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SOLID STATE DIVISION PROGRESS REPORT for Period Ending March 31, 1986

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SPECIAL DEDICATION

This issue of the Solid State Division Progress Report is dedicated to the memories of two scientists who had long and valued associations with the division. Wallace C. Koehler died at his home in Oak Ridge on April 1, 1986, after a brief bout with cancer, and Thomas S. Noggle died at ORNL on July 1, 1986, as the result of a heart attack.

Wally Koehler was a pioneer in the development and use of neutron scattering techniques for the study of condensed matter. His outstanding work at ORNL has helped to lay the foundation on which neutron scattering programs throughout the world have been built. He was especially interested in investigating the magnetic properties of rare-earth materials, and he became a leading authority on this subject. His recent research involved small-angle scattering techniques, and as the Director of the ORNL Center for Small-Angle Scattering Research, he developed this activity into a highly successful user program, accommodating over 100 scientists annually.

Tom Noggle was a senior member of the scientific staff whose research activities at ORNL covered a variety of topics in the materials sciences. He initiated an electron microscopy program in the division, participated in many experiments to determine the effects of nuclear radiation on materials, and was recently involved in utilizing ion beam techniques for the preparation and characterization of materials with unique properties. He was an exceptionally talented experimentalist, who gained intense satisfaction from direct involvement in new and challenging research. His latest experiments were part of a new initiative to prepare thin films and multilayered materials by ion beam deposition.

Both of these men performed many important scientific tasks for the Solid State Division, ORNL, and the Department of Energy. Their scientific skills and the close friendships with division members are greatly missed.

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ACRONYMS, ABBREVIATIONS, AND INITIALISMS

ACA — average crystal approximation	LPVD — laser photochemical vapor deposition
ADP — adenosine diphosphate	LTNIF — Low-Temperature Neutron Irradiation Facility
AES — Auger electron spectroscopy	NSLS — National Synchrotron Light Source
APFIM — atom probe field ion microscopy	OIC — optical integrated circuit
AR — antireflection	PAN — polyacrylonitrile
ATNIF — ambient temperature neutron irradiation facility	PB — polybutadiene
ATP — adenosine triphosphate	PBT — poly(butylene terephthalate)
bcc — body-centered cubic	PCSA — polarizer compensator sample analyzer
BCS — Bardeen-Cooper-Schrieffer	PEP — phosphenol-pyruvate
BE — binding energy	PET — poly(ethylene terephthalate)
BL — buried layer	Phe — phenylalanine
BSR — Bulk Shielding Reactor	PK — pyruvate kinase
CED — critical energy deposition	PVD — plasma vapor deposition
CP — central peak	RBS — Rutherford backscattering
CPA — constant phase angle	RFS — renormalized forward scattering
CVD — chemical vapor deposition	RPA — random phase approximation
DFZ — dislocation-free zone	RTA — rapid thermal annealing
DIDG — diffusion-induced dislocation guide	SANS — small-angle neutron scattering
DIGM — diffusion-induced grain boundary motion	SAXS — small-angle x-ray scattering
DLA — diffusion limited aggregation	SCR — self-consistent renormalization
DOS — density of states	SIMS — secondary ion mass spectrometry
DPA — displacements per atom	SPE — solid phase epitaxial
EELS — electron energy loss spectroscopy	SPLEED — spin-polarized low-energy electron diffraction
ELM — electron lifetime model	SRO — short-range order
EPR — electron paramagnetic resonance	STEM — scanning transmission electron microscopy
FAS — fatty acid synthetase	TE — transverse electric
fcc — face-centered cubic	TEM — transmission electron microscopy
FF — fill factors	THF — tetrahydrofuran
FG — fine grain	TM — transverse magnetic
FLL — flux-line lattice	TRE — time-resolved ellipsometry
FQHE — fractional quantum Hall effect	TRR — time-resolved reflectivity
FWHM — full width at half maximum	UCST — upper critical solution temperature
HF — Hartree-Fock	UHMWPE — ultrahigh molecular weight polyethylene
HFIR — High Flux Isotope Reactor	VCA — virtual crystal approximation
HVEM — high-voltage electron microscope	WAND — wide-angle neutron diffractometer
IA — impulse approximation	WAXD — wide-angle x-ray scattering
ICRH — ion cyclotron resonance heating	XPS — x-ray photoelectron spectroscopy
IQHE — integer quantum Hall effect	XTEM — cross-section transmission electron microscopy
JET — Joint European Torus	ZOLD — zeroth-order log normal
LDA — local density approximation	
LEED — low-energy electron diffraction	
LG — large grain	

INTRODUCTION

The reporting period covered by this progress report of the Solid State Division includes the eighteen months from October 1, 1984, through March 30, 1986. No major changes have occurred in the research areas of interest to the Division during this period, and emphasis has continued along most directions that were reported in the last progress report. A very large part of the Division's research comes under the broad classification of mission-oriented basic research because of its relationship to the materials problems that exist in advanced energy technologies.

The development and expansion of users' programs, whereby scientists outside ORNL can utilize equipment located at the Laboratory, have continued to be a very important part of the Division's activities. The Solid State Division has the responsibility for four of these programs: (1) the National Center for Small-Angle Scattering Research (NCSASR); (2) the Neutron Scattering Users' Program at the HFIR; (3) the Surface Modification and Characterization (SMAC) Collaborative Research Center; and (4) the Low-Temperature Neutron Irradiation Facility (LTNIF). Construction of the LTNIF has been completed recently at the Bulk Shielding Reactor, and final tests are being made before making it available to users within the next few months; it will be the main facility within the United States for basic research to study the effects of neutron radiation on materials. Both the LTNIF and the NCSASR, which is operated through a joint agreement between the Department of Energy and the National Science Foundation, have been established mainly for users, and the in-house research programs are therefore relatively small. The other two programs permit users to utilize the neutron scattering facilities at the HFIR and the accelerators and lasers of the SMAC facility at times that do not interfere with the programmatic requirements of DOE. An extensive expansion of the SMAC facility was initiated several years ago and is now nearing completion; when this expansion is finished, at least twice as many users can be accommodated. Although informal arrangements for collaborative research on major ORNL facilities have always been possible, these more formalized users' programs help to ensure that our facilities are used for the best possible research.

Members of the Solid State Division are also involved in other established programs of cooperative research. Special arrangements have been made through DOE for collaborative research in neutron scattering with scientists from Ames Laboratory and scientists from Japan. The neutron scattering program at Ames was moved to ORNL when the Ames Laboratory Research Reactor was shut down, and the cooperative program with the Japanese was negotiated under the umbrella of the U.S.-Japan Science and

Technology Agreement. The budgets and staff for these programs are relatively modest, and both of them have been highly successful for several years. Members of the Solid State Division are also involved in two participating research teams (PRT) at the National Synchrotron Light Source at Brookhaven National Laboratory. One PRT with the University of Pennsylvania now operates a facility on the VUV ring to investigate the properties of surfaces; the other PRT, which includes scientists from ORNL and several universities, operates a very flexible diffractometer on the x-ray ring.

Ongoing users' activities and other scientific interactions are very important to members of the Solid State Division staff, because they provide stimulating interactions with many scientists outside ORNL. These collaborations will undoubtedly become even stronger in future years with the availability of the LTNIF and completion of the SMAC facility expansion. Moreover, because of very strong recommendations by national committees for a new advanced steady-state neutron source in the USA, ORNL has begun plans for another major experimental facility, which has been designated the Center for Neutron Research (CNR). It will be built around a research reactor with the highest neutron beam intensities in the world for neutron scattering, and it will also have unsurpassed facilities for materials irradiation and isotope production. The CNR, which obviously will be very important for the Solid State Division, will be built as a national user facility; it is anticipated that 700 to 1,000 different scientists will perform experiments there each year.

Several programs and a number of scientists in the Division have received special recognition during this reporting period. The 1985 Division of Materials Solid State Physics Award for Significant Implication for Energy Technology was given to B. R. Appleton, C. W. White, and O. E. Schow for their research on "Surface Modification of Materials by Ion Beam Processing." Members of the Solid State Division have won six of these special DOE Materials Sciences Awards during the past five years, and this record is particularly gratifying because judges for the competition are program managers at competing DOE laboratories. During this period, B. C. Sales and L. A. Boatner won a 1985 IR-100 Award for their work on "Lead-Iron Phosphate Process for High-Level Radioactive Waste Disposal"; these two scientists were also selected by Science Digest among the 100 Top Innovators of 1985. W. C. Koehler received a special DOE award in recognition of his outstanding research and research leadership in neutron scattering, and B. C. Larson received the prestigious Bartram E. Warren Award, which is given every three years by the American Crystallographic Society for an outstanding research accomplishment in diffraction physics. Larson was cited for his studies of pulsed-laser annealing in silicon by time-resolved x-ray measurements with nanosecond resolution. Martin Marietta Energy Systems recognizes special achievements by ORNL staff members with monthly and annual awards, and a number of Division members received these awards during the reporting period. The most significant was the selection of B. C. Sales as the 1985 Inventor of the

Year within the Martin Marietta Energy Systems organization and the subsequent award to him of the Jefferson Cup by Martin Marietta Corporation. A complete list of the awards received by Division members is given in the report.

The Solid State Division also received two very important awards during the reporting period. In January, 1985, a plaque was presented to the Division for its outstanding safety record; members of the Division have never experienced a lost-time injury on the job since the Division was established in 1952. In January, 1986, the Division was the corecipient with the Metals and Ceramics Division of the ORNL Director's Award for 1985. This award is given annually to divisions which have had particularly outstanding accomplishments during the previous year.

The arrangement of this progress report has been chosen to emphasize the major areas of solid state science in which the Solid State Division conducted research during the reporting period. These areas are Theoretical Solid State Physics, Surface and Near-Surface Properties of Solids, Defects in Solids, Transport Properties of Solids, Neutron Scattering, and Synthesis and Properties of Novel Materials. There is a chapter of the report for each of these major research areas, and the chapters are divided into sections to emphasize specific topics. A brief introduction to each of the chapters indicates the scope and goals of the research and gives a few highlights of recent investigations. Because of very close interactions that exist among scientists of the Division, a number of research summaries do not fit uniquely into only one section of the report. Those summaries with overlapping interests have been placed into one of the appropriate sections on a somewhat arbitrary basis.

1. THEORETICAL SOLID STATE PHYSICS

The theoretical research program covers a wide range of topics and disciplines. This diversity is due primarily to the interaction with experimental programs within the division and to a number of important collaborative efforts with other theoretical and experimental programs in the United States and abroad. For organizational purposes this work is grouped loosely into three general categories: Electronic, Vibrational, and Magnetic Properties; Surfaces and Interfaces; and Rapid Solidification and Dopant Studies in Semiconductors. While these titles reflect clearly the difficulty in trying to categorize the research under a few headings, they do provide an indication of the type of work which is currently being pursued.

Much of the work described in this chapter relies heavily on the use of large core high-speed computers. The development of appropriate numerical techniques and the relevant computer programs necessary for applying the complex theories of condensed matter to realistic systems is no less important than the development of the theory itself. The analysis of LEED profiles to determine surface crystallography, the prediction of high-energy spin waves in itinerant ferromagnets, the investigation of ion-solid interactions including channeling, and the study of the various phases of matter formed during rapid solidification of undercooled silicon are just a few examples of the important role played by computer techniques in the research described below. The development of such techniques has long been a strength of the division's theory program and has become a vital tool in fulfilling its primary role—to provide backup and support for the division's experimental programs as well as guidance and direction for future research activities.

ELECTRONIC, VIBRATIONAL AND MAGNETIC PROPERTIES

EXCITATION SPECTRUM AND DISSIPATION IN THE INTEGER AND FRACTIONAL QUANTUM HALL EFFECT OF Si(110) SURFACE: PART I¹

M. Rasolt   F. Perrot²
A. H. MacDonald³

The discovery of the integer quantum Hall effect (IQHE) by v. Klitzing et al.⁴ and the fractional quantum Hall effect (FQHE) by Tsui et al.⁵ is one of the more surprising and exciting events in recent condensed matter physics research. The IQHE was first observed in a Si MOSFET⁴ with the

two-dimensional inversion layer pointing along the Si(100) surface. It was subsequently observed also in a GaAs heterojunction.⁵ What are observed in the experimental measurements (at very high magnetic field perpendicular to the inversion layer) are plateaus in the transverse conductance as a function of the magnetic field H , with values of the conductance which are precisely integral multiples of the conductance unit $\sigma_0 = e^2/h$ (Fig. 1.1).⁴ At the same time the longitudinal Hall resistance drops to zero^{4,5} (at $T=0$), which represents a dissipationless flow of the electrons in the two-dimensional inversion layer (i.e., the system is superconducting). Particularly surprising in these experimental observations is the insensitivity of the value of these plateaus to sample preparation (i.e., the conductance to

Fig. 1.1. A plot of the Hall transverse resistance ρ_{xy} as a function of magnetic field B or equivalently filling factor ν [$\nu \equiv N/N_T$, where N is the number of carriers in the inversion layer, and $N_T = eH^2/(hc/e)$ are the number of lowest Landau levels in an area L^2 (see text)]. The IQHE correspond to the plateaus at $\nu = 1, 2, \dots$; note the precision of the value of the plateau $\rho_{xy} = \frac{1}{\nu} \frac{h}{e^2}$ or equivalently $\sigma_{xy} = \nu e^2/h$. The FQHE corresponds to the plateaus at $\nu = 1/3, 1/5$, etc.

very high precision remains an integer value of σ_{xy} .

Most aspects of the IQHE can be understood using the single-electron picture in the following way. For a noninteracting two-dimensional system of electrons in an area L^2 , the number of lowest Landau levels N_T is $N_T = eH^2/\phi_0$, where ϕ_0 is the magnetic flux $\phi_0 = hc/e$. The plateaus occur when all of these Landau levels N_T are occupied (i.e., when the number of electrons N in the inversion layer is equal to N_T). Clearly when all these states are occupied, the spectrum of excitations has a gap $\Delta = \hbar\omega_c$ (ω_c is the cyclotron frequency), which is the energy required to excite an electron to the next Landau level. For example, this gap forbids any excitations and correspondingly forbids any dissipation as well, which is in agreement with the experimental observation.⁴ In short, using general gauge arguments, first suggested by Laughlin,⁶ it can be shown that this gap in the excitation spectrum is sufficient to sustain the IQHE. Due to the generality of such

gauge arguments, it can be shown that indeed these plateaus are insensitive to the details of the samples. However, the width of the plateaus does depend on the amount and type of impurities, whose effect is to localize part of the extended states in the inversion layer.⁶

The FQHE, unlike the IQHE, shows plateaus when the occupation of N_T is fractional (for example, when $\nu \equiv N/N_T = 1/3$). Obviously there is no single particle g.p. in the excitation spectrum when ν is fractional; thus, the FQHE must be a consequence of a gap in the collective excitation spectrum of the two-dimensional electron fluid. Such a ground state wave function which shows the appropriate spectrum of excitations with a gap at $\nu = 1/3$ was first constructed by Laughlin,⁷ and this wave function seems to explain successfully the FQHE in GaAs.

Our contribution was to make definite predictions concerning both the IQHE and FQHE when the underlying band structure of the two-dimensional electron fluid shows a time reversal valley degeneracy.¹ To be more specific, if we take a Si(110) surface for the inversion layer of the two-dimensional electron fluid, the two valleys of lowest energy lie along the $\langle 100 \rangle$ and $\langle 010 \rangle$ axes⁸ (Fig. 1.2). These two valleys are energetically perfectly degenerate (Fig. 1.2), and it is this degeneracy which we have exploited to make experimental predictions for the IQHE and FQHE in Si(110). Before we turn to the consequence of this degeneracy, we contrast this with the situation in GaAs and Si(100). In GaAs the valence band is in the center of the Brillouin zone (Fig. 1.2), and there is only one valley which is occupied. In the Si(100) surface the perfect degeneracy of the $\langle 100 \rangle$ and $\langle 010 \rangle$ valleys is lifted by the (100) surface (Fig. 1.2), and again only one valley is occupied. Therefore, both of these systems have no valley degeneracy and are properly described by an excitation spectrum containing a gap.⁷ The Si(110) surface, however, cannot have a gap in the excitation spectrum as we argue next.

We start by making an effective mass approximation for the electrons in the two valleys.¹ The effective mass Hamiltonian for these electrons is then given by

$$H_{\text{eff}} = \frac{1}{2m} \sum_{\alpha, i} \left(\mathbf{p}_{i, \alpha} - \frac{e}{c} \mathbf{A}(\mathbf{r}_{i, \alpha}) \right)^2 + \frac{1}{2} \sum_{\alpha, \beta} \sum_{i \neq j} v(\mathbf{r}_{i, \alpha} \mathbf{r}_{j, \beta}), \quad (1)$$

where $\mathbf{p}_{i, \alpha}$ and $\mathbf{r}_{i, \alpha}$ are the momentum and positions of the i th electron in valley $\alpha = 1$ or $\alpha = 2$, $\mathbf{A}(\mathbf{r}_{i, \alpha}) = 1/2 \mathbf{H} \times \mathbf{r}_{i, \alpha}$ is the vector potential, and m is the effective mass given by the curvature at the minima of the two valleys (Fig. 1.2). H_{eff} is identical to a spin 1/2 Hamiltonian in a uniform magnetic field $\mathbf{H}$ with no Zeeman splitting. In other words, the valley index α maps exactly to the spin-up, spin-down index of an itinerant electron ferromagnet, and it is therefore invariant under SU(2) spin rotation (which in our case is really valley rotation). However, because the

Fig. 1.2. (a) The six pockets of the carriers in the valley band of bulk Si (k_1 is along $\langle 100 \rangle$, k_2 is along $\langle 010 \rangle$, and k_3 is along $\langle 001 \rangle$). When the surface of the inversion layer points along the $\langle 100 \rangle$ direction, it is well established that the four pockets b, c, e, and f are lifted relative to a and d. The $\langle 100 \rangle$ inversion layer further breaks the symmetry of a and d, leaving only one pocket occupied. For Si(110), however, the two pockets at a and e can easily be seen to be degenerate, providing the type of SU(2) invariance discussed in the text. (b) Band structure $E(k)$ of GaAs and Si as a function of k . The shaded areas are the conduction electrons which make up the quantum fluid discussed in the text. As is clearly seen, GaAs is a direct gap semiconductor, and this quantum fluid is made up of only one component of electrons. Silicon is an indirect gap semiconductor, and this quantum fluid is made up of two components of electrons; one at $\alpha = 1$ [valley a, Fig. 1.2(a)] and one at $\alpha = 2$ [valley b, Fig. 1.2(a)].

high magnetic field forces all the electrons into the lowest Landau level, all the electrons have the energy $\hbar\omega_c$, and it costs no kinetic energy to valley polarize the ground state (i.e., put all of the electrons in one valley, or equivalently create a ferromagnetic state in our spin analog). Such a polarization will clearly gain exchange energy (Hund's rule), and the two-dimensional electron fluid is almost certain to be ferromagnetic. Continuing with our spin analog, we then have a Heisenberg-like itinerant ferromagnet, and such a Hamiltonian is known to include gapless Goldstone modes (i.e., "magnons" or here referred to as "valley waves") in its spectrum of excitations.

The form of the dispersion of these valley waves was found to be

$$\omega(q) = \frac{1}{2L^2} \sum_{q_1} v(q_1) \left\{ \left[e^{i(\vec{q}_1 \cdot \vec{q} - \vec{q}_1 \cdot \vec{q})/2} - 1 \right] + \left[e^{i(\vec{q}_1 \cdot \vec{q} - \vec{q}_1 \cdot \vec{q})/2} - 1 \right] (S(q_1) - 1) \right\}, \quad (2)$$

where $v(q_1) = 2\pi e^2 / (cL|q_1|)$, L is the magnetic length $L = (\hbar c / eH)$, ϵ is the dielectric constant for Si and q , and $q_1 = q_{1x} + iq_{1y}$ [i.e., complex

forms for the two-dimensional $q = (q_x, q_y)$; $\bar{q}$ is the complex conjugate of q]. Most important in our calculation [i.e., Eq. (2)] is $S(q_1)$, which is the structure factor of the two-dimensional electron fluid. $S(q_1)$ takes a particular form depending on the proposed ground state. For example, the Laughlin ground state yields one particular form for $S(q_1)$, but other exciting possibilities exist⁹; measurement of our valley waves could help answer some of these controversial questions.⁹

In Fig. 1.3 we present a plot of these valley waves [Eq. (2) with a Laughlin $S(q_1)$] along with

Fig. 1.3. The dispersion $w(q)$ of the collective excitations in Si(110) inversion layer of the FQHE at $\nu = 1/3$. The dashed curves are the density-density modes which are found in both GaAs and Si(110). The excitations have a gap for the full range of momentum q . This gap sustains the FQHE in GaAs and provides no possible dissipation (see text). The solid curve is the dispersion curve for valley waves which exist only in Si(110). The gapless behavior as $q \rightarrow 0$ is a consequence of the valley degeneracy (see text).

the usual excitations (with a gap) which are found in the single valley case discussed above. Clearly our valley waves close the gap i.e. the excitation spectrum of a multivalley semiconductor [like Si(110)] and therefore (according to our discussion) will invariably have a profound effect on the measurement of either the IQHE or FQHE in such a system. It is expected that such measurements will add profoundly to our understanding of the nature of this quantum fluid.

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EXCITATION SPECTRUM AND DISSIPATION IN THE INTEGER AND FRACTIONAL QUANTUM HALL EFFECT OF Si(110) SURFACE: PART II¹

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The effective mass Hamiltonian for the degenerate two valleys of a Si(110) MOSFET [Eq. (1) in Part I]³ contains most of the electron-electron interactions. As we showed in Part I, the H_{eff} was fully invariant under spin rotation [i.e., SU(2)]. Terms going beyond this effective mass approximation

$$H = H_{\text{eff}} + H', \quad (1)$$

violate the full SU(2) symmetry. For example, there will be terms in H' in which one electron is scattered from one valley to the other. There also are small symmetry breaking terms¹ that arise from the fact that the form factors of the Bloch functions have an opposite dependence on the wave vectors. We were able to consider the effect of such symmetry breaking terms¹ [i.e., H' in Eq. (1)] on the valley waves dispersion $w(q)$ in Eq. (2) of Part I. What we showed¹ is that, in the absence of impurities (in the inversion layer), H must conserve separately the number of electrons in each of the two valleys (i.e., in our spin analog this means that H commutes with the operator S_z). This follows directly from wave vector conservation parallel to the interface and means that a Heisenberg-like Hamiltonian H_{eis} can be written for Eq. (1); i.e.,

$$H_{\text{eis}} = AS \cdot S + BS_z^2. \quad (2)$$

In Eq. (2) the first term has the full SU(2) invariance (i.e., H_{eff}), while BS_z^2 breaks this symmetry and corresponds to H' in Eq. (1). We were able to calculate B for the Si(110) MOSFET and found $B < 0$. The broken SU(2) symmetry accordingly selects an Ising-like ground state for the valley wave polarization in Si(110). If B turned out positive, there would exist an easy axis in the x - y spin plane of Eq. (2) and the ground state would be x - y -like. Corresponding to this Ising ground state, we found¹ that the valley wave dispersion $w(q)$ [Eq. (2) in Part I] has a gap $\Delta = 4B$ at $q = 0$ (Fig. 1.4). We found¹ this gap to be very small, Δ of the order of 10^{-9} eV.

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Fig. 1.4. A sketch of the valley-wave dispersion for the Ising and x-y ground states at small q . The effect of the symmetry-breaking terms is to introduce a gap Δ in the Ising case and a linear dispersion in the x-y case. The slope of the dashed tangent line, in each case, is the critical velocity. The inset is a sketch of the longitudinal resistivity versus the current density j in the Ising case.

To observe the effect of these valley waves on the IQHE or FQHE in Si(110), we need to dissipate energy into the valley waves from impurities residing in the inversion layer. The level of dissipation dE/dt is given by¹

$$\frac{dE}{dt} = \frac{8\pi}{\hbar} \frac{N}{L^2} \sum_j |u(z_j)|^2 \int \delta(\omega(q) - \mathbf{v} \cdot \mathbf{q}) \omega(q) \frac{d^2q}{(2\pi)^2}, \quad (3)$$

where $u(z_j)$ is the matrix element of the impurity potential at position z_j between the Bloch states of the two different valleys in the inversion layer and $\mathbf{v}$ is the drift velocity of the two-dimensional electron fluid. Figure 1.4 summarizes our results:¹ according to the Landau construction, the slope of the dashed tangent line is the critical velocity v_c . For $\Delta = 10^{-9}$ eV we find a critical velocity $v_c = 80$ m/s, below which no dissipation takes place, while above v_c dissipation via the valley waves is possible. If we put $10^{11}/\text{cm}^2$ electrons in the inversion layer, this v_c leads to a critical current density $j_c = 10^{-4}$ A/cm. From Eq. (3) we find a level of dissipation or, equivalently, a longitudinal Hall resistance $\rho_{xx} = 10$ ohms for a reasonable level of impurities

in the inversion layer. All of these predicted values (i.e., ρ_{xx} , j_c , and Δ_0) are easily accessible to experimental observation, and we are eagerly awaiting the first experimental results on the IQHE and FQHE of a Si(110) MOSFET. We expect such results to provide a deeper understanding of this fascinating effect.

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PREDICTION OF HIGH-ENERGY SPIN-WAVE EXCITATION IN IRON¹

J. A. Blackman² T. Morgan²
J. F. Cooke

Itinerant-electron theory has been very successful in giving a description of the low-temperature spin waves in the 3d transition-metal ferromagnets nickel and iron. Recent predictions³ of distinct high-energy collective excitations above 100 meV in nickel were subsequently confirmed by inelastic neutron scattering using the hot source at the Institut Laue-Langevin. Some discrepancies in detail exist between theory and experiment, but in broad terms, they are in agreement. We report here some results of calculations for iron, an itinerant-electron ferromagnet with spin-splitting energy ≈ 2 eV, some 5 times the value in nickel. From these calculations, we predict the existence of new collective excitations in Fe which exist both throughout the Brillouin zone and to energies much higher than were previously thought possible.

The theory on which the calculations are based is the same as that used previously for nickel. The expression for the transverse part of the inelastic neutron scattering cross section was derived using a generalized random phase approximation and depends in a very complicated way on the spin-polarized band structure, as well as on matrix elements of a screened Coulomb electron-electron interaction. These matrix elements can be expressed uniquely in terms of symmetry-dependent constants $W_{\mu\nu\lambda\xi}$, which have no band- or wave-vector dependence and are the only terms in the theory which depend explicitly on the screened interaction. Each of the four subscripts of W is a symmetry label which ranges over the ten symmetry terms (s, p, and d) used in an expansion of the electronic wave functions in terms of symmetry orbitals.

Since the screened interaction is not known in practice, the $W_{\mu\nu\lambda\xi}$ are treated as parameters. There are several different, symmetrically correct choices for the form of W , which can be characterized by a small number of parameters. The simplest is to include, in addition to the diagonal terms, elements of the type $W_{\mu\nu\nu\mu}$, with the condition $W_{\mu\nu\nu\mu} = W_{\nu\mu\mu\nu}$ for all ν , where μ and ν label orbitals belonging to the same irreducible representation. Because of the particular form of

the rotation matrices associated with the cubic point group, it suffices to implement this addition to W for the e_g components only. The numerical results presented in this paper were obtained using this two-parameter approximation, where the two parameters were chosen to reproduce the measured moment and its symmetry character. Once the parameters are fixed, the cross section is determined uniquely. The cross-section expression was numerically evaluated with wave functions and electronic energies obtained from a self-consistent solution of the band-structure equation, and Brillouin-zone sums were evaluated using the tetrahedron method.

Results for q along $[100]$ are shown in Figs. 1.5 and 1.6 in the form of the spin-wave dispersion curve and a contour plot of the scattering intensity. These results were obtained from constant q -calculations of the cross section as a function of energy. Peaks in the scattering cross section correspond to spin waves only if the energy of the peak coincides with a resonance in the particle-hole Green's function (i.e., to a particle-hole bound state). The most remarkable feature of these results is the prediction of "optic" modes with the energy of the upper branch

Fig. 1.5. Spin-wave dispersion curve for q along the $[100]$ direction.

Fig. 1.6. Intensity contours, in arbitrary units, for q along the $[100]$ direction.

reaching about 750 meV at the zone boundary. Notice also the relatively complicated nature of the contour plot at about halfway to the zone boundary. It is possible to express the scattering cross section as the sum of contributions with different symmetries. When this is done for $q = [0.5, 0, 0]$, three of the terms in the sum show well-defined peaks, each one corresponding to a vanishing of the real part of a pole in the electron-hole Green's function. One can, therefore, understand the behavior in terms of three interacting spin-wave modes: two optic and one acoustic. The lowest energy branch in Fig. 1.5 was not continued beyond $|q| = 0.5$ because its corresponding peak is too broad to be considered a collective excitation. Because of problems associated with defining what is and what is not a spin wave, we feel contour plots of the type given in Fig. 1.6 are a better way to display the results than the plotting of dispersion curves.

With regard to the symmetry, the acoustic mode has mixed e_g and t_{2g} character, while the "optic" modes derive from interband transitions having virtually pure e_g character. Results for q along [111] have also been obtained. As in nickel, a single branch extends to the zone boundary with energy transfers occurring up to slightly over 200 meV.

With regard to the sensitivity of the results to the form of the potential, we have also considered the effect of including $W_{\mu\nu\nu\mu}$ terms for the t_{2g} component. Preliminary results indicate that this can have fairly strong effects for the [111] and [110] directions, but has no effect at all in the [100] direction. Calculations for more general forms of W are currently under way.

The experimental observation of the high-energy excitations is, therefore, likely to provide a very exacting test of models for both the band structure and the screened electron-electron interaction in the ferromagnetic transition metals. The number of modes found, along with their measured dispersion curves, will provide important information about the magnitude of the various W parameters. In addition, the search for the high-energy collective ("optic") excitations predicted in iron should provide both an exciting challenge for experimentalists working at the limits of capability of reactor sources and a novel high-energy-transfer experiment on a spallation source.

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SPIN WAVES IN FERROMAGNETIC TRANSITION METALS II: IRON AND ITS ALLOYS¹

R. Bechara Muniz²   J. F. Cooke
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A new formula for the spin-wave stiffness constant D in a ferromagnet was derived recently by Edwards and Muniz³ and applied to Ni and its alloys. It was found that D in Ni is fairly insensitive to the precise details of the ground-state band structure, the main determining factor being the exchange splitting Δ in the d band. The strongly positive nature of D found in Ni indicates an intrinsic stability of ferromagnetism, with no tendency toward an antiferromagnetic state. In Fe, with two fewer electrons per atom, the situation is quite different. In particular, Fe is on the borderline between ferromagnetism and antiferromagnetism in the 3d transition series. Although bcc Fe is ferromagnetic, fcc Fe (stabilized by alloying or in small particles) is antiferromagnetic; also, the neighboring element Mn is antiferromagnetic. In this work we investigate D in bcc Fe and its alloys, remembering that any tendency for D to become negative indicates an instability of the ferromagnetic state.

One of the most striking results obtained from this study is that the stability of ferromagnetism in bcc Fe relies on hybridization between the

d and sp bands. The inadequacy of d -band-only models for Fe was already suggested by previous work. Even with sp bands included fully, we find that D in bcc Fe is remarkably sensitive to the precise band structure. The most satisfactory ground-state band structure we have tried is essentially that used by Cooke, Lynn, and Davis⁴ in their calculations of the transverse dynamical susceptibility $\chi(q, \omega)$. As they already found, this leads to spin-wave energies in good agreement with experiment in pure Fe. This new formula for D is very convenient for extending the investigation to the behavior of D throughout an alloy series, with varying electron number and exchange splitting. We have used it to calculate the variation of D with composition in alloys of Fe with Ni, Co, Mn, Cr, and V. The results are obtained within the virtual crystal approximation (VCA), which should work reasonably well for all of these alloys, except for FeV. This is because it has been shown from model calculations that VCA results for D compare relatively well with the coherent potential approximation results in transition-metal alloys with $|\Delta Z| < 2$, where ΔZ is the difference between the atomic numbers of the two alloy components.

In evaluating the formula for D , the k -space integrations were performed by the linear analytic tetrahedron method with 6144 tetrahedra in the irreducible part of the Brillouin zone. A large number of tetrahedra is necessary for accuracy due to a rather large cancellation between the two terms in the formula for D . Our results clearly show that, within this parameterized model for the electronic structure of Fe, D is very sensitive to the choice of the "paramagnetic" bands. The important question to be answered is: whether this sensitivity of D to the band structure in Fe is a real effect or due to an inadequate tight-binding description of the momentum matrix elements which is implicit in the calculation. We are not sure of the answer, but we cannot rule out the possibility that the real differences between bands may determine the stability of the ferromagnetic state in bcc Fe. Even within the parameterized scheme, we have not yet been able to determine precisely the features of the band structure which are important for getting a good value of D . If the sensitivity of D to the band structure is a real effect, then a calculation of D in Fe is a very sensitive test of the spin-density functional used to calculate the band structure.

We conclude that hybridization between d and sp electrons is essential for the proper stability of the ferromagnetic state in bcc Fe. Even when hybridization is included, our calculations suggest that spin-wave stiffness constant D in Fe is very sensitive to precise details of the band structure. Using essentially the same ferromagnetic band structure as that of Cooke et al.,⁴ we obtain a value of D for pure Fe in good agreement with experiment. The new formula for D is extremely convenient for investigating the variation of D with composition in alloy systems. We find good agreement with experiment for alloys of Fe which cover a wide range of electron concentration and magnetization. This gives strong support to the present approach, which is based on the tight-binding parameterization first applied to spin-wave calculations by Cooke et al.⁴

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PARAMAGNETIC FORM FACTORS OF HCP TRANSITION METALS¹

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In the past two decades the induced moment form factor has been measured for a large number of transition metals, and these data provide detailed information on the response of the metals to an external magnetic field. The moment distribution is determined by the energy levels and wave functions of the metallic electrons. The induced moment consists of an orbital contribution and a spin contribution. The spin contribution has been calculated for most transition metals. However, for a long time it was not possible to compute the orbital contribution for itinerant electrons, and one traditionally analyzes this part by using the atomic model. Realistic calculations of the orbital contribution are of fundamental importance in assessing the validity of theoretical models. Recently, we have been able to formulate the orbital form factor problem in such a way that it can be calculated accurately for cubic transition metals. We have now extended the same consideration to hcp transition metals.

In a magnetic form factor measurement, one detects the spin-flip ratio of polarized neutrons. If the lattice has one atom in a unit cell, the nuclear scattering amplitude is a constant, and the result of the measurement can be directly compared with the Fourier transform of the magnetization density. The hcp structure has two atoms in a unit cell. We choose the unit cell such that the atoms are situated one at the origin and the other at δ . The nuclear contribution has the expression $F_N(G) = b[1 + \exp(iG \cdot \delta)]$, where F_N is the nuclear structure factor, b is the nuclear scattering amplitude, and G is a reciprocal lattice vector. The Fourier transform of the magnetization density for the unit cell is proportional to the generalized susceptibility function $X(G)$. The spin-flip ratio $F(G)$ is given by $F(G) = 4\text{Re}(b^*(G)X(G)/|b(G)|^2)$. If we normalize $F(G)$ in the forward direction to the static susceptibility, we can write

$$F(G) = X'(G) + \frac{\sin G \cdot \delta}{1 + \cos G \cdot \delta} X''(G), \quad (1)$$

where X' and X'' are the real and imaginary parts of $X(G)$, respectively. In general, $X(G)$ can be written in terms of spin and orbital contributions $X(G) = \alpha_s X_s(G) + X_o(G)$, where α_s is the appropriate enhancement factor. The expressions for $X(G)$ and $X_o(G)$ are rather complicated and will not be reproduced here. They, of course, depend

explicitly on the electronic energy bands and wave functions.

The energy bands and Bloch wave functions for the hcp metals were calculated by the self-consistent nonrelativistic KKR method in the muffin-tin approximation. The Kohn-Sham approximation for the exchange-correlation potential was used. The energy levels and wave functions were determined in the $1/24$ irreducible sector of the Brillouin zone over a mesh of 990 points. The wave functions consist of two sets of spherical harmonics with $l < 2$, one centered around each atom.

For the matrix elements we extend the muffin-tin orbitals into two overlapping atomic spheres and approximate the unit cell integral by the sum of the atomic sphere integrals. For states outside the irreducible sector, we use the group of symmetry operations of the hcp structure to rewrite the matrix element as one whose states are within the irreducible sector but the corresponding operator is transformed. The final sum over the Brillouin zone is calculated by using the tetrahedron technique.

A comparison of results for the orbital part of the form factor calculated from the atomic and itinerant models can be summarized as follows. The itinerant theory predicts a more rapid decrease with wave vector than atomic theory and a definite asymmetry associated with wave-vector direction. This behavior is similar to that found for the spin contribution. In contrast to the atomic model, numerical results can be obtained on an absolute scale from itinerant theory for paramagnetic metals. A comparison of results for the orbit and unenhanced spin contributions for zirconium has shown that the orbital and unenhanced spin contributions for zirconium are comparable, while for Sc, Y, and Lu the orbital contribution is approximately 10% or less of the unenhanced spin contribution at $|G| = 0$. In all cases, the spin and orbital terms become comparable as $|G|$ is increased. If for zirconium we choose $\alpha_s = 1.1$, which yields the measured static susceptibility at $|G| = 0$, then we obtain the results for the total form factor shown in Fig. 1.7. As can be seen, the agreement with experiment is quite good.

Comparisons of the type shown in Fig. 1.7 can be misleading. The agreement one gets is dependent, to a great extent, on the way the experimental data are normalized. Realistic tests of theoretical predictions can only be made on the basis of a comparison to experimental data obtained on an absolute scale. A more sensitive test of the theory could be made if the spin and orbital contributions could be separated, because of the theoretical problems associated with calculating α_s and the relatively small orbital contribution (particularly at small $|G|$) found for a number of materials. While we conclude from our work thus far that calculations based on itinerant electron theory are in reasonable agreement with experiment, we anticipate that more sensitive tests will be possible in the near future.

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Fig. 1.7. Comparison of itinerant electron (total) form factor and experimental results for zirconium.

CRYSTALLINE PROPERTIES OF RUTILE CALCULATED WITH A SIMPLE SHELL MODEL

J. C. Wang   Mark Mostoller

Recently the computer program (HADES II) developed by Harwell for calculating defect energies in cubic ionic crystals was modified (HADES III) and applied to crystals of lower symmetry such as α -alumina, Na β -alumina, and rutile.^{1,2} However, there are some problems with these new results. It was shown³ that the potential model used by Catlow et al.¹ in defect studies of TiO_2 does not give reasonable phonon structure or static properties; in fact, the potential model does not yield a stable rutile crystal structure. The site energies calculated for Na^+ ions in stoichiometric Na β -alumina are also questionable.⁴ To understand the origin of these discrepancies and to search for viable potential models, we have developed a computer code similar to the PLUTO part of the Harwell programs. For given interionic interactions and crystal symmetry, the code can determine the equilibrium structure, lattice energy, elastic constants, and dielectric constants.

The code was tested using the potential model reported by Catlow et al.¹ for rutile with the same cutoff distance for short-range interactions used by these authors.⁵ Our results (in parentheses) are compared with those reported by Catlow et al. in Table 1.1 (CATLOW 1). As can be seen from the table, there are serious discrepancies between the two sets of numbers. As found before³ by using a variety of cutoff distances for the short-range interactions, some elastic and dielectric constants are negative, indicating that the crystal is unstable. It turned out that these discrepancies are due to

the fact that Catlow et al.⁶ did not fully relax the structure in their calculations. Our results demonstrate that properties calculated using the PLUTO program for a crystal are meaningless unless the structure is first fully relaxed.

In a later publication, Catlow et al.⁷ reported another potential model for rutile. A quartic spring constant was added to the core-shell elastic energy term for both the oxygen and titanium ions, and the structure was "fully" relaxed. However, as shown in Table 1.1 (CATLOW 2), we were unable to reproduce their results. Our calculations show that their new potential does not predict the dielectric constants satisfactorily.

Because the current potential models for rutile are unsatisfactory, we have used our code to determine simple-shell-model parameters by fitting observed properties of the material. We increased the cutoff distance for the short-range interactions to 20 Å to avoid abrupt changes of these interactions at the cutoff boundary. The experimental⁸ and calculated properties are compared in Table 1.1. The values of the potential parameters obtained are summarized in Table 1.2. As can be seen, our potential gives the best agreement between observed and calculated properties; the largest discrepancy occurs with C_{33} (about 30%). In general, the parameters are quite different from those of Catlow et al.^{1,7} The van der Waals coefficients C_6 in particular differ greatly, and their relative magnitudes in our model are contrary to physical expectations. All of the calculations for rutile suggest that the simple shell model with central two-body potentials is inadequate to describe the properties of this material. The simple shell model also exhibits puzzling features when applied to higher symmetry insulators like the alkali halides. A more fundamental model that leads naturally to noncentral interactions and includes higher polarizabilities has been developed,⁹ demonstrating a need to reexamine potential models in current use for insulators.

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Table 1.1. Comparison of crystalline properties calculated with various potential models for rutile with experimental results. Numbers in parentheses are corresponding values of the results of Catlow et al. obtained in this work with the crystal structure fully relaxed.

	This work	Experimental results	CATLOW 2	CATLOW 1
a	4.36501	4.59373	4.51099 (4.51211)	— (4.66809)
c	3.01863	2.95812	3.20362 (3.20410)	— (3.16934)
u_c	0.311727	0.3053	0.30449 (0.310168)	— (0.312084)
u_s	0.307593	0.3053	— (0.310745)	— (0.319963)
E	-114.77	-126.0	— (-112.47)	-109.90 (-110.34)
C_{11}	29.64	27.01	26.81 (26.96)	25.33 (17.45)
C_{12}	18.48	17.66	19.85 (19.99)	17.80 (9.75)
C_{13}	19.12	14.80	19.76 (19.45)	20.90 (21.96)
C_{33}	47.84	48.19	55.23 (55.97)	77.92 (50.85)
C_{44}	11.01	12.39	9.95 (10.12)	9.22 (-0.26)
C_{66}	21.23	19.30	21.27 (21.30)	22.12 (15.89)
$\epsilon_{11}(0)$	78.8	86.0	86.55 (63.96)	94.76 (-26.16)
$\epsilon_{33}(0)$	178.0	170.0	274.20 (238.67)	157.32 (-62.74)
$\epsilon_{11}(\infty)$	7.00	6.83	6.63 (2.45)	6.28 (6.37)
$\epsilon_{33}(\infty)$	8.16	8.43	7.91 (2.41)	7.99 (7.61)
r_{cut}	20.0000	—	5.5125 (5.5125)	6.4312 (6.4312)

CATLOW 1 from reference 1.

CATLOW 2 from reference 7.

Experimental results from reference 8.

a and c are lattice constants in Å.

u_c and u_s are core and shell positions of oxygen ions.

E is the lattice energy in eV.

C_{11} , etc. are elastic constants in 10^{11} dyn/cm².

ϵ_{11} , etc. are static and high-frequency dielectric constants.

r_{cut} is the cutoff distance of short-range interactions in Å.

Table 1.2. Potential model for rutile obtained from the least-squares fit to the crystalline properties listed in Table 1.1.

	This work	CATLOW 1
Cation charge/ e	4.000000	4.0
$\rho(O-Ti)/\text{\AA}$	0.400593	0.40431
$A(O-Ti)/\text{eV}$	655.096	656.74
$\rho(O-O)/\text{\AA}$	0.098500	0.149
$A(O-O)/\text{eV}$	0.175000E+9	0.227643E+5
$C_6(Ti-Ti)/(\text{eV}/\text{\AA}^6)$	797.817	0
$C_6(O-Ti)/(\text{eV}/\text{\AA}^6)$	5.5011E	0
$C_6(O-O)/(\text{eV}/\text{\AA}^6)$	0.231837E-3	27.063
Shell charge (Ti)/ e	0.878624	-35.863
Shell charge (O)/ e	-1.92943	-2.38856
Spring constant (Ti)/($\text{eV}/\text{\AA}^2$)	341.146	65974.0
Spring constant (O)/($\text{eV}/\text{\AA}^2$)	4.28433	18.413
Cutoff distance/Å	20.0000	6.4312

INDIRECT SHORT-RANGE INTERACTIONS IN INSULATORS

C. D. Mahan¹ Mark Mostoller

Over the past several decades, there has been a great deal of work on the structure and dynamics of perfect insulating crystals² and on the be-

havior of defects within them.³ Considerable success in describing insulator properties has been achieved with a simple theoretical approach called the shell model, particularly for cubic materials. In this model, the ions are represented by point ionic cores and rigid, spherical electronic shells, with the shells bound to their own cores

by isotropic springs. There are long-range Coulomb (induced dipole-dipole) interactions between the charged constituents and short-range overlap-repulsive forces acting between the shells that for defect studies are included via central pair potentials.

The simplicity and apparent successes of the shell model have led many to overlook known problems associated with it. These include the following: (1) its demonstrated inability to provide a quantitative description of the equilibrium structure and dynamics of lower symmetry materials such as TiO_2 , which has the rutile structure;² (2) the occurrence of unphysical parameter values in models fitted to experimental data;⁴ (3) violation of the Cauchy relation for the elastic constants in the alkali halides (for an equilibrated cubic crystal, the assumption of central pairwise interactions leads to the prediction $C_{12} = C_{44}$, which in fact is rarely obeyed⁵); and (4) the shell model's omission of quadrupole and higher moments, which bears on problems (2) and (3) above.^{4,5} One of us (CDM) recently made a classical study of the effects of induced quadrupole and octopole moments on the elastic constants of the alkali halides.⁵ These effects are large (5-50%) and allow deviations from the Cauchy relation.

Several phenomenological extensions of the shell model have been proposed to remedy these problems.⁶⁻⁸ Each retains the long-range induced dipole interactions. Each also allows deviations from the Cauchy relation by some mechanism that leads to indirect, noncentral two- and three-body forces. With this historical framework in mind, we have carried out a fundamental reexamination of indirect short-range interactions in insulators.

The indirect force is easily described. It involves three ions: one is the "central ion," and the others are two of its first neighbors. One neighbor moves, which induces a polarization in the central ion. This polarization induces forces which act on the other neighbor. Thus the central ion provides the medium for an indirect interaction between two of its first neighbors, as well as interactions between the central ion and each neighbor. The induced forces are non-central and cause a violation of the Cauchy relation.

Figure 1.8 shows the general arrangement of the three ions. The central ion is drawn larger only to emphasize its importance in the theory. The other two ions are first neighbors to the central ion but not necessarily to each other. The two neighbors are at equilibrium distances R_1 and R_2 from the center of the central ion, and vectors to their centers make an angle β .

Let $V(r)$ denote the potential of an electron of the central ion at position r . The contribution from the neighbor ion at R_j is $u(r-R_j)$. If this neighbor displaces an amount Q_j relative to the central ion, then the potential may be expanded as a power series in the displacements,

$$V(r) = \sum \{ u(r-R_j) - Q_j \cdot \nabla u(r-R_j) + \frac{1}{2} (Q_j \cdot \nabla)^2 u(r-R_j) \dots \} . \quad (1)$$

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Fig. 1.8. The large circle represents the central ion, while the smaller circles are two of its first neighbors. The two neighbors have nine independent sets of coupled displacements. However, the four in rectangles have zero restoring force. The remaining five have nonzero restoring forces given by spring constants g_α . If $R_1 = R_2$ and the two neighbors are equivalent and all ions have closed shells, then $g'_2 = -g_2$, and only force parameters are needed; $g'_2 = -g_2 = 0$ at $\beta = 0^\circ$ or 180° .

The second term in this series is the scalar product between the displacement vector Q_j and the force $F_j(r) = -\nabla U$. An indirect interaction between displacements of two neighbors is obtained by evaluating this expression in second order of perturbation theory:

$$\begin{aligned} \Delta E &= Q_{1\mu} Q_{2\nu} M_{\mu\nu} , \\ M_{\mu\nu} &= - \sum_l \langle g | F_{1\mu} | l \rangle \langle l | F_{2\nu} | g \rangle \\ &\quad + \langle g | F_{2\nu} | l \rangle \langle l | F_{1\mu} | g \rangle / (E_l - E_g) . \end{aligned} \quad (2)$$

The symbol $|g\rangle$ denotes the ground state of the central ion, and $|l\rangle$ denotes its excited states. The mathematical form for $M_{\mu\nu}$ is similar to that of the ionic polarizability; the difference is that the general force $F_\nu(r)$ provides the driving term rather than a multipole field such as $r^M P_M(\theta)$ which enters the polarizability. Writing the tensor $M_{\mu\nu}$ in this way makes it obvious that it is

a real tensor with, at most, nine independent parameters.

Symmetry arguments can be used to show that there are no restoring forces for the four relative motions enclosed in rectangles in Fig. 1.8. In general, there are thus only five independent parameters, and if the two neighbors are equidistant from the central ion, there are at most four, depending on the angle θ . The forms of $M_{\mu\nu}$ for the general case and for $R_1 = R_2$, $\theta = 90^\circ$ are

$$M = \begin{bmatrix} m_{11} & 0 & m_{13} \\ 0 & m_{22} & 0 \\ m_{31} & 0 & m_{33} \end{bmatrix} \xrightarrow[\theta = 90^\circ]{R_1 = R_2} \begin{bmatrix} g_2 & 0 & -g_3 \\ 0 & g_4 & 0 \\ g_1 & 0 & g_2 \end{bmatrix}. \quad (3)$$

Another case of special interest in the alkali-halides has the two neighbors at 180° . Then the tensor $M_{\mu\nu}$ is diagonal, with a coupling constant h_1 when both displacements are radial and h_2 when both displacements are tangential.

We have estimated the indirect interactions for positive ion displacements around negative central ions in the alkali halides in two ways. The first was to calculate the tensor components using the local density approximation (LDA). The second method was to estimate certain linear combinations of the parameters from lattice dynamical data, including the elastic constants. Both methods indicate that the indirect interactions are significant and that pairwise central potential models are not adequate to describe even simple insulators.

Table 1.3 shows results for $g_1 - g_3$ for several alkali halides; two values are obtained from the

Table 1.3. Indirect interactions $g_1 - g_3$; in units of e^2/V_0 .

Salt	Lattice dynamics		LDA
⁷ LiF	-0.16	-0.20	-0.24
KF	-0.31	-0.17	-0.13
RbF	-0.09	-0.11	-0.12
NaCl	-0.20	-0.24	-0.21
RbCl	-0.21	-0.17	-0.19
NaBr	-0.37	-0.21	-0.22
KBr	-0.29	-0.16	-0.19

lattice dynamical data, and one from the LDA calculations. The comparison between the LDA results and those derived from the lattice dynamics is encouraging. The estimated parameter values clearly indicate that the indirect interactions will have a substantial impact on the lattice dynamics of the alkali halides and by implication, on other insulators.

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ELECTRO-OPTIC CONTRIBUTION TO THE RAMAN SCATTERING OF ALKALI HALIDES¹

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We suggested initially and then provided a detailed theory of the electro-optic contribution to the Raman scattering in alkali halides. The phrase "electro-optic" is standard jargon in nonlinear optics to denote the contribution from the nonlinear polarizability of the individual ions. This contribution had not been previously considered as a mechanism for light scattering: our calculations showed that it was the most important process.

An electric field F applied to an ion will induce a dipole moment $p = \alpha F$, where α is the linear polarizability. If the field F is large, then a spherical ion will have a nonlinear, or hyperpolarizability γ , where $p = \alpha F + \gamma F^3$. Another hyperpolarizability B provides a dipole p from the combined perturbations of field F and quadrupole field Q .

$$p = \alpha F + (1/3!) \gamma F^3 + (1/3) B F Q. \quad (1)$$

We proposed that the two parameters γ and B are responsible for the inelastic light scattering.

Most crystals permit first-order Raman scattering, where the light scattering creates one phonon in the solid. This process is forbidden in alkali halides, because of the high degree of cubic symmetry. The application of a dc field F_0 breaks this symmetry and permits first-order Raman scattering. Our theory⁴ of this process notes that there are three components to the field: F_0 , the laser field F_L , and the field from the phonon F_q . There is no quadrupole field Q in this process, so only the hyperpolarizability γ enters. The sum $F^3 = (F_0 + F_L + F_q)^3$ has the triple cross product $6F_0 F_L F_q$, so the induced moment is

$$p = \gamma F_0 F_L F_q.$$

$$d\sigma/d\Omega = (\omega/c)^4 |n_\alpha n_\beta \gamma_{0\alpha\beta} F_{0\alpha} F_{L\beta} F_{q\gamma}|^2. \quad (2)$$

The expression for the cross section follows from the simple expression for p . The initial and

final polarizations of the light are denoted $\eta_{\alpha\beta}$. The cross section is easily found once γ is known. We used experimental values of γ and showed that it predicted Raman cross sections in agreement with the experiment. This provided the first satisfactory theory of this process.

Without any dc field F_0 , the light scattering can only occur by making two phonons. We also calculated the rate of this process and showed that it agreed with experiment.¹ Here the parameter B plays an important role in the analysis.

Only a few experimental values for γ are available, and none for B . A few theoretical calculations have been done for γ for a few ions, but just one for B . We recognized the need for extensive tables of good values of γ and B for alkali and halide ions. We developed a method of evaluating these constants and produced some values for a few ions.⁴ More calculations are planned for γ and B .

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CORRELATION ENERGY OF THE TWO-DIMENSIONAL ELECTRON GAS¹

G. D. Mahan²

The correlation energy was calculated for the two-dimensional electron gas. This work was undertaken when it was noticed that no values were available for the spin-polarized case. The spin-unpolarized case was also calculated, in order to check our results against the several published results for this case.³⁻⁴ We used the method of Singwi and Sjölander,⁵ where the correlation energy is related to pair correlations in the screening function. A summary of results is given in Table 1.4. Excellent agreement was found, for the unpolarized case, when compared with other results. The results for the spin-polarized case appeared reasonable, since the correlation energy is expected to be much smaller because the exchange energy is larger. These values will be useful in the theory of two-dimensional electron

gases, which are now produced routinely in the inversion layers of semiconductor devices.

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ANALYTIC CONTINUATION AND GREEN'S FUNCTION CALCULATIONS¹

L. J. Gray² Theodore Kaplan

Many properties of solids can be easily expressed and calculated in terms of Green's functions, and in particular, the limiting behavior of $G(E) = (E-H)^{-1}$ on the real axis. Since this function is singular on a portion of the real axis, the traditional numerical method is to add a small imaginary part to E , thereby performing the calculation just off the axis. In a recent paper, Hass, Velicky, and Ehrenreich³ proposed an interesting alternative, one designed to increase the speed of Green's function evaluations. The scheme put forth is to solve for $G(z)$ for z away from the axis and then to use an analytic continuation algorithm (based upon power series) to return to the real line. The rationale for this procedure is that $G(z)$ is given in terms of a q -space integral, q a Fourier transform variable. The singularities on the axis cause the integrand $G(q,z)$ to be a rather badly behaved function when $\text{Im}(z)$ is small, and consequently obtaining the required accuracy for the integral necessitates a time-consuming evaluation of $G(q,z)$ for a great many values of q . However, off the axis, $G(q,z)$ is much smoother, and thus $G(z)$ may be calculated much more easily. Using this method, Hass et al. report being able to do a three-dimensional coherent-potential approximation calculation within an accuracy of 2% in one-third the time of the standard approach.

We have developed another algorithm for the analytic continuation, one based upon Cauchy's theorem, and have performed an error analysis of both methods. For the analytic continuation methods to be effective, an error analysis is essential because of the "ill-conditioned" nature of the problem; by this it is meant that a small change in the initial data can produce a large disturbance in the final answer.^{4,5} Consequently, the error, starting with inaccuracies in the initial data and compounded with the subsequent numerical roundoff, will grow during the calculation and eventually, if the parameters are not chosen wisely, will overpower the desired solution. As a result, if $G(z)$ is computed initially too far off the real line, the analytic continuation back to the axis will yield nonsense. An error analysis is therefore required in order to determine appropriate starting values and to have confidence in the results obtained by using an analytic continuation approach. The results of the analysis show that the Cauchy method is more

Table 1.4. Correlation energies in Rydbergs.

r_s	$-E_c$ (unpolarized)			$-E_c$ (polarized)
	Jonson	Ceperley	Present	
0.5	0.250		0.275	0.076
1.0	0.211	0.229	0.224	0.065
1.5			0.192	0.057
2.0	0.155	0.165	0.170	0.052

stable but less accurate than the power series method. Another benefit of the error analysis is that it makes possible incorporating extrapolation in the algorithm, thereby improving upon the accuracy of the methods with little additional effort.

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COLLECTIVE PROPERTIES OF SMALL METAL PARTICLES¹

W. Ekardt²

Theoretical calculations were performed on the collective and dielectric properties of small metal spheres. This subject is of topical interest because experimentalists have recently been able to make such small spheres of controlled size and are measuring their properties. The calculations modeled the sphere as a homogeneous electron gas of finite radius. The local density approximation was used to approximate the effects of exchange and correlation. The ground and excited states were found self-consistently. The calculations were done for spheres of many different radii, partly to investigate whether the "magic numbers," corresponding to exactly filled electron shells, had lower ground state energies or special excitation properties. The collective modes were evaluated up to angular momentum $l = 10$ and over a wide range of frequencies.

A number of new results were found. The static dipole polarizability was found to deviate from the classical formula for a metal sphere. This deviation is due to quantum effects. The response was also found as a function of frequency and angular momentum l . A classical wave vector q can be associated with $q \sim l/R$, where R is the radius. It is found that electron-electron interactions become unimportant and that the free particle picture is valid, for angular momentum above a critical value $l > q_c R$, where q_c is the critical wave vector for a planar surface.

Sum rules correspond to various frequency moments $I_n = \int \omega^n \alpha(\omega) d\omega$, where $\alpha(\omega)$ is the frequency dependent polarizability. These were calculated for $n = 0, 1, 3$ for different angular momenta and are compared with results from simple theories. These sum rules provide an accurate means of estimating the frequencies of the collective modes such as surface plasmons.

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SURFACES AND INTERFACES

MULTILAYER RECONSTRUCTION OF THE NiAl(110) SURFACE

J. R. Noonan H. L. Davis

Over the past several years significant improvements have been made in the various techniques used to determine surface crystallography. For example, low-energy electron diffraction (LEED) analysis has been improved to the point where it is a tool that can now be used to determine distances between atoms in surfaces to an accuracy better than 0.02 Å. This, in turn, has enabled several LEED studies¹⁻⁴ to be performed on monatomic, unreconstructed, metallic surfaces. The results from these studies have clearly demonstrated the existence of an effect referred to as multilayer relaxation. A surface is said to have undergone multilayer relaxation when two or more of the spacings between its atomic layers differ from the spacings that exist in the bulk crystal. These differences between spacings have components perpendicular and, depending on the symmetry of the surface, parallel to the surface plane.^{4,5} Also, since it is now understood that multilayer relaxation is driven by a redistribution of electronic charge at the surface-vacuum interface, its study by LEED provides very important information about interactions between pairs of atoms which are in nonuniform, nonbulk environments.

Recently LEED analysis has also been extended to the study of some binary alloy systems. In particular, results for $Mg_3Al(100)$,⁶ $Pt_{1-x}Ni_x(111)$,⁷ and $NiAl(110)$ ^{8,9} have been reported. Just as the studies of monatomic surfaces provide information about interactions between like atoms, the LEED studies of binary surface systems can provide information about interactions between different types of atoms in nonuniform environments. Thus, in order to obtain as much information as possible about a specific binary surface, it was decided to expand our previous study of $NiAl(110)$, which was limited in that it considered only the crystallography of the outermost layer of this surface.

The ordered $NiAl$ alloy has the CsCl structure in its bulk (i.e., two interpenetrating simple cubic sublattices, one of Ni and one of Al, which form a body-centered cubic structure). Thus, in the bulk crystal a (110) layer consists of equal numbers of alternating rows of all Ni and all Al atoms which are exactly coplanar. However, our earlier study^{8,9} of $NiAl(110)$ indicated that the outermost layer of this surface has a reconstruction such that the Al rows are displaced outward from the surface by 4.6% (relative to the bulk interlayer spacing), while the Ni rows are displaced inward by 6.0%. The result is a rippled reconstruction of the outermost atomic layer.

The previous LEED analysis of $NiAl(110)$ employed a data base comprised of all I-V spectra in 5 sets of beams, with each set composed of sym-

metrically related beams. However, our expanded analysis has employed a data base of all I-V spectra in 14 sets of beams. The topograph of Fig. 1.9 illustrates the dependence of the total R factor when this expanded data base has been compared with spectra calculated for various relaxations of the first layer Ni rows and the first layer Al rows. Note that the best agreement (smallest R factor) between calculated and experimental spectra occurs for the Al rows displaced outward (+) by 5.2% and the Ni rows displaced inward (-) by 4.6%. Since 1% is equivalent to 0.020 Å in interlayer spacing, these new displacement values are in good agreement with the results from our previous study. However, in the present work, results have also been obtained concerning reconstruction deeper into the surface. In particular, it has been determined that the second-layer Al rows are displaced outward by 2% while the Ni rows are also displaced outward by 1%.

Fig. 1.9. R-factor topograph obtained when 14 experimental I-V spectra are compared with spectra calculated for various displacements of the Ni rows, $\Delta d_{12}(\text{Ni})$, and the Al rows, $\Delta d_{12}(\text{Al})$, of the first atomic layer of NiAl(110). Note that the minimum R-factor value of 0.065 occurs for $\Delta d_{12}(\text{Ni}) = -4.6\%$ and $\Delta d_{12}(\text{Al}) = +5.2\%$.

An independent study of the NiAl(110) surface is being conducted by use of medium-energy ion scattering.¹⁰ Preliminary results from this work are in good agreement with the results of our LEED investigation.

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COMPARISON OF CALCULATED AND EXPERIMENTAL SPIN-POLARIZED LOW-ENERGY ELECTRON DIFFRACTION FROM THE Cu(100) SURFACE

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G. K. Walters¹

With the advent of the GaAs-polarized electron source, it is now possible to measure routinely electron-spin dependences in low-energy electron diffraction (LEED). Further, such spin-polarized LEED (SPLEED) data can be obtained in parallel with LEED intensity data with very little increase in effort or total data acquisition time. This ready availability of SPLEED data can provide an additional test of surface theoretical models in that these must correctly predict any polarization effects. Also, theoretical studies indicate that calculated polarization effects are frequently more sensitive to the choice of surface structural details than are calculated intensities.² For these reasons, a detailed theoretical and experimental SPLEED investigation of Cu(100) is under way to explore the utility of SPLEED for structure determinations of surfaces composed of low-atomic-number atoms.

Preliminary results of a detailed SPLEED study of Cu(100) are described here. Cu(100) was selected because a good structural model has already been derived for this surface by a LEED intensity analysis.³ Thus, the SPLEED data provide an additional test of this structural model. In fact, fully relativistic dynamical SPLEED calculations have been performed for the structural model and are in good agreement with the experimental SPLEED data. Calculations are continuing, however, to see whether this earlier structural model can be refined by use of SPLEED data.

The SPLEED apparatus, located at Rice University, is shown schematically in Fig. 1.10. In this apparatus a beam of spin-polarized electrons from a GaAs electron source is directed at the target surface, and the spin dependence of the intensities of the diffracted beams is measured. This spin dependence is specified by means of a spin-asymmetry parameter:

$$A(E) = \frac{1}{|P_0|} \cdot \frac{I(P_0) - I(-P_0)}{I(P_0) + I(-P_0)}, \quad (1)$$

Fig. 1.10. Schematic of SPLEED apparatus used at Rice University.

where P_0 is the spin polarization of the incident beam, and $I(P_0)$ and $I(-P_0)$ are the scattered intensities with the incident electron spins polarized parallel and antiparallel, respectively, to the y axis (indicated in Fig. 1.10). The polarization can be simply reversed, $P_0 \rightarrow -P_0$, without influencing the beam current or trajectory, by changing the sense of circular polarization of the radiation incident on the GaAs photoemitter. This flexibility makes possible simultaneous measurement of the spin-asymmetry parameters and the spin-averaged intensities of the diffracted beams. The beam currents are determined using a movable

Faraday cup. The ac component in the Faraday cup current, which is measured using phase-sensitive detection techniques, gives directly the spin dependence of the scattered intensity [i.e., $I(P_0) - I(-P_0)$]. The average dc current to the cup, which is measured using an electrometer, gives the spin-averaged intensity [i.e., $[I(P_0) + I(-P_0)]/2$].

In Fig. 1.11 are shown the measured spin-asymmetry (A-V) profiles for the (10) and (11) beams from Cu(100) obtained at normal incidence and with the [01] direction in the two-dimensional surface net parallel to the y-axis of Fig. 1.10. The data are represented by the vertical lines of Fig. 1.11, and the length of the line indicates the standard deviation about the mean of the spin-asymmetry at each energy.

The crosses (+) of Fig. 1.11 represent the results of fully relativistic dynamical SPLEED calculations performed using new computer codes specifically developed for this study. These codes first calculate the phase shifts for spin-up and spin-down electrons scattering from a rigid muffin-tin sphere. Effects due to thermal vibrations are then incorporated by use of Eqs. (37) of Feder² (minor typographical errors in these were corrected). Scattering matrices for atomic layers parallel to the surface are obtained by use of Eq. (33) of Feder,² which was corrected according to the footnote in Tamura et al.⁴ Multiple scattering between atomic layers is treated via a spin-polarized version⁵ of Pendry renormalized forward scattering (RFS) perturbation theory.⁶ The desired A-V profiles are then easily obtained via Eq. (11) of Feder.² The calculated A-V profiles presented in Fig. 1.11 were obtained using nonstructural parameters derived from an earlier LEED I-V profile analysis³ (i.e., a surface Debye

Fig. 1.11. Experimental (vertical lines) and calculated (+) spin-asymmetry profiles for the (10) and (11) beams of Cu(100).

temperature of 330 K), a truncated free atom potential with full Slater exchange, an imaginary component of the optical potential equal to 0.85 $E^{1/3}$ eV (with E in eV), and a nonreflecting surface barrier. A total of 49 beams and ten phase shifts were used to calculate the A-V profiles. Tests were performed to ensure that numerical convergence was achieved with the number of beams, the number of phase shifts, the depth that the electron beam penetrated the crystal, and the number of passes of RFS (5 to 7 were typically required).

The theoretical A-V profiles of Fig. 1.11 were calculated for the surface structure that provided the best agreement with the earlier LEED intensity data,³ namely a contraction in the spacing between the top two layers Δd_{12} of -1.45% and an expansion in the spacing between the second and third layers Δd_{23} of +2.25%, relative to the bulk spacing. The agreement between the calculated and experimental A-V profiles is seen to be good; in fact, it is the best reported to date for any SPLEED analysis. Further calculations are, however, under way to illuminate better the sensitivity of the calculated A-V profiles to changes in structural and nonstructural parameters to determine whether SPLEED data can be used to refine the earlier LEED structural model.

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THE TaC(100) SURFACE STRUCTURE

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G. R. Gruzalski

As a part of an integrated investigation of the physical properties of transition-metal carbides¹⁻⁵ at ORNL, studies have been initiated to determine the crystallography of various TaC surfaces by use of LEED I-V analysis. Also, it was decided that TaC(100) would be an excellent candidate for the first crystallographic study, since earlier work² had determined that a well-ordered surface could be prepared in a manner so that it would possess the bulk stoichiometry. Although the measurement of a complete, very detailed data base of LEED I-V spectra is still in progress, an analysis of the data presently available has established that the TaC(100) surface differs significantly from its hypothetical truncated bulk surface. That is, the preliminary analysis indicates that the surface has a rippled (1x1) reconstruction in which $\langle 1 \rangle$ chains of C atoms are displaced outward from their truncated bulk positions while the $\langle 011 \rangle$ chains of Ta are displaced inward.

The TaC(100) sample was cut from a single-crystal boule which had been previously characterized by neutron scattering⁶: the stoichiometry was about 1:1, and the bulk lattice constant was

4.4555 Å. For the present LEED study, the TaC crystal was cut, aligned, polished to expose the (100) face, and inserted in a UHV chamber. Earlier work² had determined that the sample could be cleaned by flashing to ~2000°C for approximately 20 s, and in the present work it was found that after a few such flashings the surface was essentially clean with only a residual amount of oxygen [the O Auger electron spectroscopy (AES) signal, using a cylindrical mirror analyzer, was less than 2% of the C AES signal]. This trace amount of O could not be removed by either ion bombardment or additional thermal flashing to 2600°C; however, it is believed that this residual O would not influence the results of a LEED analysis.

Once the TaC(100) surface was suitably prepared, I-V spectra for five nondegenerate LEED beams were measured using a Faraday cup as a movable retarding field analyzer (in a manner similar to LEED studies of other surfaces⁷). A preliminary analysis was then conducted in which these five experimental I-V spectra were compared with I-V spectra calculated for various structural models of the TaC(100) surface.

Three main types of structural models were considered in the LEED analysis. These were models where the Ta and C atoms of the outermost surface layer were constrained to be coplanar but the spacing between this layer and the next could differ from the value for the bulk spacing, models where the Ta and C atoms were not coplanar but the Ta atoms were displaced outward from the surface more than the C atoms and various displacements were considered, and models where the Ta and C atoms were not coplanar but the C atoms were displaced outward more than the Ta atoms. Some calculated I-V spectra for each of these model types are plotted in Fig. 1.12, where correspond-

Fig. 1.12. Calculated and experimental I-V spectra for the (11) and (12) beams diffracted from TaC(100). The experimental spectra are denoted EXP. The calculated spectra are for models: TUP = Ta atoms displaced outward by 4% (relative to the bulk interlayer spacing) and the C atoms displaced inward by 4%, TB = Ta and C are coplanar and interlayer spacing equal to bulk value, and TDW = Ta displaced inward by 4% and C displaced outward by 4% (best agreement with experiment). The numerical values associated with each calculated spectra are Zanazzi-Jones, single-beam, R factors.

ing experimental I-V spectra are also plotted. The best agreement between the calculated and experimental I-V spectra was obtained for a model where the $\langle 011 \rangle$ chains of C atoms in the outermost surface layer are displaced outward by $\sim 4\%$ (relative to the bulk interlayer spacing) and the chains of Ta atoms are displaced inward by $\sim 4\%$. These displacements of the C and Ta chains create a sawtooth ripple reconstruction of the TaC(100) surface.

Because of the success of the preliminary LEED analysis, a more extensive data base of experimental I-V spectra is presently being collected. It is anticipated that the analysis of a larger data base will not only enable details of the ripple in the outermost surface layer to be determined more accurately but will also allow information to be obtained concerning possible reconstruction in deeper layers of the TaC(100) surface. Be that as it may, the results of the preliminary analysis clearly indicate that the major features of the reconstruction are as illustrated by Fig. 1.13.

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Fig. 1.13. Model of the reconstructed TaC(100) surface which provides the best agreement between calculated and experimental I-V spectra. The $\langle 001 \rangle$ chains are into the paper.

FACTORS IN SURFACE STRUCTURE DETERMINATION BY ION BACKSCATTERING

John H. Barrett

Ion backscattering has become a widely used technique for studying the surface structure of clean crystalline solids.¹ The standard experi-

mental measurement is of one or more angular scans across nonnormal row directions in the crystal. With the aid of computer simulations of the ion scattering processes, any asymmetries that appear in the measured scans are interpreted in terms of the relaxation inward or outward of one or more atomic layers on the surface of the crystal. In some cases, a determination of the thermal vibration amplitude of one or more surface layers of atoms has also been made. However, the ion scattering results involve complicated interrelationships among the surface layer relaxations, thermal vibration amplitudes, and several other factors. Although the relaxations appear to be the only factor that can produce asymmetry in the angular scans, no systematic study has been made of how completely the relaxations can be separated from the other factors (particularly when there is more than one layer involved) or of how well a factor such as thermal vibrations that produces no asymmetry can be separated.

In addition to the inward or outward relaxation of surface layers and the thermal vibration amplitude of the surface atoms, factors that can influence ion scattering from the surface region are the thermal vibration amplitudes of atoms deeper in the bulk of the crystal, correlations of the thermal vibrations, relaxations lateral to the surface in the surface layers, and the ion-atom scattering potential. As a starting point for evaluating the effects of the factors just listed, a computer simulation of an angular scan was done for a standard set of parameters. The standard set was 0.3-MeV He on Au [011], use of the Molière potential, a thermal vibration amplitude of 8.15 pm, no correlations, and bulk termination of the lattice. After doing the simulations for the standard parameters, a series of further simulations were done in which a single factor at a time was altered or added to the calculations. For each set of simulations, two quantities were evaluated. The first was $L(0)$, the surface yield for alignment with the row direction, expressed as the effective number of surface atoms per row. The second was $W(0.4)$, the angular width of the scan at a level 0.4 atoms per row above $L(0)$; this level was arbitrarily selected because it was about the largest increase in level that could be used for all of the simulations. The angular scan for the standard parameters is shown as Curve 1 in Fig. 1.14, as are scans for two altered sets of parameters.

The simulations done with one parameter altered at a time are listed in Table 1.5. The first alteration was an increase in the thermal vibration amplitude; the plot of these results is shown as Curve 2 in Fig. 1.14. The changes produced by this alteration are very much as expected: the level of the yield is raised at all angles and the width of the scan is narrowed. The second alteration was to introduce correlations for the thermal vibrations. Since correlations have effects very much like a reduction of thermal vibration amplitude, this change was expected to, and did, produce changes in the opposite direction to those produced by an increase in vibration amplitude. The third change was an enhancement of the thermal vibrations of the first layer on the surface by a factor of 1.5. The simplest expectation is that an increase in surface vibrations would be similar

Fig. 1.14. Computer simulation of angular scans of the surface yield for 0.3-MeV He on Au [011] using the Molière potential with uncorrelated thermal vibrations and bulk termination of the lattice. Curve 1 is with a thermal vibration amplitude u_1 of 8.15 pm, Curve 2 is with a u_1 of 8.93 pm, and Curve 3 is with a u_1 of 8.15 pm and the first atom offset 5 pm transverse to the row. The points accompanying Curve 1 are the simulation results through which the curve is drawn; only the curves are shown for the other two cases.

Table 1.5. Changes in $L(0)$ and $W(0.4)$ produced by alterations of the standard parameters given in the text. The layer enhancements were by a factor of 1.5, and the pairing was a lateral displacement of the first atom (in opposite directions) for each of two types of rows. The estimated error for $\Delta L(0)$ was ± 0.01 atoms/row and for $\Delta W(0.4)$ was ± 0.05 degrees.

Alteration	$\Delta L(0)$ [at/row]	$\Delta W(0.4)$ [deg]
$u_1 = 8.93$ pm	+0.12	-0.33
Correl. vibrations	-0.15	+0.33
1 layer enhanced	+0.27	+0.13
2 layers enhanced	+0.50	-0.01
5 pm pairing	+0.05	+0.06
HF potential	+0.02	-0.39

to an overall vibration increase; this turns out to be the case for $L(0)$ but not for $W(0.4)$. The fourth alteration of the standard set was to enhance the vibrations of two layers by a factor

of 1.5. Adding the enhancement for the second atom results in a narrowing of the width. The fifth alteration was a lateral offset of 5 pm for the first atom in the row; the plot of this result is shown as Curve 3 in Fig. 1.14. This alteration was introduced for two reasons. The first was to show the effect on the symmetry of a shift of the surface atom lateral to the row by a moderate amount. The second reason was to explore the effect of paired lateral displacements of surface atoms in opposite directions. This pairing means that there are two types of rows, and Curve 3 represents one of the types. The simplest way to get the result for pairing is to average Curve 3 with its mirror image. This was done, and the results are given in the next to last line of Table 1.5. The sixth and final alteration involved using a different atomic potential in the simulations. The one selected was an approximation to the Hartree-Fock (HF) potential for Au made by Robinson.² The results obtained using it, given in the last line of Table 1.5, cannot be predicted in any simple way.

A useful way to characterize the effects of the variables or factors in the model on which the simulation is based is to divide them into separate and merged variables. The separate variables would be ones that produce some effect that can be separated in some way from those of other variables. The merged variables would be ones that produce only effects that are merged with those of other variables. In the results that have just been discussed, the only variable that appears to be separate is a displacement of surface atoms that is transverse to the rows (or with a transverse component) and that is the same for all rows. All of the other variables must be classified as merged. A consequence of the existence of merged variables is that it is virtually impossible to assign any one of them a unique value. For instance, it would appear possible to make a simultaneous introduction of correlations and a vibration amplitude of about 8.93 pm and have a resulting angular scan that would look very much like Curve 1 in Fig. 1.14. If necessary to improve the correspondence with Curve 1, one might adjust the vibration amplitude further while simultaneously including a little enhancement of the vibration amplitude of the first atom in the row or altering the potential somewhat. One might find another combination looking very much like Curve 1 by introducing the HF potential together with some reduction in overall vibrations except for an enhancement of the surface vibrations. It seems clear that variables not causing asymmetry in the scans have their effects so intimately merged that none of them can be given well-defined values. The question of how completely the effects of relaxations can be separated from the effects of the other variables requires more extensive calculations.

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THEORETICAL PREDICTIONS FOR THE SURFACE STATES ON $\text{Ge}(111)2 \times 1$ ¹

Bo E. Sernelius²

The cleaved $\text{Ge}(111)2 \times 1$ surface has two surface state bands, one bonding band below the valence band edge and one antibonding band in the bulk band gap. In pure Ge, the bonding band is filled and the antibonding is empty. These surface states are of technological importance and have attracted much interest. Very recently it has been possible to study the empty surface-state band with direct photoemission.³ For this to be possible, one has to find a way to populate the empty band. This is achieved by using n-doped Ge. In an n-doped crystal, energy is gained if the electrons close to the surface are transferred to the surface state. The charge of the resulting depletion layer and the surface-state charge cause band bending, which counteracts further electron transfer. The transfer continues until the position of the Fermi level is the same at the surface as in the bulk. On n-doped Ge the Fermi level is pinned by the antibonding band, which is now partially filled. For high doping levels the electron spill out from the bulk into the depletion region plays an important role. It produces an internal work function which has to be taken into account in the estimation of the number of electrons that are transferred to the surface state.

We determined the relation between the degree of band filling and the doping level. The relative energy shifts of the two surface states, caused by the band filling, were obtained and found to be large enough to be detected experimentally. These energy shifts are due to many-body effects. Furthermore, the position of the pinned Fermi level can be extracted from the results.

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FRactal MODELS FOR THE AC RESPONSE OF ROUGH INTERFACES¹

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The transfer of electric charge between two dissimilar materials is an ubiquitous process in modern technology, and the impedance at such interfaces plays an important role in their overall electrical properties. In particular, the impedance of the interface between a blocking electrode and an aqueous or solid electrolyte has been investigated for many decades because of its importance in electrochemistry. In the standard textbook theory, the interface is modeled simply by a resistor and capacitor in series.

It has been known since 1926 that real systems do not behave in this simple manner.³ One often finds, at least in a limited frequency range, that the frequency dependence is dominated by a term of

the form $(j\omega)^{-\eta}$, where $j = \sqrt{-1}$ and the exponent $0 < \eta < 1$. In the past decade many investigators have established that the exponent is related to the roughness of the interface.⁴⁻⁸ When the interface is made increasingly smooth, the value of η approaches unity. Efforts have been made to model the unevenness by transmission lines, but these theories predict the simple value $\eta = 1/2$ unless the R and C elements of the line are assumed to have specific spatial dependence.⁹

Since nonintegral exponents often arise from scaling, it is reasonable to examine models wherein the interface is assumed to have fractal structure.¹⁰⁻¹² In this paper we describe soluble fractal models for the ac response of a rough interface.

As a first attempt to understand the relationship between the roughness of the interface and its ac response, we construct a model interface based on the Cantor bar. Imagine a grooved surface where each groove has a structure that subdivides into N branches and the branches are similar to the whole groove when the width is magnified by the factor a , $a > N$. A cross section of this fractal model with $N = 2$ is shown in Fig. 1.15. The model was originally inspired by the observation of de Levie that well-polished metal surfaces exhibit scratches with jagged surfaces.⁵ When in contact with an electrolyte, the latter forms protrusions into the scratches, as modeled by the black part of Fig. 1.15. Although somewhat contrived, the model has the advantage that its ac response can be exactly calculated.

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Fig. 1.15. Cantor bar model of a rough interface between an electrolyte (black) and an electrode (white). Two grooves each with four stages of branching are shown.

When an ac current flows from the electrolyte (black) into the electrode (white), it encounters ohmic resistance in the electrolyte and interfacial capacitance at every segment of the surface. The equivalent circuit of the interface is shown in Fig. 1.16. The circuit branches out at every new stage of the Cantor bar. The resistance increases by a factor of a at every branch because of the reduction in the width of the bar. The

Fig. 1.16. Equivalent circuit for a groove of the rough interface model in Fig. 1.15.

number of interfacial capacitors increases in proportion with the number of branches, but the size of the capacitors remains the same. The common ground represents the electrode.

The low-frequency solution for the impedance of this network is $Z(\omega) = A(j\omega)^{-\eta}$, where A is a constant and $\eta = 1 - \ln 2 / \ln a$. The fractal dimension of the surface can be shown to be $d_s = 2 + \ln 2 / \ln a$. Consequently, the exponent can be related directly to the surface dimension (i.e., $\eta = 3 - d_s$). In the more general case where there are N branches at each stage, $\eta = 1 - \ln N / \ln a$ and $d_s = 2 + \ln N / \ln a$ so that the relation $\eta = 3 - d_s$ remains valid.

Real surfaces do not have the regularity of the Cantor bar. The rough interface is actually a disordered structure. A more realistic model would allow the branching and scaling in the fractal to vary from stage to stage. This can be accomplished by assuming the branching and scaling are random variables. In addition, the surface should be viewed as being composed of many fractal regions, each with a different fractal structure. Since these regions are connected in parallel and since the admittances add, the relevant physical quantity is the average admittance $\langle 1/Z(\omega) \rangle$, where $\langle \dots \rangle$ indicates an average over all the random variables.

For small frequencies the average admittance is found to be $\langle 1/Z(\omega) \rangle = A'(j\omega)^\eta$, where A' is a constant and η satisfies the equation $\langle N \rangle \langle a^{\eta-1} \rangle = 1$. Moreover, the fractal dimension of the surface satisfies a similar equation, $\langle N \rangle \langle a^{2-d_s} \rangle = 1$. Thus, again $\eta = 3 - d_s$.

Since the relationship between the exponent and the geometry is preserved even with the introduction of disorder, this result may be more general

and could be tested experimentally, since η and d_s can be measured independently.

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FRactal Dimension of Koch Curves

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The triadic Koch curve is frequently used in the literature as an illustration of a fractal object. Its fractal dimension is always stated without qualification as $\log(4)/\log(3) = 1.26186$.^{2,3} This is conveniently demonstrated² in the steps used to generate it (Fig. 1.17) by noting that each time a new stage is created from the old one by reducing the side length by a factor of 3, the number of sides is increased by a factor of 4.

Recently we developed several computer codes to measure the Hausdorff dimension of random fractal objects produced in the laboratory, for example, electrodeposits of nearly two-dimensional metal clusters formed under certain conditions. One of these codes designed to measure boundary lengths was tested on a Koch island, and some surprising results were obtained.

Following Richardson,² we measured the coastline of a triadic Koch island by walking dividers (compass) with opening r along the boundary. The measured length is given by $L(r) = N(r)r$, where $N(r)$ is the number of walks. We expected to obtain the fractal dimension $\bar{d}$ from the slope of the graph of $\log[L(r)]$ vs $\log(r)$:

$$\bar{d} - 1 = -d[\log(L)]/d[\log(r)] \quad (1)$$

or from the graph of $\log[N(r)]$ vs $\log(r)$:

$$\bar{d} = -d[\log(N)]/d[\log(r)] \quad (2)$$

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Fig. 1.17. The first four stages of generating the triadic Koch island. The side length of each new stage is 1/3 that of the old stage.

However, as can be seen from Fig. 1.18, the graph of $\log[N(r)]$ vs $\log(r)$ is not a straight line. It consists of steps forming a band. The "slope" of the band has an absolute value of $\log(4)/\log(3)$ which is identical to the number stated as the fractal dimension of the triadic Koch curve. Similar results were obtained for other Koch curves such as a quadric Koch island.

Another method for calculating the fractal dimension is based on a scaling argument³:

$$N(r/f) = f^{\bar{D}} N(r), \quad (3)$$

where f is a scale factor. The fractal dimension calculated from this equation is not constant but has an oscillatory behavior when plotted against $\log(r)$. Only the maximum value of $\bar{D}$ in each oscillation is equal to $\log(4)/\log(3)$.

Our results suggest that, at least, fractal dimensions quoted in the literature need clarification. It is possible that in order to describe a fractal, one needs another parameter besides fractal dimension, for example, a "fractal band width," as suggested by Fig. 1.18.

1. Oak Ridge Associated Universities research trainee from The University of Tennessee, Knoxville, Tenn.

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Fig. 1.18. The log-log plots of the number of walks vs the step length of each walk along the coastline of an island (1) bounded by a triadic Koch curve (circles) and (2) bounded by a triangle (triangles). The dimension of the latter is 1.

RAPID SOLIDIFICATION AND DOPANT STUDIES IN SEMICONDUCTORS

MODELING OF NONEQUILIBRIUM MELTING AND SOLIDIFICATION IN LASER-IRRADIATED MATERIALS¹

R. F. Wood G. A. Geist²

In the work described here, we developed the conceptual foundation, and a mathematical model based on it, for the study of heat conduction and phase change problems associated with the ultra-rapid melting and solidification induced by pulsed laser irradiation of semiconductors.³ The research was stimulated by the inability of commonly available computer programs (e.g., HEATINGS)⁴ to treat phase change problems with sufficient generality. Such programs customarily assume that melting and solidification occur at or very near thermodynamic phase change temperatures and that the introduction of interfacial kinetics into the modeling is unnecessary. The motion of phase interfaces induced by pulsed laser irradiation of materials can be so rapid that this assumption is no longer valid and strong undercooling of the liquid and overheating of the solid must be considered. This capability has been incorporated in our approach by emphasizing the enthalpy rather than the temperature and by the introduction of the state array through which the state of the material in each small volume element (e.g., a finite-difference cell) is continuously monitored and controlled. The state array also allows the simulation of bulk and interfacial nucleation effects, to be included in the modeling. At present, such simulations are handled in a fairly elementary way, but more complex treatments can be incorporated at a later time.

The sample is modeled as a slab extending in the positive x -direction and is composed of any number of materials. The laser pulse is assumed (1) to have a cross section large compared with the depth into the sample for which significant temperature changes occur and (2) to be homogeneous in the energy density (E_L) across any y - z plane; experimentally, (1) is easily realized and (2) can probably be approximated adequately. The basic contents of our approach are contained in the finite-difference (F-D) counterparts of the following equations:

$$\frac{\partial}{\partial t}(\rho h) = \frac{\partial}{\partial x} \left(K \frac{\partial T}{\partial x} \right) + S; \quad \left. \frac{\partial T}{\partial x} \right|_{x=0} = 0; \quad (1)$$

$$\rho L \frac{dx}{dt} = K_L [\text{grad } T]_{l,l} - K_S [\text{grad } T]_{l,s}; \quad (2)$$

$$v = v(T_l, \{Q_l\}); \quad (3)$$

$$A_{jk} = A_{jk}(H_j, T_l, \{C_l\}, \{N\}, \{C\}). \quad (4)$$

Equation (1) is the heat conduction equation and front-surface boundary condition, with h the enthalpy, S the laser energy term, ρ the density, and K the thermal conductivity. The lack of heat loss from the front surface of the sample is known to be a good approximation on nanosecond time-scales. At the back boundary, T is fixed at the initial temperature. That a one-dimensional treatment of the heat flow problem is acceptable as a first approximation is indicated both by the experimental conditions and transmission electron microscopy (TEM) results.

Equation (2) relates the generation rate of latent heat L to $\text{grad } T$ and the thermal conductivities in the liquid (l) and solid (s) at the l - s interface. The assumption that the interface temperature T_l is at the crystal melting point T_C yields the classical Stefan problem, in which the interface velocity, $v = dx/dt$, is determined entirely by heat flow. In a highly undercooled system, this may not be a good approximation, and Eq. (3) indicates that v may be a function of T_l and a set of interfacial rate parameters $\{Q_l\}$. For example, classical crystallization theory gives

$$v = Q_f(T_l) \{1 - \exp[-(L_C/kT_C)(T_C - T_l)/T_l]\}, \quad (5)$$

with k Boltzmann's constant and $Q_f(T_l) = Q_f^* \exp(-\Delta H^{lc}/kT_l)$. ΔH^{lc} is the activation energy for a transition of an atom from the liquid to the crystal. ΔH^{lc} and Q_f^* comprise $\{Q_l\}$ for this simple case.

Equation (4) introduces the elements A_{jk} of the state array, a concept crucial to the implementation of our approach. A_{jk} specifies the conditions under which any F-D cell will make a transition from the j -th state to the k -th. These conditions may depend on the enthalpy H_j of the j -th state, T_l , $\{Q_l\}$, a set of nucleation parameters $\{N\}$, and a set $\{C\}$ that specifies the states of adjacent F-D cells.

As an example, we consider the pulsed laser irradiation of an amorphous (a) Si overlayer on a crystalline (c) Si substrate. The state array distinguishes between c -, a -, and l -phases, fine-grain (FG) and large-grain (LG) polycrystalline (p) Si, undercooled liquid, and "mushy" c -, a -, and FG p-Si. Mushy states describe the material in a F-D cell that is a mixture of liquid and solid, as determined by the enthalpy content of the cell. The input data include K_C , K_S , K_L , L_S , L_C , T_S , T_C , values of a nucleation timer t_n and nucleation temperature T_n , a value of a kinetic timer t_k , various quantities associated with the optical properties of c -, a -, and l -Si and with the laser pulse (shape, duration, and E_L). Some of these quantities are known reasonably well for Si, some have been fixed by previous calculations on c -Si, and some do not influence greatly the calculated results. Calculations were carried out for F-D cell sizes Δx of 50 and 100 Å with time steps $\Delta t < 0.5$ ps.

Figure 1.19 shows the results of calculations designed to simulate the physical phenomenon of explosive crystallization. In this case, nucleation events (indicated by the first appearance of FG material) are confined to a region very near or at the l - s interface. Once a nucleation event occurs, the newly solidified material is allowed to serve as a seed for further growth, thus making additional nucleation events unnecessary.

Fig. 1.19. Melting and solidification of an a-Si layer on a c-Si substrate irradiated with excimer laser pulses of 0.15, 0.2 and 0.4 J/cm². The state array was set up to simulate explosive crystallization. Each letter except the left-most represents a cell size of 100 Å; the surface cell is 50 Å. The letters have the following correspondence: C, A, and L + c -, a -, and normal l -Si, respectively; s + supercooled l -Si; F (L) + FG (LG) p-Si; M + a mushy state.

The first panel on Fig. 1.19 shows what might be described as a pure explosive crystallization process. The laser pulse with $E_L = 0.15 \text{ J/cm}^2$ caused the surface to melt at 15 ns, and the melt front initially just barely penetrated beyond the first cell. After nucleation, the release of latent heat from the nucleated cell drove the melt front into the next cell. Polycrystalline material was allowed to grow off the already crystallized layer at the surface, so that after each new cell melted it could resolidify by using the material in the cell adjacent to it on the surface side as a seed. The second and third panels show the evolution of the solidification behavior as the energy density is first increased to 0.2 J/cm^2 and then to 0.4 J/cm^2 . This behavior can be described as a mixture of normal and explosive crystallization, with the results for $E_L = 0.4 \text{ J/cm}^2$ showing the simultaneous propagation of a buried molten layer into the solid and a more normal return of the melt front to the surface from the initially nucleated cell.

It should be apparent that the techniques described here are applicable to a much wider class of problems than those of laser annealing of semiconductors; the same techniques can be applied to rapid heating and cooling of metals, insulators, and ceramics. Silicon has been emphasized because it was the material entering most prominently in the development of laser annealing. As we have seen, a-Si has a latent heat associated with its melting and solidification that is almost as great as that of c-Si. True glassy materials do not melt or solidify in this way. Because of its great flexibility, our approach should provide a powerful tool for the study of glass transformation in glass-forming materials.

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4. HEATING5 is a recent version of a computer program HEATING that was originally developed by several groups of workers; HEATING is an acronym for Heat Engineering and Transfer in Nine Geometries.

THEORETICAL ANALYSIS OF EXPLOSIVELY PROPAGATING MOLTEN LAYERS IN PULSED-LASER IRRADIATED a-Si

R. F. Wood   G. A. Geist

Amorphous (a) Si, heated rapidly enough to prevent solid-phase crystallization, melts by a first-order phase transition at a temperature $T_m \sim 200 \pm 100^\circ\text{C}$ below the melting point of crystalline (c) Si ($T_c = 1410^\circ\text{C}$) with a latent heat $L_m = 0.73 L_c$.² On melting, Si becomes metallic with the reflectivity R at $\lambda = 633 \text{ nm}$ increasing

by $\sim 75\%$ and the electrical conductivity γ by a factor of ~ 20 . Therefore, nanosecond pulsed laser melting of a-Si (and other semiconductors with similar properties) at energy densities (E_L) just above the threshold for melting results in a highly undercooled liquid (l) whose formation and subsequent behavior can be studied directly by time-resolved electrical³ and optical⁴ measurements. As a consequence, powerful new techniques for studying systems far from thermodynamic equilibrium—a problem of fundamental interest to physicists, metallurgists, and materials scientists—have become available. To interpret the experimental results now appearing, we have developed mathematical techniques and a computer program (LASER8) for modeling the time evolution of highly undercooled liquid-solid systems,⁵ including the effects of interfacial kinetics and nucleation. These techniques were used here in an analysis of the pulsed laser melting of a-Si on c-Si substrates, with particular emphasis on the role of explosive crystallization.⁶

The complex situation the modeling must address is illustrated by transmission electron microscopy (TEM) measurements on thin ($<0.5 \mu\text{m}$) a-Si layers melted by nanosecond laser pulses. For E_L just above the melting threshold, a well-defined layer of fine-grained (FG) polycrystalline (p) Si is formed. As E_L is increased, a layer of large-grained (LG) p-Si appears at the surface and grows at the expense of the FG- and a-layers, until both of these disappear altogether. At sufficiently high E_L , the melt front penetrates the a-c interface and c-Si grows by *i*-phase epitaxy on the c-Si substrate. Thompson et al.³ proposed that the FG p-Si is formed from a thin molten layer that propagates by explosive crystallization. Time-resolved experimental data,^{3,4} which provide important keys for understanding this complex behavior, will be given as we proceed.

The results on Figs. 1.20 and 1.21 are for a 450-nm a-Si layer on c-Si irradiated with a 45-ns KrF laser ($\lambda = 254 \text{ nm}$). The curves of depth vs time were obtained from a form of the computer output which gives the state of every finite-difference (F-D) cell at any specified time.⁵ Figure 1.20 shows that for a laser pulse of 0.2 J/cm^2 the surface melted at $\sim 15 \text{ ns}$, after which the melt front continued to advance for another 10 ns to a depth of $\sim 20 \text{ nm}$. Nucleation then occurred, causing the *i*-Si surface layer to solidify into FG p-Si while a buried *i*-layer penetrated to $\sim 320 \text{ nm}$, leaving FG material behind it. For $E_L = 0.3 \text{ J/cm}^2$, the FG surface layer, formed by the initial melting at $T = T_m$, remelts at $T = T_c$ due to energy input from the laser and from latent heat of the a + c transition associated with the buried *i*-layer. The inset shows R at 633 nm during this time. A multilayer scattering matrix formalism incorporated into the computer program was used to calculate R . The maxima and minima produced by interference of waves reflected from the surface and the buried layer are apparent; they are even more pronounced at 1152 nm because absorption in the solidified surface region is very low at this wavelength. The curves on Fig. 1.21 show that the buried *i*-Si layer is formed for $E_L > 0.3 \text{ J/cm}^2$, but the featureless R trace means that it cannot be detected optically from the front side. It is interesting to note

Fig. 1.20. The time evolution of various states and phases of an a-Si overlayer on a c-Si substrate melted by KrF laser pulses of three energy densities. A calculated reflectivity trace for $E_L = 0.2 \text{ J/cm}^2$ is also shown. FG and LG denote fine-grained and large-grained p-Si, respectively. Other features of the figure are discussed in the text.

Fig. 1.21. The same as for Fig. 1.20, but for $E_L = 0.4$ and 0.6 J/cm^2 . The reflectivity trace is drawn schematically to indicate that the buried layer cannot be detected through the i-Si surface layer.

from Figs. 1.20 and 1.21 that the maximum penetration of the buried i-layer with increasing E_L asymptotically approaches the a-c interface, as observed experimentally. Although, it was not our intention to make a detailed comparison with experiment at this time, the results on the figures are consistent with most of the optical and TEM results.

Simple considerations, verified by the detailed computations, show how the i-Si buried layers propagate. Suppose an a-Si cell is melted by the laser and subsequently satisfies the nucleation conditions. It was assumed in constructing the

state arrays⁵ that a transition from i-Si at $T > T_a$ to FG p-Si at $T = T_c$ is then made. The heat required to raise T by $\Delta T = T_c - T_a$ is $\Delta x \rho C_p \Delta T$ (Δx = F-D cell size, ρ = density, C_p = specific heat), and the latent heat released is $\Delta x L_c$, for a net heat from this cell of $\Delta x(L_c - \rho C_p \Delta T)$. To melt an a-Si cell (with $T < T_a$) adjacent to the nucleated cell on the substrate side requires little more than the latent heat $\Delta x L_a$. For the parameters used in the computer program, $L_c - \rho C_p \Delta T = 1334 \text{ J/g}$ and $L_a = 1318 \text{ J/g}$. Therefore, when i-Si + FG p-Si in one cell, an adjacent a-Si cell will melt, provided the heat released is not conducted away too rapidly. That it is not is determined by two factors. First, the low value of K_a ($< 0.1 K_c$) in the a-Si overlayer⁶ prevents the heat from diffusing rapidly into the bulk of the material. Secondly, the laser input causes the time-averaged grad T to be from the surface to the bulk, even though for brief periods after nucleation in a cell heat flows in both directions. Once a cell has nucleated, a seed exists for the next i + FG transition, which releases more latent heat to melt the next deeper a-Si cell, and so forth. The i-layer propagates until heat is lost by conduction more rapidly than it is gained from latent heat and the laser pulse. Increased heat loss occurs as the buried layer approaches the a-c interface and is responsible for its asymptotic approach with increasing E_L .

The numbers on the 0.3 J/cm^2 curve of Fig. 1.20 indicate features that are readily correlated with experimental results. The melting onset (1) can be compared directly to the measured onset of the high reflectivity and electrical conductivity of the i-phase. The time that the i-layer begins to propagate into the solid, indicated by (2), is of great importance because it marks the formation of the buried layer by a nucleation event. For low E_L , it can be determined experimentally from the R traces; in the modeling it is determined primarily by the nucleation parameters. The maximum penetration of the buried layer (3) is correlated with the maximum depth of FG p-Si, as determined with TEM. This depth is related to a number of physical parameters, but it is particularly sensitive to the interfacial kinetics and the a-phase thermal conductivity. The buried layer velocity is given by the slopes of the relevant parts of the curves on Figs. 1.20 and 1.21. The depth of the LG p-Si (4) is also readily determined from TEM. As already indicated, it was assumed that nucleation in a cell causes the FG layer to grow into the sample via the buried layer, but in addition it was also assumed that LG p-Si grows back toward the surface from the nucleated cell. Although these assumptions appear well supported experimentally, they are easily modified in the modeling if necessary.

We have described a formalism for treating the ultrarapid solidification of highly undercooled liquids and have shown that it can reproduce most of the experimental results reported for pulsed laser melting of a-Si layers on c-Si substrates. The nature of the nucleation process is still not clear. The results on Figs. 1.20 and 1.21 suggest that nucleation occurs at or near the i-a interface, but this is not particularly informative because it is only there that the nucleation conditions are satisfied. Regardless of the

nucleation event, once it occurs, explosive crystallization evidently plays a fundamental role in explaining the experimental observations. To further define this role and shed more light on the nucleation process, it would be very useful to have simultaneous measurements of γ and R so that data are available on the same samples under exactly the same laser irradiation conditions.

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ION DAMAGE CALCULATIONS IN CRYSTALLINE SILICON¹

O. S. Oen

The advantages of ion implantation over other doping techniques used in the fabrication of semiconductor devices have become widely recognized.² The dose tolerances demanded as the microminiaturization of devices progresses necessitate the use of ion implantation. This method of controlling the introduction of dopants has stimulated interest in understanding the lattice damage produced by the implanted ions as well as the details of the implanted profile. It is important to understand the nature of the damage and its spatial extent in order to help develop techniques to remove it efficiently.³ Of particular interest are effects produced by ion channeling. In channeling the ion is constrained to move in the more open avenues of the crystal, thus greatly reducing the probability of violent collisions. As a consequence the ion range is greatly increased and the cascade damage decreased. Almost all the damage or energy loss calculations done to date have assumed the slowing down of an ion in a random or amorphous medium. A major exception is the computer program MARLOWE^{4,5} which can model crystalline, polycrystalline, or amorphous solids. Recently,⁶ there has been an interest in trying to characterize and quantify some of the channeling factors that affect damage production. Once these factors are quantified, it should be possible to design experiments to check the computational models and thereby gain a better understanding of the phenomena.

The present work used MARLOWE to investigate the effects of beam/crystal orientation and of

oxide overlayers on the damage production and implantation profile in crystalline silicon. Light (B) and heavy (Bi) ions with energies from 10 to 100 keV were studied. The Molière⁹ approximation to the Thomas-Fermi interatomic potential with a Firsov¹⁰ screening length was used to describe the binary elastic collisions. The (non-local) electronic slowing down theory of Lindhard et al.¹¹ was used for the inelastic losses. In the simulation program the incident ion is followed collision-by-collision until it either leaves the target or slows down below 15 eV. A typical run consisted of 600-2000 incident projectiles. Thermal displacements of the target atoms were included using the Debye model. In addition to following the incident ion, any Si target atom that is knocked into motion when it receives an energy greater than the displacement energy E_d (15 eV) is followed until its energy drops below E_d . The spatial position of each recoil target atom together with its energy is recorded when its energy falls below E_d . The interstitial-vacancy pairs included here are those whose separation distance is greater or equal to the second neighbor distance. The net effect of incorporating recoil atom transport is to produce a damage profile at greater target depths than that deduced from the energy loss profile of the incident projectile alone.

The calculations show that the effects of channeling on the damage profile are twofold: first, there is a large reduction of the central damage peak; second, there is a component of the damage profile that extends considerably deeper into the target than is found in conventional studies using a random target assemblage. Figure 1.22 illustrates the damage dependence of two different azimuthal angles in the beam/target orientation for 35-keV B incident upon Si(100). Here the beam/target tilt angle was 7°, and the beam divergence was 1° (a critical axial channeling angle of

Fig. 1.22. The number of displaced atoms vs depth for 35-keV B ions into Si(100) for two different tilt angles. Curve (a) here is the same as curve (c) in Fig. 1.23.

3° is estimated from Lindhard's¹² channeling theory). It is seen that the peak in the damage curve (b) is significantly smaller than curve (a). Curve (b), on the other hand, shows an enhancement in the damage tail. The integrated number of displaced atoms in case (b) is 78% of that of case (a). The reason for the differences between the two cases in Fig. 1.22 is due to the planar channeling in case (b) arising from the widely spaced (022) planes. Figure 1.22 shows that an offset angle of 7° , between the crystallographic axis of the sample and the beam direction, used in most commercial implanters is inadequate to assure randomness in device preparation. That is, in addition to an adequate offset angle, one must also carefully select the azimuthal angle of implanting.

The effects of an amorphous oxide overlayer on the damage and projectile penetration profiles are shown in Fig. 1.23. An oxide layer of only 1 nm,

Fig. 1.23. The projectile penetration profile (left) and the damage profile (right) for 10-keV B into Si(100) with amorphous SiO₂ overlayers of various thicknesses. R_N is the fraction of B reflected from the target.

corresponding to about four atomic layers, produces a noticeable change in both profiles, showing that scattering in the amorphous layer reduces the probability of ion channeling in the Si(100) substrate. When the oxide thickness is increased to 20 nm, the damage profile is qualitatively similar to an off-axis tilt of 3° or 7° . In this case it is concluded that most of the ions enter the crystalline substrate at angles that preclude channeling. It is noticed that only a small fraction of the projectiles actually stop in the oxide layer. When the oxide layer is increased from 0 to 20 nm, the location of the peak in the penetration profile decreases from a depth of about 170 to 40 nm. This rather drastic change is due to the appreciable nuclear stopping in the latter

case which is "switched" off in the former under channeling conditions. From the detailed MARLOWE output it is found that the average nuclear energy loss increases from 1/3 to 2/3 of the total energy lost as the oxide layer is increased from 0 to 20 nm. The remaining energy is lost in electronic collisions, which in the model used here, does not depend upon impact parameter. Oxide overlayers are important, not only because of the frequency of native oxide on silicon targets but also because similar results are expected for amorphous silicon overlayers since the masses of Si and O are similar. The latter is of interest since a proposed solution to the inadvertent ion channeling problem in device doping is to implant first with silicon to destroy the surface crystallinity.¹³

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BAND-GAP SHIFTS IN HEAVILY DOPED n-TYPE GaAs¹

Bo E. Sernelius²

It is a well-known fact that the bands in heavily doped semiconductors are shifted in energy due to the presence of the ionized dopant ions and released charge carriers.

The bands are shifted in such a way that the band gap decreases. However, the estimated band-gap narrowing varies among the different types of experiments. The band shifts are, in general, not rigid (i.e., different states are shifted different amounts). This causes a deformation of the density of states, for the conduction and valence

bands. This deviation from rigid band shifts means that the band-gap narrowing deduced from absorption and luminescence experiments might differ, as these experiments involve transitions between different sets of states. In Si and Ge the shifts are, to a good approximation, rigid-band shifts.

We performed a calculation for n-type GaAs within random phase approximation (RPA), taking electron-electron and electron-dopant ion interactions into account. We found that the bands were far from being shifted rigidly. The states at the band edges were shifted more than the states with Fermi momentum. Consequently, the band-gap narrowing deduced from absorption experiments is strongly underestimated. Our results were compared with those from experiments on photoluminescence, cathodoluminescence, and diode-injection luminescence and from absorption measurements. Agreement was found with all the experimental results. Earlier models used to explain the deviation between the positions of the luminescence peaks in the diode and photoluminescence experiments are no longer needed. The differences are fully explained by the deviation from rigid band shifts. Furthermore, we found no indication of nonvertical transitions in the experiments. This is an important observation since nonvertical processes are often assumed to be important and even dominating in the luminescence from heavily doped GaAs.

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BAND-GAP SHIFTS IN HEAVILY p-DOPED SEMICONDUCTORS OF ZINCBLLENDE AND DIAMOND TYPE¹

Bo E. Sernelius²

We derived the band-gap shifts in, and photoluminescence spectra from, heavily p-doped semi-

conductors of zincblende- and diamond-type crystal structure. The calculated final-state lifetimes were taken into account in the derivation of the luminescence peaks. They stem from the imaginary parts of the self-energy shifts due to electron-electron and electron-dopant ion scattering. These were derived within the same formalism as the real parts causing the band shifts. Our results were compared in detail with those from photoluminescence experiments on p-type GaAs. The lifetime broadening was found to explain fully the low-energy tailing of the luminescence peaks. This low-energy tailing is often interpreted as band-tailing effects. One assumes that the spatial fluctuations in the potential from the randomly distributed ionized dopant atoms cause a tail of localized states to develop above the valence-band edge. The intensity in the low-energy side of the peak is then interpreted as due to recombination processes involving these localized hole-states. However, we found that no assumption of band tailing was needed to explain the experimental peak shapes.

The peak shapes agreed to such an extent that a "real" band-gap narrowing could be obtained with the use of the experimental and theoretical peaks. We used "real" to denote the shifts which would be obtained in experiments where no lifetime effects are present. In contrast we used the "apparent" band-gap narrowing to denote the narrowing obtained by extrapolating the low-energy side of the peaks to the background. This is the usual way to extract the band-gap narrowing from the experiments.

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2. SURFACE AND NEAR-SURFACE PROPERTIES OF SOLIDS

Surface-related research has received increasing emphasis in the Solid State Division over the past decade. This reflects both the scientific richness and technological importance of this field. Activities in the division range from fundamental studies of atomic positions at surfaces to the science of advanced surface modification techniques such as ion implantation and laser processing. Powerful new research tools including VUV and soft x-ray instruments at the National Synchrotron Light Source (NSLS) and the 1.7-MV tandem accelerator at the Surface Modification and Characterization (SMAC) facility have been installed and are being utilized by division staff. Productive new research alliances have been formed through interactions with outside collaborators at NSLS and SMAC.

Particular growth is evident in the area of ion-solid interactions. The Surface Modification and Characterization facility is undergoing a major expansion which will double the capabilities of this collaborative research center for ion beam analysis and ion implantation. A major new research initiative, the direct ion beam deposition of thin films at low energies (tens of eV), is providing new opportunities in film growth and interface research at ion energies not previously available. Technological advances in ion implantation for corrosion resistance and more recently for the fabrication of optical waveguides continue to spin off from ion-solid interactions research.

Significant advances are also reported in other areas of surface-related research in the division. New capabilities for photoemission experiments at NSLS will complement a surface science program with established strengths in LEED analysis (see Chapter 1), surface structure, and adsorption. Pulsed laser processing research has achieved a new level of sophistication through direct measurements of overheating and undercooling during laser irradiation of crystalline silicon and the observation of propagating molten layers in laser-irradiated amorphous silicon. Finally, plasma materials interactions research has emphasized erosion and surface modification studies in fusion devices.

SURFACE SCIENCE

A PHOTOEMISSION STUDY OF TaC(001)¹

R. A. DiDio   D. M. Zehner
S. C. Lui²   E. W. Plummer²

While the electronic structures of refractory metal carbides have been calculated using a

variety of methods, there have been relatively few attempts to measure the band structures of these materials. This is partly due to the difficulty in obtaining high-quality single crystals that are stoichiometric, as defect states associated with carbon or metal vacancies yield spectral features not necessarily associated with the bulk band structure. We have used angle-resolved photoelectron spectroscopy with synchrotron radiation in an attempt to measure

the bulk band structure of TaC using a highly stoichiometric³ TaC(001) crystal. In addition, we have investigated the Ta 4f region to determine the effect of charge transfer on surface core levels.

The experiments were performed at the Tantalus I storage ring of the University of Wisconsin-Madison. The TaC crystal could be cleaned quite easily by heating to 2300 K for several seconds, but even at base pressures of $<10^{-10}$ Torr, it had to be flashed at 30- to 60-min intervals because of oxygen buildup. Analysis of x-ray photoelectron spectroscopy (XPS) studies has shown that the stoichiometry of the TaC crystal at the surface is 1:1 and is reproduced using this cleaning method.⁴

Figure 2.1 shows normal emission spectra from TaC(001) for a wide range of photon energies. Angle-resolved photoemission in this configuration should probe the bulk bands of TaC along the ΓX line of the bulk Brillouin zone as photon energy is varied. (Note: TaC has the NaCl crystal structure and, therefore, the Brillouin zone of an fcc crystal.) It is immediately obvious from Fig. 2.1 that the number of peaks observed is, for some photon energies, much more than what would be expected from

theoretical band structure calculations and basic group theoretical principles of angle-resolved ultraviolet photoelectron spectroscopy (UPS). It is also clear that little dispersion is seen in the upper valence band, while theoretical calculations would predict a Δ_{15} bandwidth of 3.7 to 5.7 eV, depending upon band hybridization.⁵

Nondispersion with $h\nu$ is typically associated with two-dimensional features such as surface states/resonances or with highly disordered materials such as might result from a large defect density. It is also possible that strong localization of the hole following photoexcitation can invalidate the single-particle band structure picture. Because of this, we conducted a series of off-normal measurements to determine the true electronic nature of this surface. Angular scans were performed along the high-symmetry directions of the surface Brillouin zone (SBZ) in order to measure any band dispersions as a function of $k_{\parallel}$. In these directions, dispersions were observed, and the spectral features were periodic in $k_{\parallel}$. In addition to these measurements, photon sweeps keeping $k_{\parallel}$ fixed at high-symmetry and nonsymmetry points of the SBZ were also performed. The results of these experiments are the same as for normal emission ($k_{\parallel}=0$): there are no measurable dispersions with $k_{\parallel}$ throughout the surface zone. This fact, coupled with our observations of large dispersions with $k_{\perp}$, indicates that we are observing a true 2-D system. The reason for this phenomenon is not clear, since LEED and XPS indicate that the surface is well-ordered and stoichiometric. If there were a sizable number of random defects, one would not expect to see well-defined $k_{\parallel}$ dispersions. These observations suggest that we are probing a selvage region consisting of several atomic planes that is ordered laterally, yet considerably different from the bulk. Such a region could be produced by simple multilayer relaxations, or even more substantial reconstruction in the top few atomic planes.

Other evidence of a decoupled selvage region is observed in our study of the takeoff angle dependence of emission from the Ta 4f levels.⁶ The results of this study show that the linewidth of the Ta 4f_{7/2} level at near-grazing exit (70°) is at most 50 meV wider than that at near-normal exit (15°), which, given the quality of our statistics and experimental resolution, is probably not meaningful. This fact would be unexpected if there was simple bulk termination at the (001) surface. Because of the large amount of charge transfer from Ta to C for this material (the 4f levels in TaC are shifted by 2 eV to higher binding energy than for pure Ta), the lower number of carbon neighbors for surface Ta atoms should reveal broadening on the lower binding energy side for grazing emission. Indeed, XPS studies of TaC(001) prepared with substoichiometric surfaces show a shift in the Ta 4f levels of 160 meV to lower binding energy with a 10% reduction in the surface C to Ta ratio.⁴ Our results, however, suggest that we are sampling emission from Ta atoms in the same chemical environment, which would imply different reconstructions for the Ta and C atoms

Fig. 2.1. Normal emission energy distribution curves from TaC(001).

both at the surface and in the near-surface region.

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SURFACE STATE DISPERSIONS ON Ta(001)¹

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The Ta(001) surface does not undergo the 2×2 reconstruction that has been extensively studied for W(001),³ its neighbor in the periodic table. It has been proposed that the Fermi level crossing of certain surface states on W(001) can account for the destabilization of this surface to the 2×2 phase.⁴ A recent theoretical calculation by Krakauer⁵ on the Ta(001) surface suggests that the differences between Ta and W can be explained by rigid band behavior. In this picture, the surface state believed to be responsible for W(001) reconstruction is pushed above the Fermi level on Ta(001), explaining the nonreconstruction of this surface. To test the rigid shift hypothesis, we have measured the occupied surface state dispersions of Ta(001) in the high-symmetry directions of the Ta(001) surface Brillouin zone (SBZ). Our results indicate a surface state band that disperses toward the Fermi level from 3.3-eV binding energy at $\bar{\Gamma}$, which is qualitatively similar to one that originates at 4.5 eV on W(001). We find persistent surface states in the region of the Fermi level throughout the SBZ, however, which is also true for W(001). Thus, the rigid shift appears true for one occupied band only. Krakauer's calculation does predict a surface state near the Fermi level at $\bar{\Gamma}$, but does not predict the deeper one at 3.3 eV.

Even though the measured occupied surface state dispersions of Ta(001) do not match theoretical predictions, it should be noted that they are noticeably different from those measured on W(001).⁶ In particular, on W(001), there are clear Fermi level crossings. Therefore, it is still possible that the Ta(001) surface is much more stable with respect to the 2×2 reconstruction in some way because of its surface state structure. Until calculations can at least qualitatively match experimental results, however, the exact mechanism of surface state stabilization or destabilization cannot be determined.

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AN EELS STUDY OF OXYGEN ADSORPTION ON TUNGSTEN (112)

J. F. Wendelken

The adsorption of oxygen on W(112) is characterized by a variety of low-energy electron diffraction (LEED) patterns associated with different coverages of oxygen.^{1,2} A $p(2 \times 1)$ LEED pattern is observed at a coverage of 0.5 monolayer (ML), and then a (1×1) pattern develops as oxygen atoms fill in the remaining equivalent sites as indicated in Fig. 2.2. Further oxygen may then be adsorbed in a second layer leading to a total coverage of 1.5 ML and a $p(1 \times 2)$ LEED pattern. The sites indicated are assumed sites which are consistent with previous studies. The nature of this adsorption system has been further examined here by means of electron energy loss vibrational spectroscopy (EELS).

Figure 2.2(b) shows electron-energy-loss profiles which correspond to the three coverages indicated in Fig. 2.2(a) following oxygen exposures at room temperature. At the low coverage, a loss peak at 82 meV dominates the spectrum, which includes a much weaker peak at 52 meV. At saturation coverage, the lower energy peak becomes

Fig. 2.2. (a) Assumed adsorption geometry for atomic oxygen on W(112) and (b) corresponding electron-energy-loss profiles for oxygen coverages of 0.5, 1.0, and 1.5 ML.

dominant. These two loss peaks, which behave independently, may be associated with two distinct adsorption sites with the first more tightly bound to the surface than the second. This is consistent with an earlier study² which showed the oxygen atoms at low coverage to be immobile at temperatures below 225 K, while the oxygen atoms forming the second layer were mobile at temperatures down to at least 170 K. Both loss peaks shift up in energy when the coverage increases above 0.5 ML, but the behavior of the 82-meV peak is particularly interesting in that its intensity decreases after reaching a maximum peak intensity at 0.5-ML coverage. While dipole-dipole interactions may play a part in these intensity and energy shifts, the most probable cause is surface reconstruction which has been determined³ to be a [111] lateral shift of the top layer of tungsten atoms. If the oxygen atoms in the first ML are adsorbed in bridge sites in the troughs as is generally believed, the bonding site could be strongly affected by the changing substrate geometry leading to a shift in vibrational energy as well as to a decrease in intensity due to a decrease in dipole moment. Although the oxygen adsorption is generally discussed as the formation of one layer followed by a second layer, the vibrational data in most cases indicate that some oxygen atoms are in the second layer before the first layer is complete. It has been shown that the growth of the first layer up to 0.5 ML occurs via an island mechanism. These data suggest that higher density islands may develop concurrently with some oxygen adsorbing in the second layer sites.

Adsorption of oxygen at temperatures down to 100 K was also studied. The same vibrational energies were observed as at room temperature, but an additional loss peak at 125 meV was observed for exposures above 2 L. The intensity of this peak decreased rapidly with higher adsorption temperatures. This loss peak could also be obtained following low-temperature adsorption on a surface preexposed with oxygen at room temperature to give a $p(1 \times 1)$ LEED pattern, but it could not be obtained if the surface was preexposed at room temperature to produce the 1.5-ML $p(1 \times 2)$ structure. The peak is clearly associated with oxygen since substitution of the ^{18}O isotope resulted in an energy shift from 125 to 118 meV. This is the shift expected either for a molecular or an atomic oxygen adsorbate with an infinite mass substrate. The 125-meV peak is close to a known W-O stretching mode of 130 meV and is also close to a range of energies which have been observed for dioxygen-type species on Pt(111), Pt(321), Ag(110), and Cr(110). While the vibrational energy is consistent with an atomic species bonded to a single tungsten atom, the appearance of this species only at low temperatures is not consistent with such a high vibrational energy. Upon heating the surface above 130 K, the intensity of the 125-meV peak was sharply reduced while the two lower energy peaks increased in intensity. This suggests molecular dissociation. The vibrational energy is much lower than the free molecular energy of 195 meV, but that is consistent with oxygen-metal complexes in which electron contribution

to the antibonding orbital of the oxygen molecule reduces the bond order from 2 to nearly 1.5 or 1.0 for superoxo- or peroxo-species, respectively. Comparison of the observed vibrational energy to values in the literature of oxygen-metal complexes does not allow for a positive classification of the molecular species since the deduced bond order is about 1.3. A thermal desorption measurement over this same temperature range revealed no loss of atomic oxygen, while molecular oxygen was observed desorbing quickly upon initial heating. Thus, heating the surface results in a combination of dissociation and desorption.

This study has shown that (1) two atomic adsorption sites occur for oxygen on tungsten (112), (2) the first atomic site occupied is more tightly bound to the surface and plays a significant role in the surface reconstruction, and (3) a molecular oxygen species may be adsorbed at low temperatures provided the first atomic adsorption is already populated and the second atomic site is not.

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AN XPS STUDY OF HYDROGEN-INDUCED RECONSTRUCTION OF STEPPED W(001) SURFACES¹

J. F. Wendelken

The reconstruction of the W(001) surface upon the adsorption of hydrogen near room temperature is one of the most commonly studied surface systems, due to the great variety of reconstruction phenomena which may be observed thereon. Of current interest is the influence of steps on the reconstruction process. The importance of surface steps was apparent² when unintentionally stepped surfaces revealed a different symmetry for the hydrogen-induced reconstruction ($c2mm$) vs the clean-surface reconstruction ($p2mg$), even though both produce nominally the same LEED pattern, $(\sqrt{2} \times \sqrt{2})R45^\circ$. It is now commonly accepted that the initial, low-coverage phase of hydrogen-induced reconstruction is characterized by lateral [100] displacements of tungsten atoms to form dimers which provide adsorption sites for the hydrogen atoms. At saturation coverages, the tungsten atoms move back to their normal positions. Two orthogonal displacement directions are possible in the low-coverage phase and the reconstruction occurs in domains associated with either one displacement direction or the other. It has been shown via LEED studies that (1) steps on a W(001) surface may limit the size of hydrogen-induced reconstruction domains in the direction parallel as well as perpendicular to the steps³ and (2) steps aligned near the [100] result in the selection of one of the possible displacement directions.² Arguments have been advanced for the tungsten dimers to be either parallel to the step edges⁴ or perpendicular to the step edges.⁵ In this study, the

issue of the dimer orientations is addressed by means of electron energy loss vibrational spectroscopy.

Figure 2.3 illustrates the vibrational modes, adsorption geometry, and associated vibrational spectra for hydrogen on W(001) for both the low-coverage and saturation phases. The vibrational spectra of Fig. 2.3(a) were obtained from a "flat" surface (average step separation greater than 400 Å). The wagging and asymmetric stretching modes, ν_2 and ν_3 , which are parallel to the surface are detected with impact scattering rather than dipole scattering and, thus, are better observed off the specular direction as indicated by comparison of the low-coverage spectra on and off the specular direction. At the higher hydrogen coverage the symmetric stretching mode shows a strong downward shift from 160 to 133 meV. The parallel modes also show strong shifts and are reduced in intensity.

The determination of the preferred dimer orientation on the stepped surfaces is based on the observation that if all the dimers are

oriented in the same direction in the commensurate phase, then all ν_2 and ν_3 modes will be aligned in the same directions, respectively. When a mode is observed via impact scattering, it will not be observed if it is perpendicular to a scattering plane which is a plane of mirror symmetry for the surface. Thus, if the electron scattering plane is chosen to be parallel to the step edges and the preferred dimer direction is perpendicular to the step edges, the observed vibrational spectrum should include ν_2 , but not ν_3 . In the case of the saturation (1x1)H phase, the direction of the scattering plane should have no effect, and this was observed to be the case with the stepped surfaces used for these measurements.

Vibrational measurements obtained for a stepped surface with a 30-Å average terrace width and a [100] step alignment are shown in Fig. 2.4. Spectra associated with scattering planes both parallel and perpendicular to the step edges are shown for a series of increasing hydrogen exposures in each case. The bottom

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Fig. 2.3. (a) Electron energy loss spectra obtained with the flat W(001) crystal on and off the specular direction for the commensurate phase hydrogen reconstruction (0.05 L) and off specular for the (1x1)H phase (1 L). (b) Schematic representation of commensurate phase (top) and (1x1)H structures on W(001) surface with vibrational modes indicated.

Fig. 2.4. Electron energy loss spectra vs hydrogen exposure for a stepped W(001) surface with a 30-Å average terrace width and step edges perpendicular to [100]. Scattering planes are parallel and perpendicular to the step edges.

curves correspond to an exposure at which the reconstruction just begins when the surface symmetry switches from $p2mg$ to $c2mm$; the highest exposure is near the maximum development of the commensurate reconstruction phase. It is obvious in these data that v_2 is much more intense in the spectra associated with a scattering plane which is parallel to the step edges. This alone implies that the v_2 mode is aligned parallel to the step edge (i.e., the dimers are perpendicular to the step edges). With such an alignment, the asymmetric stretch v_3 should be most obvious in the orthogonal direction; however, this is not observed. The v_1 loss peak is broadened on the low-energy side for both scattering directions, but most intensely for the parallel scattering direction, where a second peak becomes apparent at the highest exposure. The intensity of this peak grows independently of any significant change in v_1 and is at an energy of 133 meV, which corresponds to the v_1 mode of the saturation phase, hereafter designated as v_1' . Vibrational spectra obtained from stepped surfaces with 68- and 93-Å average terrace widths are similar to the spectra from the 30-Å terrace surface, but with a few differences. In particular, the wagging mode may be detected when the scattering plane is perpendicular to the step edges; however, it is still much more intense for the scattering plane parallel to the step edges. The intensity of the vibrational mode at 133 meV is again greater in both cases when observed in the scattering plane parallel to the step edges. On rare occasions, a weak shoulder near 120 meV, which may be assigned as v_3 , was observed on each of

the wider terrace surfaces at the lowest hydrogen exposures. The appearance of this loss without apparent preference for either scattering plane is probably associated with reconstruction domains which are too small to be affected by the steps.

Observations of the scattering plane dependence of the wagging mode intensity provide clear evidence that the dimers are perpendicular to the step edges and hence that the preferred atomic displacements are perpendicular to the step edges. The same tendency was found for the clean-surface reconstruction of a surface with steps having a [110] alignment.⁶ However, the lack of observation of the asymmetric stretching mode on any of the stepped surfaces when the reconstruction was fully developed is not understood at this time, but may be due to some damping mechanism for this vibrational motion which is perpendicular to the step edges. The mode observed at 133 meV is believed to represent regions of higher hydrogen density which coexist with the low-coverage domains being studied. This mixed phase situation is also observed on flat surfaces, but only after higher exposures. The scattering plane dependence of the 133-meV mode along with the exposure dependence may be interpreted to indicate that high-density hydrogen adsorption is promoted in narrow bands beneath the step edges. With this geometry, the high-density hydrogen regions may be partially shadowed by the step edges, giving rise to the observed scattering plane dependence.

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SODIUM AND OXYGEN COADSORPTION ON Cu(110)

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The study of alkali metal coadsorption with oxygen on transition-metal surfaces has been an area of intense interest for several years owing to the importance of these systems in a diverse range of technologically important areas including thermionic emission and heterogeneous catalysis. This study² makes use of electron energy loss spectroscopy (EELS), low-energy electron diffraction (LEED), and Auger electron spectroscopy (AES) to investigate the coadsorption of sodium and oxygen on Cu(110) and to determine the effect of isochronal anneals on this coadsorption system.

Results from this coadsorption study clearly demonstrate that both the binding of sodium and oxygen on Cu(110) and the structure of the surface change dramatically depending on the temperature of the surface during an isochronal anneal. In particular, an isochronal anneal of Cu(110)/Na/O to 645 K results in a significant shift in the primary vibrational loss feature from 48 to 59 meV as observed in the EELS spectra shown in Fig. 2.5. Comparison of these results with vibrational studies of various sodium oxide species clearly indicates that although sodium and oxygen do not form a surface sodium oxide compound when coadsorbed on Cu(110) at 320 K, a sodium peroxide (Na_2O_2) surface species is formed following the 645-K anneal. This is in agreement with recent results² for the coadsorption of cesium and oxygen on Ag(110), which indicate that a surface cesium oxide species is formed only following an anneal of Ag(110)/Cs/O to 620 K.

Fig. 2.5. Electron energy loss spectra from a Cu(110) surface which has been given a saturation exposure of sodium followed by 0.5 L of oxygen at 320 K and then annealed to the indicated temperatures.

In addition to this apparent change in binding of sodium and oxygen on Cu(110), this same 645-K isochronal anneal gives rise to significant changes in the observed LEED patterns. The weak (1x1) LEED pattern observed following the coadsorption of sodium and oxygen at 320 K shows that no long-range order is present other than that of the Cu(110) substrate. Following the 645-K anneal, a sharp $(2\sqrt{6}\times 3\sqrt{2})R35.3^\circ$ LEED pattern is observed corresponding to two orientational domains with unit cell dimensions that agree within 1% of those found in a room-temperature hexagonal phase of bulk sodium peroxide (Na_2O_2). This provides further evidence for the presence of a sodium peroxide species on Cu(110)/Na/O following an isochronal anneal to 645 K. Another important aspect of this new $(2\sqrt{6}\times 3\sqrt{2})R35.3^\circ$ LEED pattern is the presence of energy-dependent spot splitting indicative of a stepped surface. Careful analysis of the magnitude and energy dependence of this spot splitting indicates that this stepped Cu(110)/Na/O surface is comprised of (111) close-packed step faces that are 2.64 Å high and (110) terraces with an average terrace width of 15.5 Å. Although the step height and terrace width seem to be relatively constant, the direction of subsequent steps (i.e., up or down) appears to be random. The close correspondence of the step height with the ideal 2.55-Å bilayer height for a close-packed (111) step face of copper provides tantalizing evidence that the surface sodium peroxide actually drives the Cu(110) surface to form steps.

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OXYGEN ADSORPTION ON NiAl(110)¹

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As part of a study aimed at determining the adsorption properties of clean NiAl surfaces, the chemisorption of oxygen on the (110) surface was investigated using a variety of surface-sensitive spectroscopic techniques. Clean surface faces were prepared using Ar ion sputtering followed by anneals at $\sim 850^\circ\text{C}$, a procedure that yields a stoichiometric surface region containing a rippled top layer.² No new ordered overlayer structures due to the dissociative chemisorption of oxygen were observed by examining diffraction patterns. Instead, the intensities of the integral-order beams were gradually attenuated with increasing exposure and were completely extinguished following an exposure of ~ 3000 L.

By measuring the areas under the O(1s) core-level spectra, obtained with photoemission techniques, the amount of adsorbed oxygen was determined and is plotted in Fig. 2.6 as a function of exposure. Since no ordered overlayers containing a submonolayer quantity of oxygen were observed, no information regarding coverage

Fig. 2.6. Adsorption of oxygen on Ni(110) and NiAl(110).

could be extracted from the low-energy electron diffraction (LEED) patterns. Similar spectra were obtained following the adsorption of oxygen on a clean Ni(110) surface, and areas obtained using these data also are displayed in Fig. 2.6. The saturation plateau of this curve is believed to correspond to a coverage of two monolayers of oxygen on the Ni(110) surface.³ From a comparison of the two curves in Fig. 2.6, it appears that a similar amount of oxygen was chemisorbed on the NiAl(110) surface. In this case, however, the coverage would correspond to between one and three monolayers, depending on how one defines a monolayer: as one adsorbate atom per substrate-atom pair or per substrate atom, respectively.

Additional information about bonding was provided by examining changes with adsorption in Ni and Al core-level spectra and by comparing these observations with what has been determined previously for adsorption on Ni and Al. For Ni, the adsorption of oxygen and eventual formation of NiO results in large changes in both the binding energy and loss structure associated with the $2p_{3/2,1/2}$ spectra. In contrast, similar changes were not observed for the NiAl spectra; only a decrease in intensity was seen with increasing exposure. An examination of both the Al 2s and 2p core-level spectra showed that new chemically shifted peaks were observed following oxygen adsorption and that the intensities increased with increasing exposure. These chemically shifted core levels are very similar to those observed for adsorption of oxygen on Al surfaces, which is consistent with the formation of Al_2O_3 .⁴

In summary, these data indicate that the sticking probability for oxygen on the NiAl(110) surface is several orders of magnitude lower than that for the pure metals but that even-

tually an oxide layer is formed. Within this layer, the oxygen appears to be bound to Al in a way similar to that observed in Al_2O_3 .

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SURFACE STUDIES OF AMORPHOUS $Fe_{80}B_{20}$ ¹

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In order to complement previous ion scattering studies⁴ on amorphous and crystalline metallic glasses, we have completed an extensive study of the composition and electronic structure of this material utilizing Auger electron and x-ray photoelectron spectroscopies. Both sides of an amorphous ribbon of $Fe_{80}B_{20}$ (Allied Chemical METGLASS .605) were examined. As a consequence of preparation procedures, it might be anticipated that the two sides of the film would differ both in composition and structure. Measurements were also obtained from samples which were annealed for ~20 h at 550°C, which crystallized the bulk as verified by x-ray diffraction.

Auger electron spectroscopy was utilized to monitor surface cleanliness. Small amounts of C and O were always present on the sputtered surfaces. Annealing produced an increase in the amounts of these impurities present and also resulted in the diffusion of P, S, Cl, Si, and N to the surface, all of which could be reduced by ion sputtering. For photoemission measurements, the annealed surfaces were sputter cleaned and annealed briefly to reduce the sputter-induced damage. X-ray photoelectron data were obtained for the B-1s, Fe-2p, Fe-3s, and Fe-3p core levels for both amorphous and crystallized samples.

The composition within the surface region was estimated from the integrated areas under the Fe-2p and -3p and B-1s peaks. Since the peak areas were the same for both sides of the foil and were independent of whether the sample was crystalline or amorphous, sputtered or annealed, an average stoichiometry was calculated. Utilizing empirical sensitivity factors,⁵ a nominal composition of $Fe_{85.2}B_{15.2}$ was obtained. Using calculated atomic sensitivity factors,⁶ a composition of $Fe_{76.2}B_{24.2}$ was obtained. These estimated compositions bracket that expected from the bulk composition. In addition, since the Fe/B ratio did not change with sputtering or annealing and the Fe-3s/Fe-2p and Fe-3p/Fe-2p ratios were the same for pure iron and the foils, it seems unlikely that significant segregation or preferential sputtering has occurred.

There were no significant differences in the Fe core-level binding energies between the two sides of the foil or between the crystallized and amorphous phases. The binding energies obtained from the alloys are essentially the

same as for pure iron, with the exception of the Fe-3p level, which is consistently shifted to slightly higher binding energies in the metallic glass. The B-1s core level exhibited a slight shift (0.3-0.4 eV) to higher binding energy when the amorphous material was annealed overnight. This peak tended to shift back to lower binding energy when the annealed material was subsequently sputtered; a result which suggests that the electronic structure of the B on the sputtered surfaces is independent of whether the bulk is crystalline or amorphous. The binding energy shift induced by crystallization is small and is probably due to structural changes.

The valence band x-ray photoelectron spectra from the foils are dominated by a major peak at ~1 eV, which is due to the Fe-3d bands. The energy, shape, and width of this band are independent of whether the surfaces were sputtered or annealed, amorphous or crystalline. A weaker feature was observed at ~9 eV in spectra obtained from sputtered surfaces of both the amorphous and crystallized materials and is due primarily to B-2p levels mixing with the Fe-3d bands.

In summary, no differences are observed in the composition or electronic structure between the two sides of the foil. There is no evidence for segregation in either the amorphous or crystalline materials. The results presented here and previous ion scattering results, which indicated that crystallization did not alter the atomic scale roughness, are in agreement with earlier catalytic measurements which observed little change with surface treatment.

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ENERGY DISTRIBUTIONS OF ELECTRONS PRODUCED BY H-LIKE AND He-LIKE MULTICHARGED ION IMPACT ON Au AT GRAZING INCIDENCE¹

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In an experiment designed to investigate the feasibility of studying ion-surface interactions using the ORNL electron cyclotron resonance (ECR) multicharged ion source, we have measured energy distributions of secondary electrons produced during collisions of H-like and He-like light ions with the (110) surface of gold at grazing incidence. The study of multicharged ion-surface interactions is of considerable interest, in large part due to the significant neutralization potential energy that multicharged projectiles carry into the collision. Experiments studying

reflected ion charge state distributions and secondary electron emission coefficients for collisions with W surfaces have been reported.^{6,7} The present experiment is the first to investigate the energy distributions of secondary electrons produced during multicharged ion-surface collisions.

Beams of N³⁺, N⁶⁺, O⁶⁺, and O⁷⁺ were produced by the ORNL ECR ion source at 10-keV source potential. After charge selection and beam collimation, the ions were made incident at 5° on the (110) surface of a gold single crystal mounted in an ultrahigh vacuum chamber equipped with a 4-grid low-energy electron diffraction (LEED) system. The condition of the Au surface was determined by electron-induced Auger spectroscopy and the observation of LEED patterns. In addition, the energy distributions of the multicharged ion-induced secondary electrons were obtained by using the LEED grids in the retarding field mode and numerically differentiating curves of the transmitted secondary electron current vs retarding voltage.

Figures 2.7(a) and 2.8(a) show the secondary electron spectra observed for N⁶⁺ and O⁷⁺ incident projectiles. Both spectra show two peaks superimposed on a "kinetic emission" background having a monotonic energy dependence. The higher energy peaks at 350 and 480 eV in the case of N⁶⁺ and O⁷⁺ induced spectra, respectively, are believed to be associated with Auger decay of the K-shell vacancy in the H-like projectile via

Fig. 2.7. Secondary electron energy distributions for N⁶⁺ and N⁵⁺ incident on Au(110) at 5°, q=10 keV projectile energies.

Fig. 2.8. Secondary electron energy distributions for O^{7+} and O^{6+} incident on Au(110) at 5° , $q=10$ keV projectile energies.

electrons in highly excited states. These high-lying states are populated during the collision by resonance neutralization from the valence band of the solid. The lower energy peaks at 250 eV occur at the same energy in both spectra and are believed to be associated with Auger decay of a target-atom inner-shell vacancy created during the collision.

Secondary-electron spectra were also measured for N^{5+} and O^{6+} incident projectiles, whose ground-state configurations have filled K-shells. Although the latter spectra shown in Figs. 2.7(b) and 2.8(b) were dominated by the "kinetic emission" background, the same peaks observed for the H-like incident ions could be discerned, albeit greatly reduced in size. These spectra indicate that a small fraction of the He-like ions extracted from the ECR source are created in $1s2s$ metastable states. Since these metastable ions necessarily have K-shell vacancies, the secondary electrons they produce during surface collisions manifest the same Auger peaks as were observed for the H-like ions.

Within the $\pm 30\%$ uncertainty of the measurement of the incident ion flux to the crystal target, the area under the two peaks for both H-like incident ions corresponds to one electron per incident ion. The areas under the peaks were estimated by subtracting the measured

electron energy distributions for the He-like ions from the corresponding ones of the H-like ions, since it has been shown⁸ that the energy distribution for a given ion is "included" in that for the ion of next higher charge state as a result of the stepwise neutralization of the ions at the surface. The unit probability for filling the projectile K-shell vacancy suggested by the above electron yield is not surprising, since the projectile-based K-shell Auger process is not constrained by the ion-surface interaction time. This feature may, however, be very useful in normalizing the probability of target inner shell processes during the collision that compete with the projectile Auger transitions in filling the projectile K-shell vacancy. From the ratio of peak heights, we estimate that the probabilities of the 250-eV target process occurring are 0.32 and 0.19 for incident N^{6+} and O^{7+} , respectively.

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ION BEAM PROCESSING

LOW-TEMPERATURE EPITAXIAL DEPOSITION OF ^{30}Si AND ^{74}Ge BY ION BEAM DEPOSITION (IBD)

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There is considerable scientific and technological interest in developing a technique capable of epitaxial deposition of Si and Ge at temperatures lower than 900°C . Recent experiments have shown that IBD is capable of this for both semiconductor and metal films.

Epitaxial growth of ^{74}Ge on Ge(100) by IBD. Ge(100) single crystals were sputter-cleaned with 500-eV ^{74}Ge ions and then annealed at 600°C for 60 min in vacuum. ^{74}Ge ions were then deposited at 40 eV with a background pressure of 10^{-10} Torr that rose to 10^{-9} Torr once the ion beam was present in the deposition chamber. With the temperature of the Ge substrate held at 400°C during deposition, the ^{74}Ge films were found to grow epitaxially with the underlying substrates. Subsequent room temperature ion channeling analysis of the epitaxial film indicated a 3.9% minimum yield for the [110] direction, which is comparable to the 3% minimum yield obtained for perfect single-crystal Ge

(Fig. 2.9). Further experiments exploring the effects of ion energy and substrate temperatures are under way. The possibility of heteroepitaxy of Ge on Si(100) by IBD is also being explored, despite a lattice mismatch of 4.2% that has led to failure with conventional techniques, such as MBE, that rely only on thermal effects. It is possible that the nonequilibrium nature of the IBD process may permit this type of heteroepitaxial growth.

Epitaxial growth of ^{30}Si on Si(100) by IBD. The epitaxial growth of ^{30}Si on Si(100) has been explored as a function of surface preparation, deposition temperature, and ion beam energy. Because of the possibility of using the incoming ion energy to enhance atomic surface mobility without introducing thermal energy in the system, IBD offers the possibility of epitaxial growth at lower temperatures than expected from a thermodynamic point of view. This capability is crucial for the fabrication of future macro-integrated semiconductor and optoelectronic device structures. However, a clean, ordered surface is still needed to induce epitaxy. Therefore, some of our efforts have been devoted to the development of surface preparation techniques that do not require the high-temperature cycling ($>900^\circ\text{C}$) usually found necessary to reorder silicon surfaces after sputter-cleaning by 0.5–3 keV noble gas ions. We have found that reactive ion cleaning using 20-eV ^{37}Cl bombardment with the sample held at 600°C allowed good epitaxy to occur. Figure 2.10 shows the random and the ion channeling spectra of an IBD deposit of ^{30}Si at 40 eV on Si(100) held at 600°C after such a cleaning treatment. Good epitaxy has clearly been obtained without high-temperature annealing at any stage of the preparation. Recent experiments have shown that good epitaxy can be achieved at 400°C with 20-eV deposition

Fig. 2.10. Random and channeling spectra of 130-nm IBD ^{30}Si on Si(100) at 40 eV, 600°C . Prior to deposition the surface was sputtered with 20-eV ^{37}Cl at 600°C .

energies. We have also observed an unexpected dependence of epitaxy on the doping of the Si substrate. N-type Si crystals have shown good epitaxy (20 eV, 400°C) while P-type Si deposited under identical conditions were found to be amorphous. Further experiments are under way to determine the dependence of energy, temperature, surface cleaning, and substrate doping on the epitaxial process. Experiments involving other homoepitaxial and heteroepitaxial systems, possibly unattainable by other techniques, are also scheduled.

ION BEAM DEPOSITION TECHNIQUES

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Fig. 2.9. Random and channeling spectra of 40-nm IBD ^{76}Ge on Ge(100) at 40 eV, 400°C . Prior to deposition the surface was sputtered with 500-eV ^{76}Ge and annealed for 60 min at 600°C .

There is widespread interest in the semiconductor industry in manufacturing techniques capable of depositing pure, adherent films and epitaxial overlayers at low substrate temperatures with minimal damage to the underlying structure. This is reflected in the flurry of activity in recent years in the development of molecular beam epitaxy (MBE) and chemical vapor deposition (CVD) techniques for the fabrication of artificially structured materials. Although direct ion beam deposition (IBD) techniques have been known for years and have been examined at several laboratories recently,¹⁻⁷ progress has been hampered by the lack of a reliable, efficient, and uniform source of ions and controlled deposition conditions. In this laboratory we have developed an IBD system which for the first time combines (1) mass-and-energy-analyzed beams from an ion implantation accelerator, (2) a deceleration lens system integrated into an ultrahigh vacuum (10^{-10} Torr) deposition and analysis chamber, and (3) a sample arrangement

which allows for in situ cleaning, annealing, and sample heating during deposition. The ORNL IBD system is shown schematically in Fig. 2.11. A beam of ions is extracted from the ion source at 35 keV and is analyzed to select a single monoenergetic isotopic species. The beam is passed through a 7-deg deflection system to remove neutral particles and to induce vertical and horizontal scanning for uniformity. It then passes through three stages of differential pumping and enters the UHV chamber through a 20-mm aperture. The base pressure in the deposition chamber is 10^{-10} Torr and rises linearly with beam intensity to typically 10^{-9} Torr during deposition. The deceleration lens system consists of three electrodes: the first is a grounded aperture slightly larger than the incident beam; the second is biased at -1 keV to suppress secondary electrons; and the third, which supports the target holder, is connected via a shielded cable and a variable voltage supply to the ion source high voltage. The final energy of the ion beam is determined from the bias voltage of the power supply between the ion source and the target. This technique eliminates energy variations that could be introduced by voltage fluctuations in the ion source power supply and is an important feature for good energy definition. The present system can produce isotopic beams of most species at ener-

gies from 10 to 1000 eV and currents from 3 to 50 μ A depending on operating conditions. This system is a preliminary design that will be upgraded in the coming year.

The ability to deposit materials in UHV directly from an ion beam that is mass and energy analyzed presents several attractive features. Accurate control of deposition energies ensures control of substrate damage and favors a high uniformity of the deposit. The precise selection of the deceleration voltage allows optimization of the ion energy to avoid detrimental effects such as ion self-sputtering⁷ or to favor desirable ones like enhanced surface modification. For the latter case, the use of the ion energy rather than thermal energy to promote layer reordering may permit epitaxial growth to occur at lower temperatures than other techniques, such as MBE. The use of an ion implanter also provides complete versatility in selecting the deposited species and accurate control of the deposited dose.

The possibility of switching from one ion to another during deposition, the accuracy of the dose, and the occurrence of epitaxial growth at low temperatures make IBD especially suited for the preparation of isotopic heterostructures and quantum wells for electronic and optical devices. For more fundamental studies, the fact that IBD films are monoisotopic provides new

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Fig. 2.11. Schematic diagram of the IBD system developed at ORNL.

opportunities to explore major issues in materials research. For instance, IBD of the Si isotope of mass 30 on a Si single crystal (mass = 28.086 amu) allows mass separation by ion scattering between the deposit and the substrate. This unique feature provides an opportunity for the study of mass transport and atomic redistribution at the $^{30}\text{Si}/\text{Si}(100)$ interface during the epitaxial growth which occurs while deposition is taking place or the solid-phase regrowth induced under subsequent annealing. To explore these possibilities, the IBD of Ge^{74} and Si^{30} layers on $\text{Si}(100)$ was studied as a function of energy, dose, and substrate temperature. The first deposited layers were found to be perfectly continuous, indicating a layer-by-layer growth instead of islanding, and showed a bulk-like atomic density (4.46×10^{22} at/cm³ for Ge^{74} and 5×10^{22} at/cm³) in films that could be made as thin as 3 nm.

The interface width between the deposits and the substrate, measured by cross-section TEM, was found to be less than 1 nm for all the IBD conditions used. These characteristics were found to be the same for films grown at 40 and 200 eV. This is in agreement with the range straggling values obtained with the Monte Carlo simulation code TRIM. The number of defects created by Si and Ge ions was found to decrease rapidly with energy, but anomalous damage behavior was observed at 700 and 900 K. (A detailed analysis of the damage creation in single-crystal substrates for the present IBD experiments can be found in reference 7.) Figure 2.12 shows the first Ge/Si monoisotopic heterostructure achieved by IBD. Cross-section TEM and ion

channeling measurements established that the properties found for the deposits mentioned above were also obtained in this more complex structure: sharp interface definition, good lateral uniformity, accuracy of the dose, and high compositional purity. These results verify that IBD has the expected potential.

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EPITAXIAL GROWTH OF ^{57}Fe FILMS ON SILVER BY IBD

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The ion beam deposition (IBD) system¹ has been used to produce epitaxial (001) ^{57}Fe films on Ag (001) substrates. The ^{57}Fe was deposited at 40 eV on Ag films held at 200°C. The ^{57}Fe films grow with (001) parallel to the (001) surface of the Ag, but with the Fe (110) parallel with (100) of the silver. This 45° rotation of the iron with respect to the silver leads to a 0.8% mismatch between the lattice spacing of Fe(110) and Ag(100) in contrast with the ~30% mismatch which would occur for a parallel orientation, i.e., Fe(100) parallel to Ag(100). These orientation relationships were established by ion channeling in which [001] axial channeling is observed for both the Fe and the silver, [110] axial channeling of the Ag is accompanied by (110) planar channeling of the iron, and as shown in Fig. 2.13, [111] axial channeling in the iron is accompanied by (100) planar channeling in the silver. These results were further confirmed by TEM observations which showed that microtwins in the silver films were propagated as microtwins in the iron films. This latter observation suggests that good epitaxy of iron on silver is not limited to the special case of the (001)-oriented substrate.

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IRRADIATION DAMAGE FROM LOW-ENERGY IONS

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Irradiation damage produced in $\text{Si}(100)$ by deposition of ^{74}Ge and ^{30}Si ions at energies below 200 eV has been studied by ion channeling

Fig. 2.12. Ge/Si multilayer obtained by IBD with 65-eV ions at 300 K.

Fig. 2.13. Random and channeling ion scattering spectra of $^{57}\text{Fe}/\text{Ag}(100)$ heterostructure along the $[111]$ direction of Fe [also aligned with (100) of the Ag].

and transmission electron microscopy (TEM). The amount of damage measured by ion channeling is the number of atoms displaced from normal lattice sites in the Si substrate after deposition. The dechanneling due to the ion beam deposition (IBD) layer is taken into account, and its contribution to direct backscattering is corrected for in the data. TEM measurements of the damage localization showed that in cases where the damage peak width was within the ion scattering resolution, the damage measured in the Si substrate was confined within a 1-nm interface region between the IBD layer and the Si substrate [Figs. 2.14(s) and 2.15(a)]. This was found to

occur when the deposition energy was less than 150 eV. Comparison of the damage values obtained as a function of energy for similar doses shows that the damage decreases with energy. For 200-eV Ge, TRIM Monte Carlo simulation shows a damage distribution no deeper than 2.5 nm in Si while both the TEM and the ion scattering measure a depth of 30 nm. At 150 eV, we find 26 nm instead of the computed value 1.2 nm. A difference of more than an order of magnitude is surprising since the depth distribution of the implanted ions has been found to agree with the simulation.

Several observations seem to confirm the occurrence of radiation-enhanced defect mobility. The accumulated damage and the defect distribution depend on the substrate temperatures during IBD. If one compares the results for 65-eV Ge at room temperature and at 685 K, one finds that the damage in the Si substrate drops from 1.4 displaced atoms/ion to 0.2 displaced atom/ion for the same IBD dose. The effect is also observed for Ge and Si at 40 eV, although the damage found in the substrate at room temperature decreases by an order of magnitude from 65 to 40 eV. Heating the substrate thus helped to annihilate part of the defects produced during the irradiation. However, cross-section TEM done on layers deposited on a substrate held at 685 K [Figs. 2.14(b) and 2.15(b)] revealed a region of defect accumulation below the surface at a depth of ~60 nm with no observable damage in the surface region. This damage was distributed over a depth of 70 nm for 40 eV ^{30}Si [Fig. 2.14(b)], thus showing up as far as 130 nm from the interface. The number of displaced atoms is about 1×10^{12} at/cm² in the case of 40-eV ^{30}Si for a dose of 7.5×10^{16} at/cm² and 5×10^{14} at/cm² in the case of 65-eV ^{74}Ge [Fig. 2.15(b)] for a dose of 1.3×10^{16} at/cm². These data indicate a long-range diffusion of a small fraction of the defects produced in the substrate during IBD. To separate the annealing

Fig. 2.14. (a) Cross-section TEM micrographs of ^{30}Si on Si(100) IBD at 40 eV at room temperature. (b) Same conditions as in (a), except that the substrate was held at 685 K.

Fig. 2.15. (a) Cross-section TEM micrographs of ^{74}Ge on $\text{Si}(100)$ IBD at 40 eV at room temperature. (b) Same conditions as in (a), except that the substrate was held at 685 K.

effect from the irradiation influence, ^{30}Si layers deposited at room temperature were annealed at 700 and 900 K after deposition. However, no defect redistribution was detected, showing that the defect region found in the substrates heated during IBD resulted from the combined effect of irradiation and annealing.

The buried damage layer was observed consistently in all the heated IBD depositions, even in the cases where the deposit was epitaxial. Preliminary sputtering between 20 and 500 eV did not modify its occurrence or characteristics. The damage layer was never observed for room temperature deposits. Experimental evidence supports the hypothesis that the damage production mechanisms at work are specific to very low-energy ion bombardment. The mobility of these defects, which is apparent only if the crystal is heated at 400°C and above during irradiation, suggests that intrinsic defects are injected in the crystal during irradiation and can then diffuse. Interstitials in Si are known to be mobile at all temperatures. Parallel experiments on P-type and N-type silicon are presently being done to study this hypothesis, while computer simulations of atomic collisions in solids are being analyzed to determine the role of low-energy ion channeling, replacement sequences, and defect generation.

THERMODYNAMIC CONSTRAINTS ON LOW BEAM MIXING OF METALS ON INSULATORS¹

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Previous work has established that ion irradiation of certain metal films on insulators leads to ion beam mixing while lateral segregation and agglomeration occur for other systems.⁵ These results were explained in terms of the heats of formation of the products relative to those of the reactants. Mixing was observed

when the heats of formation of the products is less than those of the reactants; otherwise, agglomeration was observed. This is referred to as the enthalpy rule of ion beam mixing.

To determine whether the enthalpy rule appears to be generally valid and can be used to predict whether mixing will occur for a given system, experiments were carried out using a variety of film-substrate combinations. Rutherford backscattering (RBS) measurements and scanning electron microscopy (SEM) analyses were used to determine the extent of mixing and the changes in the surface topography.

The film-substrate combinations which have been examined are given in Table 2.1. In each case the film was 100–300 Å thick, and Xe was used as the bombarding projectile at a dose of $1 \times 10^{16}/\text{cm}^2$. Also indicated in Table 2.1 is the observed behavior as a result of ion irradiation. Systems which have unfavorable heats of formation show only limited ballistic interface mixing (IM in Table 2.1), no mixing (NM), or film agglomeration (SA). Those systems for which the heats of formation are favorable show substantial evidence for mixing (M) and in some cases even M where a well-defined stoichiometry is observed [stoichiometric mixing (SM)]. In almost all cases the results are in accordance with the enthalpy rule. The clearest exception is for the case of Cr on SiO_2 , where no M is predicted. In this case, M is observed at room temperature. However, if ion irradiation is carried out at elevated temperatures (660°C), the system "demixes." A number of systems in Table 2.1 remain to be evaluated, but the results to date suggest that equilibrium thermodynamic considerations have a greater influence on determining the phase formation than the non-equilibrium aspects of ion bombardment.

1. Summary of paper: p. 137 in *Ion Beam Processes in Advanced Electronic Materials and Device Technology*, ed. by B. R. Appleton, F. H. Eisen, and T. Sigmon, Materials Research Society, Pittsburgh, Pa., 1985.

Table 2.1. Mixing map. The table shows the substrates and films examined according to the interfacial reaction observed. X = system not completed; SA = segregation-agglomeration of the film; SM = stoichiometric mixing; NM = ballistic mixing; NM = no mixing, no change in the RBS spectra; ? = ambiguous identification; M = mixing.

Substrate film	Al ₂ O ₃ (s.c.) ^a	ZrO ₂ (s.c.)	SiO ₂	YPO ₄ (s.c.)	SiC (s.c.)	Si ₃ N ₄
Ni	X	X	X	X	M	NM
Au	NM	X	X	X	X	
Cu	SA	SA	SA	SA	SA	
			M (20°C)			
Cr	NM	NM	NM (600°C)	NM	M	
Ti	NM?	NM	M	NM	X	
Zr	NM	X	M	X	X	
Si	NM	M	X	NM	X	
Nb	SM	X	M	X	X	
Pd	SA	X	SA	X	X	
V	SM	X	X	X	X	
W	NM	X	SA	X	X	
Al	X	X	NM?	NM	SA	
Ta	X	X	SM	X	X	

^aSingle crystal.

2. Present address: Wright State University, Dayton, Ohio.
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4. IBM, Yorktown Heights, N.Y.
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EFFECTS OF DIFFERENT METHODS OF CALCULATING MIXED DEPTH UPON THE MIXING RATES DURING ION BEAM MIXING¹

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The dose dependence of the thickness of the mixed layer produced by ion beam mixing of metals on Si is usually reported as being either linear or parabolic. Occasionally the dose dependence of the same metal/Si systems is reported differently by different experimenters. The authors previously reported linear dependences of several metal/Si systems that had been characterized by others as parabolic.² In an effort to determine the causes of the divergent results, several methods of calculating the mixed depth were examined, and a comparison of the same data analyzed by different methods was performed.

Data representing the mixing of a metal on Si to several depths were simulated. Both stoichiometric and diffuse mixing were simulated, with and without the simulation of the effects of detector resolution. The mixed depths were then calculated from these data using the following methods: integrated area, half-height, error function, 10-90%, and moment.³ While all of the methods were accurate for data that did not include effects of the detector resolution, only the moment method showed immunity when the resolution was of the same order of magnitude as the

mixed depth. The effect of increasing resolution was to increase the power law dependence of the integrated area method, to have no effect on the moment method, and to decrease the power law dependence of the other methods.

The experimental data of the mixing of Au, Pd, V, Cr, and Pt on Si were reanalyzed by these methods. The dose dependences of ion beam mixing of Au, Pd, and V were consistent with the previously reported results. All showed nearly linear mixing by all of the methods. However, Cr on Si showed a linear dependence by the integrated area method, but showed nearly parabolic dependences by the other methods. This is probably a result of the detector resolution, which was noted to increase the power law of the integrated area method, compared to the other methods. Finally, the results of Pt on Si showed nearly parabolic dependences by all methods. These results indicate that it is possible to determine erroneously the dose dependence of ion beam mixing by using a calculation method that is sensitive to the detector resolution, such as the case of Cr on Si. Therefore, the use of the moment method is recommended, since it shows the greatest immunity to these effects.

1. Summary of paper: p. 171 in Ion Beam Processes in Advanced Electronic Materials and Device Technology, ed. by B. R. Appleton, F. H. Eisen, and T. Sigmon, Materials Research Society, Pittsburgh, Pa., 1985.

2. D. B. Poker and B. R. Appleton, J. Appl. Phys. 57, 1414 (1985).

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MIXING AND AMORPHIZATION OF Al_3Ni BY BOMBARDMENT WITH ENERGETIC PARTICLES¹

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The present study forms part of a broader program in which phase stability and ion mixing across the whole composition range of the Ni-Al system was investigated for several parameters that could potentially affect the outcome when such systems are bombarded with ions.^{5,6} Although certain structures, namely the α and Ni_2Al_3 , were not stable under bombardment (these two transformed to α and β' ,⁶ respectively), amorphization was observed only for the composition range near Al_3Ni . More recent experiments have concentrated on the detailed study of this amorphization process.

As before,⁵ thin-film sample materials were produced by vapor deposition of alternating layers of Ni and Al by a technique that provided for control and selectivity of the average concentration of the film. Average concentration of samples used in the present experiments was $\text{Al}_{77}\text{Ni}_{23}$. Heating of as-deposited films at 623 K for 1 to 2 h (equilibration) produced homogenization with formation of the compound, Al_3Ni plus Al, as expected. Samples were bombarded with either $1.3 \times 10^{16}/\text{cm}^2$ of Ne ions at 60 keV or $2 \times 10^{15}/\text{cm}^2$ of Xe ions at 300 keV. These dose-energy combinations were chosen to produce the same calculated damage energies for the two types of bombardment, the calculated displacements per atom (DPA) level being about 17 for both. Detection of structures present was by transmission electron diffraction.

Table 2.2 summarizes results of these experiments. The most obvious point is that the equilibrium structure was not produced for any particle/temperature combination by ion bombardment of the as-deposited films. Instead the amorphous structure always stood in place of the equilibrium phase, Al_3Ni . If the equilibrium structure preexisted, however, amorphization of the Al_3Ni part occurred at low but not at high temperatures, and room temperature was the

approximate crossover point. At room temperature complete amorphization occurred for Xe but not for Ne. Although some amorphization occurred for both Xe and Ne at 373 K, amorphous zones for Ne were rather sparse. Degree of amorphization for Xe was about the same as for room temperature bombardment. This latter point regarding stability of preexisting Al_3Ni will be mentioned again below. Production of amorphous, rather than crystalline Al_3Ni at all temperatures by ion mixing of as-deposited layers is attributed to difficulty in nucleation of the ordered stoichiometric compound.¹

Amorphization of preexisting Al_3Ni was studied versus fluence for Xe, Ne, and electron bombardment (1.0-MeV electrons from a high-voltage electron microscope were used in an in situ study). In all cases amorphization was produced at a damage level of 0.4 DPA at a bombardment temperature of about 100 K. At room temperature, electrons never produced amorphization, Ne produced partial amorphization (Table 2.2), and Xe produced complete amorphization, again at about 0.4 DPA. These results indicate that a critical concentration of point defects is sufficient to promote transformation to the amorphous state and that cascade effects, such as thermal spikes, are not absolutely necessary. On the other hand, some factor associated with cascades increases the temperature at which amorphization occurs for the given calculated DPA. It may be that the kinetics of simultaneous production and recovery of defects at the higher temperatures are such that the critical concentration can more readily exist over suitable volumes and for suitable times, for the higher density modes of defect formation than for the lower.

Recrystallization of amorphous Al_3Ni occurred very rapidly at about 673 K upon heating at 15 C-deg/min in an in situ transmission electron microscopy study.

Table 2.2. Ion irradiation of NiAl_3 + Al and $\text{Ni}_{23}\text{Al}_{77}$ multilayers.

T(K)	Ion	Equilibrated NiAl_3 + Al	As-deposited $\text{Ni}_{23}\text{Al}_{77}$
100 K	Xe	a + Al	a + Al
	Ne	a + Al	a + Al
300 K	Xe	a + Al	a + Al
	Ne	a + NiAl_3 + Al	a + Al
373 K	Xe	a + NiAl_3 + Al	a + Al
	Ne	a + NiAl_3 + Al	a + Al

a = amorphous.

1. Summary of papers: Journal of Materials Research (in press); to be published.
2. Los Alamos National Laboratory, Los Alamos, N. Mex.
3. Metals and Ceramics Division, ORNL.
4. Cornell University, Ithaca, N.Y.
5. M. Nastasi et al., Solid State Div. Prog. Rep., Sept. 30, 1984, ORNL-6128, p. 66.
6. M. Nastasi et al., J. Appl. Phys. 57, 1050, (1985).

COMPARISON OF THERMAL ANNEALING AND ION BEAM MIXING OF Ni-W FILMS ON Si¹

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It is generally observed that the first silicide phase induced by ion mixing is the same as that obtained by thermal annealing. It is somewhat surprising that ion mixing, which is regarded as a transient process, correlates with thermal annealing, which is regarded as a steady-state process. For thermally induced thin-film reactions, the process is driven by thermodynamics, and the formation of reaction

ION IMPLANTATION

TRAPPING OF INTERSTITIALS DURING ION IMPLANTATION IN SILICON¹

R. J. Culbertson   S. J. Pennycook

products is quite often limited by kinetic reasons. For ion-induced thin-film reaction, the kinetic restrictions are somewhat relaxed by the increased atomic mobilities during ion irradiation, but collisional effects may play a role in the compound formation. For multiple-element samples consisting of A/B/Si or AB/Si, where the masses of A and B are significantly different, ion mixing could lead to preferential mass transfer in collision cascades. The Ni-W-Si system was investigated under ion mixing and thermal annealing conditions to determine whether such differences are evident.

Under both thermal annealing and ion mixing, Ni-rich tungsten ($\text{Ni}_{87}\text{W}_{13}$) alloy films deposited on Si undergo phase separation to Ni and W silicides. This is believed to be the result of the motion of Ni (the high mobility, low-temperature silicide former) in the alloy, although the mobility of Si may be enhanced during ion mixing. In an alloy with low concentration of W, Ni atoms are able to migrate from the alloy leading to phase separation during either thermal reaction or ion mixing.

Phase separation is also observed after thermal annealing of W-rich ($\text{Ni}_{38}\text{W}_{62}$) alloy films on Si. The thermal reaction is attributed to the migration of Si at high temperatures into the Ni-W alloy matrix in which the Ni atoms are locked by the high concentration of W. Phase separation occurs by the growth of Ni silicide crystallites oriented with respect to the Si(100) substrate in order to lower the energy of the system. In the case of ion mixing, a ternary Ni-W-Si alloy is formed, due to the transient nature of the ion mixing process.

The results of layered Ni-W films on Si depend upon which element lies next to the Si substrate in both thermal annealing and ion mixing cases. This is due to the nature of the low-temperature silicide formation between Ni and Si. W silicide formed on the surface during high-temperature annealing, or a Ni-W-Si mixture formed on the surface during high-dose ion mixing.

In the case of Ni/W/Si samples, the high-temperature silicide former (W) is interposed between the Si substrate and the low-temperature silicide former (Ni). Layer reversal between Ni and W layers results during thermal annealing due to the diffusion of Ni through the W layer, reacting with the substrate to form a silicide. Si then diffuses through the Ni silicide to react with the W. However, a Ni-W-Si ternary mixture results from ion mixing. The enhanced Si mobility and the increased intermixing between Ni and W during ion mixing make the formation of a Ni-W-Si ternary mixture possible.

Ion implantation of dopants in silicon has been an important technique for achieving dopant profiles and concentrations unobtainable by other means. Especially important has been the ability to greatly exceed equilibrium solubility limits while still maintaining the dopants in the electrically active substitutional sites. For medium- to high-implanted dopant concentrations the Si surface layer is amorphized for implantation at room temperature or below. The end of range damage due to implantation has been well studied, but it has recently been demonstrated that defect complexes for group V dopants may be formed within the amorphous layer.^{2,3} Effects similar to those found in samples irradiated with electrons are expected. However, for ion implantation damage it is found that the defect complexes are stable enough to be a problem for material processing. These complexes are sufficiently stable to survive solid-phase-epitaxial (SPE) regrowth conditions, which typically involve furnace annealing at 600°C for 30 to 60 min. Annealing at higher temperatures or longer times dissolves the complexes. The release of the silicon interstitials induces a dopant diffusion transient with a large enhancement (up to five orders of magnitude) of the dopant diffusion coefficient accompanied by a lowered activation energy. The dopant atoms precipitate, and the Si interstitials condense into dislocation loops at the mean projected range; the transient dopant diffusion decreases as the dislocation loops develop.

The formation of such complexes during ion implantation requires trapping interstitials in a stable configuration for dopant-Si bonding. A model for the dopant-Si complex that explains the stability of group V dopant complexes and the relative instability of group III dopant complexes is discussed elsewhere.⁴ We believe the interstitials are generated during the ion implantation process. The dependence on implantation temperature and the complete insensitivity to regrowth velocity support this belief. Calculations⁵ of the concentration of generated interstitials have been made using the MARLOWE⁶ computer code. The dopant depth distribution is also given by MARLOWE, and excellent quantitative agreement with results of Rutherford backscattering measurements using 2-MeV He were obtained.⁵ The depth distributions obtained by MARLOWE and Rutherford backscattering analysis for Si(100) implanted with 5×10^{15} Sb-cm⁻² at 200 keV at room temperature and furnace annealed at 600°C for 60 min are shown in Fig. 2.16. The calculated profile of generated interstitials is also shown. The density of silicon is 5×10^{22} cm⁻³, so it is clear that many interstitials are generated for each lattice site over a depth bracketing the dopant profile. (Less than one displacement per

1. Summary of papers: *J. Appl. Phys.* **58**, 4172 (1985); *J. Appl. Phys.* **58**, 4178 (1985).

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Fig. 2.16. Concentration profile of implanted Sb and generated Si interstitial for 200-keV Sb implanted to a dose of $5 \times 10^{15} \text{ cm}^{-2}$ into Si(100). The experimental data are from Rutherford backscattering analysis, and the calculations are from MARLOWE.

atom is sufficient to amorphize silicon at room temperature.⁷⁾ The profile of trapped interstitials is not directly obtainable, but from measurements using multiple implantation schemes to generate uniform concentration profiles, it appears that the concentration of trapped interstitials is approximately 2% or 1% of the dopant concentration for implantation at room temperature or low temperatures, respectively. Attempts to alter the number of trapped interstitials by following with an implantation of pure Si had little effect. The additional interstitial generation was apparently countered by the breakup of existing complexes. Thus, only the last displacement is important in the formation of the stable dopant-Si complexes.

After SPE regrowth the Sb substitutional fraction was typically greater than 0.90, as determined by ion channeling measurements; thus the dopant atoms were effectively incorporated into electrically active substitutional sites. After annealing at higher temperatures and/or longer times, ion channeling results show both dechanneling in the silicon at the depth of the loops and a reduction of the Sb substitutional fraction; these observations are consistent with results from transmission electron microscopy (TEM).

Similar observations are made when As is used as the implanted dopant species, except that As does not seem to precipitate in a form visible to TEM. However, experiments with group III dopants do not show the large increase in diffusion coefficient, the reduction of the activation energy, or interstitial loop formation. All these observations are explained by the stability of the dopant-Si bond, and a model for group III and group V dopant-Si complexes has been developed⁵. Further support of the model has been provided by double-doping experiments.⁵

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DIFFUSION OF ION-IMPLANTED ARSENIC IN SILICON¹

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P. Williams²

There is a continuing interest in identification and analysis of factors that determine the distribution of ion-implanted dopants in Si. The present experiments were designed to obtain data that would be suitable for testing the accuracy of rate theory, with various modifications in respect to parameters, in predicting the spread in profile that occurs due to diffusion during implantation of ion-implanted constituents.

Silicon samples of low dislocation density (essentially "dislocation free" silicon) and relatively high dislocation density (approximately $1 \times 10^7/\text{m}^2$) were specially prepared by the Monsanto Corporation. Samples were implanted to a fluence of $1 \times 10^{15}/\text{cm}^2$ of As at 290 keV. Implantation temperatures were -180 (approximately), 300, and 600°C. The low-temperature implantations were done to provide a reference or undiffused profile. Elevated temperatures were used for the other implantations to avoid amorphization; it was thought that interpretation of the results in terms of the planned analysis would be less ambiguous if the lattice remained intact during the diffusion process. Experimental analysis of the samples was by Rutherford backscattering (RBS)/ion-channeling and by sputter ion mass spectrometry (SIMS).

Figure 2.17 shows SIMS profiles for a sample implanted at -180°C and for the two samples implanted at 300°C (high and low dislocation densities). The logarithmic plot is interesting because it illustrates the power of SIMS to detect very low fractional concentrations and thus to reveal tails in the concentration that extend to large depths. Depth calibration for the SIMS profiles was obtained by profilometry of the sputtered area. Normalized SIMS and RBS profiles were in excellent agreement in the range where both have good detectability (e.g.,

Fig. 2.17. SIMS profiles representing As concentration v. depth for Si samples implanted with $1 \times 10^{15}/\text{cm}^2$ of As ions at 290 keV.

the range which contains about 90% of the implanted dopant). Whereas SIMS provides better detectability, RBS provides better absolute concentrations and depth calibration. From Fig. 2.17 it will be noted, first, that considerable spreading of the profile occurred at 300°C, and second, that the spreading was greater for the higher dislocation density than for the lower. The same trend occurred at 600°C, but the difference between the results for the two dislocation densities was not as great as for the results of Fig. 2.17. For both dislocation densities the spread was greater at 300 than at 600°C. Despite the large amount of in-diffusion of As for the higher temperature implantations, there is almost no difference in the FWHMs for the cryogenic implant and for the low dislocation case at 300°C, for example. This observation is one reflection of the fact that the diffusion tail involves only a small fraction of the implanted As.

To summarize, there was more spread in the profile at 300 than at 600°C and more spread in the high dislocation material than in the low. Neither result is expected in terms of the usual theories of radiation-enhanced diffusion, and analysis is continuing. Explanations of the dependence on dislocation density are being sought in terms of the idea that structures or defects, introduced as a side-effect of producing the differing dislocation concentrations, override the effects of the dislocations themselves. A speculative explanation of the temperature effect is that As has enhanced mobility at the lower temperatures due to binding of Si interstitials to As impurities but that at higher temperatures the two are thermally dissociated, with the result that, in relation to their respective concentrations, either is about as equally probable as an interstitial.

LATTICE LOCATION OF BORON AND HAFNIUM DOPANTS IN Ni_3Al ALLOY BY ION CHANNELING/NUCLEAR REACTION ANALYSES

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Recent developments regarding the effect of alloying dopants on the ordered stoichiometric alloy, Ni_3Al , have formed the basis for a new class of engineering alloys known as "advanced aluminides." Addition of B dopant (0.1–0.5 at. %) greatly improves the ductility of the material, and addition of Hf (e.g., 1 at. %) contributes further to improved ductility and to high-temperature strength. These results, which allow the superior high-temperature properties of Ni_3Al to be exploited in engineering design, underscore the need for research that might lead to a better understanding of the relationship between structure and physical properties of these advanced aluminides.

The present experiments have made use of Rutherford backscattering (RBS)/ion channeling techniques in conjunction with analysis for a nuclear reaction product to study lattice locations of B and Hf dopants. Studies were of an alloy single crystal of composition $\text{Ni}_{76}\text{Al}_{23}\text{Hf}_1$ with about 0.1 at. % B added. The crystal lattice is of the Cu_3Au structure. Because of its small mass and low concentration, B is scarcely detectable by conventional RBS. Detection of ^{11}B is accomplished by measuring α particles (of ~ 3.7 -MeV energy) resulting from the nuclear reaction $^{11}\text{B}(p,\alpha)^8\text{Be}$ using protons as the incident projectile. The cross section as a function of proton energy for the reaction is broadly peaked at about 620 keV with a FWHM of about 300 keV. The present experiments made use of a proton energy of 750 keV for detection of the B. An absorber of 6- μm Al foil was needed to shield the ion detector from backscattered protons, while allowing most of the alpha particles to reach the detector.

Figure 2.18 shows angular scans in which normalized yields for 2.0-MeV He ions scattered from Ni lattice atoms and yields for α particles from the (p,α) reaction described above are plotted versus tilt angle from a $\langle 100 \rangle$ direction (left) and from a $\langle 110 \rangle$ direction (right). The octahedral interstitial site is in the center of the cubic unit cell and is thus aligned with rows of lattice atoms for a projection in a $\langle 100 \rangle$ direction. Neither octahedral nor tetrahedral sites are blocked by normal lattice rows for projections in $\langle 110 \rangle$ directions. The fact that the B yield increases relative to the random yield for alignment in a $\langle 110 \rangle$ direction means that B is interstitial. The reduction in yield coincident with that of the lattice for a $\langle 100 \rangle$ scan means that the B occupies mostly octahedral sites.

It will be noted that the minimum yield for the B is greater than that of the lattice. At least half of this difference between the minimum yield for the Ni and that of the B is due to the fact that the proton beam samples B atoms over a very large, but imprecisely known, depth range, whereas lattice yield data were selected from a region of approximately 100 nm deep near

1. Summary of paper: Proceedings of the TMS-AIME Conference (in press).

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Fig. 2.18. Comparison of yields of backscattered He ions and alpha particles from the p, α reaction in B for angular scans about a $\langle 100 \rangle$ direction and a $\langle 110 \rangle$ direction in a (nominally) Ni_3Al crystal of the composition indicated.

the surface of the crystal. Another contributing factor whose quantitative effect is not precisely known is that the smaller B atoms have larger vibrational amplitudes than those of the host atoms. Boron has low solubility in the lattice, as is attested to in part by the fact that the mechanism of ductility improvement for the additive involves segregation of the B to grain boundaries. Therefore, it is reasonable to expect that in single crystals, segregation of some of the B to dislocations and other possible favorable sites could result in some B atoms not being well blocked by lattice atoms in $\langle 100 \rangle$ directions. Other possible factors that might account for the difference include the idea that some of the B is partitioned onto the tetrahedral sites or that the (essentially) octahedral site is somewhat asymmetrical. Experiments at high temperatures may provide information that helps to explain this difference.

The atomic mass of Hf is great enough that Hf yields a good RBS analysis, even for the 1 at. % level of the present crystal, whereas the mass of Al is such that even at the 25 at. % level the yield is rather small. Therefore lattice location experiments for Hf involved comparisons between Hf and Ni yields, but not comparisons of Hf and Al yields. Figure 2.19 shows normalized RBS yields of Hf and Ni for an angular scan about a $\langle 100 \rangle$ axis. The experimental half-angle for Ni is 0.70 deg. As expected, the calculated value of 0.73 deg is somewhat (but not drastically) greater than the experimentally measured value. The measured value for Hf is 0.67 deg. The calculated value of the half-angle for Al rows containing 4% Hf (1% Hf in the alloy but all Hf on the Al sublattice) is 0.46 deg. The close coincidence of the Hf yield with that of the Ni over the angular scan is interpreted as very strong evidence that the Hf occupies mostly Ni sublattice sites. If appreciable Hf were on the Al sublattice, the measured half-angle for Hf should be less than the value calculated for Al.

Fig. 2.19. Comparison of RBS yields for Ni and Hf upon scanning through a $\langle 100 \rangle$ channel for the same crystal as was used for the experiment of Fig. 2.18.

This conclusion regarding lattice location of the Hf is in disagreement with results of experiment using electron channeling³ and atom probe⁴ techniques on crystals of approximate composition $\text{Ni}_{76}\text{Al}_{24}\text{Hf}_3$. At present it is believed that the differing conclusions are related to the differences in composition of the alloys that were studied. Experiments directed toward resolving these conflicting results are in progress.

1. Kernforschungsanlage, Jülich, Federal Republic of Germany.
2. Metals and Ceramics Division, ORNL.
3. J. Eantley, private communication.
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ION IMPLANTATION AND ANNEALING OF CaTiO_3 ¹

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Ion implantation and annealing phenomena are being studied in a variety of crystalline oxides and ceramic materials using Rutherford backscattering (RBS)/ion channeling analysis. In CaTiO_3 , we find that the implantation of Pb at modest doses turns the near-surface region amorphous. Subsequent annealing at relatively low temperatures gives rise to an amorphous-to-crystalline phase transition which appears to take place by solid-phase epitaxy. The kinetics of recrystallization can be determined by ion channeling measurements.

The channeling results of Fig. 2.20 (left) show that the implantation of Pb (250 keV, $4 \times 10^{15}/\text{cm}^2$) turns the near-surface region amorphous in the Ca, Ti, and O sublattices. In Fig. 2.20 the aligned spectrum in the implanted region reaches the random value in the Ti sublattice, and the aligned scattering yield from Ca and O are equivalent to similar steps in the

Fig. 2.20. 2.0-MeV He^+ backscattering and channeling spectra from Pb (250 keV, $4 \times 10^{15}/\text{cm}^2$) implanted CaTiO_3 . Results obtained in the as-implanted state are shown on the left. Results obtained after annealing 500°C/1 h are shown on the right.

random spectrum. The depth of the amorphous region is ~ 1100 Å. Channeling results obtained after annealing to 500°C/1 h are shown in Fig. 2.20 (right). After annealing, the aligned spectra in the implanted region are indistinguishable from those measured in the virgin region, demonstrating that the amorphous region has been recrystallized and is epitaxial with the underlying substrate. Implanted Pb is observed to be in solid solution following annealing. This is a metastable solution, because if the crystal is heated to higher temperatures, Pb will come out of solution. Figure 2.21 shows channeling results obtained after annealing to 450°C/30 min. In this case, we observe only partial recrystallization of the amorphous region. Approximately two thirds of the initial amorphous region has recrystallized epitaxially with the underlying substrate, but the near-surface region remains amorphous in each sublattice. This behavior is that expected by a solid-phase-epitaxy process where recrystallization takes place at an amorphous/crystalline interface. The position of this interface can easily be measured by ion channeling, and from these measurements the velocity of the interface can be obtained as a function of annealing temperatures. Figure 2.22 shows the measured interface velocity plotted as a function of T^{-1} . Assuming a thermally activated process of the form $V(T) = V_0 e^{-Q/RT}$, the data are in reasonable agreement with an activation energy $Q \sim 1.3$ eV for the amorphous/crystalline transition. The results in Fig. 2.22 were obtained for recrystallization along the low-symmetry direction. Preliminary results show that the kinetics of recrystallization

Fig. 2.21. Partial recrystallization of Pb (250 keV, $1 \times 10^{15}/\text{cm}^2$) implanted CaTiO_3 . This crystal was annealed at 450°C/30 min.

along the high-symmetry direction are considerably different.

1. Summary of paper to be published.
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Fig. 2.22. Temperature dependence of the amorphous/crystalline interface velocity in CaTiO_3 .

ANNEALING OF AMORPHOUS Al_2O_3 ¹

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Previous work⁴ has established that ion implantation at liquid nitrogen temperature can be used to turn the near-surface region of $\alpha\text{-Al}_2\text{O}_3$ amorphous. In that work it was shown that a stoichiometric implant (two parts Al, three parts oxygen with ion energies chosen to give the same projected range) could be used to produce the amorphous phase free of any unwanted impurities on the crystalline α -substrate. It was also demonstrated that the amorphous film could be recrystallized epitaxially with the underlying substrate by annealing at 1190°C for 30 min.

In the present work, we have studied the annealing behavior at lower temperatures. We find that amorphous Al_2O_3 transforms to crystalline $\gamma\text{-Al}_2\text{O}_3$ by annealing at temperatures as low as 800°C for times as short as 90 min. This is followed by a transformation of $\gamma\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$ at a well-defined interface. The velocity of the γ/α interface has been measured as a function of annealing temperature, and an activation energy of 3.6 eV has been determined for the $\gamma \rightarrow \alpha$ transition.

Figure 2.23 illustrates schematically the recrystallization behavior observed for amorphous Al_2O_3 on $\alpha\text{-Al}_2\text{O}_3$. A stoichiometric implant at the energies and currents indicated in Fig. 2.23

Fig. 2.23. Schematic representation of the recrystallization behavior observed in Al_2O_3 made amorphous by a stoichiometric implant.

produces an amorphous layer $\sim 1600 \text{ \AA}$ thick. Annealing at 800°C for time periods as short as 1.5 hours converts the entire amorphous region to columnar crystallites which are the γ phase of Al_2O_3 . These crystallites are $\sim 350 \text{ \AA}$ in diameter and extend from the amorphous/crystalline interface to the surface. Individual crystallites are in registry with the substrate, but they exhibit texturing relative to one another. Further heating at 800°C (for 3 h) results in a slight coarsening of the crystallites accompanied by less texturing. After annealing for 96 h at 800°C , the film of $\gamma\text{-Al}_2\text{O}_3$ appears to be continuous with little evidence of boundaries between grains.

Following the conversion of amorphous Al_2O_3 to $\gamma\text{-Al}_2\text{O}_3$, the $\gamma\text{-Al}_2\text{O}_3$ begins to transform to the α -phase at a well-defined interface which moves from the original amorphous/crystalline interfacial region toward the surface. This is illustrated schematically in Fig. 2.23 for results obtained after annealing at 800°C (96 h) and 960°C (90 min).

The position of the interface where the $\gamma \rightarrow \alpha$ transition takes place is dependent on annealing temperature and time, and this can be measured easily using Rutherford backscattering/channeling techniques. From these results the γ/α interface velocity can be determined as a function of annealing temperatures.

Figure 2.24 shows the measured velocities of the γ/α interface plotted as a function of T^{-1} . Assuming a thermally activated process of the form $V(T) = V_0 e^{-Q/RT}$, the data can be fit reasonably well with an activation energy of $\sim 3.6 \text{ eV}$ (83 kcal/mol). This is the activation energy for the growth of α from the γ phase with no nucleation required because in this experiment, nucleation sites are provided by the underlying α -substrate.

Fig. 2.24. Temperature dependence of the γ/α interface velocity in Al_2O_3 .

There are numerous investigations⁵ of the $\gamma \rightarrow \alpha$ phase transformation in Al_2O_3 . The more recent determinations⁵⁻⁸ of the activation energy for the $\gamma \rightarrow \alpha$ transition in Al_2O_3 give results that lie in the range 130–150 kcal/mol. Those experiments involved the conversion of bulk $\gamma\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$; as such they averaged over all crystal orientations, and the transformation involved both nucleation and growth of the α -phase. Our results deal with one crystal orientation only, and the activation energy determined is that for growth alone because nucleation sites are provided by the underlying substrate. To our knowledge, this is the first time the activation energy associated with growth of the α -phase has been determined for Al_2O_3 .

In summary, a stoichiometric implant at LN_2 can be used to produce a thin amorphous layer of Al_2O_3 free of any impurities on an $\alpha\text{-Al}_2\text{O}_3$ substrate. Upon annealing, the amorphous phase converts to the γ -phase. This is followed by the conversion of γ to α at a well-defined interface which moves from the underlying substrate toward the surface. An activation energy of ~ 3.6 eV has been determined from the measured γ/α interface velocity. This activation energy is that required for growth alone, since nucleation sites are provided by the underlying substrate.

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CATION TRANSPORT IN OXIDES

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Rutherford scattering is a powerful and convenient tool for measurement variations in composition within 100 to 5000 Å of a surface. By measuring such composition changes after passing current through spinel samples at elevated temperatures, we have determined transference numbers and diffusion coefficients.

If ions drift under the influence of an electric field in a material such as MgAl_2O_4 , the positive ions will move to the cathode surface. If the ambient gas is $^{18}\text{O}_2$, these cations combine with ambient oxygen to form an ^{18}O metal oxide layer. The thickness of this layer depends on time, current, and the ion transference number t_i and allows the calculation of t_i directly from measured and known values. Diffusion coefficients are obtained by making use of the Nernst-Einstein equation and the above result.

Energy spectra for 2.0-MeV ^4He backscattered from untreated spinel (o) and from the cathode surface of spinel treated for 7.5 hours at 995°C (+) are shown in Fig. 2.25. Markers show the energies at which scattering would take place from the indicated elements at the surface of the sample. Note that for the treated sample (+) there is no Al present at the surface and that a layer of ^{18}O has been built up. Also the scattering for ^{16}O has moved to lower energy, indicating greater depth in the sample. The peak just below the Mg edge is due to combined scattering from Mg near the surface and from Al below the surface. Quantitative analysis of these results indicates that a layer of Mg^{18}O ~ 120 nm thick has been grown on the cathode face of this sample, showing that Mg, and not Al, is the dominant charge carrier. Other spinel samples treated for different times and currents gave comparable results.

By the use of He ion backscattering from electric-field-treated MgAl_2O_4 spinel, we have been able to demonstrate clearly that at 1000°C magnesium is the mobile ion species while aluminum motion is negligible. Magnesium diffusion coefficients are approximately 1×10^{-13} cm²/s. The transference number, determined for the condition where significant current has flowed through the spinel sample, is less than unity and decreases with increasing current. This result is in contrast with an earlier deter-

Fig. 2.25. Energy spectra of 2-MeV ^4He ions scattered from MgAl_2O_4 spinel for untreated material (o) and from the cathode surface of a sample annealed at 995°C in an electric field of 461 V/cm (+). The arrows indicate energies at which ^4He would scatter from the indicated elements at the surface of the sample.

mination of the ionic transference number of spinel,³ in which oxygen concentration cell measurements (no current flow) indicated pure ionic conduction. It appears that current flow through spinel causes the production of electronic donors or acceptor centers which are ionized at 1000°C and contribute electronic carriers.

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ION IMPLANTATION AND ANNEALING OF ALPHA SILICON CARBIDE

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Because of its favorable high-temperature properties, silicon carbide has potential for use both as a semiconductor capable of functioning at elevated temperatures and as a refractory material for construction of structural and working parts in applications such as fission and fusion reactors, heat engines, and heat exchangers. Data of the present report were obtained as part of a continuing program designed to investigate the effects of ion beam modification of SiC surfaces. Previous experiments on alpha SiC ^{4,5} have concentrated on production of lattice disorder, amorphization, and associated property changes due to bombardment with Cr and N ions. These dopants were chosen for potential mechanical applications, but many

aspects of production and annealing of damage can be expected to be reasonably independent of dopant. The present experiments have concentrated on annealing of lattice damage and epitaxial regrowth of SiC after ion implantation treatments. Also the effects of implantation at elevated temperatures have been investigated.

Single-crystal samples, supplied by the Carborundum Company, were polished to present {0001} surfaces for study. Following ion implantation and annealing treatments that will be described, lattice damage was investigated by use of Raman spectroscopy techniques and by RBS/ion channeling techniques. After ion implantation treatments, samples were annealed to temperatures as high as 1500°C .

Previous experiments^{4,5} had established the dose dependency of the growth of lattice damage, and in particular, the minimum fluences of N and Cr necessary to produce amorphization. For 260-keV Cr this fluence was approximately $2 \times 10^{14}/\text{cm}^2$. Figure 2.26 shows RBS/ion channeling spectra for four conditions in SiC . The bottom curve and the top curve are the unimplanted-aligned and the rotating random cases, respectively. RBS/ion channeling spectra are shown for samples implanted to a fluence of $1 \times 10^{16}/\text{cm}^2$ of Cr ions at 260 keV (e.g., 50 to 100X the minimum fluence necessary to produce amorphization at room temperature). One sample was held at room temperature during the implantation, and the other was held at 750°C . The room-temperature implantation produced amorphization to a depth of about $0.29\text{ }\mu\text{m}$, whereas the sample implanted at 750°C remained crystalline and had a maximum yield that was about 50% of that corresponding to the rotating random. Approximately 50% of the implanted Cr was substitutional after the high-temperature implantation. Implanting crystals held at 750°C to doses of $8 \times 10^{16}/\text{cm}^2$ of 62-keV N ions also did

Fig. 2.26. RBS/ion channeling spectra for SiC samples: (a) virgin-aligned, (b) implanted to $1 \times 10^{16}/\text{cm}^2$ of 260-keV Cr ions at 750°C , (c) implanted to the same Cr dose at room temperature, and (d) rotating random.

not produce amorphization. Again, such a dose is approximately 100X the minimum fluence necessary for amorphization at room temperature. It is concluded that elevated temperature implantations do not produce amorphization of SiC, as has now been confirmed for several constituents in both alpha and beta SiC.

For room-temperature implantation, Raman peaks were eliminated by implantation with Cr or N, but the doses required for elimination of the peaks were greater than those necessary to produce the random yield in RBS/ion channeling experiments. Raman peaks remained after elevated temperature implantations.

The temperature dependence of damage recovery was highly dependent on whether the sample was fully amorphized or not. In Fig. 2.26 the curve for the sample implanted to $1 \times 10^{16}/\text{cm}^2$ at 750°C is very similar to that for a sample implanted to $1.5 \times 10^{14}/\text{cm}^2$ at room temperature. For that reason a curve for the latter case is not shown, and the curve that is shown should be interpreted as also representative of the data for implantation to the fluence of $1.5 \times 10^{14}/\text{cm}^2$ at room temperature. Such a sample is damaged but not amorphized. As was noted, the high-dose implantation has produced amorphization to a depth of $0.29 \mu\text{m}$ (a depth now designated as W). Figure 2.27 shows recovery of damage versus isochronal annealing temperature for the two cases, together with similar data for a sample that was implanted with N to a fluence also designed not to produce amorphization. It is necessary to use different characterizations of the damage for samples that have been amorphized than for those that have only been damaged but not amorphized. For the latter cases, the disorder parameter⁶ (in number of defects/ cm^2) determined from the area of the damaged region (Fig. 2.26) after a dechanneling function has been subtracted,⁶ was used. For

the amorphized samples the damage was characterized by W , the depth of amorphization. The samples that have only been damaged but not amorphized recover to a fairly high degree of perfection, with recovery being practically complete by 1000°C . The sample that was fully amorphized has some continuous recovery up to a temperature of 1450°C , and then epitaxially regrows very suddenly upon heating to 1500°C . Not shown are recovery data for a sample implanted to an N-dose of $8 \times 10^{16}/\text{cm}^2$, a dose that produces amorphization for N. For this case also, recovery versus temperature is very similar to that for the sample that was amorphized by implantation of Cr.

The data of Fig. 2.27 suggest that recovery of damage in SiC divides itself into two qualitatively distinct processes. The first relates to recovery of damage in material that has been damaged but not amorphized. This process applies for the low-dose samples and could also account for the gradual slope in the high-dose sample that exists up to 1450°C . Because of the shape of the damage-vs-depth curve, an amorphized region can be expected to have a damaged, but not fully amorphized, region behind it. Recovery of damage in this region would be expected to reduce the apparent value of W in the present RBS/ion channeling analysis. Finally at 1500°C true epitaxial regrowth of amorphized material occurs. One consequence of this interpretation is the conclusion that apparently recovery of single cascades of damage, such as might exist in the low-dose samples, bears no resemblance to epitaxial regrowth. Thus it would seem that a single cascade is not a small amorphized zone, at least for ion masses up to that of Cr. These conclusions depend on the idea that the amorphized layer actually does regrow rather than perhaps evaporate or become oxidized during the dramatic step that occurs at 1500°C . Arguments against these latter mechanisms include the fact that the implanted Cr is still present after the 1500°C anneal, although it is somewhat redistributed toward the surface. Also the anneals were carried out with the samples in a gas flow of purified Ar.

Raman intensity in amorphized samples recovers to a considerable degree over the broad annealing range from 300 to 1450°C and actually reaches a peak of 80% recovery for the Cr-implanted case at 1450°C just before the sudden recovery of epitaxy. Nevertheless, TEM has established that recovery of true crystallinity does not correlate with this recovery of intensity.⁷

Fig. 2.27. Recovery of ion-implanted SiC samples vs annealing temperature.

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AMORPHIZATION AND RECRYSTALLIZATION PROCESSES IN MONOCRYSTALLINE BETA SILICON CARBIDE THIN FILMS¹

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Beta-silicon carbide (β -SiC) thin films can be ion implanted to introduce electrically active dopants. However, as the dose of the implanted species is increased, the near-surface region of the semiconductor becomes progressively damaged; atomic disorder and eventual amorphization of the structure occur. In order to recrystallize the amorphous layer, annealing of the film is necessary.

As part of an ongoing study of electronic device production in β -SiC, Rutherford backscattering in an ion channeling geometry was used to study damage accumulation with dose for Al and P implantation. The damage profile results have been compared to predictions of energy deposition and vacancy and interstitial production from Monte Carlo computer simulations and have been quantified using a critical energy deposition (CED) model. In addition, transmission

electron microscopy studies on implanted samples following thermal annealing have been used to characterize the solid-phase-epitaxial (SPE) regrowth.

Thin films of monocrystalline (100) β -SiC were epitaxially grown on (100) silicon wafers via chemical vapor deposition. Each sample was then mechanically polished, oxidized, and etched in HF in order to obtain a clean, undamaged, and smooth surface. The samples were implanted at room temperature with P or Al ions at energies of 110 and 130 keV, respectively. Following implantation, in situ He backscattering spectra were obtained using 2.5-MeV ions incident along the $\langle 011 \rangle$ axial direction. The dosimetry was stepwise increased in order to measure the incremental increase in lattice damage as a function of dose.

The spectra in Fig. 2.28 illustrate the accumulation of damage in β -SiC as a result of P implantation. Also shown are a virgin spectrum from the unimplanted sample and a spectrum obtained by rotating the sample around its normal axis during the RBS analysis to approximate the yield expected from amorphous SiC. Damage increases in the sample with increasing dose until the scattering yield from the damaged region reaches the level characteristic of amorphous material. This condition initially occurs at a depth of ~ 90 nm for a dose between 3.0 and $5.0 \times 10^{14}/\text{cm}^2$. The width of the

Fig. 2.28. Rutherford backscattering spectra for P implantation into β -SiC at 110 keV.

amorphous region increases until at the highest dose, $3.0 \times 10^{15}/\text{cm}^2$, a layer amorphous from the surface down to 154 nm results.

The k_{CED} is the minimum deposited energy density needed to amorphize the crystal. To determine k_{CED} , a graph was constructed by measuring at each implantation dose the experimental minimum and maximum depths over which the implantations amorphize the crystal. These depths were then plotted with the corresponding ordinate proportional to $1/\text{dose}$. The k_{CED} is the scaling factor that normalizes a curve drawn through these experimental data that has the same shape and maximum value as a theoretical profile of damage energy versus depth calculated for P implantation into SiC using the TRIM84 computer code.³ For P implantation at room temperature, k_{CED} is $15.5 \times 10^{23} \text{ eV}/\text{cm}^3$. Using the same procedure, k_{CED} for room temperature Al implantation is found to be $15.0 \times 10^{23} \text{ eV}/\text{cm}^3$.

Deviation between the theoretical and experimental profile depths was significant for both implanted species, with the maximum in the experimental damage occurring deeper. This may indicate a need for revision of parameters in the TRIM84 code for the implantation models here. However, a more likely source of discrepancy may be in the method in which the program computes damage production from recoils, and an evaluation of the TRIM codes used is being made. It was previously suggested⁴ that the experimentally measured depth of damage in ion-implanted SiC resulted from knock-on of carbon atoms during the implantation process. It should be noted, however, that depth profiles of Si and C vacancies or interstitials produced during the recoil cascades, as calculated using the TRIMCASCADE computer code,³ do not provide adequate agreement with the experimental data either.

Amorphous layers were also produced in β -SiC by implanting Al, P, Si, and Si plus C in order to study SPE regrowth upon annealing. The former two species were implanted for p-type and n-type doping, respectively; the latter two were used for amorphization prior to subsequent dopant introduction at concentrations below which amorphization occurs. Energies and doses were chosen to give peak concentrations in the range $3\text{--}10 \times 10^{19}/\text{cm}^3$. Regrowth of amorphized layers was achieved by thermally annealing samples in 1 atm of Ar at 1600, 1700, or 1800°C for 300 s. Annealing in this temperature range is necessary for optimizing electrical characteristics of implanted layers.

Residual lattice damage in the surface-implanted regions before and after annealing was visually evaluated using cross-section transmission electron microscopy (XTEM). SPE regrowth was found to occur upon thermal annealing at temperatures as low as 1600°C. Layers implanted with Al and Si regrew as single crystals but with residual line and planar defects. For the case of amorphous layers created by P implants, polycrystalline regrowth was observed as a result of supersaturation of P in the SiC matrix. The regrowth properties of amorphous layers obtained using a lower atomic concentration of P are presently being investigated. Initial experiments have shown that

overlying implants of C and Si do not improve the regrowth properties of amorphous SiC. To understand the characteristics of the regrown implanted layer better, additional experiments are being conducted using ^{30}Si and ^{13}C .

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ION IMPLANTATION OF SURGICAL Ti-6Al-4V ALLOY¹

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Studies^{4,5} of the effects of ion implantation treatments on wear and wear-accelerated corrosion of surgical Ti-6Al-4V alloy were continued. Tests made use of an apparatus in which cylindrical alloy samples were rotated between loaded, conforming pads of ultrahigh molecular weight polyethylene (UHMWPE), with pads and samples immersed in a saline electrolyte. (In articulating hip and knee joints, alloy components rub against UHMWPE components during walking.) The apparatus provided for control and measurement of electrochemical parameters. Previous tests^{4,5} were done at a polarization condition in the "passive" region of the anodic polarization curve, so that if oxides were removed by wear, new oxide would immediately form by anodization. The electrolyte was a 0.9% NaCl solution. Ion implantation of N to a level of some 20 at. % into the surfaces of alloy samples reduced the anodic corrosion currents by factors of 1000 to 10,000. Continuous monitoring of the corrosion current was possible during those tests at anodic potential. During the present reporting period, tests were done at open circuit corrosion potential and with bovine serum added to the electrolyte. These latter conditions were intended to provide a more realistic simulation of the application than did the earlier tests. At open circuit, periodic measurements of the corrosion current were made by the Tafel extrapolation technique. Studies of the effects of implanting C as well as N have been done. In addition, the influence of applied stress on the sliding interface on the wear-accelerated corrosion was investigated for unimplanted and N-implanted alloy samples.

Figure 2.29 is a photograph showing alloy samples and one of the mating UHMWPE pads for each sample. Tests were done either in saline or in the saline-serum (10% calf serum by volume) solution. All tests were essentially at open circuit potential. The visible striations in unimplanted samples 5 and 6 of Fig. 2.29 are up to 80 μm in depth and appear the same in character as striations on samples tested at the anodic condition.^{4,5} By assessing

Fig. 2.29. Layout of Ti-6Al-4V alloy samples and matching UHMWPE for different combinations of ion implantation treatments and fluid media (serum or saline) used for the wear-corrosion tests. All tests were essentially at open circuit. The new sample was unimplanted and untested.

profilometry charts from the samples, it is possible to estimate the amount of material removed in the tests. Effective average thicknesses removed vary from 1 to 17 μm and appear to be fairly independent of polarization conditions. However, wear in unimplanted samples may be more severe with serum than in pure saline. For open circuit tests on unimplanted samples, corrosion currents were less than those obtained at the anodic polarization condition by factors of 35 to 200. Taken together, these results mean that the wear debris is relatively metal-like for the open circuit condition versus relatively oxide-like for the anodic test but that the total amount of material removed is about the same for the two polarization conditions. Alloy samples implanted with N or C remained as-new as far as visual inspection and profilometry could resolve. As-polished samples, ion-implanted samples, and implanted-and-tested samples all had average surface roughnesses of about 0.3 μm with great similarity in overall aspects of these profiles. Corrosion currents for ion-implanted samples at open circuit were reduced by a factor of about 40 over those for unimplanted samples. Again it is noted that most of the difference between the factor of 40, which is obtained at open circuit, and the factor of 1000 to 10,000, obtained at anodic potential, is due to higher oxidation at the anodic potential rather than differing degrees of effectiveness of the ion implantation treatment.

Pads associated with unimplanted alloy samples are severely scored whereas pads associated with ion-implanted samples remained virtually unaffected by the test. Wear of pads is undoubtedly caused in good part by abrasive wear debris, oxide and metallic, originating from the alloy surface. Therefore, it is not surprising that improved wear of the pads is associated with improved wear of the alloy. Because the biocompatibility of Ti and TiO_2 is excellent (e.g., possibly better than UHMWPE), many surgeons believe that reduced wear of the UHMWPE is a more important factor pertaining to inflammation, infection, loosening, and general acceptance of the surgical implant by the body than is reduced wear of the alloy. Reduced wear of both is important as regards longevity of an otherwise successful surgical implant.

For the tests described above, the average stress on the sliding interface was 2.3 MPa. Other tests were done for a stress range of 0-7 MPa, for implanted and N-implanted samples with serum and without, and also with SiC abrasive added to the interface in some cases. Sample voltage was at the passive anodic condition with continuous monitoring of corrosion current. Under this condition the corrosion current is proportional to the instantaneous fraction of alloy surface that is unprotected by oxide. As before,⁴ there was considerable statistical scatter of the data, but within the scatter there was no dependence on stress. This matrix of data is too large to discuss in detail. In general terms the interpretation is that microevents which remove an area of oxide, and thus perhaps initiate a severe wear band with further oxide removal, are statistical in nature and may depend on a number of factors, but over a wide range of stress levels there is always enough stress to initiate the event wherever the other necessary factors come into statistical coincidence.

Ion implantation of N is highly effective as a wear and wear-accelerated corrosion preventative of Ti-6Al-4V alloy for both polarization conditions studied, for both fluid media, and for all stress levels studied. Ion implantation of C is equally effective for cases where it has been studied.

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ION IMPLANTATION FOR CORROSION INHIBITION IN URANIUM

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Uranium readily oxidizes in the presence of water vapor, and the oxide that forms (UO_2) is only weakly adherent to the metallic substrate. Spalling of oxide and continuing oxidation are severe problems for U. Coating techniques such as chemical vapor deposition or plasma vapor deposition may be employed to inhibit corrosion with some success, but these techniques have shortcomings due to factors such as columnar structure of the coating, porosity, or poor adherence. One reason for poor adherence is that the coating may often be deposited on top of some amount of residual oxide. Another disadvantage of such coatings is that the thickness of material required to give sufficient protection can be appreciable.

A program designed to explore the use of ion implantation techniques for corrosion inhibition of U has been initiated. The high energy of the ion implantation process should enable production of a homogeneous treated layer which is in intimate contact with the substrate, because the energetic ions not only can penetrate the oxide layer that is sure to exist if the material has ever been exposed to air after it was cleaned but also can penetrate still further into the substrate. In addition, sputtering of such oxide is part of the ion implantation process, and once cleaned, the surface is expected to remain clean in the high vacuum of the implantation target chamber. The goal of the program is to produce an ion-implanted or ion-mixed layer that will provide sufficient protection to be practical in itself or to build a transition layer that will more readily accept a coating from a complementary coating technique than the natural substrate does.

The corrosion tests employed flat, mechanically polished coupons of ^{238}U in an arrangement in which the area to be tested was exposed to pure H_2O vapor at 100°C and a pressure of 93 Torr. The tested area was precisely limited by a seal so that for implanted samples no unimplanted area need be exposed. The total evolved hydrogen was measured as a function of time to determine the amount of oxidation that had occurred. Tests have been done for samples implanted with either N, Si, Ti, Cr, Nb, or Sb ions. These constituents (and others which have been implanted, but for which tests have not yet been done) were chosen to produce a survey with respect to several potentially important metallurgical, chemical, and process factors. Implant doses were generally high ($>1 \times 10^{17}/\text{cm}^2$) so as to produce concentrations of 10 or more at. % in the treated layer, and for some constituents more than one dose was used. Particle energies were typically 150 keV.

Figure 2.30 shows integrated corrosion versus time for three of the implant dopants. These cases represent essentially the extremes in effectiveness among the ion implantation treatments that were used. The Sb was almost totally ineffective, and the curve for Sb is almost

Fig. 2.30. Integrated corrosion vs time for U samples implanted with $1.7 \times 10^{17}/\text{cm}^2$ of Sb at 150 keV, $3.7 \times 10^{17}/\text{cm}^2$ of N at 75 keV, and $5.7 \times 10^{16}/\text{cm}^2$ of Si at 150 keV.

indistinguishable from that of unimplanted uranium. For Si and N, corrosion is almost totally arrested for about 30 h. Then after a transition region extending to about 70 h, the slope reverts to that characteristic of unimplanted U.

The corrosion test employed in the present tests is very severe. Therefore, it is expected that the offset of 30 h, achieved by the present treatments before rapid corrosion set in, might correspond to several years of exposure in realistic environments. This means that the results which have been achieved thus far are of potential practical importance, particularly when it is considered that the extreme thinness of the ion-implanted layer might be an advantage in comparison with layers produced by competing processes.

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ION-IMPLANTED WAVEGUIDES IN LiNbO_3

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For the first time it has been possible to fabricate high-quality optical waveguides by ion implanting Ti into LiNbO_3 substrates. This is an important achievement for the production of optical integrated circuits (OIC) on LiNbO_3 substrates, which are the best choice for the active switching and modulating components for optical communications and signal processing. Although ion implantation offers several distinct advantages for doping LiNbO_3 , previous studies have shown that ion bombardment initiates severe chemical decomposition of the crystal structure. The complex lattice structure of the crystal is responsible for its interesting large electrooptical, acousto-optical, and piezoelectrical properties. Only

in its well-ordered state is the crystal completely transparent for light, without undue adsorption or scattering centers. The stability of the crystal is mostly provided by Nb-O bonds, and the Li-O bonds are necessary to keep the highly mobile Li ions in place. The recoil cascades during ion implantation destroy these bonds, and the Li ions start diffusing. Segregation and surface precipitation set in, and the crystal loses its optical properties completely. These effects have been studied by ion scattering, ion channeling, secondary ion mass spectrometry (SIMS), and optical microscopy.⁴ It has been demonstrated that it is mostly Li out-diffusion which is responsible for the detrimental surface precipitates.

The present investigations have identified crucial implantation and annealing conditions which make it possible to dope LiNbO₃ with high concentrations of Ti and still maintain the structure and optical properties of the sample. Higher implant energies of 360 or 540 keV were used to deliver the Ti ions 0.2 or 0.3 μm into the crystal. Most implants were done with Ti ions at liquid-nitrogen temperature in order to reduce the detrimental Li diffusion. We were able to implant as much as 3×10^{17} Ti/cm² (Ti/Nb ratio ~ 1) without degrading the crystals. This high concentration of deeply buried Ti dopant permits a thermal treatment at sufficiently high temperatures to restore the crystalline lattice without excessive loss of dopant due to diffusion. These thermal treatments are the essential step to recover the crystallinity, and they are executed immediately after the low-temperature implant in order to shorten the time for detrimental diffusion. Anneals were performed in flowing wet oxygen gas. The oxygen was instrumental in replenishing oxygen lost during implantation. Additional water vapor is also beneficial since the indiffusion of protons into LiNbO₃ suppresses an undesirable phase transformation into the LiNb₃O₈ phase and at the same time hinders Li out-diffusion.⁵

In the "as-implanted" state, all samples are amorphous when investigated by ion channeling. The crystalline recovery is under systematic study, and we have found three characteristic temperature regimes.⁶ At approximately 600°C the coloration of the samples disappears, most probably due to the restoration of the oxygen sublattice.⁷ Around 800°C the Ti diffusion sets in and becomes noticeable. Work is under way to establish the probably different diffusion coefficients in the damaged and the nondamaged crystal lattice. Above 950°C the lattice is restored to a high degree, and all samples show very good ion channeling, practically as good as a virgin crystal in the undamaged stage.

By now we have fabricated several very good waveguides, showing losses of less than 1 dB/cm at $\lambda = 6328$ Å and carrying one or two modes of that wavelength. Work is under way to establish details of crystallographic regrowth after implant, and experiments with different ion species and MeV energies for even deeper implants are planned. A very deep implant with MeV energies might provide a guide with very good single-mode coupling to graded index

fibers, which are used to transport optical signals over large distances.

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STATUS OF THE NEW TANDEM ACCELERATOR

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The Surface Modification and Characterization (SMAC) facility has recently added a 1.7-MV tandem accelerator¹ to augment the facility's Rutherford backscattering and nuclear reaction analysis capabilities and to provide heavy-ion beams for ion implantation in the MeV-energy range. The 1.7-MV terminal voltage corresponds to beam energies of 3.4 MeV for singly charged ions such as H⁺ or He⁺ and 5.1 MeV for doubly charged ions such as He²⁺ and heavy ions. The tandem is located in a new building addition, part of which is still in the construction phase (the area below the tandem and the second floor in Fig. 2.31). As illustrated, the tandem installation consists of two negative ion sources, the 1.7-MV tandem accelerator, and beam transport for two experimental scattering chambers.

The upper source beam line in Fig. 2.31 consists of a duoplasmatron ion source and a Li charge exchange canal for H and He beams. The lower beam line has a Cs sputter source of the Middleton type² for heavy-ion beams. The ions from each source are pre-accelerated up to 120 keV to optimize the injection optics for transmission through the tandem. The "T"-shaped tandem has a usable terminal potential range 0.4-1.7 MV. The design of this machine is somewhat unconventional in that the terminal potential is achieved with a RF driver and high-voltage multiplier housed in the base of the "T" rather than with a mechanical belt or chain bringing charge to the terminal. Much higher currents can be produced by this parallel-fed high-voltage multiplier (up to 2 mA at 1.7 MV).

Following the tandem is the beam transport system consisting of a quadrupole triplet, switching magnet, and two beam lines (11 and 30 deg) each containing a steering magnet, a beam profile monitor,³ collimators, faraday cups, and a scattering chamber. The switching magnet has

Fig. 2.31. Floor plan of the SHAC facility.

mass-energy products (mE/q^2) of 260 and 35 at 11 and 30 deg, respectively. Both beam lines were designed to accommodate RBS channeling experiments (the beams can be constrained to divergences as small as 0.02 deg with a corresponding loss of intensity). Also the collimators and faraday cups are cooled in anticipation of significant beam heating effects (beam currents of 100 μA at 5 MeV may be possible in this machine). The faraday cups are cooled by means of a closed-cycle heat pipe system that provides complete electrical isolation and a cooling capacity of about 1 kW. In addition to these features, the 11-deg beam line has an electrostatic scanning system³ for ion implantation. The 11-deg beam line will be completed by October 1986.

The period covered by this report has been one of installation and development for the tandem facility. This has involved installing laboratory services such as electrical power, water, compressed air, liquid nitrogen, and dry nitrogen gas throughout the building concurrently with the accelerator installation. After

the accelerator acceptance tests, modifications were made to the source area that included reconfiguring the source area to fit into the building floor plan, installing a source gas-handling system, rebuilding the freon cooling system for more reliable operation, adding a diffusion pump to the sputter source beam line so that each beam line would have independent vacuum pumping, and adding an automatic LN_2 refill system for the diffusion pump cold traps. In addition improved electrical grounding and safety interlock features were added for personnel safety.

At this time no modifications have been made to the accelerator, although some of the fittings in the pressurized SF₆ vessel may have to be replaced in the future.

Installation of the high-energy beam line, the switching magnet, and the 30-deg beam line is complete. This includes installation of beam pipe, scattering chamber, vacuum pumping and control equipment; collimators; beam profile monitor; faraday cups; and service lines for air, water, nitrogen gas, and liquid nitrogen.

The vacuum system was designed for eventual ultrahigh vacuum operation, ease of use, and maintenance of vacuum integrity in case of electrical power or component failure. Users can cycle the scattering chamber between atmosphere and high vacuum by simply throwing a switch. Pressures in the 10^{-10} Torr range have been achieved.

Installation of the ion scattering detection equipment is complete. The detector table and mount are installed, as is a two-axis goniometer. The nuclear pulse height analysis electronics for processing the detector signals has been installed and tested. A Nuclear Data ND680 data acquisition system is available for experiments.

The tandem operation has been reliable. Tank sparks at 1.7 MV have been very rare, and except for a bad capacitor in the control board, terminal stability has been very good. Performance of the tandem has been studied primarily with the duoplasmatron. Beam intensities of 20 μ A for protons and 2 μ A for He have been measured on the low-energy faraday cup before injection into the tandem. After acceleration He beam intensities through two 2-mm-diam collimators separated by 3 m is typically 60-particle nA for energies between 0.8 and 5 MeV. The lower energy corresponds to 0.4-MV terminal potential. Below this, transmission through the tandem drops rapidly. Although no direct measurements are available, proton intensities for the same collimator geometry should be about a factor of 10 higher. As yet little data have been obtained for the sputter source and transmission of its beams through the tandem. Beam intensities of 50, 140, and 150 μ A for ^{11}B , ^{63}Cu , and ^{197}Au , respectively, have been measured on the low-energy faraday cup. However, based upon our present understanding of the transmission of the ions through the tandem and expected sputter source yields,² we estimate that we should be able to produce scanned beams for ion implantation with intensities ranging from 40- to 100-particle μ A for the following ions: ^{12}C , ^{16}O , ^{19}F , ^{28}Si , ^{32}S , ^{58}Ni , ^{63}Cu , and ^{197}Au .

1. Purchased from General Ionex Corp., Newburyport, Mass.

2. R. Middleton, *Nucl. Instrum. Methods* 214, 139 (1983).

3. Purchased from National Electrostatics Corp., Middleton, Wis.

PULSED LASER PROCESSING

OVERHEATING AND UNDERCOOLING IN SILICON DURING PULSED LASER IRRADIATION¹

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D. M. Mills²

Nanosecond resolution time-resolved x-ray scattering measurements of thermal strain have been used to measure the lattice temperatures in silicon during pulsed laser irradiation. The measurements were performed using the pulsed

time structure of the Cornell High Energy Synchrotron Source, and they have provided measurements of the temperature of the liquid-solid interface as well as the temperature distribution below the interface. The results showed the interface temperature in $\langle 111 \rangle$ -oriented silicon to be 110 ± 30 K higher during the melting phase than during regrowth and 50 ± 25 K higher during melting than regrowth on $\langle 100 \rangle$ silicon. The analyses of measurements performed at near-zero interface velocity have provided an accurate calibration of the strain associated with the equilibrium melting temperature so that the interface temperature differences could be separated into overheating and undercooling components.

The experiments were performed by synchronizing the firing of ~ 25 -ns laser pulses of 248-nm wavelength photons with the arrival time of the synchrotron x-ray pulses and step-scanning the x-ray measurements to obtain time-resolved Bragg reflection profiles. The Bragg profiles were then analyzed in terms of thermal-expansion-induced strain and converted to lattice temperatures using the thermal expansion coefficients. Figure 2.32 shows the KrF laser pulse shape and the power incident on the sample as a function of time. Also shown in Fig. 2.32 are calculations³ of the melt-front penetration depth and calculations of the interface velocity as a function of time relative to the arrival of the laser pulse. The dashed lines indicate the nominal times of 16, 27, and 45 ns at which the measurements were made.

The measurements made at 16 and 45 ns probed the interface temperatures at the times of maximum melt velocity (~ 11 m/s) and maximum regrowth velocity (~ 6 m/s), while the intermediate time of 27 ns corresponded to the time of near-zero velocity as the heat input to the interface became equal to the heat flow away from the interface into the bulk. The temperature profiles for these times were determined by nonlinear least-squares fitting of the measured profiles with scattering calculations in which the depth distribution of the thermal strain was parameterized. The resulting temperature profiles for the region near the liquid-solid interface on $\langle 111 \rangle$ -oriented silicon are shown in Fig. 2.33. The interface temperature during 11-m/s melting was found to be essentially the same as that measured at zero velocity, indicating the requirement of little overheating to drive 11 m/s melting of silicon, while ~ 100 K undercooling is apparently necessary to regrow silicon at 6 m/s. Since the 27-ns interface temperature provides a calibration of the equilibrium melting temperature, overheating and undercooling are reckoned from this temperature rather than the absolute temperatures, which are affected by uncertainties in the temperature dependence of the expansion coefficients and the elastic constants. These results are somewhat surprising, as considerations of the principle of thermodynamic microreversibility would have predicted overheating and undercooling to be more nearly proportional to their respective velocities. This large difference in the driving force required for melting and crystal growth is not fully understood at present; however, the possi-

Fig. 2.32. Time structure of the laser pulses used in the experiment and calculations of the melt-front position and the interface velocity as a function of time relative to the laser pulse. The dashed lines indicate the chosen reference time and the nominal measurement times.

bility of different surface morphologies has been suggested as an explanation. Measurements at zero interface velocity were not made on $\langle 100 \rangle$ silicon so the overheating and undercooling components on $\langle 100 \rangle$ silicon could not be specified directly, but melting would not be expected to be more difficult on $\langle 100 \rangle$ than $\langle 111 \rangle$ silicon.

Comparisons of the measured temperature profiles to depths of $\sim 2 \mu\text{m}$ below the surface with numerical heat flow calculations have shown remarkably good overall agreement. However, the measured temperature gradients have been found to be systematically somewhat higher than those calculated for temperatures above 1000°C , suggesting the possibility that under temperature gradients $> 10^6 \text{ K/cm}$, the thermal conductivities are lower than those expected from literature values.

1. Summary of paper: *J. Mater. Res.* 1, 144 (1986).

Fig. 2.33. Measured lattice temperatures near the liquid-solid interface for measurement times of 16, 27, and 45 ns.

2. Cornell High Energy Synchrotron Source and School of Applied and Engineering Physics, Cornell University, Ithaca, N.Y.

3. Performed using a computer code supplied by M. O. Thompson.

SOLUTE TRAPPING: COMPARISON OF THEORY WITH EXPERIMENT

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The dependence of the nonequilibrium partition coefficient (k) of Bi in Si upon solidification velocity v has been measured for the first time with sufficiently high accuracy to distinguish between various proposed solute trapping mechanisms. This accuracy was achieved by combining high-resolution glancing-angle Rutherford backscattering (RBS) impurity depth profile analysis with transient conductance measurements of the liquid-solid interface velocity in pulsed laser melted, ion-implanted Si(100). Our results, for the velocity range from 2–14 m/s, show a much more gradual increase in k with increasing v than those previously reported. Our results also show no evidence for a "saturation" effect (i.e., $dk/dv \rightarrow 0$ at $k < 1$, for Bi in Si). The continuous growth model of Aziz fits the data quite well, whereas the stepwise growth model of Aziz and the two-level Baker model yield values of dk/dv that are too high to fit the data.

The present work was undertaken using Bi-implanted Si, because previous work had shown that the partition coefficient was far greater than the equilibrium value at velocities of several meters/second. Transient conductivity measurements on Bi-implanted silicon on sapphire samples were used in order to determine the melt history to high accuracy. Laser annealing was carried out using a pulsed ruby laser with pulse duration of 3 and 30 ns and energy densities between 0.56 and 1.16 J/cm². These conditions allowed v to be varied between 2 and 14 m/s. Determination of the partition coefficient was performed by numerical simulation with a finite difference solution to the heat conduction equation using the measured as-implanted profile and the measured melt depth as a function of time for each sample.

Figure 2.34 shows a comparison of simulations to RBS data for a sample in which the regrowth velocity is ~ 14 m/s. A liquid phase diffusivity of 2×10^{-4} cm²/s is necessary to reproduce the observed broadening of the profile. The solid and broken lines result from simulations at $k = 0.35$ and 0.20, respectively, and these bracket the data. The best fit value is taken to be 0.28.

The results of analyses of a number of samples, along with predictions of three simple solute trapping models are shown in Fig. 2.35. In the stepwise growth model of Aziz,⁴ in which diffusionless crystallization of a monolayer and solute-solvent redistribution alternate in time, the partition coefficient is given by $k = k_e + (1 - k_e)\exp(-1/\beta)$, where k_e is the equilibrium value. The dimensionless speed β is

Fig. 2.34. Partitioning of Bi in Si at 14 m/s. Specimen irradiated with a 0.56-J/cm² 3-ns pulse. Maximum melt depth 80 nm. Bi depth profile after pulsed laser melting taken in RBS scattering geometry shown. Profiles taken with the geometry shown. Simulations with $D_L = 2 \times 10^{-4}$ cm²/s.

Fig. 2.35. Dependence of partition coefficient on velocity. Triangles and circles: estimated from heat-flow calculations. Squares: v measured by transient conductance. Continuous growth model: $v_D = 32$ m/s. Stepwise growth model: $v_D = 10$ m/s. Baker model: $v_D = 1$ m/s.

given by v/v_D , where the diffusive speed v_D is the only free parameter in the three models considered; v_D was chosen in each case to yield the best overall fit to the data. In the dilute solution limit of the continuous growth model of Aziz,⁵ expected to apply if the increase in solute potential occurs simultaneously with a steady-state advance of the interface, the partition coefficient is given by $k = (\beta + k_e)/(\beta + 1)$. In the two-level Baker model,^{4,6-8} in which the impurity is treated as diffusing in a continuum down a steep energy gradient at the interface, $k = \{\beta + \ln k_e\} / \{\beta + [(1/k_e)\ln k_e \exp(-\beta)]\}$.

For all three equations above, v appears only as the ratio v/v_D . Thus, in a plot of k vs $\log v$ (Fig. 2.35), a change in v_D produces only a rigid horizontal shift of the curves, with no change in slope. For the present data, the stepwise growth model and the two-level Baker model produce curves that rise too steeply. These models yield a partition coefficient that is much too low at 3.2 m/s and much too high at 14 m/s. The continuous growth model, on the other hand, fits the present data quite well.

Data from the original work of Baeri et al.⁹ and of White et al.¹⁰ are also shown in Fig. 2.35. While sufficient to establish that k increases far beyond k_e as v increases, their data are not accurate enough to allow definite conclusions regarding appropriate models or the presence of "saturation." Note that there is no evidence in our data for the saturation effect.

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Z-CONTRAST STEM AND RBS IMAGING OF THE FINAL THICKNESS AND DEPTH OF BURIED MOLTEN LAYERS IN AMORPHOUS SILICON¹

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S. P. Withrow

Time-resolved electrical conductance² and optical reflectivity¹ measurements³ demonstrate that low-energy density (E_f) pulsed laser irradiation of amorphous (a) silicon layers [produced on crystalline (c) silicon substrates by ion implantation] can result in the formation of a thin, buried liquid layer that propagates through the a-Si at velocities of 8-14 m/s.¹ Postirradiation cross-sectional transmission electron microscope (TEM) views⁴ typically show a region of large-grained polycrystalline silicon (LG p-Si) near the surface and fine-grained (FG) p-Si at greater depth. It has been suggested² that recrystallization of the original a-Si region occurs in two steps. The LG region results from solidification of a thin, "primary" melt. The latent heat released during this process raises the temperature of the LG p-Si above the melting temperature T_m of a-Si, and the a-Si beneath then begins to melt, resulting in formation of a thin and nearly self-propagating molten layer whose forward motion is driven by the differences in the heats of fusion of the a- and c-phases ($L_a = 0.73 L_c$ ⁵) and in their melting temperatures [$T_c - T_a = 200$ (± 50) K⁶]. Because of the difference in melting points of the a- and c-phases, the buried molten layer produced in laser-irradiated a-Si is expected to be highly undercooled relative to T_c . Thompson et al.⁶ have postulated that the FG p-Si region observed via TEM is formed by recrystallization occurring at the highly disordered back interface of this undercooled liquid layer. The high velocities that are measured for the buried layer are consistent with crystallization occurring from a highly undercooled liquid.¹

We recently used the new technique of Z-contrast scanning transmission electron microscope (STEM) imaging⁷ to obtain the first direct high-resolution images of the final thickness and depth of the buried liquid layer, via imaging of ion-implanted Cu that was transported from original locations near the top of an ion-

implanted layer to greater depths by the propagating buried liquid layer. The a-Si specimens were prepared by ion implantation of Cu ions at a dose of $5 \times 10^{17}/\text{cm}^2$, using five different implantation energies to produce a "flat" Cu profile that was confined entirely to the top 300 nm, followed by 180-keV Si ion implantation, resulting in a total a-Si thickness (determined by TEM) of 410 nm. A pulsed KrF excimer laser (248-nm, 35-ns FWHM pulse duration) was used for the laser irradiations.

It was recently shown⁷ that heavy dopants in Si can be directly imaged by detecting Rutherford-scattered transmitted electrons in a STEM using an annular detector placed around the transmitted beam. By collecting electrons scattered at large angles (>0.1 rad), one obtains an image intensity that is proportional to $Z^2 n_i Z_i^2$, where n_i is the number of atoms of atomic number Z_i under the electron probe. Very strong Z-contrast imaging is obtained, and the contrast in the image accurately reflects dopant concentration variations at peak doping levels of order 1%, provided that care is taken to avoid channeling of the incident beam which occurs in crystalline samples oriented near low-order Bragg reflections. The high-angle Z-contrast image has great sensitivity for detecting segregation phenomena and for spatially resolved elemental mapping in thin specimens.⁷

Because Cu has very low solid solubility in Si (and a low interface segregation coefficient), pulsed laser melting of Cu-implanted a-Si is expected to result in substantial surface segregation of Cu. For the same reason, if a buried molten layer is generated in Cu-implanted a-Si, segregation of Cu to a point deep inside the original a-layer should also occur, as the Cu is transported by the propagating buried layer. Two other groups have recently used RBS measurements to observe such a deep Cu segregation peak and have pointed out that it provides primary evidence that explosive crystallization is mediated by a thin, propagating molten layer.⁸ However, the depth resolution of RBS measurements is insufficient to provide precise information about the thickness of the buried layer (BL) (see below), so we have instead obtained direct measurements of its thickness from Z-contrast STEM.

Figure 2.36 shows Z-contrast STEM images of Cu that was transported by the BL and the corresponding conventional cross-sectional TEM images, following irradiation of (Cu + 180-keV Si)-implanted specimens at 0.143 and 0.167 J/cm². Comparison of the pairs of images in Fig. 2.36 shows that the Cu image of the BL does lie at the boundary between the FG p-Si and the remaining, unmelted a-Si, consistent with the model of Thompson et al.⁶ The width of the image of the deposited Cu provides a direct measure of the thickness of the buried layer at the time that it solidifies. A line scan perpendicular to the Cu image in Fig. 2.36 gave a final BL thickness of 15 nm, slightly thinner than the initial 18-nm maximum thickness estimated from TEC measurements on Si-implanted silicon-on-sapphire.⁹ Our Z-contrast measurements actually provide an upper limit on the final BL thickness, because of averaging over the nonplanar BL interface (Fig. 2.36) through the finite specimen thickness and

Fig. 2.36. (Left) Conventional cross-sectional TEM images and (right) Z-contrast STEM images of (180-keV Si + Cu)-implanted Si, following KrF laser irradiation at 0.143 (a) and (b) and 0.167 (c) and (d) J/cm².

the ~ 2.5 - μm electron probe beam diameter. Quantitative Z-contrast analysis revealed a Cu concentration $\sim 0.4\%$ above background in the BL.

Figure 2.37 shows results of 2.0-MeV He ion backscattering measurements of Cu segregation, both toward the surface and toward the a-c interface, following pulsed laser irradiation of Cu-implanted specimens. In order to accentuate the net transport of Cu by the BL, only the differences of the Cu distributions are plotted in Fig. 2.37 as a function of depth, for the as-implanted and laser-irradiated specimens. Both the net transport of Cu to greater depth with increasing E_L , throughout the low E_L range, and the beginning of substantial surface segregation at ~ 0.2 J/cm² are clear. However, the width of the region in which backscattering shows a net increase in Cu is not a measure of the BL thickness, because of the nonplanar BL interface; backscattering necessarily averages over the different BL depths found within the ~ 1 - μm ion beam diameter. Taking into account the backscattering instrumental depth resolution of ~ 21 nm at the depth of the BL and assuming the 15-nm BL thickness measured by TEM, the backscattering measurements imply a ± 24 -nm root mean square variation in the mean BL depth at 0.146 J/cm², in excellent agreement with cross-section TEM measurements of the variation in the FG p-Si depth at different locations. The total Cu backscattering yield was constant for $E_L < 0.20$ J/cm² but decreased for $E_L > 0.25$ J/cm², indicating the onset of Cu loss by vaporization from the

Fig. 2.37. Change in Cu distribution vs depth, for various E_L . [The difference yield is defined as Cu(laser-irradiated specimen) - Cu(as-implanted specimen).]

surface in the same E_L range for which surface segregation of Cu becomes significant.

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DIRECT OPTICAL MEASUREMENTS OF THE VELOCITY OF "EXPLOSIVELY" PROPAGATING BURIED MOLTEN LAYERS IN AMORPHOUS SILICON¹

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We recently reported¹ the first direct measurements of the velocity of pulsed-laser-induced "explosively" propagating buried liquid layers in amorphous (a) silicon and of the variation of buried layer velocity with depth and pulsed laser energy density (E_L), using time-resolved reflectivity measurements at visible and infrared wavelengths. (Post-laser irradiation measurements of the final thickness and depth of the buried layer were also carried out using scanning transmission electron microscopy and Rutherford backscattering methods.)²

Transient electrical conductance³ and optical reflectivity (R) and transmission measurements have been used to study rapid melting and solidification in crystalline (c) Si and a-Si, following pulsed laser melting of a shallow (<1 μm) near-surface region. For crystalline semiconductors, transient conductance measurements provide a powerful, relatively simple means for determining the position and velocity of the liquid-solid interface and the depth of melting, since the melt is continuously connected to the surface and its electrical conductivity is known. However, the interpretation of these measurements on amorphous semiconductors is complicated by the fact that a thin, propagating buried molten layer, not contiguous with the surface, may be formed. In such a case, the conductance measures the total thickness of molten material present at any time, but not its depth or velocity. As a complement to conductance measurements, time-resolved visible and infrared R or transmission measurements have advantages for dynamical studies of the formation and propagation of the buried molten layer in a-Si. Because the 1152-nm HeNe wavelength is only weakly attenuated by either c- or a-Si, interference maxima and minima appear in R(1152 nm) due to reflections by the sample surface and by the buried layer moving beneath the surface; from these the buried layer position and velocity can be determined directly as functions of time, if the depth of any additional surface melt is not too great.

A KrF excimer laser (248-nm, 45-ns FWHM pulse duration) was used to irradiate a-Si layers that were produced by Cu ion implantation at a dose of $5 \times 10^{15}/\text{cm}^2$, using five different implantation energies to produce a "flat" Cu profile that was confined to the top 300 nm, followed by 180-keV Si ion implantation at a dose of $10^{16}/\text{cm}^2$. The a-layer thickness determined by transmission electron microscopy was 410 nm ($\pm 5\%$). Time-resolved reflectivity measurements were carried out simultaneously at 633 and 1152 nm using low-power HeNe probe lasers that were aligned to be accurately colinear and centered on the same spot; the $1/e^2$ FWHM for both probe beams was measured to be about 60 μm in the plane of the front surface of the sample.

Figure 2.38 shows the 633- and 1152-nm reflectivity signals following irradiations at various KrF laser E_L . For $0.13 < E_L < 0.16 \text{ J}/\text{cm}^2$, strong interference maxima and minima are seen to modulate both R signals, due to interfering reflections from the sample surface and from the buried molten layer moving away from the surface. At higher E_L (Fig. 2.38), the duration of high R is much longer at 1152 nm than for 633 nm, and the 1152-nm signal still exhibits deep interference maxima and minima when the buried layer is at depth for which the 633-nm beam is strongly attenuated. The latter's attenuation results in part from a thin molten region at the surface (particularly at earlier times) but is also due to the hot polycrystalline Si that crystallizes behind the moving buried layer (especially at later times). The depth of the buried layer beneath the surface actually varies slightly² within the probe laser beam diameter, causing a further "phase smearing" reduction of the oscillatory R signals that is greatest at 633 nm. At low E_L the rapid decay of the 633-nm R signal,

Fig. 2.38. R (in arbitrary units) as a function of time and KrF laser E_L at visible (633 nm, —) and infrared (1152 nm, ---) probe laser wavelengths.

after its initial peak, shows that the surface has already solidified at times when the buried layer is still moving and is easily visible at 1152 nm (e.g., $E_1 = 0.158$ or 0.178 J/cm² in Fig. 2.38). In this case the buried molten layer is separated from the surface of the sample only by a layer of recrystallized fine-grained polycrystalline Si (FG p-Si), so that its velocity can be obtained as a function of depth directly from the measured time intervals between successive 1152-nm interference maxima and minima in Fig. 2.38, which correspond to optical path differences of $1/4$ -wave in the FG p-Si. Figure 2.39 is a plot of buried layer velocity vs depth obtained in this way, using the index of refraction $N(1152 \text{ nm}) = 4.0$ for FG p-Si ($1/4$ -wavelength = 72 nm in FG p-Si).

Figure 2.39 shows that the maximum buried layer velocity (13–14 m/s) observed in these experiments is just slightly below the limiting velocity of 15 m/s, above which direct amorphous regrowth from an undercooled Si melt occurs in the (100) direction.³ The average temperature in the highly undercooled buried molten layer is expected to be slightly higher than the melting

temperature of a-Si [i.e., about 200 (± 50) K below the c-Si thermodynamic melting point].^{4,5} This undercooling of the buried layer provides the driving force for the recrystallization occurring at its trailing edge.

Earlier work dealing with epitaxial regrowth at a single recrystallizing melt-crystalline solid interface has shown that the velocity coefficient of undercooling, β^u (defined by $\Delta T_u = \beta^u V$), is dependent upon crystal orientation. Larson et al.⁶ have used time-resolved x-ray diffraction measurements of lattice strain during pulsed KrF laser melting and recrystallization to estimate $\beta^u = 18.3 (\pm 5)$ K/(m/s) and $\beta^u = 8.3 (\pm 4.5)$ K/(m/s) for (111) and (100) silicon, respectively. Galvin et al.,⁷ using transient conductivity measurements on (100) SOS films irradiated with 2.5-ns ruby laser pulses, have estimated $\beta^u = 15 (\pm 5)$ K/(m/s). Thompson et al.,⁸ also using transient conductivity measurements on (100) SOS but with 28-ns ruby laser pulses, reported $\beta^u = 17 (\pm 3)$ K/(m/s).

The maximum buried layer velocity of 14 m/s that is observed in our experiments shortly after the buried layer is formed, together with its expected undercooling of about 200 K, corresponds to $\beta^u \sim 14$ K/(m/s), a value that is in good agreement with the results just quoted, taking into account the different orientations of the fine poly-Si grains that are formed in our case. Figure 2.39 also shows that the buried layer velocity is a function both of depth and of the incident laser E_1 . The sudden quenching of the buried layer velocity at the end of its travel (especially noticeable at the higher E_1 values) is caused by the rapidly increasing heat loss as the buried layer approaches the high thermal conductivity c-Si substrate.

Fig. 2.39. Buried layer velocity vs depth and laser E_1 . The data points are plotted at depths corresponding to the calculated mean depth of occurrence of successive pairs of 1152-nm reflectivity minima and maxima, in the absence of any surface melt. The points on the abscissa correspond to the final depth of the buried layer.

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HIGH-SPEED TIME-RESOLVED ELLIPSOMETRY¹

G. E. Jellison, Jr. D. H. Lowndes

A time-resolved ellipsometer has been constructed which is capable of measuring any one of the related ellipsometric parameters N , S , or C continuously as a function of time, with a

detector-dependent time resolution ranging from ~100 ns down to the low picosecond range. The related ellipsometric parameters are defined as $N = \cos 2\psi$, $S = \sin 2\psi \sin \Delta$, and $C = \sin 2\psi \cos \Delta$, where the quantities ψ and Δ are the common ellipsometric angles, given by $r_p/r_s = \tan \psi e^{i\Delta}$, and r_p (r_s) is the Fresnel reflection coefficient for light polarized parallel (perpendicular) to the plane of incidence.

The ellipsometer is of the standard polarizer-compensator-sample-analyzer (PCSA) type, where the analyzer is a Wollaston prism. (A Wollaston prism has the property that light polarized in different directions is deviated by roughly the same small angle, in opposite directions, after exiting the prism.) Using very fast photodetectors and a fast digitizer, it is possible to record the intensity of both emergent beams, whose polarizations will be mutually perpendicular. Therefore, the quantity

$$F = [I_1 - I_2]/[I_1 + I_2] \quad (1)$$

will be equal to N , S , or C , depending on the azimuthal orientations of the polarizer, compensator, and analyzer. The quantities I_1 and I_2 are the intensities of the two emergent beams. If we restrict the orientations of the polarizer, compensator, and the analyzer to modulo 45° , there are 80 possible configurations of the ellipsometer (16 of the configurations come when no compensator is in the system). It is possible to calculate the dependence of F on small deviations of the azimuthal orientations of the optical components, as well as small errors in the phase shift of the compensator, and thereby arrive at schemes where adding or subtracting the F s determined from different configurations results in the elimination of many first-order errors. (This scheme is often called zone averaging.)

Since there are no moving components to this ellipsometer, the time resolution is dependent only on the rise time of the detector system and the bin time and bandwidth of the digitizer. We have performed some experiments using p-i-n diodes as photodetectors and a Tektronix 390 two-channel digitizer (33-ns bin time, 10-bit resolution), discussed below. Theoretically, <10 ps or better time resolution is possible, using a streak camera as both the photodetector and as the digitizer; these experiments are in progress in our laboratory.

This technique has been used to study pulsed-laser-irradiated silicon, using a HeNe (633 nm) ultrastable probe laser, on the 100-ns timescale. Figure 2.40 shows N , S , and C before and after pulsed laser irradiation of (100) crystalline silicon by a KrF excimer laser (248-nm, 35-ns pulse width, $1.0\text{--}J/\text{cm}^2$ energy density). The sharp discontinuities in these parameters shortly after the onset of the KrF laser pulse are due to melting and are described in Ref. 1. Note that the quantity S changes abruptly from ~0.063 before the laser pulse to ~0.039 after the laser pulse. [The parameter S is nearly proportional to the surface layer thickness times the surface layer refractive index if this thickness and the extinction coefficient (k) of the substrate are small ($\alpha = 0.018$ for Si at 633 nm).] Subsequent laser irradiations of the same sample surface

Fig. 2.40. Values of N , S , and C obtained with ~100-ns time resolution before and after pulsed laser irradiation of crystalline silicon with a KrF excimer laser. The onset of the laser pulse is at the zero of time.

resulted in the same value of S before and after the laser pulse. Therefore, it can be concluded that the first laser pulse reduces the "effective oxide thickness" of the sample surface, probably by "burning off" organic contaminants from the sample surface.

The quantity S does not approach very close to zero after the laser pulse. This indicates that either the native oxide layer never leaves the surface during the laser melting and solidification process or that oxide regrowth is extremely rapid (taking place in <200 ns) and that it regrows to the same 2.0-nm thickness on all subsequent laser shots. This conclusion is drawn from the fact that if the oxide layer were burned off or evaporated during the laser pulse and regrew slower than within ~200 ns, the quantity S would approach very close to 0, which is not observed.

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2. G. E. Jellison, Jr., and D. H. Lowndes, Appl. Phys. Lett. 47, 720 (1985); "Time-Resolved Ellipsometry Measurements of the Optical Properties of Silicon During Pulsed Excimer Laser Irradiation," this report.

CHARACTERISTICS OF INHOMOGENEOUS MELTING OF Si DETERMINED FROM TIME-RESOLVED ELLIPSOmetry MEASUREMENTS¹

G. E. Jellison, Jr. R. F. Wood

Time-resolved ellipsometry (TRE) measurements of silicon during pulsed excimer laser irradiation have been described elsewhere in this report.² These measurements have the advantage

over normal-incidence time-resolved reflectivity measurements in that additional parameters can be measured, which can place valuable constraints on the interpretive model.

As has been mentioned,³ time-resolved reflectivity measurements indicate that the melt-in process does not occur in a homogeneous manner, but rather a more complicated procedure must be invoked to explain the observed data. If the melt-in process is assumed to be one-dimensional with a well-defined and sharp melt front separating the liquid surface layer and the solid beneath, there is only one free parameter (the liquid thickness) to use in a calculation of the reflectivity as a function of time. Since TRE measurements give two independent parameters (ψ and Δ),⁴ it is possible to calculate two values of the liquid thickness for each time. These values are shown in Fig. 2.41 for Si irradiated with 0.8 J/cm^2 (just above the melt threshold); clearly, the liquid thickness calculated from ψ is significantly less than that calculated from Δ , indicating that the simplest model of the melt-in process is not adequate.

A more realistic model is one in which the near-surface region is assumed to consist of a layer of liquid and solid coexisting (slush) just as melting begins. If the near-surface region is modeled as a liquid-solid effective medium, two free parameters (the thickness of the effective medium layer D and the fraction of solid in the liquid layer F_s) can be determined from the TRE parameters ψ and Δ as functions of time; these are shown in Fig. 2.42(a). With values of D and F_s determined, the polarized reflectivities, R_s (for light polarized perpendicular to the plane of incidence) and R_p (for light polarized parallel to the plane of incidence), can be calculated and compared with experimental values determined from the TRE experiments. This comparison in Fig. 2.42(b) shows that the model is internally consistent. The effective thickness of the liquid $[(1 - F_s)D]$ can also be calculated and is shown in Fig. 2.41, labeled EM.

Figure 2.42(a) shows that F_s decreases continuously to a value of ~ 0.2 at 12 ns after the onset of melting, when it starts to increase again to a value of 1 at 24–25 ns. During this time, the thickness of the effective medium layer remains relatively constant at $\sim 20 \text{ nm}$. For a case when the irradiation energy was much higher (1.4 J/cm^2 , not shown), F_s decreased from 1 to 0 in $\sim 7 \text{ ns}$. Therefore, even for energy densities sufficient to create a long-lived melt ($\sim 85 \text{ ns}$ in this case), it takes an appreciable amount of time for the near-surface region accessible to the 632.8-nm probe beam to melt completely.

The picture suggested by our effective medium model is one in which the liquefaction of the near-surface region occurs as a bulk process, with liquid inclusions forming within the top 20 nm and then growing as more laser energy is absorbed. The inclusions must, in general, be smaller than the wavelength of light, if the effective medium approximation is to be used. If the inclusions were larger than the wavelength of the probe beam, a model based on incoherent reflections must be used, which did not fit the data. Clearly, the effective medium model presented here represents a simplification of the

Fig. 2.41. The thickness of the liquid layer on Si as a function of time during pulsed laser irradiation just above the melting threshold (0.8 J/cm^2), calculated in three different ways. Time = 0 corresponds to the initialization of the melt. The dashed-dotted lines refer to the thicknesses calculated from the ψ vs time and the Δ vs time profiles obtained from the TRE experiments. The solid line, labeled EM, corresponds to the thickness vs time obtained by the product of the effective medium thickness times the fraction of liquid.

real situation during laser melt-in. A more realistic model would treat the near-surface region with several layers, each described by a fraction of solid and a thickness. However, it would not be possible to determine these extra parameters from the TRE measurements, since there are only two measured parameters, ψ and Δ .

1. Summary of paper to be published.

2. G. E. Jellison, Jr., and D. H. Lowndes, "Time-Resolved Ellipsometry Measurements of the Optical Properties of Silicon During Pulsed Laser Irradiation," this report; *Appl. Phys. Lett.* 47, 718 (1985).

Fig. 2.42. (a) The effective medium thickness D and the fraction of solid F_s calculated from ψ and Δ using the effective medium theory for Si irradiated with KrF excimer laser pulses of 0.8 J/cm^2 . (b) The reflectivities for light polarized parallel (R_p) and perpendicular (R_s) to the plane of incidence; the lines refer to R_s and R_p calculated from the effective medium thickness D and the fraction of solid F_s given in (a) above, while the points refer to actual experimental data points. Time = 0 corresponds to the initialization of the melt.

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TIME-RESOLVED ELLIPSONOMETRY MEASUREMENTS OF THE OPTICAL PROPERTIES OF SILICON DURING PULSED LASER IRRADIATION¹

G. E. Jellison, Jr. D. H. Lowndes

Time-resolved reflectivity measurements have been used for several years to examine the laser annealing process during and immediately after laser irradiation.² However, not all the infor-

mation in the optical reflectivity is collected from a measurement of the reflected intensity; information regarding the phase shift of the reflected light and the relative magnitudes of light reflected perpendicular and parallel to the plane of incidence is lost. This additional information can be collected, however, if a time-resolved ellipsometry experiment is performed. From these data, it is then possible to calculate the effective dielectric functions of the high-reflectivity phase and of the hot, solid silicon before and after melting.

The time-resolved ellipsometer used for these experiments was the standard polarizer-compensator-sample-analyzer (PCSA) system set at 68.2° angle of incidence. The probe beam was an ultrastable low-power cw HeNe laser ($\lambda = 632.8 \text{ nm}$), while the exciting (melting) beam was from a KrF excimer laser ($\lambda = 248 \text{ nm}$, pulse width $\sim 40 \text{ ns}$, pulse-to-pulse reproducibility $\pm 5\%$, spot size $< 5 \text{ mm} \times 5 \text{ mm}$). An avalanche photodiode was used as a photodetector, connected to a Tektronix 7912 A/D waveform digitizer for convenient data recording and subsequent transfer to a computer. Lenses were used to focus the probe beam to a $20 \times 50\text{-}\mu\text{m}$ spot on the sample surface. Zone averaging was used to reduce effects of systematic errors in the azimuthal angles of the polarizer, compensator, and analyzer. From the data taken in this experiment, we could determine the associated ellipsometric parameters N ($=\cos 2\psi$), S ($=\sin 2\psi \sin \Delta$), and C ($=\sin 2\psi \cos \Delta$) and the effective dielectric functions $\langle \epsilon_1 \rangle$ and $\langle \epsilon_2 \rangle$, all as functions of time. The overall time resolution of the system was 1 ns .

In general, there are five regions of the behavior of the dielectric function versus time: (1) after the laser pulse, but before melting, $\langle \epsilon_1 \rangle$ and $\langle \epsilon_2 \rangle$ increase monotonically, as a result of the temperature increase of the near-surface region; (2) after the beginning of the melt, but before the melt has penetrated more than ~ 2 skin depths, $\langle \epsilon_1 \rangle$ peaks, as does $\langle \epsilon_2 \rangle$ if the melt front penetrates far enough; (3) after the melt has penetrated more than ~ 2 skin depths, $\langle \epsilon_1 \rangle$ and $\langle \epsilon_2 \rangle$ take on the values of the molten phase; (4) as the melt comes back to the surface, region (2) is repeated; and (5) after the surface has resolidified, $\langle \epsilon_1 \rangle$ and $\langle \epsilon_2 \rangle$ decrease monotonically, resulting from the decrease in surface temperature after the laser pulse.

Using these measurements, we can determine the optical properties of liquid silicon at $\lambda = 632.8 \text{ nm}$; these are shown in Table 2.3. Also shown in Table 2.3 is an interpolation of the results of Shvarev et al.,³ which are in minor disagreement with the results presented here. This discrepancy could be due to (1) the interpolation used (they performed their measurements at 400 and 700 nm), (2) the polaroid polarizers used in their ellipsometer, or (3) a thin layer on the surface of their sample which was not taken into account.

As was mentioned above, the behavior of $\langle \epsilon_1 \rangle$ and $\langle \epsilon_2 \rangle$ in regions 1 and 5 can be explained in terms of the temperature changes of the near-surface region before and after melting.

Figure 2.43 shows the "effective" surface temperature before and after the surface melt derived from the values of $\langle \epsilon_1 \rangle$ and $\langle \epsilon_2 \rangle$ deter-

Table 2.3. Optical properties of liquid silicon at $\lambda = 632.8$ nm determined by time-resolved ellipsometry (this work) and by Shvarev et al.³

Author	n	k	ϵ_1	ϵ_2	R
Shvarev et al. ³	2.9	5.2	-19	30	0.73
This work	3.8	5.2	-12	40	0.71

Fig. 2.43. Effective surface temperature vs time. The panel to the left shows the temperature rise before the onset of melting, where time = 0 indicates the beginning of the laser pulse. The panel to the right shows the temperature drop after the surface has solidified. Surface temperatures are shown for two different energy densities of the KrF laser. The error bars give representative confidence limits for the measurements.

mine⁴ in these experiments and the known temperature dependence of the dielectric function⁴ for two different energy densities. The surface temperature can only be determined "effectively" because it is not possible to take the temperature-depth profile into account.

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TIME-RESOLVED AND TEM STUDIES OF THE ONSET OF NUCLEATION AND CRYSTALLITE GROWTH IN HIGHLY UNDERCOOLED LIQUID SILICON

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G. E. Jellison, Jr.

We recently used nanosecond time-resolved optical measurements at visible (633 nm) and infrared (1152 nm) wavelengths to show that one solidification mode that quite generally results from pulsed laser irradiation of ion-implanted a-Si layers is the formation of thin (~15 nm), "explosively" propagating buried molten layers that move through the a-Si at velocities of 8–14 m/s and result in formation of fine-grained polycrystalline silicon.¹ However, as shown below, these same time-resolved optical measurements also provide clear evidence of other nucleation and crystallite growth events occurring very near the highly undercooled liquid surface, at times before the formation of the buried molten layer.

Figure 2.44 shows the reflectivity signals observed for 195- and 410-nm-thick a-Si layers for various pulsed KrF (248 nm) laser energy densities. For both sets of samples the reflectivity does not have the flat-topped shape characteristic of pulsed-laser-melted c-Si. (The optical skin depths for liquid Si are about 9.6 and 12 nm at the 633- and 1152-nm wavelengths, respectively.) Instead, the reflectivity reaches an initial peak value (typically ~60%) about 10 ns after the onset of surface melting but then decays to lower values. After approximately 10 ns more, the first minimum in the reflectivity signal is observed, due to the top of the buried layer passing through a depth of about 70 nm below the surface. These results strongly suggest that nucleation and crystallite growth begin within a few nanoseconds after melting has occurred and that the latent heat of fusion released by these early crystallization events is the "trigger" for formation of the buried liquid layer. Thus, the nature of the initial nucleation and crystallization process(es) occurring in the highly undercooled primary near-surface melt is of interest.

Plan-view transmission electron microscopy (TEM) micrographs (Fig. 2.45) of the 195-nm-thick a-Si specimens reveal that very well defined Si "flakes" are present at the surface for all pulsed laser energy densities (E_1), but that striking changes occur in the structure of these flakes with increasing E_1 . The mean diameter of the flakes increases rapidly while the number density of flakes decreases continuously with increasing E_1 . Microdiffraction studies showed that the flakes formed at $E_1 = 0.17$ J/cm², just above the 0.13 J/cm² melting threshold, are mostly amorphous; flakes formed at higher E_1 are amorphous only at the center, becoming crystalline with increasing radial distance; for $E_1 = 0.45$ J/cm² the few, large diameter flakes are entirely crystalline near the sample surface, typically consisting of defective bicrystals.

Our structural studies suggest that nucleation and crystallite growth leading to formation of flakes is initiated near the liquid-amorphous Si interface, where melt undercooling is the

Fig. 2.44. Reflectivity vs time at 1152-nm (solid traces) and 633-nm (dashed traces) probe laser wavelengths, for 410-nm (left) and 195-nm (right) thick a-Si specimens, produced by ion implantation into (100) c-Si substrates. (The 410-nm-thick specimens also contain implanted Cu in the top 300 nm.)

greatest, or at the interface itself. An initial burst of very rapid radial growth is followed in this model by growth at decreasing velocities, resulting in the observed transition from primarily amorphous to primarily crystalline silicon with increasing radial distance from the

Fig. 2.45. Plan-view TEM micrographs of Si flakes formed at the surface of an originally 195-nm-thick a-Si layer, following pulsed KrF laser irradiation at (a) 0.14, (b) 0.17, (c) 0.19, (d) 0.23, (e) 0.36, and (f) 0.43 J/cm².

nucleation site. Such a transition is consistent with recent experiments which show that the amorphous phase of Si can be formed directly from an undercooled melt if the regrowth velocity exceeds about 15 m/s on a (100) interface.² Assuming an average radial growth velocity of 10 m/s, the time required to form the 100-180-nm radius flakes that were found in 195-nm thick a-Si for $E_f = 0.17$ -0.23 J/cm² lies in the range 10-18 ns, in excellent agreement with the time scale on which the reflectivity signals decay and the buried layer is formed in Fig. 2.44.

In order to obtain information about possible changes in flake morphology as a function of depth beneath the sample surface, we also examined TEM plan-view micrographs of a particular flake after each of a series of ion beam milling steps, at equal intervals of milling time. The flake diameter was found to be remarkably constant over its entire depth, but its morphology changed from highly crystalline near the specimen surface to mixed fine polycrystalline and a-Si, near its bottom boundary, just above the remaining unmelted a-Si.

Our optical and TEM studies suggest that nucleation and growth resulting in silicon flakes and recrystallization occurring at the back interface of a thin, propagating buried molten layer, resulting in fine-grained and/or a-Si, are simply two different but closely related aspects of a single process of solidification from highly undercooled liquid silicon. According to this view, the initial process of flake

nucleation and growth releases heat of crystallization that can trigger formation of the propagating, buried liquid layer. As the buried layer moves downward, the flake grows downward with it, at the velocity of the buried layer. The flake also can grow in the upward direction, though presumably more slowly because of the generally higher temperature of the liquid near the surface, which is due both to continuing heat input of the laser (the FWHM pulse duration is 35 ns) and to recalescent heating of the liquid by heat rejected as flakes continue to grow. (Quantitative consideration of recalescent heating shows that only 11% of the surface area need be covered by flakes for all of the surrounding liquid to be heated from T_a to T_c , in the absence of any heat loss to the substrate.) Thus, differences in the growth velocity of flakes in the upward and downward directions probably can account for the observed changes in flake morphology with depth and E_f . Similarly, heating of the liquid Si to $T \sim T_c$, due both to recalescence and to increased laser heating of the melt with increasing E_f , should cut off nucleation of additional flakes in the primary melt near the surface. This heating should also favor slower regrowth of large-grained polycrystalline Si in this region, especially with increasing E_f , as is observed in cross-sectional TEM micrographs.

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2. M. O. Thompson et al., *Phys. Rev. Lett.* **50**, 896 (1983).

TIME-RESOLVED REFLECTIVITY MEASUREMENTS ON SILICON AND GERMANIUM USING A PULSED KrF EXCIMER LASER¹

G. E. Jellison, Jr.   D. H. Lowndes
D. N. Mashburn   R. F. Wood

Pulsed laser melting of semiconductors has been the subject of intensive study for the last 7-8 years.² The time of the onset of melting and the melt duration depend in a complicated fashion on the parameters of the laser pulse, including its wavelength, pulse duration, and shape, as well as its energy density.

We have performed a series of time-resolved reflectivity (TRR) measurements during pulsed KrF (248 nm, pulse width 40 ns FWHM) excimer laser irradiation of both silicon and germanium. The TRR measurements were performed at two different wavelengths (632.8 and 1152 nm), using cw lasers focused on the same spot. Melting model calculations were also carried out to compare with the experiments. These are the first TRR measurements on silicon and germanium irradiated by an excimer laser under exactly the same laser conditions, the use of which provides an independent check on both the generality and the details of the melting model calculations. Among the useful characteristics of excimer lasers are good pulse-to-pulse reproducibility of pulse

width and energy density (both $\pm 5\%$, unlike ruby or Nd:YAG lasers) and a short (<10 nm) absorption length in both Si and Ge. Excimer lasers are also potentially useful for semiconductor doping and p-n junction formation, making the data presented here useful for these applications.

Figure 2.46 shows the reflectivity of both Ge (top) and Si (bottom) at 632.8 nm, as a function of time for several different energy densities near the melting threshold. The reflectivity of Si increases monotonically with time during the heating of the solid by the laser pulse until surface melting results in a large increase of the reflectivity. On the other hand, the reflectivity of solid Ge first increases and then decreases with time during laser heating (this is not clear from Fig. 2.46, but becomes obvious on an expanded scale), until melting again results in a large increase in the reflectivity.

Two observations can be made from the data presented in Fig. 2.46 for energy densities just above the threshold for melting: (1) the maximum reflectivity increases with increasing energy

Fig. 2.46. TRR of Ge (top panel) and Si (bottom panel) at 632.8 nm during pulsed KrF excimer laser irradiation. The time profile of the laser pulse is shown in the bottom panel, for which the y-axis is in arbitrary units. The numbers labeling the figure are the laser pulse energy density in J/cm^2 .

density from the value expected for the hot solid to that expected for the liquid over a finite energy range, and (2) the duration of partial melting (defined as the time the reflectivity spends above the reflectivity of the hot solid, ~42% for Si and ~50% for Ge, but below that of an optically deep liquid) undergoes a discontinuous jump with increasing energy density: no partial melt durations were observed less than ~25 ns for Ge or ~20 ns for Si. These observations imply that melting does not occur homogeneously in the near-surface region.³

Two parameters that can be determined from TRR measurements for comparison with melting model calculations are the surface melt duration and the time of onset of melting. The time of onset of melting is defined as the time after the beginning of the laser pulse at which the slope of the TRR signal changes abruptly, indicating surface melting. The surface melt durations for Si and Ge are shown in the top panel of Fig. 2.47, while the times of onset of melting are shown in the bottom panel. As can be seen, the melting threshold for Si is significantly greater than

it is for Ge. For energy densities well above the melting threshold, the melt duration increases monotonically with energy density for both materials, with the rate of increase being much larger for Ge than for Si. The lines represent the results of melting model calculations (described below) and are in good agreement with experiment.

The major problem in implementing melting model calculations is that temperature-dependent thermal and optical properties must be included in the computer code. The thermal properties are reasonably well known and are discussed in Chapter 4 of Ref. 2. However, the optical properties of Si and Ge in both the solid and liquid phases have not been sufficiently studied at 248 nm. The absorption coefficients of liquid and solid Si and Ge are large ($>10^6/\text{cm}$), and therefore are not important parameters in the melting model calculations. The reflectivities, on the other hand, are large ($>60\%$), can vary with temperature in the solid phase, and are very important in determining the amount of energy deposited in the sample. We have treated the reflectivities in the hot solid and in the liquid as fitting parameters. The best fits were obtained using the reflectivities shown in Table 2.4, resulting in the calculated melt durations and times of onset of melting shown in

Fig. 2.47. Surface melt durations (top panel) and times of the onset of melting (bottom panel), as functions of pulsed KrF laser energy density for Si and Ge. The lines represent the results of melting model calculations, while the data points indicate some of the experimental results.

Table 2.4. The optical properties of Si and Ge at 248 nm. The reflectivities were determined by comparing the experiments with the results of melting model calculations (see text).

Material	Absorption coefficient ($\times 10^6/\text{cm}$)	Reflectivity
Si, solid	1.8	0.63
Si, liquid	1.5	0.70
Ge, solid	1.6	0.60
Ge, liquid	1.3	0.65

Fig. 2.47. A comparison of the results shown in Table 2.4 with data in the literature and from our own self-reflectivity measurements shows very good agreement.

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2. Pulsed Laser Processing of Semiconductors, ed. by R. F. Wood, C. W. White, and R. T. Young, Academic Press, New York, 1984.
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MEASUREMENT OF SOLUBILITY LIMIT OF Al IN Si DURING PULSED LASER ANNEALING¹

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It is well known that pulsed laser annealing can incorporate dopants into a silicon lattice to concentrations well above the equilibrium solubility limit. The measurement of the solubility limit achieved for various dopants during recrystallization is of considerable interest and is often done by Rutherford backscattering analysis. Provided the solubility limit is exceeded, the maximum substitutional concentration can be obtained from ion channeling analysis and represents the solubility limit for the particular regrowth velocity obtained during recrystallization.

In the case of Al-implanted Si, ion channeling analysis cannot be used due to insufficient energy separation of the Al and Si profiles. We have therefore used axial electron channeling analysis to measure the solubility limit, which is based on the detection of x-ray emission from a thin sample, with which the Al and Si peaks are easily resolved and well above the Bremsstrahlung background in the spectrum.

Figure 2.48 shows the TEM cross-section image of Al⁺ (50 keV $2 \times 10^{16} \text{ cm}^{-2}$)-implanted Si (100) following 1.3 J cm^{-2} pulsed excimer laser annealing. The formation of the cell structure is clearly seen. The cells in fact begin in fairly large precipitates, identified by x-ray analysis and microdiffraction to be Al. The cell walls then continue to the surface. The depth profile of the total Al concentration was obtained from x-ray analysis. With the microscope in a scanning mode, lines were scanned parallel to the surface to average over many cells and stepped back in depth to give the concentration profile shown in Fig. 2.49. It is clear that a plateau region exists behind the maximum cell depth of 100 nm. The band of precipitates gives a peak in the profile at about 60-nm depth, which drops slightly before rising sharply at the surface. A $\langle 100 \rangle$ axial electron channeling analysis was used to determine the substitutional concentrations. The depth resolution of the channeling analysis was about 50 nm, and fair agreement was obtained between

Fig. 2.49. Al concentration profile and axial electron channeling analysis.

measurements just below and just above the band of precipitates. The solubility limit was found to be $2.75 \pm 0.75 \times 10^{20} \text{ cm}^{-3}$. The high error bars are due to the fact that this concentration is approaching the detection limit of the technique. This solubility limit is a factor of 10 lower than that of Sb under similar conditions,³ but is still a factor of 10 above the retrograde maximum solubility limit under equilibrium conditions ($2 \times 10^{19} \text{ cm}^{-3}$).

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2. Consultant from Centre National de la Recherche Scientifique, Paris, France.
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PLASMA MATERIALS INTERACTIONS

WEIGHT CHANGE MEASUREMENTS OF EROSION/DEPOSITION AT BERYLLIUM LIMITER TILES IN ISX-B¹

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A. C. England² A. Gabbard²
R. A. Zuhr

The erosion of limiters and other components exposed to high particle and heat fluxes in the plasma edge of fusion devices is a major concern in component lifetime and plasma contamination. Previous measurements of erosion using laser-induced fluorescence and surface probes have provided localized information on erosion rates and mechanisms, but have not addressed the macroscopic, long-term erosion/redeposition behavior of limiters and other plasma edge structures. In this paper, we report the use of weight change measurements to monitor the erosion and redistribution of limiter material at a beryllium rail limiter during three months of beam-heated operation in the ISX-B tokamak.

Fig. 2.48. Cross-section electron micrograph of cells formed in Al⁺-implanted Si following pulsed laser annealing.

The limiter consisted of 12 individual beryllium tiles arranged in a rail assembly and mounted at the top of ISX-B as indicated in the inset of Fig. 2.50. Each tile was approximately $10 \times 10 \times 2.5 \text{ cm}^3$ and weighed approximately 260 g. The limiter functioned as the main limiter of ISX-B for more than 3500 beam-heated discharges with typical plasma parameters $I_p = 116 \text{ kA}$, $B_T = 11 \text{ kG}$, $N_e = 4 \times 10^{13}/\text{cm}^3$, $P_B = 0.8 \text{ MW}$ (0.25), and $t = 0.3 \text{ s}$. Under these conditions, the maximum power flux to the limiter was 2 kW/cm^2 . Early in this sequence, the plasma current was raised to 155 kA for 300 discharges to test the limiter at higher power loads. The 155-kA discharges resulted in surface melting of the limiter, and general topographic features developed during this melting persisted throughout the experiment.

The individual limiter tiles were weighed to an accuracy of 1 mg prior to installation in ISX-B and following completion of the experiment. The resulting weight changes are summarized in Fig. 2.50. Overall, the limiter showed a net weight loss of 2.0 g with the central tiles losing 3.2 g and the inside tiles (those closer to the inside wall of the torus) gaining 1.2 g. Surface probe measurements³ indicate that approximately 0.2 g of beryllium was distributed uniformly around the torus. The remainder of the weight loss is presumed to be in the form of small droplets of molten material which were observed on the inside wall and at the bottom of the vacuum vessel in the vicinity of the limiter. The weight gain of the inner tiles is attributed to the flow of molten material from the central tiles to the inside, consistent with the observed

flow pattern on the limiter surface. Since the limiter was mounted horizontally, this flow was probably driven by electromagnetic forces.

The overall results indicate that limiter surface melting during the period of high current operation was responsible for most of the beryllium loss and redistribution. The horizontal flow of beryllium along the limiter surface suggests a position instability for the melt layer which could contribute significantly to local erosion during fault conditions (such as disruptions) which result in surface melting. The observed erosion was much higher than expected from sputtering, demonstrating the importance of melt layer behavior in erosion processes. The results also establish the usefulness of weight change measurements for monitoring long-term erosion/deposition at limiters and other plasma edge components.

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2. Fusion Energy Division, ORNL.

3. R. A. Langley, M. B. Lewis, and R. A. Zuhr, "Migration of Beryllium in the ISX-B Tokamak During the Beryllium Limiter Experiment," this report.

POSTMORTEM NEAR-SURFACE ANALYSIS OF BERYLLIUM LIMITER TILES FROM ISX-B¹

R. A. Zuhr

Beryllium is a promising material for plasma-side components in magnetic confinement fusion devices and is being considered for possible use in the Joint European Torus (JET). In order to test beryllium as a limiter material, a collaborative JET/ISX-B experiment was carried out in which the ISX-B tokamak was operated for more than 3000 discharges with a beryllium limiter.² At the end of the test period the limiter was removed, and the composition of the near-surface region of selected tiles was analyzed as a function of position by Rutherford backscattering. Chromium, iron, and nickel were the dominant metallic impurities in the surface with a combined concentration on the order of 10^{16} cm^{-2} . Oxygen surface coverages were generally in the mid- 10^{16} cm^{-2} range. A consistent trend in the impurity data was that heavily damaged or melted areas generally incorporated more impurities. The amount of deuterium retained near the surface was measured by nuclear reaction analysis [$D(^3\text{He}, p)^4\text{He}$]. The amounts of deuterium trapped in the tiles ranged from 1 to $5 \times 10^{17} \text{ cm}^{-2}$ over all of the surfaces exposed to the plasma. No deuterium was detectable on surfaces (the protected sides) not directly exposed to the plasma.

As in the case of other tokamaks for which the limiter surface has been analyzed, the operating surfaces of the beryllium limiter tiles from ISX-B were shown to contain a mixture of the elements present in the vacuum vessel. The amount of foreign metals found on the tiles was somewhat less than has been observed recently on other machines, probably due to

Fig. 2.50. Weight change of the individual beryllium tiles as a function of their radial position. The location of the limiter with respect to the plasma is indicated in the inset.

beryllium coating of the walls, while the amounts of retained deuterium were generally comparable, even for different limiter materials. Thus, in terms of impurity and deuterium content, the beryllium limiter behaved much like the more conventional limiter materials.

1. Summary of paper: Journal of Vacuum Science and Technology (in press).

2. P. K. Mioduszewski et al., Nuclear Fusion (in press).

THE MIGRATION OF BERYLLIUM IN THE ISX-B TOKAMAK DURING THE BERYLLIUM LIMITER EXPERIMENT¹

R. A. Langley² R. A. Zuhr
M. B. Lewis

The beryllium limiter experiment was performed to study the suitability of beryllium as a limiter material in a large tokamak such as the Joint European Torus. The beryllium limiter has been described elsewhere,³ and the plasma physics results are the subject of other studies.⁴ The objective of this particular work was to measure the migration of beryllium throughout the tokamak vacuum vessel, the attached diagnostics, and the neutral beam lines after a relatively long running period during which more than 3000 neutral beam-heated plasma discharges were conducted.

This experiment provided a unique opportunity to study migration of a limiter material because beryllium is a material which has not been used in toroidal confinement devices and occurs only in trace amounts in commonly used materials (e.g., stainless steels, graphite, and titanium carbide). The migration of beryllium is important because it can coat the internal surfaces of the vacuum vessel, thereby creating a different internal surface material than the original surface, and it is a potential health hazard during maintenance procedures. The deposition of beryllium on the internal surfaces can also have advantages; i.e., gettering of oxygen by the deposited beryllium was observed during the experiment.

Two types of samples were exposed during the experiment. The first type of sample (A) consisted of a 304-L stainless steel plate with a single-crystal silicon plate, $6 \times 8 \times 0.15$ mm, attached to the steel plate at one corner. Seven of these samples were laid on the tokamak vessel floor at a position which would place them radially in the center of the plasma; six samples were placed in various diagnostics; and six samples were placed at various locations in the neutral beam lines. The seven samples laid on the vessel floor moved during the course of the experiment radially inward to the inner wall. This movement was presumably due to eddy currents and most probably occurred during the initial phase of the experiment. The second type of sample (B) was a single-crystal silicon plate $7.6 \times 19 \times 0.4$ mm. Four of these samples were placed at the inner surface of the outer vessel wall, and four were placed on the inner

surface of the vessel top. Figure 2.51 shows these various sample locations. At the end of the beryllium limiter test, all the samples were removed from the torus and tested for beryllium content using nuclear reaction analysis [$^9\text{Be}(p,\alpha)^6\text{Li}$].

The results obtained for the deposition of atomic beryllium in the main vacuum vessel are presented in Fig. 2.51. Of all samples placed in attached diagnostics and the neutral beam lines, only one showed a level of beryllium above the minimum detectable level. This sample was placed in the heavy ion beam probe port and had 2.1 mg/m^2 of beryllium deposited on it. In all cases where samples were located in the same toroidal position but in different radial locations, the sample located nearer the inner wall had the higher value, indicating that some of the beryllium moved radially inward during the discharge. From the distribution in Fig. 2.51, it is estimated that 200 mg (~10% of the material lost from the limiter)⁵ was vapor deposited on the inner surface area.

ORNL-CONF 85-7232A2

Fig. 2.51. Plan view of the ISX-B tokamak showing the placement of samples and the position of some internal components. The amount of deposited beryllium in mg/m^2 is shown in parentheses for each sample.

Particulate deposition was observed on those samples in direct line of sight with the beryllium limiter, with the density highest nearest the limiter. The observed particles had been splat-cooled and were rather firmly attached to the sample surface. The inner wall of the vacuum chamber at the limiter position had a high density of splat-cooled beryllium. The vessel floor beneath the limiter also had considerable beryllium debris on it.

From the photograph of the wall taken at the completion of the experiment, size and spatial distributions of the particulates were obtained. Weight distributions were obtained by removing splat-cooled particles and measuring their

thicknesses as a function of diameter. The results are shown in Fig. 2.52, which provides the total number of particles in a size group and, in addition, shows the estimated average weight of a particle within a size group. Particles less than 0.1-mm diam could not be resolved, and no particles larger than 2.5-mm diam were observed in this particle distribution.

Fig. 2.52. Size distribution of particulate beryllium on the inside wall of the vacuum vessel showing average diameter and weight.

In conclusion, both atomic and particulate distributions were measured as a function of position with respect to the beryllium limiter. Considering both of these distributions, there did not appear to be any major toroidal asymmetries (i.e., with or against the ion drift direction). It was observed that there were three probable sources of beryllium; evaporation of beryllium directly from the limiter, evaporation of beryllium droplets as they pass through the plasma and are heated, and direct sputtering of beryllium from the limiter and walls. This can be a major problem in the use of beryllium as a limiter material, but adjustments can be made to the plasma parameters to minimize or alleviate this problem (e.g., limiting the power to the limiter, which was accomplished by decreasing the plasma current in this experiment).

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4. R. Isler et al., Nuclear Fusion (in press).

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SURFACE EROSION OF LONG-TERM WALL SAMPLES IN JET¹

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The erosion and deposition behavior of plasma-side surfaces can seriously impact impurity introduction, hydrogen recycling, and component lifetimes in fusion devices. While there have been numerous measurements of erosion/deposition for samples exposed in the higher particle fluxes of the plasma edge, there is little direct evidence of erosion at the wall position in present tokamaks. Wall erosion and deposition are expected to be more important for the new generation of longer pulse, higher power tokamaks such as the Joint European Torus (JET). The expectation of measurable erosion rates in JET prompted this study using long-term surface samples.

The erosion/deposition measurements were made using a recently developed⁵ self-isotope marker technique to determine net erosion or deposition of carbon in graphite samples. The chemical equivalence of the marker and host simplifies the interpretation of the experiment and allows secondary ion mass spectrometry (SIMS) analysis without matrix effects. Papyex graphite strips were implanted with ¹³C ions to doses of $2.5 \times 10^{17}/\text{cm}^2$ at 10 keV and 180 keV using accelerators at the Solid State Division's Surface Modification and Characterization facility and the University of Munich. These implants resulted in two ¹³C marker layers at 30 and 450 nm below the surface of the graphite. The shallow implant was clearly distinguishable from the ¹²C of the host by Rutherford backscattering (RBS) using 2.6-MeV ⁴He ions, while the deeper implant could be profiled using SIMS with 5-keV O sputtering.

A total of 12 implanted graphite samples were positioned at various poloidal locations in JET and were exposed to 2200 discharges between November 1984 and June 1985. These included approximately 1000 full-length (10 s) discharges with plasma currents of 1.5–4 MA and 2–5 MW of ion cyclotron resonance heating (ICRH). Following exposure in JET, the samples were analyzed using RBS for ¹³C, O, and Fe-Cr-Ni and SIMS for H, D, ¹³C, Fe, Cr, and Ni. Changes in ¹³C marker depths were determined to approximately 5 nm to measure the erosion or deposition of carbon.

The carbon erosion data are summarized in Table 2.5. The shallow ¹³C implant could not be found in any of the samples, indicating a minimum carbon erosion of 30 nm. For four samples, the deep marker also could not be found, indicating erosion in excess of 500 nm. Extrapolated to steady state, this would correspond to a loss of wall thickness of approximately 1 mm/yr. The maximum erosion occurred at the inner wall and outer midplane of the torus.

Table 2.5. Carbon wall erosion in JET during 2200 plasma discharges.

Poloidal location	Erosion (10^{18} C/cm ²)	
	Octant III	Octant V
Outer midplane	>5	>5
Outer top	3	-
Top	2	-
Inner wall (top)	>5	4
Outer wall (bottom)	>5	4
Bottom	4	-

Substantial deposition of metallic impurities was also observed on all samples. This varied from ~10 nm of Fe-Ni-Cr at most locations to more than 1 μ m immediately adjacent to the location of a stainless steel probe "accident" which occurred during the experiment.

The overall results indicate large erosion rates at the wall position in JET which equal or exceed estimates based on charge exchange neutral sputtering. There are large poloidal

variations in both erosion and deposition, and there is little evidence for the redeposition of eroded wall material back on the walls. This suggests that carbon in the plasma edge is efficiently scraped off by limiters and other structures before reaching the walls. Experiments are currently under way to investigate the deposition of wall material on the JET limiter. The results also contribute to the understanding of the "plasma pumping" effect which occurs during current ramp down at the end of JET discharges. The large erosion rates at the inner wall are consistent with large ion fluxes impacting this region during the inward shift of the plasma during ramp down.

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3. Gesellschaft für Strahlen und Umweltforschung, Neuherberg, Federal Republic of Germany.
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3. DEFECTS IN SOLIDS

The properties of defects in solids are of fundamental importance in most solid state phenomena. As a result, examples of defect-related research can be found throughout this report. In this chapter, the emphasis is on activities where fundamental understanding of defect properties is often the major focus of the research effort. This includes research activities in x-ray scattering, electron microscopy, radiation damage, fracture, and semiconductor physics. Highlights of these activities range from structural studies of icosahedral phases in aluminum alloys to a new initiative for athermal epitaxial growth using laser photochemical vapor deposition (LPVD).

Significant progress is reported on the preparation and characterization of quasi-crystalline icosahedral phases in Al-Mn alloys and on interstitial behavior in silicon. Observations of the dislocation-free zone at crack tips during fracture have been extended to thick specimens using high-voltage electron microscopy. It is expected that LPVD will provide sensitive photonic control over thin-film deposition processes leading to rapid film growth at low temperatures with improved spatial resolution and options for nontoxic precursor gases. Research on solar cells has emphasized glow-discharge implantation and surface passivation.

Two major research facilities are currently coming on line which will give the Solid State Division unique capabilities for defect studies. The Low-Temperature Neutron Irradiation Facility (LTNIF) has been completed and is providing high irradiation fluxes under special environmental conditions (such as sample temperatures as low as 3.2 K) which have not been previously available in the U.S. The division has also participated in the development and installation of the ORNL x-ray beam line at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. This beam line became operational this year and is currently being utilized in diffuse scattering and quasi-crystal experiments.

IMPURITIES AND DEFECTS

FORMATION OF ICOSAHERAL AL-Mn BY ION IMPLANTATION INTO ORIENTED CRYSTALLINE FILMS¹

J. D. Budai² M. J. Aziz³

In experiments on rapidly quenched Al-Mn alloys, Shechtman et al.⁴ have reported electron diffraction patterns exhibiting both icosahedral point symmetry and Bragg peaks. Since conventional crystallography commonly considers

these two properties to be inconsistent, the observations have generated a large number of theoretical and experimental investigations into the nature of the atomic ordering in this new structure. Several authors⁵⁻⁷ have shown theoretically that icosahedral ordering can be described as the three-dimensional quasicrystal generalization of the two-dimensional Penrose tiling. By packing three-dimensional space with two different polyhedra in a nonperiodic way, they find that the locations of the vertices preserve true long-range bond orientational order with tenfold symmetry. Moreover, the

Fourier transform of their structure appears quite similar to the electron diffraction patterns observed in Al-Mn alloys.

In this work, we have observed solid phase precipitation of quasicrystals during implantation of Mn into a crystalline Al matrix. The resulting precipitates were highly oriented with respect to the fcc matrix, and we have established a unique orientation relationship between the symmetry axes of the icosahedral phase and the crystallographic directions of the Al matrix. This relationship provides important clues for the atomic structure of the icosahedral phase and leads to speculation concerning the coherence of the quasicrystal and crystal structures.

Thin-film samples were prepared by vacuum deposition of approximately 1000-Å Al films onto cleaved (100) NaCl substrates at room temperature. The Al films were then implanted with $^{55}\text{Mn}^+$ ions at two energies (35 and 75 KeV) in order to produce roughly uniform Mn concentrations typically in the range 13-24% near the center of the films. Different samples were implanted at three different substrate temperatures (20, 150, and 275°C). After implantation, the films were removed from the NaCl substrates by placing the samples in distilled water. A transmission electron microscopy (Philips 400) examination of the Al films before implantation showed that they consist of small (typically less than ~2000 Å) grains oriented with a $\langle 111 \rangle$ axis normal to the film. The grains were randomly oriented about the film normal.

The diffraction patterns associated with the lowest temperature implantation of 20°C showed a diffuse ring centered at a scattering vector of approximately $q = 2.96 \text{ \AA}^{-1}$ as well as sharp partial rings corresponding to the textured aluminum film. A comparison of the position of this amorphous ring with the x-ray powder pattern peaks listed for the icosahedral phase by Bancel et al.,⁸ showed that it lay midway between the expected positions for the two strongest quasicrystal lines and hence suggested that the short-range interatomic distances in the implanted phase were similar to those in the icosahedral phase.

Selected area diffraction patterns from a sample implanted at the higher substrate temperature of 275°C showed periodic spot patterns, indicating that a crystalline phase had formed. Patterns taken at various orientations were indexed and found to correspond to reciprocal lattice planes of the crystalline Al_{13}Mn structure.

The selected area diffraction patterns associated with implantations carried out at an intermediate substrate temperature of 150°C showed many rings which we have indexed. All ring spacings were found to agree within experimental error with either the published peak positions for the icosahedral Al-Mn phase or with expected positions due to multiple scattering of the electrons between the Al matrix and the icosahedral phase. High-resolution x-ray diffraction measurements using the ORNL beam line at the National Synchrotron Light Source have also been obtained from these samples, and

they confirm the icosahedral peak positions for the strongest lines to within 0.005 Å. Bright field and dark field images of the icosahedral phase showed it to consist of small (less than ~500 Å) irregularly shaped grains with no preference for locating at the boundaries between Al grains.

The most surprising observation was that the diffraction from the icosahedral phase displayed a nonuniform intensity around individual rings and hence a strong degree of orientational texturing with respect to the fcc matrix. In order to explore the nature of this texturing further, microdiffraction patterns were obtained from individual grains at various orientations. Figure 3.1 shows a typical convergent beam diffraction pattern oriented with the icosahedral fivefold axis parallel to the electron beam. From a stereographic analysis of many such convergent beam diffraction patterns, we concluded that the icosahedral grains were oriented such that three mutually perpendicular twofold axes lie along the fcc [001], [110], and $[\bar{1}\bar{1}0]$ crystallographic directions as shown in Fig. 3.2. The icosahedral grains appeared to be equally divided among the three equivalent sets of crystallographic directions of this type.

Since the atomic locations within the icosahedral precipitates are not known, it is not possible to construct models of specific interfaces between the two phases which may be energetically favored. Further, the icosahedral phase is not consistent with truly crystalline translational periodicity. However, on average,

Fig. 3.1. Microdiffraction pattern along fivefold icosahedral axis. A superimposed fcc reflection is labeled Al, and other letters correspond to the icosahedral indexing scheme presented in Ref. 6 as follows: $\{111010\} = c$, $\{110000\} = d$, and $\{101000\} = f$.

Fig. 3.2. Stereographic projection showing the orientation relationship between the icosahedral (solid symbols) and fcc Al (open symbols) phases.

the atomic density is localized to planes⁹ which give rise to Bragg peaks in the diffraction patterns. Considering atomic planes in this manner, it was found that in the implanted Al-Mn films, the icosahedral $\{110000\}$ planes¹⁰ lie parallel to Al $\{001\}$ or $\{110\}$ planes but not to the close packed $\{111\}$ planes. A comparison of plane spacings shows that the icosahedral $\{110000\}$ plane and the Al $\{002\}$ plane can be made quasicohesive throughout the two phases if a 2% strain is allowed over distances of a few hundred angstroms. Considering the fact that implantation of Mn ions into Al films at 20, 150, and 275°C resulted in amorphous, icosahedral, and crystalline phases, respectively, it was concluded that the icosahedral phase formed at 150°C was the result of solid phase precipitation. The lack of icosahedral phase formation at room temperature and the observation of texturing tend to rule out direct cascade formation and amorphous phase precipitation, respectively. It is expected that this implantation technique for producing oriented icosahedral grains will provide a means of obtaining an ordered quasicrystal sample for carrying out quantitative x-ray diffraction investigations of the atomic structure of quasicrystals.

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7. A. L. MacKay, *Physica* **114A**, 609 (1982).

8. P. A. Bancel et al., *Phys. Rev. Lett.* **54**, 2422 (1985).

9. D. R. Nelson and B. I. Halperin, *Science* **229**, 236 (1985), Fig. 5.

10. The six-digit icosahedral indices are described in Ref. 7.

PRECIPITATION OF ICOSAHEDRAL Al-Mn DURING PULSED LASER MELTING¹

M. J. Aziz² J. D. Budai³

A novel metallic phase possessing both long-range icosahedral orientational order and sharp diffraction peaks was first observed⁴ in rapidly quenched Al-Mn samples formed by spraying molten alloys onto a cold, rotating copper wheel. This observation has stimulated a tremendous amount of work, including many studies directed toward developing other techniques for producing metallic phases with icosahedral symmetry. Thus far, materials exhibiting metastable icosahedral order have been produced by melt spinning, ion mixing, ion implantation, precipitation from the solid phase, solid-state reaction of thin crystalline layers, and electron beam melting.

In this investigation, we have used pulsed laser melting to form icosahedral Al-Mn with grain sizes of up to 1 μm . This technique is similar to melt spinning and e-beam melting in that they both create metastable phases from a rapidly cooled liquid. Pulsed laser melting, however, can be used to create highly uniform, plane-front, one-dimensional interface motion, allowing important physical quantities to be calculated and measured.⁵⁻⁶ In general, the quench rates attained with this technique are significantly greater than those attained by melt-spinning. We were able to produce large grains of the quasicrystal phase by deliberately reducing the quench rate by using high laser-pulse energy densities, thin films, and an insulating substrate.

Thin-film samples initially containing either amorphous, icosahedral, or crystalline phases were prepared by vacuum deposition of Al films followed by implantation of Mn ions.⁷ The samples were then irradiated using a pulsed KrF⁺ excimer laser (pulse duration 25 ns FWHM, wavelength 248 nm) focused to a small spot to obtain regions with varying laser energy. The metal films were removed from the NaCl substrate by placing the samples in distilled water and then mounted on transmission electron microscopy grids.

Typically, three distinct regions were identified in low-magnification micrographs of the area surrounding the laser spot. Closest to the laser hole was typically a single-phase region of fcc Al supersaturated with Mn (approximately 7 at. %). Further from the laser spot a region containing icosahedral grains embedded in an fcc matrix was found. Small grains of Al₆Mn were also observed in this region in samples which contained this phase before the laser melting occurred. The size of the icosahedral grains

continuously diminished with distance from the laser hole, until finally a third region was found where the sample was unaffected by the laser pulse. The structure in the region containing icosahedral grains was consistent with the nucleation of quasicrystals before significant broadening of the implant profile could occur in the liquid phase. The single-phase fcc region, which was irradiated with a greater laser intensity, was apparently at temperatures above the icosahedral melting point long enough to allow spreading of the implanted Mn peak concentration below that required for icosahedral phase nucleation.

Figure 3.3 shows a micrograph of a region containing two star-shaped icosahedral grains formed by pulsed laser treatment of a sample that was originally a two-phase mixture of fcc and Al₆Mn. From the relationship between the convergent beam electron diffraction patterns and morphology of these and other grains with other symmetry axes near to the film normal, we concluded that the most rapid growth directions (i.e., the "point" on the stars) are the threefold symmetry axes of the icosahedral structure. This observation rules out the model of Hillert for rapid growth along the fivefold axis⁷ and corroborates those of Schaefer et al.⁹ Unlike the as-implanted samples,⁷ no unique orientation relationship between the fcc and icosahedral precipitates was found in this case.

Fig. 3.3. Region containing icosahedral grains (star shapes) and Al₆Mn crystals (brick shapes) in an fcc matrix. Scale bar is 0.5 μm.

Figure 3.4(a) shows one of the larger icosahedral grains, formed by pulsed laser melting of a sample that started out as fine icosahedral precipitates in an fcc matrix. The corresponding fivefold selected area diffraction pattern from the large central grain is shown in Fig. 3.4(b). The size of the grains allows us to estimate the melt duration, assuming that growth with solute partitioning requires diffusion-controlled kinetics. With a liquid-phase diffusivity assumed to be 10^{-4} to 10^{-5} cm²/s, the time necessary for 0.5-μm radial growth is of the order 100 μs. Pulsed laser melting of

Fig. 3.4. (a) Branched structure of large icosahedral grains formed by pulsed laser melting and (b) fivefold selected area diffraction pattern from central grain.

metals and semiconductors typically produces melt durations of 0.1–1 μs. Large grains of the icosahedral phase thus can only be produced by pulsed laser melting if steps are taken to reduce the quench rate, such as by utilizing insulating substrates.

The growth of materials with icosahedral symmetry can be achieved with pulsed laser melting under well-controlled experimental conditions. This simple technique should prove quite useful by making larger grain sizes possible as well as by providing information concerning the thermodynamics and formation kinetics of these novel structures.

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ANALYTICAL IMAGING MICROSCOPY¹

S. J. Pennycook   S. D. Berger²
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We have recently developed a technique for directly imaging distributions of heavy dopants in silicon even if they are in solution, using a scanning transmission electron microscope (STEM).³ An annular detector placed around the transmitted beam is arranged to collect electrons scattered through angles much greater than those which can be employed in conventional TEM. In this angular range the scattered intensity is very sensitive to atomic number (Z) but is insensitive to structure. As the fine probe of the STEM is scanned across the sample, the

image contrast directly maps atomic number variations, providing an elemental map of the distribution of heavy elements even if they are in solution. The technique has now been quantified so that elemental concentrations can be determined directly from the image as described below. The intensity of the elemental map is of the order of 10^3 higher than those obtained by conventional analytical electron microscopy so that we refer to the technique as analytical imaging rather than elemental mapping. It is entirely complementary to conventional structure imaging, and we note that the resolution limit is at least as high (and theoretically higher) as that of conventional high resolution microscopy. A high-resolution STEM would certainly resolve the silicon lattice, and with the high sensitivity to dopants (0.1% of Bi, for example), the imaging of single dopant atoms seems entirely feasible.

The quantification of analytical images was investigated using the three dopants As, Sb, and Bi in Si to cover a wide range of Z . High dopant concentrations were obtained by ion implantation followed by solid-phase-epitaxial growth. Cross-section samples were prepared and examined at various calibrated values of detector collection angles. Line traces were taken across the images to determine the contrast $C = I_x/I_{Si}$ as defined in Fig. 3.5. The contrast can be related to the cross section σ for elastic scattering into the detector as follows

$$C = \left(\frac{\sigma_x}{\sigma_{Si}} - F_s \right) c_x, \quad (1)$$

where c_x and F_s are the dopant concentration and substitutional fraction, obtained from Rutherford backscattering analysis. A number of expressions for the cross sections σ were compared to see which gave the best prediction of the experimentally observed contrast. It was found

Fig. 3.5. Line trace across cross-section sample of Bi⁺-implanted Si following recrystallization, showing contrast due to 0.75 at. % Bi.

that simple expressions often used in electron microscopy were not accurate for a quantitative analysis but that improved calculations of screening by Molière, modified by Fleischmann,⁴ gave a consistently good fit to all three dopants. The cross section is given by

$$\frac{d\sigma}{d\Omega} = \left(\frac{m}{m_0} \right)^2 \frac{Z^2 \lambda^4}{4\pi^2 a_0^2 \theta^4} \frac{\theta}{\theta + \theta_F}, \quad (2)$$

where m = electron mass; m_0 = electron rest mass; a_0 = Bohr radius; λ = electron wavelength; θ = scattering angle; $\theta_F^2 = 2.718 \theta_0^2 (1.13 + 3.76 \alpha^2)$; θ_0 = Born screening angle given by $\theta_0 = (1.13 Z^{1/3})/137 \beta$; $\beta = v/c$ the ratio of electron velocity to the velocity of light; and $\alpha = Z/137\beta$.

Integrating over the annular detector from θ_1 to θ_2 gives

$$\sigma = \left(\frac{m}{m_0} \right)^2 \frac{Z^2 \lambda^4}{2\pi^2 a_0^2} \left[\frac{\theta_2 - \theta_1}{\theta_1 \theta_2 \theta_F} + \frac{1}{\theta_F^2} \log_e \frac{\theta_1}{\theta_2} + \frac{\theta_2 + \theta_F}{\theta_1 + \theta_F} \right]. \quad (3)$$

Figure 3.6 shows the experimental results for the Bi sample as a function of inner detector angle θ_1 (with constant outer detector angle $\theta_2 = 275$ mrad). The vertical axis η represents the reduction of the cross-section ratio from that expected for Rutherford scattering.

$$\eta = \frac{\sigma_x}{\sigma_{Si}} \frac{Z_{Si}^2}{Z_x^2}. \quad (4)$$

The Fleischmann formula overestimates η by 10-20% consistently for all three dopants. This can be allowed for in analytical imaging of

Fig. 3.6. Experimental and theoretical cross-sections of Bi relative to Si, expressed in units of the Rutherford scattering cross-sections.

these dopants, although it may not be true for elements of other groups. Other elements could easily be measured experimentally, even in the amorphous state if recrystallization were not possible.

The accuracy of the analytical image depends on removing other sources of image contrast. Thickness variations can be eliminated by careful specimen preparation. The smallest inner detector angle at which no residual diffraction contrast was observed at defects was investigated and was found to vary from 114 mrad for individual defects to 166 mrad for a dense band of defects. The nature of channeling contrast was shown to be fundamentally different from diffraction contrast, but could be eliminated by imaging under "arandom" crystal orientation. The use of images taken in channeling conditions for lattice location mapping was shown not to be feasible due to dechanneling effects. Detection limits and multiple scattering were also discussed.

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DIRECT IMAGING OF SILICIDE PIPES BY ANALYTICAL IMAGING MICROSCOPY¹

S. J. Pennycook   J. Narayan²

As the size of integrated circuit devices is reduced, the size of the interconnection lines must also reduce. To avoid increasing their resistance, metal silicides have been replacing polycrystalline silicon for the interconnection material, due to their lower sheet resistivity. They can be formed by reaction of a thin metal overlayer such as Ti on the polycrystalline silicon substrate. The silicide is stable at temperatures used in device processing, and since the native oxide on the silicon substrate is consumed in the silicide reaction, a clean interface should be produced with reproducible electrical characteristics. However, when forming a silicide layer by conventional furnace annealing, rapid diffusion of the metal down grain boundaries in the polycrystalline substrate can lead to the formation of silicide "pipes," which effectively short circuit the devices. Using analytical imaging microscopy, we have been able to image directly such a pipe for the first time. We have also shown how the formation of such pipes can be avoided by the use of a rapid-thermal-annealing (RTA) treatment instead of conventional furnace annealing.

Silicon single crystals were oxidized to form a 25-nm SiO₂ layer, upon which a layer of polycrystalline Si was grown by low-pressure chemical vapor deposition to a thickness of 250–400 nm. This layer consisted of columnar grains aligned along the deposition direction, normal to the

surface. Finally, a 30-nm layer of Ti was deposited by electron beam evaporation. The microstructures after conventional annealing and RTA were compared by analytical imaging microscopy. This technique provides images sensitive to atomic number rather than crystal structure, so that Ti-rich regions appear bright.

A cross-section electron micrograph after furnace annealing in nitrogen at 900°C for 30 min is shown in Fig. 3.7. The TiSi₂ layer at the surface shows bright compared with the polycrystalline substrate, and the thin SiO₂ layer is seen as a narrow dark band. It is clear that the TiSi₂ layer is not continuous but has broken up into islands. A long, bright finger is seen to extend almost completely through the polycrystalline layer. This is the silicide pipe formed by rapid diffusion of Ti along a grain boundary. It is not distinguishable by conventional electron microscopy but is very obvious from the analytical image. Figure 3.8 shows the same material after RTA at 1100°C for 10 s. No diffusion of Ti along grain boundaries has occurred, and the layer is continuous and relatively uniform. Some of the Ti layer has

Fig. 3.7. Analytical image after furnace annealing at 900°C for 30 min, showing silicide "pipe."

Fig. 3.8. Analytical image after RTA at 1100°C for 10 s, showing uniform "pipe-free" silicide layer.

not been consumed by the reaction and is visible as a thin bright layer at the surface.

RTA uses higher temperatures but shorter times than conventional furnace annealing and favors high activation energy E_A . It has been successful in removing extended defects in Si ($E_A \sim 5$ eV) while minimizing dopant diffusion ($E_A \sim 4$ eV). Although the activation energies in the system studied here are unknown, the RTA has favored silicide reaction in the bulk over grain boundary and surface diffusion.

In conclusion, we have shown the first direct images of silicide pipes, whose existence was previously assumed only from electrical measurements, and we have shown how their formation can be avoided by RTA.

1. Summary of paper to be published.
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DIRECT OBSERVATION OF LONG-RANGE INTERSTITIAL MIGRATION IN SILICON¹

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Ion implantation followed by solid-phase-epitaxial (SPE) growth leaves a band of damage marking the original amorphous/crystalline interface. This can act both as a source and sink for point defects. In the case of group V ion implantation into Si, the damage band acts as a net sink, since large numbers of interstitials are trapped within the recrystallized layer. With group III implantation the damage band acts as a net source, since no point defects are trapped in the recrystallized layer.

We have studied both B^+ and Ga^+ implantation and found similar results for both. To establish that no trapping mechanism occurs, analogous to that seen for group V implants, we have implanted each dopant into Si (100) which had been preamorphized by a high-energy Si^+ implant to move the damage layer deep into the crystal. Thin samples were prepared for plan-view transmission electron microscopy (TEM) and annealed in thin form to induce precipitation of the dopant. The thin regions observable by TEM consisted entirely of recrystallized Si, since the underlying damage had been removed during specimen preparation. From the observed precipitate size distribution, diffusion coefficients were obtained close to the intrinsic tracer diffusion coefficients for both B^+ - and Ga^+ -implanted samples.

The situation was very different for samples annealed in the presence of the damage layer. Figure 3.9(a) shows the damage layer resulting from Ga^+ implantation into crystalline Si (100) followed by SPE growth. Annealing in bulk, only very low temperatures were required to induce Ga precipitates to form as shown in Fig. 3.9(b). Diffusion coefficients were about 1000 times greater than tracer values. Since no defects were trapped in the recrystallized layer itself, the source of the enhancement must be point defects released from the underlying damage band. The enhancement is less than that

Fig. 3.9. Cross-section TEM micrographs of Ga^+ (100 keV 1×10^{15} cm⁻²) implanted Si (100) (a) after SPE growth and (b) after additional annealing at 780°C for 20 min.

observed with a corresponding group V implant, which is the reason that the damage layer can act as a net sink in that case; a higher concentration of interstitials is released from the dopant than from the underlying damage. The width of the damage layer can be greatly increased by implanting into "ion-beam-annealed" Si. A high-current Si^+ implantation creates a damage layer almost 0.5 μ m wide at a depth below the usual damage layer [Fig. 3.9(a)]. The damage then acts as a net source even for low concentrations of group V dopants when interstitials are also trapped in the dopant band. The diffusion enhancement due to trapped interstitials is increased by the underlying damage, showing that interstitials are the dominant species ejected from the damage layer.

We believe these are the first clear observations of long-range migration of interstitials and of the interstitialcy diffusion mechanism in Si. We plan to extract migration energies and the relative interstitial diffusivities of the common dopants.

1. Summary of paper: Journal of Materials Research (in press).

THE NATURE OF TRAPPED INTERSTITIALS FORMED DURING ION IMPLANTATION OF Si¹

S. J. Pennycook   R. J. Culbertson
J. Narayan²

Recently, we have established that during implantation of Si with group V dopants, high

concentrations of self-interstitials are trapped at the implanted dopant atoms.³ These survive solid-phase-epitaxial growth but during subsequent thermal processing lead to transient-enhanced dopant diffusion and the formation of a band of defects at the mean projected ion range. These trapping effects are not seen for group III dopants. We propose that the trapped interstitials are simply interstitial dopant atoms in a split <100> configuration. This model naturally explains why trapping effects are seen only for group V dopants.

The model is an extension of that developed by Tan, Berry, and Frank for self-interstitials and boron interstitials in Si.^{4,5} We assume that the same basic point defects will occur in the amorphous and crystalline states, since locally the tetrahedral bonding is very similar and interstitials are constructed by replacing a regular Si atom by a complex Si-X sharing the lattice site. This is denoted by I(X), and Fig. 3.10 shows the expected configuration of the neutral self-interstitial I⁰(Si), which is also expected to be the structure of isoelectronic interstitials in neighboring groups, I⁰(III) and I⁰(V). Electrons are added or subtracted to give other charge states as shown in Fig. 3.10 and will distribute so as to give a minimum energy configuration. For self-interstitials, symmetry requires an antibonding state which lowers the binding energy from that of the neutral self-interstitial. Dopant interstitials polarize, giving an electrostatic contribution to the binding energy [Figs. 3.10 (b) and 3.10(c)]. Table 3.1 summarizes the binding energy in the form of $n_c \pm n_e$, where n_c is the number of covalent bonds and n_e is the number of electrons giving an electrostatic binding (or antibinding). The neutral group V interstitial I⁰(V) is clearly more strongly bound than any other interstitial. The model therefore naturally

Table 3.1. Properties of interstitials of groups III, IV, and V in various charge states in Si, showing internal binding in the form $n_c \pm n_e$ (see text) and the type of Si in which they are stable.

Group	Charge state		
	-	0	+
III	2	1+1(p)	
IV	2-1(n)	2	1-1(p)
V		2+1(n)	2

explains why the group V interstitials can survive the solid-phase-epitaxial (SPE) growth whereas group III interstitials, which must also be formed during implantation, do not. Any group V vacancy complexes also anneal out at temperatures well below SPE growth temperatures.⁶

The activation energy for decay and migration of the interstitial is expected to be very similar.⁵ The migration energy we measure is 1.8 eV, not significantly greater than that of the neutral self-interstitials or boron interstitials. Presumably, when the trapped interstitial decays, it releases neutral self-interstitials, which can then combine with an ionized dopant atom to give I⁰(V). We, therefore, see the low-migration energy corresponding to I⁰(Si) or I⁰(V).

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Fig. 3.10. Configuration of interstitials in Si.

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GETTERING OF INTERSTITIALS BY RADIATION DAMAGE BAND IN Si¹

S. J. Pennycook R. J. Culbertson

Besides causing enhanced diffusion, we have shown that trapped interstitials² which form at the mean projected ion range as shown in Fig. 3.11(a) also give rise to a band of extended defects. The band arises as the large metastable concentration of self-interstitials condenses by aggregation into interstitial-type dislocation

Fig. 3.11. (a) Projected range and end of range defect bands in As^+ (220 keV, $1 \times 10^{16} \text{ cm}^{-2}$) implanted Si (100) annealed at $600^\circ\text{C}/20$ min. (b) Suppression of projected range defects by dual implantation with B^+ (35 keV $5 \times 10^{15} \text{ cm}^{-2}$).

loops. This band is separate from the underlying band of damage which marks the original amorphous/crystalline interface and arises simply from the annealing of the damaged crystal underlying the amorphous layer.

We have observed an interesting effect in samples following dual implantation of group V and group III dopants. The concentration of the group III dopant (boron) was made less than that of the group V dopant, so that the material remained n-type and trapped interstitials formed as usual. With Sb^+ (200 keV $5 \times 10^{15} \text{ cm}^{-2}$) and B^+ (35 keV $5 \times 10^{15} \text{ cm}^{-2}$) implanted into Si (100), enhanced Sb precipitation was observed as expected, but no band of loops formed. In the case of As, precipitates are not observable by transmission electron microscopy (although they can be seen by channeling angular scans if a sufficient fraction is in precipitate form); hence, Fig. 3.11(a) shows only the loops. In this case dual implantation with B^+ again avoids the formation of projected range loops [Fig. 3.11(b)].

We believe the mechanism to be as follows: boron has a higher diffusion coefficient than As or Sb and also has a high interstitial component to its tracer diffusion,³ whereas As and Sb prefer vacancy mechanisms under equilibrium conditions. This means that given a large supply of interstitials, the B diffusivity will be about two orders of magnitude greater than the As or Sb diffusivities. It can therefore provide an efficient mechanism for the trapped interstitials to spread further through the volume of the material than they otherwise would. They presumably are able to reach the

underlying band of defects, where addition to existing loops is energetically more favorable than the nucleation of fresh loops.

Further evidence for this mechanism involving the underlying damage band is obtained from a higher energy Sb^+ implant (300 keV, $1 \times 10^{16} \text{ cm}^{-2}$). In this case some defects were observed at the mean projected ion range. In this material the damage is further from the peak dopant concentration, 200 nm compared with only 125 nm for the 200-keV Sb^+ implant and 140 nm for the As^+ implant shown in Fig. 3.11.

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FORMATION OF STABLE SUPERSATURATED SEMICONDUCTOR ALLOYS¹

S. J. Pennycook R. J. Culbertson

It is well known that ion implantation followed by solid-phase-epitaxial growth can produce highly supersaturated semiconductor alloys with the dopants electrically active on substitutional sites. The reason that such materials have not found greater application in industry is that they often are not stable to the temperatures needed for typical materials processing steps (900 – 1000°C). The dopant in excess of the solubility limit precipitates out. This has been hard to understand, since for group V elements the tracer diffusion coefficients predict negligible precipitation up to 1000°C for times of 30–60 min.

The enhanced precipitation is caused by the release of trapped interstitials.² This release enhances the diffusion coefficients by many orders of magnitude. One prediction of the model we have developed is that the trapped interstitials would not be formed in p-type material, because they would be electronically unstable. We have tested this by double implantation of Sb^+ and B^+ into Si at doses such that the boron concentration exceeds that of the Sb. As expected, enhanced precipitation was suppressed, and diffusion coefficients close to tracer values were obtained from the observed precipitate sizes. Sb and B are immiscible and hence precipitate separately. They also are easily distinguishable in the electron microscope. Figure 3.12 shows the microstructure observed after annealing at 1100°C for 60 min. In 3.12(a) the B precipitates show dark, and the Sb precipitates show Moiré fringes if large enough, whereas in (b) the B precipitates show faint light contrast, and the Sb precipitates show dark. The Sb diffusion coefficient obtained from Fig. 3.12(b) is $4 \times 10^{-15} \text{ cm}^2\text{s}^{-1}$, somewhat less than the expected tracer value of $1.5 \times 10^{-15} \text{ cm}^2\text{s}^{-1}$.

Fig. 3.12. Double implant of Sb^+ (200 keV, $5 \times 10^{15} \text{ cm}^{-2}$) and B^+ (35 keV, $2 \times 10^{16} \text{ cm}^{-2}$) annealed at 1100°C for 60 min showing precipitates under (a) dynamical and (b) kinematical diffraction conditions.

Since the tracer diffusion coefficient of B is an order of magnitude greater than that of Sb, the B precipitates out much faster, as obvious from Fig. 3.12. This provides a method for producing stable n-type supersaturated alloys. If the Sb remains highly substitutional after the anneal (Fig. 3.13), it will be electrically active, whereas the B in precipitates presumably will not be. The B remaining in solution will compensate the Sb to some extent, and electrical measurements are being carried out to determine the extent of the compensation, but we believe we have found the basis of a useful technique for obtaining stable supersaturated n-type semiconductor alloys.

Fig. 3.13. Ion channeling analysis of super-saturated Sb in Si showing good substitutionality after high-temperature annealing.

COMPARISON OF ION MILLING TECHNIQUES FOR CROSS-SECTION TRANSMISSION ELECTRON MICROSCOPY (TEM) OF SEMICONDUCTORS¹

C. W. Boggs J. T. Luck
S. J. Pennycook

We have compared the two common methods for preparing cross-section samples of semiconductors for TEM to determine the advantages and disadvantages of each method.

In the original method used in the Solid State Division, a slice of the sample material approximately $5 \text{ mm} \times 0.5 \text{ mm}$ is mechanically polished on both sides to a thickness of $30\text{--}40 \mu$ and is mounted on a small piece of scrap silicon. This is placed in the ion milling machine with the original surface of the sample facing away from the ion gun and is ion milled. After about one half of the estimated time required to mill through the sample, it is removed from the scrap silicon carrier and remounted in order to mill from the second side. Milling continues until a notch forms, on either side of which are thin electron-transparent areas.

The second technique involves bonding two pieces of sample material face to face with a suitable glue. Epoxy is usually used, but the choices of glue and curing time and temperature must be determined for each type of material, since the glue and sample material must mill at the same rate. The sandwich is mechanically polished as before to a thickness of $30\text{--}40 \mu$ but is then mounted on a 3-mm-diam copper ring. This is mounted on a rotating stage in the ion milling machine, and two ion guns are used to mill from both sides simultaneously, until a hole forms, hopefully at the interface of the original sandwich.

In our experience, the first technique is superior at least for silicon samples. It produces samples with larger, more uniform thin areas, as seen in Fig. 3.14. This is obviously

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Fig. 3.14. TEM micrographs of silicon cross sections produced by (a) single-gun carrier-mounted technique and (b) double-gun ring-mounted technique showing thickness inhomogeneities.

of key importance. In addition, the original sample surface is naturally preserved since it never faces the ion gun, whereas in the ring-mounted method there is the danger that the surface will be lost if the glue mills faster than the sample. In the ring-mounted method, the sample can only be rinsed in solvent before it is glued to the ring, which does not result in such effective cleaning. For silicon, the original method produces better quality samples with higher reliability (specimen throughput). The only disadvantage of this method is that the sample must be removed from the carrier and mounted on a ring after thinning.

1. Summary of paper: p. 166 in Proc. 43rd Annual Meeting of Electron Microscopy Society of America, ed. by G. W. Bailey, San Francisco Press, San Francisco, 1985.

CALCULATION OF DIFFUSE SCATTERING FROM SPHERICAL PRECIPITATES IN AN ANISOTROPIC ELASTIC MATERIAL

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B. C. Larson

In order to make use of X rays to study solute precipitation in Cu₃Zn, we have extended diffuse scattering calculations for precipitates in an isotropic medium² to consider elastically anisotropic materials. The radial symmetry of the distortion fields under elastic isotropy reduces diffuse scattering calculations to a one-dimensional numerical integration² in isotropic materials; however, diffuse scattering calculations for anisotropic materials entail calculating the anisotropic distortion fields and numerical integration of three-dimensional lattice sums.

Closed-form expressions are not available for the distortions around defects in anisotropic materials; however, the Fourier transform of lattice displacements can be written in terms of the Fourier transformed elastic Green's function for arbitrary elastic anisotropy³ in cubic

materials. In this work, the distortions around cobalt precipitates in copper were calculated using reverse Fourier transformation of the q -space displacement fields, and the diffuse scattering amplitudes were calculated in the single defect approximation using the calculated lattice displacements. By restricting the calculations to small q values (i.e., diffuse scattering close to reciprocal lattice points), it was possible to use the approximation of scattering from a continuous elastic medium in which the lattice sums were converted to integrals for evaluation. The "Huang," or first-order scattering from the distortion field, was calculated analytically using the Fourier transformed displacement fields, and the higher order scattering from the lattice distortions was calculated numerically using a Gaussian function to limit the range of the integration.⁴ Mathematically, the introduction of the Gaussian function results in a small amount of q -space smearing of the scattering calculations while making it possible to limit the integration over the lattice distortions to distances ~ 10 times the radius of the precipitates without introducing termination effects in the integrations.

Diffuse scattering calculations for 50-Å radius cobalt precipitates in copper are shown in Fig. 3.15 for q parallel to the 400 reciprocal lattice vector at the (400) Bragg reflection. These calculations demonstrate the characteristic divergence of the Huang scattering as q goes to zero, and we see a rapid falloff in the intensity for larger q 's. The rapid falloff and the oscillatory nature of the scattering at large- q are a result of the form factor of the precipi-

Fig. 3.15. Scattering cross section for 50-Å spherical cobalt precipitates in copper for q parallel to the 400 reciprocal lattice point near the (400) Bragg reflection.

tates and the interferences in the scattering from the large distortions close to the precipitate surface. The rapid oscillations in the scattering for 50-Å precipitates in Fig. 3.15 would tend to be smeared out by the presence of a range of precipitate sizes; therefore, smoothly decreasing intensities would be expected for the larger q values under experimental conditions.

A further ramification of the finite size of the precipitates is the shoulder at $q \sim 0.1$ Å. This shoulder is a result of "local" Bragg-like scattering from the precipitate lattice and appears at a position q given by

$$-q/H = \epsilon, \quad (1)$$

where H is the reciprocal lattice vector and ϵ is the strain (or lattice parameter change) of the cobalt precipitate lattice relative to that of copper. Since the lattice parameter of fcc cobalt is smaller than that of copper ($\epsilon = -0.0146$ in these calculations), the shoulder appears at positive q for this case.

The magnitude of the scattering intensity and the overall q dependence of the diffuse scattering make it possible to use diffuse scattering measurements to determine the concentration and size distribution of precipitates directly from diffuse scattering measurements; the shoulder in the scattering provides an opportunity of directly determining the lattice parameter of the precipitate as well. Further information on the precipitate scattering can be obtained using synchrotron x-ray sources through the use of anomalous scattering to change the scattering factor of the precipitate atoms relative to that of the host atoms. For the case of small solute clusters in the initial stages of precipitation, diffuse scattering measurements can provide information inaccessible by electron microscopy, and the nondestructive nature of such measurements provides an opportunity for time-resolved investigations on the order of a few tens-of-seconds as well.

tion loop scattering cross sections to diffuse scattering measurements. In a continuation of research in this area, we have extended diffuse scattering calculations to three-dimensional lattice defects in order to develop techniques for investigating solute precipitation in dilute alloys and for detailed investigation of the structure of displacement cascades in irradiated materials.

In the single-defect approximation, the diffuse scattering cross section is given by

$$\frac{d\sigma(K)}{d\Omega} = (r_e f_h)^2 |A(K)|^2, \quad (1)$$

where $K = H + q$ is the scattering vector defined by a reciprocal lattice vector H and a vector q within the Brillouin zone, r_e is the classical electron radius, f_h is the scattering factor of the host atoms, and $A(K)$ is the diffuse scattering amplitude for a defect cluster. For the case of coherent, spherical precipitates of radius R_0 composed of atoms with scattering factor f_p , $A(K)$ is given in terms of lattice sums by

$$A(K) = \frac{f_p}{f_h} \left[\sum_{i=1}^{r_1 < R_0} e^{iK \cdot r_i'} + \sum_{i=1}^{r_1 > R_0} e^{iK \cdot r_i'} - \sum_{i=1}^{r_1 > 0} e^{iK \cdot r_i} \right], \quad (2)$$

where $r_i' = r_i + S_1$ is the position of the i th atom displaced S_1 from the average lattice position r_i . These sums represent the scattering from the precipitate, the scattering from the distorted host-lattice surrounding the precipitate, and the subtraction of the scattering due to the average (undistorted) lattice, respectively.

Following previously used methods² of evaluating $A(K)$ in Eq. (2), we rearrange the lattice sums and separate the lowest order term in $K \cdot S_1$ to obtain

$$A(K) = \frac{(f_p - 1)}{f_h} \left[\sum_{i=1}^{r_1 < R_0} e^{iK \cdot r_i'} + \sum_{i=1}^{r_1 > R_0} e^{iK \cdot r_i'} - \sum_{i=1}^{r_1 > 0} e^{iK \cdot r_i} (e^{iK \cdot S_1} - 1 - iK \cdot S_1) \right]. \quad (3)$$

These terms now correspond to the precipitate scattering, the so-called "Huang" scattering from the long-range displacement field, and the higher order scattering arising from the large distortions near the precipitates, respectively. For an isotropic material, $s(r) = \epsilon r$ inside the precipitate and $S(r) = \epsilon R_0^3 r/r^3$ outside the precipitate, where ϵ represents the strain of the precipitate lattice relative to the host lattice parameter. Converting the lattice sums to integrals, the first two terms in Eq. (3) can be evaluated in closed form, and because $S(r)$ is isotropic, we have been able to reduce the third term to a one-dimensional radial integral. The resulting expression for $A(K)$ is

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DIFFUSE SCATTERING FROM SPHERICAL PRECIPITATES IN AN ISOTROPIC MATERIAL

S. Iida¹ J. Z. Tischler
B. C. Larson

X-ray diffuse scattering has been shown to be a useful tool for the study of radiation-induced dislocation loops in metals.² The size distributions and concentrations of both vacancy and interstitial loops in neutron and ion-irradiated copper have been determined by fitting disloca-

$$A(K) = \frac{V_p}{V_c} \left(\frac{f_p}{f_h} - 1 \right) F(q'R_0) - \frac{\Delta V}{V_c} \frac{(H \cos(\theta_H) + q)}{q} F(qR_0) \\ + \frac{4\pi}{V_c} \int_0^\infty r^2 \left[\frac{\sin(M(r))}{M(r)} - \frac{\sin(qr)}{qr} \right] \\ + \frac{(H \cos(\theta_H) + q)s(r)}{(qr)^2} (\sin(qr) - qr \cos(qr)) dr \quad (4)$$

in which

$$V_p = 4/3 \pi R_0^3 \quad \Delta V_p = 4\pi \epsilon R_0^3 \\ q' = |q + \epsilon K| \quad M(r) = |rq + s(r)K| \quad (5)$$

$$f(x) = \frac{3}{x^3} (\sin(x) - x \cos(x)) ,$$

and θ_H is the polar angle between q and H .

This expression provides a means of calculating directly the diffuse scattering from spherical precipitates of radius R_0 . Previous work by Trinkaus³ (using a different method) provided results for inclusions in the limit of vanishing radii, in which the amplitude for direct scattering from the precipitates did not occur, nor did the form factor $F(qR_0)$ appear. Both of these factors must be considered for precipitates of more than a few angstroms diameter and are important for the 10-100-Å radius precipitates typically encountered in physical systems. Another important aspect of this expression for $A(K)$ is that only a one-dimensional integral is required for evaluating the diffuse scattering amplitude. This expression allows accurate calculation of the diffuse scattering cross sections near Bragg reflections in isotropic materials, and it also provides a reference point for the evaluation of the three-dimensional numerical integration routines required to calculate diffuse scattering from spherical precipitates in anisotropic elastic materials. The results of such calculations are presented elsewhere in this report.

1. Guest scientist from Toyama University, Toyama, Japan.

2. B. C. Larson, T. S. Noggle, and J. F. Barthorst, p. 25 in Advanced Photon and Particle Techniques for the Characterization of Defects in Solids, ed. by J. B. Roberto, R. W. Carpenter, and M. C. Wittels, Materials Research Society, Pittsburgh, Pa., 1985.

3. H. Trinkaus, Z. Angew. Phys. 31, 229 (1971).

MEASUREMENT OF THE SILICON (200) REFLECTION

J. Z. Tischler J. D. Budai¹

There have been recent reports of a nonzero structure factor for the silicon (200) reflection²

which have created some controversy since the (200) reflection in diamond-structure materials should be zero due to symmetry considerations. To investigate this problem, we have made measurements of the (200) reflection on the ORNL x-ray beam line at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory.

The (200) reflection in the diamond structure is a basis forbidden reflection. Although most basis forbidden reflections are zero only for centrosymmetric atoms, the symmetry of the diamond structure forces the (200) reflection to be exactly zero regardless of atomic shape. If the (200) structure factor F_{200} were found not to be zero, then silicon would not really have the diamond structure. Such a finding would of course affect the many fundamental studies that have been done on silicon.

We have made measurements of the silicon (200) integrated intensity at three different ϕ angles, where ϕ is the angle between the plane of diffraction and the [010] direction. At two of these orientations we found nonzero integrated intensities, but at the $\phi = 0$ orientation, no measurable intensity was observed. Comparing these measurements with 400-beam multiple scattering calculations,³ it was found that the multiple scattering contribution at the $\phi = 0$ orientation is essentially zero while multiple scattering makes a significant contribution at the other orientations.

At $\phi = 0$, the combination of the null integrated intensity measurement and the calculation of no multiple scattering contribution establishes the fact that the (200) structure factor is indeed zero. Both the multiple scattering calculation and our measurement at the other orientations show that, in general, nonzero integrated intensities are to be expected for the (200) reflection and, hence, explain the reports² of such measurements.

1. Eugene P. Wigner Fellow.

2. B. Post, ACA Meeting, Stanford, Calif., 1985.

3. J. Z. Tischler and B. W. Batterman, "A Many Beam Scattering Approximation for Weak X-Ray Reflections," this report.

A MANY BEAM SCATTERING APPROXIMATION FOR WEAK X-RAY REFLECTIONS¹

J. Z. Tischler B. W. Batterman²

The availability of powerful synchrotron x-ray sources has made it possible to investigate the details of the electronic charge distributions in Si and Ge through the measurement of basis forbidden reflections. Because these reflections arise only from the asymmetric charge distributions, they provide information for evaluating the details of electronic charge density models. However, the extremely weak nature of these reflections makes it necessary to correct the measured intensities for multiple scattering contributions from allowed (but not directly excited) reflections.³ In this work we

have shown that the usual procedure of considering three to eight multiple beams for these corrections is not adequate and that up to ~400 beams may be required for accurate results. Although the evaluation of multiple-beam diffraction from 400 simultaneous beams is in general intractable, an accurate approximation has been developed for making such calculations for cases when only the primary reflection is highly excited.

Under two-beam diffraction conditions (Fig. 3.16), two reciprocal lattice points (000) and (hkl) lie on the Ewald sphere, defining the direction of the incident beam k_0 and the diffracted beam k_f , respectively. For the case of allowed reflections, the scattering amplitude is so large that only the two reciprocal lattice points that lie on the Ewald sphere contribute significantly to the scattered intensity. However, when the structure factor of the principal reflection is very weak, multiple beam contributions [such as those defined by the (000)(h'k'l')(hkl) sequence in Fig. 3.16] can be significant even when (h'k'l') is rather distant from the Ewald sphere as long as (h'k'l') is an allowed reflection. It should be noted that the (000)(h'k'l')(hkl) scattering is sharp and makes an intensity contribution only over the scattering range of the (000)(hkl) reflection even though an intermediate reciprocal lattice vector is involved.

The direct solution of the multiple scattering problem involving N such reciprocal lattice points requires the diagonalization of a $2N$

$\times 2N$ complex matrix so that the consideration of more than ~40 beams is not feasible. However, an accurate approximation has been developed by which multiple scattering from ~400 weakly excited beams has been evaluated with only a few minutes of CPU time on a supermini size computer. The approximation is based on the fact that beams derived from reciprocal lattice points far from the Ewald sphere are very weak, and thus they couple weakly to each other. Since the total reflectivity for basis forbidden reflections is typically less than $\sim 10^{-4}$, incident photons can be reflected with sizable probability only by the principal reflection (000)(hkl) or by a single multiple reflection (000)(h'k'l')(hkl). That is, higher order multiple reflections can be neglected.

Since the scattering from all channels is coherent, the total scattering amplitude in this approximation is given by the sum of the scattering amplitude of the principal reflection and the scattering amplitudes of all of the first-order (h'k'l') contributions. Therefore, the scattering amplitude of each of the (000)(h'k'l')(hkl) contributions can be computed independently using three-beam calculations. The amplitudes can then be added coherently after taking polarization into account; it is unnecessary to solve for all of the scattering amplitudes simultaneously. Since the scattering amplitudes involved here are small and absorption rather than primary extinction limits the penetration of the beam into the crystal, the integrated intensities can be obtained immediately from F^2 , the square of the peak amplitude as given by kinematical relationships.

Figure 3.17 shows the two-beam integrated intensity for the (622) basis forbidden reflection of Ge and the effect of multiple beam scattering for three crystal orientations. The markers represent full N -beam calculations⁴ for $N = 2, 4, \dots, 30$, and the lines denote results for the approximation using N three-beam calculations for $N = 2, 3, \dots, 400$. These results indicate first of all that the successive three-beam calculations are very good approximations to the full N -beam calculations for these weakly excited reflections and secondly that several hundred beams are required to determine fully the multiple scattering contributions. We see further that the multiple beam effects vary in both magnitude and sign of their contribution to the measured intensities, depending on the particular crystal orientation. Clearly these effects must be considered in detail when measuring weak reflections, and as discussed elsewhere in this report,⁵ multiple reflections must be considered in connection with measurements of symmetry forbidden reflections because they can contribute intensity even though the principal reflection intensity is zero.

Fig. 3.16. Reciprocal-space diagram for multiple beam scattering showing the Ewald sphere, the principal reciprocal lattice vector H , and the multiple scattering geometry associated with the (h'k'l') reciprocal lattice point.

1. Summary of paper: *Acta Crystallographica* (in press).

2. School of Applied and Engineering Physics and Cornell High Energy Synchrotron Source, Cornell University, Ithaca, N.Y.

3. J. Z. Tischler and B. W. Batterman, *Phys. Rev. B* **30**, 7060 (1984).

4. R. Colella, *Acta Crystallogr. A* 30, 413 (1974).

5. J. Z. Tischler and J. D. Budai, "Measurement of the Silicon (200) Reflection," this report.

Fig. 3.17. Calculated integrated intensity as a function of multiple beam diffraction for the basis forbidden (622) reflection in Ge for three orientations, ϕ , between the plane of diffraction and the [011] direction. The markers represent N-beam simultaneous diffraction calculations, and the lines represent the approximate multibeam calculations.

ON REFRACTORY OXIDE CRYSTALS FOR CONTINUOUS-WAVE TUNABLE LASERS¹

Y. Chen R. Gonzalez²

Tunable lasers based on vacancies in ionic crystals can be expected to gain increasing importance in research and technology. A clear advantage is the broadly tunable operation that can be derived from such a system. Success in the alkali halides has already been demonstrated.^{3,4} The purpose of this study is to demonstrate that the F^+ center in irradiated MgO is not likely to produce cw tunable laser action but that MgO crystals thermochemically reduced at high temperatures and pressures are more promising.

In general, anion vacancies in alkaline-earth oxides assume two charge states: the one-electron F^+ center and the two-electron F center.

While the absorption bands of these two charge states in most oxides occur at different wavelengths, in MgO they coincide at 4.9 eV (250 nm).⁵ In MgO, CaO, and SrO irradiated with energetic particles, the preferred charge state is the F^+ center. Excitation of MgO with 4.9-eV light produces the F^+ luminescence at 2.1 eV (395 nm) with a full width at half maximum (FWHM) of 0.6 eV.⁵ Such broad emission, in principle, permits a broad tuning range for laser action.

Photoconversion is common in the alkaline-earth oxides. In thermochemically reduced crystals the natural state of the anion vacancy is the F center. In thermochemically reduced MgO the photoconversion process

has been reported. The electron released from the F center is captured by a Fe^{2+} impurity to form a Fe^+ ion.

The reverse photoconversion process

where h^+ refers to a hole, prevails in MgO irradiated with energetic particles. This process renders the use of the F^+ luminescence in irradiated crystals for cw tunable lasers doubtful. When the electron of the F^+ center is in an excited state, the strong polarization at the vacancy demands an electron from a nearby O^{2-} ion, thereby leaving behind a hole. The hole migrates and is trapped by a magnesium vacancy-charge compensated by an impurity inherently present in MgO crystals, such as Al^{3+} or H^+ , to form the V_{Al} or V_{OH} centers, whose linear configurations are $Al^{3+} - O^{2-} - [Mg \text{ vacancy}] - O^-$ and $OH^- - [Mg \text{ vacancy}] - O^-$, respectively. The O^- refers to an O^{2-} ion with the trapped hole. These trapped-hole centers give rise to broad absorption bands with a FWHM of 1.1 eV at 300 K, with peaks at about 2.3 eV (540 nm). This photoconversion effect was exhibited on a nominally pure MgO crystal previously irradiated with $5.3 \times 10^{15} \text{ n/cm}^2$ ($E > 1 \text{ MeV}$) in the ORNL Bulk Shielding Reactor. The sample temperature during irradiation was about 320 K. The sample was excited with a low-intensity 4.9-eV light, the source being a 100-W Hg lamp in conjunction with a Bausch and Lomb monochromator set at 254 nm. The spectra before and after the excitation are shown in Fig. 3.18. It is clear that trapped-hole centers, which absorb at 2.3 eV, are produced by the 4.9-eV light excitation. The absorption coefficient was 3 cm^{-1} . These centers are metastable and have a half-life for hole release of a few hours at 300 K. They obviously are a deterrent to producing cw laser action in the region of their optical absorption.

We propose that in general thermochemically reduced crystals are better candidates than irradiated crystals as laser materials. Thermochemical reduction is performed at $T \geq 2000 \text{ K}$ in a chamber containing high-pressure metallic vapor (several atmospheres) of the host constituent. The strong reducing atmosphere causes a

Fig. 3.18. Optical absorption spectra of a neutron-irradiated MgO crystal (a) before and (b) after excitation with 5.0-eV light. The sample thickness was 1.51 mm.

deficiency of oxygen ions, resulting in anion vacancies. Equally important, from the mass action law the cation vacancy concentration is dramatically reduced. Therefore, trapped-hole centers are minimized. This can be demonstrated for an MgO crystal which has been thermochemically reduced in 6 atm of magnesium vapor at about 2200 K for 2 h. The spectrum after thermochemical reduction is shown by the dotted curve in Fig. 3.19. After excitation with 4.9-eV light, the spectrum remained essentially the same (solid curve in Fig. 3.19). The absorption band at 2.3 eV due to trapped hole centers is notably absent. Furthermore, compared with Fig. 3.18, the low absorption and the flatness of the curves between 1 to 4 eV are apparent.

As noted, after thermochemical reduction the charge state of the anion vacancy is neutral (F center). During excitation into the F band, photoconversion occurs, and both F^+ and F luminescence take place, the latter being a long-lived phosphorescence with a peak at 2.3 eV (to be distinguished from the broad absorption peak at the same energy due to trapped-hole centers). The long-lived component of the F luminescence has been identified as due to the presence of H^- ions (protons in anion sites each with two electrons). Being positively charged with respect to the lattice, they serve as metastable traps for electrons excited from the F centers. If protons are completely removed from an MgO crystal prior to thermochemical reduction, as in the sample whose spectra are shown in Fig. 3.19, only the F^+ luminescence occurs. This is a highly desirable effect because the gain coefficient of the F^+ emission should be much larger than that for the F center: for the F center, the electronic wave function of the $^3T_{1u}$ excited

Fig. 3.19. Optical absorption spectra of a thermochemically reduced MgO crystal before (bottom curve) and after (top curve) excitation with 5.0-eV light. The sample thickness was 0.87 mm. The top curve is displaced upward to avoid overlapping of the two curves.

state is too diffuse; its energy level is estimated to be within 0.01 eV of the conduction band. The F^+ center does not have this problem, because the $^2T_{1u}$ excited state is sufficiently removed from the conduction band. It is therefore more desirable for tunable lasers.

Besides the absence of trapped-hole centers, other advantages offered by thermochemically reduced MgO are thermal stability and probably higher quantum efficiency of the luminescence.

In general, the trapped-hole centers in irradiated oxide crystals can be detrimental to cw tunable laser operation. It is suggested that thermochemically reduced oxides are more promising. Trapped-hole centers are not formed in thermochemically reduced refractory oxides when irradiated with photons or ionizing radiation. Furthermore, the extreme resistance of refractory oxides to form defects by particle irradiations can serve in a very positive manner: optical devices using thermochemically reduced oxides can survive an environment of strong radiation fields, such as the Van Allen belt, without appreciable optical degradation.

1. Summary of paper: *Opt. Lett.* 10, 276 (1985).

2. Guest scientist from Universidad Complutense, Madrid, Spain.

3. L. F. Mollenauer, *Opt. Lett.* 1, 164 (1977).

4. See P. Luty, *Phys. Today* 37, S-19 (1984), and references therein.

5. Y. Chen, J. L. Kolopus, and W. A. Sibley, *Phys. Rev.* 186, 865 (1969).

PROTONS AND DEUTERONS IN CRYSTALLINE OXIDES

I. DIFFUSION AND ITS IMPLICATIONS IN FUSION DEVICES¹

R. Gonzalez² Y. Chen

The infrared absorption of OD^- and OH^- ions was used to study diffusion rates of D^+ and H^+ in several oxide materials heated to high temperatures in D_2O and H_2O vapors. Deuterons were used as the main diffusion species because most oxides contain hydrogen as an impurity. The diffusion coefficients for D^+ can be obtained from knowledge of the initial infrared optical absorbance of OD^- ions, the absorbance after anneals of time t , and the absorbance at saturation (after long anneals), referred to as A_0 , A_t , and A_∞ , respectively. The diffusion coefficient can be calculated from the relationship:

$$\frac{A_t - A_0}{A_\infty - A_0} = \frac{S}{V} \frac{4}{\pi} \sqrt{Dt}, \quad (1)$$

where S is half the total sample area and V is the sample volume. We neglect the diffusion through the edges of the sample and treat the problem as one dimensional. This treatment is justified because the samples were thin (thickness $\ll S$). The equation is valid if the thickness is greater than $\sqrt{Dt}$.

In MgO , the minimum temperature (observation threshold) for D^+ diffusion is 1750 K, and the diffusion coefficient is $\sim 1 \times 10^{-6} \text{ cm}^2/\text{s}$ at 1873 K. Doped MgO crystals also have about the same diffusion coefficients, with the exception of lithium-doped MgO crystals. Deuterons diffuse much more readily in the Li-doped crystals. A method to determine accurately the ratio of the diffusion coefficients of H^+ to D^+ was made. At 1873 K, this ratio was measured to be 1.1 ± 0.1 . Removal of soluble H^+ or D^+ can be accomplished effectively by application of an electric field at high temperatures.

A novel method of enhancing diffusion, especially at low temperatures, has been demonstrated. Specifically, diffusion of deuterons and protons in rutile TiO_2 can be induced near room temperature by breaking the O-H bond by electron irradiation and sweeping these hydrogenic species along the c-axis using an electric field.

Diffusion coefficients of protons and deuterium in LiNbO_3 , KTaO_3 , MgAl_2O_4 spinel, and $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ were also measured.

1. Summary of paper: Anales de Física A 81, 1 (1985).
2. Guest scientist from Universidad Complutense, Madrid, Spain.

PROTONS AND DEUTERONS IN CRYSTALLINE OXIDES

II. CONSIDERATION FOR A TUNABLE LASER¹

Y. Chen R. Gonzalez²

Thermochemical reduction of MgO , CaO , and SrO crystals at high temperatures results in anion

vacancies and H^- ions (protons in anion sites, each attended by two electrons). Infrared absorption lines observed near 1000 cm^{-1} are shown to be due to H^- ions. The electron transition of the F^+ and F centers (anion vacancies with one and two electrons, respectively) occurs at 5.0 eV (250 nm).

At room temperature, H^- ions are the main metastable traps for electrons excited from F centers (oxygen vacancies each with two electrons), thereby causing the long-lived phosphorescence observed in thermochemically reduced crystals. Thermochemically reduced crystals possess some characteristics desirable for tunable laser materials. By removing protons prior to thermochemical reduction, the phosphorescence is destroyed and the desired F^+ luminescence takes place. Emphasis is placed on MgO crystals, since it is a widely used material, nonhygroscopic, and is therefore most likely to be useful for device applications among the alkaline-earth oxides.

1. Summary of papers: Anales de Física A 81, 20 (1985); Cryst. Latt. Def. Amorph. Mater. 12, 149 (1985).
2. Guest scientist from Universidad Complutense, Madrid, Spain.

THE LOW-TEMPERATURE NEUTRON IRRADIATION FACILITY

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C. E. Klabunde F. W. Young, Jr.

After nearly three years of design and construction, the Low-Temperature Neutron Irradiation Facility (LTNIF) was completed early in 1986 (construction of auxiliary facilities continues). Upon completion of the safety analysis, the LTNIF will be available for qualified experiments at no cost to users. It provides high radiation intensities and special environmental and testing conditions that have not previously been available in the U.S. Irradiations and tests are possible at temperatures between 3.2 and 800 K. Preliminary determination of the radiation characteristics are given in Table 3.2.

The LTNIF is located at the Bulk Shielding Reactor (BSR). Figure 3.20 shows the irradiation cryostat and its relationship to the BSR pool and reactor core. Performance tests have shown that samples can be cooled to temperatures as low as 3.2 K during irradiation and testing. At 5 K, 30 W of nuclear heating (generated in about 100 g of metal at full reactor power, for example) can be removed from experiment assemblies during irradiations. The irradiation chamber is a 37-mm-diam tube inside the lower, rectangular parallelepiped section of the cryostat, which nests inside a U-shaped gamma-ray shield in place of a missing fuel element. Just above the irradiation chamber is a 197-mm-diam test chamber for in situ testing of irradiated samples. Liquid helium and liquid nitrogen are delivered by the refrigeration system to heat exchangers surrounding the test chamber. The

Table 3.2. Preliminary radiation characteristics at the full BSR power of 2 MW.

Radiation	Intensity
Fast neutrons ($E > 0.1$ MeV)	1.8×10^{17} n/m ² s ^a
Thermal neutrons	1.5×10^{17} n/m ² s ^b
Gamma rays (in Al)	0.32 W/g ^b

^aDetermined by scaling more detailed neutronics measurements made in a hollow fuel element device to the results of measurements employing a Ni activation detector in a mockup of the cryostat.

^bDetermined by computer calculations and neutronics/nuclear heating measurements made in a hollow fuel element device.

in a natural convection loop. Because the test chamber is outside the irradiation zone, samples can be irradiated to high fluences and then tested in the absence of nuclear heating, using unirradiated test devices that may be sensitive to radiation (e.g., a superconducting magnet).

Three features of the BSR will aid LTNIF experimenters. First, the core fuel loading allows sufficient excess reactivity to permit restarting after any operating history—xenon poisoning is not an operational limitation. This is an asset for experiments that require frequent on-off reactor operations. Second, the open pool provides convenient locations for ambient-temperature and cryogenic storage and test facilities for radioactive samples. These facilities are located close to the irradiation cryostat, and they make use of pool water for biological shielding. Third, the movable core assembly affords easy insertion and removal of radiation modifiers between the core and the irradiation cryostat when modified spectra are needed.

In addition to the irradiation cryostat and its refrigeration system, several auxiliary facilities are functional and others are under construction or in planning. A computer-based, on-line data acquisition system is provided with hard-wired electrical terminals available at the cryostat top. Data can be tabulated, plotted, or transmitted to a distant computer over telephone lines for later analysis. Provisions are available for transfer of irradiated specimens at 4.2 K into the user's test device or into vessels for shipment to other laboratories. Temporary storage at 4.2 or 308 K of radioactive samples or experiment assemblies is available in the BSR pool. Short-term storage is often essential to allow decay of short-lived radioactive isotopes that are present. A 12-T superconducting magnet is on hand and will be mounted for use either in a poolside experiment devar or in the test section of the irradiation cryostat. An ambient temperature irradiation facility (ATNIF) is available for irradiation at temperatures from ambient up to a maximum of about 800 K. A 200-kV electron microscope is being procured, and a liquid helium stage and transfer device to move specimens from the irradiation cryostat to the microscope without warmup is under design. After completion of this microscope facility, it will be possible to obtain direct microscopic structural information about radiation-induced defects and their thermal annealing as it occurs in the microscope.

FRACTURE

DIRECT OBSERVATION OF DISLOCATION-FREE ZONE AT CRACK TIPS BY HIGH-VOLTAGE ELECTRON MICROSCOPY¹

S. M. Ohr² H. Saka³
Y. Zhu³ T. Imura³

Fig. 3.20. Layout plan for LTNIF at ORNL's Bulk Shielding Reactor.

sample assembly is cooled by helium in the gaseous or liquid state (depending upon the precise conditions) circulating through the irradiation chamber and past the helium heat exchanger

The dislocation-free zone (DFZ) was first observed approximately five years ago at the tips of moving cracks in bcc metals during in situ fracture experiments in an electron

microscope. Under externally applied tensile stress, dislocations were emitted from a crack tip and moved rapidly out of the area, creating a zone cleared of dislocations between the crack tip and its plastic zone. Subsequent experiments have shown that the DFZ was present in all of the bcc, as well as fcc, metals studied. Theoretically, the DFZ restores the stress singularity at the crack tip even though crack-tip deformation has occurred. It is possible to describe the state of the stress at the crack tip by a stress intensity factor. It has also been shown that the presence of the DFZ is closely related to the condition for dislocation emission from the crack tip.

One of the questions raised with respect to the DFZ is that the in situ fracture experiments in which the DFZ was observed were carried out in conventional electron microscopes with accelerating voltages of less than 200 KV. At these voltages, the maximum thickness of the foil from which useful information could be obtained was a few thousand angstroms. It was possible, therefore, that the observations reported may have been influenced by the thickness of the specimens.

In the present work, we performed in situ fracture experiments in iron and in copper-aluminum single crystals using the 1-MV high-voltage electron microscope (HVEM) located at Nagoya University, Japan. As stress was applied, cracks were nucleated at the edge of the specimen and propagated into the thicker portion of the specimen. As the crack propagated, a large number of dislocations were emitted from the crack tip and moved away immediately from the crack tip, leaving a DFZ near the crack tip. The dislocations eventually came to rest in a plastic zone some distance from the crack tip and formed dense tangles. An example of the distribution of dislocations ahead of a crack tip in iron is shown in Fig. 3.21. Because of the high accelerating voltage used, the dislocation structure could be observed in areas as thick as a few microns. Nearly all of the dislocations visible in this micrograph were emitted from the crack located at the edge of

the specimen. The number of dislocations emitted could not be measured accurately, but it was estimated to be a few thousand. It can be seen that all of the dislocations are piled up in the plastic zone in the form of tangles, but the region between the crack tip and the plastic zone ($\sim 7 \mu$ in length) is free of dislocations. In some instances, a few emitted dislocations were trapped near the crack tip by other defects, such as dislocation loops. The number of these trapped dislocations was only a very small fraction of the total number emitted. As the stress was increased further, these dislocations eventually became untrapped, left the crack tip area, and joined other dislocations in the plastic zone. As the crack propagated further into the specimen, the length of the DFZ became shorter because many of the dislocations could not escape from the tangles. As the crack approached the tangles, the stress field was so high that some of these tangles were dissolved, and the dislocations were again driven out of the crack-tip area.

It was concluded from this study that the presence of the DFZ is not limited to thin foil specimens and that the dislocations emitted from a crack tip are strongly repelled from the crack tip. The observed behavior of dislocations near a crack tip is also in good agreement with the predictions of the theory of elastic interaction between a crack and dislocations.

1. This work was partly supported by the Yamada Science Foundation, Osaka, Japan.
2. Present address: State University of New York, Stony Brook, N.Y.
3. Nagoya University, Nagoya, Japan.
4. S. Kobayashi and S. M. Ohr, *Phil. Mag. A* 41, 81 (1980).

Fig. 3.21. Distribution of dislocations in the vicinity of a crack tip observed in an iron single crystal using an HVEM. Specimen thickness was a few microns.

CRACK TIP DEFORMATION AND CRACK PROPAGATION IN PURE IRON¹

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S. M. Ohr²

We have shown the dislocation behavior at crack tips and its relationship to the onset of crack propagation through in situ transmission electron microscopy (TEM) experiments in various bcc and fcc metals and alloys. However, very few studies have been made on iron, which is the base metal for many structural materials used in various energy systems, because of the material's strong ferromagnetism and consequent effects in TEM. In the present study, an attempt was made to characterize the mode and geometry of crack-tip deformation and crack propagation involved in this bcc metal.

The mode and geometry of crack-tip deformation were, in general, similar to those observed in other bcc metals, such as molybdenum, niobium, and tungsten. Edge or screw dislocations were emitted from the tip of the propagating cracks, left the crack-tip area

rapidly, and piled up in a plastic zone, leaving behind a dislocation-free zone (DFZ) between the crack tip and the plastic zone. Typical crack-tip deformation is shown in Fig. 3.22, where the crack-tip-emitted screw dislocations are piled up on the active (101) slip plane that is coplanar with the crack plane ahead of the 3.2- μ m-long DFZ. The plastic zone shown represents pure shear deformation, and the crack is an anti-plane shear crack of mode III type, which was most frequently observed in other bcc metals. As was noted in many other cracks studied, the active slip system had the highest crack-tip Schmid factor among all possible slip systems at the crack-tip area. The crack-tip-generated dislocations were frequently cross-slipped out of the original slip plane into other {110} and {112} planes. Those dislocations often interacted with other dislocations (not visible in Fig. 3.22) generated from sources other than the crack, such as grain boundary ledges and junctions.

TEM observations of crack propagation were also performed in pure iron, as shown in Fig. 3.23. As applied stress was increased, a crack propa-

Fig. 3.22. Electron micrograph of a pileup of screw dislocations ahead of a mode III crack in pure iron.

Fig. 3.23. Crack propagation along a zigzag path observed in pure iron. The crack propagated by a combination of modes I and III.

gated in a zigzag manner by activating two slip systems alternately at the crack tip. In this process after emitting dislocations and moving certain distances, the crack suddenly stopped its propagation, changed its direction, and propagated along the new direction by emitting dislocations on another slip system. It was noted that many of the dislocations emitted were piled up in the vicinity of the crack and formed complex dislocation-cell walls. The crack-tip dislocation activities were thus limited in a region between the cell walls. The local zigzag mode is quite similar to that observed in bcc molybdenum. That is, the crack propagated by a combination of opening mode (mode I) and shear mode (mode II or III) components. However, the geometry was distinctly different from that of molybdenum. While slip traces and thus the zigzag paths in molybdenum make an angle of approximately 30 degrees with each other, the zigzag path in iron followed the perpendicular slip traces, which are identified as traces of dominant slip planes in iron, {110} or {112}.

1. Summary of paper to be published.
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IN SITU TRANSMISSION ELECTRON MICROSCOPY STUDIES OF CRACK TIP DISLOCATIONS IN MOLYBDENUM¹

C. G. Park   S. M. Ohr²

From a series of transmission electron microscopy (TEM) observations, it is now well established that when plastic deformation occurs ahead of propagating cracks, dislocations emitted from the crack tip are rapidly driven out of the area and piled up in a plastic zone, creating a dislocation-free zone (DFZ). The observation of the DFZ, which is a manifestation of the difficulty associated with dislocation emission from the crack tip, has contributed significantly to understanding the mechanism of ductile and brittle crack propagation. The relationship between the behavior of crack tip dislocations and the mode of crack propagation depends on the crack geometry and the loading conditions. In the present study, we have examined the effect of loading conditions on the distribution of dislocations, on the DFZ, and on the crack-tip slip systems during in situ TEM deformation of bcc metals, with an aim to find a parameter that is responsible for determining the geometry of crack-tip deformation.

Depending on the loading geometry, all three modes of crack-tip deformation have been observed. In all of the cases studied the presence of the DFZ immediately ahead of the crack tip was confirmed by imaging 4-5 different diffraction conditions. Table 3.3 lists the sizes of the DFZ and the plastic zone and the number of dislocations associated in the plastic zone for a number of experiments on molybdenum. In general, the DFZ ahead of a shear crack of mode III was shorter than DFZs of mode I and II cracks. This observation indicates that the emission of screw dislocations from the crack

Table 3.3. The sizes of the DFZ and the plastic zone and the number (N) of dislocations associated in the plastic zone observed under three different modes of loading in molybdenum.

Mode	DFZ	Plastic Zone	N
I	8.8 μm	>16 μm	420
	9.0	>8	160
	19.8	>7	80
	5.5	>8	250
II	8.8	12	100
	2.5	14.5	120
	16.0	>5	70
	15.8	---	---
	9.9	>7	85
	12.0	>8	120
III	7.2	>4	70
	1.4	>12	350
	3.5	>25	---
	3.6	>15	>400
	2.7	>28	300
	2.5	20.5	130
	3.0	15	250
	2.5	>20	>300
	2.5	4	45
	3.2	>16	>200
	1.5	>10	280

tip is easier under the mode III loading condition. The dislocations distributed in the plastic zone were not in the form of an exact inverse pile-up as previously reported.³ That is, the maximum density was not nearest the crack tip; instead, it was generally located at a distance 7-8 μm away from the crack tip (Fig. 3.24).

The size of the DFZ depended on the number of dislocations in the plastic zone, the grain size, and the loading condition, as predicted by the dislocation model of fracture.⁴ Figure 3.25 shows the variation of the DFZ in two different stages of crack propagation in molybdenum. Between (a) and (b) the applied stress was increased and the crack propagated. The total number of dislocations emitted from the crack tip increased from 70 to 280, and the length of the DFZ decreased from 5.5 to 1.5 μm . During this process the grain boundary appears to have acted as a barrier to dislocation motion. More detailed examination indicated that these dislocations interact with grain boundaries in very complex ways. When the stress was removed, some of the dislocations that were piled up only against the grain boundary moved backward to the crack tip and were annihilated.

In all of the crack-tip deformations analyzed, the choice of the crack-tip slip system was dictated by two factors: the dislocation emission condition from the crack tip for each mode of loading and the crack-tip Schmid factor,

Fig. 3.24. TEM picture of a 2.5- μ m long DFZ and a pileup of screw dislocations ahead of a mode III crack in molybdenum.

Fig. 3.25. Distribution of dislocations ahead of a propagating crack in molybdenum. As applied stress increased from (a) to (b), the crack propagated and the size of the DFZ decreased.

representing a relative resolved shear stress in the crack-tip area. That is, the mode of crack-tip deformation was determined first by the ratio of the component of applied stress to the critical stress intensity factor for dislocation emission for each mode. It was found that the mode III crack-tip deformation is statistically favored over modes I and II. Then, within each mode of deformation, the slip system possessing the maximum crack-tip Schmid factor was activated from the tips of propagating

cracks. The results are in good agreement with the DFZ theory of fracture.⁴

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DISLOCATION SHIELDING MODEL OF FRACTURE UNDER REVERSE LOADING¹

S.-J. Chang² S. M. Ohr³

The distribution of dislocations in the plastic zone ahead of a crack tip during cyclic loading has been studied theoretically by Weertman⁴ and Bilby and Heald⁵ by extending the method proposed by Bilby, Cottrell, and Swinden (BCS).⁶ The BCS model of fracture, however, is inadequate in describing the crack-tip processes because the model predicts the density of dislocations to be infinite at the crack tip, giving rise to zero local stress intensity factor. Recent TEM studies of crack propagation have shown that a dislocation-free zone (DFZ) is present immediately ahead of the crack tip. It was also observed when the applied load was reduced that some of the dislocations in the plastic zone returned to the crack tip and were annihilated at the crack tip, but the number of dislocations returning to the crack tip was appreciably greater⁷ than the number predicted by the BCS theory.

In the present study, we have applied the DFZ model of fracture^{8,9} to investigate the distribution of dislocations in the plastic zone during cyclic loading. Starting from the equilibrium distribution of dislocations with a DFZ between the crack tip and the plastic zone, the applied stress was allowed to decrease, and an integral equation was set up for the new distribution function. The method of solving the integral equation by superposition, used in the BCS model, could not be used because the stress distribution in the DFZ was not constant and was a sensitive function of the distance from the crack tip. It was, therefore, necessary to introduce an approximation scheme to obtain a solution of the integral equation. It was found that two distinct types of distributions of dislocations were possible during reverse loading. The first of these consisted of only positive dislocations, whereas the second was a mixture of positive and negative dislocations. The negative dislocations were found when the local stress intensity factor became more negative than the critical stress intensity factor for dislocation emission (i.e., $k(-k_c)$).

Two distinctly different distributions of dislocations that are possible during reverse loading are shown in Fig. 3.26 and Fig. 3.27. Figure 3.27 shows a series of distributions in which the applied stress is reduced beyond a certain threshold value. As the applied stress is lowered, the number of dislocations in the plastic zone is reduced, indicating that some of the dislocations returned to the crack tip and were annihilated. The size of the DFZ increases, but the local stress intensity factor decreases because the applied stress is reduced. This trend continues as the applied stress becomes increasingly negative so that the local stress intensity factor is less than $-k_c$; negative dislocations are emitted from the crack tip, resulting in a distribution of both positive and negative dislocations (Fig. 3.27). As the

Fig. 3.26. Distribution of positive dislocations ahead of the DFZ under reverse loading.

Fig. 3.27. Distribution of positive and negative dislocations under reverse loading.

applied stress becomes more negative, the negative dislocations dominate the distribution near the crack tip.

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BEHAVIOR OF CRACK TIP DISLOCATIONS UNDER CYCLIC LOADING

C. G. Park   T. C. Estes
S. M. Ohr¹

Direct observations of the motion of the crack-tip-generated dislocations during loading/unloading conditions for fcc metals have been reported² previously, but no studies have been performed to date on the motion of dislocations under a cyclic (tension/compression) loading condition. We have extended the direct observations of crack-tip deformation by TEM to study the effect of cyclic loading on the motion of the crack-tip-generated dislocations.

Figure 3.28 shows some of the results obtained in bcc molybdenum. By applying a tensile stress, a crack was propagated and formed an edge dislocation pileup ahead of the crack tip. As the stress was increased, the mode II crack propagated by emitting a number of edge dislocations that moved along a new slip plane to form a second dislocation pileup shown in Fig. 3.28(a). As the stress was reduced, the dislocations in the second pileup started to move backward to the crack tip, and some of them were annihilated at the crack tip. When the stress was completely removed, as shown in Fig. 3.28(b), less than half of the dislocations were left in the plastic zone and had redistributed themselves. According to the dislocation theory of fatigue,³ the above crack-healing process is caused by the repulsive force exerted by dislocations in the

plastic zone overcoming a friction stress which now opposes the dislocation motion to the crack. As the tensile stress increased again, dislocations were reemitted from the crack tip and moved along the identical slip plane.

In another series of experiments, after a tension and relaxation cycle which produced very similar results (i.e., same fracture mode and same Burgers vectors for the dislocations), a compressive stress was applied. In this case, new dislocations were generated, which pushed the existing dislocations away from the crack, and the crack propagated further. An interaction of those two kinds of dislocations and a possible antishielding of the crack are currently under investigation.

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ELASTIC SOLUTION OF AN EDGE DISLOCATION NEAR A WEDGE CRACK¹

S.-J. Chang²   S. M. Ohr³
R. Thomson⁴

Direct observation of crack propagation during in situ tensile deformation in an electron

Fig. 3.28. Electron micrograph of crack-tip dislocations under (a) tensile loading and (b) complete unloading conditions observed in molybdenum.

microscope has shown that crack-tip deformation under mode I loading condition occurs by the emission of edge dislocations on slip planes that are inclined to the crack plane.⁵ When edge dislocations are emitted on an inclined plane, the plastic slide-off occurs at the crack tip, and as a consequence the crack, which was originally sharp, becomes a wedge crack. It was shown⁶ that the stress field around a wedge crack was drastically different from that of a sharp crack and that it was no longer possible to apply the usual elasticity solution to describe the crack tip processes. In the present study, we have examined the elastic interaction of a wedge crack of an arbitrary angle and an edge dislocation by applying the method of complex variables. For a semi-infinite crack, a simple analytical solution has been found.

In order to obtain a solution, the wedge plane z is transformed to a half plane $w = a + ib$ by

$$z = g(w), \quad (1)$$

where $g(w) = w^p$ ($1 < p < 2$). The method used for a screw dislocation⁶ does not apply for the case of an edge dislocation. Since p is in general not an integer, the analytical continuation of $g(w)$ induces a discontinuous displacement $[D]$ in the w -plane, and its magnitude along the real axis is given by

$$2\mu[D] = \kappa[\Phi] - (\bar{g}/g') [\Phi'] - [\phi], \quad (2)$$

where μ and κ are constants and Φ and ϕ are the stress functions. In order to obtain a solution for a fictitious distribution of dislocations, $f(u)$ is assumed along the real axis of the w -plane to remove the discontinuous displacement $[D]$. The resulting integral equation for $f(u)$ is

$$\int_0^\infty [1 + D_b(u, u')] bf(u') du' = -[D(u)]. \quad (3)$$

In this equation, $[D_b]$ is the discontinuous displacement at u along $v = 0$ due to the presence of a dislocation of unit Burgers vector at u' . In order to obtain the solution for an edge dislocation near a wedge crack, this integral equation must be solved for $f(u)$. The complete solution is then obtained by superposition.

NEW MECHANISM IN HYDROGEN EMBRITTLEMENT: CHEMICAL DRIVING FORCE FOR DISLOCATION MOTION¹

C. G. Park   J. C. M. Li²
S. M. Ohr³

The effects of hydrogen on plastic deformation and fracture behavior in iron and steels have been reviewed in order to understand the basic mechanism of hydrogen embrittlement. A mechanism has been proposed, based on the concept termed diffusion-induced grain boundary motion (DIGM)^{4,5} or diffusion-induced dislocation glide (DIGG)⁶ in which grain boundaries or dislocations are induced to move when solute atoms diffuse along grain boundaries or dislocations more rapidly than through the lattice. The initial motivation for such effects is believed to be the difference in free energy of solute atoms across the boundary or the dislocation.

The proposed mechanism consists of two major parts. The first is on the effect of hydrogen on plastic behavior. That is, during charging or discharging of hydrogen, a large chemical driving force can be generated and converted into mechanical effects of moving dislocations. A necessary condition is that hydrogen diffuses faster along dislocations than through the lattice, so that hydrogen dissolution or removal can be facilitated by the motion of dislocations. The fact that a dislocation can be a short circuit for the diffusion of solutes has been well accepted. It is also proposed that, when hydrogen fugacity is high, it can overcome the nucleation barrier so that some surface sources of dislocations can be activated. The newly created dislocations are then capable of spreading the hydrogen into the lattice.

The chemical driving force exerted on a dislocation line, through which hydrogen diffuses with fugacity f_0 and from which hydrogen of fugacity f gets injected into the lattice, is given approximately by the following equivalent shear stress:

$$\tau = \frac{nkT}{b^2} \ln \frac{f_0}{f}, \quad (1)$$

where n is the number of hydrogen atoms trapped per unit length of dislocation when the dislocations move forward by a distance b , k is the Boltzmann constant, T is the temperature, and b is the Burgers vector of the dislocation. Thus, for instance, a ratio (f_0/f) of 2 of hydrogen fugacities and a value of $n = 10^{10}$ hydrogen atoms/m will have a chemical driving force equivalent to a shear stress of 306 MPa at 200 K. This is certainly sufficient to move dislocations.

The mechanism can explain several controversial effects of hydrogen on the plastic behavior of iron and its alloys in a consistent manner. For instance, the following results obtained during in situ electron microscopy⁷ and during mechanical tests can be explained: (1) Sudden softening upon charging (this includes a sudden drop of flow stress and an instant increase of the creep rate or the rate of stress relaxation)

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is caused by an instant movement of dislocations to reduce the chemical potential of hydrogen. The effect is transient, diminishes with further hydrogen charging, and stops at saturation. This explanation seems to account for the data better than does the concept that hydrogen reduces the Peierls barrier for dislocation motion. (2) Hardening after further charging that is observed results from increased dislocation density. This effect is more persistent, and it is removed by aging at high temperature. (3) Sometimes, further softening upon discharging can be caused by the instant increase of chemical stress on the dislocations; of course, if this increased dislocation motion resulted in loss of dislocations from the metals, the work hardening rate would then decrease.

Concerning the effect of chemical driving force on crack propagation and hydrogen embrittlement, we propose that the large fugacity gradient at the crack can cause the emission of a large number of dislocations at the crack tip, even without any external stress. Unlike the case of shielding in which the emitted dislocations can reduce the stress intensity factor introduced by the applied stress, the dislocations emitted by the chemical stress can exert a large stress intensity factor on the crack tip that can propagate the crack. Since the induced stress intensity factor is maximum along the slip plane on which the dislocations are emitted, a brittle crack will tend to follow the dislocations. This mechanism explains the so-called slip plane decohesion that is frequently observed during hydrogen embrittlement.

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SEMICONDUCTOR PHYSICS AND PHOTOVOLTAIC CONVERSION

THE REFRACTIVE INDEX OF SILICON AT ELEVATED TEMPERATURES AT SEVERAL LASER WAVELENGTHS¹

G. E. Jellison, Jr.   H. H. Burke²

It has been known for many years that the refractive index n of silicon increases with temperature T for photon energies less than the direct band gap (3.4 eV at 25°C). For photon energies greater than the indirect band gap

(1.12 eV), the only data in existence are those of Jellison and Modine,³ from which accurate values of the extinction coefficient k could be obtained. Values of n were not as accurate due to uncertainties in the angle of incidence.

In order to measure the refractive index of Si at elevated temperatures, a high-temperature nulling ellipsometer that could use several different lines from Ar⁺ and HeNe lasers was constructed. In order to measure n accurately, it was also necessary to determine the angle of incidence accurately.⁴ Because cw lasers are used as probe beams, any changes that may occur in the angle of incidence, due for example to geometric changes of the sample holder as a function of temperature, can easily be monitored by triangulation.

It was found that n was a linear function of temperature from 25 to ~750°C for all wavelengths longer than 450 nm but that the coefficient of the linear term was a function of wavelength. That is,

$$n(\lambda, T) = n_0(\lambda) + a_n(\lambda) T \quad (1)$$

From Ref. 1, we know that k can be expressed as

$$k(\lambda, T) = k_0(\lambda) \exp(T/T_0) \quad (2)$$

where $T_0 = 430^\circ\text{C}$. Therefore, we can calculate the normal incidence reflectivity, which is given by

$$R(\lambda, T) = [(n-1)^2 + k^2] / [(n+1)^2 + k^2] \quad (3)$$

To a good approximation,

$$R(\lambda, T) = R_0(\lambda) + a_r(\lambda) T \quad (4)$$

The linear coefficients a_n and a_r are functions of wavelength and are shown in Fig. 3.29. As a check, the reflectivity at normal incidence was also measured at elevated temperatures, where it was found that R was linear with temperature. The values of $a_r(\lambda)$ determined from these elevated temperature reflectivity measurements are shown in the top panel of Fig. 3.29 by the open circles. It is also possible to correct the data originally presented in Ref. 1 for the small changes in the angle of incidence with temperature at one wavelength (in this case, 633 nm) and to determine $a_n(\lambda)$ and $a_r(\lambda)$ at any other wavelength from the corrected data. These results are also shown in Fig. 3.29 by the crosses.

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Fig. 3.29. The linear temperature coefficient of the refractive index a_n (bottom panel, $\times 10^{-4}$) and of the reflectivity a_r (top panel, $\times 10^{-5}$) determined from nulling ellipsometry experiments ($\square$), reflectivity measurements ($\circ$), and the data of Ref. 1 ($\diamond$).

PICOSECOND LASER AND STREAK CAMERA FACILITIES DEVELOPMENT

D. N. Mashburn

A Nd:glass laser capable of generating <10-ps pulses has been built using many components of an existing Nd:YAG laser. The oscillator cavity includes an active mode locker, a 55% flat output coupler, 6-m radius of curvature rear mirror in contact with a saturable absorber, and a Brewster-cut laser rod pumped by two linear flash-lamps set in a diffuse reflector.

The mode locker is a temperature-controlled acousto-optic modulator driven at its resonant frequency of 55.955 MHz at RF power levels up to 10 W.

The saturable absorber dye, $C_{50}H_{43}O_2 \cdot ClO_4$ (Eastman #5) dissolved in 1,2 dichloroethane, flows through the optical cavity in a 0.5-mm-thick laminar stream confined between the rear mirror and an AR-coated window. The solution is circulated and filtered during operation, because the optical power density in the dye, which must be very high for saturation to occur, can readily cause breakdown and mirror/window damage if particulates are present. The dye concentration can be adjusted precisely with a built-in dye injector and is typically 10–20 $\mu\text{g}/\text{mL}$ for the shortest pulses.

The laser rod is 95-mm long $\times$ 4-mm diam athermal phosphate glass doped with 6% neodymium and clad with samarium-doped, thermally matched glass to a total diameter of 7 mm. This configuration filters the flashlamp light, fluorescently converts ultraviolet radiation to a better match to the Nd absorption lines, and focuses the pump light into the rod center. These features somewhat offset the much higher pumping requirements of Nd:glass compared with Nd:YAG and make it feasible to use the existing YAG flashlamp cavities and power supplies for this laser.

With the optical cavity length adjusted to match the modulator optical frequency, good mode-locking was observed at a pump energy of 43 J. The Quantel pulse slicer for the YAG laser easily selects a single pulse from the 40–50 pulses in the pulse train that is emitted; amplification factors of 50 to 100 are possible in the existing Nd:glass amplifier stages.

A streak camera has been used to observe the second harmonic (green) light from this laser. Pulses of 10-ps duration, the resolution limit of the camera, have been recorded. The streak camera has been interfaced to our experiment-control computer, the control scheme has been worked out, and the major elements of a picosecond time-resolved ellipsometry experiment have been tested.

FACILITIES FOR LASER PHOTOCHEMICAL VAPOR DEPOSITION

D. H. Lowndes D. N. Mashburn

We recently began development of facilities that are needed for research on laser photochemical vapor deposition (LPVD), a versatile new method for growth of thin films and artificially structured materials at temperatures that are significantly lower than is possible using existing film growth methods. The technical approach of LPVD is to use intense ultraviolet pulsed laser radiation (either in the flowing gas stream directly above a growing film or normally incident upon the film) to produce selectively and nonthermally large concentrations of excited atomic or molecular species; film nucleation and growth are initiated and controlled by this laser-induced nonequilibrium chemical environment. Unlike the thermal "cracking" of molecules on a hot substrate that is used in all conventional chemical vapor deposition (CVD) processes, a UV photochemical growth mechanism results in film growth at very low substrate temperatures and has a number of additional advantages.

Not only does LPVD combine low-temperature and spatially selective growth (growth limited to the laser-illuminated region), but also LPVD's direct photonic control over growth shows promise for providing rapid film growth (governed by the pulsed laser repetition rate) while still maintaining precise control over growth (individual laser pulses corresponding to submonolayer resolution). Other advantages of pursuing a photochemical approach to film growth include the possibility of developing nontoxic, thermally stable precursor gases and LPVD's potentially

broad applicability to incorporate semiconductors, metals, and ceramics (insulators) into artificial materials structures.

Because of the safety and environmental concerns that are necessarily involved in work requiring the use of toxic and/or flammable compressed gases, considerable care is being taken in planning and design of the laboratory area. Selection and purchase of an appropriate vacuum pump, a caustic-spray exhaust gas scrubber, a toxic gas monitor, and a fully integrated set of gas cylinder cabinets and experimental work area that are all housed within a common vented enclosure, have been completed. Conceptual design of the overall safety and environmental protection systems is also complete. Special emphasis is being placed on source gas purity, which is a primary factor governing the ultimate electronic properties that can be achieved in semiconductor thin films. In conjunction with several commercial vendors, a gas-handling system that we believe will set a new standard for compactness, speed of gas mixture switching, and source gas purity has been designed. This system can be operated entirely under laboratory computer control for eventual use in highly reproducible fabrication of multilayered artificially structured materials. Design of a prototype reaction chamber and a laser beam-handling optical system is currently under way for use in preliminary experiments that are required to gather needed design data.

HIGH-EFFICIENCY GLOW-DISCHARGE-IMPLANTED SILICON SOLAR CELLS

R. D. Westbrook   R. F. Wood

The cell fabrication techniques used in the work described here involved glow-discharge implantation of the front and back sides of the silicon wafers with phosphorus and boron from various source gases, followed by a conventional furnace thermal annealing cycle during which an oxide layer of ~ 100 Å was grown for extrinsic surface passivation.¹ The application of anti-reflection (AR) coatings was eliminated as an undesirable complication at this stage; they will be applied after further optimization of the processing. Three-inch, p-type silicon wafers of 0.3-Ω-cm resistivity were used throughout the studies.

Although glow-discharge implantation has proved to be a very useful technique, it has one disadvantage for studies of extrinsic passivation (i.e., it is difficult to obtain a well-controlled light dose of the implanted ions). Work by Spitzer et al.² on surface passivation of cells made by conventional ion implantation indicates that a sheet resistivity ρ_s of >100 Ω/□ is needed to obtain the maximum benefits of extrinsic surface passivation. Values of ρ_s generally obtained with typical glow-discharge implantation conditions are in the range 20–80 Ω/□, too low for effective surface passivation by oxide growth. Our first goal, therefore, was to find methods to decrease the implanted dose, and these will be discussed next.

Experiments were carried out which established that heavy molecular ions, such as those likely to be in the plasma of the PF_5 gas we have generally used as a phosphorus source in the discharge implantation, are stopped almost completely in the ~ 20 -Å-thick native oxide layer on the Si wafers. The most direct evidence for this comes from the comparison of van der Pauw measurements on implanted samples annealed before and after oxide stripping. Typically, samples from which the oxide layer was not stripped gave values of ρ_s in the range 20–40 Ω/□, whereas stripping before annealing gave $\rho_s > 300$ Ω/□, indicating that most of the phosphorus from the PF_5 had been removed with the oxide. Confirmation of this result was obtained from Auger measurements. With BF_3 , our most commonly used boron source, the oxide layer is readily penetrated by these lighter ions, and the stripping experiments show very little difference between stripped and unstripped samples.

One may wonder why the implantation conditions cannot be arranged to give the desired dose. The difficulty is that the glow-discharge apparatus must be operated within a fairly restricted range of conditions on the voltage, current, and charge transfer if a stable plasma with good lateral uniformity is to be obtained. These conditions will vary with each gas, and the required parameters for a desired dose and profile, particularly the voltage, may not be attainable at all in some cases.

Several possible solutions to the foregoing problem were investigated:

1. Use of different combinations of dopant and carrier gases (e.g., PF_5 , PH_3 , PH_3 in Ar, PH_3 in H, BF_3 , BF_3 in H, B_2H_6 , and B_2H_6 in H).
2. Sputtering of the native oxide layer to reduce its thickness and, therefore, the amount of dopant, after implantation but before annealing.
3. Stripping of the native oxide layer before annealing, perhaps in conjunction with (1); this allows only the tail of the dopant distribution that penetrated the oxide layer to be effective in doping.

Each of these approaches can yield the desired result, but each also has some drawbacks, and we have not yet established which one gives the most reproducible results.

Table 3.4 shows the results for several cells made by glow-discharge implantation and furnace annealing. The numbering of the cells indicates the dates on which they were fabricated and shows that steady progress has been made in increasing the efficiencies. The efficiencies η of cells numbered on 7-10-85-1 A and B, 7-10-85-2 A and B (confirmed by measurements at SERI), and 3-19-86-1 A and B are very high. The excellent quality of the cells is also indicated by the very good values of the diode factor A_1 and the dark current I_0 . On stripping of the passivating oxide layer on cell 7-10-85-1 B, V_{oc} dropped by 25 mV and I_{sc} by 0.7 mA; similarly for cell 3-19-86-1 B, $\Delta V_{oc} = 24$ mV and $\Delta I_{sc} = 0.9$ mA. The oxide passivation is clearly effective, but the relatively low values of ρ_s (<100 Ω/□) indicate

Table 3.4. Performance of furnace-annealed cells. The dopant/carrier gas combination is indicated in parentheses in the first column. The cell labeled SPIRE was made by conventional ion implantation and furnace annealing.

Cell No.	$V_{oc}(mV)$	$J_{sc}(mA/cm^2)$	FF	η	A_1	$I_0 (A/cm^2)$	$\rho_s(Q/\square)$
10-29-84-1 A (PF ₅)	608	23.7	79.3	11.5	1.06	$7 * 10^{-12}$	86
B	609	23.3	78.9	11.4			
3-27-85-1 A (PH ₃ /Ar)	607	23.3	78.6	11.1	1.0	$2.1 * 10^{-12}$	64
B	600	23.1	79.4	11.1			
3-28-85-2 A (PH ₃ /Ar)	603	23.0	79.0	11.0	1.03	$3.0 * 10^{-12}$	46
B	603	23.0	79.1	11.0			
7-10-85-1 A (PF ₅)	616	23.8	79.1	11.6	1.00	$1.1 * 10^{-12}$	88
B	618	23.5	79.1	11.5			
7-10-85-1 B (stripped)	592	22.8	78.0	10.6			
7-10-85-2 A (PF ₅)	615	23.4	79.8	11.6	1.03	$2.3 * 10^{-12}$	70
B	618	23.4	79.9	11.6			
3-19-86-1 A (PF ₅)	626	23.6	79.2	11.9	1.03	$1.3 * 10^{-12}$	84
B	625	23.7	79.3	11.9			
3-19-86-1 B (stripped)	601	22.8	77.0	10.8			
Spire	620	23.2	78.0	11.2	1.07	$4.0 * 10^{-12}$	189
(stripped)	580	22.5	77.5	10.2			

that our processing of this type of cell is still not optimized. The cell labeled "Spire," made from a wafer provided by Spire,³ shows a ΔV_{oc} of 40 mV and ΔI_{sc} of 0.7 mA on stripping. From an analysis of our experience to date, we conclude that somewhat higher values of both V_{oc} and I_{sc} can be gained by further optimization of these cells to achieve an efficiency of 12% before application of an AR coating. A good two-layer AR coating should then result in cells with $\eta = 18\%$ AM1, which we believe is about the best that can be achieved with our present processing facilities. More important than the attainment of the highest possible efficiency is the demonstration that low-cost, nonmass-analyzed implantation can yield cells with excellent efficiencies.

ANTIREFLECTION COATINGS FOR PLANAR SILICON SOLAR CELLS¹

G. E. Jellison, Jr. R. F. Wood

A computer code has been written to calculate the effect of antireflection (AR) coatings on silicon solar cells. The code calculates the collected current for any one of four hypothetical solar cells with different quantum efficiency spectra. The cells are assumed to be illuminated with any one of four different illumination spectra. Component films of two-layer coatings were simulated by the refractive index versus wavelength (dispersion relations) of 12 different films found in the literature. In addition, the existence of a thin oxide layer between the AR coating and the solar cell can be incorporated into the calculations to simulate the behavior of a passivation layer.

The computer code is capable of optimizing the thickness of each of the individual layers to obtain the largest short circuit current, if the solar cell quantum efficiency spectrum, the illumination spectrum, and the constituents of AR coating are given. In determining the optimum thicknesses, the code also calculates the curvatures of the current versus the thicknesses of the individual layers, which shows the decrease in the short circuit current if an AR coating is not fabricated with optimum thicknesses.

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2. M. B. Spitzer, S. P. Tobin, and C. J. Keavney, *IEEE Trans. Electron Devices*, ED-31, 546 (1984).

3. We wish to thank M. B. Spitzer for providing us with the wafers from which these cells were made. The efficiency of the "Spire" cell shown in Table 3.4 is not representative of the highest efficiency Spire cells.

In evaluating the quality of an AR coating, we found that the most useful quantity, from a theoretical point of view, was the ratio X of the collected current with the given AR coating to the collected current with a perfect AR coating (defined as one that gives zero reflectance over the entire solar spectrum). This quantity differs from the conventional improvement ratio, which is defined as the ratio of the collected current with the given AR coating to the collected current with no AR coating, denoted as X_1 . The quantity X_1 is readily accessible experimentally, but gives no indication of how much further improvement is possible with a better AR coating, since the maximum value of X_1 is dependent upon the quantum efficiency spectrum and the illumination spectrum. On the other hand, X is not readily accessible experimentally, but has an upper bound of 1, giving a very good indication of how much further improvement is possible.

Several general conclusions can be drawn from the results of the computer calculations.

(1) In evaluating AR coatings of a solar cell, care must be taken about the quality of the solar cell being examined. A poor solar cell can give a higher value of either X or X_1 than can a good solar cell, although the total collected current will be less. The optimum thickness τ for obtaining the best possible collection current will also be dependent upon the quality of the solar cell.

(2) In a similar manner, the illumination spectrum used to test the solar cell must be taken into account. In particular, a peaked source, such as an ELM lamp, can lead to higher values of X or X_1 from a particular AR coating than will a solar simulator closely matched to the solar spectrum. Minor differences can also be observed in the optimum thickness of layers of an AR coating between AMO and AM1.5 sunlight, indicating that the design of the AR coating should take into account whether the solar cell is intended for space or terrestrial use.

(3) In general, optimized two-layer coatings give higher collectible currents than single-layer coatings; in addition, these coatings are less sensitive to errors in the thicknesses of the two films than are similar single-layer coatings made of the same material as the inner film.

(4) Several materials are suitable for AR coatings. Particularly, Ta_2O_5 , TiO_2 , and Si_3N_4 were found to be suitable for single-layer coatings, while two-layer coatings consisting of SiO_2 or MgF_2 as the outer layer and Ta_2O_5 , TiO_2 , or ZnS as the inner layer were found to give high values of X or X_1 . Of course, the suitability of a material as an AR coating depends critically on the optical properties of the material itself, which often varies according to preparation procedures.

(5) An interlying passivation layer adversely affects the optical impedance match between the AR coating and the solar cell. However, if this layer is thin (<10 nm), the resulting decrease in collectible current is not severe. For thicker passivation layers, the collectible current decreases, and the sensitivity to errors in the thickness of the layers becomes greater; this is

particularly true for cells with double-layer AR coatings.

(6) The angle of incidence of the illuminating light has a very small effect on the performance of the AR coating, if the angle is <20 deg.

(7) Three-layer coatings give an improvement over two-layer coatings so small that the extra complication of adding the third layer is probably not worth the effort.

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INTRINSIC AND EXTRINSIC SURFACE PASSIVATION OF LASER-PROCESSED SILICON SOLAR CELLS

R. F. Wood   R. D. Westbrook

It is useful to contrast two approaches to the problem of passivating the surfaces of a silicon solar cell and to list the advantages and disadvantages of the two approaches.

Intrinsic Passivation. This approach relies on the formation of strong built-in electrical fields to keep minority carriers away from the surfaces where the recombination rate is high. Surface states, caused by dangling bonds and other effects, are still present, but the minority carriers do not see them. Pulsed laser annealing of glow-discharge-implanted wafers² has proved particularly useful in forming the p^+nn^+ and n^+pp^+ structures needed for this approach to passivation. Moreover, with glow-discharge ion implantation, shallow implants can be obtained, and subsequent laser annealing results in very high dopant concentrations that may even exceed the solubility limit.

Extrinsic Passivation. In this approach, surface passivation is obtained by thermal growth of an oxide or other type of layer that compensates or eliminates the surface states so that the surface recombination velocity is greatly reduced.³ Dopants may be introduced into the wafers either by conventional thermal diffusion from an external source or by ion implantation followed by thermal annealing. The thermal treatments required in either case are well suited to the growth of the passivating oxide layers.

The advantages of intrinsic passivation via laser annealing are that the processing is simple and the temperature of the wafer is never raised above ambient, except within the first ~ 10 μ m of the annealed surface, and even there for periods of only microseconds. The disadvantages are those to be expected from heavy doping (e.g., bandgap narrowing, low mobility, etc.). The disadvantages of extrinsic passivation are the complexity of the processing and the high temperatures ($>800^\circ\text{C}$) to which the entire wafer is subjected. The principal advantage of extrinsic passivation is that heavy doping effects can be avoided while still obtaining the required reduction in the surface recombination velocity.

The highest efficiencies reported⁴ to date for intrinsically passivated single-crystal Si cells are $\sim 16.5\%$ AM1, but with optimization of the processing and of the antireflection (AR)

coatings this figure can probably be raised to ~18%, as we demonstrate here. The highest efficiencies reported⁵ for extrinsically passivated cells have approached 19% AM1, and there is optimism that this figure can be pushed to 20% with processing and cell structure modifications designed to improve the response of the base region.

Table 3.5 shows the results for several laser-processed cells with a $p^{+}nn^{+}$ structure made by glow-discharge implantation of BF_3 to form the emitter and PH_3/H_2 to prepare the back-surface region for good ohmic contact. Although the cells are not yet fully optimized, the efficiencies η are quite respectable, and the short circuit currents I_{sc} are very good; the fill factors (FF) are somewhat low. With a good two-layer AR coating on the cells, the efficiencies would be ~17.5% AM1. The high values of V_{oc} , the open circuit voltage, and the low value of the sheet resistivity ρ_s illustrate the intrinsic surface passivation effect due to high dopant concentration in the emitter region. The highest values of V_{oc} for furnace-annealed cells without oxide passivation that have been obtained with this material are slightly less than 600 mV.

Table 3.6 shows some preliminary results of attempts to passivate laser-annealed cells by thermal oxide growth. That some processing

Table 3.5. Intrinsically passivated laser-annealed cells. All of these cells were taken from the same 0.3 Ω -cm n-type wafer.

Cell	V_{oc} (mV)	I_{sc} (mA/cm ²)	FF	η	ρ_s ($\Omega/\square$)
1	612	23.7	77.7	11.5	30
2	613	23.7	78.4	11.6	
3	613	23.7	78.3	11.6	
4	608	23.7	71.4	10.5	
5	612	23.7	77.6	11.5	
6	614	23.7	78.5	11.6	

Table 3.6. Laser-annealed, oxide-passivated cells. The high V_{oc} and loss of ~40 mV on cells 3^a and 11^a show that the oxide passivation is very effective.

Cell	V_{oc} (mV)	I_{sc} (mA)	FF	η	ρ_s ($\Omega/\square$)
2	624	22.7	77.7	11.2	95
3	625	23.0	77.2	11.3	
7	624	22.8	77.3	11.2	
11	624	22.9	76.9	11.2	
12	624	22.8	77.4	11.2	
3 ^a	584	22.4	78.5	10.5	
11 ^a	584	22.4	78.1	10.5	

^aAfter stripping of the oxide layer.

problem arose with these cells is indicated by the low FF and the currents. Nevertheless, on stripping of the oxide layers on cells 3 and 11, V_{oc} dropped by ~40 mV. We conclude, therefore, that there is nothing inherently incompatible with oxide passivation and laser processing of solar cells, but low-temperature techniques for growth of effective oxide layers will be required if all of the advantages of laser processing are to be retained.

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4. TRANSPORT PROPERTIES OF SOLIDS

This chapter contains reports on studies of a variety of transport properties of various solids.

Metal-solid electrolyte interfaces generally exhibit an impedance to current flow that is related to the roughness of the interface. Different models have been developed to account for the experimental results, most recently fractal models of the interface. Contributions in this chapter, and also in Chapter 1, report the recent work on this subject. The enhancement in ionic conductivity by incorporating submicron particles of insulating material into the ionic conductor has been studied both experimentally and theoretically. An interesting correlation between deformation of the composite and its conductivity is shown.

The mechanism by which zinc oxide ceramics act as a varistor is under investigation. Phenomenological models successfully explain the varistor response to fast current and voltage pulses in terms of a voltage-dependent barrier resistance and capacitance. Although much progress has been made, some of the physics of this system remains elusive.

In the continuing effort to determine the transport properties of transition-metal carbides, the optical and electrical properties of niobium carbide of several nonstoichiometric compositions are reported. An investigation using x-ray photoelectron spectroscopy has provided clear evidence for defect electronic states in substoichiometric tantalum carbide.

In investigations of superconductors, observations of flux line lattices via small-angle neutron scattering have shown anisotropy in the lattice V_3Si . Also, flux line pinning by the grain boundary in niobium bicrystals has been analyzed. Some results from studies of the preparation of thin films of transition-metal nitrides, their superconductive properties and the change in these properties resulting from introduction of defects by irradiation, are also reported.

INTERFACES

MODEL FOR THE INTERFACIAL IMPEDANCE BETWEEN A SOLID ELECTROLYTE AND A BLOCKING METAL ELECTRODE¹

J. C. Wang   J. B. Bates

It is quite common to determine the conductivity of an ionic material by measuring its impedance when sandwiched between a pair of blocking electrodes. In doing so, it is inevitable that the measured impedance includes the

contribution from the interfaces between the electrolyte and the electrodes. An accurate determination of the conductivity of the material, therefore, sometimes depends crucially on a suitable model of the interfacial impedance.

In practice,² it is often found that in order to describe the experimental results satisfactorily, the interfacial impedance is in the form

$$Z(\omega) = A(j\omega)^{-n} , \quad (1)$$

where $j = \sqrt{-1}$, $1/2 < n < 1$, and A is independent of frequency ω . This fractional-power-law

dependence on ω is sometimes referred to as a constant-phase-angle element³ or a non-Debye capacitor.^{4,5} The complex impedance graph of Eq. (1), $-\text{Imag}(Z)$ vs $\text{Real}(Z)$, is a straight line forming an angle of $\pi\alpha/2$ with the real axis. The purpose of this work is to demonstrate that pores on the electrodes may produce such an impedance and that the value of α can be related to the shape of the pores.

We adopt the model developed by de Levie.^{6,7} For a blocking electrode, the impedance of a pore can be approximated with that of a transmission line: The resistance per unit length, $r(x)$, is determined by the resistivity of the electrolyte in the pore and the pore cross section, and the corresponding capacitance per unit length $c(x)$ is determined by the double-layer capacitance at the electrolyte-electrode interface in the pore and the interfacial area.

Scarama⁸ found that a semi-infinite rc ladder network and a distributed rc transmission line can give the impedance shown by Eq. (1). We have generalized his results to provide a systematic way to find other rc ladder networks and transmission lines that have the same impedance. We found that a horn-shaped pore with radius given by

$$R = a(1+bx)^{-\alpha} \quad (2)$$

can give an impedance very close to the form described by Eq. (1) over a wide frequency range. In Eq. (2), a is the radius at the pore opening ($x=0$), and α and b are two parameters that define the shape of the pore. Pores described by Eq. (2) with several values of α are put side by side in Fig. 4.1 to show schemat-

Fig. 4.1. Schematic diagrams of an interface full of horn-shaped pores with radius $R(x)$. The pores filled with electrolyte are represented by the shaded areas. An interface with greater value of α is taken to be smoother.

ically the texture of the surface formed. Since the interface becomes a plane when $\alpha \rightarrow \infty$, surfaces with pores of greater α are taken to be smoother.

For an interface full of horn-shaped pores with a given α , the total impedance can be calculated by dividing the impedance of one pore by the number of pores. The impedance graphs corresponding to the cases of Fig. 4.1 are shown in Fig. 4.2. It can be seen that the smoother the surface, the greater the phase angle. This trend is qualitatively consistent with our experimental observations.² Notice that the impedance graphs for the surfaces shown in Fig. 4.1 lie between that of a flat surface (ideal capacitor, $\alpha=1$) and that of a surface full of long channels ($\alpha=1/2$).

It is interesting to see what happens if $r(x)$ and $c(x)$ of a pore are disordered. We have studied the case in which $r(x)$ and $c(x)$ are first specified by Eq. (2) and then are allowed to fluctuate about these values by $\pm 20\%$ randomly

Fig. 4.2. The impedance graphs of interfaces full of pores with shapes shown in Fig. 4.1. Each pore has a radius of $1\text{ }\mu\text{m}$ at the opening and a depth of $10\text{ }\mu\text{m}$. The sample is assumed to have a cross section of 5 mm^2 and a resistivity of $3 \times 10^{-4}\text{ ohm-cm}$. The double layer capacitance per unit area of the electrolyte-metal interface in the pore is assumed to be $44.3\text{ }\mu\text{F}$. The figure shows that the smoother the interface, the greater the slope of the impedance graph.

at all x . The resultant impedance of the transmission line can still be described by Eq. (1) quite well with the same value of n . This implies that the smoothness of the interface inside a pore is not a crucial requirement for the existence of the impedance described by Eq. (1).

The impedance of an interface containing many pores can be calculated by putting the impedance of the individual pores in parallel. If each pore is assumed to have an impedance given by Eq. (1) and the various pores are described by a distribution in n , then it can be demonstrated numerically that the resultant impedance can still be described roughly by Eq. (1) with some effective value of n , $\bar{n}$, provided the distribution is not too broad.

When an interface has an impedance of the form described by Eq. (1), it is often found² that the value of n decreases with T . This result can be explained qualitatively with the present pore model. It can be demonstrated that when the resistivity of the electrolyte in a pore is changed with T through a thermally activated process, the change of the pore impedance depends on the value of n :

$$Z(\omega, T)/Z(\omega, \infty) = \exp[(1-n)E_a/kT] \quad (3)$$

where $Z(\omega, \infty)$ is the impedance at $T = \infty$ and E_a is the activation energy for conduction. For an interface containing many pores with different values of n , the effective value for the interface, $\bar{n}$, will, therefore, also change with T . The value of $\bar{n}$ is mainly determined by pores with greater n at low T because their impedances are smaller [Eq. (3)]. At high T , the dominance by these pores is reduced. Therefore, the value of $\bar{n}$ decreases with T .

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IMPEDANCE OF METAL-SOLID ELECTROLYTE INTERFACES¹

J. B. Bates   J. C. Wang
Y. T. Chu

The impedance of the interface between a solid electrolyte and a metal contact at which

the mobile ions accumulate (blocking contact) can be represented by the function $Z_1(\omega) = A(j\omega)^{-n}$ over many decades of frequency ω , where $0 < n < 1$, $j = \sqrt{-1}$, and A is a constant. (If the interface behaved as a perfect capacitor, then $n = 1$ and $A = 1/C$.) With $D = A \sin(n\pi/2)$, Z_1 can be written as

$$Z_1 = \frac{D}{\omega^n} \cot(n\pi/2) - j \frac{D}{\omega^n} \quad (1)$$

The total impedance of the electrolyte bounded by two metal contacts is given by $Z = R_b + 2Z_1$, where R_b is the dc electrolyte resistance. The first term of Eq. (1) contributes a frequency-dependent real term to the total impedance, a characteristic of the circuit element represented by Z_1 , which is often referred to as a constant phase angle (CPA) element. The objective of this study was to relate the parameter n to the microstructure of the interface.

Platinum or silver contacts (~5000 Å thick) were sputtered onto polished or as-cut faces of single-crystal and polycrystalline specimens of β - and β' -alumina. The sizes of surface features were estimated from electron micrographs of the uncoated faces. Impedance measurements were made from 0.1 Hz to 10 MHz at temperatures from -134 to 450°C. Examples of the impedance data are shown in Fig. 4.3. The frequency dependence of $\text{Re}(Z)$ is evident in Fig. 4.3 and is proportional to ω^{-n} ($n=0.81$) over about three decades in frequency. The downturn in $\text{Re}(Z)$ near 0.5 Hz

Fig. 4.3. Example of the two-point impedance of the cell Pt/Ag β -alumina/Pt. The solid lines through the data points are the real and imaginary components of the CPA impedance with $D = 8 \times 10^6$ and $n = 0.81$. The inset is the graph of $-Im(Z)$ vs $Re(Z)$.

is caused by small errors in the measured phase angle which, for values approaching 90° , introduce large errors in $\text{Re}(Z)$. At high frequencies, $\text{Re}(Z)$ approaches a constant value determined by the dc resistance of the electrolyte. On the other hand, $-\text{Im}(Z)$ follows the ω^{-n} dependence over the full frequency range of this example, which spans more than five decades.

The results of the impedance measurements show that there is a correlation between the frequency exponent n and the range of feature sizes at the metal-electrolyte interfaces: n ranged from 0.98 when the surface features² were 0.2 μm or smaller to 0.78 when the features were about 1 to 10 μm . The frequency exponent also changed with temperature above 25°C to ~ 0.6 at 400°C .

Two models have been examined to account for the dependence of n on surface texture and temperature. (1) A Cantor bar was used³ to represent the rough interface between an electrolyte and a metal electrode. The electrical analogue of this interface consists of a branching resistor network, with each resistor R connected to ground by a capacitor C . For low frequencies, $\omega \ll 1/RC$, and in the limit of an infinite number of stages, the impedance of the analogue circuit is

$$Z(\omega) = kR(j\omega RC)^{-n} \quad (2)$$

where k is a scale factor. The frequency exponent is directly related to the fractal dimension $\bar{d}$ of the Cantor bar: $n = 1 - \bar{d}$. The relationship of $\bar{d}$, and therefore n , to the roughness of the interface predicted by this model agrees qualitatively with the experimental results. (2) A rough interface was represented by pores on the surface of the electrolyte. The impedance of a pore was based on a transmission line with distributed resistance and capacitance, and for horn-shaped pores, the impedance given in Eq. (2) was obtained. The frequency exponent was found to depend on the shape of the pore in a manner consistent with the experimental results. Thus both the Cantor bar and pore models of a metal-electrolyte interface show that the frequency exponent n of Eq. (1) is directly related to the microstructure of the interface. Also, as a consequence of Eq. (2) and the fact that the electrolyte resistance R is temperature dependent, both models correctly predict the observed decrease of n with increasing temperatures above 25°C (see reference 4).

STRUCTURES OF COPPER LEAVES GROWN BY ELECTRODEPOSITION

Y. T. Chu   J. B. Bates
W. T. Stribling¹

A wide variety of nonequilibrium growth and aggregation models have attracted much attention in recent years following the simple diffusion limited aggregation (DLA) model proposed by Witten and Sander.² In the DLA model a two-dimensional cluster is grown from a seed by addition of one particle at a time released far from the cluster along a random walk trajectory. The DLA model leads to a cluster having a self-similar ramified structure with a fractal dimension $\bar{d} = 1.66$ in two-dimensional Euclidean space.

We have found that "two-dimensional" copper leaves grown by electrodeposition have a fractal structure similar to the DLA clusters. (In this case, the "particles" are Cu^{2+} ions that are reduced at the growing interface.) These leaves were grown at 25°C on a glass table covered with a 1-mm thick film of 0.8 M CuSO_4 contained in a larger reservoir of the solution. A copper wire ring immersed in the solution below the glass table was the anode, and the cathode was a polished pencil lead which just touched the surface of the solution. When a dc voltage (6-9 V) was applied between the electrodes, the copper leaf grew along the top of the glass table from the tip of the cathode.

In order to measure the fractal dimension of the copper leaves, a computer connected to a television camera was used to digitize shadows of the leaves with a resolution of 512 by 512 pixels. The digitized data stored on a magnetic tape were used to reconstruct the leaves and analyze their properties. The fractal dimension of the copper leaves was determined from the relation: $N \sim R^{\bar{d}}$, where R is the radius of a circle measured from the geometrical center of the copper leaf images and N is the total number of pixels within the circle. The fractal dimension, taken as the slope of the graph of $\log(N)$ vs $\log(R)$, was 1.67, 1.63, 1.62, and 1.57 for the copper leaves grown at 6, 7, 8, and 9 volts, respectively. The reason that the fractal dimension of the leaves grown at higher voltages is slightly less than the predicted value (1.66) of the DLA model could be due to the fact these leaves had much fine structure which was below the resolution limit of the camera.

During the copper electrodeposition experiments, occasionally a paper-thin layer composed of many fine copper particles surrounded by a fine metallic copper wire grew at a very high rate at the air solution interface. The shapes of the thin layers were very similar to the snowflake-like patterns obtained in a modified DLA model proposed by Vicsek.³ In this model, the sticking probability of a particle depends on the local curvature of the interface, and the position of a particle added to the growing interface is relaxed to a site with the highest number of occupied nearest neighbors. This model thus simulates the Gibbs-Thomson boundary condition for the solidification interface of an undercooled liquid. It applies to our experiments because the electric field in the solution

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satisfies the Laplace equation, and the strength of the field depends on the local curvature of the interface. Moreover, it is logical that copper particles added to the boundary relax to sites with the largest number of nearest neighbors, because these sites have the lowest potential energy.

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CORROSION OF Na β - AND Na δ -ALUMINA IN CO₂-H₂O¹

J. B. Bates R. L. Anderson²

It was shown in a recent study³ that Na β -alumina reacts with H₂O and CO₂ at 25°C resulting in the formation of a surface layer of NaHCO₃ at high CO₂ pressures or a surface layer of hydrated Na₂CO₃ at low CO₂ pressures. The following reactions were suggested:

and

Both of these reactions involve the replacement of Na⁺ ions by H₃O⁺ ions in the surface region of β -alumina accompanied by the formation of a crust of bicarbonate or carbonate on the specimen. The bicarbonate and hydrated carbonate were identified from infrared reflectance measurements after treatment of polycrystalline specimens in H₂O-saturated CO₂ and in H₂O-saturated air, respectively. After several days of exposure to H₂O-saturated CO₂, it was estimated that the bicarbonate layer was on the order of 20 to 50 μm thick. A further investigation of the corrosion of Na β - and Na δ -alumina as revealed through a series of micrographs has been made as a function of time of exposure to H₂O-CO₂.

Freshly prepared surfaces of single-crystal and polycrystalline specimens of Na β - and Na δ -alumina were examined in a scanning electron microscope before and after treatment in a flowing stream of H₂O-saturated CO₂ (P_{CO₂} = 10⁵ Pa, P_{H₂O} = 3 kPa) and H₂O-saturated air (P_{CO₂} = 33 Pa) at 25°C for periods from one day to several weeks. Examples of micrographs made before and after exposure of a single crystal of Na β -alumina to H₂O-saturated CO₂ are shown in Fig. 4.4. After 22 h of treatment, formations of NaHCO₃ ranging in sizes from ~10 to ~1 μm were distributed over the surface. The larger formations had a dendritic-like structure, and some of these continued to grow with increasing

(a)

(b)

(c)

Fig. 4.4. Electron micrographs showing growth of NaHCO₃ on a polished face normal to the conduction layers of a single crystal of Na β -alumina after exposure to H₂O-saturated CO₂ for (a) 0 h (1000X), (b) 72 h (500X), (c) 72 h (250X), — = 10 μm at 1000X.

exposure. After 72 h the dendritic structures were as large as 40 to 50 μm across and on the order of 10 μm thick. On other regions of the surface, film growth was evident, and large bubbles were observed on some sections of the film. As can be seen in Fig. 4.4(c), some of the NaHCO_3 formed ridges parallel to the conduction layers (cleavage planes). Underneath these ridges are small cracks along which the crystal tends to cleave. After 8 days of exposure to H_2O -saturated CO_2 , much of the surface was covered by a dense dendritic growth of NaHCO_3 about 15 to 20 μm thick.

The same kind of dendritic formations of NaHCO_3 found on single crystals of $\text{Na}\beta$ -alumina also were observed on the surfaces of polycrystalline specimens. In addition, needle-shaped formations were seen on some specimens. These are similar to the structures observed by Singh⁴ on polycrystalline $\text{Na}\beta$ -alumina and attributed to an unidentified Na_2O -rich phase.

The growth of the various formations on the single-crystal and polycrystalline specimen is believed to result from crystallization of the bicarbonate through surface and/or vapor transport after it has been produced in the reaction, possibly due to the moist environment of the treatment chamber. At low surface coverage, these processes likely have no effect on the kinetics of the reaction which produces the bicarbonate.

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THE DISPERSION OF BULK POLARITONS IN $\alpha\text{-Al}_2\text{O}_3$ MEASURED BY INFRARED REFLECTION¹

Y. T. Chu J. B. Bates

Polaritons result from the strong coupling of an electromagnetic wave with an elementary excitation of a crystal. The existence of polaritons was first demonstrated experimentally by Henry and Hopfield² in GaP by means of forward and near-forward Raman scattering. Using the Raman scattering technique, one can determine the polariton dispersion curves by varying the angle between the direction of incident beam and the direction of the scattered beam in the crystal.

The polariton dispersion curves can also be measured by infrared reflection due to the fact that polaritons are already inherent in the solution of Maxwell's equations for a crystal characterized by its dielectric function. If one neglects damping in the expression of the dielectric function, the calculated spectrum exhibits high reflectivity regions ($R=1$) bounded by steeply rising and falling edges. The frequencies corresponding to these edges depend on the values of the wave vector. Analysis shows that these edges are close to the frequencies of

the polariton modes. Since the edges of the measured high reflectivity bands ($R=1$) are smooth, the inflection points of these bands are taken as the frequencies of the bulk polaritons. Thus the polariton dispersion curves can be determined by measuring the inflection points obtained for different wave vectors.

We consider a transverse magnetic (TM) polarized wave incident upon a uniaxial crystal. The orientation of the c -axis is arranged to be parallel to one of the Cartesian coordinates. Hence, the dielectric tensor for a uniaxial crystal is in diagonal form, and the dielectric function is characterized by the principal values ϵ_1 and ϵ_x . The reflectivity R can be written as follows³:

$$R(\theta, \omega) =$$

$$\left| \frac{\epsilon_x^{1/2} \epsilon_z^{1/2} \frac{\omega}{c} \cos \theta - N \left(\frac{\omega^2}{c^2} \epsilon_z - k_x^2 \right)^{1/2}}{\epsilon_x^{1/2} \epsilon_z^{1/2} \frac{\omega}{c} \cos \theta + N \left(\frac{\omega^2}{c^2} \epsilon_z - k_x^2 \right)^{1/2}} \right|^2, \quad (1)$$

where θ is the incident angle, ω is the angular frequency, c is the velocity of light in vacuum, N is the refractive index of the medium outside the crystal, ϵ_x and ϵ_z are the dielectric functions of the crystal, and k_x is the wave vector along the x -direction. The latter is determined by

$$k_x = \frac{\omega}{c} N \sin \theta. \quad (2)$$

If one neglects damping, the factor $\frac{\omega}{c} \sqrt{\epsilon_z}$ in Eq. (1) is just the wave vector k_0 of the transverse bulk polaritons propagating along the x -axis with the lattice displacement parallel to the z -axis. Thus Eq. (1) can be transformed into:

$$R(\theta, \omega) = \left| \frac{\epsilon_x^{1/2} k_0 \cos \theta - N (k_0^2 - k_x^2)^{1/2}}{\epsilon_x^{1/2} k_0 \cos \theta + N (k_0^2 - k_x^2)^{1/2}} \right|^2, \quad (3)$$

From the above equation, total reflection ($R=1$) occurs when either one of the terms in the numerator of this equation is imaginary or equal to zero. Thus the regions of total reflection can be determined, if the following conditions are satisfied:

$$\text{For ciz: I. } \epsilon_1 < 0, \quad (4a)$$

$$\text{II. } \epsilon_1 > 0, \quad k_0^2 - k_x^2 < 0; \quad (4b)$$

For ciz or cix:

$$\text{I. } \epsilon_z < 0, \quad \epsilon_x < 0, \quad (5a)$$

$$\text{II. } \epsilon_z > 0, \quad \epsilon_x < 0, \quad k_0^2 - k_x^2 > 0, \quad (5b)$$

$$\text{III. } \epsilon_z > 0, \quad \epsilon_x > 0, \quad k_0^2 - k_x^2 < 0. \quad (5c)$$

The frequencies corresponding to the edges of high-reflectivity regions determined from conditions (4a) and (5a) are the TO or LO mode frequencies, and they are independent of the wave vector. On the other hand, the frequencies corresponding to those edges determined from conditions (4b), (5b), and (5c) with $k_y^2 - k_x^2 = 0$ are the polariton mode frequencies, and these frequencies depend on the wave vector.

Here we present the experimental and theoretical results for the case of ciz only, since the cases of cix and cly can be treated in the same way. For the case of ciz , we have $\epsilon_2 = \epsilon_1$. Since there are two modes¹ for E1c in single-crystal α - Al_2O_3 , there are three polariton dispersion curves. In Fig. 4.5 the solid curves are the calculated polariton dispersion curves, and the areas marked by the vertical lines are the high-reflectivity regions determined from conditions (5a)–(5c). The experimental spectra for various values of λ (defined as $\frac{\epsilon_2}{\epsilon_1} k_y$ or $\frac{\epsilon_2}{\epsilon_1} k_x$) are plotted in Fig. 4.6. Note that the spectra with $K > 1$ were measured by direct contact of the crystal to the case of the KRS-5 prism (refractive index = 2.35). The closed circles are the inflection points on the boundaries of the high reflectivity bands, and they correspond to the closed circles in Fig. 4.5.

Although the polariton dispersion curves can easily be obtained by infrared reflection, a few shortcomings exist in this method. In order to measure a large portion of the dispersion curves, a prism with a high refractive index is required. Note that the dispersion curve in the low-frequency region shown in Fig. 4.5 cannot be measured, because the values of the wave vector are too large to be achieved with the available prism. Moreover, some measured high-reflectivity bands are too weak to be able to locate the inflection points for small values of K .

Fig. 4.5. Bulk polariton dispersion curves of Al_2O_3 (solid lines) for the case ciz . The positions of the TO and LO mode frequencies are indicated by the dashed lines. The areas marked by the vertical lines are the high-reflectivity regions. The closed circles and crosses are the experimental results determined from the inflection points on the edges of the high-reflectivity bands in the measured spectra.

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OPTICAL MEASUREMENT OF THIN AMORPHOUS Al_2O_3 AND γ - Al_2O_3 ON α - Al_2O_3 SINGLE CRYSTALS¹

Y. T. Chu   J. B. Bates
C. W. White   G. C. Parlow²

The optical dielectric functions for thin amorphous Al_2O_3 and γ - Al_2O_3 films have been determined by infrared reflection. The amorphous Al_2O_3 film was prepared by ion implantation of an α - Al_2O_3 single crystal, and the γ - Al_2O_3 film was obtained by thermally annealing the amorphous Al_2O_3 film.

A stoichiometric implant (2 parts Al^+ and 3 parts O^+) with the substrate held at 77 K was used to produce an amorphous layer free of any impurities on the (0001) face of a single-crystal α - Al_2O_3 substrate. The ion energies

used (90 keV for Al and 55 keV for O) were chosen to give a projected range of 800 Å for each species. The doses were $4 \times 10^{16}/cm^2$ for Al and $6 \times 10^{16}/cm^2$ for O. Both Rutherford backscattering (RBS) ion channeling and transmission electron microscopy were used to verify that following implantation the near-surface region was amorphous to a depth of 1500 Å.

The measured infrared reflectivity spectra with transverse electric (TE) polarization and 30° incident angle of the amorphous Al_2O_3/α - Al_2O_3 sample and an α - Al_2O_3 single crystal are plotted as solid and dashed curves, respectively, in Fig. 4.7. It is seen that absorption by the

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Fig. 4.6. Reflectivity spectra measured at $K = 0.407, 0.530,$ and 1.175 for ciz . The closed circles (corresponding to those in Fig. 4.5) are the inflection points on the edges of the high reflectivity bands.

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Fig. 4.7. Measured reflectivity spectra with TE polarization and 30° incident angle on the amorphous $Al_2O_3/\alpha-Al_2O_3$ sample (solid curve) and $\alpha-Al_2O_3$ single crystal (dashed curve). The open circles are the calculated reflectivity for the amorphous $Al_2O_3/\alpha-Al_2O_3$ sample.

amorphous layer reduces the reflectivity in the region between 600 and 900 cm^{-1} . We found that the change in reflectivity could be accounted for by assuming a single classical oscillator model for the dielectric function of the amorphous layer:

$$\epsilon(\omega) = \epsilon_\infty + \frac{S\omega_t^2}{\omega_t^2 - \omega^2 - i\omega\gamma} \quad (1)$$

where ϵ_∞ is the limiting value of ϵ at high frequency; ω_t , S , and γ are the transverse optical mode frequency, strength, and damping of a classical oscillator, respectively. With the known dielectric function for an $\alpha-Al_2O_3$ single crystal³ and the Fresnel reflectivity formula for a three-layer system,⁴ we were able to fit by least-squares⁵ the calculated reflectivity to the experimental reflectivity by adjusting the values of the parameters involved in Eq. (1). The best fit values are $\epsilon_\infty = 2.8$, $\omega_t = 706\text{ cm}^{-1}$, $S = 2.21$, and $\gamma/\omega_t = 0.322$. The calculated reflectivity is plotted as open circles in Fig. 4.7. A few results from our analysis are worth noting. (1) The LO mode frequency $\omega_L = 944\text{ cm}^{-1}$ as determined from $\epsilon(\omega_L) = 0$ with damping neglected in Eq. (1). Bruesch et al.⁶ reported that $\omega_t = 690\text{ cm}^{-1}$ and $\omega_L = 950\text{ cm}^{-1}$ were obtained by infrared transmission measurements on a sputtered Al_2O_3 film (thickness = $5100\text{ \AA}$) on a $Si(111)$ wafer. (2) The index of refraction for the amorphous Al_2O_3 film in the visible region given by $N = \sqrt{\epsilon_\infty} = 1.67$ is in good agreement with the results obtained from measurements on an anodic aluminum oxide film ($1.66 < N < 1.68$).⁷

The amorphous Al_2O_3 layer annealed at $965^\circ C$ for 90 min most likely transformed to $\gamma-Al_2O_3$.⁶ The measured reflectivity of the annealed sample is plotted as the solid curve in Fig. 4.8. It is clear that the reflectivity is quite different from that for $\alpha-Al_2O_3$ (dashed curve) in the regions $450\text{--}550\text{ cm}^{-1}$ and $700\text{--}900\text{ cm}^{-1}$. An attempt to determine the optical dielectric function for $\gamma-Al_2O_3$ has been made by assuming that there are

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Fig. 4.8. Measured reflectivity spectra with TE polarization and 30° incident angle on the $\gamma-Al_2O_3/\alpha-Al_2O_3$ sample (solid curve) and $\alpha-Al_2O_3$ single crystal (dashed curve). The open circles are the calculated reflectivity for the $\gamma-Al_2O_3/\alpha-Al_2O_3$ sample.

three classical oscillators involved in the dielectric function. The best-fit values are $\epsilon_\infty = 2.9$, $\omega_{c1} = 515 \text{ cm}^{-1}$, $S_1 = 1.22$, $\gamma_1/\omega_{c1} = 0.052$, $\omega_{c2} = 744 \text{ cm}^{-1}$, $S_2 = 0.32$, $\gamma_2/\omega_{c2} = 0.0797$, $\omega_{c3} = 808 \text{ cm}^{-1}$, $S_3 = 0.147$, and $\gamma_3/\omega_{c3} = 0.0522$. The calculated reflectivity is plotted as open circles in Fig. 4.8. The calculated LO mode frequencies are $\omega_{L1} = 584 \text{ cm}^{-1}$, $\omega_{L2} = 774 \text{ cm}^{-1}$, and $\omega_{L3} = 851 \text{ cm}^{-1}$. These TO and LO mode frequencies are in good agreement with those obtained from a thin $\gamma\text{-Al}_2\text{O}_3$ film that was prepared by annealing a sputtered Al_2O_3 film at 1000°C .⁶

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DIELECTRIC RESPONSE OF STABILIZED ZIRCONIA

J. B. Bates K. A. Wegenke¹

The cubic phase of zirconia (ZrO_2) can be stabilized at room temperature by replacing ~10 to 30% of the zirconium ions with aliovalent cations such as Y^{3+} or Mg^{2+} . The charge imbalance created by the impurity ions is compensated by the formation of oxygen vacancies (~4 to 17% oxygen sites vacant), and the resulting defect structure is a good O^{2-} ion conductor at elevated temperatures. For example, the mobility of O^{2-} is $4 \times 10^{-7} \text{ cm}^2/\text{Vs}$ at 500°C for $0.72(\text{ZrO}_2) \cdot 0.14(\text{Y}_2\text{O}_3)$.

As a consequence of the motion of O^{2-} ions, the impedance Z of single crystals of zirconia in the frequency range dominated by the bulk response (i.e., above the range dominated by electrode effects) deviates markedly from that of a simple parallel RC circuit. An example from a series of measurements on a 1-mm-thick crystal with silver electrodes (17 cm^2) is shown in Fig. 4.9. The sharp increase in $\text{Im}(Z)$ below $f = 1 \text{ Hz}$ is due to the metal contact,² and the change in slope of $\text{Re}(Z)$ and $\text{Im}(Z)$ above $\sim 3 \times 10^5 \text{ Hz}$ is due to a stray capacitance in the measuring circuitry. The solid lines through the data points were calculated from the model impedance discussed in the text. The impedance below 10 Hz is dominated by the metal-electrolyte interface while the impedance at higher frequencies is dominated by the bulk response.

$$Z(\omega) = \left[\frac{1}{R_b} + B(j\omega)^n \right]^{-1} + Z_i \quad (1)$$

where R_b is the bulk resistance, R is a constant, $j = \sqrt{-1}$, n is characteristic frequency exponent ($n = 0.85$ in this example), and Z_i is the interface impedance of the same functional form discussed elsewhere in this report.² In the special case of an ideal dielectric, $n = 1$ and

Fig. 4.9. Impedance of a single crystal of stabilized cubic zirconia with sputtered silver electrodes. The measurements in (a) and (b) were made with two instruments in order to cover nine decades in frequency. The open circles are the real values of Z , and the open triangles are the negative imaginary values of Z . The solid lines through the data points were calculated from the model impedance discussed in the text. The impedance below 10 Hz is dominated by the metal-electrolyte interface while the impedance at higher frequencies is dominated by the bulk response.

$B = 1/C$, where C is the geometric capacitance of the sample, and the terms inside the brackets in Eq. (1) then represent the admittance of a parallel RC circuit with constant R and constant C .

The frequency-dependent bulk impedance in Eq. (1) can originate from one of two sources:

(1) a frequency-dependent conductivity and/or
(2) a frequency-dependent capacitance. While a distinction between these sources can be made in theory, it has not been possible to distinguish between them experimentally. In either case, a complex bulk capacitance $C_b^*(\omega)$ can be defined, $C_b(\omega) = Y_b(\omega)/j\omega$, where $Y_b(\omega)$ is the bulk admittance: $Y_b(\omega) = Z_b^{-1}(\omega) = \frac{1}{R} + B(j\omega)^n$. The complex dielectric function is then given by

$$\epsilon(\omega) = \frac{d}{A\epsilon_0} C_b^*(\omega) = \epsilon'(\omega) - j\epsilon''(\omega) \quad (2)$$

where d is the sample thickness, A is the area of the electrode, and ϵ_0 is the vacuum permittivity. From the defining relationships for C_b and ϵ ,

$$\epsilon''(\omega) = \frac{1}{E_0\omega} [\sigma_0 + K\omega^n] \quad (3)$$

where σ_0 is the dc conductivity and $K = \frac{dB}{A} \cos \frac{n\pi}{2}$.

The term $\sigma_0 + K\omega^n$ in Eq. (3) is defined as the frequency-dependent conductivity, and the claim has been made³ that the frequency exponent n assumes the values of 0.85 below and 0.64 above a transition frequency, ω_p , based on a graphical presentation of $\epsilon''(\omega)$ data. As shown in Fig 4.9, we find that the $\text{Re}(Z)$ and $\text{Im}(Z)$ can be closely fit by a single frequency exponent with a value $n = 0.87$. The transition frequency ω_p corresponds to the frequency ω_{max} at which $-\text{Im}(Z)$ is a maximum. It can be shown from Eq. (1) that $\omega_{\text{max}}^n = 1/R_b B$. Since $1/R_b$ is thermally activated, $\ln \omega_{\text{max}} = -\frac{E_a}{nkT} + \text{constant}$, where E_a is the activation energy for ionic conduction (≈ 1 eV). The slope of the graph of $\ln \omega_{\text{max}}$ vs $1/T$ from our measurements gives $E_a = 1.14$ eV for $n = 0.87$, which is close to the value we obtained from four-point conductivity measurements. This result supports our analysis of the dielectric response of stabilized zirconia, but there remains the problem of understanding the physics behind the empirical function, $B(j\omega)^n$. It is worth noting that the inverse of this function has also been used to represent the impedance of a metal-solid electrolyte interface,² thus underscoring its apparent universal character.

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MODEL FOR THE COMPOSITION DEPENDENCE OF CONDUCTIVITY OF AN IONIC CONDUCTOR CONTAINING SUBMICRON PARTICLES OF AN INSULATOR¹

J. C. Wang N. J. Dudney

The ionic conductivity of several metal halides such as LiI, AgI, and CuCl can be enhanced by

orders of magnitude by the addition of submicron particles of some insulators such as Al_2O_3 , SiO_2 , and fly ash.^{2,3} Generally, the conductivity of these composite systems increases with the volume fraction f of the insulating particles, goes through a maximum between $f=0.1$ and $f=0.5$, and drops rapidly at higher volume fractions. It is believed that the enhancement is due to the existence of a high-conductivity layer surrounding each particle.

In this paper, we assume the existence of this high-conductivity layer and extract information about its structure by calculating the composition dependence of the total conductivity using a very simple model. We assume that the insulating particles, each with its high-conductivity layer, are arranged on a simple cubic lattice embedded in the conducting material to form a cubic composite sample. (See Fig. 4.10)

To analyze the conduction process, we divide each slice (with thickness d) of the sample into two layers and divide each layer into two regions. In Layer 1 (L1) the current mainly flows in the high-conductivity regions (denoted R1 in Fig. 4.10). In Layer 2 (L2) the current mainly flows from particle to particle in Region 3 (R3). To calculate the total conductivity of the composite system, we put the two resistors corresponding to R1 and R3 in series and two resistors corresponding to R2 and R4 in series. The two resultant resistors are connected in parallel to calculate the total conductivity.

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Fig. 4.10. Schematic diagram showing the arrangement of insulating particles on a simple cubic lattice embedded in a conducting medium. The layer with enhanced conductivity outside each particle is represented by the contours.

It is possible to fit various experimental results with the present model by adjusting the structure of the high-conductivity layer surrounding each particle. The result for lithium iodide containing alumina particles is shown in Fig. 4.11. The dimension of the particles is chosen arbitrarily to be 1000 Å. If the actual size is different from this value by some factor, the conductivity-composition graph shown in Fig. 4.11 is still valid, provided the structure of the enhanced high-conductivity layer is scaled by the same factor.

Fig. 4.11. Conductivity vs volume fraction graphs for LiI containing alumina particles. The calculated curve is shown by the solid line. The experimental results are taken from Ref. 1 assuming the volume fraction of alumina particles to be the same as the molar fraction.

The structure of the high-conductivity layer extracted from the above fitting is the following: The conductivity shows a sharp maximum at about 90 Å away from the surface of each particle and tails off rapidly toward both the bulk of the medium and the surface of the particle. The tailing off toward the surface is required by the rapid decrease of conductivity at large f in Fig. 4.11, and that toward the bulk is dictated by the rapid increase of conductivity at small f . This structure of the high-

conductivity layer is probably a combined result of carrier concentration and mobility.

It is concluded that by allowing the current to flow around particles in one layer and from particle to particle in another, the present model can account for the composition dependence of conductivity of an ionic conductor containing insulating particles quite well.

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EFFECTIVE MEDIUM CALCULATIONS OF A COMPOSITE ELECTROLYTE

N. J. Dudney

A model for the enhanced ionic conduction for a composite with an ordered array of insulating particles has been described by Wang and Dudney.¹ In this report an alternative model is described. Here the composite is assumed to be a random array of nearly spherical grains of the conducting (matrix) phase and nearly spherical insulating particles. The interfaces between matrix grains, as well as the matrix/particle interfaces, may provide high conductivity paths through the composite.

An effective medium calculation² was made to estimate the conduction along the interfaces in the composite and also through the lattice. Because the conductivity of the insulating particles is very small, the effective medium theory predicts a lattice conductivity given by $\sigma = \sigma_m(1-3f/2)$, where f is the volume fraction of alumina below the percolation limit at $f = 2/3$ and σ_m is the lattice conductivity of the conducting phase. The effective conductance for the interface, C_i , was calculated by modeling the interface as a cubic array of resistors. Each resistor was randomly given one of three values corresponding to the conductance along a matrix/matrix grain boundary, a matrix/particle interface, or a particle/particle interface. The fraction of each of these types of interfaces, and therefore C_i , depends upon the composition of the composite and the relative sizes of the particles and matrix grains. The expression for the total conductivity of the composite is

$$\sigma = \sigma_m \left(1 - \frac{3f}{2}\right) + 2C_i \left[\frac{1}{r_m} + f\left(\frac{1}{r_p} - \frac{1}{r_m}\right)\right],$$

where r_m is the radius of the matrix grains and r_p is the radius of the alumina particles. For $f > 2/3$, the lattice conductivity is set equal to zero.

The curves in Fig. 4.12 are examples of the calculated conductivities of a composite relative to $\sigma_m = 1$. For these particular calculations, the interface conductances were taken

Fig. 4.12. Calculated conductivity of AgCl containing 0.3- μ m alumina particles. The AgCl grain size may be constant (dashed curve) or composition-dependent (solid curve).

from calculations of the interfacial space-charge layers for AgCl³; however, these calculations would be equally appropriate for enhanced interfacial conductance due to other mechanisms. Values chosen for the conductances of the AgCl/AgCl, AgCl/Al₂O₃, and Al₂O₃/Al₂O₃ interfaces were 3×10^{-5} , 6×10^{-3} , and 3×10^{-15} ohm⁻¹, respectively. The maximum conductivity of the composites from these calculations were ~30–45 times larger than the conductivities for $f = 0$.

In general, the effective medium calculations demonstrate that the matrix/particle interface must be more conductive than the matrix/matrix grain boundaries in order for there to be an enhanced conductivity for the composite. The maximum in the conductivity occurs near the composition $f \approx r_p/(r_m + r_p)$. See the dashed curve in Fig. 4.12 that was calculated for $r_p = 0.3 \mu\text{m}$ and $r_m = 1 \mu\text{m}$. Experimental observations reported for β -AgI/Al₂O₃ particle composites showed that the maximum in the conductivity always occurred at $f \approx 0.2$ for r_p between 8 and 0.06 μm .⁴ This suggests that r_m must be decreasing along with r_p . It is possible that r_m is also a function of f . For a comparison, the solid curve in Fig. 4.12 was calculated assuming $r_p = 0.3 \mu\text{m}$ and $r_m = f^{-1/3}$ with a maximum value of 30 μm for small f . This gives a rapid increase in the conductivity for $f < 0.05$. Such enhancements due to only 1–5 vol % alumina particles have been reported for β -AgI composites.⁵

In summary, this model for the ionic conductivity of a composite electrolyte differs from other models mainly by including the possibility of rapid conduction along boundaries between two grains of the conducting phase. Several experimental observations of the change in conductivity with composition and alumina particle

size may be related to changes in the grain size of the conducting matrix phase.

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CALCULATIONS OF THE INTERFACIAL SPACE-CHARGE POLARIZATION FOR LiI AND β -AgI¹

N. J. Dudney

Recent reports have shown that the ionic conductivity of compounds, such as β -AgI and LiI, can be enhanced by factors of 50 to 500 by addition of 10–40 vol % of submicron Al₂O₃ particles.^{2,3} Some researchers claim that this effect is due to an increased concentration of ionic charge carriers forming a diffuse space-charge layer near the charged surface of the alumina particles.² The goal of the present study is to test this proposed mechanism.

Calculations of the interfacial space-charge polarization for LiI and β -AgI are very similar to the calculations for AgCl described earlier.⁴ Basically, at thermodynamic equilibrium there may be a net charge at a surface or interface that is compensated by an excess of oppositely charged lattice site defects in a diffuse layer near the interface. Changes in the concentrations of the ionic charge carriers give a local change in the conductivity. Assuming the defect mobilities near the interface are the same as those in the bulk, integration of the excess defect concentrations across the space-charge layer gives the excess conductance along the interface, C_i .

Silver interstitials and vacancies are the major point defects in β -AgI. The concentration of divalent cation impurities was assumed to be ~10 ppm. Lithium iodide is a Schottky material. Nominally pure LiI contains ~70-ppm divalent cations. The Debye length λ for these materials, shown in Fig. 4.13, is characteristic of the thickness of the space-charge layer. At room temperature λ is <25 Å. The dashed line indicates the Debye length for intrinsic LiI with <<70-ppm impurities.

The magnitude and sign of the charge for surfaces and interfaces of LiI and β -AgI are unknown, so the space-charge polarization was calculated for several extremes. For β -AgI, the site fraction of the silver vacancies, or alternatively the silver interstitials, was assumed to approach saturation at the interface. Both of these extreme cases gave a high conductivity layer at the interface. The calculated interfacial conductances are shown in Fig. 4.14. The

Fig. 4.13. Debye length for LiI and β -AgI.

Fig. 4.14. Relative excess conductance of β -AgI interface (points on curves a and b) and LiI interface (points on curve c). Curves a and b correspond to the maximum interfacial concentrations of silver vacancies and interstitials, respectively. Curve c is for the maximum interfacial concentration of lithium vacancies.

values of C_i/σ_∞ , where σ_∞ is the bulk conductivity far from the interface, can be thought of as the width of a layer of bulk material with a conductance equal to the excess conductance due to the space-charge layer. The largest interfacial conductance, curve b, corresponds to an accumulation of silver interstitials, which are the most mobile defects, in the space-charge layer. For LiI, only accumulation of the lithium vacancies enhances the conductivity near the interface since the mobility of the iodine vacancies is very low. The maximum conductance for this case is shown as curve c.

For AgCl/ Al_2O_3 particle composites, an effective medium model was used to estimate the conductivity^{1,5}; however, this is not necessary

to test the validity of the space-charge layer model for composites of LiI and β -AgI. The results for the maximum interfacial conductance from Fig. 4.14 can be compared directly with the reported enhanced conductivities due to the alumina particles. For a significant enhancement in the conductivity, the size of the LiI or β -AgI grains must be $\ll (C_i/\sigma_\infty)$.

From an extensive study of β -AgI with 0.06- μm alumina particles, enhancements of 50 times for dried alumina particles and 2000 times for as-received alumina particles were reported.² The grain size of the β -AgI was reported² to be $\sim 10 \mu\text{m}$. Clearly, the largest value of C_i/σ_∞ for β -AgI in Fig. 4.14 is at least three orders of magnitude lower than what would be necessary to account for the fiftyfold enhancement.

Composites of LiI and activated $\gamma\text{-Al}_2\text{O}_3$ have enhanced conductivities of ~ 100 times over that of pure LiI.³ For this enhancement to be due to an interfacial space-charge polarization, the LiI grain size must be $< 5 \text{ nm}$. Although the grain size for these composites was not reported, $< 5 \text{ nm}$ seems unreasonably small given that the reported x-ray diffraction lines corresponding to the LiI phase were sharp.

In conclusion, these calculations show that the interfacial space-charge polarization for LiI and β -AgI is not large enough to account for the large enhancements in the ionic conductivity reported for composites made with submicron alumina particles. Experimental work on AgCl/ Al_2O_3 composites suggests an alternative mechanism which may contribute to these large enhanced conductivities.⁶

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ENHANCED IONIC CONDUCTIVITY IN AgCl- Al_2O_3 COMPOSITES INDUCED BY PLASTIC DEFORMATION¹

N. J. Dudney

The dramatic effect of dispersed alumina particles on the ionic conductivity of materials such as β -AgI and LiI has been discussed in several other contributions.^{2,3} In this study, the conductivities of pure AgCl versus AgCl-alumina composite samples were measured after preparation and during a series of subsequent mechanical and thermal treatments. The results indicate that plastic deformation of the materials is essential to achieving an enhanced ionic conductivity.

In all earlier studies of the enhanced conductivity of AgCl/ Al_2O_3 and other composite

materials, the samples were prepared as pressed pellets. In this work, the samples of pure AgCl and AgCl containing ~4 vol % alumina were prepared directly from molten AgCl. An alumina paper composed of 3- μ m-diam alumina fibers was used rather than alumina particles. The alumina paper soaked up the molten AgCl giving a homogeneous composite without the need for mixing and pressing procedures. The samples were thin disks, ~1.5-mm thick $\times$ ~1-cm diam, with densities >94% of the theoretical value. Three-point conductivity measurements were made at frequencies of 100 Hz to 10 kHz using pressureless silver contacts. Effects of the electrode impedance were avoided at the higher frequencies. The most significant conductivity results for the as-prepared samples and after various treatments and anneals are summarized in Table 4.1.

Table 4.1. Room temperature conductivity measured at 10 kHz after each step in the sequential sample treatment.

Treatment	$10^8 (\text{ohm-cm})^{-1}$	
	AgCl	AgCl/Al ₂ O ₃
Prepared from molten AgCl	1.56	1.73
Pressed at ~125 MPa	4.61	5.49
Annealed overnight at 250°C	1.48	3.85
Pressed at ~280 MPa	13.1	19.6
Annealed 3 days at room temp	7.99	15.5
Annealed overnight at 250°C	1.98	7.57
Annealed 2 h at 400°C	2.00	7.51
Remelted AgCl	≥ 1.85	≥ 1.69

The conductivity of the as-prepared composite was about equal to that of the pure AgCl sample. This indicates that the existence of the AgCl/Al₂O₃ interface in the composite does not result in an enhanced conductivity. Any interfacial space-charge layers² or enhanced carrier mobilities along the interfaces in the undeformed composite are insufficient to give a significant increase in the sample conductivity.

When the samples were pressed uniaxially under a load of 900 or 2250 kg (initial pressures of 125 or 280 MPa), there were comparable increases in the conductivities of both the pure and composite samples. The deformed composites had a uniform opacity indicating a homogeneous distribution of the alumina fibers. There appears to be a monotonic increase of the conductivity with increasing deformation.

For the pure AgCl sample, the conductivity decreased to its initial value when the sample was annealed at 250°C. The alumina fiber composite, however, maintained a twofold to fivefold enhanced conductivity even after being annealed at 400°C. Only after remelting and resolidifying the AgCl matrix did the conductivity of the composite material return to its as-prepared value. Apparently the alumina

fibers stabilized the deformation-induced defects responsible for the enhanced conductivity.

The observed magnitude of the enhanced conductivity and also the annealing behavior for these AgCl materials are quite similar to results reported by Johnston for deformed AgBr crystals.⁴ From his work, Johnston concluded that the high conductivity occurred in regions with high dislocation densities. A similar mechanism is probably responsible for the enhanced conductivity of the pure and composite samples in this work. Because the composite samples prepared in other studies were all pressed pellets, it seems likely that deformation is also important in these observations of the enhanced ionic conductivity.

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ELECTRICAL AND OPTICAL PROPERTIES

FAST PULSE RESPONSE OF ZINC OXIDE VARISTORS

F. A. Modine R. B. Wheeler

Zinc oxide varistors are ceramic aggregates of ZnO grains with a few percent of added impurities such as Bi, Sb, and Co. Although varistors are electrical insulators at low voltages, they become conductors at high voltages. The electrical pulse response of varistors is of great practical importance because varistors are used primarily for transient surge suppression. Thus, it is surprising that varistor fast-pulse response has not been thoroughly studied, even though the response time of ZnO varistors limits their ability to protect against fast pulses. This limitation is especially relevant to military applications. Military defense requires a surge suppressor to protect communications and weapons electronics from the very fast electromagnetic pulses produced by high-altitude nuclear explosions. Moreover, pulse response studies reveal transient characteristics that provide a more stringent test of varistor theory than do the steady state characteristics upon which most varistor models are based.

The pulse response of a ZnO varistor is dependent upon its intrinsic properties and the type of circuit in which it is used. Figure 4.15(a) shows the voltage response of a varistor to a fast current pulse. Initially, the voltage V rises at a rate determined by the current I and the varistor capacitance C ,

$$\frac{dV}{dt} = I/C \quad (1)$$

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Fig. 4.15. The pulse response of a varistor. Part (a) shows the voltage response to a current pulse from a high-impedance source. Part (b) shows the current response to a voltage pulse from a low-impedance source. The upper-most curves represent the current in both cases.

Then the voltage overshoots the varistor breakdown voltage and approaches steady state from above. This is known as the "voltage overshoot" phenomenon. For slow rise times no overshoot is observed, but an overshoot of 30% can be obtained for high currents. At the end of the current pulse, the voltage drops precipitously before assuming an exponential decay with a time constant determined by the varistor capacitance and the resistance R of the external circuit,

$$\frac{dV}{dt} = -V/RC \quad (2)$$

Several factors influence voltage overshoot. The overshoot is enhanced by transition-metal dopants such as cobalt and manganese that are added to improve varistor nonlinearity. Consequently, the magnitude of the overshoot is correlated with the nonlinearity, which is defined by the phenomenological equation,

$$I = (V/V_0)^\alpha \quad (3)$$

where α is the nonlinearity factor (typically $\alpha=5-50$) and V_0 is a constant. The overshoot can be reduced by sacrificing nonlinearity, but this is not usually acceptable. Subsequent pulses give reduced overshoot if they are not well delayed in time (e.g., 50 μs). After many large current pulses, the overshoot increases if the polarity is reversed.

The capacitance of a varistor can be calculated from its pulse response by using either Eqs. (1) or (2). This capacitance is slightly less than that found from ac admittance measurements made between 10 Hz and 10 MHz. No such difference is found for a mica capacitor of similar value. Thus, the capacitance from pulse response measurements conflicts with a large increase in capacitance that is both inferred from ac admittance measurements made as a function of voltage¹ and predicted by a theoretical model of varistor conduction.² The increase in capacitance inferred from admittance measurements may be a consequence of phase shifts that originate in the trapping and detrapping of charge in the grain boundaries rather than being a real increase.¹

Figure 4.15(b) shows the current response of a varistor to a fast voltage pulse. These results have the same origin as those of Fig. 4.15(a). The initial current spike is due to charging of the varistor capacitance. Then the current slowly rises from an initial value achieved during the short time required to charge the capacitor to a steady state value. This increase in current from an initial value to a steady state value is the complement of voltage overshoot and is therefore called "current undershoot." The trailing edge of the pulse response is dominated by the discharge of the varistor capacitance.

A relationship between current undershoot and voltage overshoot is obtained from Eq. (3) by assuming that both phenomena are due to a transient change in α from an initial value α_i to a steady state value α_s .

$$\ln(I_s/I_i) = \alpha_i \ln(V_i/V_s) \quad (4)$$

where the subscripts s and i denote values at steady state and immediately after the rise time of the applied pulse, respectively. The voltage overshoot is less than the current undershoot because a varistor tends to arrest its voltage overshoot much as it arrests any overvoltage.

Figure 4.16 shows the varistor current I_i that is observed immediately after the rise of the voltage pulse plotted against the steady state current I_s . The current undershoot is constant over a wide current range, but it varies with varistor type. In contrast, the voltage overshoot increases as the current increases because the voltage peak occurs earlier.

The rise time of the current undershoot varies with voltage, and the shape of the undershoot suggests the relationship

$$I = I_s - (I_s - I_i)/(1 + t/\tau) \quad (5)$$

Fig. 4.16. The current immediately after the rise of a voltage pulse plotted against the steady-state current for three different varistors.

where I_0 and I_1 denote the steady state and initial current, respectively, and τ is a time constant. At low voltages τ can be more than 10 μ s, but at high voltages τ can be so short that no current undershoot is observable.

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FREQUENCY DEPENDENCE OF THE ADMITTANCE OF ZINC OXIDE VARISTORS

F. A. Modine R. B. Wheeler

The admittance of zinc oxide varistors was studied to obtain information on varistor conduction that has direct bearing on transient response, theoretical models, and power-loss mechanisms. In the simple Schottky-barrier model of a varistor, the current at low applied voltages is contributed by thermal activation of electrons over grain boundary barriers and by the capacitance of double-depletion layers that form at the barriers. The conductivity per unit area of grain boundary is

$$G = (eA/k_B)T \exp(-eV_B/k_B T) , \quad (1)$$

where e is the electron charge, A is the Richardson constant, k_B is the Boltzmann constant, T is the temperature, and V_B is the barrier height. The capacitance per unit area of grain boundary is

$$C = \epsilon/4\pi d = \epsilon D/4\pi Q , \quad (2)$$

where ϵ is the ZnO dielectric constant, d is the depletion layer thickness, D is the donor density, and Q is the charge per unit area of grain boundary. The barrier height is determined by the donor density and grain boundary charge:

$$V_B = eQ^2/\epsilon D . \quad (3)$$

When identical varistor grains are assumed and the series and parallel contributions of the 10^7 – 10^{11} grains/cm³ in a typical varistor are combined, a representation of a varistor as the electrical equivalent of a resistor and capacitor in parallel is obtained. (Both the conductivity and the capacitance are directly proportional to varistor area and grain size and inversely proportional to varistor thickness.) The grain resistivity of ZnO adds a very small series resistor to this parallel combination, but this can be ignored in comparison to the barrier impedance for the frequencies considered. Thus, a simple model of the electrical properties of a varistor is obtained. Given information on the grain size from microscopy or from breakdown voltages (i.e., assuming ~ 3.2 V per barrier at breakdown), varistor parameters are deduced from electrical measurements on this basis. While this model may be useful for many such purposes, it is unrealistic because the impedance of a zinc oxide varistor has a frequency dependence that does not at all correspond to its predictions.

Figure 4.17 shows the capacitance C and dissipation D of a varistor that were obtained from ac measurements of the in-phase and quadrature varistor currents.

$$C = R/\omega \quad (4)$$

and

$$D = G/\omega C , \quad (5)$$

Fig. 4.17. The capacitance and dissipation factor of a low-voltage varistor are indicated by the solid and dashed curves, respectively.

where G and B are the measured conductance and susceptance, respectively, and ω is the frequency in radians/sec. The dispersion of the capacitance and the loss peak between 10^5 and 10^6 Hz are typical of many measurements made at ORNL and at other laboratories. Neither of these aspects of varistor impedance has been given a good explanation. However, it has been noted¹ that the dispersion of the capacitance could be due to (1) trapping and detrapping of charge in the varistor barriers or (2) variations in the Schottky-barrier heights (i.e., not all grain boundary barriers are identical). In marked contrast to the simple expectation of a dissipation that changes in proportion to frequency, it is constant to within a factor of 2 for a frequency change of at least 6 orders of magnitude.

Although it has been given little notice, the general features of varistor impedance can be associated with a non-Debye capacitance,² which is represented phenomenologically as a constant-phase-angle circuit element. Moreover, it is an interesting case because depletion-layer capacitance is a manifestation of the change in donor charge induced by band bending rather than being a polarization effect. The non-Debye capacitance gives rise to an impedance with real and imaginary parts in constant ratio as a function of frequency, and thereby constant dissipation. Figure 4.18 shows conductance and susceptance versus frequency for the same varistor providing the data of Fig. 4.17.

The principal features of non-Debye capacitance are described by an admittance of the form

$$Y = K(j\omega)^n = K\omega^n[\cos(\pi n/2) + j\sin(\pi n/2)] \quad (6)$$

where K is a constant, $j = (-1)^{1/2}$, ω is the frequency in rad/s, and n is a noninteger exponent. The exponent may be evaluated from the slope of the curves in Fig. 4.18 or from the ratio

Fig. 4.18. The conductance and susceptance of a low-voltage varistor are indicated by the solid and dashed curves, respectively.

$$\tan(\pi n/2) = B/G = 1/D \quad (7)$$

From the slope of the susceptance, $n = 0.95$, and from the dissipation factor, $n = 0.95 \pm 0.02$ for the data shown. Measurements made on a variety of varistor types have yielded the range of values: $0.88 < n < 0.99$, where the highest values are found for fine-grained varistors. (Because D is small, the same results are obtained from plots of the impedance as from plots of the admittance.)

Many examples of non-Debye behavior are known,² but the phenomenon remains poorly understood. In the case of varistors, it is probably associated with inhomogeneity in the grain boundary barriers. Fine-grained varistors with uniform grain sizes such as those made from sol-gel or urea process powders exhibit less non-Debye behavior and have lower loss. In any event, non-Debye capacitance appears to be an important contributor to varistor power dissipation under quiescent operating conditions, and the thermal and electrical stability of varistors can be improved by decreasing this power dissipation.

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VOLTAGE DEPENDENCE OF THE ADMITTANCE OF ZINC OXIDE VARISTORS

F. A. Modine R. B. Wheeler

The changes in the ac admittance of a varistor that are induced by a dc bias voltage were measured to obtain information about the voltage dependence of varistor capacitance. The voltage-induced changes in capacitance provide a test of the predictions of theoretical models. Moreover, the capacitance of a varistor influences its pulse response. An increase in capacitance with voltage tends to reduce voltage overshoot, but a decrease in the capacitance enhances voltage overshoot.¹

Figure 4.19 shows a varistor capacitance that is inferred from ac admittance measurements. With increasing dc bias voltage, the capacitance decreases slightly, then increases by as much as two orders of magnitude for low-measurement frequencies with lesser increases at higher frequencies, and finally plunges to negative values at breakdown voltages. Although there is a theoretical model² of the varistor barrier that predicts a huge increase in capacitance near breakdown, negative values cannot represent true capacitance. The voltage dependence of the capacitance is more plausibly a consequence of phase shifts that originate in the trapping and detrapping of charge in the grain boundary barriers. This premise was supported by a perturbation calculation of the small-signal ac admittance of a varistor barrier with an applied dc voltage bias.

Time-dependent equations for a Schottky-type grain boundary barrier were derived using (1)

Fig. 4.19. The voltage dependence of the capacitance of a varistor as obtained from ac admittance measurements. The solid and dashed curves are for frequencies of 10 and 100 Hz, respectively.

the Richardson-Dushman approach to thermal activation over a barrier, (2) Poisson's equation to calculate band bending, (3) Fermi statistics to calculate the rate of electron emission from traps, (4) current conservation, and (5) charge conservation. Several simplifying assumptions were made: (1) the barrier current due to tunneling is negligible, (2) minority carrier contributions are negligible, (3) the distribution of electron traps is monoenergetic, (4) the trapping cross section is constant, (5) the Fermi level is coincident with the conduction band edge, (6) the number of electron traps is finite, and (7) most electron traps are filled at zero voltage bias. Although these assumptions are similar to those made by Pike in a similar calculation,³ a different mathematical formulation of the problem was made, and different results were obtained.

The equations for the varistor current and the interface charge under steady state conditions were obtained from the time-dependent equations by setting time derivatives to zero. The small-signal admittance was calculated as the harmonic perturbation about the steady state solution of these equations by considering the perturbations to be functions of $j\omega$ and by formally setting the time derivatives equal to $j\omega$. The admittance was obtained in the form of a ratio of polynomials in $j\omega$, and the conductance and capacitance were obtained by evaluating the real and imaginary parts of this ratio:

$$Y = G + j\omega C = [a + b(j\omega) + c(j\omega)^2] / [d + e(j\omega)] \quad (1)$$

where G and C represent the apparent values of conductance and capacitance, respectively, and the coefficients $a-e$ are functions of varistor parameters and the applied voltage. The form of Eq. (1) permits either positive or negative

values of apparent capacitance, depending on the values of the coefficients $a-e$. (The capacitance will appear to be negative if the pole of the admittance function is nearer the origin of the complex plane than are the zeros.)

The apparent varistor capacitance was calculated from Eq. (1) using parameter values that give agreement between computed and measured steady state varistor behavior, for example, the dc current as a function of voltage and the capacitance in the absence of applied voltage. The steady state solutions yielded a varistor nonlinearity peaking at 38 and a temperature coefficient of the breakdown voltage of $-10^3/K$, both in good agreement with experiment. Figure 4.20 shows that the calculated capacitance exhibits an increase with voltage and a frequency dependence that is in good agreement with measurements, but it does not go negative.

The calculations support the contention that the large increase in varistor capacitance as a function of voltage is more apparent than real, but they fail to explain the negative values of capacitance observed at breakdown voltages. The results reveal that negative values are plausible, but they are not obtained for the parameter values assumed. Some additional factors such as the generation and trapping of holes may lead to the phase shifts that are interpreted as negative capacitance.⁴

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3. G. E. Pike, *Phys. Rev. B* **30**, 795 (1984).
4. F. A. Modine and R. B. Wheeler, "Minority Carriers in Zinc Oxide Varistors," this report.

Fig. 4.20. The voltage dependence of the capacitance of a varistor single barrier as obtained from a perturbation calculation of the ac admittance. The solid and dashed curves are for frequencies of 10 and 100 Hz, respectively.

MINORITY CARRIERS IN ZINC OXIDE VARISTORS

F. A. Modine R. B. Wheeler

Minority carriers (i.e., holes) may profoundly influence ZnO varistor performance even though the Fermi level in varistors is near the conduction band edge of a wide band-gap material. Mahan et al.¹ have proposed a model of varistor conduction in which breakdown is triggered by hole creation when the conduction band in the grain interior drops below the top of the valence band at the grain interface. As direct evidence of holes, Pike² has observed band gap electroluminescence in ZnO varistors. Moreover, it can be argued that holes contribute to the varistor phenomena of voltage overshoot and negative capacitance.^{3,4} Thus, understanding the role of minority carriers may be a key to understanding ZnO varistors.

Electrons crossing a varistor barrier with energy exceeding the band gap can generate electron-hole pairs by impact ionization. The holes are attracted to the barrier by the band bending and can be trapped in a barrier potential whose shape and height are altered by the presence of the holes (Fig. 4.21). By the methods of Mahan et al.,¹ the barrier potential can be expressed as a quadrature.

$$\int_U^V [\xi(U-\mu_h)^{5/2} + U]^{-1/2} dU = 2nX, \quad (1)$$

where V is the barrier height, U is the potential, μ_h is a chemical potential for holes that is measured relative to the unbarriered valence band, X is distance from the interface, and ξ and n

are constants. If $U < \mu_h$, the term in ξ is zero, and parabolic band bending is obtained.

Poisson's equation can be used to calculate the barrier charge from the barrier potential.

$$Q = (\epsilon n / 2\pi) [V + \xi(V - \mu_h)^{5/2}]^{1/2}, \quad (2)$$

where ϵ is the ZnO dielectric constant and Q is the sum of the depletion-layer charge and the hole charge on one side of a barrier. Because it is now known that there is no insulating material in the interface between grains, it is assumed that the valence band on both sides of the barrier is filled with holes to the same chemical potential, instead of using the assumption of Mahan et al. that holes are trapped only in the forward biased side of the barrier (Fig. 4.21). The total depletion-layer and hole charge, which because of charge neutrality requirements equals the electron charge trapped at the grain boundary, is given by

$$S \equiv Q/Q_0 = \{ [V_L + \xi(V_L - \mu_h)^{5/2}]^{1/2} + [V_R + \xi(V_R - \mu_h)^{5/2}]^{1/2} \} / 2(V_B)^{1/2}, \quad (3)$$

where V_R and V_L denote the barrier heights of the forward- and reverse-biased barriers, respectively, and Q_0 and V_B denote the grain boundary charge and the barrier potential, respectively, when no voltage is applied and no holes are present. From Eq. (3), the barrier heights can be calculated as functions of Q , μ_h , and the applied voltage $V = V_R - V_L$,

$$V_L = V_B [S - V/(4V_B S)]^2 - \xi(V_L - \mu_h)^{5/2}, \quad (4)$$

and

$$V_R = V_B [S + V/(4V_B S)]^2 - \xi(V_L - \mu_h)^{5/2}. \quad (5)$$

Because ξ is a large number, holes cause a large reduction in the barrier height, and only a few are needed to promote varistor breakdown.

In order to determine the varistor current as a function of voltage, it is necessary to determine the number of holes that are trapped and their chemical potential. However, so little is known of hole generation and trapping that only a speculative treatment is attempted. At varistor breakdown voltages, it is assumed that holes are generated and trapped in proportion to the electron current and that the trapped holes either escape from the barrier potential by thermal activation or they decay by a recombination process. The equation for hole trapping then takes the form,

$$\frac{dP}{dt} = gJ_0 \exp(-8V_L) - J_h \exp(-8\mu_h) - P/\tau, \quad (6)$$

where P is the number of trapped holes, g is a factor less than unity that describes the probability that an electron crosses the barrier and

Fig. 4.21. In the model of Mahan et al., holes are trapped as shown for the grain boundary barrier on the left; in this work, it is assumed that holes are trapped as shown for the barrier on the right.

generates a hole that is trapped, $J_0 \exp(-\beta V_L)$ is an approximation to the over-barrier electron current, $J_h \exp(-\beta \mu_h)$ is the current of holes escaping from the barrier, $\beta = e/k_B T$, and τ is a recombination time constant. Although g is a function of the trapping cross section for holes as well as the number of unoccupied hole states, it is assumed to be nearly constant because few holes get trapped.

If Eq. (6) is applied to each barrier separately, a dilemma emerges; the holes escape from a barrier at a faster rate than they are generated. This is concluded by noting that $g < 1$, $V_L > \mu_h$, and $J_h > J_0$. The constants J_0 and J_h are proportional to the electron and hole densities of states in the conduction and valence bands, respectively; thus, J_0 and J_h are proportional to the electron mass $m_e = 0.38$ and hole mass $m_h = 1.8$, respectively. The dilemma can be resolved by assuming that the holes escaping from one barrier are for the most part swept to another barrier where they are trapped again before they can recombine. The retrapping effectively reduces the value of J_h so that holes can accumulate. This conjecture implies that varistor properties should depend upon the number of barriers, if the number is relatively small. There is some evidence that nonlinearity may depend upon varistor thickness in some cases. However, this evidence is not conclusive because of problems with varistor stability.

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MODELS OF THE PULSE RESPONSE OF ZINC OXIDE VARISTORS

F. A. Modine R. B. Wheeler

A complete explanation of varistor pulse response will require a time-dependent model of varistor conduction. However, the simpler case of steady state conduction is not yet well understood. Many theoretical models of varistor conduction have been proposed, but most have lost credibility as more experimental evidence emerged. Theoretical models in which conduction is controlled by double Schottky barriers are well accepted at present, but debate continues about conduction mechanisms, charge trapping, minority carrier contributions, and other details of such models. Although the transient characteristics of varistors are difficult to interpret, they are very important because they provide a more stringent test of varistor theory than do the steady state characteristics upon which most varistor models are based.

A simple phenomenological model of varistor pulse response provides a surprisingly realistic

description of a varistor's pulse response. The varistor is represented as the parallel combination of a resistance R and a capacitance C , both of which are assumed to be voltage dependent. When a voltage V_s is applied to a varistor by a source with impedance R_s , the equation for the varistor voltage is

$$\frac{dV}{dt} = [(V_s - V)/R_s - V/R]/C - (V/C) \frac{dC}{dt} \quad (1)$$

The resistance and capacitance are assumed to have the voltage dependencies derived for currents thermally activated over a Schottky barrier and conducted through a double-depletion-layer capacitance

$$R = R_B + R_0 \quad (2)$$

$$1/R_B = J/V = J_0 [\exp(-\beta V_L) - \exp(-\beta V_R)]/V \quad (3)$$

and

$$C = 2C_0 / [(V_L/V_B)^{1/2} + (V_R/V_B)^{1/2}] \quad (4)$$

where R_B and R_0 are nonlinear and linear contributions to the resistance, respectively; J denotes the current through the varistor, J_0 is a function of temperature but is otherwise a constant; $\beta = e/k_B T$ is inverse temperature converted to voltage; C_0 is the varistor capacitance without applied voltage; V_B is the barrier height without applied voltage; and V_L and V_R , respectively, denote the heights of the reverse- and forward-biased barriers when a voltage is applied.

The changes in the barrier voltages that are induced by an applied voltage are phenomenologically described as

$$V_L = V_B - \gamma V/N \quad (5)$$

and

$$V_R = V_B + (1-\gamma)V/N \quad (6)$$

where γ is the fraction of the applied voltage that appears across the reverse-biased barrier and N is the number of barriers. A value of $\gamma < 0.5$ is expected.

It is assumed additionally that the resistance and/or the capacitance follow the applied voltage with an exponential time constant τ in a manner described by the equations

$$\frac{dR}{dt}(V, t) = - [R(V, t) - R(V, \infty)]/\tau \quad (7)$$

and

$$\frac{dC}{dt}(V, t) = - [C(V, t) - C(V, \infty)]/\tau \quad (8)$$

where $R(V, \infty)$ and $C(V, \infty)$ are used to denote the steady state values that are found from Eqs. (2) to (6). Alternatively, equations could be

written for the conductance and the reciprocal capacitance without qualitatively changing the results.

Equations (1)–(8) were solved by the Runge-Kutta method for representative parameter values. The solutions display the voltage overshoot seen in a varistor's response to a current pulse and the current undershoot seen in a varistor's response to a voltage pulse.¹ Figure 4.22 shows voltage overshoot that is computed when C is assumed to lag the voltage and R has no explicit time dependence. The overshoot increases for larger current pulses, and larger current pulses

Fig. 4.22. A computer model of a varistor's fast pulse response shows a voltage overshoot that increases with the amplitude of an applied rectangular current pulse.

cause an abrupt drop to lower voltages on the trailing edge of the pulse. Moreover, there is a memory of past pulses that is shown in Fig. 4.23. These results agree with experimental observations. Similar results are obtained when only R is assumed to lag the applied voltage.

The good description of varistor pulse response given by Eqs. (1)–(8) implies that the phenomena are explicable in terms of a time lag in the response of a varistor to a voltage. It seems logical to associate this lag with a delayed buildup of charge in the barrier region, which is a suggestion first made by Eda,² and to attempt a more exact treatment. However, self-consistent, time-dependent equations of a double Schottky barrier that include electron trapping fail to predict varistor pulse response. Little or no voltage overshoot is predicted because electron trapping in the barrier region causes a delayed increase in the barrier resistance, instead of the decrease that causes an overshoot. Some addition to, or modification of, the theory is required. The addition of hole trapping in the barrier region appears promising.³ Electron trapping causes an increase in the barrier

Fig. 4.23. A computer model of a varistor's fast pulse response exhibits memory effects. Less voltage overshoot is induced by subsequent current pulses that are not greatly delayed.

resistance, but hole trapping would cause a decrease.

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ELECTRONIC BARRIERS PRODUCED AT ZnO SURFACES BY ION IMPLANTATION AND ANNEALING¹

E. Sonder   R. A. Zuhr
J. R. Martinelli²

Modern varistors are made of polycrystalline ZnO, doped to create Schottky-like barriers at the grain boundaries.³ To allow the study of tailored single-barrier junctions, we have implanted ZnO crystals with Bi, Sb, and transition metals. The electrical properties and the distribution of Bi and Sb were measured in the implanted crystals as a function of annealing temperature.

Figure 4.24 shows the current-voltage behavior of a sandwich of two implanted ZnO crystals, with the implanted faces in contact and the back faces having sputtered Pt low-resistance contacts. After implantation, before heating, the sandwich exhibits ohmic behavior with a resistance $\sim 1 \times 10^5$ ohms. Upon heating to 600–800°C the resistance increases ~ 2 orders of magnitude, and there is no evidence of breakdown for voltages up to 500 V. Heating to 1000°C is necessary before the 2-1/2 volt breakdown, characteristic of varistor barriers, is observed.

Figure 4.25 is a portion of the Rutherford backscattering (RBS) spectrum of ZnO implanted

Fig. 4.24. Electrical characteristics of two ZnO crystals implanted with Bi, Sb, Mn, Co, and Cr, with the implanted faces in contact. The curve labels indicate anneal temperatures in °C.

Fig. 4.25. Portions of ^4He backscattering spectra of ZnO implanted with Bi, Sb, Mn, Cr, and Co. The areas under the two peaks indicate, respectively, the amounts of Bi and Sb remaining after the indicated anneals: $\blacksquare$, before heating; $\blacktriangle$, 800°C; $+$, 1000°C; $\times$, 1200°C followed by 900°C.

with the five varistor-forming dopants most often present in commercial varistors (Sb, 4×10^{15} ; Bi and Cr, 2×10^{15} ; Mn and Co, 1×10^{15} atoms/cm²). The two peaks correspond to scattering from Sb (1.73 MeV) and Bi (1.83 MeV), respectively. These results indicate that there is no significant change in the Sb or Bi distribution for anneals up to 800°C. At 1000°C much of the Bi disappears, and at 1200°C Bi is no longer detectable. It is presumed that the

implanted ions have diffused to the surface where evaporation can take place.

The fact that the bismuth, as implanted, does not give rise to a barrier indicates that the presence of this element in the bulk of ZnO is not sufficient; a surface (or grain boundary) is necessary, and presumably trivalent Bi either acts to adjust the oxygen/zinc ratio⁴ at the surface or produces surface electron traps. Our ion scattering results show clearly that no thick Bi layer is necessary to produce varistor action. This is in accord with observations of actual varistor grain boundaries⁵ where no Bi-rich phase separated the ZnO grains.

The high-resistance behavior we observed after 600–800°C annealing was unexpected. We propose two possible explanations. One is that the implanted impurities or the radiation-produced defects⁶ readjust during the 600–800°C anneal to form centers that give rise to deep electronic traps. Such electron trapping would produce a thick enough insulating layer to stand up under voltages up to 500 V. The other possibility is that multiple small-angle grain boundaries exist in the surface region of the ZnO crystals. These could be due to the presence of boundaries in the original crystal or due to creation of them during sample preparation (slicing and polishing) or implantation.

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3. For a review, see Advances in Ceramics 7, edited by M. F. Yan and A. M. Neuer, American Ceramics Society, Columbus, Ohio, 1983.

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ROLE OF SHORT-CIRCUITING PATHWAYS IN REDUCED ZnO VARISTORS¹

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Electrical measurements and secondary ion mass spectrometry (SIMS) observations have been made to elucidate the mechanisms involved in the degradation of ZnO varistors at elevated temperatures in reducing atmospheres. By measuring samples prepared with different additives or different amounts of additives, we have shown that the degradation sensitivity depends to some extent on varistor composition but can be highly variable for different varistors of the same formulation. Even different sections of a single degraded varistor can differ greatly as is demonstrated by comparison of the current-voltage characteristics of 2×2 mm cut pieces of a given varistor. The results indicate that oxygen moves out (into) varistor samples during

reduction (reoxidation). The SIMS penetration profiles depicted in Fig. 4.26 indicate that after reduction (degradation) and reoxidation in $^{18}\text{O}_2$, the oxygen-18 has penetrated up to 100 nm into the ZnO crystallites and is present in large amounts throughout the varistor pellets. In order to account for the large variation in behavior of different sections of reduced varistors and for the rapid degradation that is inconsistent with any reasonable bulk or grain boundary diffusion coefficients, it is proposed that flaws, such as microcracks in the varistors, act as conduits for oxygen at elevated temperatures. A circuit model in which a reduced varistor is characterized by short-circuiting regions around such flaws predicts an electric field versus current density that is similar to that observed in experiments.

1. Summary of paper: *J. Appl. Phys.* 58, 4420 (1985).
2. General Electric Company, Schenectady, N.Y.

Fig. 4.26. Depth profiles of ^{18}O below the fracture surface of varistors that had been reduced and reoxidized in $^{18}\text{O}_2$. Samples I and F7 are varistors of different composition, reduced 2 h at 780°C and reoxidized 18-3/4 h at 580°C . Sample C has been reduced and oxidized at 290°C , respectively, for 1-1/4 and 3-3/4 h. Sputtering rate was ≈ 1 nm/s.

APPLICATION OF ELECTRONIC GRAIN BOUNDARY BARRIERS TO GAS SENSORS

E. Sonder

Recent studies of ZnO varistors^{1,2} have indicated that at elevated temperatures reducing atmospheres degrade the grain boundary barriers that give rise to the varistor's high resistance. Since a lowering of the grain boundary barriers increases the conductivity of a varistor ceramic by more than six orders of magnitude, it seemed that the near-surface region of a varistor-like sample might be a sensitive sensor of oxygen pressure. Consequently, we studied resistance changes due to ambient atmosphere of a piece of a commercial varistor and a number of highly porous specially sintered ZnO ceramics containing common varistor additives.

The measurements were made by attaching wires to the ends of samples with platinum paste and placing the samples inside a silica tube that could be heated and within which the gas could be changed. The resistance was calculated from the measured current through the sample and the applied voltage, the latter being supplied by a 1.5- or 4.5-V dry cell. The samples were normally $1 \times 2 \times 10$ mm in size.

Figure 4.27 shows results for a piece of commercial varistor material measured at 190°C and one of our porous samples measured at room temperature. For solid ZnO ceramics, we typically found resistance changes greater than a factor of 2 for changing the gas from Ar to oxygen at temperatures between 180 and 260°C . The upper curve of Fig. 4.27 depicts changes of resistance of a factor of 6. Such changes, as well as observed response times of < 1 min, are comparable to the response of some commercial gas sensors. Changing from oxygen to CO/CO_2

Fig. 4.27. Resistance changes in zinc oxide ceramics due to changed ambient gases. (a) piece cut from V130LA10A varistor, measured at 190°C ; (b) highly porous, cloth-like, ZnO ceramic containing Bi, Sb, Co, Cr, and Mn additives, measured at room temperature. The labels next to the curves indicate the ambient gas.

mixtures produced larger changes in our samples. The rate of change of the resistance upon switching gas was a strong function of temperature, becoming slower at lower temperatures. As indicated by the lower curve in Fig. 4.27, a porous cloth-like (large surface area) sample of ZnO containing Bi, Sb, Mn, Co, and Cr^{3+} exhibited oxygen partial pressure sensitivity at room temperature. However, not all the porous samples we produced behaved identically; most required higher temperatures before they showed significant changes in resistance as the gas ambient was changed. Development of a sensor that operates at room temperature would allow production of simpler, cheaper, and perhaps more reliable devices, since heaters and heater controls would not be necessary.

The results depicted in Fig. 4.27 also exemplify an observed degradation. The rate of change of resistance dR/dt upon initial reduction with Ar gas is significantly faster than it is after cycling. It appears that after numerous cycles there is additional slowing down of dR/dt . The initial rate of oxidation appears to be constant, but there is a slowing of the final rate of approach to the initial (oxidized) resistance after the sample has been cycled repeatedly.

It is clear that electronic barriers at grain boundary intersections with the surface do indeed react to changes in ambient oxygen pressure at temperatures not far above room temperature. Our measurements suggest two time constants, a rapid one reflecting changes at the surface and a slower one, presumably reflecting changes of grain boundary barriers deeper within the sample. Significant development is necessary before a practical device can be realized. Different compositions and physical states must be tried to find the conditions necessary for room temperature operation and to minimize degradation upon repeated cycling.

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2. E. Sonder, L. M. Levinson, and W. Katz, *J. Appl. Phys.* **58**, 4420 (1985).

3. Compositions were similar to those used for varistors described by E. Sonder, T. Quinby, and D. L. Kinser, *Bulletin American Ceramic Society* (in press).

ELECTRICAL PROPERTIES OF NIOBIUM CARBIDE

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The electrical properties of single-crystalline NbC_x were studied for 3 specimens with $x = 0.98$, 0.87, and 0.76. The specimens were unoriented disks having lateral dimensions of about 5 mm and thicknesses of about 1 mm. Electrical measurements were made using a fully automated van der Pauw apparatus with a 4.2–300 K temperature range. Accurate resistivities were easily measured, but the small highly conductive specimens required hundreds of measurements to obtain statistically meaningful Hall coefficients.

Figure 4.28 shows electrical data obtained for $\text{NbC}_{0.98}$. Measurements of the Hall coefficient have been fitted to a Gaussian distribution, and the temperature dependence of the resistivity has been fitted to the empirical equation

$$\rho = \rho_0 + AT + B \exp(-T_0/T) \quad (1)$$

which has been used previously to describe the resistivities of transition-metal carbides.

The parameters fitted to the electrical data for each of the specimens are given in Table 4.2. An increase in the contribution of defect scattering to the electrical resistivity with decreasing carbon content is apparent, and defect scattering is dominant for $\text{NbC}_{0.76}$. The exponential term in Eq. (1) describes a tendency of the resistivity to saturate at high temperatures; the saturation probably results from a thermally activated scattering mechanism rather than from structure in the electronic density of states at the Fermi level. The Hall coefficient is largest in magnitude for $\text{NbC}_{0.87}$, rather than exhibiting a monotonic dependence on composition. The change in the Hall coefficient with composition reveals changes in the carrier density that might be related to defect states that are introduced near to the Fermi energy.

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Fig. 4.28. The electrical properties of $\text{NbC}_{0.98}$. The inset shows the distribution of values measured for the Hall coefficient of a single sample at room temperature.

Table 4.2. Parameters fitted to the electrical data for niobium carbide. The Hall coefficient is computed from a Gaussian curve fitted to the measurements. The resistivity at 300 K is included for quick reference. The resistivity of $\text{NbC}_{0.76}$ is almost constant with temperature.

Parameter	$\text{NbC}_{0.98}$	$\text{NbC}_{0.87}$	$\text{NbC}_{0.76}$
ρ_0 ($\mu\Omega\cdot\text{cm}$)	24.0	121.6	153.4
A ($\mu\Omega\cdot\text{cm}/\text{K}$)	0.022	0.005	—
B ($\mu\Omega\cdot\text{cm}$)	22.9	9.5	—
C (K)	278	474	—
$\rho(300)$ ($\mu\Omega\cdot\text{cm}$)	38.5	125.1	155.2
R_H (mm^3/C)	-0.084	-0.137	-0.026

OPTICAL PROPERTIES OF NIOBIUM CARBIDE

F. A. Modine C. Y. Allison¹
R. H. French²

The optical properties of single-crystalline $\text{NbC}_{0.87}$ were studied. Specular reflectance was measured between 0.025 and 11 eV, and ellipsometric measurements were made between 1.2 and 4.5 eV. The measured reflectance is shown together with a calculated reflectance phase in Fig. 4.29. From the infrared to the near ultraviolet, the reflectance is accurate within a couple percent, but the uncertainty is greater in the vacuum ultraviolet, where a small sample causes great difficulty. The phase was obtained by first performing a Kramers-Kronig inversion of the reflectance amplitude with an approximate extension beyond 11 eV. Then a correction proportional to energy was added to achieve agreement with the phase found by ellipsometry.

From the reflectance amplitude and phase (r and ϕ), the optical constants (n and k), the dielectric functions (ϵ_1 and ϵ_2), and the opti-

cal conductivities (σ_1 and σ_2) were calculated using the relations

$$\text{re}i\phi = (n+ik-1)/(n+ik+1) \quad (1)$$

and

$$\epsilon_1 + i\epsilon_2 = (n+ik)^2 = 1 + 4\pi(\sigma_1 + i\sigma_2)/(-i\omega) \quad (2)$$

The optical conductivity, shown in Fig. 4.30, is more readily related to electrical measurements and to theoretical band structure calculations than are other optical functions.

Values for the electronic transport parameters were estimated from the optical conductivity. The dc electrical conductivity is taken to be the real part of the optical conductivity at zero energy, and the relaxation energy $\hbar\gamma = \hbar/\tau$ (where τ is the carrier relaxation

Fig. 4.29. The reflectance and reflectance phase for $\text{NbC}_{0.87}$. The dashed curve is the phase.

Fig. 4.30. The real and imaginary parts of the optical conductivity for $\text{NbC}_{0.87}$. The real part is represented by a solid curve and the imaginary part by a dashed curve.

time) is assumed to be the energy of the lowest energy peak of the imaginary part of the optical conductivity. These estimates are in good agreement with electrical measurements,³ if a single carrier with an effective mass of unity is assumed and parameters are obtained from the electrical data using the relations

$$4\pi\omega = \omega_p^2 = 4\pi Ne^2/m, \quad (3)$$

and

$$R_H = -1/Nec. \quad (4)$$

The parameters obtained from optical and electrical measurements are compared in Table 4.3.

Table 4.3. Electron transport parameters for $\text{NbC}_{0.87}$ as found from optical and electrical measurements. The dc electrical conductivity, relaxation rate, and plasma frequency are denoted by σ , γ , and ω_p , respectively.

Parameter	Optical	Electrical
$\hbar\sigma$ (eV)	4.60 ± 0.10	4.75 ± 0.10
$\hbar\gamma$ (eV)	1.2 ± 0.4	1.05 ± 0.05
$\hbar\omega_p$ (eV)	8.2 ± 1.5	7.9 ± 0.2

The optical conductivity at energies higher than a few eV results from interband transitions. A calculation of the interband contributions was made by convolving the partial densities of states obtained from the band-structure calculations of Klein et al.⁴ The result shows strong interband transitions between admixed carbon p states and metal d states at energies between 5 and 9 eV; the optical results (Fig. 4.30) show the strongest contributions between 4 and 8 eV. Because the partial densities of states are for a stoichiometric crystal and because the calculation neglects matrix elements and selection rules, the agreement is considered reasonably good.

DEFECT STATES IN SUBSTOICHIOMETRIC TANTALUM CARBIDE¹

G. R. Gruzalski D. M. Zehner

The search for a satisfactory understanding of the electronic structure of substoichiometric group-IVB and -VB transition-metal carbides (i.e., those deficient in carbon) has been relatively recent. Although some theoretical studies have suggested that removing carbon has little effect upon the shape of the density of states (DOS), other than a broadening of the sharp features, most have suggested that "defect" states are formed, that these states are associated with carbon vacancies, and that their ground states lie just below the Fermi level E_F , near the minimum in the DOS of the p-d bands. Few experimental investigations have supplied information relevant to the question of whether or not these defect states exist; those that have, however, are more or less consistent with the theoretical studies finding defect states just below E_F .

The above ideas regarding defect states were tested by using x-ray photoelectron spectroscopy (XPS) to determine core-level binding energies (BE) and valence-band structure of several TaC_x near-surface regions, which varied in composition from $x = 0.5$ to $x = 1.0$. Auger electron spectroscopy (AES) measurements were also made. In this report our observations are interpreted in terms of (1) an added negative charge in the vicinity of tantalum atoms owing to the presence of carbon vacancies and (2) the corresponding redistribution of tantalum states (i.e., the formation of occupied defect states). It also is suggested that as x decreases charge may transfer away from carbon atoms remaining in the crystal.

In Fig. 4.31(a) are shown tantalum-4f XPS spectra from (100) surfaces of tantalum carbide having different carbon-to-tantalum ratios x . Also shown for comparison is one spectrum from a clean, well-ordered (100) surface of pure tantalum. As x decreases, the spectra from the tantalum-carbide surfaces broaden somewhat, and the valley regions between peaks fill in, suggesting there was more than one distinguishable tantalum site in those near-surface regions deficient in carbon. The spectra also shift toward the Fermi level as x decreases. Similar results were observed for tantalum-4d spectra.

In Fig. 4.31(b) are shown carbon-1s spectra from surfaces of different x . In contrast with the tantalum-4d and -4f spectra, these exhibit no significant broadening with decreasing x . Also, the overall change in BE is more than a factor of 2 smaller than that for the tantalum-4d and -4f core levels.

Shown in Fig. 4.32 are valence-band XPS spectra from surfaces of different x . The peak near 5 eV BE derives from a hybridization of carbon-2p and tantalum-5d states.² As x decreases from 0.97 to 0.52, the position of this p-d peak shifts toward E_F by about 0.6 eV. A lower-lying carbon-2s peak (not shown) also appears to shift somewhat and in the same direction. In addition, the relative intensity in the spectra between about 1 and 2 eV BE increases as x decreases.

1. Oak Ridge Associated Universities faculty research participant from Oklahoma State University, Stillwater, Okla.

2. DuPont Central Research, Wilmington, Del.

3. F. A. Modine, C. Y. Allison, and T. W. Haywood, "Electrical Properties of Niobium Carbide," this report.

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Fig. 4.31. (a) XPS Ta-4f spectra and (b) C-1s spectra from (100) surfaces of tantalum carbide having different carbon-to-tantalum ratios x . Also shown in (a) is one spectrum from clean, well-ordered Ta(100). Binding energies are with respect to the Fermi level.

When tantalum and carbon combine to form tantalum carbide, charge is transferred from the tantalum atoms to the carbon atoms.³ Hence, in light of the tantalum core-level shifts, it may be reasonable to assume that, when a carbon atom is removed, the "tantalum" electrons that would have transferred to that carbon atom remain instead in the vicinity of the tantalum atoms. In addition to this interpretation being intuitive, it is consistent with the theoretical results in ref. 3, in that those results show a net transfer of charge to tantalum states with decreasing x .

The shift of the p-d valence-band peak toward E_F as x decreased also is consistent with the

Fig. 4.32. Uncorrected XPS valence-band spectra from surfaces having different carbon-to-tantalum ratios x . Spectra are shown to 9 eV BE only.

idea that a decrease in x results in added negative charge in the vicinity of the tantalum atoms. That this shift is somewhat smaller than the corresponding shift of the tantalum-4d and -4f core levels can be ascribed to hybridization effects.

Although it is difficult to determine the carbon-2s BE, it appears that it changed with x more than the carbon-1s BE did. This result is surprising because it may suggest that carbon-2s states are mixing with tantalum states more than indicated by theory.³

The additional intensity appearing in the valence-band spectra between about 1 and 2 eV BE is interpreted as being due to photoemission from occupied defect states that were created as carbon was removed. It is suggested that these states are primarily tantalum states that have redistributed spatially and energetically in order to accommodate the added negative charge resulting from the presence of carbon vacancies.

If one assumes that changes observed in the valence band are similar to those recently calculated^{4,5} for other transition-metal carbides and nitrides, then one is led to conclude that, with respect to an absolute energy scale, both the Fermi level and the carbon-1s level decrease with decreasing x . If this is an accurate description of what happens in tantalum carbide, then in addition to what already has been said about the redistribution of charge caused by the presence of carbon vacancies, one might further suppose that as x decreases charge also transfers away from the carbon atoms remaining in the crystal. This interpretation is consistent with theoretical results in ref. 3 and with our present understanding of changes

observed in carbon KVV AES spectra from surfaces of different x .

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SUPERCONDUCTIVITY

FLUX-LINE PINNING BY THE GRAIN BOUNDARY IN NIOBIUM BICRYSTALS

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B. C. Cai ³	Y. T. Chou ³

Studies of flux-line pinning by the grain boundary in niobium bicrystals have yielded a number of insights over the past several years.⁴⁻⁶ Among these is the confirmation that a localized superconducting state exists on the grain boundary in a parallel magnetic field well above the upper critical field H_{c2} , where the superconductivity vanishes in the bulk. In addition, strong evidence exists that the flux-line pinning interaction arises from the scattering of conduction electrons by the grain boundary. In our own work⁶ both electrical and SANS data strongly suggest that the grain boundaries in these bicrystals are faceted—possibly because of pinning of the grain boundary to small interstitial gas precipitates during sample growth.

The present work focuses on the strong rectification effect observed in one sample, in which the applied magnetic field is parallel to the [111] and the [001] crystal directions in the two grains when it is in the plane of the grain boundary and perpendicular to the current direction. The critical current (and pinning force) can be larger by more than a factor of 2 when the resulting driving force moves flux lines from the [100] grain into the [111] grain. A small component of this rectification arises from the geometrical matching (higher critical current) and mismatching (lower critical current) of the curved flux lines with the faceted grain boundary and is also seen in samples with symmetric tilt boundaries. However, the large rectification observed in this case appears to arise mainly from the intrinsic anisotropy of superconducting niobium—the critical fields H_{c1} and H_{c2} , the magnetic flux density B , and the flux-line lattice (FLL) are substantially different in the two grains. ($B = 0$ when $H = H_{c1}$, and $B = \mu_0 H_{c2}$ when $H = H_{c2}$.)

In the absence of any reasonable theory for how the observed large rectification could occur, correlations were sought with other physically observable features of the mixed state. The maximum average pinning forces per unit area of

grain boundary F_b^+ in the strong-pinning direction and F_b^- in the weak-pinning direction are shown in Fig. 4.33 as functions of flux density and temperature. As the lower plots show, the field dependence is nearly independent of temperature and shows no signature of the crossover point near $B = 0.6 \mu_0 H_{c2}$, where B is identical in both grains. The temperature dependence of F_b shows a marked anomaly in that it decreases with decreasing temperature at the lowest temperature. The difference $F_b^+ - F_b^-$ at 1.9 K is much smaller than at higher temperatures and may arise solely from the geometrical matching described above.

We speculate that the rectification effect at intermediate temperature and its near disappearance between 2.6 and 1.9 K is connected with an instability in the FLL. Figure 4.34 shows the hexagonal lattice in the [111] grain and the two equivalent isosceles lattices in the [001] grain observed in this sample at 4.8 K. Also shown are the two equivalent square lattices observed below 2 K in a single-crystal sample when B was in the [001] direction.⁷ The excess pinning force $F_b^+ - F_b^-$ would seem to be associated with the decrease in FLL shear strength as the temperature is lowered until the FLL in the [001] grain undergoes its structural phase transition near 2 K. A SANS investigation has been initiated to clarify our picture of the FLL structure in this bicrystal and its temperature dependence.

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FLUX-LINE-LATTICE ANISOTROPY IN V_3Si : OBSERVATION AND INTERPRETATION

D. K. Christen	H. R. Kerchner
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Small-angle neutron scattering (SANS) measurements of the flux-line-lattice (FLL) morphology in the high- T_c Al5 compound V_3Si have been extended and interpreted using a realistic theoretical description of the anisotropic mixed state free energy.¹ V_3Si belongs to a small class of intrinsically high- κ , clean, type-II superconductors, such that at low magnetic flux density the interflux-line forces are dominated by the microscopic field interaction. Previously, our observations of correlations between the FLL symmetry and of the real crystal-axis parallel to the applied field were analyzed using a phenomenological approach, where the influence

Fig. 4.33. (a) The maximum average pinning force per unit area of GB inhibiting FL motion from the [001] grain into the [111] grain plotted vs the upper critical flux density B_{c2} at four temperatures; (b) the reduced peak value of $F_b(\Gamma)$ plotted vs reduced flux density B/B_{c2} for the conditions of (a); (c) same as (a) but for FL motion in the opposite direction; (d) same as (b) but for the FL motion of (c).

of the normal FL cores was completely ignored and an ansatz anisotropic magnetic penetration depth $\lambda(\hat{r})$ was introduced into the London theory. The present approach treats the weak nonlocality in the electrodynamic response and anisotropy both in the Fermi surface and in the electron-phonon interaction of the cubic material to obtain a reciprocal space power series expansion for the mixed state free energy. Within this free energy, Fermi surface averages of the (anisotropic) superconducting energy gap $\Delta_{\mathbf{k}}$ and moments of the Fermi velocity $v_{\mathbf{k}}$ are parameterized.

One feature of the theory is the prediction of an approximately linear dependence of the FLL unit-cell symmetry on the flux density B , for crystalline axes where the lowest order $n=1$ terms in the interaction apply. This is the case for applied fields parallel to $\langle 110 \rangle$ and $\langle 112 \rangle$ axes, where the ratio of predicted symmetry dependences is described by

$$\frac{1 - (b/a)_{\langle 112 \rangle}}{1 - (b/a)_{\langle 110 \rangle}} = -1/3. \quad (1)$$

As seen in Fig. 4.35, this general behavior is observed experimentally and agrees semiquanti-

tatively for the value of the Fermi-surface averages shown. Likewise, for the sample orientation where $H \parallel \langle 100 \rangle$, the observed FLL morphology yields the second order $n=2$ term. These results are summarized in Table 4.4. The relevant averages of the Fermi velocity have not yet been evaluated from band theory, but we may compare our results with those inferred from measurements and theory for the anisotropy in the upper critical field H_{c2} . If the anisotropy of $\Delta_{\mathbf{k}}$ can be neglected, the $n=1$ Fermi surface average deduced from the $H \parallel \langle 111 \rangle$ data is identical with the one that governs H_{c2} anisotropy near the critical temperature T_c . Those results yield $\langle v_{\mathbf{k}}^2 - 5v_{\mathbf{k}}^x \rangle / \langle v_{\mathbf{k}}^2 \rangle = -0.21$. A possible means to resolve this discrepancy between H_{c2} and FLL anisotropy is to conclude that $\Delta_{\mathbf{k}}$ is strongly anisotropic due to anisotropy in the electron-phonon interaction. Resolution of this problem will require a detailed, reliable measurement of the gap anisotropy as well as theoretical evaluations of the relevant Fermi-surface averages of $v_{\mathbf{k}}$ and $\Delta_{\mathbf{k}}$.

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Fig. 4.34. Schematic illustration of bicrystal showing the orientation of the two grains, the directions of positive field H and current I , and the observed FLL (solid circles) at 4.8 K. Also shown are the square FLL's observed in a single-crystal sample for temperatures below 2 K and for H [001].

ION-IRRADIATION-INDUCED DISORDER EFFECTS IN VANADIUM NITRIDE

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Early investigation of the effect of neutron irradiation on the superconducting critical tem-

Fig. 4.35. The observed FLL symmetry b/a and c/a as a function of the flux density B , for the applied field parallel to $\langle 110 \rangle$ and $\langle 112 \rangle$ crystal axes. The curves shown are obtained from the current theory for $n=1$ and the Fermi-surface averages $\langle (v_k^2 - 5v_{k_x}^2)/\Delta_k^2 \rangle \langle \Delta_k^2 \rangle / \langle v_k^2 \rangle^2 = 0.29$.

Table 4.4. Fermi surface averages evaluated from fits to the FLL symmetry data. The H_i are sums of cubic harmonics of angular momentum i .

n	$H_{2n+2}(v_k)$	$\langle v_k^{2n+2} H_{2n+2}(v_k) / \Delta_k^{2n} \rangle \langle \Delta_k^2 \rangle^n / \langle v_k^2 \rangle^{n+1}$
1	$1 - 5v_{k_x}^2 / v_k^2$	0.29
2	$1 - 20v_{k_x}^4 / v_k^4$ $+ 21 v_{k_x}^6 / v_k^6$	0.012

perature T_c of Bi-phase, rocksalt-structured superconducting compounds revealed that they were much less sensitive to radiation damage than their AlS-phase counterparts.³ Since the Bi-phase superconductors are second only to the AlSs in highest T_c value, the effect of radiation-induced disorder is of technological as well as purely scientific interest; therefore, the effect of lattice disorder, induced by nitrogen ion bombardment, on the superconducting and normal state properties of VN has been studied. T_c , the residual resistivity ρ , the

residual resistance ratio RRR, and the upper critical field H_{C2} of three thin films of VN have been measured as a function of the incident ion fluence ϕ .

The preparation technique of the virgin films has been described in detail elsewhere.⁴ Briefly, the VN films were formed by heating films of pure V metal, approximately 100 nm thick, in 1 atm of very high purity N_2 gas. This produced VN films, 125 to 155 nm thick, with T_C 's of 8.28 to 8.75 K, ρ 's of 55.6 to 34.2 $\mu\Omega\text{-cm}$, and RRR's of 1.54 to 1.76. H_{C2} of these films was then measured as a function of temperature. The samples were then bombarded with 45- and 340-keV nitrogen ions, in a ratio of 1:15, in order to produce a uniform energy deposition profile. After irradiation, the parameters of the samples were measured, the dose was doubled, and the parameters were measured again.

T_C is shown as a function of fluence in Fig. 4.36. T_C is found to decrease with fluence to a saturation value at fluences greater than 1×10^{16} N-ions/ cm^2 . The T_C behavior can be well described as an exponential decay function of form:

$$T_C(\phi) = T_C(\infty) + [T_C(0) - T_C(\infty)] \exp[-c\phi], \quad (1)$$

where $T_C(0)$ is the undamaged value, $T_C(\infty)$ is the saturation value, and c is a decay constant related to the deposited energy. The c value is found to be constant for all samples, contrary to previous reports,⁴ and corresponds to a deposited energy density of 14.2 eV per VN molecule. The striking result of this analysis is that the saturation value of T_C depends on the starting value. This is quite different from the Al5 compounds where, for a given material, the saturation value of T_C is independent of the starting value.⁵ A proposed model for this result will be discussed later.

The effect of radiation on ρ is shown in Fig. 4.37. As is shown, ρ increases to a saturation

Fig. 4.36. T_C and the coefficient to the renormalized electronic heat capacity γ^* as a function of fluence ϕ for three samples.

Fig. 4.37. ρ and the upper critical field slope at T_C , $H_{C2}(T_C)$, as a function of fluence ϕ .

tion value at the same fluence as T_C . ρ can also be described by an exponential function of the form:

$$\rho(\phi) = \rho(0) + \rho(\infty) \{1 - \exp[-d\phi]\}, \quad (2)$$

where $\rho(0)$ is the unirradiated value, $\rho(\infty)$ is the saturation value, and d is the appropriate decay constant. d is constant for all samples, and $\rho(\infty)$ is sample dependent.

From the slope of the H_{C2} vs T curve at T_C , $H_{C2}(T_C)$, and ρ , one can calculate the coefficient of the electronic heat capacity γ^* and thus the electronic density of states at the Fermi level $N_F(0)$, both renormalized by many-body corrections. H_{C2} is shown in Fig. 4.37 as a function of fluence; it increases with increasing fluence up to a fluence of about 1×10^{15} N-ions/ cm^2 , where it levels off and then decreases, in most cases, at higher fluences. γ^* is obtained from the Bardeen, Cooper, and Schrieffer relation⁶:

$$-H_{C2}(T_C) = a\gamma^*, \quad (3)$$

where $a = 4.48 \times 10^4$ K/0e $\Omega\text{-cm}$. Values obtained from this expression are shown in Fig. 4.36. Since the renormalized density of states is proportional to γ^* , this is also a plot of $N_F(0)$ as a function of fluence.

These results suggest a simple qualitative model based on the electron lifetime model (ELM).⁷ According to the ELM, the decrease in the conduction electron relaxation time, resulting from lattice disorder, has the effect of broadening or smearing out the density of states (DOS). This broadening reduces the DOS at the Fermi level $N_F(0)$ in most materials. In the case of the Al5 materials the Fermi level is on or near a peak in the DOS; thus the ELM results in a drastic decrease in the DOS and therefore the T_C . However, in the case of the Bi materials, and VN in particular, the Fermi level is actually on the side of a large peak, and thus the ELM

still has the effect of reducing the DOS but to much less extent.

This model is also consistent with the fact that the saturation T_C in VN is dependent upon the initial value. T_C of our samples is limited by the impurity content, which has the effect of moving the Fermi level to a lower value of the DOS. Since the Fermi level falls on the side of a peak in the DOS, after smearing there is still some slope to the DOS around the Fermi level, resulting in different postirradiation $NV(0)$ values for samples with different initial $NV(0)$ and thus different saturation T_C values. This argument is further reinforced by our measurement of γ^* [or $NV(0)$]. Here we see that the initial γ^* values, as well as the saturated values, are higher for higher T_C .

In an attempt to form a coherent picture of the effects of ion bombardment on Bi-phase superconductors, a study is currently under way in which thin films of TiN are irradiated with nitrogen ions. While it is still early in the investigation, the results are qualitatively similar to those of VN. T_C decreases exponentially with incident ion fluence, as does the RRR, while ρ increases exponentially. Findings of this investigation will be reported at a later date.

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ANNEALING STUDIES OF ION-DAMAGED VN_x

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Previous investigations^{3,4} have dealt with the effect of N-ion damage on the superconducting parameters of Bi-structure VN_x ($x < 1$). The purpose of the work reported here is two-fold: (1) to examine the recovery in the damaged material of the superconducting transition temperature T_C and the resistance ratio Γ , defined as the resistance at 295 K to the resistance at 10 K, by thermal isochronal annealing studies from room temperature to a temperature at which the sample was fabricated ($\sim 1200^\circ\text{C}$) and (2) to investigate the effect of heat treatment of the sample to higher tem-

peratures under otherwise identical conditions in order to provide information on the formation, stoichiometry, and stability of the compound using measurements of T_C and Γ .

A VN film, 180 nm thick and prepared on a sapphire substrate,³ was irradiated with 45- and 350-keV N ions to a total fluence of 1.87×10^{15} N ions/cm² in order to produce spatially homogeneous lattice disorder. The increase in N concentration due to this process is estimated to be negligibly small ($\sim 0.01\%$). T_C was found to decrease from 7.7 to 3.9 K while Γ decreased from 1.3 to 1.0. The heat treatments, consisting of 10-min isochronal anneals, were carried out in high-purity N₂ gas at a pressure of one atmosphere. Following each annealing step of 50 or 100°C over the temperature range from 20 to 1500°C, measurements of T_C and the electrical resistance were made in a variable temperature cryostat using the standard four-probe method. Annealing temperatures were determined with a thermocouple or, at higher temperatures, with a two-color pyrometer. At several stages of the anneals, x-ray diffraction was used to monitor the lattice parameter and to explore the effect of thermal ordering on the sample.

Fig. 4.38 shows a plot of T_C defined as the midpoint of the superconducting-to-normal transition with the bars indicating the width of the transition vs the annealing temperature T_A . Recovery of T_C is quite discernible at modest temperatures and proceeds more rapidly above 200°C. Annealing at 900°C, well below the temperature at which the sample was made, results in almost complete recovery of T_C to the pre-irradiation value of 7.7 K, and on annealing to higher temperatures this value is exceeded. This result suggests that the thermal ordering process is ameliorated by radiation-induce-

Fig. 4.38. The superconducting T_C vs the T_A for ion-damaged VN.

defects as has also been observed in annealing studies of damaged Al₅ superconductors. With heat treatments to higher temperatures one can anticipate that variations in T_c may reflect changes in stoichiometry as well as the degree of ordering. In the present case, annealing at 1500°C increases T_c to 9.0 K. This would indicate that the N concentration and perhaps the degree of order increased as T_A increased. However this is at variance⁵ with recent studies of stoichiometry in VN powders at thermal equilibrium in which it was found that the N concentration was reduced by heat treatment in this higher temperature regime.

For comparison with the T_c data, Fig. 4.39 shows a plot of Γ vs T_A . The recovery of Γ with T_A is qualitatively consistent with the recovery of T_c from 20 to ~1100°C and can be understood as arising from annealing of defects and ordering in the lattice. At 1100°C, Γ has increased to a value of $\Gamma = 5.0$, but on annealing to higher temperatures Γ is observed to decrease sharply. X-ray diffraction studies for the 1100 and 1500°C anneals revealed no striking changes in the lattice parameter. The decrease in Γ is more in accord with the reported study of VN powders, and work is in progress to extend the times of heat treatment at high temperatures in an effort to reconcile the discrepancies. In addition, measurements of $H_{c2}(T)$, the temperature dependent upper critical field, as well as T_c and ρ , will be made to provide additional insight.

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Fig. 4.39. Γ vs T_A for ion-damaged VN.

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FORMATION, PROPERTIES, AND ION IRRADIATION EFFECTS OF HEXAGONAL MoN

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Much effort has been focused on the formation and stabilization of the B1 (rocksalt)-structure phase of MoN, because of the theoretical prediction of a high $T_c = 30$ K.² In thermodynamic equilibrium, however, the stable stoichiometric phase has a hexagonal structure, comprised of a supercell containing 8 MoN units. We have initiated a study to form high-quality thin films of this material and to investigate several normal and superconducting state properties. Hexagonal MoN appears to possess several desirable characteristics that may render it useful for tunneling device applications—in particular, a respectably high $T_c = 13$ K and a low residual resistivity $\rho_0 = 6 \mu\Omega\text{-cm}$, leading to a relatively small value of the magnetic field penetration depth $\lambda = 70$ nm. The latter is important, for example, in limiting the dynamic inductance of Josephson junctions, thereby increasing the sensitivity.

The MoN films were fabricated by reacting purified Mo films with NH_3 at temperatures of 700 to 750°C. Prior to the reaction, the starting Mo films were degassed in a UHV chamber at $T = 1550^\circ\text{C}$ for 10 to 20 minutes. This vacuum anneal resulted in residual resistivity ratios of almost 100 and was found to be essential for the subsequent formation of consistently high-quality MoN. After reaction, the resulting MoN structure was characterized using x-ray diffraction and was found to be single-phase hexagonal, with typical lattice parameters $a = 0.572$ nm and $c = 0.563$ nm, in close agreement with those measured for bulk stoichiometric MoN.

The two best MoN films had low-temperature resistivities about $6 \mu\Omega\text{-cm}$ and resistivity ratios slightly over 10. Measurements of the upper critical field as a function of temperature were analyzed according to the theory of Werthamer, Helfand, and Hohenberg (WHH), including the effects of Pauli paramagnetic limiting, spin-orbit scattering, and electron-phonon renormalization.³ From the slope $dH_{c2}/dT|_{T_c}$, we obtain a renormalized electronic specific heat coefficient γ^* of up to 20 mJ/mole K^2 , a large value relative to the B1-structure nitrides. The observed extrapolated $H_{c2}(0) = 4.5$ T for the two cleanest samples, with a Ginzburg-Landau parameter κ of 6 to 7.

To assess the effect of lattice disorder on this material, we have begun properties studies after irradiation with high-energy N-ions. For ambient temperature irradiations, we chose dose combinations of 45² and 340-keV N ions such that

a nearly uniform damage profile existed over a film thickness up to 150 nm, with very little implantation of nitrogen—so no new chemical species is introduced and the stoichiometry is essentially unaffected. At the lowest fluence $\phi = 1 \times 10^{16}$ N/cm², the average deposited energy is less than 1 eV/atom and results in a T_c reduction of about 1 K, along with a substantial increase in the residual resistivity to 60 $\mu\Omega$ -cm and in the upper critical field to $H_{c2}(0) = 7.5$ –8 T. We find a reduction in γ^* to 3.3 mJ/mole K², while the thermal part of the resistivity at room temperature dropped by a factor of 0.45. These effects follow monotonically with increasing dose, until saturation occurs above $\phi = 1 \times 10^{16}$ N/cm², where $T_c = 9.5$ K, $\rho_0 = 140$ $\mu\Omega$ -cm, and $\gamma^* = 2.3$ mJ/mole K², with $H_{c2}(0)$ over 10 T. This observed saturation ratio $T_{c,sat}/T_{c0}$ of almost 3/4 is the highest of which we are aware for any ordered-compound superconductor (e.g., for the Al₅ structure superconductors, the ratio is about 0.2).⁴ In this regime the WHH theory cannot fit the $H_{c2}(T)$ curves, which are too linear at low temperatures. We are investigating the possible influence of weak electron localization as a source of this effect. At present, we are ascribing the above trends to electron-lifetime reductions in the electronic density of states at the Fermi surface and to disorder-induced modifications in the phonon spectrum. The latter effect would account for the observed reductions in the electron-phonon coupling manifested in the strong deviations from Matthiessen's rule.

ITINERANT ELECTRON FERROMAGNETISM IN Fe-ALLOYED, Ni₃Al BASED MATERIALS

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Ni₃Al crystallizes in an ordered Li₂ (Cu₃Au-type) structure and is a well-known, weak itinerant ferromagnet for which studies of materials prepared off-stoichiometry have shown that the critical Ni concentration is 74.5 at. % Ni. With the addition of Fe, the single-phase ordered structure can be retained up to ~12 at. % Fe, provided that each two Fe atoms are accommodated by removal of one Ni atom and one Al atom from the stoichiometric compound, as was done in the fabrication of the materials investigated here.

Alloys containing 1, 3, 6, and 10 at. % Fe were arc melted and then annealed for homogenization and ordering. The magnetization of the samples M(H,T) was measured in magnetic fields up to 5 T in two vibrating sample magnetometers to span a temperature interval from 4 to 400 K. The experimental results were then analyzed in terms of two general theoretical formulations for weak itinerant ferromagnetism [viz., the Stoner theory and the self-consistent renormalization (SCR) theory of spin fluctuations]. The analysis indicates that while the Stoner theory appears to account readily for the variation in Curie temperature and the spontaneous magnetization at T = 0 with Fe concentration, the SCR theory provides a better description of the temperature dependence of the spontaneous magnetization.

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5. NEUTRON SCATTERING

The neutron scattering program at ORNL has many of the same current trends that are evident in various national studies of neutron scattering. We have a growing involvement with outside users, a more diverse scientific program, and a strong desire to upgrade the neutron scattering instruments.

Approximately two-thirds of the experiments in diffraction and inelastic scattering involve outside users, usually in collaboration with one of our staff. We have formalized the user program by enlisting an external Proposal Review Committee in addition to the existing Advisory Committee. This user structure is separate from the National Center for Small-Angle Scattering Research, which continues to be utilized fully by outside users.

The major new scientific trend in diffraction is our entry into the study of time-dependent phenomena using the wide-angle neutron diffractometer (WAND), constructed with funds from the Japan Atomic Energy Research Institute as part of the U.S.-Japan Cooperative Program on Neutron Scattering. This instrument, coupled to a beautiful furnace allowing very rapid but controlled temperature changes, has enabled the study of kinetics of phase transitions in several alloy systems. In inelastic scattering, there is a growing interest in polarization analysis experiments on magnetic systems and a decline in interest in phonon dispersion measurements. In small-angle scattering, the polymer work continues to be the most active area, but work on colloid systems, alloys, and biological samples is growing.

Within available resources, ORNL and DOE have been supportive in beginning to meet the need for new facilities. An addition to the HFIR building has just been completed, providing a cryogenics laboratory for testing and maintenance of our low-temperature equipment and office space for users. A new building is to be constructed in the HFIR area to house the entire neutron scattering staff and visiting scientists. Over the past two years, ORNL funds have been provided to begin planning a new reactor and associated experimental facilities. This Center for Neutron Research (CNR) is a major goal of ORNL; our hope is to make it the world's premier center for neutron scattering research. Initial DOE funding for R & D on a new research reactor is contained in the proposed FY 1987 budget. On the negative side, the Oak Ridge Research Reactor will probably cease operation in FY 1987. This will require a shift of the Ames Laboratory Neutron Scattering Program to the HFIR.

Most of our instruments at the HFIR are now about 20 years old and are in need of replacement or major repair. The first step in this improvement

program will be at HB-4, where it is planned to construct a removable array of Soller-slit collimators and detectors to allow the correlation chopper to be converted into a high-resolution powder diffractometer. This would become a dual purpose instrument capable of operation as either a correlation chopper or as a powder diffractometer. A new, more powerful computer is a necessary part of this improvement. It should be noted that this project is in response to user demand for a good powder diffractometer. The value of all our triple-axis instruments could be increased by rebuilding them to make better use of vertically focusing monochromators. This is particularly true for the polarized-beam instrument where polarization analysis experiments are always difficult because of intensity limitations. A logical plan would be to replace these instruments with new ones which would be designed for transfer to the CNR when it is ready.

SMALL-ANGLE SCATTERING

THE NATIONAL CENTER FOR SMALL-ANGLE SCATTERING RESEARCH (NCSASR)¹

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The activities of the National Center for Small-Angle Scattering Research for the period December 1, 1984-March 31, 1986, are summarized. Included are descriptions of the replacement of the two-dimensional detector on the 30-m SANS instrument, the replacement of the rotating anode generator for the 10-m SAXS facility, progress in interfacing the IBM personal computers to the instruments, and a description of the use of the facilities.

30-m SANS facility. Over most of the period surveyed in this report, the detector in use on the 30-m instrument was the first one built in the laboratory (SANS I), and the second detector (SANS II) was in use at the 10-m SANS facility at the Oak Ridge Research Reactor. Measurement of the ³He pressure on SANS I indicated that a leak existed which was slow enough that it was possible to maintain normal operation with very little inconvenience to the NCSASR users. This situation became time-consuming for NCSASR staff, however, in view of the more frequent recalibrations which were needed, and as soon as the third detector SANS III was available, it was installed in late February. After over a month's service in the evacuated flight path, tests revealed no measurable leak, and indications were that the machine calibration remained unchanged during that period.

10-m SAXS camera. The new 12-kW Rigaku rotating anode x-ray generator, jointly funded by DOE and NSF, was delivered on schedule in December 1984 and was fully operational in February 1985. Since then, the SAXS facility with a much more

powerful source has been once again made available to users. The smooth performance of the system over the year has greatly reduced the difficulties of users caused by the deterioration of the previous 10-year-old x-ray generator. Automatic sample changers and sample orienters have been designed and built to take advantage of the increase in flux of up to an order of magnitude.

User-interface upgrade. For some time the existing spectrometer software has occupied all of the (nonexpandable) available memory of the ModComp computers, effectively preventing any upgrade to a more modern, user-friendly software architecture. To overcome this problem, we are replacing one user terminal on each spectrometer by an IBM PC/XT desktop computer, which will act as a smart user interface, allowing menu-driven spectrometer operation with greatly enhanced facilities for experimental control and data analysis. The interrupt-driven ModComp interface software has been written and tested, and a first version of the user interface software is being evaluated. The new system is designed to be highly expandable, and ideas from users will be incorporated as they evolve.

Use of the facilities. The use of the NCSASR facilities in terms of user days or discipline days is given in Tables 5.1 and 5.2 over the period October 1, 1984-September 30, 1985. In Table 5.1 are listed the category of use, the number of users (each user is counted only once), the number of visits (all users in the category), and the number of user days for the neutron N and x-ray scattering X equipment. (If two people in a measuring team make two visits each of four days duration, 16 user days are recorded.) In this presentation we have included the name of the local contact in the list of users if he is part of a collaborative experiment, makes a full contribution to the conception, execution, and interpretation of the experiment, and may be expected to be a cosuthor of any publication resulting from the work.

Several conclusions can be drawn from the tables. The SANS facilities are used most heavily by the university community with strong

Table 5.1. User report, FY 1985 (October 1, 1984–September 30, 1985).

Sector	Users		Visits		User-days	
	N	X	N	X	N	X
Industrial	16	10	20	10	72	30
University	46	18	91	28	429	88
ORNL	16	3	74	45	325 ^a	128
Other government laboratories	1	1	1	1	4	5
Foreign	10	1	29	1	127 ^b	2
Total	89	33	215	85	957	253

^aORNL use includes NCSASR staff participation with users. The local contact is counted as a member of the user team if he is a full collaborator in the experiment.

^bThis is large because a foreign scientist, R. Triolo, was local contact for four months during the year.

for the SANS instruments. Use of SANS by colloid chemists continues to increase.

1. The NCSASR is operated under an agreement between the Department of Energy and the National Science Foundation (Interagency Agreement DOE No. 40-637-77, NSF No. DMR-7724458).

2. Instrumentation and Controls Division, ORNL.

3. Computing and Telecommunications Division, Martin Marietta Energy Systems, Inc.

INCOMPATIBILITY AND SEGREGATION IN MIXTURES OF DEUTERATED AND PROTOMATED MACROMOLECULES¹

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For over a decade small-angle neutron scattering studies of polymers have been based on the assumption that the thermodynamic interactions between polymer molecules are independent of deuteration, or alternatively, that the Flory

Table 5.2. Use of scattering facilities by discipline.

Discipline	Number of discipline days									
	I		U		ORNL		OGL		F	
	N	X	N	X	N	X	N	X	N	X
Polymers	41	12	224	86	88	70	-	5	10	-
Colloids	10	12	108	2	90	11	-	-	91	2
Materials, metallurgy, and physics	21	6	46	-	95	47	4	-	26	-
Biology	-	-	51	-	52	-	-	-	-	-
Total	72	30	429	88	325	128	4	5	127	2

participation from industrial scientists. NCSASR scientists are forming active, ongoing research collaborations with many of the users. This is, of course, by mutual consent and is beneficial to both the staff and to the user communities.

Efforts to form a base of biologists who use the SANS equipment are showing success. Similarly, materials and metallurgy specialists in the university and industrial communities are beginning to take advantage of the 30-m instrument. The use of the x-ray facilities by these groups is lower than expected. This may be due in part to the difficulties associated with the previous generator and also to the fact that the x-ray instruments of one kind or another do exist in many laboratories. Further, the technique of choice for metallurgists is often electron microscopy. The polymer community has been a faithful customer for the 10-m SAXS as well as

interaction parameter χ_{HD} between labeled and unlabeled molecules of the same species is zero. However, calculations³ have indicated that χ_{HD} may be finite and of the order of 10^{-3} – 10^{-4} . This had led to the suggestion⁴ that for sufficiently high molecular weights, demixing could occur in mixtures of deuterated and hydrogenous molecules of the same species and that this could lead to the measurement of χ_{HD} .

Such experiments have been performed for the first time in binary mixtures of deuterium labeled and unlabeled 1-4 polybutadienes.^{1,5} By regarding the labeled and unlabeled molecules as different species with volume fractions ϕ_H and ϕ_D , the interaction parameter ϕ_{HD} between them may be estimated by fitting the random phase approximation⁶ (RPA) to the measured scattering data. Figure 5.1 shows the measured cross section for a blend of deuterated ($\phi_D = 0.31$) and hydrogenous ($\phi_H = 0.69$)

Fig. 5.1. $dI(Q)/dQ$ vs Q for blend of 69 vol % protonated and 31% deuterated 1,4-polybutadiene at the critical composition. The curves were obtained from the homogeneous mixture scattering function by adjusting χ_{HD} (one adjustable parameter).

polybutadienes, which is fitted to the RPA for different temperatures. Note that the zero- Q intensities exceed by large factors the value ($dI(0)/dQ \sim 10^2 \text{ cm}^{-1}$) expected for $\chi_{HD} = 0$. The data were calibrated in absolute units (cm^{-1}), and the polymerization indices of the H- and D-species ($Z_H = 960$, $Z_D = 4600$) were measured independently by chromatographic methods. The single chain functions were represented by Debye (Gaussian) coils with $R_g = l_K(Z/6)^{1/2}$, where $l_K = 0.69 \text{ nm}$ is the Kuhn length for polybutadiene.⁶ Thus, χ_{HD} is the only adjustable parameter in the fit, and the RPA was shown to give an excellent representation of the data for various blend compositions, temperatures, and chain lengths. It was also demonstrated that the system exhibited an upper critical solution temperature (UCST) as predicted by Buckingham and Hentschel.³ This finding is remarkable in that to the authors' knowledge there was previously no example of a UCST in high-molecular weight polymers, where lower critical solution temperature (LCST) transitions have been universally observed. Figure 5.2 shows a plot of χ_{HD} as a function of inverse temperature T^{-1} (K^{-1}), which reaches the value of the spinodal at $T_S = 242.1 \pm 0.7 \text{ K}$. Below this temperature the blends phase separate due to isotope effects alone. In the homogenous state above T_C the critical exponents exhibited the mean field values, and at room temperature ($T = 296 \text{ K}$) the value of $\chi_{HD} = 8.8 \times 10^{-4}$, which is within a factor of 3 of the value predicted by theory.^{1,3} Similar measurements on the polystyrene system corroborate the prediction of a universal isotope effect.⁷

Since a χ value of 10^{-3} – 10^{-4} is in general much smaller than the values measured between different species, it does not invalidate the previous SANS measurement of χ parameters for polymer blends. However, the correction for this effect should

Fig. 5.2. Plot of χ_{HD} vs T^{-1} for blend of deuterated ($\phi_D = 0.31$) and hydrogenous ($\phi_H = 0.69$) polybutadienes.

be considered when these methods are applied to measurements of smaller χ parameters. Similarly the effect of a finite χ_{HD} does not invalidate the vast majority of investigations using the SANS techniques, as segregation effects are important only in high molecular weight systems and have generally not been observed. In the bulk state most systems studied previously are solids at room temperature and have been exposed for only a limited time period in the liquid state, which may not be sufficient for the development of equilibrium compositional fluctuations. The polybutadiene system is characterized by a glass transition temperature, $T_g < -90^\circ\text{C}$, and is thus liquid at room temperature, thereby facilitating the attainment of equilibrium.

In future the effect of a finite χ_{HD} must be carefully evaluated for liquid systems by comparing molecular weights measured by SANS and independently by chromatographic techniques. This is possible providing the SANS data are taken in absolute units, and previously unexplained effects observed in such systems may be attributable to the effect of a finite χ_{HD} .^{8,9}

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SMALL-ANGLE NEUTRON SCATTERING STUDY ON THE MORPHOLOGY OF SEDED EMULSION POLYMERIZED LATEX PARTICLES¹

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Emulsion polymerization has become one of the most important methods of polymer synthesis and results in particles (latexes) consisting of one or more monomers, polymerized by sequential addition. The morphology of the latex markedly affects the properties of the bulk polymers, though there has been no general agreement on the actual structure of the latex particle. The core-shell model³ developed in the 1970s postulates that during sequential monomer addition the first monomer polymerizes in the form of a spherical core, the surface of which serves as the locus of polymerization for the second monomer, thus giving rise to a core-shell morphology. This model has received not only much attention but also significant criticism, and the same evidence has been used to argue both for and against it. This is partly because the techniques previously used (electron microscopy, soap/surface group titration, etc.) do not directly observe the surface itself, and information on this component must be inferred indirectly. Direct observation of the surface may be obtained by small-angle neutron scattering (SANS) in combination with contrast variation methods.⁴ In this investigation, core particles were polymerized with styrene and methylmethacrylate monomers to form a 50:50 random copolymer. The monomer feed was then changed to trideuteriomethacrylate. By contrasting out the polystyrene/polymethylmethacrylate (PS/PMMA) core in an H₂O/D₂O mixture, SANS experiments can determine whether the deuterated PMMA-D₃ forms a shell on the original core. Experiments were performed on the ORNL 30-m SANS instrument. For measurements on the unlabeled core latexes (sample A), pure D₂O was used, and for the partially deuterated core-shell latexes (sample B), the proper mixture of D₂O:H₂O needed to contrast match the core was calculated to be 25% deuterium oxide. Sample concentration was 10 wt %, and the latex suspensions were enclosed in disc-like quartz cells of 1- or 2-mm path length.

After correcting for instrumental smearing effects by indirect Fourier transform methods,⁴ the data were converted to an absolute differential scattering cross section and compared with both solid sphere and hollow shell scattering functions. The desmearing procedure yields experimental values of R_g and the zero-Q cross

section $d\Sigma(Q)/d\Omega$.⁴ The fitting procedure used was a steepest descent nonlinear minimization employing the method of ridge analysis.⁵ It was found that sample A was best fitted with a solid sphere scattering function and sample B with a hollow sphere scattering function. The results of these fits are shown in Figs. 5.3 and 5.4 for samples A and B, respectively.

Due to dispersion of the particle size, it is necessary to employ a particle distribution func-

Fig. 5.3. Comparison of experimental SANS data and theoretical scattering function of PS-PMMA core latexes in D₂O. (Sample A)

Fig. 5.4. Comparison of experimental SANS data and theoretical scattering function of PS-PMMA-H core latex with PMMA-D₃ shell. Core contrast matched in 25:75% solution of D₂O/H₂O. (Sample B)

tion to account for deviations from ideality. In this work, a zeroth-order log-normal probability distribution (ZOLD) was used.⁶ The parameters used are consistent with the known dimensions of the samples, based upon stoichiometric calculations. The calculation yields a ratio of the core plus shell radius to the core radius of 1.3, which is consistent with the experimental SANS result of 1.2. Data for sample A are fit best by a solid sphere scattering function, composed of a random copolymer of polystyrene and PMMA. Fitting the data obtained for sample B to a hollow sphere (i.e., the shell region of a core-shell structure) supports our concept of a composite core-shell structure formed by the seeded emulsion polymerization.

The results of the fitting procedure gave a shell size of 140 Å with a mean distribution of 60 Å. This wide variation in the width of the shell indicates that it is in the latter stages of polymerization, where the greater variation in the size of the particles occurs. Based on these dimensions obtained from the ZOLD fitting procedure, the radius of gyration R_g and the zero-angle scattering cross section $dI(0)/d\Omega$ may be calculated for both the core and core-shell latexes. The results shown in Figs. 5.3 and 5.4 indicate that the proposed core-shell structure and dimensions are consistent, not only with the observed R_g but also with the absolute magnitude of the measured zero-angle cross section obtained from the indirect Fourier transform desmearing routines.

The overall sizes of these particles have also been determined by transmission electron microscopy and light scattering. These results are shown in Table 5.3, which lists the overall diameter. As can be seen, there is close agreement between the data obtained by microscopy and light scattering and those obtained by neutron scattering. This confirms that the particle dimensions calculated from the neutron scattering data are consistent with other techniques.

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CONFORMATION OF POLYBUTADIENE IN THE NETWORK STATE BY SMALL-ANGLE NEUTRON SCATTERING¹

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The reactive forces in elastomers arise through conformational changes of the chains themselves, and there is considerable current interest in determining the response of individual molecules to a macroscopic deformation or swelling of the sample. Small-angle neutron scattering (SANS) from partially labeled (deuterated) samples can provide direct information on the deformation of the whole molecule down to the average statistical segment and offers the possibility of checking the various models which have been developed to relate the macroscopic and microscopic properties of polymers, as for example, in theories of rubber elasticity.

This report describes a set of experiments on the dimensions of polybutadiene (PB) molecules in the linear, cross-linked, and swollen states. The networks were randomly cross-linked with peroxide so as to approximate those used in many studies as well as in practical applications. Linear PB molecules containing 0.16 volume fraction of PB(D₆) in 0.84 volume fraction of PB(H₆) matrix were made by dissolving the polymers in tetrahydrofuran (THF) and melt pressing after evaporating the solvent. To prepare randomly cross-linked networks, an appropriate amount (0.1 % w/v) of cross-linking agent was included before solvent evaporation, and the samples were partially cured in a compression molding operation at 120°C at a pressure of 45 psi for 20 min and then placed in a nitrogen atmosphere chamber for 4 h at 130°C.

The scattering experiments were performed at the 10-m SANS spectrometer at the Oak Ridge Research Reactor using neutrons of wavelength $\lambda = 4.75$ Å and a fixed sample-to-detector distance of 4.65 m. Absolute calibration of the data gave the measured differential scattering cross section $dI/d\Omega(Q)$ in units of cm^{-1} and was checked for all samples by comparing the molecular weight of the deuterated molecules measured by SANS and chromatographic techniques for both swollen and unswollen samples. The difference (3%) was within the statistical errors of the measurements after correction for incoherent backgrounds. SANS experiments were performed on linear and cross-linked materials, in addition to networks swollen by a factor of 4.67 in toluene.

The molecular weight M_w and the radius of gyration R_g were calculated from the intercept

Table 5.3. Comparison of SANS results with other techniques.

Sample	Outer diameters (Å) from different techniques		
	SANS ZOLD	Electron microscopy	Light scattering
A core	1010 ± 50	900 ± 150	1120 ± 120
B core plus shell	1200 ± 60	1070 ± 150	1300 ± 120

and the slope, respectively, of Zimm plots in the Guinier region and also by fitting a Debye (Gaussian) coil to the scattering data by least-squares regression techniques. A typical plot of both procedures is shown in Fig. 5.5. In general, the Zimm results were higher than those derived from the Debye fits because part of the data was taken at Q values for which $QR_g > 1$. Such effects are well known, and correction techniques are available in the literature.³ The final values of R_g and M_w are shown in Table 5.4, after correction for mismatch between the molecular weights of the D- and H- molecules.⁴

Three deformation models—chain affine, junction affine, and phantom network—were used to determine the theoretical relationship between the molecular and the macroscopic deformation defined by the ratio of swollen and unswollen volumes, Q . If the deformation is chain affine,

$$R_g^* = R_g Q^{1/3} \quad (1)$$

where R_g^* is the radius in the swollen state and R_g is the undeformed value. For the junction affine deformation, in which only the cross-link junctions deform affinely with macroscopic swelling, the expected value of R_g is given by⁵

$$R_g^* = R_g \left(\frac{Q^{2/3} + 1}{2} \right) \quad (2)$$

For tetrafunctional networks ($f = 4$), Pearson⁶ derived the following expression for the phantom network model

$$R_g^* = R_g \left(\frac{Q^{2/3} + 3}{4} \right)^{1/2} \quad (3)$$

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Fig. 5.5. Debye (Gaussian) coil and Zimm fits for a cross-linked blend of 16% polybutadiene- D_6 molecules in polybutadiene- H_6 matrix.

Table 5.4. Characterization of PB(D_6)/PB(H_6) polymers via SANS experiments.

Sample code	Zimm plot ^a		Debye fit		Average of Zimm Debye values ^b	
	M_w	$R_g(\text{\AA})$	M_w	$R_g(\text{\AA})$	M_w	$R_g(\text{\AA})$
Uncross-linked	37,100	89.6	35,300	86.1	31,700	82.2
Cross-linked	44,500	85.7	43,600	84.1	38,550	79.5
Swollen	42,000	103.5	40,600	109.3	36,100	99.6
Value of α		1.18		1.28		1.23

^aCorrected for effects of finite angular range by methods of ref. 3.

^bCorrected for effects of mismatch between the polymerization indices of the H and D molecules by methods of ref. 4.

The values of α , the ratio of deformed and undeformed radii, calculated from Eqs. (1)–(3) using the experimental swelling ratio $Q = 4.67$ are, respectively, 1.67, 1.37, and 1.20. The following conclusions may be drawn from the experiment. Every sample was observed to fit the Debye form factor for random coil molecules, indicating that the chains exhibit Gaussian conformations in the linear, cross-linked, and swollen states. Chemical cross-linking does not affect the molecular dimensions as measured by R_g . This confirms one of the important assumptions underlying the theory of rubber elasticity. The R_g of the elastic chains in the swollen network is about 23% larger than in the dry network, even after being swollen to 4.67 times its original volume. The R_g measured after swelling agrees better with the theoretical phantom network model than with the affine deformation models. For the linear (uncross-linked) material, the SANS data yield a value of $R_g/M^{1/2} = 0.35 \text{ \AA g}^{-1/2}$. Intrinsic viscosity data in an ideal solvent yield $0.34\text{--}0.42 \text{ \AA g}^{-1/2}$, indicating that the dimensions in the bulk polymer are close to those in ideal solvents as has been generally found for amorphous polymers.

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KINETICS OF POLYMER FIBER ANNEALING¹

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The change of materials processing conditions affects the morphology and thus the physical, chemical, and mechanical properties of materials. Microstructural changes occurring during the process of crystallization in as-spun poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) have been monitored using wide-angle x-ray diffraction (WAXD), small-angle x-ray scattering (SAXS), optical birefringence, shrinkage measurements, and specific gravity. The fibers have been isothermally crystallized at different temperatures between 100°C and 200°C and at constant tensions of 2, 5, and 12 g for annealing times ranging from 100 to 1050 ms. Morphological changes in these fast crystallization processes were thoroughly investigated, and the results were analyzed in combination with those obtained by other physical techniques.

Shrinkage and birefringence results from PET show a competition between two processes, chain recoiling on one hand and crystallization on the other. A consistent correlation among WAXD, SAXS, shrinkage, and birefringence results were demonstrated. However, for PBT the crystallization process prevails over the chain recoiling process.

For PET SAXS data show a fibrillar morphology. Based on WAXD results, the crystallization is envisioned as a two-stage process: first the formation of defective fibrils, then the formation of more perfect crystals. WAXD results also demonstrate a remelting phenomenon in samples which have experienced positive shrinking.

As to PBT, density measurements show that the rate of crystallization increases with temperature. WAXD shows that the orientation of polymer chains within the crystals remains constant with time and temperature. SAXS shows the development of small-angle Bragg peaks as the annealing time is increased. A two-lobe arc pattern is the characteristic pattern as expected. The value for long period spacing ranged from 100 to 120 Å, increasing with temperature.

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NEUTRON SCATTERING FROM MIXED MAGNETIC AND NONMAGNETIC COLLOIDS¹

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Ferrofluids are stable colloidal suspensions of small ($\approx 15 \text{ nm}$) diam, approximately spherical superparamagnetic particles dispersed in water or oil. The ferrofluid (FF) magnetization M , which is proportional to the volume fraction of magnetic material n , reaches a typical saturation value of 500 Gauss in applied fields of a few kilogauss. It has recently been shown that a single layer of micron-sized, nonmagnetic spheres suspended in a ferrofluid may be ordered in a variety of ways by the application of a small magnetic field.⁵ The spheres displace FF and behave in an external field as magnetic holes with aligned moments. Interactions between these large effective moments may produce chain-like aggregates or 2-D crystals, observable with an optical microscope. In three dimensions, if the FF is regarded as a continuum, correlations between dispersed nonmagnetic spheres of diameter d are solely determined by $(\mu^*)^2 = \mu^2/k_B T$, where μ is the magnetization of the FF displaced. This situation is realized for micron-sized particles [$(\mu^*)^2 \approx 50,000$ at saturation]. For much smaller guest particles, density variations in the FF may cause significant fluctuations in $(\mu^*)^2$ ($\approx 40\%$ for $d = 50 \text{ nm}$) and may be correlated with the positions of the nonmagnetic particles. In the limit when nonmagnetic and ferrofluid particles are of comparable size, the concept of an effective moment for the nonmagnetic species is no longer valid, and the system models a novel binary liquid in which dipole-dipole and central interactions coexist. In this paper, we report small-angle neutron scattering (SANS) results on such a liquid, comprising polymethylmethacrylate (PMMA) spheres ferrodistributed in a cobalt FF chosen to have small intrinsic anisotropy for this preliminary investigation.

PMMA spheres of 37.4-nm diam were dispersed at 6.5% volume fraction in an oil-based magnetite ferrofluid. The mixed suspension contained 9.3%

volume fraction of ferrofluid particles (18-nm total diam). Treating the system as a two-component macrofluid, the scattered intensity may be written

$$I_2(Q) = x f_2^2(Q) S_{22}(Q) + 2[x(1-x)]^{1/2} f_1(Q) f_2(Q) S_{12}(Q) + (1-x) f_1^2(Q) S_{11}(Q), \quad (1)$$

where subscripts 1 and 2 refer to FF and PMMA particles, respectively; $f_i(Q)$ is the particle form factor; $S_{ij}(Q)$ is the partial structure factor for correlations between particles of types i and j at momentum transfer Q ; and x is the relative number density of FF particles. In the approximation that adding a dilute suspension of PMMA does not significantly perturb the FF structure, $S_{11}(Q)$ may be expected to be the same in the mixture as in the pure FF, so that the difference in intensity $\Delta I(Q)$ between PMMA+FF and FF alone will be given by just the first line of Eq. (1). An interesting feature of this result is that the FF form factor appears only linearly, so that magnetic contributions to the scattering will average to zero in an unpolarized beam experiment. Therefore, only the nuclear contribution to the FF scattering enters the second term of Eq. (1). A comparison of the experimental intensity [Fig. 5.6(a)] with this approximation [Fig. 5.6(b)], using the theory of Ashcroft and Langreth⁶ to evaluate the $S_{ij}(Q)$, shows fairly good agreement. In particular, a study of the separate terms which enter the calculation shows that the large peak which appears in the difference data has its origin primarily in cross correlations between the two types of particles present. We are now extending the theory along the lines used in the one-component FF⁷ to analyze data taken on systems in which the constancy of $S_{11}(Q)$ can no longer be assumed on formation of a binary system.

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PENETRATING BACKGROUND CORRECTION TO THE COLLOIDAL ONE-COMPONENT MACROFLUID MODEL¹

John B. Hayter

Many dispersions of charged colloidal particles exhibit strong interparticle correlations, due to the long-range nature of the Coloumb interactions.

Fig. 5.6. (a) Measured difference scattering $\Delta I(Q)$ vs momentum transfer Q for a PMMA-FF mixture relative to the scattering from the pure FF. (b) Theoretical $\Delta I(Q)$ (see text).

Such correlations dramatically alter the intensity distributions observed in scattering experiments designed to measure colloidal properties, and their understanding forms a central problem in interpreting scattering data. In the case of spherical particles, one generally successful approach has been to model the colloidal suspension as a one-component macrofluid (OCM)² and to apply the integral equation methods of liquid theory. In this context, the mean spherical approximation (MSA)³ has proved particularly apposite, once its low-density limitations have been overcome by appropriate renormalization techniques (RMSA).⁴ The OCM is based on the Ornstein-Zernike equation for the colloidal particles alone,

$$h(r) = c(r) + nh(r) * c(r), \quad (1)$$

supplemented by the RMSA closure relations $g(r) = 0$, $r < d$ (the hard core condition) and $c(r) = -V(r)/k_B T$, $r > d$. Here, n is the number density of colloidal particles of diameter d interacting through the pair potential $V(r)$; $c(r)$ is the direct correlation function; $h(r) = g(r) - 1$, where $g(r)$ is the pair correlation function; and $*$ represents a convolution. $V(r)$ is taken to have a screened Coloumb form,

$$V(x) = [z^2/d\epsilon k_B T(1+k/2)^2] \exp[-k(x-1)]/x, \quad r > d, \quad (2)$$

where z is the effective charge on the particle, $x = r/d$, and $k = \kappa d$, with κ^{-1} being the Debye length of the dispersion medium. Both the MSA and OMSA yield analytic solutions which give apparently excellent results when applied to the analysis of experimental data.

Recently, Naegle et al.⁵ have explored the use of the so-called primitive model (PM) to extend such studies, using an MSA solution due to Blum.⁶ While this model is only useful at high densities, it offers the attractive added feature of providing explicit counter-ion distributions. Both macroions (species 1) and counter-ions (species 2) are considered, so that Eqs. (1) and (2) are replaced by

$$h_{ij}(r) = c_{ij}(r) + \sum_{k=1}^2 n_k h_{ik}(r) a_{kj}(r) \quad (1a)$$

and

$$V_{ij}(r) = z_i z_j / \epsilon r, \quad r > d_{ij}, \quad d_{ij} = (d_i + d_j)/2 \quad (2a)$$

with obvious equivalent MSA closure conditions. In the point counter-ion limit ($d_2 \rightarrow 0$), the PM may be reduced to a one-component model in which the effective potential is given by Eq. (2).⁵ The latter is a more realistic model than the OCM, however, since the ions which maintain electro-neutrality are restricted to the volume between the macroions. In the OCM, we may formally write $g_{12}(r) = 0$ for all r , so that the counter-ions may occupy any spatial position and form a penetrating background. We shall now demonstrate that for each point-ion limit of the PM, there is an equivalent OCM system. This is of more than academic interest, since the OCM is extremely rapid to compute, an important practical feature when analyzing experimental data. Consider a real system characterized by charge z , screening k , and volume fraction $\phi = \pi n d^3/6$. Following Hansen,⁷ it is straightforward to show that the presence of a penetrating background will reduce the charge on the OCM model particle to $z(1-\phi)$, so that for the OCM to model a physical system with charge z , the OCM calculation must be performed for an effective charge

$$z^* = z/(1-\phi). \quad (3)$$

The effective system so created can no longer exhibit correlations which are equivalent to the real system, however, unless the Coulomb coupling between particles, defined as $2V(x=\phi^{-1/3})/k_B T$, is the same in both cases.⁴ From Eqs. (2) and (3), this amounts to the requirement that the screening in the effective system be given by

$$k^* = k - 2\phi^{1/3} \log(1-\phi). \quad (4)$$

The pair distribution function $g(r)$ computed for the system (z^*, k^*, ϕ) in the OCM approximation will then be expected to mimic the $g(r)$ calculated in the point-ion limit of the PM for the physical

system defined by (z, k, ϕ) . The typically good agreement between the two methods is evident in Fig. 5.7.

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Fig. 5.7. $g(x)$ vs x for a colloidal system defined by $\phi = 0.327$, $k = 4.74$, $z = 20$, and $d = 5.0$ nm. (—) Primitive model⁵ with $d_2 = 0$; (---) background corrected MSA.

SELF-CONSISTENT CALCULATION OF MICELLAR IONIZATION¹

John B. Hayter

Evans et al.² have developed a theory of "dressed micelles" which establishes a method of calculating the effective micellar ionization directly from measurable experimental parameters. Since one of the great successes of small-angle neutron scattering (SANS) in recent years has been the development of techniques to estimate the effective ionization of micelles in solution (e.g., Ref. 3), a large body of experimental data is available with which to test this theory, and Chao et al.⁴ have recently attempted such a comparison. However, the latter authors were unable to rederive the original theoretical expressions. They therefore assumed (incorrectly) that the theory was erroneous and used an earlier, less accurate expansion method.⁵ The theory of Evans et al. thus remained to be tested. We have recently undertaken to do this and have found that while the theory is fairly good under conditions of high screening, it fails for small screening, a feature which was anticipated by the authors.² We are now able to show that this failure is

related to an inconsistency in the original approximation and that a self-consistent reevaluation of the theory leads to good results even for small screening.

We follow Evans et al. and start from the Poisson-Boltzmann equation in spherical symmetry:

$$\frac{d^2 y}{dx^2} + \frac{2}{x} \frac{dy}{dx} = \sinh y. \quad (1)$$

The dimensionless variables are defined by $y = (e\phi/k_B T)$ and $x = \kappa r$, where $\phi(r)$ is the potential at distance r from the center of the micelle and κ^{-1} is the Debye length. The boundary conditions are

$$y \rightarrow 0 \text{ as } x \rightarrow \infty,$$

and

$$\left. \left(\frac{dy}{dx} \right) \right|_{\kappa = \kappa_R} = -(4\pi e^2)/(\epsilon \kappa a k_B T) \equiv -s,$$

where R is the micelle radius, a is the area per surfactant head-group in the micelle, and s is the scaled surface charge per unit area. Setting $y_0 = y(\kappa R)$, Eq. (1) may be integrated once to yield

$$s^2 = 4 \sinh^2(y_0/2) - \int_0^{y_0} \frac{4}{x} \frac{dy}{dx} dy. \quad (2)$$

The approximation of Evans et al. consists of replacing (dy/dx) in the integrand in Eq. (2) by the exact result for planar boundary conditions, namely $(dy/dx) = -2 \sinh(y/2)$, and arguing that the most important contribution to the integral comes from the region $x \approx \kappa R$. A second integration then yields their basic equation:

$$s^2 = 4 \sinh^2(y_0/2) + (16/\kappa R) [\cosh(y_0/2) - 1]. \quad (3)$$

Eq. (3) is inconsistent with the boundary condition implied by the planar approximation used in its derivation, namely that $s = -2 \sinh(y_0/2)$. Since good physical arguments support the contention that the integral is dominated by the contribution near the surface,⁵ an erroneous boundary value may be expected to dominate the answer. The central feature of the present work lies in replacing the above planar approximation by a similar functional form, but with self-consistent normalization of the boundary value: $(dy/dx) = -[s/\sinh(y_0/2)] \sinh(y/2)$. The second integration then evaluates to

$$s^2 = 4 \sinh^2(y_0/2) + 8s [\cosh(y_0/2) - 1] / [\kappa R \sinh(y_0/2)], \quad (4)$$

which replaces Eq. (3) as the basic equation of the dressed micella theory. Setting $z = \cosh(y_0/2)$, Eq. (4) becomes

$$(4z^2 - \alpha)^2(z+1) - \beta^2(z-1) = 0, \quad (5)$$

with $\alpha = s^2 + 4$ and $\beta = 8s/\kappa R$, from which the surface potential y_0 may be obtained by solving for z given any value of the scaled charge s . The derivation of the micellar degree of ionization δ then follows that given by Evans et al., yielding (after some lengthy and tedious algebra) the remarkably simple analytic result

$$\delta = 1 - (4/\kappa R s) [(1+w^2)^{1/2} - (1+\kappa^2 R^2)^{1/2}], \quad (6)$$

where $w = (\kappa R/2)(z+1)$. Reference to Fig. 5.8 shows that Eq. (6) gives a generally good description of micellar ionization over a wide range of κR .

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Fig. 5.8. Theoretical vs experimental degrees of ionization δ for micelles formed by the indicated surfactants at several ionic strengths, encompassing the range $0.19 < \kappa R < 12.7$. The theoretical values are computed without fitting, using parameters derived from SANS experiments. The circled points are for systems with a high concentration of added Br^- , for which polarizability effects (not included in the present theory) are expected to be important.

SANS STUDY OF LIPOPOLYSACCHARIDE MICELLES¹

John B. Hayter Mildred Rivera²
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A variety of physical techniques has been used to measure the architecture and conformation of bacterial lipopolysaccharide (LPS). While some investigators suggest that extracted LPS exists generally in bilayer form,³ others have indicated that LPS may form nonlamellar aggregates,⁴ especially under conditions of high pH. The primary goal of the present study was to confirm recent suggestions⁵ that, at pH values above 9.0, LPS self-assembles into long tubular micelles and to obtain quantitative estimates of the micellar dimensions in solution. To this end, we subjected the LPS suspensions to hydrodynamic shear during small-angle neutron scattering (SANS) experiments, so that any anisotropy in the aggregates appeared as an equivalent asymmetry in the two-dimensional SANS scattering patterns.⁶

LPS was isolated from *Escherichia coli* strain D21f2 and was purified by differential centrifugation. The purity was verified using colorimetric assays. The sodium salt was obtained by dialysis against NaEDTA, and the sample was lyophilized, weighed, and resuspended for the SANS measurements at 10 mg/mL in either 50-mM sodium borate (pH 9.0-9.5) or sodium phosphate (pH 6.0 and 7.4) and five H₂O/D₂O ratios. The pH was measured with a combination glass electrode, without correction for the presence of D₂O. Absolute intensity contrast variation measurements as a function of the H/D ratio at pH 9.1 yielded an average micellar weight of $11 \pm 1 \times 10^6$ Daltons, corresponding to a mean aggregation number of 4860 ± 500 . The variation of intensity $I(Q)$ with momentum transfer Q differed significantly at pH 9.1 from that at either lower or higher pH. In particular, the Kratky plots [$Q^2 I(Q)$ vs Q] at pH 6.0 and 7.4 are consistent with loosely coiled tubular micelles of diameter $2a \approx 10$ nm and several hundred nm in length, whereas at pH 9.1, these plots develop a qualitatively different structure. A preliminary analysis shows that the latter is consistent with loose pairing of tubular micelle sections.

Anisotropic scattering patterns were observed when a viscous shear, G ($0 < G < 2 \times 10^4$ s⁻¹), was applied in the temperature range 10-25°C. The anisotropy was more pronounced at lower temperatures, and it was significantly pH dependent (Fig. 5.9). Analysis in terms of the rotational diffusion of rod-like segments shows that the characteristic stiffness length is of order 100 nm at pH 9.1 and is smaller at higher or lower pH. This increased rigidity is consistent with the tentative conclusion that some form of correlation develops between pairs of tubular sections at pH 9.1. The pH specificity may indicate that the conformational changes are driven by charge interactions within and between the polar headgroups of the monomers forming the micelles; such interactions are known to have profound influence on the shapes of micelles formed by smaller surfactant molecules. Independently of any model of the interactions, however, we are able to conclude firmly from the scattering asymmetry that highly

Fig. 5.9. SANS asymmetry, measured as the axial ratio of constant intensity contours for D21f2 LPS as a function of applied shear G at several temperature and pH values.

anisotropic micelles having a maximum rigidity at pH 9.1 are formed by LPS in solution.

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SHAPE ANALYSIS OF THE HISTONE OCTAMER IN SOLUTION¹

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Recently, two low-resolution x-ray crystal structures of nucleosome core particles^{3,4} and a 3.3-Å resolution map of the histone octamer⁵ were published. The histone octamer structure differed surprisingly in shape from that of the histone octamer in core nucleosomes as shown by the crystallographic studies. The discrepancy was addressed by proposing that core nucleosomes are artifacts generated by removing H1 and linker DNA from chromatin, concluding that crystallographic studies of core particles generate maps of structures which do not represent the native chromatin subunit.⁵

Since small-angle neutron scattering (SANS) affords the opportunity to make direct measurements of the size and shape of biomolecules in solution, we performed a SANS study of the histone octamer in conditions similar to those employed for crystallization.

In 2 M NaCl the radius of gyration R_g is approximately 30.0 Å, while it ranges from 32.1 to 32.7 Å in $(\text{NH}_4)_2\text{SO}_4$. These values are larger than the 28.4-Å R_g calculated from the histone portion of the x-ray crystal structure of the core nucleosome.⁴

The length distribution functions $P(r)$ for the octamer in various experimental conditions are shown in Fig. 5.10. Examination of the R_g data in Fig. 5.10 reveals several features.

Fig. 5.10. $P(r)$ functions for (---) histone core from nucleosome x-ray structure; (—) histone octamer in 2 M NaCl; and (-.-) histone octamer in 3.5 M $(\text{NH}_4)_2\text{SO}_4$.

First, the octamer in 2 M NaCl is slightly larger than the octamer in the core particle crystal structure, although its shape, as judged from the shape of the length distribution function, is similar to that of the core particle octamer. The maximum chord length through the molecule in 2 M NaCl is about 90 Å, compared with about 85 Å for the octamer in the core particle. Second, in 3.5 M $(\text{NH}_4)_2\text{SO}_4$, the octamer appears significantly larger and more extended than it does in either 2 M NaCl or core particles. According to the $P(r)$, the longest chord through the octamer in $(\text{NH}_4)_2\text{SO}_4$ is at least 110 Å and perhaps as great as 130 Å.

To analyze the scattering data for the shape of the octamer, scattering was calculated for homogeneous ellipsoidal and cylindrical models. The R_g of each model was maintained at the experimentally determined value while axial ratios were varied. In all cases ellipsoids yielded the best fits. The length distribution function analysis and best ellipsoidal approximations of the 2 M NaCl and core nucleosome octamers show that the maximum chord through these two structures is about 20 Å shorter than through their $(\text{NH}_4)_2\text{SO}_4$ counterpart.

A comparison of the compact octamer in core nucleosomes with the octamer structure suggests some of the changes which may be involved in the transition of the compact octamer to its extended conformation. Figure 5.11 shows a schematic comparison of the crystallographically determined structures of (a) the histone octamer in $(\text{NH}_4)_2\text{SO}_4$ and (b) the nucleosome core particle.^{3,4} Structure (a) is similar in size and shape to the octamer in 3.5 M $(\text{NH}_4)_2\text{SO}_4$ described in this study. In the presence of DNA under physiological solvent conditions, the histone subunits associate more tightly, as in (b).

Fig. 5.11. Schematic comparison of the crystallographically determined structures of (a) the histone octamer in $(\text{NH}_4)_2\text{SO}_4$ and (b) the nucleosome core particle.

The most important implication of this study is that the octamer crystallized in $(\text{NH}_4)_2\text{SO}_4$ and the octamer in crystals of core nucleosomes^{3,4} are very closely related, and their seeming disparities are reconcilable. The radii of gyration of core nucleosome octamer and octamer in $(\text{NH}_4)_2\text{SO}_4$ and their respective length distribution functions correspond to the major differences between the two x-ray structures. Since the histone octamer in 2 M NaCl is shaped similarly to the octamer in core nucleosome crystals, extension of the long axis of the octamer in 3.5 M $(\text{NH}_4)_2\text{SO}_4$ must be attributed to a factor other than the removal of DNA. This study demonstrates that the elongated 3.5 M $(\text{NH}_4)_2\text{SO}_4$ octamer is primarily the result of a specific salt effect and, as such, does not provide grounds for postulating an entirely different nucleosome structure.

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SMALL-ANGLE NEUTRON SCATTERING OF RABBIT MUSCLE PYRUVATE KINASE¹

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Being an important regulatory glycolytic enzyme, skeletal muscle pyruvate kinase (PK) has been studied extensively. Much information is known about the kinetic mechanism, and some aspects of its regulatory behavior have been examined.⁴ The enzyme catalyzes the reaction phosphoenol-pyruvate (PEP) + adenosine diphosphate (ADP) $\rightleftharpoons$ pyruvate + adenosine triphosphate (ATP) and requires a divalent cation, preferably Mg^{2+} , and a monovalent cation K^+ for activity. In vivo, the production of ATP plays a major role in the energy flux of the cell. Thus, PK naturally holds a key position in the glycolytic pathway, and therefore, its activity can be expected to be subjected to a pattern of regulation. L-phenylalanine (Phe) has been shown to exert an allosteric inhibition on PK⁵ although the in vivo significance of Phe as an allosteric effector is unclear.

The overall effect of Phe on the structure of PK is to cause an "expansion" of the molecule whereas the substrate PEP and metal ions, Mg^{2+} and K^+ , which are required for activity, cause a "contraction." The detailed structural features that are associated with this change are not defined. In an effort to probe further at the molecular dimensions and overall shape of PK as a function of solution conditions, this study was initiated using small-angle neutron scattering (SANS) to map structural changes that occur upon binding of ligands to PK.

The structural information about PK revealed by SANS strongly reflects that PH and ligands cause specific changes in the molecular dimensions of PK. The scattering data were collected in H_2O and D_2O , and the results from both contrasts are internally consistent. The radius of gyration decreases by about 1 Å in the presence of the substrate PEP but increases by about the same magnitude in the presence of the allosteric inhibitor Phe. With increasing pH, the radius of gyration of PK increases. Mg^{2+} and K^+ also influence the structure of the enzyme significantly since in their absence the radius of gyration again increases by about 1 Å. A summary of R_g values in D_2O and H_2O is shown in Table 5.5.

Length distribution analysis indicates that under all experimental conditions which increase the radius of gyration there is a pronounced increase observed in the probability for interatomic distances between 80 and 110 Å. These SANS results indicate a "contraction" and "expansion" of the enzyme when it is in its active and inactive forms, respectively. Using the α -carbon coordinates of crystalline cat muscle pyruvate kinase, the scattering curve was simulated, and it matches the solution scattering profile of the inactive form (Fig. 5.12). These observations are consistent since the crystals were grown in the absence of divalent cations.⁶

From the $P(r)$ distributions, it can be inferred that the major difference between the PEP- and the Phe-induced enzyme forms is an increased probability of interatomic distances in the range 80–110 Å. Since the active site lies in a cleft

Table 5.5. Summary of R_g values in D_2O and H_2O .

PD _{app}	Ligands	R_g (Å)
8.5	—	39.6 $\pm$ 0.1
	—	39.7 $\pm$ 0.1
	2 mM PEP	39.0 $\pm$ 0.1
	1 mM Phe	40.3 $\pm$ 0.1
	6 mM Phe	40.2 $\pm$ 0.1
	12 mM Phe	40.2 $\pm$ 0.1
	no Mg^{2+} , K^+	40.2 $\pm$ 0.1
7.5	—	39.6 $\pm$ 0.1
	12 mM Phe	40.3 $\pm$ 0.1
9.5	—	40.2 $\pm$ 0.1
	12 mM Phe	40.5 $\pm$ 0.2
pH		
6.5	—	40.8 $\pm$ 0.6
	15 mM Phe	41.9 $\pm$ 0.7
	2 mM PEP	39.8 $\pm$ 0.6
7.5	—	39.7 $\pm$ 0.6
	15 mM Phe	40.6 $\pm$ 0.4
	2 mM PEP	38.8 $\pm$ 0.6
8.5	—	39.8 $\pm$ 0.8
	15 mM Phe	40.0 $\pm$ 0.4
	2 mM PEP	39.3 $\pm$ 0.4

Fig. 5.12. Small-angle scattering of rabbit muscle pyruvate kinase. (—) A solid line experimental scattering curve from inactive form of pyruvate kinase. (....) Scattering curve calculated using the α -carbon coordinates of crystalline cat muscle pyruvate kinase.

between adjacent domains of each PK subunit,⁷ a reasonable possibility is that the cleft is opening and closing in response to defined solution conditions in a manner analogous to that of

hexokinase.^{8,9} PEP and the cations, Mg^{2+} and K^+ , cause the domains to move together, "priming" the enzyme for catalytic activity. Phe and high pH, on the other hand, cause this interdomain region to open up, rendering PK inactive. Inclusion of these structural data further supports the simple two-state model proposed for pyruvate kinase.¹⁰

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THE SHAPE OF FATTY ACID SYNTHASE¹

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Eukaryotic fatty acid synthetases (FAS) are multifunctional enzymes consisting of domains which are proposed to comprise the seven sites of catalytic activity.⁴ The FAS derived from animal tissues are homodimers of near 480,000 molecular weight, and each of the two subunits contains all catalytic properties.

Electron microscopy studies of the synthase isolated from animal tissue (chicken liver) show fields comprised of the molecules in various shapes and sizes. The monomer structures could be related to each other by assuming that the subunit is rod-like in open form and is capable of nearly closing to form a C. Similarly, the dimeric structures may consist of two rods or two stacked C's and forms between these. The rods measure 200 by 50 Å on their major and minor axes, respectively. If the rods close to form a ring, the diameter of the ring would be 64 Å. The C-shaped structures observed in the electron micrographs have a diameter ranging from 70 to 100 Å, representing the degree to which they are closed.

It is well known that negative staining and dehydration procedures employed in electron microscopy visualization of macromolecules may result in considerable distortion of the molecule and give rise to structures which are an artifact of these procedures. A delineation of the shape of the active form of animal FAS by small-angle neutron scattering was undertaken to distinguish which of these structures (two parallel rods or two stacked C's) represent the active form of the enzyme.

The small-angle neutron scattering measurements were carried out at 20°C over a period of

48 h. It was demonstrated that the enzyme loses no activity over this time period. The enzyme was prepared at several concentrations ranging from 5 to 15 mg/ml and was dialyzed into buffers containing D₂O or H₂O. The final D₂O concentrations in the samples and buffers were determined by neutron transmission measurements. Sample and buffer were run in pairs of matched cells to avoid systematic errors due to differences in cell thickness or cell transmission. Repeated measurements were made on samples and buffers by cycling them automatically every few hours. The various H₂O buffer runs also serve to calibrate the detector sensitivity so that the scattering can be placed on an absolute scale.

The radially averaged scattering curves of intensity $I(k)$ as a function of $k = (4\pi/\lambda)\sin\theta$ were analyzed to determine R_g by the application of Guinier's law. R_g values were also obtained as a result of applying the indirect Fourier transform method of Moore⁵ to evaluate the length distribution function $P(r)$. The $P(r)$ function is intuitively very useful since it correlates directly to the size, shape, and density distribution of a molecule. The forward scattering $I(0)$ and the maximum chord length D_{max} through the molecule are also determined in the analysis. Table 5.6 summarizes the radius of gyration R_g and D_{max} values obtained in the experiment. The D_{max} determined from the $P(r)$ analysis is 170 Å, which is in close agreement with the Stoke's diameter (164 Å) calculated from hydrodynamic measurements of the enzyme.

Table 5.6. R_g and D_{max} values for chicken liver fatty acid synthase in H₂O and D₂O.

	H ₂ O (Å)	D ₂ O (Å)
R_g (indirect fourier transform)	58.0	57.9
Guinier	58.5	57.6
D_{max}	170	165

Several modeling techniques were used to ascertain the probable shape of FAS. Geometric shape models were calculated with the constraint that each maintain its R_g at the experimental value. A sphere-shaped model was ruled out based on the poor fit by the model scattering curve to the experimental data over nearly the entire k -range. A hollow cylinder, which approximates two stacked C's gave an equally poor fit to the experimental data. Models consisting of an oblate isotropic ellipsoid, an elliptical cylinder, and a solid cylinder gave overall respectable fits to the experimental scattering data, although none fit well in the k region 0.035–0.98 Å⁻¹. The dimensions of these various models are summarized in Table 5.7.

A large number of discrete models were considered in view of the electron microscopy, indicating that the dimer may be comprised of side-by-side rods or two stacked Cs. A stacked C model

Table 5.7. Dimensions of the geometric shapes which gave best fit to the scattering data for the dimeric fatty acid synthase with a R_g of 58.5 Å.

Geometric shape	Dimensions of the radius and height (Å)
Sphere	77
Isotropic ellipse	20.9 and 92.1
Solid cylinder	83 and 21 height
Elliptical cylinder	73.5, 91.5, and 21 height
Hollow cylinder	25, 80, and 26 height

100 Å thick with inside and outside radius of 25 and 50 Å, respectively, and a 40-Å gap in each C was seen to deviate markedly from the experimental data. Two side-by-side cylindrical rods of 25-Å radius and 200-Å length gave an improved fit to the scattering data. The fit of the side-by-side rods could be improved by changing the shape to two elliptical cylinders which overlap each other. The resulting model consisted of two side-by-side elliptical cylinders with overall dimensions of $150 \times 136 \times 60$ Å and major and minor axes of 70.7 and 60 Å, respectively. The elliptical cylinders overlap by 5.2 Å. Comparison of several model scattering curves to the experimental data are presented in Fig. 5.13.

Fig. 5.13. Comparison of experimental scattering curve to scattering curves from elliptical cylinder model and stacked C's model of FAS.

This study demonstrates that the active subunit of FAS from animal tissue is a linear rod-like structure and that the dimeric enzyme consists of two such subunits arranged side by side. The stacked C's structure seen in electron microscope fields does not exist in solution according to the neutron scattering analysis.

It is likely that the stacked C's arrangement is an artifact produced as a result of the harsh negative staining and dehydration procedures employed in preparing the enzyme for electron microscopy visualization.

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SURFACE ROUGHENING AND THE FRACTAL NATURE OF ROCKS¹

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Microgeometry of rocks is a subject of much scientific interest and practical importance. Rocks can be viewed as highly disordered two-phase systems, networks of pore space, and continuous grain space, separated by a random interface. This disordered nature of materials can be used to study fundamental statistical physics and to understand how randomness on a microscale affects physical properties on a macroscale. This knowledge is of importance for extracting geological information from petro-physical measurements and may provide key information about petroleum resources and extraction applicability.

A detailed small-angle neutron scattering (SANS) study was performed to probe the virgin structure of three basic types of sedimentary rocks: sandstones, shales, and carbonates (limestone and dolomites). SANS is a powerful technique for studying the microgeometry of rocks and other porous materials, because neutrons can penetrate thick bulk samples and they are scattered by the interior structure of the sample. The scattering due to the exterior surface is negligible and thus insensitive to how the sample was prepared. Three sample-to-detector distances (3, 9, and 17 m) were employed to achieve a wider q range 0.002 – 0.2 Å⁻¹ with 4.75 Å neutrons. A total of 26 rocks from different geological origins were studied, including 12 sandstones, 4 shales, 4 limestones, and 6 dolomites. Sandstones and shales are a mixture of quartz and clay. The quartz is considered to be transparent to neutrons, due either to the low contrast or the larger size of crystallites. A fractal dimension (D) analysis³ of scattering data provides nonuniversal dimensions for sandstones and shales ranging from $D = 2.25$ to $D = 2.96$. Some typical data are shown in Fig. 5.14. These variations are very likely related to the morphology of clay as revealed qualitatively by scanning electron microscopic investigations. Thus, one may conclude that clay is the source of fractal behavior of sandstones and shales.

However, the scattering from carbonates is fundamentally different and is not consistent with a fractal dimension analysis. The geometry

Fig. 5.14. SANS intensity distributions of several sandstones and shales. The solid line is a best fit using ref. 3 to obtain the fractal dimension D .

of these rocks may be described by the solid-on-solid model with nonfractal rough surfaces. A geological reasoning is offered to explain that the formation of carbonate rocks is a relatively simple process and that the surface roughness is primarily determined by the competition between thermal fluctuations and the surface tension during a dissolution and reprecipitation process of carbonates as the environment (temperature, pressure, etc.) changes.

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X-RAY SCATTERING STUDIES OF GRAPHITE FIBERS¹

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High-performance polymer composites play an extremely important role in today's energy and other related technologies. Graphite fiber is one of the commonly used reinforcing components in composite materials. The aim of this work is to achieve a better understanding of the microstructure of graphite fibers.

Commercial carbon and graphite fibers are produced either by the controlled pyrolysis and graphitization of certain organic precursors, principally rayon and polyacrylonitrile (PAN),

or extruded pitch. The structural features of three different graphite fibers were studied via small- and wide-angle x-ray techniques. Samples included low (AS4) and high (HMS) modulus PAN and melt-spun pitch-based (VSB-16) fibers. Graphitization, degree of orientation, crystallite size, and microporosity were analyzed. By wide-angle x-ray diffraction (WAXD), VSB-16 was found to have the highest degree of graphitization, the highest degree of orientation, and the largest crystallite regions; AS4 has the poorest graphitized structure. The microvoid structures in these graphite fibers were investigated by small-angle x-ray scattering (SAXS), and the detailed scattering patterns which revealed the drastically different features are shown in Fig. 5.15. SAXS from glycerin-soaked fibers indicates the scattering at very small angles ($2\theta < 10$ mrad) is dominated either by fairly large pores or by total reflection of X rays at the fiber surface. The pores in HMS and VSB-16 fibers are inaccessible to glycerin, and those in AS4 fibers are partially accessible. The pores in PAN-based HMS and AS4 fibers are of needle-like shape, and those in VSB-16 are ellipsoidal. The porosity is 12.6%, 8.4%, and 4.5% in HMS, AS4, and VSB-16 fibers, respectively. The experimental evidence is consistent with a sheath/core fiber morphology.

Deviations from Porod's law [$I(q) \sim q^{-4}$, $q = 4\pi/\lambda \sin(\theta/2)$] were observed at large scattering angles and were attributed to scattering from fractal aggregates of carbon atoms as clusters in the graphite crystallites and/or fractal boundaries of pores. The fractal dimension of the aggregates is 2.3 ± 0.1 , 2.8 ± 0.2 , and 3.0 ± 0.2 for AS4, HMS, and VSB-16 fibers, respectively. Speculations about the fractal nature of aggregation may stimulate some new insight into the graphitization process, paracrystallinity, and the material strength of graphite fibers.

1. Summary of paper to be published.
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CHARACTERIZATION OF SPINODALLY DECOMPOSED $\text{Fe}_{0.6}\text{Cr}_{0.39}\text{Co}_{0.099}$

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Characteristic distances describing the scale of the spinodal microstructure obtained from transmission electron microscopy (TEM), atom probe field ion microscopy (APFIM), and small-angle neutron scattering (SANS) were compared. Only the decomposition of the ferrite phase into a modulated isotropic microstructure consisting of a chromium-enriched α' phase and an iron-rich phase was considered.

The SANS curves show an interference peak at $K^* = 2\pi/\Lambda$, where Λ is the periodicity in the

Fig. 5.15. SAXS isointensity contour patterns for graphite fibers HMS, AS4, and VSB-16, as measured at two sample-to-detector distances 5.12 m (above) and 1.12 m (below).

microstructure. TEM and FIM yield a direct measure of this periodicity with lineal analysis of the micrographs. From atom probe composition profiles, the average thickness of the α' phase τ and the periodicity of the modulations λ may be obtained. Atom probe microanalysis can also yield composition and volume fraction measurements not obtainable directly from SANS or easily measured with TEM.

Several of these measurements are summarized in Table 5.8. A comparison of these data reveals that the parameters related to the periodicity of the microstructure (i.e., λ from TEM and FIM micrographs, λ from AP composition profiles, $2\pi/k^*$ and linear correlation lengths from SANS, and autocorrelation analysis of the AP composition profiles) are in general agreement. The Guinier radius R_g obtained from SANS, usually taken as an estimate of the size of a precipitate, can be compared to the thickness of the α' phase τ measured from the AP composition profile. The trend in these two parameters correlates although their magnitudes are slightly different.

SANS characteristic wavelength measurements display a change in the coarsening kinetics as indicated by the discontinuity in the time exponent occurring between 24 and 72 h. After approximately the same aging time, this discontinuity is also observed in the compositions of the two

phases, the thickness of the chromium-enriched α' phase, and the change in volume fraction, but is not observed in the other AP/FIM or TEM data sets. This observation indicates that the SANS data are influenced by changes in the local composition or volume fraction in addition to the scale of the microstructure.

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HELIUM GAS CONTENT AND SIZE OF BUBBLES IN NICKEL FOLLOWING ISOCHRONAL ANNEALING

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The investigation of helium implanted into nickel has been investigated by SANS where isotopic scattering differences have been used. In an earlier study He^3 and He^4 were implanted in natural nickel. Estimates of helium density in the helium bubbles formed after annealing were made, but ambiguities in the interpretation of the ratio of scattering intensity for samples with the two isotopes led to uncertain results. In the present investigation ^{58}Ni was used so that the scattering intensity ratios yielded a

Table 5.8. Comparison of characteristic distance measurements (nm).^a

Aging time at 525°C (n)	Micrographs		Atom probe			SANS		
	FIM	TEM	Composition profile		Autocorrelation	$2\pi/K^*$	l_c	R_g
	(Å)	(Å)	λ	τ	$(k_2 - k_1)d$			
2	5.3	-	4.9	2.6	4.6	4.4	5.7	1.6
8	6.4	5.8	6.2	3.0	6.1	5.0	6.6	1.8
24	7.9	7.4	7.7	2.9	8.3	5.8	7.5	2.1
72	9.5	10.2	9.2	3.4	11.0	7.8	9.7	2.7
192	12.6	11.0	2.8	4.4	14.0	10.1	13.5	3.6
485	15.3	14.6	17.1	4.2	18.0	12.1	16.3	4.1
Time exponents								
a_0	0.20	0.22	0.22	0.10	0.25	0.19	0.20	0.18
a_1	0.16	0.22	0.18	0.05	0.24	0.10	0.12	0.11
a_2	0.23	0.22	0.27	0.14	0.26	0.25	0.26	0.23

^a λ and Λ are the mean center to center distances of the α' regions; τ is the linear thickness of the α' phase; k_1 and k_2 are the first and second maxima in the autocorrelation analysis of the composition profile; d is the distance between measurements; K^* is the scattering vector at the SANS intensity maximum, where $K = 4\pi \sin \theta / \lambda$ with 2θ the scattering angle and λ the neutron wavelength; l_c is the linear correlation length given by 2π times the ratio of the first to second moments of the scattering curve; R_g is the Guinier radius given by the $\sqrt{3}$ times the slope the straight line portion of the plot of log intensity versus K^2 ; a_0 is the time exponent (i.e., slope) of the overall log-log plot of parameter versus aging time; and a_1 and a_2 are time exponents for a two-segment representation of these data.

clear determination of the helium density. It was found that, in two-hour anneals beginning at low temperatures and ending at 1000°C, helium was collected at increasingly higher densities in the voids produced by the original He implantation. At 1000°C the bubbles became equilibrated through bubble growth, which was revealed in the analysis of bubble size.

The scattering curves reveal a bimodal size distribution which is consistent with TEM observations of large bubbles which appear preferentially at the nickel foil surface. It is inferred that the small bubbles grow in the interior of the material. From the scattering results it appears that the growth of both the large-size and small-size bubbles start at the same temperature.

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SMALL-ANGLE X-RAY SCATTERING (SAXS) INVESTIGATION OF THE METASTABLE MISCIBILITY GAP IN THE Al-Li SYSTEM

S. Spooner

A metastable miscibility gap in the Al-Li alloy system has been suggested in recent phase diagram calculations by Sigli and Sanchez.¹ Differential scanning calorimetry experiments by several investigators support the calculation through obser-

vation of endothermic reactions in the vicinity of 100°C. Direct structural verification of the miscibility gap is being undertaken in SAXS measurements of several alloys which have been heat treated at 95, 110, and 125°C. Al-Li alloys containing 4.1, 5.5, 6.5, and 7.2 at. % lithium were prepared from pure components melted in a boron nitride crucible. After solution annealing at 550°C, samples were quenched into an oil held at one of the above temperatures and decomposition proceeded for times up to 16 h. SAXS measurements on samples of the four compositions held at the three temperatures for 16 h were made at 2 and 5 m on the 10-m SAXS machine.

Distinctly different scattering patterns can be attributed to two precipitation structures. In Figs. 5.16(a) and 5.16(b) the scattering intensity is multiplied by k^2 , where k is the scattering vector. The area under the curves is proportional to the density difference times the volume fraction of the precipitate in the structure. Figure 5.16(a) shows that in the 4.1 at. % Li alloys, scattering arises from a small number of independently scattering precipitates of about 10 nm. Figure 5.16(b) shows scattering that is characteristic of a high density of small precipitates formed in the 7.1 at. % Li alloys at all three temperatures. The density and size result from a rapid decomposition process that must occur within the miscibility gap. Figure 5.17 summarizes the observations on a portion of the calculated phase diagram where the open circles indicate the structure formed by nucleation and growth and the closed circles indicate the high-precipitate density from the decomposition within

Fig. 5.16. (a) Plots of $k^2 I(k)$ versus k of the 4.1 at. % alloy aged for 16 h at 95 (short dashes), 110 (long dashes), and 125°C (solid) show scattering at small angles, which indicates the precipitation of independently scattering particles. (b) Scattering from the 7.1 at. % Li alloy shows scattering at higher angles having an interference maximum that indicates a high density of small precipitates as might be expected from a spinodal decomposition process.

Fig. 5.17. A portion of the phase diagram calculated by Sigli and Sanchez is shown with the indication of the structures found in the scattering experiments. Note that the high-density structures shown by closed circles fall within the calculated miscibility gap.

the miscibility gap. The corroboration of the calculation is very good. Further analysis of the decomposition kinetics is under way.

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DIFFRACTION

TEMPERATURE DEPENDENCE OF THE INDUCED MAGNETIC FORM FACTORS OF HEAVY FERMION SUPERCONDUCTORS¹

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The unusual electronic and magnetic properties⁸ of the heavy fermion superconductors CeCu_2Si_2 , UPt_3 , and UBe_{13} have caused speculation that the superconductivity exhibited by these substances

involves a mechanism different from that of normal Bardeen-Cooper-Schrieffer (BCS) superconductors. We have used polarized neutron scattering to study the wave vector dependent susceptibilities of these substances in hopes of shedding some light on the nature of the superconducting state.

Each single-crystal sample was placed in a cryostat with a superconducting magnet on a polarized-beam neutron spectrometer. Most of these data were taken on the HB-1 spectrometer at the High Flux Isotope Reactor, using the helium dilution refrigerator facility obtained through the U.S.-Japan Cooperative Program on Neutron Scattering. Some of the data at higher temperatures were taken at the Brookhaven High Flux Beam Reactor. Magnetic fields between 6 and 50 kOe were used, with the field direction perpendicular to the neutron scattering plane. In this configuration, the ratio of the elastic scattered intensity with incident neutron beam polarized parallel to the magnetic field to the scattered intensity with incident beam polarized antiparallel to the field is directly related to the sample susceptibility at the scattering wave vector.⁹ By measuring this ratio at various Bragg positions, the wave vector dependence of the susceptibility can be explored.

In general, the susceptibility of the magnetic electrons should have both spin and orbital components, each component showing a wave vector dependence through the appropriate form factor. In a BCS superconductor, the spin susceptibility decreases rapidly below the superconducting transition temperature. This occurrence was demonstrated several years ago using a V_3Si sample, with a polarized neutron technique identical to that employed in the present experiment.¹⁰ (The V_3Si result was checked and confirmed during the course of our experiment.) The various proposals for exotic superconductivity in heavy fermion superconductors give differing predictions for the behavior of the spin susceptibility, but several predict that there should be no great change in susceptibility below the transition temperature.

At 4 K (above T_c), the form factors measured for $CeCu_2Si_2$, UBe_{13} , and UPt_3 agree very well with calculations of the ionic Ce^{3+} and U^{3+} f-electron form factors. Preliminary results of the $CeCu_2Si_2$ measurement have been published.¹¹ The uncertainty in each measured point is about 10%, due almost entirely to neutron counting statistics.

At very low temperatures (<100 mK, well below T_c), the measured form factors for these samples are identical, within experimental uncertainty, to the 4-K results. This is also true at intermediate temperatures and for various values of magnetic field down to 6 kOe.

The lack of temperature dependence in these form factor measurements is consistent with some of the exotic superconductor theories. However, as mentioned above, these measurements are sensitive to both spin and orbital susceptibilities. It is possible that strong spin-orbit coupling effects in these materials completely mask any changes in spin susceptibility. The theory of such spin-orbit effects is currently being investigated.

These measurements show that the distributions of magnetic moments within the heavy fermion superconductors $CeCu_2Si_2$, UBe_{13} , and UPt_3 match the calculated f-electron distributions of Ce^{3+} and U^{3+} ions. No large changes in the wave vector dependent susceptibility are observed below the superconducting transitions of these samples.

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OBSERVED CORRELATIONS BETWEEN ELECTRON SCATTERING AND THE LOW-TEMPERATURE SPIRAL-MAGNETIC ORDERING IN SINGLE-CRYSTAL HOLMIUM

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Holmium is one of the rare-earth transition metals which undergoes rather complex magnetic ordering at low temperatures. Below $T_N = 131$ K the material orders antiferromagnetically by the formation of a helical spiral structure, whereby magnetic moments in a given base plane are parallel and aligned perpendicular to the hexagonal c-axis, and there exists a fixed-turn angle between the direction of alignment in consecutive base planes. The turn angle decreases monotonically with decreasing temperature down to $T_c = 20$ K, where the spiral periodicity locks in to a well-defined value and the moments lift out of the base planes, producing a conical structure and a net ferromagnetic moment along the c-axis. Previous microscopic investigations of the spiral modulation using neutron diffraction¹ and, more recently, high-resolution synchrotron x-ray diffraction² have revealed low-temperature lock-in periodicity behavior that is sample dependent, where both commensurate and incommensurate modulations have been observed. Although it is known that the ordering arises from a delicate balance and interplay between the predominant indirect magnetic exchange interaction and other contributions such as the anisotropic magnetoelastic and crystal field energies, a complete and quantitative theoretical description of the phenomenon has not yet been possible.³

Here we report the observation of low-temperature lock-in behavior that differs for the same holmium sample after having undergone different

vacuum heat treatments, and we find correlations between these effects and the residual electron scattering. For this study we used the high-resolution double-perfect-crystal small-angle neutron diffractometer at the High Flux Isotope Reactor to measure the temperature-dependent scattering angle of the $(000)^+$ spiral magnetic satellite in a high-quality holmium single crystal grown at ORNL.

The sample was in the form of a thin plate, about $13 \times 7 \times 2 \text{ mm}^3$, with the c - and b -axes in the plane of the plate. Scattering measurements were performed in transmission with the b -axis vertical, using neutrons of $1.3\text{-\AA}$ wavelength, with the specimen situated between $\langle 113 \rangle$ -oriented perfect Si monochromator and analyzer crystals. To enable four-terminal electrical resistance measurements, a separate sample was sliced from the same holmium ingot and was shaped such that the long transport direction was a crystal a -axis. After initial characterization in the "as-grown" state, both samples were annealed together in a Ta susceptor and were heated by rf induction inside an all-metal UHV chamber at pressures $< 1 \times 10^{-9}$ Torr.

The results of the heat treatments and scattering measurements are summarized in Fig. 5.18. As grown, the a -axis sample had a residual resistance ratio $r = R(295 \text{ K})/R(4.2 \text{ K}) = 56$, among the highest we have found reported in the literature. As seen in Fig. 5.18, the lock-in modulation wave vector is near the commensurate value $1/6 c^*$, which has been observed previously. However, peak widths for $T < 20 \text{ K}$ were broad and skewed toward larger K , suggestive of recent work reporting coexistence of domains having both $2/12 c^*$ and $2/11 c^*$ modulation.² In all cases the observed peak widths are substantially larger than the calculated instrumental resolution, indicating a distribution in the spiral periodicity. Moreover, the peaks are found to increase in breadth with lower temperatures.

The high-temperature anneal at 1025°C was culminated with a relatively rapid cooldown, which resulted in an increase in the residual resistivity such that r dropped to 11. Repeating the scattering measurements, we found the low-temperature modulation centered at $K = 2/11 c^*$ but with skewing of the peaks toward lower K . The correlations with r were confirmed by a third extended duration anneal at 510°C , which yielded a partial recovery to $r = 36$ and an observed lock-in near $1/6 c^*$ at $T = 4.2 \text{ K}$. In this case, however, there was increased hysteresis just below 20 K , with some peaks indicating broad distributions centered near $2/11 c^*$ and $2/12 c^*$. Based on the present results, therefore, we might speculate that the sample of Ref. 2 had a resistance ratio somewhere between 36 and 56, although it is not stated in the article. The detailed microscopic mechanisms behind the above observations are uncertain, but we may develop a reasonable picture for the origin of the correlation. The sample contains some impurities (probably oxygen due to the large affinity) that are initially clustered or precipitated out of solution in the as-grown crystal. This leaves the crystal matrix relatively pure and the residual electron scattering small. The high-temperature anneal (and rapid cooldown)

Fig. 5.18. The scattering vector K of the $(000)^+$ magnetic spiral reflection in holmium as a function of temperature. (a) The full temperature range explored. (b) Expanded view of low-temperature data. The legend indicates the sample thermal anneal history, residual resistance ratio r , and the thermal history (T increased or decreased) of a given measurement. The low-temperature modulation is seen to cluster near $2/12 c^*$ and $2/11 c^*$, depending on r . Here, $c^* = 2\pi/c$ is the holmium c -axis reciprocal lattice vector. The curves are visual guides.

homogenizes the impurities into solution, thereby increasing the residual resistivity. Finally, the low-temperature anneal at 510°C partially precipitates the impurities, again drawing them out of solution.

Credence is lent to this scenario by additional SANS results taken on the 30-m machine, which revealed scattering from larger microstructures in the as-grown and 510°C-annealed sample than in the sample when annealed at 1025°C. The delicate energetic balance that determines the low-temperature lock-in behavior apparently is biased by the impurity distribution. One possibility is an alteration in the anisotropic magnetoelastic and/or the exchange energies due to small internal strains from the solute atoms or precipitates. For example, it is known that thermal history and internal strains can affect the bulk magnetic and elastic properties of other rare-earth metals.⁴

Efforts are in progress to clarify these observations by extending the properties studied using a purer starting material.

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THE WIDE-ANGLE NEUTRON DIFFRACTOMETER¹

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The wide-angle neutron diffractometer (WAND) built in cooperation with the Japanese Atomic Energy Research Institute at Tokai, Japan, has been in routine use during the period covered by this report. Japanese scientists have carried out several experiments using the unique features of this facility, and their results are described elsewhere in this document in detail. In addition to these experiments, some major modifications to the machine have been made. One megabyte of computer memory has been added so that more programs can be used simultaneously. Also, routine data links to ORNL's large computer systems are now in use. A dial-up telephone connection modem has been added to the computer so that the status of experiments can be monitored from any terminal with access to a phone and modem.

A significant decrease in gain of the detector was noticed, and this had to be compensated for by an increase in gain of the AIM-204 electronic module. This probably indicates that the gas in the detector is becoming contaminated with O₂ and H₂O vapor from outgassing. This process seems to have reached saturation in the past couple of months and hopefully has now stabilized.

Significant progress has been made in data analysis programs which are too big to be run on the PDP 11/44 on-line computer. The Solid State

Division Data General Eclipse computer has been used primarily to write programs which, in addition to many of the same calculations that the PDP 11/44 can do on-line, can also draw high-quality contour maps and projections of intensity data in reciprocal space. Rietveld profile analysis of powder patterns is also being implemented. It would not be practical to carry out these kinds of calculations on the on-line PDP 11/44 computer.

Archive data storage is becoming a problem due to the large number of relatively expensive disk packs needed to store data. Magnetic tape storage seems to be the only logical answer to this problem and would have the further advantage of making it possible for users to take copies of their data back home with them. This method is being investigated presently.

1. Research carried out at the Oak Ridge National Laboratory under the U.S.-Japan Cooperative Program on Neutron Scattering.
2. Guest scientist from the Japan Atomic Energy Research Institute, Tokai-mura, Japan.

OBSERVATION OF THE NEUTRON DIFFRACTION ROD PATTERN OF YFe₂O₄ WITH THE WIDE-ANGLE NEUTRON DIFFRACTOMETER (WAND)¹

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H. R. Child

Iron rare-earth oxide of the form RFe₂O₄ has a basically hexagonal-layered crystal structure and shows a strongly two-dimensional magnetic character.^{3,4} Crystallographically, all iron atoms occupy 18h sites in the hexagonal R $\bar{3}m$ structure, but electronically, divalent and trivalent irons coexist on the equivalent sites. Like magnetite, strong electron exchange interactions exist between iron atoms in the same layer. Consequently, magnetic ordering depends on the stoichiometry, namely on the oxygen content. A two-dimensional magnetic ordering develops in oxygen-deficient YFe₂O₄, while a three-dimensional ordering occurs in stoichiometric YFe₂O₄.

With a conventional double-axis neutron diffractometer, a one-dimensional diffraction rod in the reciprocal space associated with two-dimensional magnetic ordering would be measured point by point along the rod. However, a curved position-sensitive one-dimensional detector measures the diffraction intensity along an arc on a certain plane in the reciprocal space. When the sample is turned about an axis perpendicular to the plane defined by the counter, the arc scans the plane. Figure 5.19 shows the contour map of the diffraction intensity of an oxygen-deficient YFe₂O₄ sample at 9 K in the reciprocal (hhi) plane measured with WAND. The contours are drawn between 0 and 500 counts/monitor unit with an interval of 50 counts/monitor. The development of (1/3 1/3 t), (2/3 2/3 t), and (4/3 4/3 t) diffraction rods is obvious at this temperature. Some weak circular contours which are centered on the origin are polycrystalline diffraction rings coming from the aluminum sample container. Though a fan-shaped five-degree moving collimator

Fig. 5.19. Contour map of neutron diffraction in the (hkl) plane of YFe_2O_4 . Rods of intensity along the lines $(1/3 \ 1/3 \ l)$, $(2/3 \ 2/3 \ l)$, and $(4/3 \ 4/3 \ l)$ are observed indicating two-dimensional magnetic order.

is installed in the WAND to reduce background coming from scattering by any materials in the main neutron beam, including the background by air scattering, it cannot be made fine enough to remove the scattering from the sample container without losing intensity unreasonably. Tails are seen for some strong nuclear Bragg peaks $(1 \ 1 \ 0)$, $(0 \ 0 \ 9)$, $(0 \ 0 \ 12)$, and $(1 \ 1 \ 12)$ toward low angles (i.e., toward origin) along the counter arc. They are due to counter characteristics for high counting rates. Weak diffraction points at $(1/2 \ 1/2 \ 0)$, $(1/2 \ 1/2 \ 9/2)$, $(1/2 \ 1/2 \ 6)$, and $(1/2 \ 1/2 \ 12)$ are due to a slight half wavelength contamination which was not completely eliminated by the graphite filter. It should be noted that the contour levels are set low as described above to show the weak scattering, thus sacrificing information concerning the strong peaks. The $(1 \ 1 \ 0)$ spot, for example, is as strong as 50000 in the same units, while the $(1/3 \ 1/3 \ l)$ rod is no higher than 500 and the strongest aluminum circular diffraction $(1 \ 1 \ 1)$ is lower than 200. Most of the tails of the strong fundamental spots are also lower than a few hundred.

The present results show very clearly that the WAND is very efficient in investigating low-dimensional magnetic materials because of the

comprehensiveness of the result. The wide-angle counter collects 2048 channels of data while at the same time covering 130° of scattering angle. The original data collected for Fig. 5.19 are comprised of about 1000 measurements; in other words, Fig. 5.19 is drawn by treating about 2 million data points accumulated on the disc file. From the accumulated data, it is possible to produce other displays, for example, a section of Fig. 5.19 along a certain line like $(1/3 \ 1/3 \ l)$ or a two-dimensional perspective profile.

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quadrant in the reciprocal space can be carried out in several days, accumulating diffraction intensity at about 20 million points in the 2θ-ω-φ space or the reciprocal space.

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A FURNACE FOR RAPID CHANGE OF TEMPERATURE¹

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M. Iizumi²

Real-time experiments on time-dependent phenomena are one of the most interesting research subjects using the wide-angle neutron diffractometer (WAND) which was installed at the High Flux Isotope Reactor. In some alloy systems, time-dependent phenomena such as order-disorder transitions or phase separations take place at high temperatures. To investigate them in detail, it is necessary to change the temperature as rapidly as possible over a wide temperature range. Therefore, we designed and fabricated a new furnace which is able to control temperature changes at a very high rate. Its performance is sufficient to carry out some kinetic measurements by the use of WAND.

The furnace makes use of circular infrared lamps for rapid heating and high-pressure gas jets for rapid cooling. A schematic drawing of the furnace is shown in Fig. 5.22. A sample (A) is mounted on a holder (B) which is made of transparent quartz. These are placed in a quartz tube (C) (diam 80 mm) which can be evacuated. The heating elements are a pair of circular infrared lamps (D) over and under the sample. To get a high heating rate and uniform temperature, the reflector (E), which is a gold-coated aluminum alloy 2 mm in thickness, roughly focuses images of the lamps on the sample. The high-pressure gas blows against the sample from many small holes in two rings (F) which are also made of quartz. The gas flow is controlled by valves (G). The sample temperature is measured by two chromel-alumel thermocouples. A test showed that a heating rate of 1000°C/min can easily be obtained. In cooling, the average cooling rate was about -500°C/min.

Using this furnace on the WAND, the relaxation processes of the order-disorder transitions in CuZn and Ni₃Mn alloys were investigated. Observations were made on the decay of superlattice peaks in the ordered state and the growth of short-range order (SRO) in the disordered state. It is well known that CuZn exhibits a second-order transition; therefore, the time constant is expected to be quite short. However, an electrical resistivity experiment indicated that the time constant for growth of SRO at about 5 degrees above the transition temperature is over

Fig. 5.22. Schematic drawing of the furnace: A - sample, B - holder, C - quartz tube, D - infrared lamp, E - reflector, F - ring for gas blow, G - valve for high-pressure gas.

one hour.³ If the time constant is of this order of magnitude, the process should be easy to observe. However, our measurements showed a time constant for the decay of a superlattice peak of less than 5 s. In this work, the (111) superlattice intensity was observed after the temperature was suddenly changed from 450 to 465°C (the transition is at 470°C). Ten-second time slices were stored for the first 5 min, with 120 repetitions to build up counting statistics. The intensity fell by a factor of about 5 from its value at 450°C on a time scale too short to be observed by this technique. That is, the first 10-s time interval gave the same result as all succeeding intervals. The sample temperature changed to close to the final value within a few seconds but then exhibited some damped oscillations, so it was not reasonable to attempt shorter time slices. The experiment on the growth of SRO investigated by changing the temperature from 550 to 475°C also showed that the time constant is short. Thus our result is rather different from that of the electrical resistivity measurement. Although we cannot explain this difference at present, the result obtained here seems to be consistent with the neutron diffraction study of this alloy on SRO.⁴ In that study, SRO peaks at various temperatures were clearly observed in a series of quick scans of 90-min duration.

For Ni₃Mn, it is known that the transition is first order and that the time constant is fairly long.^{5,6} The (211) peak was observed after a sudden temperature change from 470 to 490°C (the transition temperature is about 510°C). Ten-min time slices were accumulated for the first 12 h. Figure 5.23 shows the decay of the integrated intensity with time. The time constant obtained from these data is about 30 min. This result is

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Fig. 5.23. Integrated intensity of the (211) superlattice peak of Ni_3Mn as a function of time.

consistent with the previous reports. The growth of SRO was investigated by the change of temperature from 600 to 515°C. Since the intensity was small and had a broad distribution, the counting statistics were poor. However, the result indicates that the time constant is over 10 min.

In conclusion, rapid temperature changes can be accomplished satisfactorily by this system. The temperature of a sample can be changed within a second for a change of about 10 degrees. Although a small oscillation of the temperature was observed after a rapid change, this should be reduced by the use of a higher performance temperature controller. Then it would be possible to investigate time-dependent phenomena with a time constant of the order of a second.

ORDERING KINETICS IN Ni_3Mn

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H. R. Child

Recently the kinetics of first-order phase transitions have received great attention from both theoretical and experimental viewpoints. In these time-dependent phenomena, order-disorder transitions are one of the most fundamental problems. Hence, many theoretical studies and computer simulations have been done on this subject. As a result, it has been appreciated that in the late stage of the transition the growth of the ordered region follows a power law in time and that the structure factor of a superlattice peak indicates scaling behavior with respect to space and time.

To study this ordering process, a Ni_3Mn alloy is an ideal system for two reasons. (1) Since Ni and Mn atoms have similar size, the elastic strain generated by the phase transition should be small. (2) The time constant involved is fairly long. Therefore, a neutron diffraction study on the relaxation process of this alloy was performed by Collins and Teh,³ and one on the ordering kinetics was done by Wakabayashi.⁴ However, as they used a conventional neutron diffractometer and an ordinary furnace, it took over 30 min after a change of temperature for the first diffraction pattern to be obtained. Hence, it was impossible to observe the early stage of the process. In contrast, our system using the wide-angle neutron diffractometer (WAND) and a furnace for rapid change of temperature is suitable for clarifying the behavior in the very early stage. We utilized this system to investigate the whole process from the initial to final stage of the order-disorder phase transition in Ni_3Mn .

Figure 5.24 shows the time dependence of the (211) superlattice peak after the temperature was abruptly changed from 600 to 470°C across the transition temperature around 510°C. The temperature of the sample reached equilibrium in about 15 s. In order to get the initial stage result, time-resolved measurements for 1 min were done for the first 30 min. To increase counting statistics, these measurements were repeated 30 times, and data for 1-min intervals were accumulated. For the final stage, time-resolved measurements for 6-min intervals were repeated 5 times. As shown in Fig. 5.24, it is observed that the peak becomes sharp with time. This shows the development of order. The width of the peak is shown as a function of time in Fig. 5.25. It is found that the time dependence of the width follows a power law which shows crossovers; at the beginning, the width remains almost constant, but after time τ_0 , it follows a power law with an exponent of about $1/4$, and then after time τ_1 , the exponent changes to $1/2$. The initial stage when the width remains almost constant is considered to be the period of the formation of the ordered regions. In the next stage, these ordered regions start to grow. For this stage, Furukawa recently proposed exponents of $1/3$ and $1/4$, which come from a diffusion-reaction process.⁵ Our result in the intermediate stage suggests that the exponent is $1/4$ rather than $1/3$. The late

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Fig. 5.24. Time dependence of the (211) superlattice peak of Ni_3Mn when the temperature was abruptly changed from 600 to 470°C.

Fig. 5.25. Time vs width. The exponent of the power law shows crossovers at τ_0 and τ_1 . (τ_0 indicates the width at τ_0 .)

stage was most extensively studied. The exponent of $1/2$ was predicted by several authors by considering the motion of the interfaces,^{6,7} and this prediction was verified by experiments on Cu_3Au by Hashimoto et al.⁸ and Noda et al.,⁹ and on Ni_3Mn by Wakabayashi.⁴ Our result in the late stage also agrees with these results. Thus, the result indicates that the ordering process changes from an initial stage of the formation of ordered regions to an intermediate stage of slow growth by a diffusion-reaction process and then to a late stage of fast growth by motion of the interfaces. The time dependence of the integrated intensity of the superlattice peak indicates that the ordered regions are formed in a very early stage.

Up to the present, several authors have reported that ordering kinetics show a critical behavior near the transition temperature.^{8,9} However, the detailed properties are not clear yet. Therefore, we investigated the temperature dependence of the ordering kinetics. The results at various temperatures show the same behavior as the result at 470°C with respect to the power law. Hence, we could obtain the temperature dependence of the time τ_0 , when the width begins to follow the power law of $1/4$. The result indicates that τ_0 diverges as the temperature approaches the transition temperature T_c , which was estimated as 509°C. The slope of the plot of $(T_c - T)$ versus τ_0 on a log-log scale is about -1. This value is interesting since Collins and Teh obtained a similar value in their experiment on the relaxation process in the ordered state.³ Theoretically, Langer¹⁰ discussed critical behavior of the time constant and obtained the value of -1. Furthermore, Suzuki also proposed $(T_c - T)^{-1}$ dependence of the time constant in his scaling theory of the growth of order.¹¹ However, the correspondence of these theories with experiment is not clear at present. More extensive work is necessary.

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CRYSTALLIZATION KINETICS IN AMORPHOUS Fe-B-Si AND Fe-P-Si ¹

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Since the crystallization behavior and thermal stability of amorphous metals closely relate to their properties as materials, many studies have been done using a variety of techniques. Although diffraction experiments are a powerful technique for investigating these properties from a microscopic viewpoint, extensive work has not yet been done because of the difficulty of in situ experiments in this technique. However, because the wide-angle neutron diffractometer (WAND) is able to do real-time experiments, we investigated the kinetics of crystallization of amorphous $\text{Fe}_{79}\text{B}_{13}\text{Si}_9$ at 450, 465, 480, 500, and 520°C and $\text{Fe}_{80}\text{P}_{14}\text{Si}_6$

at 395, 410, 430, and 450°C. The WAND made it easy to follow the growth of Bragg peaks as a function of time at each temperature.

The time dependences of the fraction of the crystal phase in FeBSi at various temperatures are shown in Fig. 5.26. These data were fitted to the Avrami equation,

$$1-x = \exp [-(Kt)^n], \quad (1)$$

where x is the fraction, K is the rate, and the constant n is the exponent which relates to the mechanism of nucleation and growth in the transition. The result shows that the exponents n at various temperatures are almost equal to 2.5. This result indicates that the transition takes place by the same mechanism over a wide temperature range. In other words, when time is scaled by a characteristic time at each temperature, the crystallization kinetics follows a universal form. The exponent of 2.5 suggests that the crystallization mechanism is a constant nucleation and diffusion controlled three-dimensional growth.

The temperature dependence of the rate K can be fitted to the Arrhenius law,

$$K = K_0 \exp (-E_a/kT), \quad (2)$$

where K_0 is some constant, E_a is the activation energy, k is the Boltzman constant, and T is the temperature. From this relation, the activation energy E_a is estimated at 4.0 ± 0.3 eV.

The results for FePSi were analyzed similarly.

1. Research carried out at the Oak Ridge National Laboratory under the U.S.-Japan Cooperative Program on Neutron Scattering.
2. Guest scientist from Japan Atomic Energy Research Institute, Tokai-mura, Japan.

Fig. 5.26. The time dependence of the fraction of crystal phase in $\text{Fe}_{79}\text{B}_{13}\text{Si}_9$ at various temperatures.

INELASTIC SCATTERING

MOMENTUM DISTRIBUTION OF ^3He

H. A. Mook

Liquid ^3He and ^4He are materials whose properties are determined to a large extent by quantum effects. Of particular importance is the fact that ^4He is subject to Bose-Einstein statistics while ^3He is a Fermi liquid. Inelastic neutron scattering is capable of measuring the single-particle momentum distribution of these materials which then can be compared with theoretical calculations. Such a measurement is best done with the use of high-energy neutrons so that the impulse approximation (IA) is valid. However, high resolution is needed in the experiment to see details of interest so that medium-energy neutrons are generally used and the data are analyzed in such a way that errors from the nonvalidity of the IA are minimized. In this manner, considerable information has been obtained for ^4He including the observation of Bose condensation.

^3He , however, has a very large cross section for neutron absorption (10,000 b) so that measurements are difficult. Nevertheless, by using the ultrasonically pulsed time-of-flight spectrometer, reasonable data could be obtained, and the scattering function $S(Q, E)$ for ^3He was measured at 30 different momentum transfers varying from 3 to $9 \text{ \AA}^{-1}$. From these data, the momentum distribution was obtained for ^3He for a temperature of 0.37 K, where the material is in the Fermi-liquid regime. Interactions in the liquid ensure that there are modifications in the statistical behavior of the liquid from an ideal gas; however, as a first approximation, comparison with the ideal gas behavior is reasonable. Figure 5.27 shows the measured momentum distribution for ^3He compared to the ideal gas Fermi distribution given by

$$n(p) = \frac{1}{\exp[(E - E_F)/k_B T] + 1}. \quad (1)$$

Least-squares analysis showed that the best fit was obtained for a Fermi temperature $E_F/k_B =$

Fig. 5.27. $n(p)$ for ^3He at 0.37 K. The solid line is a least-squares fit by the ideal-gas Fermi distribution for $T_F = 1.8$ K.

1.8±0.2 K. This result is in good agreement with generally accepted values and represents the first direct observation of the Fermi surface of ^3He by neutron scattering.

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TEMPERATURE DEPENDENCE OF THE MAGNETIC EXCITATIONS IN Gd

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Much of the current interest in the spin fluctuations of ferromagnets at finite temperatures centers around the question of whether spin-wave-like modes persist at $T > T_C$. In the case of the Heisenberg ferromagnets, both theory and experiment suggest that damped spin-wave modes do persist at $T > T_C$, at least in the region of large wave vector q . Recently, we reported² an inelastic neutron scattering study of the spin fluctuations in the Heisenberg ferromagnet Gd in which we concluded that spin-wave-like modes do not occur in the $\langle 00L \rangle$ direction for $T/T_C > 1.09$ even at the zone boundary. This was an unexpected result since spin-wave modes apparently persist to $T/T_C = 2$ in the similar Heisenberg systems EuO and EuS. This difference in behavior was attributed to the energetics of the systems relative to kT ; e.g., the zone boundary spin-wave energies of EuO and EuS are comparable to kT_C while that of Gd along $\langle 00L \rangle$ is only about 0.6 kT_C . It was suggested that spin-wave-like modes should persist in Gd along $\langle hh0 \rangle$ where the zone boundary spin-wave energy becomes approximately equal to kT_C . Subsequent $\langle hh0 \rangle$ data showed this to be the case. Here, we give a brief comparison of the temperature dependences of the magnetic excitation spectra of Gd in the $\langle 00L \rangle$ and $\langle hh0 \rangle$ directions.

The neutron cross section for magnetic scattering from a Heisenberg ferromagnet is proportional to the dynamic structure factor, which can be written as

$$S(q, \omega) = (g^2 \mu^2)^{-1} \chi(q) \omega (n_\omega + 1) F(q, \omega). \quad (1)$$

Here, $\hbar\omega$ is the energy transfer, n_ω is the Bose factor, and $F(q, \omega)$ is the spectral weight function which describes the spin dynamics. Several approximate forms have been suggested for $F(q, \omega)$ at $T > T_C$. One of the more useful of these is the damped harmonic oscillator form, which can be written as

$$F(q, \omega) = \frac{2}{\pi} \frac{\langle \omega_q^2 \rangle}{q} \frac{\beta q}{(\omega^2 - \langle \omega_q^2 \rangle)^2 + 4 \beta^2 \omega^2}, \quad (2)$$

where $\langle \omega_q^2 \rangle$ is the second moment of the frequency distribution and βq is the damping parameter related to the relaxation time of the random forces. This function reduces to the correct limits at both low and high temperatures and includes correlations via the damping, so it is expected to have a wide range of applicability.

The effects of temperature on the magnetic excitations at large q are illustrated in Fig. 5.28, which shows the spectra obtained at $Q = 003$ ($q = 2\pi/c$) for several temperatures near T_C . At 250 K, the spectrum shows a well-defined spin-wave peak near 2.9 THz. With increasing temperature, this peak moves down in energy and becomes broader. In addition, an asymmetry develops with extra intensity being shifted into the low-energy region. The raw intensity data shown in Fig. 5.28 were fitted to a constant background plus a magnetic intensity corresponding to a convolution of Eq. (1) with the instrumental resolution and with $F(q, \omega)$, given by the damped harmonic oscillator function of Eq. (2). The solid curves in Fig. 5.28 and Fig. 5.29 represent such fits with the parameters given in Table 5.9. The peak in $F(q, \omega)$ appears at

$$\omega_{\text{PEAK}}^2 = \langle \omega_q^2 \rangle - 2 \beta q^2, \quad (3)$$

so that $\omega_{\text{PEAK}} = \langle \omega_q^2 \rangle^{1/2}$ only when βq is small. The minimum condition for spin-wave-like behavior is that $\omega_{\text{PEAK}} > 0$. The parameters of Table 5.9 show that this condition is met at 320 K for the zone boundary spectrum along $\langle hh0 \rangle$ but not along $\langle 00L \rangle$.

The existence of spin-wave modes at $T > T_C$ is presumably associated with the presence of magnetic short-range-ordered regions that exist over long enough correlation lengths and time scales to support short-wavelength, high-frequency spin waves. To examine this relationship, we define a critical wave vector q_c as the q value where ω_{PEAK} becomes finite and a critical energy $\hbar\omega(q_c)$

Fig. 5.28. Magnetic excitation spectra of Gd at $Q = 003$ for several temperatures near T_C .

Fig. 5.29. Magnetic excitation spectrum of Gd at $Q = 1/2 \ 1/2 \ 2$ at $T = 320 \text{ K}$.

Table 5.9. Characteristic frequencies and damping parameters of Gd.

Q	T	$\langle \omega_q^2 \rangle^{1/2}^a$	β_q^a	ω_{PEAK}^a
003	250	2.93	0.32	2.89
003	273	2.68	0.75	2.46
003	282	2.53	0.97	2.13
003	287	2.56	1.24	1.87
003	292	2.39	1.29	1.54
003	320	2.17	1.54	0
1/2 1/2 2	320	3.20	1.72	2.08

^aFrequencies are in THz.

as the low-temperature spin-wave energy at q_c . Both q_c and $\hbar\omega(q_c)$ approach zero at temperatures just below T_c but become finite at $T > T_c$. In molecular field theory, the inverse correlation length κ_1 is proportional to $[(T-T_c)/D]^{1/2}$ so that $\hbar\omega(q_c) = Dq_c^2$ should be proportional to

$(T-T_c)q_c^2/\kappa_1^2$. A comparison for the two directions $\langle 00L \rangle$ and $\langle hh0 \rangle$ at 292 and 320 K is given in Table 5.10. In agreement with the above considerations, we find that q_c is proportional to κ_1 ($q_c \approx 7 \kappa_1$) for both directions and both temperatures and that $\hbar\omega(q_c)$ is approximately the same for the two directions at a given temperature. Thus, the occurrence of spin-wave modes above T_c is related to the magnetic short-range order and to the energetics of the system relative to kT .

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SPIN DYNAMICS OF A Cu-Mn SPIN-GLASS ALLOY¹

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Y. Tsunoda²

Neutron diffuse scattering measurements³ on Cu-Mn spin-glass alloys reveal two distinct types of magnetic short-range order. There are ferromagnetic spin-pair correlations which produce diffuse peaks around each Bragg peak and at the $(1 \ 1/2 \ 0)$ positions of the atomic short-range order as well as antiferromagnetic correlations which yield relatively sharp peaks at $Q = (1 \ 1/2 \pm \delta \ 0)$, where δ is concentration dependent. Since the complicated spin-glass behavior of these alloys is determined by the interactions between and within these ferromagnetic and antiferromagnetic regions, it is important to know the spin dynamics associated with each type of correlation. The dynamics of the ferromagnetically coupled pairs has been thoroughly studied in the low-Mn concentration region by Murani and coworkers,⁴ who find a broad distribution of relaxation times that changes continuously with temperature. Much less is known about the dynamics of the antiferromagnetic correlations. In a previous report,⁵ we described constant-energy measurements on a Cu-21% Mn alloy which showed that both types of spin correlations exist at temperatures ranging from well below to well above the spin-glass freezing temperature T_f , even at rather large energy transfers. We have now extended these measurements to a Cu-10% Mn alloy and have

Table 5.10. The critical wave vectors, critical energies, and inverse range parameters of Gd.

Direction	T(K)	$q_c(\text{\AA}^{-1})$	$\kappa_1(\text{\AA}^{-1})^a$	$\hbar\omega(q_c)[\text{THz}]$
00L	292	0.72	0.11	2.3
00L	320	1.09	0.14	3.5
hh0	292	0.36	0.06	1.7
hh0	320	0.57	0.08	2.6

^aReference [3].

directly determined the relaxation times associated with the two types of spin correlations from constant-Q data.

Constant-energy scans were also made for the Cu-10% Mn alloy, and the observed elastic scattering at a few fixed temperatures is shown in Fig. 5.30. Here, the characteristic features of the Cu-Mn diffuse scattering are shown in the $T = 10$ K scan; there is a broad peak at $(1\ 1/2\ 0)$ and two relatively sharp satellite peaks at $(1\ 1/2 \pm \delta\ 0)$. Both nuclear and magnetic scattering are contained in the $(1\ 1/2\ 0)$ peak while the

Fig. 5.30. Elastic neutron scattering along $Q = (1\ 1/2\ 0)$ for Cu-10% Mn at selected temperatures.

satellite peaks arise from the antiferromagnetic spin-pair correlations. As the temperature is increased, the magnetic contribution to this elastic scattering decreases at all three peak positions. The opposite occurs for the inelastic scattering, which increases with increasing temperature. This behavior is consistent with a distribution of relaxation times that shifts toward faster times with increasing temperature.

Constant-Q scans were made at $Q = (1\ 1/2\ 0)$ and $(1\ 1/2 - \delta\ 0)$ for the Cu-10% Mn alloy to determine directly the relaxation times associated with the two types of spin correlations. The 295-K results are shown in Fig. 5.31. Here, the spectra consist of an intense elastic peak superimposed on a broad quasielastic peak. At this temperature, the elastic peak is purely nuclear in origin, while the quasielastic peak arises mainly from the magnetic scattering. The data were fitted to a constant background plus a Gaussian elastic peak plus a magnetic contribution given by

$$I(Q, \omega) = I_0 \int \int d\Delta q d\Delta \omega R(\Delta q, \Delta \omega) \frac{k'}{k} \omega(n_\omega + 1) \times g(E) \frac{\Gamma}{\omega^2 + \Gamma^2} \quad (1)$$

Fig. 5.31. Excitation spectra of Cu-10% Mn at $Q = (1\ 1/2\ 0)$ and $(1\ 1/2 - \delta\ 0)$ at $T = 295$ K. The solid curves are fitted to the data as described in the text.

where I_0 is an amplitude, the double integral is a convolution with the instrumental resolution, n_0 is the Bose factor, and $g(E)$ is the fraction of the monitor count given by neutrons with the incident energy E . The fitted curves are shown in Fig. 5.31 along with the fitting parameter Γ , the inverse relaxation time. Within the experimental error, Γ is the same at the two positions. This supports the previously suggested⁵ model in which small ferromagnetic clusters are imbedded within much larger antiferromagnetic clusters. These composite clusters exist even at temperatures well above T_f and fluctuate in time while maintaining their spatial correlations. These fluctuations slow down with decreasing temperature, but even at temperatures well below T_f , fluctuating spin clusters are still observed. This is consistent with Murani's description of the dynamics of the ferromagnetic correlations. The present results indicate that both types of spin-pair correlations follow the same spin dynamics.

1. Research performed at the Oak Ridge National Laboratory under the U.S.-Japan Cooperative Program on Neutron Scattering.
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SPIN WAVES IN A RANDOM ANISOTROPY ANTIFERROMAGNET $K_2Co_xFe_{1-x}F_4$

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The low-temperature spin-wave excitations in the random anisotropy antiferromagnet $K_2Co_xFe_{1-x}F_4$ have been calculated by computer simulation across the whole concentration range $0 < x < 1$. These simulation results are in much better agreement with inelastic neutron scattering data^{2,3} than with the results of calculations using an average crystal approximation (ACA).^{4,10}

A random anisotropy magnet is a system in which the magnetic sites in the crystal lattice are randomly occupied by two different magnetic species with differing (orthogonal) spin anisotropies. The general form of the phase diagram for such systems has been studied, both theoretically and experimentally, during the past decade.⁵ There are four phases in the temperature-concentration plane; at high temperatures there is a paramagnetic phase, while at low temperatures, there are three ordered phases as a function of the concentration. The phase transition lines which separate these phases correspond to second-order phase transitions which meet in a tetracritical point. For systems like $K_2Co_xFe_{1-x}F_4$, which are a mixture of a uniaxial antiferromagnet (K_2CoF_4) and a planar antiferromagnet (K_2FeF_4), the three ordered phases are a uniaxial phase, a planar phase, and a mixed phase. In the uniaxial and planar phases, there is only long-range magnetic

order in either the uniaxial or the planar spin components, respectively, while in the mixed phase, which is intermediate in concentration between the other two phases, there is long-range magnetic order in both spin components. The phase diagram for $K_2Co_xFe_{1-x}F_4$ has been found experimentally⁶ to have the form described with the low-temperature transitions from the uniaxial phase to the mixed phase and mixed phase to the planar phase occurring at the concentrations $x = 0.50 \pm 0.05$ and $x = 0.10 \pm 0.06$, respectively.

Prior to the present work, calculations of the low-temperature properties of random anisotropy systems have used one form or another of an ACA.⁷ In such calculations, each site in the lattice is assumed to have an average environment, and hence the ground state is therefore specified by an average spin orientation angle for each of the two species. Since these ACA calculations ignore fluctuations in the local environment of sites, the resulting spin-wave dispersion relations have a delta-function relationship between energy and wave vector.⁸ These calculations also predict that there will be a soft mode at the transition from the uniaxial to the mixed phase.

For comparison with our computer simulation results, we have also performed ACA calculations for the $K_2Co_xFe_{1-x}F_4$ system. In these calculations and also in the computer simulations, the $K_2Co_xFe_{1-x}F_4$ system has been modeled as a two-dimensional antiferromagnet on a square lattice with the exchange parameters, etc., taken from the values for the pure system end members. These ACA calculations predict the transitions from the uniaxial phase to the mixed phase and from the mixed phase to the planar phase to be at concentrations $x = 0.285$ and $x = 0.205$, respectively, in poor agreement with experiment. In Fig. 5.32, the ACA dispersion relations for $K_2Co_{0.6}Fe_{0.4}F_4$ are shown by the dashed lines along with the experimentally measured spin-wave peak positions of Higgins et al.² The poor agreement between these ACA calculations and experiment is repeated for the other experimentally measured spin waves at concentrations $x = 0.20$ and $x = 0.27$. Since the orientation of the spins changes with concentration, so does the polarization of the spin waves. If the x and z directions are respectively defined to be the directions of planar and uniaxial order, then in Fig. 5.33(a) the lowest spin-wave energies for each polarization are shown as a function of concentration. Figure 5.33(a) clearly shows the soft mode at the phase boundary between the uniaxial and mixed phases.

The $K_2Co_xFe_{1-x}F_4$ system was modeled in the computer simulations on a two-dimensional 60×60 square array. Each site in the lattice was randomly occupied using a random number generator, and periodic boundary conditions were applied. The ground state orientations of the spins and the spin-wave excitations were calculated using modified versions of the algorithms due to Walker and Walstedt⁹ and Alben and Thorpe,⁹ respectively. A detailed description of the simulation method is given elsewhere.¹⁰

These computer simulations predict that the low-temperature boundaries between the uniaxial phase and the mixed phase and between the mixed phase and the planar phase occur at concentrations $x = 0.50$ and $x = 0.10$, respectively, in good

Fig. 5.32. The dispersion relations predicted for $K_2Co_{0.6}Fe_{0.4}F_4$ by the ACA (dashed lines) and the computer simulations (solid lines) are shown along with the experimental results.

agreement with experiment. In Fig. 5.32, the solid lines show the predictions of the computer simulations for the spin-wave peak positions in $K_2Co_{0.6}Fe_{0.4}F_4$. The simulation results are in good agreement with the experimental data, giving accurate predictions of the widths and structure factors of the excitations as well as the peak position. There is equally good agreement between the simulation results and experimental measurements at the concentrations $x = 0.202$ and $x = 0.273$ as well.

In Fig. 5.33(b), the computer simulation results for the peak positions of the lowest lying spin-wave excitations in $K_2Co_xFe_{1-x}F_4$ are shown for various concentrations. The arrows in Fig. 5.33(b) indicate the positions of the phase boundaries, clearly showing that there is no soft mode at the transition from the uniaxial phase to the mixed phase.

Fig. 5.33. The lowest spin-wave energies in $K_2Co_xFe_{1-x}F_4$, as calculated by the ACA (a) and by the computer simulations (b), are shown as a function of concentration. For the ACA results, the x-x and y-y polarized spin waves are degenerate in the uniaxial phase, and x-x and z-z polarized spin waves are degenerate in the mixed phase.

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PHONON DISPERSION CURVES OF NONSTOICHIOMETRIC Nb_2Ge^1

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Recently, considerable progress has been achieved in the experimental determination of the phonon dispersion curves of A15 compounds; a

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complete data set is now available for Nb_3Sb ,⁴ and the data for Cr_3Si ,^{5,6} and Mo_3Si ,⁷ although more limited, give a clear picture of the lattice dynamics of these materials. However, these three compounds are all nonsuperconducting or nearly nonsuperconducting. Thus, for an understanding of the electron-phonon interaction in Al5 materials, additional investigations on high- T_c compounds are desirable. Unfortunately, single crystals of high- T_c Al5s of sufficient size for inelastic neutron scattering investigations are difficult to grow, except for V_3Si , which however has very unfavorable neutron scattering properties for the determination of the phonon dispersion curves. After we were able to grow a small crystal (0.1 cm^3) of nonstoichiometric $\text{Nb}_3(\text{Ge}_{0.8}\text{Nb}_{0.2})$, which is a moderate- T_c material ($T_c = 6 \text{ K}$), we tried to determine its phonon dispersion curves as a next step toward a better insight into the electron-phonon interaction in this class of materials.

Despite the small size of the sample, most of the branches along the main symmetry directions have been determined. The experimental results for the $[\bar{1}00]$ direction are shown in Fig. 5.34. In contrast to the phonon spectra of other superconducting compounds,⁸ no drastic anomalies were observed, and temperature effects were found to be small. The results can be well described by a Born-von Kármán model (Model I) with axially symmetric forces up to the seventh nearest neighbors (7NN). The force constants for three models are listed in Table 5.11 along with one of the models for Nb_3Sb from Ref. 4. Model II treats the first neighbor interaction as a general force and allows two different kinds of axially symmetric 7NN force constants. Model III allows general forces for the 2NN and 3NN interactions. The continuous curves in Fig. 5.34 are based on Model II calculations. From Table 5.11, it is readily seen

Fig. 5.34. Phonon dispersion curves of $\text{Nb}_{3.2}\text{Ge}_{0.8}$ at room temperature. Lines are the result of a fit based on the 7-NN Born-von Kármán model (Model II).

that for both compounds the force constants beyond the third NN shell are of minor importance.

The major differences between the lattice dynamics of the two compounds were found to be a reduction of (1) the Nb-Ge interaction by 35% compared with the Nb-Sb interaction and (2) the

Table 5.11. Axially symmetric force constants for Models I-III of Nb_3Ge . F denotes longitudinal, and G transverse force constants. For comparison, the force constants of Model III for Nb_3Sb (Ref. 3) are given (column X).

Number of NN pairs	Specifi- cation	Distance (a_0 units)	Force constants (10^3 dyn/cm)							
			I		II		III		X	
			F	G	F	G	F	G	F	G
1	(A-A) ^I	0.500	57.37	-9.65	56.48	-12.74	59.59	-12.22	64.1	4.6
2	(B-A) ^I	0.559	26.76	1.93	28.36	-8.65	5 parameters	-10.22	45.5	0.5
3	(A-A) ^{II}	0.612	22.33	0.27	18.11	0.09	6 parameters		13.5	2.6
4	(B-B) ^{II}	0.866	-2.83	-0.81	-2.48	1.34	-3.70	0.89	-0.9	0.8
5	(B-A) ^{II}	0.901	3.12	-0.54	2.16	0.54	1.89	0.05	3.4	-1.9
6	(A-A) ^{III}	0.935	4.33	-0.25	4.80	-0.31	6.02	-0.35	1.2	0.4
7 _L	(A-A) ^{IV}	1.000	0.22	-0.26	3.80	0.17	2.54	0.85	4.7	0.4
7 _T	(A-A) ^{IV}	1.000	0.22	-0.26	0.63	1.13	-0.16	-2.99	4.7	0.4
8	(B-B) ^{II}	1.000	0	0	-1.22	-3.26	0.13	1.99	3.1	-0.1
No. of parameters			14		19		26		16	
rms deviation (THz)			0.127		0.111		0.101		0.116	

low-frequency modes in $\text{Nb}_3(\text{Ge}_{0.8}\text{Nb}_{0.2})$ which involve a "buckling" of the Nb chains.

A discussion of the electron-phonon coupling in Nb_3Ge compared with the isoelectronic Nb_3Sn (Ref. 9) has recently been published¹⁰ by one of the authors.

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LATTICE DYNAMICS OF BCC Sr

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The electronic structure of the divalent alkaline-earth metals Ca, Sr, and Ba is quite simple. Below the Fermi level E_F , the electronic bands are practically free-electron-like. The d-bands in these metals are only slightly above the Fermi level, and as a result, the electronic wave functions at E_F contain a substantial admixture of d-character arising from hybridization of the free-electron-like states with the d-bands. As a result, the structure and physical properties of these metals are quite sensitive to the d-occupation number.

Because of the relatively simple structure of these metals, it has been assumed that their lattice dynamical properties can be adequately described within the framework of the pseudopotential theory of metals. In recent experiments² on bcc Ba, however, it was found that along the $[\xi 00]$ symmetry direction the frequencies of the longitudinal dispersion curve are lower than those of the transverse branch. This anomalous feature of the dispersion curves was attributed to the hybridization near the Fermi level of the free-electron-like states with the d-bands. This interpretation has been supported² by first-principles frozen-phonon calculations. These calculations showed, in addition, that the observed

anomaly is quite sensitive to the position of the d-bands relative to the Fermi level.

To provide additional support for this interpretation, we performed measurements of the dispersion curves of bcc Sr, in which the d-bands lie higher than in Ba. Strontium is stable in the bcc phase between approximately 830 K and its melting point (~1040 K).

A large single crystal of bcc Sr was grown in situ and was used to measure the dispersion curves, at 930 K, along the $[\xi 00]$, $[\xi \xi 0]$, and $[\xi \xi \xi]$ symmetry directions. Along the $[\xi 00]$ symmetry direction the frequencies of the longitudinal curve are higher than those of the transverse branch, whereas, as noted above, the relative ordering of these branches is reversed in bcc Ba. This result is consistent with the theory, since in bcc Sr the d-bands lie higher than in Ba and therefore the hybridization of the free-electron-like states with the d-bands is not significant. The data were also used to evaluate the elastic constant, the phonon density of states, and the lattice specific heat of bcc Sr.

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LATTICE DYNAMICS OF BCC Cs

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Cesium is considered as the prototype for pressure-induced s+d (and p+d) transitions, an effect quite common in solids (I, Xe, Cs, Ba, La) with partly occupied or empty d-bands. Such s+d (and p+d) electronic transitions are of central importance to theories of the systematic of the high-pressure structural transformations of these solids.

Cesium crystallizes in the bcc structure just above room temperature; it transforms to the fcc phase at approximately 23 kbar, and it undergoes an isomorphic transition (fcc→fcc), characterized by a 9% decrease in volume, at approximately 42 kbar. Although it is generally accepted that the high compressibility and phase transformations of Cs are related to pressure-induced s+d electronic transitions, the effect of the s+d transfer on the elastic and lattice dynamical properties of Cs and the mechanism driving the isomorphic transition are not well understood. Of particular interest is the pressure dependence of the phonon frequencies, since Grüneisen parameter measurements as a function of pressure suggest that they exhibit anomalous behavior in the vicinity of the isomorphic transition.

As a first step in this project, we measured the ambient pressure dispersion curves of this metal. For this study, we were able to grow several single crystals of Cs of sufficient size for the systematic study of the dispersion curves along the $[\xi 00]$, $[\xi \xi 0]$, and $[\xi \xi \xi]$ symmetry directions. We find that the phonon frequencies are extremely low (≤ 1 THz) and that the dispersion curves are typically of free-electron-like metals.

Actually the measured frequencies agree to within 10% with calculations performed using the pseudopotential theory of metals. The experimental results were also used to evaluate the elastic constants, phonon density of states, and the lattice specific heat of bcc Cs; the results are in

quite good agreement with those obtained by other experiments.

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6. SYNTHESIS AND PROPERTIES OF NOVEL MATERIALS

Research on the synthesis, preparation, and characterization of new and novel materials represents a cornerstone on which future developments in the areas of solid state physics and materials science will be based. Investigations of this type often play a central role in the resolution of current problems in a number of basic research areas as well as problems of significant technological importance. The goals of the effort on the synthesis and properties of novel materials are to contribute to the resolution of outstanding materials problems that are related to the principal research goals of DOE and to develop new high-technology materials for energy-related applications. In carrying out these goals, high-quality research specimens are prepared and characterized using a variety of modern techniques. Implicit in these activities are the development of new techniques for both materials synthesis and the determination of materials properties. Research materials prepared and characterized in this work are employed in research efforts within the ORNL Solid State Division and in other ORNL divisions, as well as at other DOE laboratories, industrial research centers, and university laboratories. Numerous collaborative efforts are carried out involving other research groups, and the results of these efforts provide "feedback" into the research on materials synthesis and crystal growth. The entries in this section span a wide range of materials types including complex oxides in the electronics materials class, refractory oxides for high-temperature applications, refractory metals and alloys, transition-metal carbides, actinide elements, and advanced ceramics. A major ongoing effort involves a new class of glasses discovered in this program that have potential applications in the waste disposal area, as optical materials, and as glass-to-metal seals.

MATERIALS SYNTHESIS AND CHARACTERIZATION

PHYSICAL AND CHEMICAL CHARACTERISTICS OF LEAD-IRON PHOSPHATE NUCLEAR WASTE GLASSES¹

B. C. Sales   L. A. Boatner

Lead-iron phosphate glasses appear to be a promising new storage medium for many major categories of defense and commercial high-level nuclear wastes. Relative to borosilicate nuclear waste glasses, which represent the current reference primary storage medium, lead-iron

phosphate nuclear waste glasses have several distinct advantages: (1) an aqueous corrosion rate which is between 100 and 1000 times lower, (2) a formation temperature that is 100 to 250°C lower than the temperature (1150°C) required for a comparable borosilicate glass, and (3) a much lower melt viscosity in the temperature range 800-1050°C. The processing technology for producing lead-iron phosphate nuclear waste glasses is also similar to that developed for processing borosilicate nuclear waste glasses in many respects.

The lead-iron phosphate nuclear waste glasses can be prepared by melting in either stabilized zirconia, platinum, or alumina crucibles. For

defense-waste-loaded glasses, platinum crucibles appear to be the preferred choice followed by zirconia, but for commercial-waste-loaded glasses zirconia crucibles may perform better. All of the waste oxides and silicates in both the simulated defense waste and in the simulated commercial waste were completely dissolved in the lead-iron phosphate melt at 1050°C with the exception of ZrO_2 (a constituent of commercial waste), whose solubility is relatively very low.

The results of extensive corrosion tests on lead-iron phosphate glasses indicate that these glasses are extremely resistant to aqueous corrosion when the solution pH is between about 5 and 9 and the solution temperature is below about 125°C. At temperatures above 125°C, the hydrothermal corrosion rate of defense-waste-loaded lead-iron phosphate glasses rapidly increases. Commercial-waste-loaded lead-iron phosphate glasses are resistant to corrosion for solution temperatures below 150°C.

Crystallization studies on lead-iron phosphate nuclear waste glasses indicate that these glasses can be annealed for prolonged periods of time

(450 h at 500°C) without exhibiting any detectable crystallization or phase separation as a result of the heat treatment. Subsequent corrosion tests on heat-treated glasses indicated no measurable change in the corrosion rate. In another set of crystallization experiments it was determined that at $680 \pm 25^\circ\text{C}$ the crystallization rate during cooling was a maximum for lead-iron phosphate glasses and that these glasses had to be cooled through this temperature region ($680 \pm 25^\circ\text{C}$) at a rate greater than $1\text{--}10^\circ\text{C}/\text{min}$ to prevent crystallization. These crystallization studies indicate that it should be possible to produce a single uncracked cylindrical monolith of lead-iron phosphate nuclear waste glass approximately 15–30 cm in diameter by 3 cm long with a minimum of crystallization. The largest cylinder of lead-iron phosphate nuclear waste glass produced in our laboratory was 6 cm in diameter and 5 cm high (Fig. 6.1).

A summary of pertinent thermal, physical, and chemical characteristics of lead-iron phosphate nuclear waste glasses are given in Tables 6.1 and 6.2. Although all of the experimental results

Fig. 6.1. Samples of lead-iron phosphate glass loaded with simulated defense waste.

Table 6.1. Summary of thermal, physical, and chemical properties of lead-iron phosphate glasses loaded with simulated defense waste.

Property	Measured value	Temperature	Glass compositions ^a
Glass melting temperature	1050°C	-	1-D, 2-D
Glass pouring temperature	900°C	-	1-D, 2-D
Preferred melting crucible	Platinum		1-D, 2-D
Glass density	$4.7 \pm 0.1 \text{ g/cm}^3$	25°C	1-D, 2-D
Waste loading	7.73 g/cm^3	25°C	1-D, 2-D
Corrosion rate in water	$<0.001 \text{ g/m}^2\text{-d}$	90°C	1-D
Maximum hydrothermal temperature ^b	125°C	-	1-D
Critical cooling rate ^c	1-5°C/min	50-1000°C	1-D
Temperature of maximum rate of crystallization	$680 \pm 25^\circ\text{C}$	-	1-D
Annealing temperature	470°C	-	1-D
Glass transition temperature	477°C	-	1-D
Softening temperature	518°C	-	1-D
Thermal expansion coefficient	$11.0 \times 10^{-6}/^\circ\text{C}$	40-450°C	1-D
Heat capacity	$0.1\text{-}0.16 \text{ cal/g-}^\circ\text{C}$	50-350°C	1-D
Thermal conductivity	$0.006 \pm 0.001 \text{ W/cm-}^\circ\text{C}$	30-90°C	3-D

^aThe details of the glass compositions are given in J. Non-Cryst. Solids 79, 83 (1986).

^bAbove this temperature the corrosion rate rapidly increased with increasing temperature.

^cThe slowest rate at which the glass can be cooled without the occurrence of any bulk crystallization.

reported in this article were obtained on laboratory-scale samples using glasses loaded with simulated nuclear waste, it is hoped that the results of the research will stimulate full-scale evaluations of the possible use of lead-iron phosphate glass as a primary storage medium for high-level nuclear waste.

INVESTIGATION OF THE STRUCTURAL PROPERTIES OF LEAD-IRON PHOSPHATE GLASSES USING LIQUID CHROMATOGRAPHY AND RAMAN SCATTERING SPECTROSCOPY¹

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J. B. Bates   L. A. Boatner

The techniques of high-performance liquid chromatography and Raman scattering spectroscopy have been employed in investigations of the structural properties of several crystalline reference compounds and of a series of lead-iron

1. Summary of paper: J. Non-Cryst. Solids 79, 83 (1986).

Table 6.2. Summary of thermal, physical, and chemical characteristics of lead-iron phosphate glasses loaded with simulated commercial waste.

Property	Measured value	Temperature	Glass compositions ^a
Glass melting temperature	1050°C	-	I-C
Glass pouring temperature	900°C	-	I-C
Preferred melting crucibles	Zirconia, Pt	-	I-C
Glass density	5.0 ± 0.1 g/cm ³	25°C	I-C
Waste loading	0.32 g/cm ³	25°C	I-C
Corrosion rate in water	<0.001 g/m ² -d	90°C	I-C
Maximum hydrothermal temperature ^b	150°C	-	I-C
Critical cooling rate ^c	1-10°C/min	50-1000°C	I-C, 2.5-C
Temperature of maximum rate of crystallization	680 ± 25°C	-	I-C
Annealing temperature	490°C	-	I-C
Glass transition temperature	502°C	-	I-C
Softening temperature	544°C	-	I-C
Thermal expansion coefficient	10.3 × 10 ⁻⁶ /°C	50-500°C	I-C
Heat capacity	0.1-0.16 cal/g-°C	50-350°C	I-C

^aThe details of the glass composition are given in *J. Non-Cryst. Solids* 79, 83 (1986).

^bThis temperature is the maximum temperature at which aqueous corrosion tests were conducted.

^cThe slowest rate at which the glass can be cooled without the occurrence of any bulk crystallization.

phosphate glasses: $[1-x] \text{Pb}(\text{PO}_3)_2 + [x] \text{Fe}_2\text{O}_3$, $0 < x < 0.22$. Linear phosphate chains up to 13 PO_4 tetrahedra in length, as well as the cyclic phosphate ions trimetaphosphate and tetrametaphosphate, could be resolved by the liquid chromatography column. From the chromatography results and the results of associated experiments, it is concluded that liquid chromatography can be used to catalog the structural units present in lead-iron phosphate glasses with $x > 0.06$. The chromatograms from glasses with $x > 0.06$ are accurately described by the flexible chain model of Parks and Van Wazer.³ Raman scattering measurements on lead-iron

phosphate glasses showed an asymmetric broadening of the dominant band at $\Delta\nu = 1150 \text{ cm}^{-1}$ that increased with increasing iron concentration. This broadening is most probably due to the creation of $\text{O} = \text{PO}_3^{2-}$ and groups and $\text{O} = \text{PO}_3^{3-}$ orthophosphate groups by the addition of iron oxide to lead-metaphosphate glass.

The liquid chromatogram for pure lead-metaphosphate glass $[\text{Pb}(\text{PO}_3)_2]$ is shown in Fig. 6.2 for $x = 0$. Chains of PO_4 tetrahedra from P_1 (orthophosphate) to P_{12} are clearly resolved in the chromatogram along with two cyclic phosphate ions, trimetaphosphate P_{3m} and tetrametaphosphate P_{4m} . The trimetaphosphate and tetra-

Fig. 6.2. Liquid chromatograms of the series of lead-iron phosphate glasses: $[1-x] \text{Pb}(\text{PO}_3)_2 + [x] \text{Fe}_2\text{O}_3$ for $0 < x < 0.22$. The tendency of iron to produce a structure with shorter chain lengths is apparent.

metaphosphate ions are composed of 3 or 4 PO_4 tetrahedra arranged in a ring-like configuration. The broad envelope in the chromatogram, which is clearly visible after 40 min, is most likely due to the presence of longer phosphate chains ($>\text{P}_{12}$) and larger cyclic phosphate ions in solution which remain unresolved with the analytical column used. As iron oxide is added to lead metaphosphate, the chromatograms (Fig. 6.2) show a definite trend toward the presence of shorter and shorter phosphate chains in solution as well as a decrease in the concentration of the cyclic phosphate ions. For the glasses with the two highest concentrations of iron ($x = 0.152$ and $x = 0.216$) it is possible to make a reasonable estimate of the average phosphate chain length since all of the linear chains appear to be resolved by the analytical column. For $x = 0.152$

the average chain length computed from the chromatogram was 4.2, and for $x = 0.216$ it was 2.6.

A very simple model, first described by Parks and Van Wazer,³ was found to be in excellent agreement with the chromatograms of lead-iron phosphate glasses for glasses with $x > 0.06$. The model neglects the possibility of ring structures and assumes that the phosphate chains are infinitely flexible and can lie in any conceivable configuration. For the lead-iron phosphate glasses investigated here, the metal-to-phosphorus ratios exclude the possibility of branching phosphate groups and of unreacted metal oxide. In this limit, the "flexible chain model" of Parks and Van Wazer predicts that the weight fraction $w(n)$ of total phosphorus contained in the various chains is

$$w(n) = \frac{n}{\bar{n}'(\bar{n}'-1)} \left| \frac{\bar{n}'-2}{\bar{n}'-1} \right|^{n-2} [1-f_0] \quad (1)$$

for $n = 2, 3, 4, \dots$

and $\bar{n}' > 2$

where n is the chain length, $\bar{n}'$ is the average length of chains with a length greater than or equal to 2, and f_0 is the weight fraction of phosphorus present as orthophosphate. In fitting the chromatograms, the orthophosphate fraction is taken from the chromatogram and substituted into Eq. (1). For the glasses with $x = 0.15$ and $x = 0.22$, the value of $\bar{n}'$ is determined from the chromatogram and is used in Eq. (1). For the lower concentrations of iron oxide, the average chain length $\bar{n}'$ is treated as an adjustable parameter. A comparison between Eq. (1) and the chromatograms for $x = 0.06, 0.085, 0.15$, and 0.22 is shown in Fig. 6.3. The agreement between the flexible chain model and the chromatograms is within the experimental error which arises during the analysis of each chromatogram.

The lead-oxygen and iron-oxygen bonds are considerably more covalent than alkali-oxygen or alkaline-earth-oxygen bonds. It is for this reason that the flexible chain model should provide a better description of the lead-iron phosphate chromatography data than it does of the chromatography data previously reported for alkali and alkaline-earth phosphate glasses.

The lead-iron phosphate glasses with $x = 0$ and $x = 0.03$ contained a substantial fraction of unresolved higher polyphosphates ($>\text{P}_{12}$) and large amounts of both pyrophosphate and cyclic phosphate ions and the chromatograms from the two glasses with $x = 0$, $x = 0.03$ are not described by Eq. (1). Hence, no attempt was made to fit these two chromatograms to the flexible chain model.

The Raman spectrum obtained from pure lead-metaphosphate glass $[\text{Pb}(\text{PO}_3)_2]$ is characteristic of the Raman spectra from all metal metaphosphate glasses. A sharp band at about 1150 cm^{-1} is the dominant feature of the spectrum and has been assigned to a symmetric out-of-chain stretching vibration of PO_2 groups. As iron oxide is added to lead-metaphosphate glass, the most noticeable change that occurs in the Raman spectra is the asymmetric broadening of the band at 1150 cm^{-1} .

OPTICAL PROPERTIES OF Nd^{3+} IN LEAD-PHOSPHATE GLASSES¹M. J. Weber² L. A. Boatner
B. C. Sales

Fig. 6.3. Comparison of the chain-length distributions of lead-iron phosphate glasses as measured using liquid chromatography (●) and as calculated using the model of Parks and Van Wazer² [(Eq. 1)] (Δ).

The high-energy side of this band tends to remain sharp independent of the amount of iron oxide that is added to the glass, whereas the low-energy side of this band broadens even for low concentrations of iron oxide. If the dominant Raman modes of the end and orthophosphate groups occur at frequencies lower than the frequencies of the symmetric PO_2 vibrations, it is reasonable to expect that the sharp band at about 1150 cm^{-1} will be broadened in an asymmetric manner similar to that observed here. To test this hypothesis, the Raman spectrum was measured for samples of lead-metaphosphate glass, $\text{Pb}(\text{PO}_3)_2$; lead-pyrophosphate crystals, $\text{Pb}_2\text{P}_2\text{O}_7$; lead-orthophosphate crystals, $\text{Pb}_3(\text{PO}_4)_2$; iron-metaphosphate glass, $\text{Fe}(\text{PO}_3)_3$; iron-phosphate crystals, $\text{Fe}_3(\text{P}_2\text{O}_7)_3$; and iron-orthophosphate crystals, FePO_4 . These data show that virtually all of the Raman intensity from lead pyrophosphate (end groups) and lead orthophosphate occurs on the low-energy side of the 1150 cm^{-1} bend of lead metaphosphate. The same trend is observed for the three iron-phosphate compounds.

The optical absorption and emission properties of Nd^{3+} ($[\text{Xe}]\text{4f}^3$) ions in a series of alkaline-earth (Mg, Ca, Sr, Ba) and other divalent (Zn, Cd) and trivalent (Al, Nd) modifier metaphosphate glasses have been described previously.³ For the divalent alkaline earths, it was found that the Nd^{3+} spectroscopic properties varied systematically with the alkaline-earth atomic number. In the case of Zn and Cd, the other divalent cation network modifiers studied, the data did not conform to the trend observed for Nd^{3+} in the alkaline-earth metaphosphates. The observed differences in the behavior of the two types of cations are attributed to their different electronic structures [i.e., the divalent alkaline earths are closed shell ions of the type $\dots\text{ns}^2\text{p}^6$ ($n = 2, 3, 4, 5$), while Zn and Cd have a noble gas configuration and an $\dots\text{ns}^2\text{p}^6\text{d}^{10}$ ($n = 3, 4$) outer shell].

In the present work, the earlier investigations are extended to encompass lead-phosphate glasses including the lead metaphosphate composition. Divalent lead has a $6s^2$ outer shell, is easily polarized, and forms a $\text{M}(\text{II})\text{-O}$ bond with the most covalent character. Several of the optical properties of Nd^{3+} in the metaphosphate glasses were found to exhibit extremes when lead was the modifier cation. This observation led us to investigate the spectroscopic properties of Nd^{3+} in phosphate glasses with lead concentrations greater than that corresponding to the metaphosphate composition.

Absorption and fluorescence spectra of Nd^{3+} were recorded at room temperature using apparatus and techniques described previously.⁴ Table 6.3 summarizes the physical and spectroscopic properties for a lead metaphosphate glass and for a higher lead-content phosphate glass. For comparison, the extreme values measured earlier for other divalent cation metaphosphate glasses are given in the final column of the table. The modifier ion which exhibited the observed extreme value is noted in parentheses. Although the lead metaphosphate glass transmitted above 280 nm , the absorption edge of the higher lead-content glass was shifted slightly to longer wavelengths with a tail that had an absorption coefficient of 6 cm^{-1} at 300 nm .

The Nd^{3+} spectra observed for lead-phosphate glasses were very similar to those shown in Ref. 2, but they exhibited a slight narrowing of the band widths and small changes in band intensities of transitions between J states. Intensity changes have also been observed for silicate glasses with comparable PbO content.⁵ The strong covalent character of the Pb-O bond effectively reduces the ligand field at the Nd^{3+} site. The resulting small overall Stark splitting accounts for the narrower effective linewidth for the $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ emission in Table 6.3.

All of the Judd-Ofelt intensity parameters for Nd-doped lead-phosphate glasses are smaller than those for the other divalent-cation

1. Summary of paper to be published.

2. Analytical Chemistry Division, ORNL.

3. J. R. Parks and J. R. Van Wazer, *J. Amer. Chem. Soc.* **79**, 4890 (1957).

Table 6.3. Comparison of the spectroscopic and physical properties of Nd^{3+} -doped lead-phosphate and various metaphosphate ($\text{M} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}, \text{Zn}, \text{Cd}$) glasses at 295 K. The extreme values measured for metaphosphate glasses are given.

Glass	$1\text{Nd}_2\text{O}_3$ - 49PbO-50P ₂ O ₅	$1.7\text{Nd}_2\text{O}_3$ - 53.6PbO-44.7P ₂ O ₅	$1\text{Nd}_2\text{O}_3$ - 49MO-50P ₂ O ₅
Physical properties:			
Density (g/cm ³)	4.56	5.07	2.48(Mg)-3.83(Cd)
Refractive index n_D	1.71	1.75	1.50(Mg)-1.62(Cd)
Abbe number v_D	61	58	66(Mg)-56(Cd)
$^2F_{3/2} \rightarrow ^4I_{11/2}$ fluorescence:			
Peak cross section (pm ²)	3.5 $\pm$ 0.1	3.6 $\pm$ 0.1	2.4(Mg)-3.9(Ba)
Peak wavelength (nm)	1054	1054	1055(Cd)-1056(Ba)
Effective linewidth (nm)	25.2	25.1	28.5(Ba)-33.9(Mg)
Radiative lifetime (μ s)	320	300	290(Ba)-430(Mg)
Judd-Ofelt intensity parameters:			
Ω_2 (pm ²)	2.6 $\pm$ 0.2	2.0 $\pm$ 0.2	3.9(Cd)-5.3(Mg)
Ω_4 (pm ²)	3.5 $\pm$ 0.3	3.6 $\pm$ 0.3	4.2(Mg)-5.6(Ba)
Ω_6 (pm ²)	4.3 $\pm$ 0.1	4.2 $\pm$ 0.1	4.3(Mg)-5.6(Ba)

metaphosphate glasses. This is a consequence of the high polarizability of P_2^{2+} and the directional nature of the Pb-O bond. The Ω_2 parameter, which is derived principally from the hypersensitive $^4I_{9/2} \rightarrow ^4F_{5/2}$ transition at ~ 580 nm, decreases with increasing PbO content and has the smallest value observed in any oxide glass. The only glasses exhibiting smaller Ω_2 values are halide-containing glasses;⁵ these glasses also have weak local fields and narrow linewidths.

The fluorescence decays, measured in samples containing 0.1 wt % Nd_2O_3 to reduce nonradiative relaxation by ion-ion interactions, were nonexponential with lifetimes less than the radiative lifetime predicted from the Judd-Ofelt parameters. The difference is attributed to the presence of a small quantity of water in the glasses as evidenced by infrared absorption bands in the vicinity of 3 μ m characteristic of hydroxyl groups in phosphate glasses. The predicted branching ratios for fluorescence from the $^4F_{3/2}$ state to levels of the ^4I_j manifolds were within a few percent of the values predicted for other phosphate glasses.

Several of the spectroscopic properties of Nd^{3+} in lead metaphosphate glass represent extremes for metaphosphate host glasses with divalent modifier cations. The observed behavior of optical properties in the high-lead-content phosphate glasses can therefore be used to tailor the host glass composition for absorption and luminescence applications.⁶ Although the intensity parameters for rare earths are small, the peak cross sections are relatively large, and the radiative lifetimes are short because of the narrow band widths and high refractive index. The predicted nonlinear refractive index coefficient n^2 in the visible and infrared regions is estimated to be large, $>5 \times 10^{-20}$ m²/W, for PbO concentrations of >50

mol %. Hence, lead-phosphate glasses are not attractive for laser applications where effects of self-focusing are detrimental.

1. Summary of paper: J. Non-Cryst. Solids 74, 167 (1985).
2. Lawrence Livermore National Laboratory, Livermore, Calif.
3. M. J. Weber, R. A. Saroyan, and R. C. Ropp, J. Non-Cryst. Solids 44, 137 (1981).
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5. M. J. Weber, p. 327 in Proceedings of the International Conference on Lasers '82, STS Press, McLean, Va., 1982.
6. M. J. Weber, D. C. Ziegler, and C. A. Angell, J. Appl. Phys. 53, 4344 (1982).

LEAD-INDIUM PHOSPHATE AND LEAD-SCANDIUM PHOSPHATE GLASSES: A NEW CLASS OF OPTICAL MATERIALS¹

B. C. Sales L. A. Boatner

Investigations of the properties of lead-phosphate glasses have been carried out for over 25 years. These glasses have been of interest primarily as a result of their low preparation temperatures and low softening points—characteristics that made them ideal materials for fundamental studies of glass devitrification and the glass transition. Commercially, lead-phosphate glasses have been of limited interest because of their poor chemical durability when exposed to aqueous environments. Recently, however, we have found that the addition of iron

oxide to lead phosphate could drastically improve the chemical durability of the resulting glass without substantially raising either the preparation temperature or the melt viscosity.²

Lead-iron phosphate glasses represent a very durable group of glasses and have several potential uses (e.g., these glasses represent an excellent storage medium for many types of high-level nuclear waste). Lead-iron phosphate glasses, however, strongly absorb light in the visible region (the glasses are black in appearance), and hence lead-iron phosphates are of no use for optical applications that require the transmission of light (i.e., lead-iron phosphate glasses would be useless as lenses, prisms, etc.).

A variety of metal oxide additives were investigated as possible alternatives to iron oxide in the hope that other constituents could simultaneously stabilize lead-phosphate glass without coloring or tinting the resulting material. The oxides investigated included MgO, Al₂O₃, CaO, Sc₂O₃, TiO₂, V₂O₅, Cr₂O₃, MnO₂, CoO, NiO, Cu₂O, ZnO, Ga₂O₃, Y₂O₃, ZrO₂, In₂O₃, La₂O₃, CeO₂, and Cd₂O₃. Of all the oxides investigated, only In₂O₃ and Sc₂O₃ met all of the requirements; namely, (1) the oxides could be dissolved in the lead-phosphate melt at reasonable temperatures (less than 1000°C), (2) the chemical durability of the lead-phosphate glass was greatly enhanced by the addition of the metal oxide, and (3) the resulting glass exhibited no measurable absorption of light with wavelengths between 3000 and 8000 Å (i.e., the glass was clear in the visible wavelength region). Of the two additives (In₂O₃ or Sc₂O₃), the In-doped lead-phosphate glass had

somewhat better performance and preparation characteristics, and hence, most of the optical and chemical characterization was done with this material. In addition, Sc₂O₃ is difficult to obtain and is quite expensive. This makes the lead-indium phosphate glass more attractive for purely economic reasons. A summary of the experimental results obtained on lead-indium phosphate glass is given in Table 6.4.

1. Summary of paper to be published.
2. B. C. Sales and L. A. Boatner, Science 222, 45 (1964).

EPR OBSERVATIONS OF TRIVALENT TITANIUM IN ORTHOPHOSPHATE SINGLE CRYSTALS¹

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M. A. Aronson²

Electron paramagnetic resonance (EPR) observations of the unusual trivalent state associated with a d¹ electronic configuration for Zr and Hf,^{3,4} elements that are generally found in the tetravalent state, have provided the impetus for other investigations of ions with unusual valence states. In particular, the ground state spectroscopic properties of the 3d¹ electronic configuration ion Ti³⁺ have been investigated using EPR spectroscopy. Trivalent titanium was incorporated as a dilute impurity in single crystals of the tetragonal, zircon-structure hosts ScPO₄, YPO₄, and LuPO₄. The crystals were grown by means of a flux technique in which the

Table 6.4. Summary of experimental results on lead-indium-phosphate-based glass.

Composition (wt %)	65% PbO, 29% P ₂ O ₅ , 6% In ₂ O ₃
Melting and fining temperature	900°C
Pouring temperature	800–900°C
Melting crucibles	alumina, zirconia
Density	5.4 ± 0.1 g/cm ³
Index of refraction	1.780–1.836 (650–400 nm)
Ultraviolet absorption edge	~300 (nm)
Infrared absorption edge	~2800 (nm)
Dispersion	Abbe number = 30 ± 1
Thermal expansion coefficient	12.0 × 10 ⁻⁶ (30–380°C)
Glass transition temperature	436°C
Softening point	459°C
Chemical durability classes ^a	CR1, FRO, SR 51
Aqueous dissolution rate (25°C)	<1 × 10 ⁻⁷ g/cm ² -day (5 < pH < 9)
Aqueous dissolution rate (90°C)	<1 × 10 ⁻⁷ g/cm ² -day (5 < pH < 9)
Critical cooling rate ^b	10°C/min

^aSee the introduction of the Schott Glass Optical Catalog for definitions of these durability classes.

^bThe slowest rate at which the glass can be cooled without the occurrence of any bulk crystallization.

appropriate host and titanium oxides were reacted with lead-hydrogen phosphate at 1360°C. Excess PbHPO_4 decomposed to form a $\text{Pb}_2\text{P}_2\text{O}_7$ flux, and the crystal growth process was carried out by slowly cooling the resulting mixture to ~900°C. Unequivocal identification of the magnetic resonance of Ti^{3+} depends on the observation of a characteristic hyperfine spectrum consistent with the known abundance of the two odd titanium isotopes. Since the natural abundance of ^{47}Ti and ^{49}Ti is only 7.28 and 5.11%, respectively, isotopically enriched samples were also prepared. An intense EPR spectrum due to Ti^{3+} was observed in the as-grown LuPO_4 crystals, and it was not necessary to perform a low-temperature irradiation to produce the trivalent state. The increased intensity of the eight hyperfine structure lines for the enriched ^{49}Ti isotope ($I=7/2$) unequivocally identified the titanium EPR spectrum. By varying the crystal orientation with respect to the external magnetic field, it was established that the trivalent titanium impurity is located substitutionally in a rare-earth cation site and that the magnetic axes of the paramagnetic ion are coincident with the crystallographic axes of the tetragonal orthophosphate hosts. The EPR spectrum obtained for isotopically enriched $^{49}\text{Ti}^{3+}$ in LuPO_4 at 77 K with the crystallographic c-axis parallel to the external magnetic field is shown in Fig. 6.4. The spectroscopic parameters, g , g_1 , $^{49}\text{A}_1$, and $^{49}\text{A}_2$, were obtained by fitting the usual axially symmetric spin Hamiltonian,

$$H = \mu_B \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + A_1 I_z S_z + A_2 (I_x S_x + I_y S_y), \quad (1)$$

with $S = 1/2$.

The spin-Hamiltonian parameters determined for Ti^{3+} in LuPO_4 , YPO_4 , and ScPO_4 , as well as the previously reported parameters for Zr^{3+} and Hf^{3+} in the same three hosts, all have $g_1 > g_2$ and $A_1 > A_2$. This demonstrates that the orbital ground state is described by the symmetric wave function $(1/\sqrt{2}) [|+2\rangle + |-2\rangle]$, which transforms as $(x^2 - y^2)$. Attempts to fit the experimental data for any of these d^1 ions to the theory of Abragam and Pryce in order to calculate the energy separation between the orbital levels produced by the crystal field have been unsuccessful. Whatever the origin of the additional effects that must be taken into account in order to fit the experimental data, it is clear that coupling to other electronic levels is important. This is evidenced by the observation that the g and A values for the Ti^{3+} and Zr^{3+} ions that can be measured at room temperature are different than the values determined at 77 K. At room temperature, the departures of the g values from the free electron value (Δg_1 or Δg_2) are slightly larger for these two ions, and the hyperfine values are slightly smaller than their respective values at 77 K. It should also be noted that the Δg 's increase for each trivalent d^1 ion in the order of the series of hosts (ScPO_4 to LuPO_4 to YPO_4) and that they also increase as the principal quantum number goes from 3 to 5. The trend of increasing Δg 's as the host is varied as indicated implies that

Fig. 6.4. EPR spectrum of isotopically enriched Ti^{3+} at 77 K in a single crystal of LuPO_4 with the applied magnetic field parallel to the fourfold symmetry axis of the tetragonal crystal. The 76.27% abundance of ^{49}Ti increases the intensity of the eight ^{49}Ti lines relative to the six ^{47}Ti lines and the central even Ti ($I=0$) line. The absorption lines (shown in a first derivative presentation) are labeled by the bar diagram below the spectrum.

the strength of the crystal-field interaction with the d electron in the ScPO_4 , LuPO_4 , and YPO_4 hosts is in descending order of magnitude. A similar descending order of magnitude for the crystal-field interaction has been observed for the d^5 configuration ion Fe^{3+} in these same hosts. With the completion of these investigations, results are now available for a series of three isovalent d^1 configuration ions (i.e., Ti^{3+} , Zr^{3+} , and Hf^{3+}) in a series of three isostructural tetragonal-symmetry hosts (i.e., LuPO_4 , YPO_4 , and ScPO_4). The trends evidenced by the g -values determined for these nine different systems should provide an indication for the direction of future theoretical efforts to account for the important spectroscopic properties of single d -electron systems.

1. Summary of paper: Journal of Chemical Physics (in press).

2. Oak Ridge Associated Universities research trainee from Pennsylvania State University, State College, Pa.

3. M. M. Abraham et al., J. Chem. Phys. **81**, 5362 (1984).

4. M. M. Abraham, L. A. Boatner, and J. O. Ramey, J. Chem. Phys. **83**, 2754 (1985).

EPR STUDIES OF EXCITED STATES IN THE GROUND MANIFOLD OF Ce^{3+}

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Recently a positive identification was made³ for a Ce^{3+} resonance occurring between the levels of an excited-state doublet for both $^{23}\text{Ce}^{3+}$ and $^{140}\text{Ce}^{3+}$ doped into the zircon-structure host single-crystal LuPO_4 . This resonance was identified as a transition arising from an excited-state doublet by establishing that lowering the sample temperature reduced the intensity of the observed EPR signal. In this case the measured axial g values of the doublet were fitted to a wave function of the form $\alpha|\pm 5/2\rangle + \beta|\pm 3/2\rangle$. New EPR lines that correspond to transitions within the two remaining higher lying excited doublets [i.e., $(\alpha|\pm 3/2\rangle - \beta|\pm 5/2\rangle$ and $\gamma|\pm 1/2\rangle - \delta|\pm 7/2\rangle)$] of the ground state manifold for Ce^{3+} in LuPO_4 have now been observed for Ce^{3+} in LuPO_4 . EPR observations of all three excited doublets have also been made for the case of Ce^{3+} in another zircon structure host crystal (i.e., isostructural YPO_4). The resulting g -value predictions for the Ce^{3+} ground state have also been verified by Zeeman effect studies of the Ce^{3+} optical absorption in YPO_4 .

In Table 6.5, the measured axial g values g_1 and g_2 are listed along with the calculated g values and the resulting wave functions for the four Ce doublets in LuPO_4 . The excited state resonances may be observed at both 4.2 and 77 K, and the results at both temperatures are given in Table 6.5. Small tetragonal, crystal-field-induced admixtures of the excited $|\pm 1/2\rangle$ wave-function into the ground $|\pm 7/2\rangle$ level produce a finite, albeit small, g_1 value for the ground

doublet. This small g_1 value will result in a much lower transition probability for a magnetic resonance transition between the levels of the $\gamma|\pm 7/2\rangle + \delta|\pm 1/2\rangle$ doublet than that found for the other higher lying doublets. The fact that a resonance transition for the lowest lying doublet is not observed can be attributed to this effect. Although the magnetic resonance spectrum of the ground doublet has not been observed, the expected g values may be calculated by using the Mohr circle construction. The tetragonal crystal-field admixture can be expressed as $\tan 2\theta$, where $\tan 2\theta$ is equal to twice the off-diagonal crystal-field matrix element divided by the difference in the diagonal elements. Therefore, for the $|\pm 7/2\rangle$ and $|\pm 1/2\rangle$ admixtures, $\tan 2\theta$ is given by

$$\tan 2\theta = \frac{2(\sqrt{35}/5)b_4^0}{(-12b_2^0 + 2b_4^0 - 6b_6^0 - 4g \mu_B H)} \quad (1)$$

and the corresponding expression for the $|\pm 5/2\rangle$ and $|\pm 3/2\rangle$ admixture is

$$\tan 2\theta = \frac{(2\sqrt{3})b_4^0}{(-4b_2^0 + 10b_4^0 + 14b_6^0 - 4g \mu_B H)} \quad (2)$$

where the b^0 are the Stevens crystal-field parameters. The values of $\tan 2\theta$ for the two different admixtures may be calculated from the coefficients of the wave functions listed in Table 6.5. (The coefficients are merely $\cos\theta$ and $\sin\theta$.) In this manner, $\tan 2\theta = 0.7736$ and 0.7811 for the first admixture at $T = 77$ K and 4.2 K, respectively, and $\tan 2\theta = 0.3782$ and 0.3988 for the second admixture at $T = 77$ K and 4.2 K, respectively. The ratio of the two admixtures is found to be approximately two and not about four, as would be expected if

Table 6.5. Wave functions and g values for $\text{LuPO}_4:\text{Ce}^{3+}$.

		Calculated		Measured	
		g_1	g_2	g_1	g_2
77 K	$0.9837 \pm 1/2\rangle - 0.1798 \mp 7/2\rangle$	1.424	7.436	1.424(2)	-
	$0.9463 \pm 3/2\rangle - 0.3233 \mp 5/2\rangle$	4.155	4.07	4.15(1)	4.07(1)
	$0.9463 \pm 5/2\rangle + 0.3233 \mp 3/2\rangle$	8.00	4.07	8.00(2)	4.07(1)
	$0.9837 \pm 7/2\rangle + 0.1798 \mp 1/2\rangle$	12.95	0.25	-	-
4.2 K	$0.98205 \pm 1/2\rangle - 0.1886 \mp 7/2\rangle$	1.373	7.402	1.373(1)	7.402(5)
	$0.9455 \pm 3/2\rangle - 0.3255 \mp 5/2\rangle$	4.13	4.096	4.12(1)	4.10(1)
	$0.9455 \pm 5/2\rangle + 0.3255 \mp 3/2\rangle$	7.976	4.096	7.98(1)	4.096(4)
	$0.98205 \pm 7/2\rangle + 0.1886 \mp 1/2\rangle$	2.9	0.27	-	-

b_2^0 were dominant parameters in the denominators of the expressions shown for $\tan 2\theta$. Thus, the parameters b_4^0 and b_6^0 cannot be neglected in Eqs. (1) and (2); since b_2^0 is negative, it can be concluded that b_4^0 (and probably b_6^0) are both positive for Mn^{2+} in LuPO_4 . It is clear that the admixtures are larger at the lower temperature (Table 6.5) and that, therefore, the levels are closer at 4.2 K than at 77 K.

Axial g values were also measured for the excited Mn^{2+} levels in YPO_4 , and resonances from all three excited levels were observed at 77 K. Only one resonance could be seen at 4.2 K, however, due to thermal depopulation of the two higher lying doublets. The g values and wave functions for the four doublets at 77 K were also calculated. The values of $\tan 2\theta$ for the $|\pm 5/2\rangle$ and $|\pm 3/2\rangle$ admixture at 77 and 4.2 K are calculated to be 0.5924 and 0.5943, respectively, while the $\tan 2\theta$ value for the $|\pm 7/2\rangle$ and $|\pm 1/2\rangle$ admixture is 0.2133 at 77 K. It can be seen that, since the admixtures of the wave functions for Mn^{2+} in YPO_4 are smaller than the corresponding admixtures for Mn^{2+} in YPO_4 , the tetragonal crystal field in the YPO_4 host is stronger than it is in the LuPO_4 host (i.e., the energy levels are farther apart in YPO_4 than they are in LuPO_4). Furthermore, since the ratio of the two different admixtures for YPO_4 at 77 K is larger than the ratio for LuPO_4 , it can be concluded that the effect of the b_4^0 and b_6^0 parameters relative to the b_2^0 parameter in the denominators of the expressions for $\tan 2\theta$ is smaller for YPO_4 . It is still true, however, that in YPO_4 (just as in LuPO_4) the signs of b_4^0 (positive) and b_2^0 (negative) are different and that the crystal-field-induced admixtures are less at 77 K than at 4.2 K.

1. Summary of paper to be published.
2. Lawrence Berkeley Laboratory, Berkeley, Calif.
3. M. M. Abraham and L. A. Boatner, *Phys. Rev. B* **26**, 1434 (1982).

EPR AND THERMOLUMINESCENCE INVESTIGATIONS OF Mn^{2+} IN LuPO_4 , YPO_4 , AND ScPO_4 ¹

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M. M. Abraham   L. A. Boatner

Divalent manganese has been incorporated in both single crystals and powders of the zircon-structure hosts LuPO_4 , YPO_4 , and ScPO_4 . The single-crystal specimens were grown by slowly cooling a $\text{Pb}_2\text{P}_2\text{O}_7$ flux from 1360°C, and finely divided powders of these materials were also prepared using a molten urea precipitation technique.

The EPR spectrum obtained for a single crystal of manganese-doped ScPO_4 is shown in Fig. 6.5. The five fine-structure groups, each of which exhibits six hyperfine lines, establish that the manganese ions are in the 2+ valence state (i.e., $S = 5/2$ and $I = 5/2$ for the 100% abundant ^{55}Mn isotope). The variation of magnetic field position of the fine-structure groups as a function of the magnetic field orientation identified the

Fig. 6.5. EPR spectrum of Mn^{2+} in a ScPO_4 single crystal is shown in (a) and (b) for the applied magnetic field parallel and perpendicular to the c crystallographic axis, respectively. From the five fine-structure groups of six hyperfine lines each, it is clear that the manganese ions are in the 2+ valence state. The extra lines with small intensity that can be seen in (a) are caused by manganese ions in lower symmetry sites.

local symmetry of the crystalline electric field at the Mn^{2+} site. Observations of this variation in other planes established that the spectrum with the orientation of the magnetic field parallel to the c axis of the crystal is an absolute maximum (i.e., the z axis of the magnetic complex is along the crystallographic c axis), that the symmetry of the crystalline electric field is tetragonal, and that the Mn^{2+} ion is substitutional for a Sc^{3+} ion. Curiously, even though the aliovalent ion requires some type of charge compensation to maintain charge neutrality, the necessary charges are sufficiently far removed from the Mn^{2+} site so as not to disturb the original tetragonal symmetry of the site. Extra lines with low intensity that can be seen in Fig. 6.5(a) are due to manganese ions in lower symmetry sites. The relative intensities of the tetragonal symmetry spectra and these lower symmetry spectra varied from one crystal growth run to another, and the lower symmetry spectra were identified as having orthorhombic symmetry and as representing Mn^{2+} in four magnetically nonequivalent but symmetry-related sites in the ScPO_4 host lattice. For Mn^{2+} in LuPO_4 single crystals, both tetragonal and orthorhombic symmetry spectra were also observed.

Examination of Mn^{2+} -doped LuPO_4 revealed the presence of the same type of orthorhombic spectrum that was observed in some specimens of Mn^{2+} -doped ScPO_4 . Again, the four orthorhombic Mn^{2+} spectra for the LuPO_4 host were magnetically inequivalent, but were characterized by the same crystal-field magnitude and symmetry.

In the case of manganese-doped YPO_4 single crystals, only the orthorhombic Mn^{2+} spectra were observed, and no evidence of a tetragonal spectrum was found. The usual fourfold degeneracy of the orthorhombic EPR transitions was observed when $\mathbf{H}$ was parallel to the fourfold c axis of the crystal, and four equivalent absolute extremes for the magnetic field positions occurred when $\mathbf{H}$ was oriented at an angle of 26° relative to the c axis in any one of the four equivalent $\{ca\}$ planes. These are the same characteristics found for the orthorhombic Mn^{2+} system in ScPO_4 and LuPO_4 . The nonequivalence of the four magnetic sites in YPO_4 can be seen in Fig. 6.6, where the

Fig. 6.6. Angular variation in the (ca) plane of the $\Delta M_s = \pm 1$ fine-structure transitions for a single crystal of $\text{YPO}_4 \cdot \text{Mn}^{2+}$. The magnetic field positions of each hyperfine group are represented by a single point. There is a fourfold degeneracy when $\mathbf{H}$ is parallel to the crystallographic c axis. In this plane, the transitions split into three components with intensities of 1:2:1 when the field is moved away from the c axis. A complete angular variation of all the transitions was not practical due to the effects of line broadening. Two of the four magnetic z axes (z^1 and z^2) lie in this plane at angles of $\pm 26^\circ$ from the c axis of the crystal. The secondary maxima for which $\mathbf{H} \parallel \mathbf{a}$ were chosen as the magnetic y axes (y_1, y_2).

angular variation in the (ca) plane for some of the fine-structure transitions is plotted. When the magnetic field was moved away from the c direction, the transitions split into three components with relative intensities of 1:2:1, but the complete angular variation of all the transitions could not be followed since the lines also

broadened considerably as a function of angle. Mn^{2+} -doped powders of the hosts $ScPO_4$, $LuPO_4$, and YPO_4 were also investigated.

Finally, thermoluminescent properties of the three Mn-doped zircon-structure orthophosphates were investigated. Whether all or some of the observed glow peaks are extrinsic or intrinsic remains a question for additional study, but certainly, a thermoluminescence single-peak theory is inadequate to explain the unusual resolved structure observed.

1. Summary of paper: J. Chem. Phys. **83**, 6113 (1985).
2. Guest scientist from Universidad Nacional Autónoma de México, México, D.F.

DISORDER-INDUCED DYNAMIC FLUCTUATIONS IN KTi¹

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This work is an outgrowth of a recent study³ of quasielastic light scattering in the perovskite ferroelectric $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ with $x = 0.032$, in which an intense, singular central peak (CP) was observed near the second-order phase transition from the cubic phase to a rhombohedral ferroelectric phase at $T_c = 38$ K. These earlier results, in which the fluctuations responsible for the CP were attributed to disorder in the form of polarized clusters of displaced ions on the Ta/Nb sublattice, have now been extended to include samples of $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ with higher Nb concentrations (i.e., $x = 0.1$ and $x = 0.28$). Both of these concentrations are above the multicritical point on the KTaO_3 - KNbO_3 phase diagram, and therefore the crystals display a series of transitions to tetragonal, orthorhombic, and rhombohedral ferroelectric phases that are typical of perovskite oxide.

Light scattering spectra were obtained using the 5145-A line of an argon laser tuned to the absorption of an I_2 filter, which completely eliminated the elastically scattered laser light. The Raman and quasielastic components were dispersed by either a double monochromator alone or by a triple-pass Fabry-Perot interferometer followed by the double monochromator. Central components in the light scattering spectra are observed beginning at temperatures above the cubic-tetragonal transition at T_{C1} , and these components persist with increasing intensity into the tetragonal and orthorhombic phases at T_{C2} and T_{C3} , respectively.

Below T_{C1} the CP increases in intensity. This effect is illustrated in Fig. 6.7, which shows the intensity transmitted through the I_2 filter and double monochromator when the latter is centered on the laser frequency and set for a bandwidth of 5 cm^{-1} . In the $x = 0.1$ sample (solid curve, upper temperature scale, Fig. 6.7), a small singularity is observed at T_{C1} , and the CP intensity increases in the tetragonal phase. Following the transitions at T_{C2} and T_{C3} , the intensity of the CP rapidly decreases and becomes negligible in comparison with the Brillouin components in the rhombohedral phase. The CP intensity in the single

Fig. 6.7. Temperature dependence of the central component intensity within 2.5 cm^{-1} of the laser line. Solid curve and upper temperature scale are for $x = 0.10$; dashed curve and lower temperature scale are for $x = 0.28$.

domain $x = 0.28$ sample between T_{c1} and T_{c2} is illustrated by the dotted curve in Fig. 6.7. There is a step at T_{c1} , followed by a gradual increase until T_{c2} is reached. In the orthorhombic phase below T_{c2} very strong scattering of the incident laser light by the domain structure precluded further measurements in this sample when poled along $\langle 001 \rangle$.

The characteristics of the observed spectra can be understood on the basis of an order-disorder model for the phase transition and the structure of the polar phases. In this model, at a temperature above T_{c1} the ions of the (Ta,Wb) sublattice are displaced from central positions in the octahedron of oxygen ions to eight equivalent positions along cube diagonals. Below T_{c1} preferential occupation of four of these equivalent sites on a plane parallel to a cube face lead to the tetragonal polar ordering. At T_{c2} , two sites on a line parallel to a cube edge are most populated, leading to the orthorhombic phase; at T_{c3} , only one of the cube diagonal sites is favored, resulting in the rhombohedral phase. In the tetragonal phase, fluctuations in the occupations of the four equivalent sites account for the E-symmetry central component. For the orthorhombic phase, a B_2 symmetry CP is expected due to hopping between the two equivalent occupied sites. In the rhombohedral phase, however, no degeneracy of the thermally occupied sites exists at low

temperatures; this accounts for the disappearance of the CP deep in the rhombohedral phase. The absence of a softening of the $TO_1(A)$ mode as T_{c1} is approached from below is also consistent with the order-disorder nature of the transition.

1. Summary of paper: *Solid State Commun.* 55, 451 (1985).
2. Indiana University, Bloomington, Ind.
3. Edward Lee, L. L. Chase, and L. A. Boatner, *Phys. Rev. B* 31, 1438 (1985).

PROTONIC CONDUCTION IN ACCEPTOR-DOPED KTaO_3 CRYSTALS¹

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From a fundamental viewpoint, protonic conduction is of interest because the proton is a unique charge carrier that does not possess an electronic shell about the nucleus and is also the lightest element. Most protonic conductors have hydroxyl as a major constituent, so that H^+ is present at a high concentration and often forms complex molecules or radicals. It is of interest to develop an understanding of protonic migration in an oxide host under sufficiently dilute conditions that the protons do not interact with each other. KTaO_3 , when acceptor doped with 3d transition-metal ions, constitutes such a host. It has previously been shown that H^+ (or D^+) can be introduced into this material, giving rise to an extremely sharp OH^- (or OD^-) absorption band in the infrared.³ In the present work, the ionic conductivity of this system has been investigated, and other techniques have been employed that help to characterize the defects present.

Single crystals of KTaO_3 used in these experiments were grown by means of a flux technique. The nominal acceptor dopant concentrations (Cu^{2+} , Fe^{3+} , or Ni^{3+}) were in the range 0.1–1.0 mole %; however, mass spectrographic analysis of the Cu-doped samples showed that actual concentrations were in the range of 0.01%. Following a heat treatment at $\sim 900^\circ\text{C}$ for a few hours in an atmosphere of water vapor (argon gas passing through water at room temperature), the doped crystals showed an OH^- infrared band. When the samples were treated at 900°C in vacuum (~ 30 m Torr) for a few hours, the IR band was eliminated. Furthermore, complete exchange between H^+ and D^+ was accomplished at 900°C by using D_2O vapor. No OH^- or OD^- band was ever observed in a nominally pure crystal.

Electrical conductivity measurements were carried out using an automated ac bridge (Model CGA-83, Andeen Associates, Cleveland, Ohio) that covered the frequency range 10 Hz–100 kHz. Guarded electrodes were employed to eliminate surface conduction, and complex impedance analysis was used to obtain the bulk conductivity.

A representative conductivity plot of $\ln \sigma T$ versus $1/T$ for Ni-doped KTaO_3 is shown in Fig. 6.8. In this case, the lowest curve is for a sample without H^+ , while the other curves are for various samples for which the values of a_{OH} are denoted.

Fig. 6.8. Conductivity plots for H^{3+} -doped $KTaO_3$ for various values of α_{OH} .

The results show that introduction of protons greatly increases the electrical conductivity and that the activation energy for samples containing H^+ falls within the narrow range 1.02–1.10 eV. So long as the measurement temperature is maintained below $\sim 400^\circ\text{C}$, there is no evidence for irreversibility either in these measurements or in the height of the IR absorption band. Similar results have been obtained for $KTaO_3$ with other iron group dopants. The results show that when acceptor dopants are present in $KTaO_3$, it is possible to introduce H^+ or D^+ in the form of OH^- or OD^- and that the material then becomes almost entirely a proton (or deuteron) conductor.

1. Summary of paper: Solid State Ionics (in press).
2. Columbia University, New York, N.Y.

RESONANCE ELECTRONIC RAMAN SCATTERING IN ERBIUM PHOSPHATE CRYSTALS¹

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Electronic Raman scattering effects in rare-earth crystals have been the subject of numerous studies since the initial work of Hougén and Singh in 1963.⁴ Most of the experiments, however, were

performed using a nonresonant experimental configuration, with the exciting line well removed in frequency from any electronic transition of the subject rare-earth ion. There are only a few reports of resonance electronic Raman scattering in trivalent rare-earth doped crystals, and in these resonance Raman studies, enhancement factors on the order of 5 at most were reported. In the present work, resonance enhancement factors of 10–100 have been observed for electronic Raman transitions within the ground $^4I_{15/2}$ multiplet of Er^{3+} that was both concentrated and diluted in phosphate crystals. The resonance excitation occurs between the crystal field levels of the $^4F_{7/2}$ multiplet and the $^4I_{15/2}$ ground levels. This represents the first time that such large enhancement effects have been observed.

The nonresonant electronic Raman spectrum of $ErPO_4$ and the experimental procedure employed in all of these studies have been reported previously.⁵ In the previous work, the excitation sources were the 514.5- and 457.9-nm lines of an argon-ion laser, and the electronic Raman spectra produced by those two lines were identical. When the argon-ion laser blue line at 488.0 nm ($20,486.7\text{ cm}^{-1}$ in vacuum) is incident on the crystal, however, drastic changes occur in the Raman spectra. The line at 488.0 nm is coincident with the $^4F_{7/2}$ multiplet, which now contributes significantly to the electronic Raman intensities. Another favorable factor is that the oscillator strengths of the transitions between the ground multiplet and the $^4F_{7/2}$ excited multiplet are relatively large (on the order of 5×10^{-6} as determined by laser absorption measurements), which classifies them among the strongest transitions of the Er^{3+} ion).

Resonant and nonresonant Raman spectra were obtained for both pure $ErPO_4$ and 1% Er^{3+} in $LuPO_4$. The nonresonant electronic Raman intensities for $ErPO_4$ were on the order of a few hundred counts per second for the existing experimental conditions. Using the identical experimental arrangement and similar laser input powers of about 50 mW, resonant Raman signals as high as 10,000 counts per second were observed.

Erbium phosphate systems are promising candidates for studies of resonance enhancements of other nonlinear optical processes. Since the electronic Raman intensities are greatly enhanced by the intermediate $^4F_{7/2}$ resonance, two-photon absorption or four-wave mixing should also be significantly enhanced by the same intermediate resonance.

1. Summary of paper: Optics Letters (in press).
2. Lawrence Berkeley Laboratory, Berkeley, Calif.
3. Carleton University, Ottawa, Ontario, Canada.
4. J. T. Hougén and S. Singh, Phys. Rev. Lett. **10**, 406 (1963).
5. P. C. Becker et al., Phys. Rev. B **31**, 8102 (1985).

CRYSTAL GROWTH AND CHARACTERIZATION PROGRAM

CRYSTAL GROWTH AND CHARACTERIZATION PROGRAM

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The impact and effectiveness of the crystal growth and characterization program is increased deliberately by pursuing a policy of working with scientists in other ORNL divisions, other national laboratories, university research laboratories, and industrial laboratories. Depending on the degree of involvement of the program staff members, samples are provided to others on either a collaborative or loan basis. Measurements are generally carried out using these samples that are either supplementary or complementary to ongoing research efforts in the ORNL Solid State Division. Some representative examples of the nature and diversity of the research arising from this activity are given in Table 6.6 along with a listing of some of the laboratories that benefit from this policy.

1. Guest scientist from Universidad Nacional Autónoma de Mexico, Mexico, D.F.

CRYSTAL GROWTH OF ACTINIDE- AND PROMETHIUM-DOPED SINGLE CRYSTALS

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Single crystals of the zircon-structure materials ScPO_4 , YPO_4 , and LuPO_4 containing an estimated 3 wt % ^{244}Cm ($t_{1/2} = 16$ yr) were grown by the flux method. The crystals, up to $1 \times 1 \times 5$ mm in size, formed in platinum containers on cooling high-temperature $\text{Pb}_2\text{P}_2\text{O}_7$ solutions from 1360 to 950°C at 1°C/h in air. The crystals often exhibited a red self-luminescence characteristic of Cm^{3+} . This luminescence was particularly strong in the case of $\text{LuPO}_4:^{244}\text{Cm}$. Single crystals of ZrSiO_4 (zircon) containing up to 5 wt % ^{237}Np ($t_{1/2} = 2 \times 10^6$ yr) were grown from $\text{Li}_2\text{O} \cdot 6 \text{ MoO}_3$ solutions by cooling in air from 1350 to 950°C at 1°C/h, using covered platinum containers. The crystals grew in the form of tetragonal prisms up to $3 \times 3 \times 4$ mm in size. Both the actinide-doped orthophosphate and zircon single-crystal specimens are being investigated at Lawrence Berkeley Laboratory and ORNL by optical and EPR techniques.

The Bridgman technique was used under 1.1 atm of argon to grow SrCl_2 crystals (a cubic, fluorite-structure material) containing ~0.5 wt % ($^{147}\text{Pm}_{0.2}\text{Sm}_{0.8}$) Cl_2 , (~6 Ci of activity). Crystals up to $6 \times 6 \times 12$ mm formed in a conical-bottom quartz ampoule that was lowered at a rate of 1 mm/h through a resistance-heated furnace

at 900°C. The crystals were initially blue and exhibited a red self-luminescence. They darkened after several days, however, due to self-irradiation from ^{147}Pm (0.26-MeV β^- , $t_{1/2} = 2.6$ yr). These crystals are being grown for Lawrence Livermore National Laboratory for the purpose of evaluating new laser systems based on promethium as the laser active ion.

TOP-SEEDED SOLUTION GROWTH OF Nb_3Sn AND FLOAT-ZONE GROWTH OF Cr_3Si

Y. K. Chang	H. E. Harmon

The stoichiometric A15 compound Nb_3Sn has a high superconducting transition temperature and a large critical current density in high magnetic fields. While single crystals of Nb_3Sn are of interest for use in numerous experimental investigations, the high peritectic temperature (2130°C), reactive nature, and high vapor pressure of the material at high temperatures have been obstacles to producing high-quality single crystals. According to the Nb-Sn phase diagram,¹ Nb_3Sn dissolves in tin at a temperature above 930°C, and it is possible to nucleate Nb_3Sn crystals at a temperature significantly below its melting point. Experiments on the growth of Nb_3Sn have been carried out using the top-seeded solution-growth method at temperatures of about 1200°C. This temperature is safely below the point where serious vaporization losses occur. Additionally, the growth chamber could be filled with 4-5 atm of argon to reduce evaporation. Since molten tin has a tendency to wet copper, an anodized aluminum hearth was used for casting Nb_3Sn . Precast Nb_3Sn ingots and a sufficient amount of tin were melted in an alumina crucible in an rf induction crystal-growth system. The precast Nb_3Sn compound was found to dissolve more easily than pure Nb metal in a tin flux. A Nb single crystal, used as a seed to nucleate Nb_3Sn crystals from the tin flux, was pulled at a rate of about 1-2 mm/day, and small Nb_3Sn crystallites with dimensions up to 2 mm were successfully nucleated on the surface of the Nb seed. X-ray powder diffractometry showed that the lattice parameters of these crystals are in good agreement with those of the stoichiometric composition.

Cr_3Si , another A15 compound, melts congruently at $1770 \pm 10^\circ\text{C}$. Although Cr_3Si is not a superconductor, when the element Cr in Cr_3Si is replaced by its neighboring element V to form V_3Si , the compound V_3Si exhibits strong superconducting behavior. Since high-quality single crystals of V_3Si have been successfully grown previously in our laboratory by the float-zone method, this technique has now been extended to the growth of single crystals of Cr_3Si . Feed rods were prepared by melting Cr pellets over Si disks in an arc melter. The material was crushed and remelted inductively in a water-cooled silver boat system several times to ensure homogeneity. The resulting rods were zone refined at approximately 5 mm/h in an argon atmosphere. Single crystals of Cr_3Si about 8 mm in diam and 40 to 50 mm long were prepared, and their lattice parameters were identified by means of diffrac-

Table 6.6. Loan of samples for research outside the Research Materials Program.

Material	Type of study	To whom sent	Organization
SrCl ₂ :Pm	Fluorescence	M. Shinn	LLNL
TiC	Resistivity	F. Modine	ORNL
TiC	Wear properties	M. Kaminsky	ANL
TiC	Analytical microcopy standards	K. Krishnan	LBL
TaC	Defect properties	C. Allison	Oklahoma State University
ZrC	Wear properties	M. Kaminsky	ANL
VC	Analytical microcopy standards	L. Krishnan	LBL
Pb-Fe phosphate glasses	Evaluation of nuclear waste storage	W. Lutze	Hahn-Meitner Institut, Berlin, FRG
Pb-Fe phosphate glasses	Evaluation of nuclear waste storage	C. Jantzen	Savannah River Laboratories
Pb-Fe phosphate glasses	Evaluation for possible commercial use	K. Brown	Spectrol Electronics
Pb-Fe phosphate glasses	Liquid chromatography studies	R. Ramsey	ORNL
Nb+50 wt % Ti	Neutron scattering	D. Christen	ORNL
Nb	SIMS	N. Karam	North Carolina State University
AgPd	Metallurgy	C. Sparks	ORNL
V ₃ Si	X-ray measurements	J. Staudenmann	Ames Laboratory
V ₃ Si	Anisotropy of Tc	L. Schwartzkopf	Mankato State University
Rare-earth Cu ₂ Si ₂	HIXE measurements	S. Raman	ORNL
Al ₂ O ₃	HIXE measurements	S. Raman	ORNL
MgO	Infrared measurements	A. Sievers	Cornell University
CaO	Optical lasers	Y. Chen	ORNL
MgO:Al	TEM	R. Gonzalez	University of Madrid, Spain
LuPO ₄ :Ce ²⁺	Optical absorption	N. Edelstein	LBL
LuPO ₄ :Ce ²⁺	Optical absorption	N. Edelstein	LBL
ScPO ₄ :Ce ²⁺	Optical absorption	N. Edelstein	LBL
YPO ₄ :Ce ²⁺	Optical absorption	N. Edelstein	LBL
ZrSiO ₄	Optical absorption	N. Edelstein	LBL
ZrSiO ₄ :Np ²³⁷	Optical absorption	N. Edelstein	LBL
ScPO ₄ , LuPO ₄ , ScPO ₄ , YPO ₄ , LuPO ₄ :Mn	Thermoluminescence	E. Muñoz P.	UNAM, Mexico
MgO:Mn	EPR	J. Boldú O.	UNAM, Mexico
	Spin lattice relaxation	R. Stapelton	University of Illinois
LaPO ₄	Infrared absorption	N. Edelstein	LBL
SrCl ₂ :U	Optical absorption	N. Edelstein	LBL
SrCl ₂ :Cu	Optical studies	L. Chase	LLNL
SrCl ₂ :Sm	Optical studies	L. Chase	LLNL
KTaO ₃ :Co	Conductivity	A. Nowick	Columbia University
Pb ₂ F ₂ O ₇	X-ray measurements	D. Mullica	Baylor University
Cd/YbPO ₄	X-ray measurements	D. Mullica	Baylor University
KTaO ₃	Neutron scattering	M. Hagen	ORNL
K _{1-x} TaO ₃	Neutron scattering	C. Loong	ANL

tometry. These samples will be used in physical property measurements including studies of phonon spectra.

1. J. P. Charlesworth, I. Macphail, and P. E. Madsen, *J. Mater. Sci.* 5, 580 (1970).

GROWTH OF TRANSITION-METAL CARBIDE SINGLE CRYSTALS

C. B. Finch

The rf induction-heated float-zone method was used to grow $8 \times 8 \times >10$ -mm single crystals of $VC_{0.80}$ and $TiC_{0.95}$. The crystals of both materials were relatively homogeneous in terms of their composition along the growth axis. The float-zone growth process was carried out under 8 atm of He at $\sim 2600^\circ\text{C}$ and 2800°C for $VC_{0.80}$ and $TiC_{0.95}$, respectively. The experiments utilized 12.0-cm long, 1.2-cm-diam ceramic starting rods whose compositions had been reported by Japanese authors¹ as ideal for producing a uniform composition along the boule growth axis. Float-zone translation rates were 1.0 cm/h for $VC_{0.80}$ and 1.5 cm/h for $TiC_{0.95}$. Bottom spindle rotation at ~ 10 rpm was employed with no top rotation. The molten zone height was approximately 1.0 cm for a 1.2-cm-diam rod. Figure 6.9 shows typical as-grown boules of $VC_{0.80}$ and $TiC_{0.95}$. The final compositions of both $VC_{0.80}$ and $TiC_{0.95}$ were determined by carbon analyses at the start (bottom) and finish (top) of the boule. These single crystals will be used in optical and surface properties investigations in the ORNL Solid State Division.

1. S. Otani et al., *J. Cryst. Growth* 61, 1 (1983).

GROWTH OF AgPd CRYSTALS BY PULLING FROM THE MELT

Y. K. Chang

Single crystals of silver-palladium alloys with wide concentration ranges are required for x-ray diffraction, photoemission, and positron annihilation experiments in order to verify the interesting results obtained from recent band structure calculations. Early attempts to grow crystals of an alloy containing 50 at. % Pd by the induction float-zone method failed due to the difficulty of maintaining a molten zone. During this reporting period other attempts have been made to grow AgPd single crystals by pulling from the melt. A AgPd charge was first melted in an alumina crucible held inside a graphite susceptor that was coupled to an rf induction coil. This assembly was rotated for stirring and for obtaining uniform heating. A 6-mm polycrystalline rod was used as a seed to pull AgPd crystals in a water-cooled growth chamber that was filled with 4.5 atm of argon gas for the purpose of suppressing the vaporization of silver. One of the resulting crystals is shown in Fig. 6.10(a). After pulling at a rate of about 10 mm/h for more than 7 mm, the pulling rate

was lowered to 5 mm/h for about 14 mm and then lowered to 3 mm/h for the rest of the growth. It was found that the grain boundaries have a tendency to run parallel to the growth direction and that the grain size increases with decreasing pulling rate. Grains several millimeters wide were found near the end of the crystal. It appears that a necking process and possibly a slower pulling rate may be necessary for preparing large grain crystals. A Laue x-ray photograph taken 10 mm from the end of the boule is shown in Fig. 6.10(b). This crystal will be cut into thin bars and used as seeds in future growths to minimize defect generation and propagation.

GROWTH OF A NIOBIUM-TITANIUM BICRYSTAL

Y. K. Chang

For two decades, niobium-titanium alloys have been used as windings in superconducting magnets. Recent interest in investigating the flux-line-lattice interaction with grain boundaries in NbTi by means of small-angle neutron scattering has resulted in a demand for bicrystals of this material. Both random and well-defined grain boundaries are desired for these experimental studies. The approach employed in growing a crystal of this type was to select a randomly oriented bicrystal (cut from a crystal prepared in this laboratory) for use as a seed. This bicrystal was then joined to a precast and swaged $Nb_{0.34}Ti_{0.66}$ polycrystalline rod by means of induction melting. Two vertical float-zone passes were made. The purpose of the first pass was primarily to smooth and thicken the rod. The second pass was carried out at about 7 mm/h for the actual crystallization process. For the second and final pass, the molten zone was translated down to 1 mm below the beginning of the first pass in order to make contact with the bicrystal seed. To suppress excess vaporization of Ti at the growth temperature ($\sim 1850^\circ\text{C}$), the growth chamber was filled with 3.2 atm of argon gas. A bicrystal 8 mm in diameter and 45 mm in length, having a grain boundary running through the middle along the length of the ingot, was successfully prepared by means of this technique. Such a grain boundary is shown in Fig. 6.11 with two etched slices cut from the beginning and the end (separated by 43 mm) of the bicrystal. The grain boundary runs almost exactly through the middle of the cross section surface, and its shape is only slightly altered from the beginning of the growth to the end.

STRUCTURE OF DICROMATE-TYPE LEAD PYROPHOSPHATE, $Pb_2P_2O_7$ ¹

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D. A. Grossie² L. A. Boatner
B. C. Sales

Compounds with compositions of the type $X_2Y_2O_7$ provide an illustration of the important role that cation size plays in determining the structural properties of crystals; three structural classes, determined by the ionic radii of both

VC

(a)

(b)

Fig. 6.9. (a) $VC_{0.8}$ single-crystal rod grown by floating zone method. (b) $TiC_{0.95}$ single-crystal rod grown by floating zone method.

the X and Y atoms, have been described for these materials. Crystals in which the ionic radius of the Y atom is greater than 0.6 Å crystallize in the stopite-type structure where the Y atoms are octahedrally coordinated. When the ionic radius of the Y atom is less than 0.6 Å and the ionic radius of the X atom is less than 0.97 Å, the thortveitite-type structure is realized. If the X atom has a radius greater than 0.97 Å, crystallization with the dichromate-type structure occurs. A detailed single-crystal structural analysis of the compound $Pb_2P_2O_7$ (i.e., lead pyrophosphate) has been carried out because this compound is perhaps the closest crystalline analog of an unusual new family of amorphous materials (i.e., lead-iron phosphate glasses).³

The local structural properties of crystalline lead pyrophosphate should bear some relationship to those of the disordered lead-iron phosphate (and lead-phosphate) glasses, and accordingly an understanding of the atomic structure of crystalline lead pyrophosphate can provide insight into the microscopic origin of the unusual physical and chemical characteristics exhibited by lead-iron phosphate glasses.

Single crystals of lead pyrophosphate used in the structural refinement were prepared by slowly cooling a molten mixture of high-purity PbO and P_2O_5 (added as $NH_4H_2P_2O_4$). After heating the mixture to 1000°C in air, the molten liquid was repeatedly stirred to ensure compositional homogeneity throughout the melt. The melt temperature

(a)

(b)

Fig. 6.10. (a) A AgPd crystal (50 at. % Ag) prepared by means of pulling from the melt. (b) A Laue x-ray photograph of AgPd taken about 10 mm from the end of the boule.

was then reduced to 900°C followed by a slow cooling of the melt (about 2°C/h) to 750°C. Optically clear lead pyrophosphate single-crystal plates measuring about $5 \times 5 \times 1 \text{ mm}^3$ could be easily removed from the solidified melt. Energy dispersive x-ray analysis and powder x-ray diffraction analysis indicated that the crystals had the proper lead-to-phosphorus ratio. Diffraction data were collected using an Enraf-Nonius CAD-4F diffractometer and a clear colorless Pb_2O_7 crystal measuring $0.168 \times 0.336 \times 0.360 \text{ mm}$. Lattice constants and the orientation matrix were obtained through a least-squares refinement of 25 accurately centered reflections. Intensity data were collected using the ω -2 θ scan technique with a variable scan rate determined by a fast prescan. Phosphorous and oxygen atoms were located by difference Fourier techniques using the Pb atoms to phase the electron density map. Lead pyrophosphate, $\text{Pb}_2\text{P}_2\text{O}_7$, crystallizes in the triclinic space group $P1$ ($Z = 4$). The lattice parameters are $a = 6.941(2)$, $b = 6.966(2)$, $c = 12.751(4) \text{ \AA}$, $\alpha = 96.82(3)$, $\beta = 91.14(3)$, and $\gamma = 89.64(3)^\circ$.

A stereo view of the structural unit with all lead atoms fully coordinated is shown in Fig. 6.12. Assignment of coordination numbers for the large divalent cations, Pb^{2+} , was made by geometric and distance considerations and through the application of the bond valence model. The coordination numbers are eight for Pb(1) and Pb(4) and nine for Pb(2) and Pb(3). Pb(1) is coordinated to eight oxygen atoms arranged as a hybrid of D_{2d} and D_{3d} symmetries approximating a biaugmented trigonal prism. Pb(2) and Pb(3) are both nine coordinated and have the geometric configuration of a distorted monocapped square antiprism. Pb(4) is bonded to eight oxygen atoms, best described as a severely distorted square antiprism. The four unique phosphorus atoms are tetrahedrally coordinated (mean O-P-O angle 109.3°), and adjacent tetrahedra share one vertex to form distinct diphosphate groups. The P_2O_7 groups are repeated through lattice translations to form sheetlike structures.

1. Summary of paper: Journal of Solid State Chemistry (in press).

2. Baylor University, Waco, Tex.

3. B. C. Sales and L. A. Boatner, Science 226, 45 (1984).

DETERMINATION OF THE STRUCTURE OF SYNTHETIC PEROVSKITE CaTiO_3 BY X-RAY DIFFRACTOMETRY¹

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A determination of the crystal structure of synthetic perovskite (calcium titanate) has been carried out by means of single-crystal x-ray diffraction.

The single crystals of CaTiO_3 employed in the present crystallographic investigations were grown using a flux technique. A starting mixture consisting of 100.8 g KF, 45.0 g LiF, 11.85 g CaO , and 12.85 g TiO_2 was placed in a 200-ml platinum

Fig. 6.11. Grain boundary of a NbTi crystal. Two slices were chemically etched after being cut from the beginning (left) and finish (right) of the bicrystal.

Fig. 6.12. Stereo view of the structural unit of $\text{Pb}_2\text{P}_2\text{O}_7$. The lead atoms are shown fully coordinated.

crucible and heated to $\sim 1215^\circ\text{C}$ in air using a furnace that employed SiC heating elements. Following a 4-h soak at the maximum temperature, the system was cooled at 1.0°C/h to $\sim 875^\circ\text{C}$. Single crystals of CaTiO_3 formed in this process were entrained in the solidified mixed LiF-KF flux that is water soluble and was easily removed. After a preliminary optical examination to eliminate samples with flux inclusions, several single crystals of CaTiO_3 were selected and ground into spheres. One of the ground crystals was mounted on a glass fiber and transferred to the goniometer head on an Enraf-Nonius CAD-4F autodiffractometer. All x-ray measurements were made at 291 K using graphite-monochromated MoK_α radiation. Calcium titanate CaTiO_3 crystallizes in the orthorhombic space group Pcmm (No. 62, $Z = 4$) with $a = 5.367(2)$, $b = 7.622(3)$, and $c = 5.425(1)$ Å. A reliability factor of 0.040 was obtained for 197 independent reflections with $R^2 > 3\sigma$ ($R^2 =$

0.041). Important averaged bond lengths are Ca-O(1), 2.721; Ca-O(2), 2.717; Ti-O(1), 1.945; and Ti-O(2), 1.952 Å. The titanium atoms are octahedrally bonded to six oxygen atoms, and the calcium metal atoms are surrounded by twelve oxygen atoms forming a distorted tetracapped tetragonal polyhedron, a distorted cuboctahedron. The titanium atoms in this structure are 6-coordinated by oxygen atoms to form almost perfect octahedra throughout the structure. Each of the oxygen atoms is also 6-coordinated in an octahedral fashion as can be seen from the stereo view of the CaTiO_3 unit cell shown in Fig. 6.13.

1. Summary of paper to be published.
2. Baylor University, Waco, Tex.

Fig. 6.13. A representative stereo diagram of the molecular packing within the unit cell of calcium titanate. Calcium atoms are the large filled-in circles, titanium atoms are the large unfilled circles, and the small open circles represent oxygen atoms.

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J. F. Wendelken, G.-C. Wang, J. M. Pimbley, and T.-M. Lu, "Characterization of Surface Defect Structure by Low-Energy Electron Diffraction"

R. F. Wood, A. Geist, A. Solomon, D. H. Lowndes, and G. E. Giles, "Modeling of Bulk Nucleation and Multiple Phase Front Propagation in Pulsed Laser Melted a-Si" (invited paper)

D. M. Zehner, G. R. Cruzalski, J. F. Wendelken, R. A. DiDio, and E. W. Plummer, "Adsorption and Dissociation of O_2 on Cu(110)"

Thirtieth Annual Conference on Magnetism and Magnetic Materials, San Diego, California, November 27-30, 1984:

J. F. Cooke, S. H. Liu, and A. J. Liu, "Paramagnetic Form Factors from Itinerant Electron Theory"

W. H. Li, C. H. Perry, J. B. Sokoloff, J. W. Lynn, R. M. Nicklow, W. G. Stirling, and D. McK. Paul, "A Polarized Neutron Measurement of 'Forbidden' Magnon Scattering in Pt_3Mn "

H. A. Mook and J. W. Lynn, "Measurements of the Magnetic Excitations above T_c in Fe and Ni" (invited paper)

R. M. Nicklow, R. M. Moon, S. Kawarazaki, N. Kunitomi, H. Suzuki, T. Ohtsuka, and Y. Morii, "Nuclear Spin Ordering Observed by Neutron Diffraction" (invited paper)

O. A. Pringle, H. A. Mook, and M. B. Maple, "Small-Angle Neutron Scattering of $\text{Er}_{0.8}\text{Ho}_{0.2}\text{Rh}_2\text{B}_4$ "

Y. Tsunoda, N. Kunitomi, and J. W. Cable, "Magnetic Excitations in CuMn Spin Glass Alloy"

American Vacuum Society 31st National Symposium, Reno, Nevada, December 3-7, 1984:

R. A. DiDio, D. Heskett, J. M. Mendenar, E. W. Plummer, and D. M. Zehner, "The Pathway to Dissociation of O_2 on $\text{Cu}(100)$ and $\text{Cu}(110)$ "

H. L. Davis and J. R. Noonan, "Atomic Rippling of a Metallic Ordered Alloy Surface— $\text{NiAl}(110)$ "

J. F. Wendelken and G.-C. Wang, "Hydrogen-Induced Reconstruction of Stepped $\text{W}(001)$ Surfaces Studied with LEED and EELS"

R. A. Zuhr and W. R. Wampler, "Time-Resolved Impurity Fluxes in the Textor Plasma Edge"

Interagency Users Workshop on Plasma-Based Surface Engineering Technologies, Champaign, Illinois, December 12-14, 1984:

David B. Paker, "Surface Modification by Ion Implantation and Ion Beam Mixing" (invited paper)

International Conference on Neutron Scattering in the '90s, Jülich, Federal Republic of Germany, January 14-18, 1985:

R. M. Moon, "A Review of Current and Proposed Reactor Upgrades" (invited paper)

Fifty Second Annual Meeting of the Academy of Orthopaedic Surgeons, Las Vegas, Nevada, January 24-29, 1985:

J. M. Williams, G. M. Stevens, and R. A. Buchanan, "Wear Improvement of Surgical Ti-6Al-4V Alloy by Ion Implantation"

Ninth Annual Condensed Matter Physics Conference of the Australian Institute of Physics, Wagga Wagga, New South Wales, February 6-8, 1985:

T. R. Finlayson and H. G. Smith, "New Thoughts on an Old Problem: In-Ti" (invited paper)

Egyptian Physical Society Meeting, Minia, Egypt, February 17, 1985:

R. A. Weeks, G. Kordas, Milson Silva, Jose Martinelli, and B. R. Appleton, "Modification of Silica Glass by Ion Implantation" (invited paper)

American Adhesion Society Annual Meeting, Savannah, Georgia, February 24-27, 1985:

J. F. Fellers, M. Y. Tang, G. G. Rice, and J. S. Lin, "SAXS Characterization of Graphite, Kevlar® and Cellulose Fibers with Some Fractal Theory Interpretation"

Annual Meeting of the Metallurgical Society of AIME, New York, New York, February 24-28, 1985:

S. M. Ohr, S.-J. Chang, C. G. Park, and R. Thomson, "Coexistence of Brittle and Ductile Fracture in bcc Metals" [J. Met. 36(12), 83 (1974)]

S.-J. Chang and S. M. Ohr, "Inclined Dislocation Emission at a Shielded Crack Tip" [J. Met. 36(12), 82 (1984)]

C. G. Park and S. M. Ohr, "TEM Studies of Low Temperature Fracture in Molybdenum" [J. Met. 36(12), 82 (1984)]

Joint Spring Meeting of the Texas Section of the American Physical Society and the Texas Section of the AAPPT, Houston, Texas, March 8-9, 1985:

B. L. Davis and J. R. Noonan, "Rippled Relaxation of the NiAl(110) Surface" [Bull. Am. Phys. Soc. 30, 1110 (1985)]

D. Heidorn, H. E. Rorschach, C. F. Hazelwood, and R. M. Nicklow, "Neutron Scattering Studies of Water in Macromolecular Systems" [Bull. Am. Phys. Soc. 30, 1108, (1985)]

Polymer and Textile Research Association 1985 Annual Meeting, Knoxville, Tennessee, March 21-22, 1985:

J. F. Fellers, J. S. Lin, M. Y. Tang, and G. E. Rice, "SAXS Characterization of Graphite, Kevlar® and Cellulose Fibers with Some Fractal Theory Interpretation"

Fourth Oxford Conference on Microscopy of Semiconducting Materials, Oxford, England, March 25-27, 1985:

S. J. Pennycook, R. J. Culbertson, and E. Fogarassy, "Z-Contrast Imaging and Electron Channeling Analysis of Dopants in Semiconductors"

American Physical Society Meeting, Baltimore, Maryland, March 25-29, 1985:

B. R. Appleton, "Surface Modification and Characterization Collaborative Research" (invited paper)

M. M. Abraham, M. A. Aronson, L. A. Boatner, and J. O. Ramey, "EPR Observations of Hf^{3+} and Ti^{3+} in Orthophosphate Single Crystals" [Bull. Am. Phys. Soc. 30, 370 (1985)]

J. B. Bates, J. C. Wang, and R. L. Anderson, "AC Frequency Response of Metal-Solid Electrolyte Interfaces" [Bull. Am. Phys. Soc. 30, 346 (1985)]

S. J. Chang and S. M. Ohr, "Dislocation-Free Model of Fatigue Crack Propagation" [Bull. Am. Phys. Soc. 30, 617 (1985)]

L. L. Chase, J. Sokoloff, and L. A. Boatner, "Quasielastic Scattering from Polarization Fluctuations in KTN" [Bull. Am. Phys. Soc. 30, 272 (1985)]

Y. Chen and R. Gonzalez, "Tunable Lasers Using Thermochemically Reduced Oxide Crystals" [Bull. Am. Phys. Soc. 30, 419 (1985)]

D. K. Christen, H. R. Kerner, S. T. Sekula, and Y. K. Chang, "Observation and Interpretation of Flux-Line Anisotropy in V_3Si " [Bull. Am. Phys. Soc. 30, 609 (1985)]

Y. T. Chu and J. B. Bates, "Investigation of Surface and Bulk Polaritons on Uniaxial Al_2O_3 Crystals by Attenuated Total Reflection" [Bull. Am. Phys. Soc. 30, 245 (1985)]

J. F. Cooke, J. A. Blackman, and T. Morgan, "New Interpretation of Spin-Wave Behavior in Nickel" [Bull. Am. Phys. Soc. 30, 615 (1985)]

H. L. Davis and J. R. Noonan, "Truncation-Induced Layer Relaxations of the Al(311) Surface" [Bull. Am. Phys. Soc. 30, 459 (1985)]

P. C. Eklund, J. L. Zarestky, J. G. Spolar, W. A. Kamitakahara, and R. M. Nicklow, "Charge Transfer Induced Changes in the Phonon Dispersion of GIC's" [Bull. Am. Phys. Soc. 30, 241 (1985)]

G. R. Gruzalski, D. M. Zehner, and G. W. Ownby, "Electron Spectroscopic Studies of Tantalum Carbide" [Bull. Am. Phys. Soc. 30, 410 (1985)]

G. E. Jellison, Jr., and D. H. Lowndes, "Time-Resolved Ellipsometry Measurements of Pulsed Laser-Irradiated Silicon Using a KrF Excimer Laser" [Bull. Am. Phys. Soc. **30**, 401 (1985)]

H. R. Kerchner, D. K. Christen, and S. T. Sekula, "The Anisotropic Flux-Line-Flux-Line Interaction in High-Field Superconductors" [Bull. Am. Phys. Soc. **30**, 609 (1985)]

W. C. Koehler, "The National Center for Small-Angle Scattering Research" (invited paper)

W.-H. Li, C. H. Perry, J. B. Sokoloff, J. W. Lynn, and R. M. Nicklow, "Polarized Neutron Scattering Studies of the Intermetallic Ferromagnet Pt_3Mn " [Bull. Am. Phys. Soc. **30**, 615 (1985)]

S. a. Liu, "A Fractal Model for Charge Diffusion Across a Rough Interface" [Bull. Am. Phys. Soc. **30**, 564 (1985)]

J. W. Lynn and H. A. Mook, "Direct Observation of Spin Wave Excitations Above T_c in Nickel and Iron" [Bull. Am. Phys. Soc. **30**, 615 (1985)]

J. H. Magill, J. M. Schultz, and J. S. Lin, "In Situ SAXS Measurements of the Crystallization of TMPS" [Bull. Am. Phys. Soc. **30**, 249 (1985)]

J. R. Martinelli, E. Sonder, R. A. Weeks, and R. A. Zuhr, "Diffusion Coefficients and Transference Numbers in MgO " [Bull. Am. Phys. Soc. **30**, 469 (1985)]

K. P. McAlea, J. M. Schultz, G. D. Wignall, and K. H. Gardner, "Small-Angle Neutron Scattering Studies of Polyethylene Terephthalate" [Bull. Am. Phys. Soc. **30**, 494 (1985)]

F. A. Modine, T. W. Raywood, and C. Y. Allison, "Optical and Electrical Properties of Titanium Carbide" [Bull. Am. Phys. Soc. **30**, 570 (1985)]

H. A. Mook, "Poster of the Neutron Scattering Facilities at the HFIR" (invited paper)

Mark Mostoller and J. C. Wang, "Ionic Potential Models in Insulators Having the Rutile Structure" [Bull. Am. Phys. Soc. **30**, 281 (1985)]

J. R. Noonan and H. L. Davis, "The Atomic Structure of the $\text{NiAl}(110)$ Surface" [Bull. Am. Phys. Soc. **30**, 459 (1985)]

Perla N. Peszkin, J. M. Schultz, and J. S. Lin, "Microstructure Development of PET Fibers by Means of X-ray Scattering" [Bull. Am. Phys. Soc. **30**, 291 (1985)]

Mark Rasolt, "Lifetime of an Electron Hole Plasma in Silicon in the Picosecond Range" [Bull. Am. Phys. Soc. **30**, 575 (1985)]

B. C. Sales, R. S. Brazell, J. B. Bates, and L. A. Boatner, "Liquid Chromatography and Raman Spectroscopy Studies of Lead-Iron Phosphate" [Bull. Am. Phys. Soc. **30**, 236 (1985)]

E. Sonder, J. R. Martinelli, R. A. Weeks, and R. A. Zuhr, "The Use of $^{18}\text{O}(\text{p},\alpha)^{15}\text{N}$ Reaction to Study Cation Diffusion in MgO " [Bull. Am. Phys. Soc. **30**, 469 (1985)]

C. Stassis, J. D. Axe, C. F. Majkrzak, and J. Arthur, "Induced Moment Magnetic Form Factors of UBe_{13} and UPt_3 " [Bull. Am. Phys. Soc. **30**, 356 (1985)]

J. C. Wang and J. B. Bates, "Model for the Interfacial Impedance between a Solid Electrolyte and a Blocking Electrode" [Bull. Am. Phys. Soc. **30**, 246 (1985)]

G. D. Wignall and F. S. Bates, "Critical Behavior in Binary Blends of Proteo- and Deutero-1,4-Polybutadiene" [Bull. Am. Phys. Soc. **30**, 541 (1985)]

F. W. Young, Jr., R. R. Coltman, Jr., C. E. Klatonde, and H. R. Kerchner, "The National Low-Temperature Neutron Irradiation Facility" [Bull. Am. Phys. Soc. **30**, 391 (1985)] (invited paper)

NATO Advanced Studies Conference on Scaling Phenomena in Disordered Systems, Oslo, Norway, April 10-31, 1985:

L. J. Gray, S. H. Liu, and T. Kaplan, "A Fractal Model for Charge Diffusion Across a Rough Interface"

1985 Spring Meeting of the Materials Research Society, San Francisco, California, April 15-18, 1985:

G. C. Farlow, C. W. White, C. J. McHargue, B. R. Appleton, G. J. Clark, and J. E. E. Baglin, "Ion Bombardment of Metal Films on Insulators" (invited paper)

G. R. Gruzalski, D. M. Zehner, and G. W. Ownby, "Electron Spectroscopic Studies of Tantalum Carbide"

D. B. Poker and B. R. Appleton, "Effects of Different Methods of Calculating Mixed Depth Upon the Mixing Rates during Ion Beam Mixing"

R. A. Weeks, Milson Silva, G. Kordas, D. L. Kinser, Jose Martinelli, and B. R. Appleton, "Magnetic Properties of Ions Implanted in Glass; Fe in SiO₂"

Sixth European Photovoltaic Solar Energy Conference, London, England, April 15-19, 1985:

R. Ruckteschler, R. F. Wood, and R. D. Westbrook, "Development of Laser-Processed High-Efficiency n⁺pp⁺ Silicon Solar Cells"

Workshop on Ion Mixing in Surface Layer Alloying II, California Institute of Technology, Pasadena, California, April 19-20, 1985:

D. B. Poker, "Calculation of Mixed Depth for Some Metal-Si Systems" (invited paper)

Federation of American Scientists for Experimental Biology, Anaheim, California, April 21-26, 1985:

G. J. Bunick and E. C. Uberbacher, "X-ray Structure of the Nucleosome Core Particle" [Fed. Proc. 44, 870 (1985)]

1985 Spring Meeting of the American Physical Society, Crystal City, Virginia, April 14-27, 1985:

J. B. Roberto, "Plasma Materials Interactions in Controlled Fusion Machines" [Bull. Am. Phys. Soc. 30, 788 (1985)]

One Hundred Eighty Ninth National Meeting of the American Chemical Society, Miami Beach, Florida, April 28-May 3, 1985:

John B. Bates, "Ionic and Molecular Transport in Beta- and Beta"-Alumina Solid Electrolytes" (invited paper)

John B. Hayter, "Advances in Small-Angle Scattering from Surfactant Microphases" (invited paper)

O. I. Thompson, J. M. O'Reilly, and W. C. Koehler, "Small-Angle Neutron Scattering of SDS Micelles and Solubilizates"

Society of Plastic Engineers Meeting, Washington, D.C., April 29-May 2, 1985:

G. D. Wignall, "Small-Angle Neutron Scattering Facilities and Polymer Research at Oak Ridge"

Fifth Annual Symposium of the Tennessee Valley Chapter of the American Vacuum Society, Knoxville, Tennessee, April 30-May 2, 1985:

H. L. Davis and J. R. Noonan, "Multilayer Relaxation in Metallic Surfaces" (invited paper)

G. C. Farlow, C. W. White, C. J. McHargue, G. J. Clark, and J. E. E. Baglin, "Ion Beam Mixing of Metal Films on Insulators"

G. R. Gruzalski, D. M. Zehner, and G. W. Ownby, "Surface Spectroscopic Studies of Tantalum Carbide"

American Fiber Society Symposium on Cellulose—Today's Polymer of the Future, Atlanta, Georgia, May 1-3, 1985:

Ming-Ya Tang, John F. Fellers, and J. S. Lin, "Fractal Structures in Cotton Cellulose as Characterized by SAXS"

Eighty-Seventh Annual Meeting of the American Ceramic Society, Cincinnati, Ohio, May 5-9, 1985:

Y. Chen, R. Gonzalez, and K. L. Tsang, "Diffusion of Deuterium and Hydrogen in Rutile TiO_2 Crystals at Low Temperatures" [*Am. Ceram. Soc. Bull.* 64, 449 (1985)]

J. R. Martinelli, R. A. Weeks, E. Sonder, and R. A. Zuhr, "Cation Motion in MgAl_2O_4 " [*Am. Ceram. Soc. Bull.* 64, 464 (1985)]

S. Spooner, P. Angelini, P. F. Becher, A. Bleier, W. D. Bond, and J. Brynestad, "Investigation of the Synthesis and Processing of Submicron Ceramic Powders by TEM and Small-Angle X-ray Scattering (SAXS)"

F. A. Modine, D. H. Lowndes, E. Sonder, and J. R. Martinelli, "Laser Fabrication of Electrodes on Zinc Oxide Varistors" [*Am. Ceram. Soc. Bull.* 64, 465 (1985)]

T. C. Quinby, E. Sonder, and D. L. Kinser, "Preparation of Varistor Powders by the Urea Process" [*Am. Ceram. Soc. Bull.* 64, 465 (1985)]

E. Sonder, T. C. Quinby, and D. L. Kinser, "Properties of Varistors Prepared by the Urea Process" [*Am. Ceram. Soc. Bull.* 64, 465 (1985)]

Topical Conference on Basic Properties of Optical Materials, Gaithersburg, Maryland, May 7-9, 1985:

John A. Wooliam, George H. Bu-Abbud, David L. Mathine, David Poker, David Ingram, and Peter Pronko, "Optical Properties of Ion Beam Irradiated Molybdenum Laser Mirrors as Studied by Ellipsometry"

Energy Beam-Solid Interaction and Transient Processing Symposium of the Materials Research Society—European Spring Meeting, Strasbourg, France, May 13-15, 1985:

C. W. White, M. J. Aziz, J. Narayan, and B. Stritzker, "Melting of Crystalline and Amorphous Silicon by Ruby, XeCl , and KrF Excimer Laser Irradiation"

International Conference on Materials and Mechanisms of Superconductivity, Ames, Iowa, May 29-31, 1985:

D. K. Christen, H. R. Kerchner, S. T. Sekula, and Y. K. Chang, "Flux-Line Lattice Anisotropy of V_3Si : Observation and Interpretation"

J. R. Thompson, J. T. Ellis, D. K. Christen, J. D. Lewis, and S. T. Sekula, "Formation, Ion Modification, and Annealing of VN"

Symposium on Low-Q Diffraction, Los Alamos, New Mexico, May 30, 1985:

J. B. Hayter, "Exploring Liquid Structure with SANS" (invited paper)

ASM Conference on the Applications of Ion Plating and Implantation to Materials, Atlanta, Georgia, June 3-5, 1985:

J. M. Williams, R. A. Buchanan, and E. D. Rigney, Jr., "Improvement in Wear Performance of Surgical Ti-6Al-4V Alloy by Ion Implantation of Nitrogen or Carbon"

International Conference of Ultrasonic Attenuation and Internal Frictions in Solids, Urbana, Illinois, June 3-7, 1985:

D. B. Poker, R. B. Schwarz, and A. V. Granato, "Second Order Elastic Constants of Pd, $\text{PdH}_{0.7}$, and $\text{PdD}_{0.7}$ between 1.7 and 50 K"

Fourth Conversation in Biomolecular Stereodynamics, Albany, New York, June 4-6, 1985:

Edward C. Uberbacher and Gerard J. Bunick, "X-ray Structure of the Nucleosome Core Particle"

International Symposium on Physics of Complex and Supramolecular Fluids, Annandale, New Jersey, June 17-21, 1985:

John B. Hayter, "An Introduction to Ferrofluid Structure" (invited paper)

Twenty-Seventh Annual Electronic Materials Conference, Boulder, Colorado, June 19-21, 1985:

J. A. Edmond, B. R. Appleton, and K. F. Davis, "Ion Implantation and Thermal Annealing of P and Al Dopants in High-Purity Beta Silicon Carbide Single-Crystal Thin Films"

Annual Canadian Association of Physicists Congress, Fredericton, N.B., Canada, June 24-26, 1985:

Mark Rasolt, "Critical Behavior of a Dilute Interacting Bose Fluid" (invited paper)

ACS Northeast Regional Meeting, New Paltz, New York, June 26, 1985:

W. C. Koehler, "The National Center for Small-Angle Scattering Research" (invited paper)

Workshop on Hybridized f-Electron Systems, Los Alamos, New Mexico, June 26-28, 1985:

S. H. Liu, "Theory of Thermal Power in Heavy Fermion Systems"

Seventh International Conference on Ion Beam Analysis, Berlin, Federal Republic of Germany, July 7-12, 1985:

J. Roth, W. Moller, D. Poker, and K. Wittmaack, "Radiation Enhanced Mixing of ^{13}C in ^{12}C "

Third International Aluminum-Lithium Conference, Oxford, England, July 9-11, 1985:

S. Spooner and D. B. Williams, "Combined Small-Angle X-ray Scattering and Transmission Electron Microscopy Studies of Al-Bi Binary Alloys"

Radiation Effects in Insulators III Conference, University of Surrey, Guilford, United Kingdom, July 15-19, 1985:

B. R. Appleton, G. C. Farlow, L. A. Boatner, C. W. White, G. M. Beardsley, W. H. Christie, P. Ashley, and C. Bahr, "Ion-Induced Materials Interactions in Optical Materials,"

G. C. Farlow, C. J. McHargue, C. W. White, and B. R. Appleton, "Annealing Studies of $\alpha\text{-Al}_2\text{O}_3$ Implanted Bromine"

Twenty-Third International Field Emission Symposium, Wheeling, West Virginia, July 15-20, 1985:

M. K. Miller, L. L. Horton, and S. Spooner, "A Comparison of Characteristic Distance Measurements by AP, TEM, and SANS"

Pennsylvania State University Conference on Tailoring Multiphase and Composite Ceramics, State College, Pennsylvania, July 17-19, 1985:

K. L. More, R. F. Davis, B. R. Appleton, and D. Lowndes, "Non-Equilibrium Surface Conditions and Microstructural Changes following Laser Annealing and Ion Beam Mixing of Ni Overlayers on SiC"

Gordon Research Conference on Spin-Polarized Quantum Systems, Antrim, New Hampshire, July 22-26, 1985:

Mark Rasolt, "Bose Condensation in a Dilute Bose Fluid: Application to Helium in Vycor"

Seminar on Melting and Freezing, Los Alamos, New Mexico, July 31-August 2, 1985:

B. C. Larson, "Nanosecond Resolution Time-Resolved X-ray Study of Silicon during Pulsed-Laser Irradiation" (invited paper)

Eleventh International Conference on Atomic Collisions in Solids, Washington, D.C., August 4-9, 1985:

R. J. Culbertson and S. J. Pennycook, "Radiation Damage and the Capture of Si Atoms during Implantation of Dopant Ions into Si"

N. Herbots, B. R. Appleton, T. S. Noggle, R. A. Zuhr, and S. J. Pennycook, "Ion-Solid Interactions during Ion Beam Deposition of Ge on Si at Very Low Ion Energies"

Ordean S. Oen, "Ion Damage Calculations in Crystalline Silicon"

J. Roth, W. Moller, D. Poker, and K. Wittmaack, "Radiation-Enhanced Mixing of ^{13}C and ^{12}C "

Forty-Third Annual Meeting of the Electron Microscopy Society of America, Louisville, Kentucky, August 5-9, 1985:

Julia T. Luck, C. W. Boggs, and S. J. Pennycook, "Comparison of Ion Milling Techniques for Cross-Sectional TEM of Semiconductors"

S. J. Pennycook, "Electron Channeling Analysis and Z-Contrast Imaging of Dopants in Semiconductors" (invited paper)

Seventeenth Annual Symposium on Optical Materials for High-Power Lasers, Boulder, Colorado, August 15, 1985:

P. G. Snyder, G. H. Bu-Abbud, J. Oh, J. A. Woollam, D. B. Poker, D. Aspnes, D. Ingram, and P. Pronko, "Study of Mo, Au, and Ni Implanted Molybdenum Laser Mirrors by Spectroscopic Ellipsometry"

Fifth International Conference on Solid State Ionics, Lake Tahoe, California, August 18-25, 1985:

J. B. Bates and J. C. Wang, "Impedance of Metal-Solid Electrolyte Interfaces"

J. B. Bates and R. L. Anderson, "Corrosion of Na β - and Na β' -Alumina in CO_2 - H_2O "

Wing-Kit Lee, A. S. Nowick, and L. A. Boatner, "Protonic Conduction in Acceptor-Doped KTaO_3 Crystals"

S. H. Liu, T. Kaplan, and L. J. Gray, "A Fractal Model for the AC Response of a Rough Interface" (invited paper)

J. C. Wang and N. J. Dudney, "Model for the Composition Dependence of Conductivity of an Ionic Conductor Containing Submicron Insulator Particles"

J. C. Wang and J. B. Bates, "Model for the Interfacial Impedance between a Solid Electrolyte and a Metal Electrode"

American Crystallography Society Meeting, Palo Alto, California, August 19-22, 1985:

B. C. Larson, "Nanosecond Resolution X-ray Studies of Silicon during Pulsed-Laser Irradiation" (invited paper)

Edward C. Uberbacher and Gerard J. Bunick, "X-ray Structure of the Nucleosome Core Particle"

International Conference on Neutron Scattering, Santa Fe, New Mexico, August 19-23, 1985:

R. R. Arons, J. W. Cable, and R. M. Nicklow, "Crystal-Field Splitting in the Rare-Earth Deuterides"

R. R. Arons, J. W. Cable, A. Heidel, and W. Zinn, "Magnetic Phase Diagram of Ce Deuteride"

J. W. Cable, R. M. Nicklow, and Y. Tsunoda, "Spin Dynamics of a Cu-Mn Spin Glass Alloy"

John B. Hayter, "Structure and Hydrodynamics of Colloidal Systems" (invited paper)

W. C. Koehler, "The 30-m SANS Facility of the ORNL-NSF-DOE National Center for Small-Angle Scattering"

W. C. Koehler, G. J. Bunick, H. R. Child, J. B. Hayter, J. S. Lin, L. Maddox, S. Spooner, and G. D. Wignall, "The National Facility for Small-Angle Neutron Scattering - Five Years' Operating Experience"

H. A. Mook, "Momentum Distribution of ^3He "

A. Patel, S. S. Stivala, S. P. Daniele, J. D. Gregory, G. J. Bunick, and E. C. Uberbacher, "Small-Angle Neutron Scattering Studies from Solutions of Bovine Nasal Cartilage Proteoglycan"

International Conference on Magnetism, San Francisco, California, August 26-30, 1985:

J. W. Cable, R. M. Nicklow, and N. Wakabayashi, "Temperature Dependence of the Magnetic Excitations of Gd"

J. F. Cooke, J. A. Blackman, and T. Morgan, "New Interpretation of Spin-Wave Behavior in Nickel and Iron" (invited paper)

S. H. Liu, A. J. Liu, and J. F. Cooke, "Paramagnetic Form Factors of HCP Transition Metals"

J. R. Thompson, H. R. Kerchner, and S. T. Sekula, "Itinerant Electron Ferromagnetism in Fe-Alloyed, Ni_3Al -Based Materials"

Second International Conference on the Physics of Phonons, Budapest, Hungary, August 26-31, 1985:

B. Salce, T. Calemczuk, B. Bonjour, R. L. Mignoni and L. A. Boatner, "Low-Temperature Thermal Properties of KTaO_3 and $\text{KTa}_{0.97}\text{Nb}_{0.03}\text{O}_3$ "

B. Salce and L. A. Boatner, "Static Electric Field Effects on the Thermal Conductivity of Pure KTaO_3 and $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ Crystals"

Advanced Study Institute on "Laser Surface Treatment of Metals," San Miniato, Italy, September 2-13, 1985:

M. J. Aziz, "Solute Trapping: Comparison of Theory and Experiment"

One Hundred Ninetieth National Meeting of the American Chemical Society, Chicago, Illinois, September 8-13, 1985:

B. R. Appleton, "Surface Modification of Materials" (invited paper)

John F. Fellers, Ming Y. Tang, and J. S. Lin, "A SAX Study of Cellulose with Fractal Interpretation" (invited paper)

J. B. Hayter, "Applications of Macrofluid Theory to Surfactant Solutions" (invited paper)

Materials Research Society's Ninth International Symposium on the Scientific Basis for Radioactive Waste Management, Stockholm, Sweden, September 9-11, 1985:

E. Schiewer, W. Lutze, L. A. Boatner, and B. C. Sales, "Characterization of Lead-Iron Phosphate Glass"

Conference on "Vibrations at Surfaces IV," Bowness-on-Windermere, England, September 15-19, 1985:

J. F. Wendelken, "An EELS Study of Hydrogen-Induced Reconstruction on Stopped $\text{W}(001)$ Surfaces"

American Society for Metals Meeting, Huntsville Chapter, Huntsville, Alabama, September 19, 1985:

B. R. Appleton, "Ion Beam and Laser Processing of Solids" (invited paper)

Frontiers of Neutron Scattering Conference, Cambridge, Massachusetts, September 23-24, 1985:

R. M. Moon, "Spin Densities: Past, Present, and Future" (invited paper)

M. K. Wilkinson, "Early History of Neutron Scattering in Oak Ridge" (invited paper)

Symposium on Surface Structure by LEED and Other Techniques, Erlangen, Federal Republic of Germany, September 23-25, 1985:

J. R. Noonan and H. L. Davis, "The Structure of Selected Binary Alloy Surfaces" (invited paper)

Ion Implantation Symposium of the American Society of Metals Meeting, Toronto, Canada, October 10-14, 1985:

C. W. White and M. J. Aziz, "Energy Deposition, Heat Flow and Crystal Growth during Pulsed Laser Irradiation of Semiconductors" (invited paper)

C. W. White, G. C. Farlow, B. R. Appleton, C. J. McHargue, P. S. Sklad, L. A. Boatner, and B. C. Sales, "Ion Implantation and Ion Beam Mixing of Insulating Materials" (invited paper)

TMS-AIME Conference, Symposium on Irradiation Effects Associated with Ion Implantation, Toronto, Canada, October 14-15, 1985:

W. A. Coghlan, M. H. Rhee, and J. M. Williams, "Effect of Microstructure on the Arsenic Profile in Implanted Silicon"

Metallurgical Society of AIME Fall Meeting, Toronto, Canada, October 14-17, 1985:

C. G. Park and S. M. Ohr, "Crack Tip Dislocation Behavior in Pure Iron," [*J. Met.* 37(8), 5 (1985)]

Eighteenth Annual Synchrotron Radiation Center User's Meeting, Stoughton, Wisconsin, October 21-22, 1985:

R. A. DiDio, D. M. Zehner, S. C. Lui, E. W. Plummer, and W. Eberhardt, "A Photoemission Comparison of Ta(001) and TaC(001): Core and Valence Studies"

R. A. DiDio, D. M. Zehner, S. C. Lui, and E. W. Plummer, "Surface State Dispersions on Ta(001)"

R. H. Gaylord, S. C. Lui, J. M. Mundenar, E. W. Plummer, R. A. DiDio, and D. M. Zehner, "A Study of the (110) and (111) Faces of the Ordered Alloy NiAl"

Transplutonium Program Meeting, Knoxville, Tennessee, October 24-25, 1985:

G. D. Mahan, "Theories of Actinide Metals and Compounds" (invited paper)

Second International Conference on Fundamentals of Fracture, Gatlinburg, Tennessee, November 4-7, 1985:

S.-J. Chang, S. M. Ohr, and R. Thomson, "Elastic Solution of an Edge Dislocation Near a Wedge Crack" [ORNL/TM-9783 (October 1985), p. 138]

S.-J. Chang and S. M. Ohr, "Dislocation-Free Zone Model of Fracture Under Cyclic Loading" [ORNL/TM-9783 (October 1985), p. 139]

C. G. Park and S. M. Ohr, "TEM Studies of Crack Tip Dislocations in BCC Metals," [ORNL/TM-9783 (October 1985), p. 160]

International Symposium on Flux Pinning and Electromagnetic Properties in Superconductors, Fukuoka, Japan, November 11-14, 1985:

H. R. Kerchner, D. K. Christen, E. M. Lee, A. DasGupta, B. C. Cai, and T. Y. Chou, "Flux-Line Pinning by the Grain Boundary in Niobium Bicrystals"

Workshop on the Investigation of Fundamental Interactions with Cold Neutrons, Gaithersburg, Maryland, November 14-15, 1985:

J. Arthur, "An Effective Vibration Isolation System for Perfect-Crystal Neutron Interferometry"

Seventh Battery and Electrochemical Contractors' Conference, Crystal City, Virginia, November 18-22, 1985:

J. B. Bates and R. J. Lauf, "Development of New β "-Alumina Electrolytes" (invited paper)

Thirty-Second National Symposium of the American Vacuum Society, Houston, Texas, November 19-22, 1985:

R. E. Clausing, L. Heatherly, J. von Seggern, K. C. Tschersich, R. C. Isler, P. K. Mioduszewski, J. E. Simpkins, and R. A. Zuhr, "Cleanup and Gettering during the Beryllium Limiter Experiment in ISX-B"

R. A. DiDio, D. M. Zehner, S. C. Lui, E. W. Plummer, and W. Eberhardt, "A Photoemission Comparison of Ta(001) and TaC(001): Core and Valence Studies"

R. A. Langley, R. A. Zuhr, and M. B. Lewis, "The Migration of Beryllium in the ISX-B Tokamak during the Beryllium Limiter Experiment"

D. M. Lind, K. D. Jamison, F. B. Dunning, G. K. Walters, and H. L. Davis, "An Experimental/Theoretical Comparison of Spin-Polarized Low-Energy Electron Diffraction from the Cu(110) Surface"

J. R. Noonan and H. L. Davis, "The Al Termination of the Annealed NiAl(111) Surface"

J. B. Roberto, P. H. Edmonds, A. C. England, A. Gribbard, and R. A. Zuhr, "Weight Change Measurements of Erosion/Deposition at Beryllium Limiter Tiles in ISX-B"

R. A. Zuhr, "Postmortem Near-Surface Analysis of Beryllium Limiter Tiles from ISX-B"

Fifty-Second Meeting of the Southeastern Section of the American Physical Society, Athens, Georgia, December 2-4, 1985:

R. R. Coltman, Jr., H. R. Kerchner, C. E. Klabunde, and F. W. Young, Jr., "A Report on the Workshop on Low-Temperature Neutron Irradiation"

G. D. Mahan, "Theory of Raman Scattering in Alkali Halides" [*Bull. Am. Phys. Soc.* **30**, 1777 (1985)] (invited paper)

R. M. Nicklow, "Poster of Neutron Scattering Facilities at HFIR"

S. Spooner, "National Center for Small-Angle Scattering Research"

S. P. Withrow, "Surface Modification and Characterization Collaborative Research Center"

1985 Fall Meeting of the Materials Research Society, Boston, Massachusetts, December 2-7, 1985:

B. R. Appleton, J. Narayan, D. Fathy, G. C. Farlow, C. W. White, C. J. McHargue, and L. A. Boatner, "Ion Beam and Laser Mixing of Metal Films on Insulators"

B. R. Appleton, G. M. Beardsley, L. A. Boatner, W. H. Christie, G. C. Farlow, and P. R. Ashley, "Ion-Induced Alterations of Optical Materials"

M. J. Aziz, J. Y. Tsao, M. O. Thompson, P. S. Peercy, and C. W. White, "Solute Trapping: Comparison of Theory and Experiment"

R. J. Culbertson and S. J. Pennycook, "Trapping of Interstitials during Ion Implantation in Silicon"

J. A. Edmond, S. P. Withrow, and R. F. Davis, "Amorphization and Recrystallization Processes in Monocrystalline Beta Silicon Carbide Thin Films"

G. C. Farlow, C. W. White, C. J. McHargue, P. S. Sklad, and B. R. Appleton, "Annealing Studies of Amorphous Al_2O_3 Formed by Ion Implantation"

E. P. Fogarassy, C. W. White, D. H. Lowndes, and J. Narayan, "Laser-Induced Oxidation of Heavily Doped Silicon"

M. Herbots, B. R. Appleton, S. J. Pennycook, T. S. Noggle, and R. A. Zuhr, "Ion Beam Deposition of Ge and Si on Si at 40-200 eV: Effect of Ion Energy and Substrate Temperature on Interface and Damage Formation"

G. E. Jellison, Jr., D. H. Lowndes, D. N. Mashburn, and R. F. Wood, "Time-Resolved Reflectivity Measurements of Silicon and Germanium Using a Pulsed Excimer Laser"

T. Kaplan, S. H. Liu, and L. J. Gray, "A Fractal Model for the ac Response of a Rough Interface"

B. C. Larson, J. Z. Tischler, and D. M. Mills, "Overheating in Silicon during Pulsed-Laser Irradiation?"

D. H. Lowndes, G. E. Jellison, Jr., S. J. Pennycook, S. P. Withrow, D. N. Mashburn, and R. F. Wood, "Direct Imaging of 'Explosively' Propagating Buried Molten Layers in Amorphous Silicon Using Optical, TEM, and Ion Backscattering Measurements"

J. R. Martinelli, E. Sonder, and R. A. Zuhr, "Electronic Barriers Produced at ZnO Surfaces by Ion Implantation and Annealing"

S. J. Pennycook, "Transient-Enhanced Diffusion in Heavily Doped Silicon" (invited paper)

B. C. Sales, R. S. Brazell, J. B. Bates, and L. A. Boatner, "Liquid Chromatography and Raman Spectroscopy Measurements of Lead Iron Phosphate Glasses"

C. W. White, P. S. Sklad, L. A. Boatner, G. C. Farlow, C. J. McHargue, B. C. Sales, and M. J. Aziz, "Ion Implantation Damage and Annealing in Crystalline Oxides"

American Society for Metals Meeting, Dayton Chapter, Dayton, Ohio, January 8, 1986:

B. R. Appleton, "Surface Modification of Solids Using Ion Beams and Lasers"

Gordon Research Conference, Santa Barbara, California, January 6-10, 1986:

F. S. Bates, G. D. Wignall, and W. C. Koehler, "Isotope Effect in Blends of Deuterated and Protonated (Normal) Polymer Molecules by Small-Angle Neutron Scattering"

Aspen Conference on Frontiers of X-ray Research, Aspen, Colorado, January 20-25, 1986:

B. C. Larson, "Nanosecond Resolution X-ray Studies" (invited paper)

Tenth Annual Condensed Matter Physics Conference of the Australian Institute of Physics, Wagga Wagga, New South Wales, February 5-7, 1986:

T. R. Finlayson and H. G. Smith, "The Lattice Dynamics of PdTe_2 " (invited paper)

Biophysics Meeting, San Francisco, California, February 9-13, 1986:

Thomas G. Consler, Gerard J. Bunick, and James C. Lee, "Small-Angle Neutron Scattering Studies of Rabbit Muscle Pyruvate Kinase"

Gordon Research Conference on Dynamics of Macromolecular and Polyelectrolyte Solutions, Santa Barbara, California, February 17-21, 1986:

J. B. Hayter, "Scattering Studies of Systems with Shear or Field-Induced Anisotropy" (invited paper)

Annual Meeting of the Metallurgical Society of AIME, New Orleans, Louisiana, March 2-6, 1986:

M. J. Aziz, "Interface Response Functions for Rapid Alloy Solidification: Theory and Experiment" [*J. Met.* 37(11), 41 (1985)] (invited paper)

S.-J. Chang and S. M. Ohr, "Dislocation-Free Zone Model of Fracture Under Cyclic Loading" [J. Met. **37**(11), 70 (1985)]

T. R. Finlayson and H. G. Smith, "Neutron Scattering from Pre-Martensitic In-Ti Alloys" [J. Met. **37**(11), 57 (1985)] (invited paper)

C. G. Park and S. M. Ohr, "Dislocation-Free Zone Ahead of Crack Tip in BCC Metals" [J. Met. **37**(11), 87 (1985)]

S. J. Pennycook, "Z-Contrast Imaging and Electron Channeling Analysis of Dopants in Semiconductors" [J. Met. **37**(11), 110 (1985)] (invited paper)

Stephen Spooner, "SANS Characterization of Precipitation in a Cu-0.5% Co Alloy" [J. Met. **37**(11), 89 (1985)]

Stephen Spooner, M. K. Miller, and L. L. Horton, "Multiple-Technique Examination of Spinodal Decomposition in Fe-28.6 wt% Cr-10.6% Co" [J. Met. **37**(11), 129 (1985)]

S. Spooner, D. B. Williams, and C. M. Sung, "Evidence for the Metastable Miscibility Gap in Al-Li from Small-Angle X-ray Scattering" [J. Met. **37**(11), 129 (1985)]

Workshop on Solid State Reactions after Ion Implantation Detected by Nuclear Methods, Cöttengen, Federal Republic of Germany, March 10-12, 1986:

S. Mantl, D. Poker, R. Reichelt, and E. Kasper, "Ion Channeling Experiments on W/Mo and Si/SiGe Strained Layered Superlattices"

Second University of California Conference on Statistical Mechanics, Davis, California, March 26-29, 1986:

Mark Rasolt and A. D. J. Haymet, "Phase Transitions in a Third-Rank-Tensor Hamiltonian"

First Annual Meeting of the Center for Materials Processing, Knoxville, Tennessee, March 24-25, 1986:

J. S. Lin, L. D. Hulett, J. M. Dale, T. M. Rosseel, Darell Warner, B. Stoll, and J. F. Fellers, "X-ray Scattering and Positron Annihilation Studies of Graphite Fibers and Their Epoxy Composites"

American Physical Society Meeting, Las Vegas, Nevada, March 31-April 4, 1986:

J. Arthur, H. A. Mook, M. B. Maple, M. Decroix, S. E. Lambert, C. Rossel, F. Holtzberg, and R. Baillif, "Temperature Dependence of Magnetic Order in EuMo_6S_8 " [Bull. Am. Phys. Soc. **31**, 441 (1986)]

Michael J. Aziz and T. Kaplan, "Interface Response Functions for Rapid Alloy Solidification" [Bull. Am. Phys. Soc. **31**, 424 (1986)]

F. S. Bates and G. D. Wignall, "The Isotope Effect in Mixtures of Deuterated and Normal Polymers" [Bull. Am. Phys. Soc. **31**, 567 (1986)]

L. A. Boatner and C. W. White, "Ion Channeling Investigations of Heavy Ion- and Laser-Induced Damage in KTaO_3 Single Crystals and Recovery by Annealing" [Bull. Am. Phys. Soc. **31**, 475 (1986)]

T. Brun, S. Susman, K. Volin, J. E. Jorgensen, and H. G. Smith, "High-Temperature Transition in the Fast Li Conductor, $\beta\text{-LiAl}$ " [Bull. Am. Phys. Soc. **31**, 580 (1986)]

G. H. Bu-Abbud, P. G. Snyder, J. E. Oh, J. A. Woollam, D. P. Poker, D. F. Aspnes, D. Ingram, and P. Pronko, "Optical Properties of Ion-Implanted Mo" [Bull. Am. Phys. Soc. **31**, 701 (1986)]

J. D. Budai and M. J. Aziz, "Formation of Icosahedral Al-Mn by Ion Implantation and by Pulsed Laser Melting" [Bull. Am. Phys. Soc. **31**, 268 (1986)]

Y. K. Chang and W. Uelhoff, "Characterization of Czochralski-Grown Cu_3Au Single Crystals by γ -ray Diffractometry" [Bull. Am. Phys. Soc. **31**, 221 (1986)]

D. K. Christen, H. R. Kerchner, E. M. Lee, and S. T. Sekula, "Grain Boundary Flux Pinning in Niobium Bicrystals" [Bull. Am. Phys. Soc. **31**, 239 (1986)]

Y. T. Chu, J. B. Bates, C. W. White, and G. C. Farlow, "Optical Investigation of Alumina Films Prepared by Ion Implantation of α - Al_2O_3 Single Crystals" [Bull. Am. Phys. Soc. 31, 639 (1986)]

J. F. Cooke, J. A. Blackman, and T. Morgan, "High-Energy Spin Waves in Ferromagnetic Nickel and Iron" [Bull. Am. Phys. Soc. 31, 562 (1986)]

R. A. DiDio, D. M. Zehner, S. C. Lui, and E. W. Plummer, "Surface State Dispersion on Ta(001)" [Bull. Am. Phys. Soc. 31, 371 (1986)]

R. D. Edge, T. Datta, E. R. Jones, C. Almasan, J. W. Cable, and H. N. Ledbetter, "Neutron Diffraction Study of Interstitial Carbon and Nitrogen on Magnetic Properties of FCC Fe-Cr-Ni Alloys" [Bull. Am. Phys. Soc. 31, 563 (1986)]

J. T. Ellis, J. R. Thompson, J. M. Williams, D. K. Christen, and J. D. Lewis, "Ion Irradiation of Vanadium Nitride Films" [Bull. Am. Phys. Soc. 31, 337 (1986)]

T. R. Finlayson, W. Reichardt, and H. G. Smith, "The Lattice Dynamics of Layered-Structure Compounds" [Bull. Am. Phys. Soc. 31, 608 (1986)]

G. R. Gruzalski and D. M. Zehner, "Defect States Associated with Carbon Vacancies in Tantalum Carbide" [Bull. Am. Phys. Soc. 31, 402 (1986)]

S. Iida, B. C. Larson, and J. Z. Tischler, "Diffuse Scattering from Spherical Precipitates in Isotropic Materials"

T. Kaplan, S. H. Liu, and L. J. Gray, "Fractal Models for the AC Response of Rough Interfaces" [Bull. Am. Phys. Soc. 31, 629 (1986)]

S. C. Lui, J. Mendenar, E. W. Plummer, R. A. DiDio, and D. M. Zehner, "Surface Properties of the (111) Face of NiAl" [Bull. Am. Phys. Soc. 31, 479 (1986)]

G. D. Mahan, "Theory of Magnetoresistance in High Magnetic Fields" [Bull. Am. Phys. Soc. 31, 554 (1986)] (invited paper)

David E. Meltzer and Kevin S. Bedell, "Spin Waves and Spin Diffusion in Fermi Liquids: Bounds on Effective Diffusion Coefficients" [Bull. Am. Phys. Soc. 31, 486 (1986)]

F. A. Modine, C. Y. Allison, and T. W. Haywood, "Optical and Electrical Properties of Niobium Carbide" [Bull. Am. Phys. Soc. 31, 701 (1986)]

H. A. Mook, D. N. Theodorou, and U. W. Suter, "Elastic Coherent Neutron Scattering of Glassy Protonated and Fully Deuterated Atactic Polypropylene" [Bull. Am. Phys. Soc. 31, 567 (1986)]

T. S. Noggle, B. R. Appleton, N. Herbots, and R. A. Zuhr, "Epitaxial Growth of ^{57}Fe Films on Silver by Ion Beam Deposition" [Bull. Am. Phys. Soc. 31, 323 (1986)]

X. Quan, I. Gancarz, J. T. Koberstein, and G. D. Wignall, "Morphological Characterization of Triblock Copolymers-Homopolymer Blends" [Bull. Am. Phys. Soc. 31, 566 (1986)]

Mark Rasolt, F. Perrot, and A. H. MacDonald, "Valley Wave in the Integer and Fractional Hall Effect in Si and Ge" [Bull. Am. Phys. Soc. 31, 554 (1986)]

Mark Rasolt, "Critical Behavior of a Dilute Interacting Bose Fluid" [Bull. Am. Phys. Soc. 31, 522 (1986)]

B. C. Sales and L. A. Boatner, "Structural Relaxation of Enthalpy in Lead-Iron Phosphate Glasses" [Bull. Am. Phys. Soc. 31, 228 (1986)]

S. T. Sekula, M. Althouse, D. K. Christen, J. T. Ellis, and J. R. Thompson, "Annealing Studies of Ion-Damaged VN" [Bull. Am. Phys. Soc. 31, 337 (1986)]

Bo E. Sernelius, "Band-Gap Shifts in Heavily Doped GaAs" [Bull. Am. Phys. Soc. 31, 299 (1986)]

K. W.-K. Shung, "A Study of Electron-Electron Interaction in Graphite Intercalated Graphite (GIC)" [Bull. Am. Phys. Soc. 31, 643 (1986)]

J. L. Soubeyroux, J. J. Rhyne, S. K. Malik, H. A. Mook, M. S. Torikachvili, K. N. Yang, and M. B. Maple, "Ferromagnetism in CeRh_3B_2 " [Bull. Am. Phys. Soc. 31, 649 (1986)]

W. G. Stirling, M. E. Hagen, and G. H. Lander, "The Temperature Dependence of the Magnetic Excitations in USe_2 for $T < 1.5\text{T}_N$ " [Bull. Am. Phys. Soc. 31, 242 (1986)]

J. Z. Tischler and B. W. Batterman, "A Many Beam Approximation for Analysis of Weak X-ray Reflections" [Bull. Am. Phys. Soc. **31**, 578 (1986)]

J. Tombrello, H. T. Tohver, and Y. Chen, "Electron Paramagnetic Resonance Identification of the H⁺ Ion in CaO" [Bull. Am. Phys. Soc. **31**, 529 (1986)]

J. C. Wang, J. B. Bates, Y. T. Chu, and W. T. Stribling, "Fractal Dimensions of Koch Curves" [Bull. Am. Phys. Soc. **31**, 628 (1986)]

J. C. Wang and Mark Mostoller, "Crystalline Properties of Rutile Calculated with Simple Shell Model" [Bull. Am. Phys. Soc. **31**, 579 (1986)]

J. F. Wendelken, "A Vibrational Study of Oxygen Adsorption on Tungsten(112)" [Bull. Am. Phys. Soc. **31**, 480 (1986)]

G. D. Wignall, F. S. Bates, and S. B. Dierker, "Phase Behavior of Amorphous Binary Mixtures of Normal and Perdeuterated 1,4-Polybutadienes" [Bull. Am. Phys. Soc. **31**, 567 (1986)]

D. M. Zehner and G. R. Gruzalski, "Oxygen Adsorption on NiAl(110)" [Bull. Am. Phys. Soc. **31**, 479 (1986)]

SEMINARS

SOLID STATE DIVISION SEMINARS AT ORNL

During this period D. H. Lowndes served as Seminar Chairman October 1984—continuing. The following seminars were held:

- "Experimental Studies of Crystal Surface Vibrations by Inelastic Helium-Atom Scattering," J. G. Skofronick, Florida State University, Tallahassee, Florida
- "Dielectric Studies of Interfacial Phenomena," A. K. Jonscher, Chelsea College, University of London, London, England
- "Heavy Fermion Systems: An Overview,"¹ S. H. Liu, Solid State Division, ORNL
- "Examples of Cold Neutron Three-Axis Spectroscopy with Polarization Analysis," R. Pynn, Institut Laue-Langevin, Grenoble, France
- "The Development and Application of a Channel-Cut Double-Crystal Instrument for Neutron Small-Angle Scattering," D. Schwann, Institut fuer Festkörperforschung, Kernforschungsanlage, Jülich, Federal Republic of Germany
- "Many-Body Effects in Deep Whole Spectra of Simple Metals,"¹ K. Shung, The University of Tennessee, Knoxville, Tennessee
- "Introduction to the Quantum Hall Effect," S. M. Girvin, National Bureau of Standards, Washington, D.C.
- "UV and Soft X-ray Studies of Molecular Dissociation: O₂ on Cu(110)," R. A. DiDio, University of Pennsylvania, Philadelphia, Pennsylvania
- "The Reactor ORPHEE and Its Experimental Facilities," B. Farnoux, Laboratoire Leon Brillouin, Commission Energie Nucleaire, Saclay, France
- "Quantum Correlation and Measurements," A. R. Mackintosh, Physics Laboratory, University of Copenhagen, Denmark
- "Polarized Neutron Scattering Studies with a Pulsed Spallation Source," Y. Endoh, Tohoku University, Sendai, Japan
- "Structure and Electronic Properties of Amorphous Semiconductor Superlattices," P. D. Persans, Exxon Corporate Research Science Laboratories, Annandale, New Jersey
- "Exploring Possibilities for High-Temperature Superconductivity in Nitrides and Hydrides,"² D. A. Papaconstantopoulos, U.S. Naval Research Laboratory, Washington, D.C.
- "Atomic Interface Structure Determination by Ion Channeling and Blocking: the NiSi₂-Si(111) Interface," E. J. van Loenen, FOM Institute for Atomic and Molecular Physics, Amsterdam, The Netherlands
- "Probing the Electron-Phonon Interaction in Metals," J. C. Swihart, Indiana University, Bloomington, Indiana
- "Crystal Growth for Research," H. Wenzl, Institut fuer Festkörperforschung, Kernforschungsanlage, Jülich, Federal Republic of Germany
- "The Influence of Displacement Cascades on Radiation Effects at High and Low Temperatures," R. S. Averback, Argonne National Laboratory, Argonne, Illinois
- "Interaction of Low-Energy Ions with Solid Surfaces," M. Aono, National Institute for Research in Organic Materials, Ibaraki, Japan

- "Materials for Tunable Infrared Lasers," K. German, Burleigh Instruments, Fishers, New York
- "Fluctuation as Explanation in Microscopic Physics,"² T. A. Welton, Physics Division, ORNL
- "The Formation of Metal Silicides on Dislocation and Twins in Silicon," D. M. Vanderwalker, State University of New York, Stony Brook, New York
- "Recent Advances in Electronic Structure Calculations for Impurities in Metals," R. Zeller, Kernforschungsanlage, Jülich, Federal Republic of Germany
- "Point Defects and Their Transport in Silver Halides," A. L. Laskar, Clemson University, Clemson, South Carolina
- "Magnetic Phase Transitions in CoCl_2 -Graphite Intercalation Compounds," G. F. Dresselhaus, Bitter National Magnet Laboratory and the Massachusetts Institute of Technology, Cambridge, Massachusetts
- "Phase Diagram Basis and Kinetic Factors in the Study of Glass-Forming Alloys," C. G. Woychik, IBM Advanced Packaging Technology Laboratory, Endicott, New York
- "Half-Metallic Ferromagnetism," F. M. Mueller, Los Alamos National Laboratory, Los Alamos, New Mexico
- "Picosecond Interactions with Semiconductors," H. Kurz, Harvard University, Cambridge, Massachusetts, and Technical University of Aachen, Aachen, Federal Republic of Germany
- "Time-Resolved Small-Angle Neutron Scattering," A. R. Rennie, Institut fuer Physikalische Chemie, Universität Mainz, Mainz, Federal Republic of Germany
- "Theoretical and Experimental Investigations of Surface States of Solids," A. A. Lucas, University of Namur, Namur, Belgium
- "Collective Multiple Excitations in Small Metal Particles: Critical Angular Momentum for the Existence of Collective Surface Modes," W. Ekardt, Fritz Haber Institut der Max Planck Gesellschaft, Berlin, Federal Republic of Germany
- "Applications of the Replica Method to Some Disordered Systems," M. J. Stephens, Rutgers University, New Brunswick, New Jersey
- "High Mobility of Excitons in Cuprous Oxide at Low Temperatures," D. P. Trauernicht, University of Illinois, Urbana, Illinois
- "Resonant Interband Raman Scattering in Metals and Semimetals," P. Eklund, University of Kentucky, Lexington, Kentucky
- "Recent Simulation Studies of Inorganic Solids," C. R. A. Catlow, University College, London, England
- "Formation, Structure, and Superconductivity of Some Rapidly Quenched, Metastable, Vanadium-Based Alloys," H. R. Khan, Forschungs Institut fuer Edelmetalle und Metallchemie, Schwäbisch Gmünd, Federal Republic of Germany
- "Physics of Amphiphile Solutions near Phase Transitions," V. DeGiorgio, University of Pavia, Milan, Italy
- "Transport in Fractal Media," A. Lehehaute, Laboratoires de Marcoussis, Centre de Recherches CGE, Marcoussis, France
- "Vibrational Anomalies Due to Sliding Charge Density Waves in TaS_3 ," J. Brill, University of Kentucky, Lexington, Kentucky
- "An Atomic Model for the M-Center in InP ," J. Van Vechten, IBM Thomas J. Watson Research Center, Yorktown Heights, New York
- "Theory of Alloy Phase Stability,"² P.E.A. Turchi, University of California, Berkeley, California
- "Neutron Spectroscopy of Hydrogen Tunneling," A. Magerl, Institut Laue-Langevin, Grenoble, France
- "Icosahedral Order in Four Dimensions and in the Real World," J. P. Straley, University of Kentucky, Lexington, Kentucky
- "Hg-Cd-Te Film Growth by Molecular Beam Epitaxy," J. W. Cook, North Carolina State University, Raleigh, North Carolina

- "Quantum Theory of Polymers (Hartree-Fock Energy Bands: Treatment of Disorder and Correlation)," J. Ladik, University of Erlangen-Nürnberg, Erlangen, Federal Republic of Germany
- "Microfocused Ion Beams for Materials Analysis," D. Kingham, VG Scientific, East Grinstead, England
- "Solid-Electrolyte Interfaces as Composite Media," M. Tomkiewicz, Brooklyn College of CUNY, New York, New York
- "Cold Neutron Scattering Applied to Solid State Chemistry," C. Poinsignon, Institut Laue-Langevin, Grenoble, France
- "Defects in Amorphous Metals," J.C.M. Li, University of Rochester, Rochester, New York
- "Electron Energy Loss Spectroscopy and Its Application to Structure and Bonding at Surfaces," L. Kesmodel, Indiana University, Bloomington, Indiana
- "Twisted Nematic Droplets," R. Williams, Rutherford Appleton Laboratory, Chilton, Didcot, United Kingdom
- "Neutron Scattering at the New DHRUVA Reactor," B. A. Dasannacharya, Bhabha Atomic Research Centre, Bombay, India
- "Static and Dynamic Neutron Depolarization Experiments near the Curie Temperature of Ni and Fe," T. Rekveldt, Interuniversitair Reactor Instituut, The Netherlands
- "Energy Transfer at Surfaces: Vibrational Line Shapes and the Electron-Hole Mechanism," D. C. Langreth, Rutgers University, New Brunswick, New Jersey
- "Concepts of Magnetism from Band Theory," J. Kübler, Technical University, Darmstadt, Federal Republic of Germany
- "Magnetic Structures and Excitation of Neodymium and Praseodymium," K. McEwen, Institut Laue-Langevin, Grenoble, France
- "MBE-Tailored Ferromagnetic Films and Multilayers," W. Zinn, Institut für Festkörperforschung, Jülich, Federal Republic of Germany
- "Study of Sodium Ion Motion in Beta-Alumina by Quasi-elastic and Inelastic Neutron Scattering," G. Lucazeau, Université de Paris-Nord, Paris, France
- "Electron Structure of the 4f and 5f Elements," B. Johansson, Uppsala University, Uppsala, Sweden
- "Statistical Mechanics and Small-Angle Neutron Scattering of Micellar Fluids," R. Triolo, University of Palermo, Palermo, Italy
- "Neutron Diffraction Studies of Oriented Nuclei in Crystals," M. Steiner, Hahn-Meitner-Institut, Berlin, Federal Republic of Germany
- "Characterization of Micro/Macroscopic Modeling of Equiaxed Solidification," M. Rappaz, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland
- "Effects of Heavy Doping on the Electronic Structure of Semiconductors,"¹ B. E. Sernelius, The University of Tennessee, Knoxville, Tennessee
- "Evaluation of Fluoride Glass for Optical Devices," W. A. Sibley, Oklahoma State University, Stillwater, Oklahoma
- "Electronic Structures and Total Energies of Transition Metal Surfaces and Interfaces," C.-L. Fu, Northwestern University, Evanston, Illinois
- "MBE-Grown Gallium-Arsenic Barrier Transistors," C. Y. Chang, Semiconductors and Systems Laboratory, National Chengkung University, Tainan, Taiwan
- "Phase Separation in Solid ^3He - ^4He Mixtures," S. N. Ehrlich, University of Illinois, Urbana, Illinois
- "Problems Associated with Residual Gas Analysis as a Surface Diagnostic Method in Plasma-Surface Interactions," W. Hofer, Kernforschungsanlage, Jülich, Federal Republic of Germany
- "Introduction of Dopants into Semiconductor Surfaces by Surface Melting of Thin Evaporated Films," Z. Burshtein, Nuclear Research Center, Negev, Israel

- "Band-Gap Shifts in Heavily Doped GaAs,"¹ B. E. Sernelius, The University of Tennessee, Knoxville, Tennessee
- "Localized Excitations along the Magnetic Chain in CsMgBr_3 ," B. Gaulin, McMaster University, Hamilton, Ontario, Canada
- "Fractal Nature of a Diffusion Front and Its Relation to Percolation: States, Dynamics, and Anomalous Noise," B. Sapoval, Ecole Polytechnique Palaiseau, Cédex, France
- "Spin Waves in Heavy Fermion Systems,"¹ D. Meltzer, The University of Tennessee, Knoxville, Tennessee
- "Beam-Solid Interactions and Defect Studies," B. R. Appleton and C. W. White, Solid State Division, ORNL, and L. K. Mansur, Metals and Ceramics Division, ORNL
- "Oxygen-Induced CO Bonding Changes on $\text{Cr}(110)$ Surface," N. Shinn, National Bureau of Standards, Gaithersburg, Maryland
- "Lattice Inharmonicity in Alkali-Graphite Intercalation Compounds," S. E. Hardcastle, University of Illinois, Urbana, Illinois
- "The Method of Recurrence Relations and Its Applications to Many-Body Problems," M. H. Lee, University of Georgia, Athens, Georgia
- "Spin Dynamics of Amorphous Invar Materials," J. Fernandez-Baca, University of Maryland, College Park, Maryland
- "Ion-Implanted Optical Wave Guides in LiNbO_3 ,"³ C. Buchal, Kernforschungsanlage, Jülich, Federal Republic of Germany; "Ion Beam Modification of Ceramics,"³ C. J. McHargue, Metals and Ceramics Division, ORNL
- "Resonant Two-Photon Photoionization Cerium-Doped CaF_2 ," G. Pogatschnik, University of Connecticut, Storrs, Connecticut
- "Nonequilibrium Current Fluctuations in Semiconductors," C. Stanton, Cornell University, Ithaca, New York
- "Stability and Instability in Crystal Growth," P. Taylor, Case Western Reserve University, Cleveland, Ohio
- "Electrical Measurements of Cancerous and Normal Cells in Vitro," I. Giaever, General Electric Research and Development Center, Schenectady, New York
- "Itinerant Magnetism in Transition Metal Systems,"¹ J. F. Cooke, Solid State Division, ORNL
- "Superconductivity and Magnetic Order in Ternary Rare-Earth Rhodium Boride Compounds," S. Lambert, University of California, San Diego, California
- "Ion Beam Research Facilities and Experimental Capabilities in the Metals and Ceramics Division,"³ M. B. Lewis, Metals and Ceramics Division, ORNL; "The Surface Modification and Characterization Facility,"³ B. R. Appleton, Solid State Division, ORNL
- "Commensurate-Incommensurate Magnetic Phase Transitions in the Rare-Earth Hydrides," R. R. Arons, Kernforschungsanlage, Jülich, Federal Republic of Germany
- "Perturbed Angular Correlation: A New Solid State Technique for Studying Defect Structures on an Atomic Scale," T. Wichert, Chalk River Nuclear Laboratories, Ontario, Canada
- "Valley Waves in the Integer and Fractional Quantum Hall Effect of a Silicon MOSFET,"¹ M. Rasolt, Solid State Division, ORNL
- "Site Conversion and Activated Dissociative Adsorption on Nickel(111) Surfaces," M. B. Lee, Massachusetts Institute of Technology, Cambridge, Massachusetts

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¹Solid State Division Research-in-Progress Seminar Series.

²Metals and Ceramics Division and Solid State Division Joint Theoretical Seminar.

³Metals and Ceramics Division and Solid State Division Joint Seminar Series on Beam-Solid Interactions and Defect Studies.

LECTURES AND SEMINARS

- B. R. Appleton—Vanderbilt University, Nashville, Tennessee, "Ion Beam and Laser Processing in Materials Research"; University of North Carolina, Chapel Hill, North Carolina, "The Use of Ion Beam and Laser Processing in Materials Research"; Auburn University, Auburn, Alabama, "Materials Research with Ion Beams and Lasers"; National Bureau of Standards, Washington, D.C., "Ion Beam and Laser Processing of Solids"; Yale University, New Haven, Connecticut, "Materials Research Using Ion Beams"
- M. J. Aziz—California Institute of Technology, Pasadena, California, "Crystal Growth Kinetics Far from Equilibrium"; Harvard University, Cambridge, Massachusetts and IBM, Yorktown Heights, New York, "Measurements of Solute Trapping Resulting from Pulsed Laser Irradiation of Si and Ge"; Instituto di Fisica, University of Catania, Italy, and Dartmouth College, Hanover, New Hampshire, "Solute Trapping: Comparison of Theory and Experiment"
- J. H. Barrett—University of North Carolina, Chapel Hill, North Carolina, "Study of Clean Surfaces by High Energy Ion Scattering"
- J. B. Bates—Emory University, Atlanta, Georgia, "Ionic and Molecular Transport in Superionic Conductors"
- J. D. Budai—Harvard University, Cambridge, Massachusetts, "Studies of Icosahedral Al-Mn Formed with Ion Beams and Pulsed Lasers"
- G. J. Bunick—Oak Ridge National Laboratory, Oak Ridge, Tennessee, "X-Ray Structure of the Nucleosome Core Particle"
- Y. Chen—Wake Forest University, Winston Salem, North Carolina State University, Raleigh, North Carolina, and University of Alabama—Birmingham, Birmingham, Alabama, "Tunable Lasers Based on Defects in Refractory Oxides"; University of North Carolina, Chapel Hill, North Carolina, and University of Wisconsin, Milwaukee, Wisconsin, "Opportunities and Problems for Wavelength Tunable Lasers in Refractory Oxides Using Vacancy Defects"
- H. L. Davis—University of Texas, Austin, Texas and Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Federal Republic of Germany, "Multilayer Relaxation at Metallic Surfaces"; Universität Osnabrück, Osnabrück, Federal Republic of Germany, "Multilayer Relaxation at Metallic Surfaces as Determined by High Precision LEED"; Università Degli Studi di Firenze, Firenze, Italy, "Use of Precision LEED Analysis to Measure Multilayer Relaxation at Metallic Surfaces"; University of Pennsylvania, Philadelphia, Pennsylvania, "An Overview of LEED Procedures and Their Use to Measure Multilayer Relaxation in Metallic Surfaces" and "Comparison of Surface Structure Results Obtained by LEED and HERS—A Review of Some Important Differences"; University of West Virginia, Morgantown, West Virginia, "Multilayer Relaxation at Metallic Surfaces—Theoretical Motivation and LEED Results"
- W. Ekardt—National Bureau of Standards, Washington, D. C., University of California, Berkeley, California, University of California, Stanford, California, University of California, Irvine, California, and EXXON, Annandale, New Jersey, "Size Dependent Photoabsorption and Photoemission of Small Metal Particles"
- G. C. Farlow—Wright State University, Dayton, Ohio, "Rutherford Backscattering Analysis of Implanted Ceramics"
- J. B. Hayter—Massachusetts Institute of Technology, Cambridge, Massachusetts, "Small-Angle Scattering in Anisotropic Systems"; Kodak Research Laboratories, Rochester, New York, "Small-Angle Neutron Scattering from Micelles and Colloids"; University of Missouri—Columbia, Columbia, Missouri, "Recent Advances in Neutron Small-Angle Scattering"; AT&T Bell Laboratories, Murray Hill, New Jersey, "Small-Angle Neutron Scattering Studies of Order in Colloidal Dispersions"
- N. Herbots—Summer Course, University Extension of California, Palo Alto, California, "Aluminum Metalization for VLSI"; University of California, Berkeley, California, "The Effect of Arsenic Segregation on the Sintering of Ohmic Contacts Between Aluminum and Shallow Junctions of Silicon"; Hewlett-Packard Laboratories, Palo Alto, California, "Stabilization of Aluminum-Polysilicon Contacts by N-Type Segregating Dopants"; Arizona State University, Phoenix, Arizona, "A Combined Analysis Study of Interactions between Thin Films of Aluminum and Polysilicon during Sintering"; Stevens Institute of Technology, Hoboken, New Jersey, "Ion Beam Deposition of Germanium and Silicon at 40–200 eV and Ion Beam Epitaxy of Iron on Silver at 65 eV"
- H. R. Kerchner—University of Arkansas, Fayetteville, Arkansas, "Superconductivity—The Phenomenon and Its Applications"

- W. C. Koehler—The University of Tennessee, Knoxville, Tennessee, "Small-Angle Neutron Scattering in Polymer Research"
- B. C. Larson—University of Missouri, Columbia, Missouri, University of North Dakota, Grand Forks, North Dakota, and Concordia College, Moorhead, Minnesota, Institute of Physics, Academia Sinica, Beijing, Peoples Republic of China, Photon Factory, Tsukuba, Japan, and NHK Research Laboratory, Tokyo, Japan, "Nanosecond Resolution Time-Resolved X-ray Study of Silicon during Pulsed-Laser Irradiation"; Chinese University of Science and Technology, Hefei, People's Republic of China, "Crystal Defect Studies Using X-ray Scattering"
- J. S. Lin—East Tennessee State University, Johnson City, Tennessee, "Small-Angle X-ray and Neutron Scattering"
- S. H. Liu—Argonne National Laboratory, Argonne, Illinois, "Heavy Fermion Systems"; Rensselaer Polytechnic Institute, Troy, New York, and University of Missouri, Rolla, Missouri, "Surface Electronic States"; University of California, Berkeley, California, "Fractals in Condensed Matter Physics"
- D. H. Lowndes—Perkin-Elmer Corporation Research Laboratories, Danbury, Connecticut, "Pulsed Laser Processing of Silicon: Fundamental Studies and Applications to Photovoltaic Cells"; Sandia National Laboratories, Livermore, California, "Time-Resolved and TEM Studies of Solidification from Highly Undercooled Liquid Silicon"; The University of Tennessee, Knoxville, Tennessee, "Pulsed Laser Processing of Electronic Materials"
- G. D. Mahan—University of Rochester, Rochester, New York, University of California, Santa Barbara, California, Washington University, St. Louis, Missouri, University of Houston, Houston, Texas, and University of Virginia, Charlottesville, Virginia, "Quantum Boltzmann Equation"; University of California, Irvine, California, "Light Scattering in Alkali Halides"; University of North Carolina, Chapel Hill, North Carolina, "Forces Between Ions"; Louisiana State University, Baton Rouge, Louisiana, "Forces in Ionic Solids"
- D. N. Mashburn—Lawrence Livermore National Laboratory, Livermore, California, "Design of an Optical Delay Pulse Stretcher Capable of Handling 50 W Copper Laser Beams," "Installation Plan for the Copper Laser Optical Delay System," "Optical Delay System Procurement and Fabrication Plan," "Optical Delay System Assembly and Alignment Facility Design," "Optical Delay System Installation in the LLNL Laser Development Facility Copper Laser Chain," "Alignment Techniques for Achieving Precise Optical Alignment of the LDF Lasers in Spite of Excessive Support Structure Deflection," and "Optical Delay System Operational Performance in the LDF Copper Laser Chain"; Los Alamos National Laboratory, Los Alamos, New Mexico, "Electrooptics from GeMSAEC Bioanalyzer to the 16 Micron Raman Laser"
- H. A. Mook—Institut Laue-Langevin, France, "Neutron Scattering Studies of Itinerant Electron Ferromagnets"
- R. M. Moon—University of Florida, Gainesville, Florida, "Spin Density Measurements with Polarized Neutrons"; Atomic Energy Research Establishment, Harwell, England, "The Center for Neutron Research"
- J. R. Noonan—Imperial College, London, England, "Multilayer Relaxations at Surfaces: Experimental Limitations"; FOM-Institute, Amsterdam, The Netherlands, "Multilayer Relaxations at Surfaces of Metals and Alloys"
- S. M. Ohr—Vanderbilt University, Nashville, Tennessee, "Electron Microscope Studies of Crack Tip Deformation in Metals"; Nagoya University, Nagoya, Japan, "Dislocation Theory of Fracture"; Kyushu University, Fukuoka, Japan, and Osaka University, Osaka, Japan, "Electron Microscope Studies of Fracture"; Tokyo University, Tokyo, Japan, "In Situ Observation of Crack Propagation"; Tohoku University, Sendai, Japan, "Direct Observations of Crack Propagation"; Kyoto University, Kyoto, Japan, "Dislocation-Free Zone Model of Crack Tip Deformation"; Hitachi Scientific Instruments, Mito, Japan, "Recent Developments in Electron Microscopy in Materials Science"; Science University of Tokyo, Tokyo, Japan, "Dislocation-Crack Interactions"
- C. G. Park—Seoul National University and Korea Advanced Institute of Science and Technology, Seoul, Korea, "In Situ TEM Studies of Crack Tip Deformation in BCC Metals"; Korea Standards Research Institute, Dae Deog, Korea, "TEM Studies of Low-Temperature Fracture in Molybdenum" and "New Idea in Hydrogen Embrittlement"
- S. J. Pennycook—Microelectronics Center of North Carolina, Research Triangle Park, North Carolina, "Transient Diffusion from Interstitial Trapping During Solid-Phase-Epitaxial Growth of Silicon Alloys"; IBM Thomas J. Watson Research Center, Yorktown Heights, New York, "Enhanced Diffusion, Lattice Location, and Direct Imaging of Dopants in Semiconductors"

- D. B. Pökel—Kernforschungsanlage, Jülich, Federal Republic of Germany, "Ion Beam Modification of Surfaces: Smoothness of Laser Mirrors and Mixing of Materials on Silicon"
- M. Rasolt—University of Aachen, Aachen, Federal Republic of Germany, "Plasmon-Phonon Assisted Recombination of the e-h Plasma in Si at High Carrier Density"; University of Delaware, Newark, Delaware, "Bose Condensation in a Dilute Bose Fluid: Application to Helium in Vycor"; Harvard University, Cambridge, Massachusetts, Rutgers University, New Brunswick, New Jersey, Cornell University, Ithaca, New York, University of Kentucky, Lexington, Kentucky, and Clemson University, Clemson, South Carolina, "Valley Waves in the Quantum Hall Effect of Silicon"
- S. Spooner—University of Virginia, Charlottesville, Virginia, "Study of Phase Transformations with Small-Angle Scattering"; Emory University, Atlanta, Georgia, "Neutron Scattering Probe of Solids"; University of North Carolina, Raleigh, North Carolina, "Study of Phase Transformations Using Small-Angle Scattering"
- J. F. Wendelken—Fritz-Haber Institute, Berlin, Federal Republic of Germany, Institut für Festkörperphysik, Universität Hannover, Hannover, Federal Republic of Germany, and Cavendish Laboratory, Cambridge, England, "Step Effects on the Reconstruction of Tungsten(001) Surfaces"
- C. W. White—University of Minnesota, Minneapolis, Minnesota, "Materials Modifications Using Ion Beams and Lasers"
- J. M. Williams—ORGP Superintendent's Meeting, Oak Ridge, Tennessee, AVS-Oak Ridge Chapter Meeting, Oak Ridge, Tennessee, and the University of Alabama, Birmingham, Alabama, "Ion Beam Processing of Materials"; Johnson & Johnson Products, Inc., Braintree, Massachusetts, "Ion Implantation Effects in Surgical Ti-6Al-4V Alloy"
- F. W. Young, Jr.—North Carolina State University, "The Melting-Transformation in Silicon"
- R. A. Zuhr—Kernforschungsanlage, Jülich, Federal Republic of Germany, "Summary of Collection and Resistance Probe Measurements of Hydrogen Fluxes in TEXTOR"

AWARDS

B. R. Appleton	DOE's 1985 Materials Science Research Competition Award: Significant Implication for Energy Technology Category Martin Marietta Significant Event Award, August 1985
M. M. Abraham	Martin Marietta Energy Systems Patent Award, 1985
L. A. Boatner	Martin Marietta Energy Systems Patent Award, 1985 Martin Marietta Energy Systems Publication Award, 1985 1985 IR-100 Award for Radioactive-Waste Disposal Process 100 Top Innovators Award Competition, Science Digest, 1985
J. D. Budai	Eugene P. Wigner Fellowship, 1985
Y. Chen	Martin Marietta Energy Systems Patent Award, 1985
J. F. Cooke	Martin Marietta Significant Event Award, July 1985
N. Herbots	Martin Marietta Significant Event Award, August 1985
W. C. Koehler	Special DOE Award for Recognition of Neutron Scattering Research, 1986 Martin Marietta Significant Event Award, February 1986
B. C. Larson	American Crystallographic Association Bertram E. Warren Diffraction Physics Award, 1985 Martin Marietta Energy Systems Technical Achievement Award, 1985 Martin Marietta Significant Event Award, December 1985
S. H. Liu	Martin Marietta Significant Event Award, October 1985
D. H. Lowndes	American Physical Society Fellowship, 1985
H. A. Mook	Martin Marietta Energy Systems Inventor Award, 1985 Martin Marietta Significant Event Award, July 1985
T. S. Noggle	Martin Marietta Significant Event Award, August 1985
S. M. Ohr	Martin Marietta Energy Systems Technical Achievement Award, 1985
Mark Rasolt	American Physical Society Fellowship, 1985 Martin Marietta Significant Event Award, September 1985
B. C. Sales	Martin Marietta Energy Systems Inventor of the Year Award, 1985 Martin Marietta Energy Systems Inventor Award, 1985 Martin Marietta Energy Systems Patent Award, 1985 Martin Marietta Energy Systems Publication Award, 1985 Martin Marietta Corporation, Jefferson Cup - Inventor Award, 1985 1985 IR-100 Award for Radioactive-Waste Disposal Process 100 Top Innovators Award Competition, Science Digest, 1985
O. E. Schow	DOE's 1985 Materials Science Research Competition Award: Significant Implication for Energy Technology Category
J. Z. Tischler	Martin Marietta Significant Event Award, December 1985
C. W. White	Materials Research Society WOODY Award, 1984 DOE's 1985 Materials Science Research Competition Award: Significant Implication for Energy Technology Category

G. D. Wignall	American Physical Society Fellowship, 1985
J. M. Williams	Martin Marietta Energy Systems Inventor Award, 1985
R. A. Zuhr	Martin Marietta Significant Event Award, August 1985
Solid State Division	ORNL Director's Award in Recognition of Outstanding Accomplishments, 1985 (co-recipient with Metals and Ceramics Division) Distinguished Safety Performance Award, 1984

SCIENTIFIC PROFESSIONAL ACTIVITIES

- M. M. Abraham   Member, Editorial Board, KINAM Revista de Física
Adjunct Professor, Universidad Nacional de Autonomo de México
- B. R. Appleton   Member, Solid State Sciences Committee of the National Research Council
Director, ORNL/DOE Surface Modification and Characterization Collaborative Research Center
Councillor, Materials Research Society
Member, Nominating Committee, Long-Range Planning and Publications Committee of the Materials Research Society
Member, Panel on Materials Science of the National Materials Advisory Board for State-of-the-Art Monitoring of Advanced Processing of Electronic Materials
Member, Editorial Board, Nuclear Instruments and Methods in Physics Research
Member, Editorial Board, Nuclear Science Applications
Member, Editorial Board, Materials Letters
Member, Editorial Board, Radiation Effects
Chairman, MRS Symposium on Ion Beam Processes in Advanced Electronic Materials and Device Technology, San Francisco, California, 1985
Co-editor, Ion Beam Processes in Advanced Electronic Materials and Device Technology, Materials Research Society, Pittsburgh, Pennsylvania, 1985
Adjunct Professor, North Carolina State University, Raleigh, North Carolina
- J. H. Barrett   Lecturer, ORAU Traveling Lecture Program, 1985-1986
- J. B. Bates   Associate Editor, Solid State Ionics
Adjunct Professor, The University of Tennessee, Knoxville, Tennessee
Member, Scientific Committee, 5th International Conference on Solid State Ionics, Lake Tahoe, California, 1985
Member, DOE Working Group on Beta-Alumina, 1984-1985
Co-Chairman, Gorion Research Conference on Solid State Ionics (to be held in 1986)
- L. A. Boatner   Member, Corporate Affiliates Committee, Finance Committee, and Membership Committee, Materials Research Society
Member, Program Committee, Ninth International Symposium on the Scientific Basis for Nuclear Waste Management, Stockholm, Sweden, 1985
Associate Editor, Materials Letters
Chairman, Working Group on Radiation Effects in Crystalline Nuclear Waste Forms, Bryson City, North Carolina, 1985
- G. J. Butick   Research Assistant Professor, The University of Tennessee Graduate School of Biomedical Sciences
- Y. Chen   Co-Chairman, Materials Research Society Symposium on Defect Properties and Processing of High-Technology Nonmetallic Materials, Boston, Massachusetts, 1985
Adjunct Professor, North Carolina State University, Raleigh, North Carolina, 1985
Co-Editor, Defect Properties and Processing of High-Technology Nonmetallic Materials, Materials Research Society, Pittsburgh, Pennsylvania (to be published)
- R. R. Caltman, Jr.   Adjunct Professor, Department of Physics and Astronomy, Clemson University, Clemson, South Carolina
- H. L. Davis   Session Chairman, American Physical Society Meeting, Baltimore, Maryland, 1985
Visiting Professor, Physics Department, Rice University, January-June, 1985

- Treasurer, Fifth Annual Symposium and Equipment Exhibit of the Tennessee Valley Chapter, American Vacuum Society, Knoxville, Tennessee, 1985
 Session Chairman, International Seminar on Surface Structure Determination by LEED and Other Methods, Erlangen, Federal Republic of Germany, 1985
 Session Chairman, American Physical Society Meeting, Las Vegas, Nevada, 1986
 Treasurer, Sixth Annual Symposium and Equipment Exhibit of the Tennessee Valley Chapter, American Vacuum Society, Oak Ridge, Tennessee, 1986
 Member, Session Organizing Committee, American Physical Society Meeting, Baltimore, Maryland, 1985
 Member, Committee to Select Recipient of ORNL's Health and Safety Research Division's Annual Excellence in Research Award, 1985
 Treasurer, Tennessee Valley Chapter, American Vacuum Society, 1985-1986
- G. R. Gruzalski   Lecturer, ORAU Traveling Lecture Program, 1985-1986
- J. B. Hayter   Member, EXXON Review Panel on Polymer Research, 1985
 Participant, NSF Workshop on Surfactant Solutions and Microemulsions, Los Angeles, California, 1985
 Chairman, Working Group on High-Resolution Spectroscopy, Shelter Island, New York, 1984
 Weissberger-Williams Lecturer, Kodak Research Laboratories, Rochester, New York, 1985
 Session Chairman, 189th National ACS Meeting, Miami, Florida, 1985
 Member, Review Panel on Low-Q Diffractometer Design, Los Alamos National Laboratory, Los Alamos, New Mexico, 1985
 Co-Chairman, Working Group on User Needs at an Advanced Steady-State Neutron Facility, Washington, D.C., 1985
- L. H. Jenkins   Member, Wigner Fellowship Committee, ORNL
 Member, Ph.D. Recruiting Steering Committee, ORNL
 Chairman, Exploratory Studies Committee, ORNL, 1984-1986
 Member, Materials Sciences Functional Group, BES/OPA
- W. C. Koehler   Director, ORNL-NSF-DOE National Center for Small-Angle Scattering Research
 Research Member, Editorial Advisory Board, Journal of Magnetism and Magnetic Materials
- B. C. Larson   Lecturer, ORAU Traveling Lecture Program, 1984-1985
 Member, Advisory Committee, Cornell High Energy Synchrotron Source
 Consultant-Lecturer, Chinese University Development Project, 1985
- J. S. Lin   Adjunct Professor, Department of Chemical, Metallurgical, and Polymer Engineering, The University of Tennessee, Knoxville, Tennessee
- S. H. Liu   Member, Executive Committee, Division of Condensed Matter Physics, American Physical Society, 1985-1987
 Session Chairman, (two sessions) American Physical Society, Baltimore, Maryland, 1985
 Visiting Professor, University of California, Berkeley, California, 1986
- D. H. Lowndes   Session Chairman, Materials Research Society Meeting, Boston, Massachusetts, 1984
 Member, Solar Energy Research Institute University Research Participation Review Panel, Philadelphia, Pennsylvania, 1985
 Member, DOE University Research Instrumentation Review Panel, 1986
 Adjunct Professor, Department of Physics, The University of Tennessee, Knoxville, Tennessee, 1985-1986
- G. D. Mahan   Member, Swedish Review Panel on Semiconductor Physics, 1984-1985
- D. N. Mashburn   Member, Technology Evaluation Committee, Martin Marietta Energy Systems, Inc.
 Member, Laser Utilization Planning Center Committee, The University of Tennessee, Knoxville, Tennessee
 Member, Martin Marietta Energy Systems, Inc., Inventors Forum
- R. M. Moon   Member, NAS-NRC Evaluation Panel for the Center for Materials Science, National Bureau of Standards

- Member, Organizing Committee, Workshop on Scientific Opportunities with Advanced Facilities for Neutron Scattering, Shelter Island, New York, 1984
- Chairman, Organizing Committee, Workshop on an Advanced Steady State Neutron Facility, Gaithersburg, Maryland, 1985
- R. M. Nicklow   Member, Research Committee, U.S.-Japan Cooperative Program on Neutron Scattering
                          Member, Program Committee, International Conference on Neutron Scattering, Santa Fe, New Mexico, 1985
                          Session Chairman, International Conference on Neutron Scattering, Santa Fe, New Mexico, 1985
- J. R. Noonan   Chairman, Scholarship Committee, Tennessee Valley Chapter, American Vacuum Society
                          Member, Executive Board, Tennessee Valley Chapter, American Vacuum Society, 1985-1987
                          Chairman, Publications Committee, American Vacuum Society, 1985-1986
                          Member, Publication Policy Committee, American Institute of Physics, 1984
- S. M. Ohr   Chairman, Second International Conference on Fundamentals of Fracture, Gatlinburg, Tennessee, 1985
                          Vice-Chairman, The Chemistry and Physics of Materials Committee, The Metallurgical Society of AIME
                          Member, Nuclear Metallurgy Committee, American Society for Metals
                          Symposium Organizer, High Resolution Electron Microscopy of Electronic Materials Annual Meeting of the Metallurgical Society of AIME, New Orleans, Louisiana, 1986
                          Fellow, Yamada Science Foundation, Japan
- C. G. Park   Member, Mechanical Metallurgy Committee, the Metallurgical Society of AIME
                          Session Chairman, Fall Meeting of the Metallurgical Society of AIME, Toronto, Canada, 1985
                          Member, Local Committee, Second International Conference on Fundamentals of Fracture, Gatlinburg, Tennessee, 1985
- S. J. Pennycook   Co-Chairman, Session Chairman, Materials Research Society Symposium on Oxygen, Carbon, Hydrogen, and Nitrogen in Crystalline Silicon, Boston, Massachusetts, 1985
                          Lecturer, ORAU Traveling Lecture Program, 1985-1986
- D. B. Poker   Guest Scientist, Kernforschungsanlage Jülich, Federal Republic of Germany, July 1985-June 1986
- M. Rasolt   Guest Scientist, Physics Department, Harvard University, Boston, Massachusetts, September-December, 1985
                          Guest Scientist, Center European de Calcul Atomique et Moleculaire, Orsay, France, November-December, 1984
                          Lecturer, ORAU Traveling Lecture Program, 1984-1985
- J. B. Roberto   General Co-Chairman, Materials Research Society Annual Meeting (to be held in 1986)
                          Co-Chairman, Materials Research Society Symposium on Advanced Particle and Photon Techniques for the Characterization of Defects in Solids, Boston, Massachusetts, 1984
                          Co-Editor, Advanced Photon and Particle Techniques for the Characterization of Defects in Solids, Materials Research Society, Pittsburgh, Pennsylvania, 1985
                          Member, Editorial Advisory Board, Journal of Nuclear Materials
                          Member, Program Committee, Materials Research Society
- S. T. Sekula   Adjunct Professor, Department of Physics, The University of Tennessee, Knoxville, Tennessee
- H. G. Smith   Member, Neutron Diffraction Commission, International Union of Crystallography
                          Member, Program Committee, Neutron Scattering Symposium—Advances and Applications (to be held in 1987)
- E. Sonder   Adjunct Professor, Vanderbilt University, Nashville, Tennessee, 1985

- S. Spooner   Member, Ph.D. Recruiting Committee, ORNL
 Member, Structures Activity, Materials Science Division, American Society for Metals
 Member, Physics and Chemistry of Materials Committee, AIME
 Lecturer, ORAU Traveling Lecture Program, 1984-1985
- J. R. Thompson   Guest Scientist, Kernforschungszentrum Karlsruhe, Federal Republic of Germany, September 1985-March 1986
- J. C. Wang   Lecturer, ORAU Traveling Lecture Program, 1984-1985
- J. F. Wendelken   Chairman, Sixth Annual Symposium, Tennessee Valley Chapter, American Vacuum Society, Knoxville, Tennessee, 1986
- C. W. White   President, Materials Research Society, 1984
 Co-Editor, Pulsed Laser Processing of Semiconductors, Academic Press, New York, 1985
 Chairman, Awards, Nominating, and Long Range Planning Committees, Materials Research Society, 1985
 Principal Editor, Journal of Materials Research, 1985-1986
 Member, Editorial Board, Nuclear Instruments and Methods
 Member, Editorial Board, Materials Letters
- G. D. Wignall   Adjunct Professor, Department of Chemical, Metallurgical, and Polymer Engineering, The University of Tennessee, Knoxville, Tennessee
 Member, Board of Directors, American Crystallographic Association Special Interest Group on Small-Angle Scattering, 1985
 Lecturer, ORAU Traveling Lecture Program, 1985-1986
- M. K. Wilkinson   Executive Secretary, DOE Basic Energy Sciences Laboratory Program Panel
 Member, Organizing Committee, 1985 International Conference on Magnetism
 Member, Advisory Committee, Department of Physics, University of South Carolina
 Member, DOE Basic Energy Sciences Council on Materials Sciences
 Member, Program Advisory Committee, National Synchrotron Light Source, Brookhaven National Laboratory
 Adjunct Professor, School of Physics, Georgia Institute of Technology, Atlanta, Georgia
 Consultant to Steering Committee, U.S.-Japan Cooperative Program on Neutron Scattering
 Member, DOE Basic Energy Sciences Neutron Scattering Review Committee
 Chairman, ORNL Committee on Guests and Users
 Member, ORNL Emergency Review and Advisory Committee
 Member, ORNL Steering Committee, Center for Neutron Research
- J. M. Williams   Co-Chairman, Materials Research Society Symposium on Biomedical Materials, Boston, Massachusetts, 1985
 Member, International Organizing Committee, Surface Modification of Metals by Ion Beams Conference (to be held in 1986)
- R. F. Wood   Editor, Solid State Physics, Computer Physics Communications, North-Holland, New York
 Co-Editor, Pulsed Laser Processing of Semiconductors, Academic Press, New York, 1985.
 Member, Advisory Committee, International Conference on Defects in Insulating Crystals, Salt Lake City, Utah, 1984
 Member, Professional Education Resources Committee, ORNL
 Member, ORNL/UT Distinguished Scientist Program Committee, 1985
 Co-Chairman, Martin-Marietta Energy Systems Technical Achievement Awards Committee, 1984
 Member, Martin-Marietta Energy Systems Technical Achievement Awards Committee, 1985
 Member, Corporate Fellows Advisory Committee on Science and Technology
 Co-Organizer, Symposium on Excimer Laser Applications to Materials Processing, Fiber Laser '86 SPIE Conference, Cambridge, Massachusetts (to be held in 1986)
 Member, Proposal Review Panel for Basic Research Program of Office of Naval Research

F. W. Young, Jr.

Member, Executive Committee, American Association for Crystal Growth
 Member, Conference Committee (Chairman) and Awards Committee, American Association for Crystal Growth
 Member, Editorial Board, Topics in Crystal Growth
 Member, Council, Materials Research Society
 Member, External Affairs Committee (Chairman) and Long Range Planning Committee, Materials Research Society
 Vice-Chairman, Materials Physics Topical Group, American Physical Society
 Session Chairman, American Physical Society Meeting, Baltimore, Maryland, 1985
 Member, Committee for International Prize for New Materials, American Physical Society
 Member Materials Science Advisory Committee, Southeastern Universities Research Association

D. M. Zehner

Co-Chairman, Education Committee, American Vacuum Society, 1984
 Member, Executive Committee, Surface Science Division, American Vacuum Society, 1984
 Member, Executive Board, Tennessee Valley Chapter American Vacuum Society, 1984
 Co-Chairman, Education Committee, Materials Research Society, 1984

R. A. Zuhr

Session Chairman, Workshop on Analysis and Comparison of Surface Probe Measurements made on TEXTOR, Jülich, Federal Republic of Germany, 1985

PERSONNEL CHANGES

New Staff Members

A. Scientific Staff

J. A. Budai, AT&T Bell Laboratories, Murray Hill, New Jersey
R. A. DiDio, University of Pennsylvania, Philadelphia, Pennsylvania
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D. N. Mashburn, transferred from Oak Ridge Gaseous Diffusion Plant
J. B. Roberto, transferred from Central Management Offices (completion of temporary assignment)

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M. J. Aziz (voluntary resignation)
W. E. Brundage (retirement)
T. B. Cook (voluntary resignation)
W. C. Koehler (deceased)
T. S. Noggle (deceased)
O. A. Pringle (voluntary resignation)
J. B. Roberto (transferred to Central Management Offices; temporary assignment)

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R. L. Burrell, Secretary (retirement)
L. C. Cunningham, Secretary (voluntary resignation)

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