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PROGRESS REPORT
For Period Ending September 30, 1978**

M. K. Wilkinson, Director
F. W. Young, Jr., Associate Director

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Acronyms, Abbreviations, and Initialisms

aBR – anti-Beevers-Ross	J-T – Jahn-Teller
AES – Auger electron spectroscopy	JAERI – Japan Atomic Energy Research Institute
ASF – augmented space formalism	KFA – Kernforschungsanlage
ATA – average <i>t</i> -matrix approximation	KKR – Korringa-Kohn-Rostocker
bcc – body-centered cubic	LCAO – linear combination of atomic orbitals
BCS – Bardeen-Cooper-Schrieffer	LEED – low-energy electron diffraction
BNL – Brookhaven National Laboratory	LLL – Lawrence Livermore Laboratory
BR – Beevers-Ross	LSS – Lindhard, Scharff, Schiøtt
BSR – Bulk Shielding Reactor	LTIF – Low-Temperature Irradiation Facility
CENS – Centre d'Etudes Nucléaires de Saclay	MCD – magnetic circular dichroism
CL – crystal lattice	MCL – minority carrier lifetime
CLS – characteristic loss spectroscopy	MHD – magnetohydrodynamics
CNRS – Centre National de la Recherche Scientifique	MIT – Massachusetts Institute of Technology
CPA – coherent potential approximation	mO – mid-oxygen
CSM – critical-state model	NASA – National Aeronautics and Space Administration
DGS – degenerate ground state	NBS – National Bureau of Standards
dHvA – de Haas-van Alphen	NBSR – National Bureau of Standards Reactor
DLTS – deep level transient spectroscopy	NEMA – National Electrical Manufacturers Association
DOE – Department of Energy	NFS – Nuclear Fuel Services
dpa – displacements per atom	NMR – nuclear magnetic resonance
dPS – deuterated polystyrene	NRC – National Research Council
EBFZ – electron-beam float-zone	NSF – National Science Foundation
EBR – Experimental Breeder Reactor	NTD – neutron-transmutation-doped
ELS – energy loss spectroscopy	ORAU – Oak Ridge Associated Universities
ENDOR – electron nuclear double resonance	ORNL – Oak Ridge National Laboratory
EPR – electron paramagnetic resonance	ORR – Oak Ridge Research Reactor
EURATOM – European Atomic Energy Community	PICS – positive ion crystallography of surfaces
EXAFS – extended x-ray absorption fine structure	PoCIS – poly(ortho-chlorostyrene)
fcc – face centered cubic	RTNS – rotating target neutron source
FLL – flux-line lattice	SANS – small-angle neutron scattering
FWHM – full width at half maximum	SEM – scanning electron microscope
hcp – hexagonal close packed	SIMS – secondary ion mass spectroscopy
HFIR – High Flux Isotope Reactor	SRO – short-range order
IEEE – Institute of Electronic and Electrical Engineers	TEM – transmission electron microscopy
IIT – Illinois Institute of Technology	TPA – traveling pseudo-fermion approximation
ILL – Institut Laue-Langevin	UHV – ultra-high-vacuum
IMS – intermediate mixed state	XES – x-ray energy spectroscopy
IRML – Isotope Research Materials Laboratory	XFS – x-ray fluorescence spectroscopy
ISX – Impurity Study Experiment	

Introduction

During the 17 months covered by this Progress Report, there have been significant changes in the research programs conducted by the Solid State Division. The initiation of such changes began about four years ago when the Atomic Energy Commission was replaced by the Energy Research and Development Administration (ERDA), and these changes have continued with the formation of the Department of Energy (DOE). With the very broad missions of ERDA and DOE in the development of new energy systems, many different types of programs in the materials sciences are necessary. Every advanced energy technology has severe materials problems, and the solutions of these problems must rely heavily on information obtained from scientific research. During this relatively short period of time, the Solid State Division has entered a number of new research areas, and about half of the Division's current programs are closely related to the nonnuclear energy technologies. Although some increase in support has accompanied this change in emphasis, much of the new research has resulted from a redirection of previously existing work. It is particularly gratifying that this transition has been accomplished smoothly and that the new programs are already characterized by very interesting and productive investigations.

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, Crystal Growth and Characterization, and Isotope Research Materials. Each of them constitutes a major section of the report, and additional subdivisions are included within the sections. There are short introductions preceding the major sections to indicate the scope and goals of the research and to give a few highlights of recent investigations. These introductions reflect many of the changes that have taken place in programs of the Division. It is also their intent to give a clearer picture of the manner in which the individual programs are interrelated and to indicate how research activities of the Solid State Division contribute to various programs of ORNL and DOE.

Because of the very close interactions among programs of the Division, many of the research summaries in this report would have been equally appropriate in two or more subsections. A particularly good example of this interaction is the new work involving ion implantation and laser annealing of semiconductors. Oak Ridge National Laboratory has been one of the leading laboratories in this exciting area of materials research, with particular emphasis on the development of better photovoltaic materials for solar cells. The characterization and understanding of the unique materials produced by these techniques have required a wide variety of skills and experimental facilities, and significant contributions have been made by a large fraction of the Division's scientists. There has also been a close overlap of interests in the study of superconducting materials by conventional methods and by various techniques of neutron scattering. Of course, almost all of the experimental programs are closely tied to ongoing theoretical investigations and to programs concerned with materials preparation and characterization. It is hoped that the arrangement of the report minimizes difficulties in finding particular research summaries of interest.

A very close research collaboration now exists with members of the neutron scattering group of Ames Laboratory. With the shutdown of the Ames Laboratory Research Reactor on December 31, 1977, these scientists are continuing their research program using the research reactors at ORNL. Some of the Ames Laboratory neutron scattering equipment has been installed at the ORR, and this equipment, together with ORNL equipment at the ORR and HFIR, is available to scientists of both laboratories. The joint authorship on several neutron scattering research summaries is an indication of the strong collaboration that has developed.

Plans are now in progress to make the unique experimental facilities of the Solid State Division more available to scientists from universities and other research laboratories. Although informal arrangements of this type currently exist and have existed for many years, it is believed that a more formal users' program will ensure the most effective utilization of these facilities. A program devoted exclusively to users was initiated in January 1978 under an interagency agreement between DOE and NSF. Through this agreement, a National Center for Small-Angle Scattering Research was established at ORNL under the administration of the Solid State Division. This Center now operates the existing ORNL small-angle x-ray and small-angle neutron scattering facilities on a part-time basis. Within the next year, it will also operate a very sophisticated small-angle neutron scattering facility currently under construction at the HFIR. This users' mode of operation for the National Center for Small-Angle Scattering Research and for other unique facilities at ORNL will undoubtedly strengthen future interactions between members of the Solid State Division and scientists from other organizations.

1. Theoretical Solid State Physics

The theoretical work in the Division has broadened in scope as the experimental programs designed to accomplish the mission of DOE have evolved. The result is a wide range and variety of work including the use of well-established theories in developing concepts of technological importance, state-of-the-art interpretations of various spectroscopies, and explorations of the boundaries of existing theories. With one new heading added this year, this section of the progress report is subdivided into five subsections: Surfaces, Lattice Dynamics and Alloys, Particle-Solid Interactions, Laser Annealing, and Electronic and Magnetic Properties.

A number of advances have been made in areas of long-standing interest within the Division. For example, the first-principles calculations of phonon spectra in high T_c transition metal superconductors undertaken several years ago are now coming to fruition. Good agreement between calculations and experiment has been achieved for Nb; in particular, the anomalous dip observed in the longitudinal dispersion curve along the [001] direction is reproduced rather well by the calculations. Contrary to conclusions reached by others working with more restricted models, this anomaly does not arise in any simple way from Fermi surface effects, p - d matrix elements, or resonant screening precursive of a d -electron charge density wave. Instead, the anomaly appears to reflect a complex interplay of effects within the full dielectric response function. Work on alloys has continued, and emphasis remains on phonons in disordered systems because of the experimental neutron scattering program in the Division. A connection has been made between the augmented space formalism elaborated here and recent work by others showing how a certain class of proper analytic treatments of disorder can be generated.

Two powerful tools for surface structure analysis are ion scattering and LEED; computer programs to interpret the results of these spectroscopies continue to be both used and further refined. Computer simulation of the backscattered energy spectrum of He⁺ ions from a clean W(100) crystal indicates that the surface layer relaxes inward or outward by no more than 6% of the bulk interlayer spacing. This observation is in disagreement with a contraction of 11% deduced from LEED analysis at another laboratory; the discrepancy may reflect different methods of surface preparation. State-of-the-art multiple-scattering LEED calculations have shown that a contraction of approximately 10% occurs for the Cu(110) surface and have eliminated the so-called "missing-row" model for the 2×1 reconstructed Au(110) surface. Two of the conventional simplifying assumptions made in LEED analysis have come into question as the quality of both experimental data and theoretical analysis has improved sufficiently so that remaining differences may be ascribed to limitations of the model. Preliminary results indicate that both anisotropic surface vibrations and the direction and depth dependence of the optical potential may contribute to resolving these remaining discrepancies.

In the area of the particle-solid interactions, emphasis has shifted over the past few years from problems associated with radiation damage from fission reactors to questions of interest for advanced energy technology, although some work does continue on the

former. The computer program MARLOWE has been used to study reflection from and sputtering of various targets in the binary collision approximation. The sputtering of amorphous Cu targets by low-energy atoms and of Au (001) surfaces by 700-eV Xe⁺ ions has confirmed the usefulness of the planar surface binding model; in this model, the surface binding is overcome only by the normal component of the escaping particle velocity. Good agreement with experiment was achieved for the sputtering of Au (001) surfaces. MARLOWE was also used to simulate the reflection and sputtering of H and T from Ti, Fe, and their hydrides. The role of disorder and static displacements or relaxation induced by radiation damage in the A15 compounds (of interest because of their high superconducting transition temperatures) was studied by experiments and calculations performed for backscattering of channeled 1.9-MeV ⁴He in V₃Si crystals. It was found that the electron-phonon and electron-defect interactions are of comparable importance in the damage-related degradation of the electrical conductivity.

Oak Ridge National Laboratory has been one of the leading laboratories in the recent intense exploration of laser annealing for preparation of semiconductor device materials. Theoretical interest has thus far been concentrated on the rapid transients produced in the first few microns of the samples by the laser pulses. Typically, a single crystal of Si or some other semiconductor is ion implanted to a high concentration of acceptor or donor impurities, yielding a sample with a nonuniform dopant vs depth profile and a substantial amount of lattice damage. Following pulsed laser annealing at sufficient power densities, the dopant is much more uniformly distributed, crystal perfection is restored to an extraordinarily high level, and virtually all of the dopants are electrically activated. The physical processes that occur during and after laser irradiation to produce these desirable characteristics may be briefly summarized as follows: (1) melting occurs as energy is deposited in the surface region of the sample, and the melt front quickly sweeps into the crystal; (2) in the liquid region, diffusion takes place orders of magnitude faster than in the solid, resulting in efficient redistribution of the impurities; (3) after reaching the maximum depth, the melt front advances back to the surface as epitaxial regrowth occurs. The dependence of the resulting material characteristics on such parameters as the laser energy density, sample reflectivity and absorption coefficients in the liquid and the solid, and impurity segregation from the solid to the melt are explored in seven reports in this section, as well as in a number of other contributions in other sections.

The subsection entitled "Electronic and Magnetic Properties" this year includes further work on the electronic structure of defects in insulators and a serendipitous application of methods developed for alloys to a biological problem. It contains a very nice application of methods developed for pure bulk properties (band structure and phonon spectra) to the treatment of defects in metals. A general theoretical formulation of this problem was given years ago, but realistic calculations have been slow to follow because of their complexities.

SURFACES

STUDIES OF DEFECTS AND SURFACES BY CHANNELING¹

John H. Barrett

Two examples are given here of ways in which channeling has been used to study defects and surfaces of solids. These examples were chosen to indicate topics of current interest and ways in which uses of channeling are evolving.

One problem that is common to both of the applications which will be discussed, as well as to many other uses of channeling, is the way in which the results are normalized. Because absolute measurements are very difficult to make, the usual procedure is to express the results for Coulomb scattering, nuclear reactions, or other close encounter processes relative to yields for a random, or completely unchanneled, direction in the solid. However, it is very difficult to select a truly random direction. One commonly used technique is to use a "rotating random," a procedure in which the

beam is directed several degrees away from a major crystal axis and then rotated through 360° (or only 180° , 90° , or 60° if use is made of symmetry) about that axis. An analysis of this technique was made using computer simulation of the ion trajectories, and the technique was shown to be accurate within 1 to 2% if the angle from the axis is several times the critical angle for channeling for that axis. Another technique, also shown to be accurate to within 1 to 2%, is to go to a direction or to scan a small range of directions that are away from all major axes or planes of the crystal and normalize by comparing to a computer simulation for the same direction(s).

Most uses of channeling to locate positions of atoms in solids utilize qualitative features of the results, such as the depth and width of the channeling dip for an impurity compared to the dip for the host, or the possible presence of a peak at the center of the impurity dip or symmetrical pairs of off-center peaks. However, in some cases, the interpretation — or some part of it — depends on quantitative features of the results. In the latter situation, computer simulation furnishes the most accurate method of producing quantitative theoretical results to use in interpreting the measurements. An example can be given by considering some experimental results for an Al-0.09 at. % Mn alloy.² The qualitative features of the results established that the Mn atoms trapped radiation-produced interstitials with a resulting dumbbell configuration, but the exact position of the Mn atom in the mixed dumbbell could not be determined solely from these qualitative features.² By use of computer simulation in conjunction with the experimental results, the author was able to establish that a Mn atom in a trapped dumbbell is displaced 1.43 ± 0.05 Å from its lattice site.

In using ion backscattering under channeling conditions to study surfaces, one problem is to separate the peak in the backscattering energy spectrum due to the surface from the background contribution resulting from the bulk. The separate surface and subsurface contributions were studied using computer simulation, and two methods of extracting the surface scattering were shown to be capable of an accuracy of a few percent. Computer simulation was also applied to the analysis of experimental results for the scattering of He ions from a Pt(111) surface.³ The analysis showed that these experimental results implied an outward relaxation of 0.22 ± 0.03 Å for the surface layer.

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3. J. A. Davies et al., *Phys. Lett.* 54A, 239 (1975); *Nucl. Instrum. Methods* 132, 609 (1976).

SURFACE SCATTERING FROM W SINGLE CRYSTALS BY MeV He⁺ IONS¹

John H. Barrett L. C. Feldman²
R. A. Zuhre R. L. Kauffman²
P. J. Silverman²

The backscattered energy spectrum of a beam of MeV ions incident along a major axial direction of a single crystal displays a peak at high energy that represents the interaction of the beam with the surface region of the solid. Measurements of the size of this peak were made as a function of the energy of He⁺ ions incident on a clean W(100) crystal, and these measurements are in good agreement with classical models of channeling.

The size of the surface peak was found to be a smooth function of ρ/R , where $R = 2(Z_1 Z_2 e^2 d/E)^{1/2}$, ρ is the root-mean-square thermal vibrational amplitude parallel to the surface, $Z_1 e$ and $Z_2 e$ are the charges of the ions and target atoms, d is the atomic spacing along the row or axis, and E is the incident ion energy. The surface peak is made up of a full contribution from the first atom in each row plus partial contributions from other atoms further down in the row that depend on the exposure the latter get to the ion beam because of thermal vibrations and relaxation of the surface atoms. Because the functional dependence on ρ/R of the surface peak size is the same for the [110] and [111] incident beam directions, which are inclined to the surface normal, as for normal incidence, an upper limit may be set on the magnitude of the relaxation of the surface monolayer on a clean W(100) crystal. This limit is $\leq 6\%$ of the interlayer spacing, which is in disagreement with a contraction of 11% deduced for W(100) by an analysis of LEED data.³ The discrepancy may be due to different methods of surface preparation.

The measured values of the surface peak lie uniformly higher over the entire energy range studied than do values calculated by computer simulation using thermal vibrations appropriate in the bulk of the crystal, suggesting enhanced vibrations of the surface atoms. Good agreement between calculations and experiments is obtained for isotropic enhancement factors over the bulk vibrations of (a) 1.8 for the first layer only, (b) 1.6 for each of the first two layers, or (c) 1.5, 1.3, and 1.2 for the first, second, and third layers. The last set of

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1. Summary of paper: *Phys. Rev. Lett.* 39, 38 (1977).
2. Bell Laboratories, Murray Hill, N.J.
3. B. W. Lee et al., *J. Vac. Sci. Technol.* 14, 291 (1977).

SOME EFFECTS OF ANISOTROPIC VIBRATIONS IN LEED¹

Martin Uchida H. L. Davis

Early calculations for LEED were made for rigid lattices; that is, no effects of surface thermal vibrations were considered. As workers in the field became more aware of the importance of thermal effects in experimental I-V profiles, attempts were made to simulate vibrational effects by renormalizing the interaction potentials with Debye-Waller factors. However, this approach was shown to be inadequate by Duke and Laramore because of the importance of multiple-scattering events.^{2,3} Duke and Laramore employed quantum-field-theoretic methods to generalize and formalize the treatment of thermal vibrations in LEED theory. One main result of their work was that for the case of isotropic vibrations, when the multiple scatterings from an individual site are assumed to proceed quasi-statically, the general formulation reduces to just a renormalization of the single-site *t*-matrix by the Debye-Waller factor (strictly speaking, its square root). Although it is clear from their work that a similar type of renormalization would occur in the case of anisotropic vibrations, most questions concerning effects of anisotropic thermal vibrations in LEED have been neglected. Because the anisotropy in mean square vibrational amplitudes could be of the order of 50%, it is important to determine how this might influence the results of LEED calculations. To this end, we have initiated a study of the effects of anisotropic thermal motions in LEED.

For preliminary work, it was assumed that anisotropy exists only between the vibrational displacements parallel and perpendicular to the surface. Using a formalism we developed for such anisotropy, illustrative LEED calculations have been performed for a Cu(100) surface. For these, a surface region model was adopted in which only the topmost layer vibrated anisotropically while the remaining layers vibrated isotropically. Although this might appear to be an oversimplification, an inspection of Table 6.3 of Pendry⁴ indicates that it could be a reasonable zero-order approximation to physical

reality. The calculations were performed for room temperature and the incident electron beam normal to the surface. A Debye temperature of 300 K was used to specify both the vibrations parallel to the surface in the topmost layer and the isotropic vibrations in the remaining layers. The mean square vibrational amplitudes perpendicular to the surface in the topmost layer were assumed to be 50% larger than those parallel. This value was picked to provide what might be considered a realistic, but slightly extreme, case for the vibrational amplitudes perpendicular to the topmost layer.

Some results from our calculations are presented in Figs. 1.1 and 1.2. To our knowledge, these are the first dynamical LEED calculations that have included any vibrational anisotropy. Although all propagating reflected beams were determined in the calculations, we present here only those for the specular beam and the (01) nonspecular beam. For comparison we also show the results obtained with the usual isotropic version of the present model, where $\theta_D = 300$ K was used for the vibrations in all layers. It is fortunate that the two curves of each figure are quite similar to each other, at least with respect to their major features. If these similarities had not been obtained, serious questions would arise concerning a considerable amount of recent work that has employed LEED to infer surface crystallographic features (e.g., to obtain interlayer spacing for clean surfaces and bond lengths for adsorbed species). Thus, if some of the prominent peaks had been shifted with respect to each other by, say, 2 to 6 eV, conclusions based on the comparison of LEED calculations with experimental data might be questioned. However, some shifts of these peaks of the order of 1 eV do occur, and whether or not the shifts increase when other, and perhaps more realistic, models of vibrational anisotropy are used is a proper topic for future work. It is also to be remembered that the results of Figs. 1.1 and 1.2 are for the incident beam normal to the surface, and it might be argued that effects caused by the type of anisotropy used would be minimal for normal incidence.

If attention is directed toward the finer features of Figs. 1.1 and 1.2, one sees easily detectable differences in the locations of minor peaks and shoulders and in the shapes of some of the major peaks. These differences appear slightly more pronounced for the nonspecular beam (Fig. 1.2) than for the specular beam (Fig. 1.1). A like observation can be made for most of the other nonspecular beams considered in this investigation but not illustrated here. Any attempt to generalize whether or not similar observations will emerge from calculations where the incident beam is not normal to the

Fig. 1.1. Results for the (00) beam reflected from the two models described in the text. Curve "A" is for the model with anisotropic vibrations, and Curve "T" is for the model with isotropic vibrations. Different intensity normalizations have been used for the two curves, and the hash marks at left denote the intensity zeros.

Fig. 1.2. Results for the (01) beam reflected from the two models described in the text. Curve "A" is for the model with anisotropic vibrations, and Curve "T" is for the model with isotropic vibrations. Different intensity normalizations have been used for the two curves, and the hash marks at left denote the intensity zeros.

surface would, at present, be highly speculative. However, it does appear from our work that caution must be maintained and that fine detail in LEED calculations should not be used to infer information about surface crystallography, especially in cases where the vibrational anisotropy is expected to be relatively large.

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DETERMINATION OF A Cu(110) SURFACE CONTRACTION BY LEED INTENSITY ANALYSIS¹

H. L. Davis J. R. Noonan L. H. Jenkins

During the last decade, considerable progress has been made toward establishing LEED as a quantitative tool for surface crystallography. One result of LEED crystallography has been the demonstration that open faces of some fcc metals have the first atomic layer contracted

toward the second layer. For the (110) surfaces of Al and Ni, this contraction is about 5% of the bulk interlayer spacing,^{2,3} and it is of interest to determine whether open surfaces of other fcc metals exhibit similar contractions. Thus, we initiated a Leed study of the Cu(110) surface and found preliminary evidence that this surface is also contracted.⁴ We have now completed the analysis of normal incidence LEED data for the Cu(110) surface and conclude that this surface undergoes a contraction of $15.0 \pm 2.5\%$.

The experimental data used in our analysis are displayed as the bottom curves in the individual frames of Fig. 1.3. These I-V profiles were collected from a Cu sample that had been cut, lapped, and electropolished to expose the (110) face. After the initial sample preparation and orientation, the sample was mounted in a UHV chamber, repetitively cleaned by Ar ion sputtering, and then annealed to produce a surface that exhibited no contaminant Auger signals. The process led to well-focused diffraction beams characteristic of a clean, ordered Cu(110) surface. The data were collected by using a small, moveable Faraday cup to track the diffracted beams as a function of energy. Several advantages are gained by using a Faraday cup system to collect the data. Principally, it allows data to be collected at large angles, whereas spot photometer systems

Fig. 1.3. Measured I-V profiles for six nonspecular beams compared with the computed set of profiles for $\Delta d_{11} = -10\%$ and $v_0 = 8.5$ eV.

typically are limited to less than 60° because they must measure the fluorescent spot on the viewing screen. In addition, the cnp system measures the absolute intensity of the beam. Using this system, the sample was aligned normal to the incident beam to within $\pm 0.1^\circ$ (ref. 4). Six groups of symmetrically equivalent beams (namely the {01}, {10}, {11}, {12}, {02}, and {20} groups of beams) were measured. The fact that, within sets of symmetrically equivalent beams, data were reproducible to within $\pm 12\%$ in intensity and ± 1 eV in energy indicates that the experimental variables, such as sample alignment, stray field cancellation, electron beam coherence, and sample preparation, were all within manageable levels.

The six measured I-V profiles were compared with the results of an extensive series of dynamical LEED calculations. These calculations used computer codes created at ORNL, which were based on the Δ -layer KKR formalism of multiple scattering and renormalized-forward-scattering perturbation theory.^{5,6} The calculations were performed at 1 eV intervals between 40 and 220 eV. The electron scattering phase shifts were obtained from the Chodorow potential,⁷ and the calculations were performed using 8 phase shifts, 47 beams, 14 atomic layers, and 3 to 5 passes of renormalized forward scattering. In addition, the atomic vibrations in the surface region were modeled by using a rigid lattice of "blurred atom" scatterers to have the calculations correspond to the crystal being at room temperature.⁸ The amount of blurring was determined by using an isotropic Debye model, and a surface-region Debye temperature of 250 K provided the best fit to the data. Finally, the optical potential was composed of an energy-independent, real component v_0 , and an energy-dependent imaginary part β . For a given set of calculations, v_0 was held constant but was varied from one set to another to optimize the agreement between the data and calculated results. Then β , which is used to simulate absorption of the elastic beam, was modeled as $\beta = 0.85 E^{3/2}$, where E is the energy of the incident beam and β and E are in electron volts.³

The assumption that all atomic layers in the surface are in lateral registry with their bulk positions was used throughout our investigation. However, a series of calculations was performed in which the first, d_{12} , and second, d_{23} , interlayer spacings were varied independently from the value for the interlayer spacings in the bulk. The sets of I-V profiles resulting from these variations were then compared with the experimental profiles in two ways. First, the profiles were evaluated visually to determine which computer run had the "best" agreement with the data. This visual comparison

then was refined by making a numerical estimation of the "best" fit; that is, a structural reliability factor R as defined by Zanazzi and Jona⁹ was used to compare the six measured profiles with the calculated results.

The best agreement between the experimental and calculated profiles was found for those calculations corresponding to the first atomic layer contracted toward the second by $10.0 \pm 2.5\%$ (relative to the bulk spacing) and the second to third layer spacing being within 2.5% of the bulk value. Some subjectivity was removed from our determination of the "best fit" by the use of the multi-beam R -factor analysis. Some results of this analysis are displayed in Fig. 1.4, where the R -factor is plotted topographically as a function of the first interlayer spacing and the real component of the inner potential. The R -factor would be zero if perfect agreement were obtained and would be approximately unity if two randomly related sets of profiles were compared. As is readily apparent from Fig. 1.4, the best agreement for the analysis is for a 10% contraction of the surface atomic layer and an inner potential of 8.5 eV. Variation of the spacing between the second and third atomic layers does not further reduce the R -factor beyond the minimum of Fig. 1.4.

Fig. 1.4. Six-beam R -factor contour map to illustrate the effects of both the amount of contraction of the first layer (Δd_{12} relative to the bulk layer spacing) and changes in the real component of the inner potential v_0 .

The final agreement obtained by our analysis is illustrated in Fig. 1.3, which compares the measured I-V profiles with the ones calculated for the conditions producing the minimum R -factor of Fig. 1.4. The beam-to-beam comparisons given in Fig. 1.3 are quite typical for the final result of a LEED analysis and should be considered as producing "reasonable to good agreement"; that is, although the experimental curves are not reproduced in every detail, most of the major features are seen in the calculated curves. However, we wish to mention our consideration of the major discrepancy between the calculated and experimental profiles, which occurs in the energy region near 60 eV. This discrepancy is seen especially in the (10) and (11) beams in Fig. 1.3, where peaks occur in the data that are not reproduced by the calculations. At present, we believe that these additional peaks are due either to an incomplete modeling of the inelastic losses or to anisotropic lattice vibrations. Models are now being constructed to test these possibilities. Although we are not certain of the cause of the discrepancy, tests have been performed indicating that its occurrence should not affect the crystallographic conclusions found by our analysis in any major way. However, we do feel that further analysis of the 60-eV region is very desirable because it might contribute to the development of a more general theoretical model for LEED.

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A LEED ANALYSIS OF THE RECONSTRUCTED Au(110) SURFACE¹

J. R. Noonan H. L. Davis

Surface reconstruction is said to occur for a clean surface when it produces a LEED spot pattern indicating that the two-dimensional unit cell of the surface is different from the one that would be obtained by a simple truncation of the bulk material. However, LEED

studies have shown that for most low-Miller-index metal surfaces only slight displacements of the atomic layers in the direction perpendicular to the surface are found; that is, there is no reconstruction. Thus, because they appear anomalous, considerable interest exists in those few low-Miller-index metal surfaces that do reconstruct. Of particular interest at present is the determination of the geometric structure of these reconstructed metal surfaces. We have therefore initiated a LEED analysis of the Au(110) surface, which is reconstructed at room temperature. Interestingly, the clean (110) surfaces of Cu and Ag are not reconstructed.

It has been shown previously that the clean Au(110) surface at room temperature produces half-order LEED diffraction beams in the (001) direction,^{2,3} which leads to a (1 × 2) spot pattern with respect to the normal, truncated, (110) surface as shown in Fig. 1.5a. A direct inference from this pattern is that the two-dimensional unit cell length has doubled with respect to the truncated bulk in the (001) direction but remains the same in the (110) direction. Any further details of the crystallography of the surface, via LEED, can be obtained only by a detailed analysis of the intensity of the individual spots as a function of the energy of the incident beam. Even without such an analysis, speculations have been made concerning the geometric structure of the Au(110)-(1 × 2) surface.^{2,3} One popular model arising from these speculations is the "missing-row" model, in which the surface is assumed to have every other close-packed row missing. This model, which is entirely compatible with the (1 × 2) spot pattern, is illustrated in Fig. 1.5b. In our analysis, we decided to test the possible validity of this model first. At present, the main conclusion from our continuing analysis is a negative one: the missing-row model is incompatible with the LEED intensity data.

In our investigation, the Au(110) sample was cleaned and annealed in vacuum and then aligned perpendicular to the incident electron beam to within 0.1°. Details of these procedures are given elsewhere,^{1,4,5} but they result in the clear spot pattern of Fig. 1.5a. The intensity vs energy data were collected using a Faraday cup as a retarding field analyzer. This cup was free to rotate above the sample and was focused at a point in the surface; I-V profiles were obtained for 15 inequivalent, nonspecular beams and their symmetry-related counterparts. Because structure in symmetrically related profiles agreed to within ±1 eV in position and ±5% in intensity, we believe that experimental variables such as sample alignment, electromagnetic field cancellation, beam coherence, and sample preparation were within acceptable limits. From the 15 distinct I-V profiles

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Au(110) - (1x2)

49 eV
(a)

○ FIRST LAYER
◐ SECOND LAYER
● THIRD LAYER

(b)

Au(110) - (1x2): (a) LEED Pattern and (b) "Missing Row" Model.

Fig. 1.5. (a) Display of the Au(110)-(1 x 2) LEED pattern at 49 eV; and (b) the missing-row model for the reconstructed surface in which every other close-packed chain is missing from the surface.

measured, six were selected to be used in our preliminary analysis and are given in Fig. 1.6 as the bottom curves in the separate frames.

To test the validity of the missing-row model, multiple-scattering LEED calculations based on this model were performed at 1-eV intervals from 20 to 220 eV. These were done using ORNL-developed computer codes for surfaces with simple overlayers, which are based on the layer KKR formalism and renormalized-forward-scattering perturbation theory.^{6,7} We employed eight phase shifts for the Au potential,⁸ 47 beams for bulk-type layers, 94 beams for the top layer, and a surface Debye temperature of 140 K. To check the sensitivity of the results to minor structural variations in the model (e.g., distances between atomic layers), and also to other, constructural input parameters (e.g., the inner potential), various sets of calculations were performed in which both structural and non-structural parameters were varied over reasonable ranges.

Figure 1.6 compares the experimental profiles with one set of calculated profiles. The set of calculated profiles picked for Fig. 1.6 is one of the "least bad"

agreement with the data. As is seen from a visual inspection of the various frames of Fig. 1.6, very unsatisfactory agreement is found between the experimental profiles and those calculated using the missing-row model. This judgment was reinforced when the experimental and calculated profiles were compared numerically using the reliability factor, or *R*-factor, analysis of Zanazzi and Jona.⁹ The number in parentheses in each frame of Fig. 1.6 represents the single-beam *R*-factor as defined by Eq. (12) of Zanazzi and Jona, and the total six-beam *R*-factor, defined by Eq. (14) of Zanazzi and Jona, is 0.68. Now Zanazzi and Jona postulate that if a multi-beam *R*-factor is greater than 0.5 the structural model used must be considered doubtful. For all sets of calculated profiles based on variations of the missing-row model, we have found a six-beam *R*-factor greater than 0.6. We therefore consider it unlikely that this model is realistic for the Au(110)-(1 x 2) surface.

The inability of the missing-row model to reproduce adequately the experimental I-V profiles means that our further work on the Au(110)-(1 x 2) system will be more difficult. By seemingly eliminating the relatively simple structure of the missing-row model, we have

Fig. 1.6. Comparison between computed I-V profiles for the missing-row model and measured profiles for six nonspecular beams. (a) An (0,1) beam (defined in the (001)); (b) the (1,0) beam (in the (110)); (c) the (1,2); (d) the (0, $\frac{3}{2}$); (e) the (1, $\frac{1}{2}$); and (f) the (1, $\frac{3}{2}$) beams. The upper curve in each frame is the computed profile, and the lower curve is the measured one. The numbers in parentheses are the single-beam R -factors.

made it necessary to consider calculations for more complex arrangements of the surface atoms consistent with the LEED diffraction pattern. Some of the work required to treat more complex models is now in progress. Hopefully, this work will eventually lead to reasonable agreement between experimental and calculated profiles and thus finally elucidate the geometric structure of the Au(110)-(1 X 2) surface.

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OPTICAL POTENTIAL FOR ELECTRON SCATTERING FROM SURFACES

Mark Rasolt H. L. Davis

The spatial variation of the optical potential has so far been neglected in the study of electron interactions with metallic surfaces. In the interpretation of LEED, photo-emission, and Auger spectroscopy, both the imaginary and real parts of the optical potential are assumed to be isotropic and to depend weakly only on

the magnitude of the momentum of the scattered electron. However, present theoretical calculations are unable to reproduce all important details of the data obtained in the application of these electron spectroscopies.¹ Because differences between the data and calculations could be due partially to an incorrect modeling of the optical potential, we have begun a first-principles calculation of the anisotropic contributions to the optical potential. Preliminary results indicate that these terms are large and comparable in magnitude to the isotropic contribution. We are presently attempting to incorporate these results in a LEED calculation so that their effects can be assessed quantitatively.

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ELECTRON SCATTERING FROM ORIENTED MOLECULES

Martin Uehla J. F. Wendelken H. L. Davis

A study has been initiated to consider the elastic and inelastic low-energy electron scattering from oriented molecules. The electron scattering cross sections have been calculated using the $X\alpha$ multiple-scattering method for N_2 and CO. The accuracy of the theoretical approach was tested by comparing it to data from gas-phase measurements. Reasonable agreement between theory and experiment was found for the gas phase, raising the possibility that the calculated differential elastic and inelastic cross sections for oriented molecules might prove useful for the study of molecules adsorbed on surfaces.¹ Thus far, preliminary tests performed for the case of CO adsorbed on the Cu(110) surface indicate that differential scattering cross sections calculated by considering only the oriented molecule, without any inclusion of the effects due to the substrate, are insufficient to explain the observed angular patterns. The discrepancy between the calculated and experimental curves is due mainly to two effects neglected in the calculations. The first is the neglect of the long-range dipole contribution to the scattering, which dominates the cross sections in and near the specular direction. Second, in the oriented molecule approximation, the calculated angular pattern is that due to scattering from the oriented molecule only, and no multiple scattering from the atoms of the substrate is considered. However, it is now known that

by including the effects due to the multiple scattering from the substrate the angular pattern of the scattered electrons may be substantially modified. Inclusion of the two above-mentioned effects in the calculations remains an open problem at present.

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ELEMENTARY EXCITATIONS IN THE SURFACE REGION OF A SEMI-INFINITE SOLID¹

Mark Mostoller Theodore Kaplan

A variety of methods has been proposed for calculating the properties of elementary excitations at solid surfaces. Kalkstein and Soven,² for example, have presented an exact Green's function theory based on the tight-binding or LCAO formalism. Within the tight-binding framework, several approximate methods have also been employed; slab calculations have proven to be useful for both electronic³ and vibrational⁴ states, as has the real-space recursion method of Haydock, Heine, and Kelly.⁵

Our method shares some elements of the three approaches mentioned above. The starting point is an orthogonal tight-binding Hamiltonian for electrons, or a Born-von Kármán model for phonons. The only other assumption made is that the various planes of atoms parallel to the surface share a common two-dimensional translational symmetry so that a two-dimensional transform with respect to surface wave vectors can be performed. We emphasize that, unlike slab or real-space recursion calculations, the method is exact within the confines of these starting assumptions. An overlayer ordered in a commensurate superlattice of the substrate surface net can also be treated, as can interfaces when the constituents share a common two-dimensional Bravais lattice.

After taking the transform with respect to surface wave vectors, the desired elements of the Green's function are developed in terms of a matrix continued fraction. An exact termination of the continued fraction can be performed when a level is reached at which the planar transforms of the Hamiltonian or dynamical matrix settle down to their bulk values. Below some number of planes down into the crystal, the interatomic interactions will no longer be perturbed by the presence of the surface. We can imagine cleaving the crystal at the plane where this occurs, leaving a semi-infinite crystal with all elements of the Hamiltonian the same as

in the bulk. The Green's function in the surface region of this hypothetical, cleaved, perfect bulk crystal, which we refer to as the terminated bulk, is that which terminates the continued fraction. It can be determined either by the methods outlined by Kalkstein and Soven² or by using standard numerical techniques for solving coupled second-order equations.

The combination of matrix continued fraction and conventional Green's function approaches naturally separates effects arising from termination of the perfect bulk crystal from effects due to perturbed interactions in the surface region. The computationally difficult part of the problem is to calculate the Green's function for the terminated bulk over the desired mesh of wave vectors in the two-dimensional Brillouin zone. Once this calculation is done, the effects of changes in the interactions in the surface region on such quantities as spectral functions and dispersion relations in the surface region can be found by straightforward matrix manipulation, and layer-dependent densities of states can be calculated by integrating the appropriate spectral functions over the surface Brillouin zone.

The size of the matrices that must be manipulated is determined by the range and dimensionality of the interatomic interactions. Let n specify the interplanar range of the interactions: atoms in plane 1 interact with atoms in planes 1 to n , those in plane 2 with atoms in planes 2 to $n + 1$ (and in plane 1), etc. Let n_H denote the dimension of the interatomic interactions; for example, for lattice vibrations in monatomic Bravais crystals, $n_H = 3$, while $n_H = 9$ for electrons described by an s - p - d tight-binding Hamiltonian. The overall dimension of the matrices manipulated in our approach is $[n_H(n - 1)] \times [n_H(n - 1)]$. To illustrate this more graphically, consider the (110) surface of an fcc crystal with first- or first- and second-neighbor interactions. The range n of the interplanar interactions is three for either case, so $n - 1 = 2$. For phonons at this surface, the matrices involved in our approach are 6×6 in overall size, while for electrons described by an s - p - d tight-binding model they are 18×18 's.

To test some of the computational aspects of our approach, we have performed calculations for several simple model electronic systems, namely, s electrons at various surfaces of cubic crystals, with first- and second-neighbor interactions allowed. Although s -band tight-binding calculations are not of intrinsic interest, these systems provide the simplest cases for which our equations do not reduce to scalar equations, but instead are 2×2 or 3×3 matrix equations. Applications to more realistic problems such as lattice vibrations or electrons in d -band metals would, as noted, involve larger matrices, but the structure of the calculations would remain the same.

In our calculations, the terminated bulk Green's functions were found by the method outlined by Kalkstein and Soven.² A small but finite imaginary part was added to the energy throughout the calculations, making it possible to use very simple and direct procedures to evaluate the necessary integrals.

Figure 1.7 gives illustrative results for s electrons in an fcc (110) crystal with first-nearest-neighbor (1nn) interactions. The range n of the interplanar interactions is three for this case, so the matrices involved are 2×2 . For the results shown, all site-diagonal elements of the Hamiltonian were set equal to zero, and the 1nn interactions in the bulk were taken to have the value 1.0. The interactions $h_{1nn}(L, L')$ between first neighbors in planes L and L' in the surface region were assigned the

Fig. 1.7. Surface region and terminated bulk and infinite bulk densities of states for s electrons in an fcc (110) crystal. Plane 1 and plane 2 results in the surface region [full curves, $\rho(L; E)$] and in the surface region of the terminated bulk [dashed curves, $\rho_b(L; E)$] are at the bottom and middle; the infinite crystal density of states $\rho_0(E)$ is at the top.

following values: $h_{1nn}(L, L) = h_{1nn}(\text{bulk}) = 1.0$; $h_{1nn}(1, 2) = 0.6$; $h_{1nn}(1, 3) = 0.8$. The imaginary part of the energy used was 0.02.

The curves in Fig. 1.7 exhibit some expected features. The density of states in the surface layer differs significantly from the terminated bulk results (bottom) because of the 40 and 20% reductions in the first-neighbor interactions between planes 1, 2 and 1, 3 respectively. In the second layer (middle), the surface region and terminated bulk results are more similar to one another, and both are closer to the infinite bulk density of states (top). No surface bound states appear for this example.

Our calculations for these simple electronic models have demonstrated the advantage of separating the effects of cleavage from those produced by additional perturbations in the surface region. Almost all of the computer time required is spent in evaluating the terminated bulk Green's functions, which can be calculated once and then stored; a relatively small amount of time is needed to perform the matrix multiplications and inversions that yield the Green's function in the surface region. We believe that our calculations for these simple models also demonstrate the feasibility of performing similar calculations for more realistic models for electrons or phonons in the surface region of semi-infinite crystals.

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LATTICE DYNAMICS AND ALLOYS

FIRST-PRINCIPLES CALCULATION OF THE PHONON SPECTRUM OF Nb¹

J. F. Cooke

The fundamental relationship between lattice dynamics and superconductivity is the electron-phonon interaction. If sufficiently strong, this interaction can generate an effective attractive interaction between electrons that leads to the highly correlated superconducting ground state. In systems where the electron-phonon interaction is strong enough to induce superconductivity at high transition temperatures T_c , we now also expect to find anomalies in the phonon spectra.

Neutron scattering experiments² have established that characteristic phonon anomalies do indeed occur in transition metal, transition metal compound, and other superconductors with high T_c . The effects that have been observed indicate a definite correlation between high superconducting transition temperatures and certain types of phonon anomalies. It is currently believed that this correlation can be understood in terms of the dielectric response formalism, which provides a direct link between the phonon spectrum and the electronic properties of the system. Because of the complexity of the theory and the difficulty in obtaining accurate numerical results, there has been considerable disagreement as to the origin of the phonon anomalies and their relationship to high superconducting temperatures. For example, one of the most widely accepted views is that the anomalies are generated from peaks which occur in the dielectric screening matrix, that is, resonance screening. To determine whether this or possibly other mechanisms are operative, one must carry out first-principles calculations of the phonon spectra.

During the past few years, computer programs for carrying out first-principles phonon spectra calculations in transition metals have been developed at ORNL. These include programs for calculating the electronic energies, wave functions, and appropriate matrix elements as well as performing Brillouin zone and reciprocal lattice vector sums. Problems associated with slow convergence of the reciprocal lattice vector sums have been overcome by using a modified Ewald procedure. These programs require as input the charge on the ions (nucleus plus core electrons), the electron-ion potential, and the periodic crystal potential. There are no adjustable parameters.

Numerical results have been obtained thus far for Nb for phonon wave vectors q along the [100] and [111] directions. The ionic charge was taken to be 5e, and the electron-ion potential was obtained from an atomic Hartree-Fock calculation for a Nb atom with five electrons removed from the outermost shells. This potential was then spherically averaged and divided into a Coulomb and a non-Coulomb part. The non-Coulomb part of the potential was found to be highly localized about lattice sites, thereby considerably simplifying the entire calculation. Electronic energies and wave functions were generated from a KKR band structure calculation based on a self-consistent crystal potential proposed by Papaconstantopoulos.³ Brillouin zone sums were evaluated using the tetrahedron method with 2048 tetrahedra in the irreducible $1/48$ th of the zone.

For q along [100], the square of the phonon frequency can be written as a sum of two terms. One term, $\chi C(q)$, is generated by the direct interaction between

the ions, which results from the overlap of the Coulomb tails of the electron-ion potential. The other term, $XE(q)$, is generated by the indirect interaction between the ions, which is mediated by the conduction electrons. The first term depends only on the ionic charge and type of lattice and is plotted in Fig. 1.8. The symbols L and T refer to the contributions to the longitudinal and transverse acoustic modes respectively. The contributions from $XE(q)$ depend on the inverse of the dielectric screening matrix and therefore represent the difficult part of the calculation. Numerical results for $XE(q)$ are also plotted in Fig. 1.8.

Fig. 1.8. Contributions to the phonon frequency for Nb along [100] from the ion-ion (XC) and the electron-ion (XE) interactions. Subscripts L and T refer to longitudinal and transverse acoustic modes respectively.

The important thing to notice about the results for XE_L is that there are no peaks or dips at $|q| = 0.7$, which is where an anomalous dip occurs in the longitudinal branch of the phonon dispersion curves for Nb. This absence, in turn, implies that there are no peaks in the dielectric screening function for this direction. A more detailed investigation of the numerical results for the inverse of the screening matrix shows that this is indeed the case. The closed circles in Fig. 1.8 are values of $XE_{L,T}(q)$, which are in effect experimental points obtained from the measured phonon spectra and the unambiguous values of $XC_{L,T}(q)$. The smooth behavior

of these points is a direct experimental proof that the anomaly in the [100] LA phonon mode in Nb does not result from resonance screening.

The phonon spectra (in THz) can be determined from the results given in Fig. 1.8 by using the relation $\omega_{L,T}^2(q) = 669.49[XC_{L,T}(q) + XE_{L,T}(q)]$. The theoretical and experimental phonon spectra are shown in Fig. 1.9. The anomaly around $|q| = 0.7$ is reproduced very well by the calculation, as is the overall phonon bandwidth. The transverse phonon branch is also reproduced reasonably well.

Fig. 1.9. Comparison between theory and experiment for the longitudinal and transverse acoustic phonon modes along [100] for Nb.

The results along the [111] direction are more tentative. The calculated zone-boundary phonon frequencies are in good agreement with experiment. However, as one moves in toward the zone center, the square of the phonon frequency very quickly becomes equal to the sum of four very nearly equal terms of different signs, giving rise to convergence problems in the calculations.

In summary, it has been shown that the anomaly in the transverse acoustic phonon branch along [100] can be obtained from a first-principles calculation based on the dielectric response formalism. This anomaly does not appear to come from any resonance screening phenomena, but instead from a difference of two smooth functions of q . Interestingly enough, the same conclusion can be drawn from the experimental phonon spectra. Unfortunately, this makes it difficult to pinpoint the microscopic origin of the anomaly. A number of different approaches are currently being pursued in an effort to sort out the detailed correlation between the [100] anomaly and the electronic band structure.

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PHONONS IN DISORDERED ALLOYS: SINGLE PSEUDO-FERMION APPROXIMATION¹

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Several years ago, the average t-matrix approximation (ATA) was developed for phonons in disordered alloys with mass (diagonal) disorder only.^{3,4} Since then, no generalization with the same applicability has been made to the physically more relevant case of alloys with both mass and force constant (off-diagonal) disorder.

In a recent publication, Mills has established the necessary criteria for constructing approximations that will generate analytic Green's functions for diagonally disordered alloys.⁵ Diehl and Leath⁶ have synthesized these criteria with the augmented space formalism (ASF)^{7,8} and called it the pseudo-fermion approach. Using Kaplan and Gray's⁹ construction of augmented space, which includes off-diagonal disorder, one can employ the pseudo-fermion approach to generate new theories for off-diagonally disordered systems.

We have applied this approach to develop a more general ATA for phonons in alloys. Adapting nomenclature from Mills, the approximation we have used can be described as the non-self-consistent single traveling pseudo-fermion approximation (TPA).

As an example, we have applied the TPA to a one-dimensional A - B alloy with nearest-neighbor forces. In Fig. 1.10 we compare densities of states obtained with the TPA and "exact" numerical results⁹ for three concentrations of B atoms, $c_B = 0.01$, 0.25 , and 0.5 . For

Fig. 1.10. Comparison of the densities of states obtained with the TPA (smooth curves) and the "exact" numerical results (histograms) for linear chains with $M_A = 1.0$, $M_B = 0.5$, $\phi_{AA} = 1.0$, $\phi_{AB} = 1.5$, $\phi_{BB} = 1.5$. (a) $c_B = 0.01$, (b) $c_B = 0.25$, and (c) $c_B = 0.5$.

each case, the alloys have atoms with masses $M_A = 1.0$ and $M_B = 0.5$ and force constants $\Phi_{AA} = 1.0$, $\Phi_{AB} = 1.5$, and $\Phi_{BB} = 1.5$. The TPA results exhibit the typical ATA behavior,⁴ comparing well with exact results for c_B (or c_A) small, but giving poorer agreement for intermediate concentrations. To improve upon this approximation, one would have to generalize the approach to a self-consistent form. Such a generalization of the TPA will be reported in the near future.

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ON A COHERENT LOCATOR APPROACH TO LATTICE VIBRATIONS IN ALLOYS WITH DIAGONAL AND GEOMETRICALLY SCALED OFF-DIAGONAL DISORDER¹

Mark Mostoller Theodore Kaplan

Some years ago, a major advance in the theory of alloys was made with the introduction of the coherent potential approximation (CPA). As originally presented, the CPA was a single-site, mean-field theory for diagonal disorder only, that is, for mass changes for lattice vibrations and for random site-diagonal energies for electrons. Changes in the interatomic force constants or transfer integrals were not included in the CPA.

Subsequent to this early work, a number of methods were proposed to include off-diagonal disorder within the framework of a single-site CPA approach. For lattice vibrations, the present authors extended the CPA to include force constant changes as well as mass disorder for alloys in which the force constants superimpose linearly.² In simple binary alloys of the form $A_{1-c}B_c$, this is the so-called additive limit, in which the AB force constants are the arithmetic average of the AA and BB force constants, $\Phi_{AB} = (\Phi_{AA} + \Phi_{BB})/2$.

Somewhat more work has been done to include off-diagonal disorder for electrons in alloys. Fukuyama,

Krakauer, and Schwartz presented the electronic version of the CPA in the additive limit.³ Earlier, Shiba⁴ described a single-site coherent locator approach for the case in which the interatomic transfer or hopping integrals scale geometrically, $\Phi_{AB} = \sqrt{\Phi_{AA}\Phi_{BB}}$. Blackman, Esterling, and Berk generalized the coherent locator treatment to include arbitrary changes in the transfer integrals.⁵

Except in the additive limit, it has not been clear that the coherent locator approach can be applied to lattice vibrations. The reason for this uncertainty is that translational invariance imposes an additional formal constraint for phonons that is not required for electrons. Let $\Phi(l, l')$ be the force constant matrix connecting sites l and l' in the alloy. Then, so that no vibrations be excited in a uniform translation of the crystal, the force constants must satisfy

$$\Phi(l, l) = - \sum_{l' \neq l} \Phi(l, l'). \quad (1)$$

If there is disorder in the off-diagonal (interatomic) force constants, then this is necessarily reflected by changes in the diagonal (intra-atomic) terms in the Hamiltonian. In the additive limit, Eq. (1) is satisfied automatically by appropriately defined perturbations associated with single sites.² In general, however, and in the geometric limit, it is not possible to represent the force constant changes in the alloy as a sum of perturbations associated with single sites.

Grünwald has recently proposed a coherent locator treatment for lattice vibrations in the geometric limit.⁶ In this approach, which we will call the CPA-G, all of the correlations between off-diagonal and diagonal disorder that follow from Eq. (1) are not included. Instead, Eq. (1) is used to derive two sum rules for the configurationally averaged Green's functions in the alloy. Imposing these as additional constraints on the coherent locator development leads to a closed set of equations from which the site-diagonal, CPA-G self-energy can be calculated. We have shown that this theory reduces to a virtual crystal form for the special case of "equal" mass and force constant changes and that it fails to give satisfactory spectral limits for one- and three-dimensional model alloys.

With geometric scaling, the interatomic force constants can be written in the form

$$\Phi(l, l') = \lambda(l)\Phi^{\text{eff}}(l, l')\lambda(l'), \quad l \neq l', \quad (2)$$

where $\lambda(l) = 1$ if there is a host atom at the site l and $\lambda(l) = \lambda$ for a defect atom at l . The mass disorder is

expressed in terms of the quantity $\epsilon = 1 - M_d/M$, where M_d and M are the defect and host masses respectively.

For the special case of "equal" changes in the masses and force constants, that is,

$$\epsilon = 1 - \lambda, M_d/M = \lambda, \quad (3)$$

the CPA-G self-energy turns out to be a real constant independent of frequency, and the alloy appears like a perfect crystal with (real) masses or force constants modified from their values in the host. Phonons in the alloy for this case are not broadened but have infinite lifetimes. If ω_0 is the maximum host crystal frequency, then

$$\omega_0' = \omega_0 \sqrt{1 - c\epsilon}$$

is the maximum frequency predicted for the alloy.

Figure 1.11 shows CPA-G and exact results for a linear chain for an example of the special case of "equal" mass and force constant changes. The CPA-G density of states compares poorly with the exact results: it is a virtual crystal-like curve in which the only effect of alloying is a change of bandwidth to a value roughly 20% too low.

Fig. 1.11. CPA-G (smooth curve) and exact (histogram) results for equal mass and force constant changes.

Figure 1.12 compares CPA-G and exact results for force constant changes only. The CPA-G theory yields a spectrum appreciably narrower than the exact results and also has a peak where the exact calculations show a

Fig. 1.12. CPA-G and exact results for force constant changes only.

valley between the host crystal band edge and the first impurity peak.

We conclude that the single-site coherent locator approach proposed by Grünewald for alloys with both mass disorder and force constant changes that scale geometrically has a number of limitations. Like other single-site CPA theories, it can at best give only an approximate, overall picture of alloy properties and cannot reproduce structure in spectral functions arising from pair and larger cluster correlations. However, unlike the CPA for mass defects or its extension to include force constant changes in the additive limit, the CPA-G reduces to a virtual crystal form for certain sets of parameters (corresponding to "equal" mass and force constant changes) at all concentrations in one, two, or three dimensions. From the results found for disordered linear chains, it also appears that the CPA-G does a relatively poor job of predicting alloy bandwidths, underestimating noticeably in some instances, overestimating in others.

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LATTICE VIBRATIONS AT SURFACES

Mark Mostoller

Approximate vibrational densities of states for atoms in the surface region of solids can be calculated in several ways. One of these is the recursion method,¹ computer programs to implement this approach have been under development for several years. Previously reported versions of these programs were able to treat unrelaxed surfaces within a truncated Born-von Kármán force model,² simulating the semi-infinite solid by clusters of thousands of atoms. A rotationally invariant force model and surface-specific force constant changes have now been incorporated in the calculations.

A rotationally invariant force model is one in which no vibrational modes are excited in a rigid rotation of a crystal. In bulk solids with inversion symmetry, for example, in infinite pure materials that crystallize in the fcc, bcc, and NaCl structures, rotational invariance follows automatically from the inversion symmetry. In semi-infinite solids, this is not the case. A rotationally invariant, first- and second-neighbor ($1nn$ and $2nn$) bond-angle model for the interatomic forces like that described by Keating has been built into the surface vibration programs.³ It is equivalent to the conventional $1nn$ and $2nn$ Born-von Kármán model in the bulk but is automatically rotationally invariant at surfaces, where a truncated or cleaved Born-von Kármán model is not.

Atomic relaxation and electronic charge redistribution change the interatomic forces in the surface region in ways that are surface-specific and difficult (if not impossible at present) to determine *ab initio*. We therefore treat the force constants near the surface phenomenologically, allowing changes in what appear to be the most important forces for the particular surface under consideration. This is a computationally inefficient but apparently appropriate approach at this time.

Figure 1.13 shows some illustrative results for the Pt(755) or $6(111) \times (100)$ surface. This is an example of the high Miller index, regularly stepped surfaces of particular interest at present because they are crystallographically well defined and because increased chemical activity is known to occur at steps.⁴ The top curve in the figure gives the density of states for an atom at the top of a step for vibrations along the $[111]$, or step-normal direction, assuming a truncated Born-von Kármán model with no force constant changes in the surface region. The middle curve shows results obtained with the rotationally invariant force model, again with no force constant changes in the surface region other than those due to "missing" atoms in the cleaved

Fig. 1.13. Vibrational densities of states along the $[111]$ or step-normal direction for step-edge atoms at a Pt(755) surface. Top - Born-von Kármán model, no force constant changes; middle - rotationally invariant model, no force constant changes; bottom - rotationally invariant model, $1nn$ bonds between atoms at the top and bottom of the steps increased by 10,000 dynes/cm.

crystal. The bottom curve was calculated using rotationally invariant forces, with the $1nn$ bonds between atoms at the top and bottom of the steps increased by roughly 25%. A shift in the spectral density toward higher frequencies is seen as we move from the truncated Born-von Kármán model to the rotationally invariant bond-angle model, with no changes in the model parameters. A further buildup in spectral density at higher frequencies occurs when the bonds at the steps are strengthened.

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SYSTEMATIC APPROACH TO THE PROBLEM OF DISORDERED SYSTEMS¹

Martin Ukleb

In this work, we discuss how a model disordered problem can be simply reformulated and the averaged Green's functions calculated in an orderly and systematic fashion by methods of quantum field theory. For convenience and definiteness, we consider a theory described by a random binary (tight-binding) Hamiltonian with diagonal and off-diagonal disorder. The method reported here is similar in spirit to the field theoretic work of Mookerjee,² however, the description presented here is simpler and works for off-diagonal disorder as well.

The electronic properties of the model substitutional A-B alloy are described by a tight-binding Hamiltonian H with site-diagonal matrix elements that take on two possible values (e_A, e_B) and off-diagonal elements that have three allowed values ($W_{AA}, W_{AB} = W_{BA}, W_{BB}$), depending on the occupation of the particular sites considered. For convenience, we use here a notation appropriate for nearest-neighbor interactions only, but the formalism is not restricted to this case. The concentrations of the A and B constituents are denoted by c and $1 - c$ respectively. It can be shown that the Hamiltonian for such a system can be written in a matrix form as a certain direct product over all sites of the sample and that the configurationally averaged quantities in the alloy can be calculated as certain expectation values of the appropriate function of the Hamiltonian between its eigenvectors spanning the augmented Hilbert space.^{2,3} It is convenient to write the Hamiltonian in second quantized form (compare with ref. 2). To this end, we define $\Delta = e_A - e_B$, $\gamma = 2(W_{AB} - W_{BB})$, $\lambda = W_{AA} - 2W_{AB} + W_{BB}$, and

$$F = \begin{pmatrix} c & \sqrt{c(1-c)} \\ \sqrt{c(1-c)} & 1-c \end{pmatrix}. \quad (1)$$

We then introduce modified electron creation and annihilation operators that have an extra internal index attached to take care of the disorder. For binary alloys, this extra quantum number takes on only two values, designated by $\uparrow$ and $\downarrow$. Thus we have the anticommutation rules

$$(\psi_{i\alpha}, \psi_{j\beta}^\dagger) = \delta_{ij}\delta_{\alpha\beta}, \quad (\psi_{i\alpha}, \psi_{j\beta}) = 0. \quad (2)$$

The Hamiltonian can be split into parts describing an ordered system (H_0), the diagonal disorder interaction

H_D , the off-diagonal disorder interaction H_{OF} , and the "interacting" off-diagonal interaction H_{IOF} .

$$H = H_0 + H_D + H_{OF} + H_{IOF}, \quad (3)$$

where

$$H_0 = \sum_i e_B \psi_{i\alpha}^\dagger \psi_{i\alpha} + \sum_{ij, i \neq j} W_{BB} \psi_{i\alpha}^\dagger \psi_{j\alpha}, \quad (4a)$$

$$H_D = \Delta \sum_i \psi_{i\alpha}^\dagger F_{\alpha\beta} \psi_{i\beta}, \quad (4b)$$

$$H_{OF} = \gamma \sum_{ij, i \neq j} \psi_{i\alpha}^\dagger F_{\alpha\beta} \psi_{j\beta}, \quad (4c)$$

$$H_{IOF} = \lambda \sum_{ij, i \neq j} \psi_{i\alpha}^\dagger F_{\alpha\beta} \psi_{i\beta} \psi_{j\gamma}^\dagger F_{\gamma\delta} \psi_{j\delta}, \quad (4d)$$

where the summation convention is in effect, sums are taken over two or more repeated indices, Latin indices denote space points, and Greek indices correspond to the extra degrees of freedom arising from disorder. The configurationally averaged quantities are now calculated as expectation values between the full ground state $|\Omega\rangle = |\Omega\rangle \otimes |F_0\rangle$, where $|\Omega\rangle$ is the ground state of the nonrandom electronic Hamiltonian H_0 and $|F_0\rangle$ is the ground state of the internal (disorder) space, which in this case is the state where at each site i the index α takes on the value $\uparrow$ (i.e., all "spins" are ordered and pointing "up").

One can now proceed with an orderly perturbation expansion, taking H_0 as the unperturbed Hamiltonian and treating H_D, H_{OF} , and H_{IOF} as perturbations. For a theory with diagonal disorder only, $H_{OF} = H_{IOF} = 0$, and the sole perturbation is H_D . The averaged Green's function in this case is given by the sum of all connected time-ordered products

$$iG_{\uparrow\uparrow}(x, x') = \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \times \int dt_1 \dots dt_n \langle \Omega | T[H_D \psi_{\uparrow}(x) \psi_{\uparrow}^\dagger(x')] | \Omega \rangle_c. \quad (5)$$

It can be shown that by summing a certain infinite class of graphs one recovers the CPA.

Having summed an infinite class (CPA) of diagrams

formed by repeated applications of H_D , one may attempt to sum certain classes of diagrams with off-diagonal disorder. The diagrams due to repeated application of H_{OF} may be systematized as follows: between any two successive applications of H_{OF} , we can have arbitrarily many applications of H_D . These will be included by replacing the bare propagator $P_{\alpha\beta}$ between any two H_{OF} 's with G_{CPA} determined previously. Further, the same class of graphs can be summed as in the case of the CPA by performing the calculation in momentum space. Instead of the fixed coupling constant Δ that appears in the case of diagonal disorder, one now obtains a momentum-dependent coupling constant $\gamma(k)$. Finally, a certain infinite subset of diagrams due to H_{OF} can also be simply included by assuming the random phase approximation, which reduces the four-fermion vertex to two fermion vertices, resulting in a simple renormalization of H_D and H_{OF} .

The class of graphs that remains to be considered is the one formed by bubble diagrams. The treatment of these will be reported in another publication.

with displacements having the proper correlations. This continuation process is accomplished by using the $N - M$ retained displacements, M new random numbers, and the calculated matrices.

The continuation procedure has been applied to two situations of interest: (1) a linear row of N atoms and (2) a bcc cubic cell. In the row case, the selection of N is arbitrary, and M is 1. In the case of the bcc cell, N is 10 (the center of the previous cell as well as of the current cell is included) and $M = 5$. The continuation procedure has been tested and been found to give statistically correct correlations for both of these cases. An expression that provides an accurate asymptotic form for long-range correlations for the row case has been developed and may prove useful in increasing the value of N beyond what may otherwise be available. Extensive detail of the calculations has been provided in the bcc cell case, and consideration is given to the alternate possibilities of always moving in the same direction to an adjacent cell or of moving in one direction at the first change and then in another at the second change.

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PARTICLE-SOLID INTERACTIONS

MODELLING DISPLACEMENT CORRELATIONS IN COMPUTER SIMULATIONS OF PARTICLE-SOLID COLLISIONS¹

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The thermal vibrations of lattice atoms are known to have a significant influence on the propagation of energetic charged particles through crystals, particularly on directional phenomena such as channeling and blocking. Theoretical models of these effects have almost always assumed uncorrelated motions; however, substantial equal-time displacement correlations are in fact present.³ We have developed a method, utilizing matrices calculated from the correlations of the lattice atoms in the bulk, for including correlations in computer simulation models of ion-lattice interactions.

In general, one wishes to deal with the correlations among some group of atoms, say of number N . Initially, these may be selected by using N random numbers and one of the calculated matrices. In going from one collision to the next in the lattice, one discards M of the group of atoms, retains $N - M$, and adds M new atoms

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CHANNELING IN V₃Si: ATOMIC DISPLACEMENTS AND ELECTRON-PHONON/DEFECT INTERACTIONS¹

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Yields of backscattered ions for channeling, or alignment of the ion beam with a major crystallographic direction, have been measured for 1.9-MeV ⁴He ions in V₃Si crystals at several temperatures and after various doses of ions. The measured values for the scattering by V atoms were compared to values calculated using the previously developed expression³

$$\chi_V = C_V \pi \rho_V^2 + C_{V_3Si} \pi \rho_{V_3Si}^2, \quad (1)$$

where χ_V is the V scattering relative to what it would be for a random (unaligned) direction, ρ_V and ρ_{V_3Si} are the numbers of V and Si rows per unit area, ρ_V and ρ_{V_3Si} are the root-mean-square displacements $(x^2 + y^2)^{1/2}$ of

the V and Si atoms parallel to the surface due to thermal vibrations or to defects, and C and C' are constants. Values of ρ_V and ρ_{V1} calculated using a phonon density of states measured at room temperature⁴ together with previous channeling results² were used to estimate a value of 1.7 for C and of 1.0 for C' . Equation (1) was then used to infer values of ρ_V^2 as a function of the temperature and of the dose of ^4He ions. The mean square displacement of the V atoms increases with ^4He dose at a rate of approximately $10^{-3} \text{ \AA}^2$ per 10^{17} ions cm^{-2} . Therefore, the effect of radiation is not just the production of antisite disorder without accompanying displacements of antisite and neighboring atoms. There is also evidence of phonon stiffening for doses of 0.75×10^{17} to 1.5×10^{17} ions cm^{-2} , but this stiffening disappears again at a dose of 2.5×10^{17} ions cm^{-2} . The increase in ρ_V^2 due to irradiation explains the large increase in electrical resistivity in the defect state. The fact that increases in ρ_V^2 due to temperature or to defects produce comparable increases in electrical resistivity indicates that the electron-phonon and electron-defect couplings are of comparable magnitude.

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COMPUTER SIMULATION OF LOW-ENERGY SPUTTERING IN THE BINARY COLLISION APPROXIMATION¹

Mark T. Robinson Marc Hou²

The sputtering of amorphous Cu targets by low-energy atoms has been investigated in the binary collision approximation using the computer program MARLOWE. Particular attention was given to the influence of the surface binding model on the results. Calculations were made of the dependence of the sputtering yield on the incident particle direction, energy, and mass. Angular, energy, and yield distributions of the ejected atoms were evaluated. Comparisons with experimental results on polycrystalline targets show that the planar surface binding model (in which the surface binding is overcome only by the normal component of the escaping particle velocity) is to be preferred over the isotropic surface binding model (where the total velocity overcomes the binding), especially

with regard to the angular and energy distributions. Calculated yields are in reasonable agreement with experiment at energies below about 1 keV but deviate at higher energies, apparently because of crystal correlation effects that are neglected in the amorphous model.

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COMPUTER SIMULATION OF MONOCRYSTAL SPUTTERING

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The computer program MARLOWE¹ has been used to study the sputtering of Au (001) surfaces by normally incident 700-eV Xe⁺ ions. The model parameters used in the calculation are collected in Table 1.1. The value

Table 1.1. Model parameters used for MARLOWE investigations of the sputtering of Au (001) surfaces by 700-eV Xe

Parameter	Value
Lattice constant, a	4.0783 Å
Debye temperature, θ_D	180 K
Minimum energy for motion, E_m	4.5 eV
Particle cutoff energy, E_c	4.0 eV
Lattice binding energy, E_b	0.5 eV
Surface binding energy, U_s	4.0 eV
Maximum impact parameter, p_c/a	0.62
Molière potential parameters, a_{11}	
Xe-Au	0.0731 Å
Au-Au	0.0750 Å

of E_b was chosen to give reasonable energy losses along (011) collision sequences. The total binding energy ($E_b + U_s$) is about 18% larger than the cohesive energy of Au. Two surface binding models were compared: in the planar model, U_s must be overcome by the normal component of the escaping particle's velocity; in the isotropic model, the total speed can overcome this barrier. The former model is probably more realistic.

Figure 1.14 shows the dependence on target thickness of the sputtering yields calculated for a static lattice

Fig. 14. Sputtering of Au {001} surfaces by normally incident 700-eV Xe, as calculated with MARLOWE. (a) Distribution of incident particle penetrations; (b) the yields of sputtered atoms as functions of target thickness.

using the planar binding model. The reflection (ordinary) yield reaches a limiting value for targets thicker than about $2a$ (5 atomic layers, 3.16 Å). The transmission yield, on the other hand, reaches a maximum at about the target thickness where the reflection yield becomes constant and then decreases. The upper portion of the figure shows the distribution of Xe penetration depths. Some 22% of the Xe atoms are reflected; these reflected atoms rarely penetrate beyond the third or fourth layer of atoms. Thus, the reflection sputtering

yield and the reflection of the primary particles are determined in the same near-surface region of the crystal.

Calculated sputtering yields for several different conditions are collected in Table 1.2, which also lists the only available experimental data.² A considerable difference (30 to 60%) will be noted between the calculations based on the different surface binding models. Because the planar model is supported by recent dynamical calculations,³ it is gratifying that it gives better agreement with experiment. Although some adjustment of the model might improve this agreement, the accuracy is sufficient until more calculations and more experiments are available. The negligible effect of the inelastic loss model on the calculated results was expected: only some 2% of the primary energy is lost in electron excitation. More interesting is the rather small effect of thermal displacements. The insensitivity of the results to temperature is a consequence of the small importance of linear collision sequences in sputtering under the conditions of these calculations.

The ejected angular distributions calculated in two cases are shown in Fig. 1.15. If the sputtered atoms followed a cosine distribution, the function plotted would everywhere be unity. The actual calculated dependence is shown in Fig. 1.15, plotted as a function of μ^2 , where $\mu = \cos \theta$ and θ is the polar angle of ejection. Aside from the required fourfold symmetry in ϕ (the azimuthal ejection angle), both the static and the 120 K distributions show three marked crystallographic features imposed on a rather uniform background:

1. A ridge of high ejection intensity corresponding to the intersections of the {111} planes with the surface. This ridge includes ejection in such directions as $\langle 110 \rangle$ and $\langle 112 \rangle$ but seems to be mainly a planar feature.
2. A ridge of high intensity corresponding to particles ejected in the {100} planes perpendicular to the target surface.
3. A spot of high ejection intensity corresponding to the $\langle 110 \rangle$ directions.

Thus, although linear collision sequences are rare in these calculations, there are still very marked Wehner spots near $\langle 110 \rangle$, accompanied by radial and circum-polar streaks, much as observed experimentally.

The $\langle 110 \rangle$ Wehner spots in Fig. 1.15 are located about 50 deg from the normal, in reasonable agreement with observations on {001} surfaces of Ag,⁴ Cu,^{4,5} and Au⁵ under various bombardments. Both the outward shift of the spot and the considerable tail on the large-angle side are produced by the refractive effects of the planar

Table 1.2. Sputtering yields for 700-eV Xe normally incident on Au targets

Target	Islands: loss	Temperature	Calculated sputtering yield (Au/Xe)	
			Islands loss	Thermal blending
Amorphous	Yes	Static	3.578 ± 0.054	2.568 ± 0.043
Polycrystalline	Yes	Static	5.161 ± 0.059	3.221 ± 0.044
(001)	Yes	Static	4.809 ± 0.055	3.606 ± 0.013
(001)	Yes	120 K	4.845 ± 0.027	3.679 ± 6.023
(001)	No	120 K	5.093 ± 0.076	3.661 ± 0.065

Experimental yields for Xe⁺ ions on polycrystalline Au (ref. 2)

Ion energy, eV 400 500 600 700

Observed yield, Au/Xe 2.5, 3.0, 3.4, 3.7^a^aExtrapolated.

Fig. 1.15. Angular distributions of Au atoms sputtered from (001) surfaces by normally incident 700-eV Xe atoms. Parts (a) through (c) show distributions in two phases of ejection; (c) shows the overall pattern.

binding energy. It appears likely that most of the {100} planar ejection is associated with surface-refracted {110} ejections, although this is not quite certain. The {111} planar ejection shows an outward shift that decreases as the azimuth moves away from {100}. It may be concluded from this behavior that atoms ejected well away from {110} directions have higher velocities than those close to them. This result is also in agreement with observations.⁴ There is no evidence in the calculations for a {001} Wehner spot. This is consistent with experiments that show such spots mainly for higher bombardment energies and lighter target elements.^{4,5}

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COMPUTER SIMULATION OF THE REFLECTION OF H AND THE SPUTTERING OF H FROM METAL HYDRIDES

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Reflection of 0.1- to 2-keV H atoms from Ti, Fe, and their "metal hydrides," together with the H sputtered from the latter, has been calculated using the binary collision cascade program MARLOWE. The fraction of particles and energy reflected was found to decrease with increasing H content of the metal hydride, and this decrease is independent of the incident ion energy. It was found that the heavy metal atoms of the metal hydride are responsible for the reflection and that most of the sputtering is produced by the reflected ion as it exits through the surface layer. It was also found that T ions sputter H from "FeH" much more effectively than H ions sputter T from "FeT."

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LASER ANNEALING

CALCULATIONS OF HEAT FLOW AND MELT-FRONT MOTION DURING PULSED LASER ANNEALING OF Si

R. F. Wood G. E. Giles¹ J. C. Wang

Earlier calculations² of the temperature distribution and melt-front motion in Si during pulsed laser annealing have now been greatly extended. We give here a brief description of the computer program HEATING5,³ with which the calculations were made, and illustrate with a few specific results the type of information that can be obtained with it. Parts of this information can be used to calculate the dopant-profile motion during laser annealing in a manner described in the following contribution to this report.⁴

HEATING5 solves steady state and transient heat conduction problems in one, two, and three dimensions for Cartesian, cylindrical, or spherical coordinates. The physical problem is approximated by a system of nodes, each associated with a small volume. To define the nodes, a set of orthogonal planes is superimposed on the problem. The planes may be unequally spaced, but they must extend to the outer boundaries of the material system. Heat may flow from any given node to each adjacent node along paths parallel to each coordinate axis. Thus, for a three-dimensional problem, heat may flow from an internal node to each of its six neighboring nodes. The system of equations describing the temperature distribution is derived by performing a heat balance about each node. For example, the finite-difference, heat-balance equation for node i lying in the bulk of the sample is

$$C_i \frac{T_i^{n+1} - T_i^n}{\Delta t} = P_i^n + \sum_{m=1}^6 K_m^n (T_m^n - T_i^n) \quad (1)$$

Here, T_m^n is the temperature of node m adjacent to node i at time t_n ; K_m^n is the conductance between nodes i and m ; C_i is the heat capacitance of the material in the small volume around node i ; and P_i^n is the heat generation rate in this volume at time t_n . Because planes go through the nodes and divide the surrounding volume into octants and because the material is homogeneous between any two successive planes along any axis, a node may be composed of as many as eight

different materials, and the heat flow path between adjacent nodes may traverse as many as four different materials positioned in parallel. For a three-dimensional problem, one C , one P , and six K s will be associated with each internal node at a particular time, t_n . By choosing the increments between lattice lines small enough, the solution to the system of equations yields an accurate approximation to the appropriate differential equation.

The HEATING5 program is a very powerful and versatile tool for laser annealing calculations. It allows most physical parameters to vary with temperature and/or position in the material and allows both melting and vaporization of the material to be included. From a series of calculations of temperature profiles as a function of time, it is possible to extract the position of the melt front (liquid-solid interface) as it first penetrates into the crystal and then recedes back to the surface. Figure 1.16 shows examples of this type of result for 16-nsec (FWHM, triangular-shaped) laser pulses of various energies. On the figure, E_a is the absorbed energy density, which is just the product of the incident laser

Fig. 1.16. Melt-front location as a function of time for various absorbed energy densities. Each laser pulse was assumed to be triangular in shape with a FWHM of 16 nsec. The transition zone is defined in the text.

energy density and the factor $1 - R$, where R is the reflectivity of the sample. The solid curves give the position of the melt front as a function of time. The region between the dashed curves and the solid curves is a transition (or "slush") zone in which the material is in the process of melting but has not become completely

molten. For the 0.25-J/cm^2 pulse, melting does not occur, but a region within about $0.025\text{ }\mu\text{m}$ of the surface does reach the transition state and remains there for about 10 nsec. Figure 1.17 shows the melt-front motion for a much more energetic laser pulse than those

Fig. 1.17. Melt-front location as a function of time for an absorbed energy density of 1.05 J/cm^2 . The full curve was calculated with a model that incorporated the latent heat of fusion only. The dashed curve incorporated both the heat of fusion and the heat of vaporization.

used to generate the curves in Fig. 1.16. In this case, the material actually reaches the temperature of vaporization, but, because of the high latent heat needed, vaporization does not actually occur. However, comparison of the two curves in Fig. 1.17 shows that inclusion of the latent heat of vaporization does modify the melt-front motion.

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CALCULATION OF DOPANT REDISTRIBUTIONS INDUCED BY PULSED LASER ANNEALING

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During laser annealing of ion-implanted Si with Q-switched lasers, the near-surface region of the sample melts and extremely rapid diffusion of the implanted dopant occurs in the liquid. In those cases where the melt front penetrates well beyond the implanted dopant profile, rather good fits to the experimental data can be obtained by assuming that the region of the profile is instantaneously melted, stays molten for a certain period of time, and then is instantaneously resolidified.² This "instantaneous-melt" approximation fails when the maximum melt-front penetration occurs within or just beyond the implanted profile, and improved approximations in which the actual motion of the melt front is included must be constructed. We have employed three types of models to deal with this moving boundary problem.

The first model is derived from the Green's function formulation of the one-dimensional, mass-diffusion problem. In the "instantaneous-melt" approximation, the profile after laser annealing is given by

$$\rho(x, t) = \int_0^{\infty} [G(xt | x_0 t_0) \rho_i(x_0, t_0)] dx_0 \quad (1)$$

$t_0 = 0$

in which ρ_i and ρ are the implanted and final profiles, respectively, and $G(xt | x_0 t_0)$ is the Green's function for diffusion in a semi-infinite slab. For assumed values of the diffusion parameters, a fit of ρ to the experimental profile determines the time t during which the implanted region must have remained molten. This time should be consistent with that obtained from calculations of the melt-front motion.² Obviously, when the melt front does not penetrate beyond the implanted profile, a single time during which the entire profile is allowed to diffuse cannot be assigned in even an approximately correct manner. A simple approximation that, though difficult to justify rigorously, gives surprisingly good results and yet remains within the spirit of Eq. (1) is obtained from the following procedure. From a plot of the melt-front location as a function of time, the time during which any point in the sample remains molten can be determined.² Substituting values of x and t from such a plot into Eq. (1) with a suitably modified form of $G(xt | x_0 t_0)$ and carrying out the integration over x_0 gives our first approximation to the diffused profile. It is interesting to note that melt-front

curves (see Fig. 1 of ref. 2) are often nearly triangular in shape. If the curves are assumed to be triangular, velocities of melt front penetration into and out of the sample can be assigned and the maximum penetration of the melt front varied to give a best fit (in a least squares sense) to the experimental curves. Figure 1.18

Fig. 1.18. Comparison of experimental and theoretical dopant profiles of As in Si.

shows the results of such a procedure applied to experimental data³ for As implanted in Si and laser annealed with laser pulses of 0.63, 1.07, and 1.41 J/cm². The fit is clearly very good.

In spite of the apparent success of the above-described procedure, the validity of the approximations on which it is based are difficult to establish for all cases

likely to be encountered in laser annealing. We have therefore developed another model using a finite-difference formulation of the diffusion equation,

$$\frac{\partial \rho(x, t)}{\partial t} = \frac{\partial}{\partial x} \left[D \frac{\partial \rho(x, t)}{\partial x} \right], \quad (2)$$

with appropriate boundary conditions. The diffusivity D can be a function of x and t , and this flexibility is used to change from values characteristic of the liquid ($D_l \approx 10^{-4}$ cm²/sec) to those characteristic of the solid ($D_s \approx 10^{-12}$ cm²/sec) at the moving liquid-solid interface. The sample is imagined to be oriented perpendicular to the x axis with its front face at $x = 0$ and its x dimension divided into cells with Δx of the order of 100 Å or smaller. As the melt front penetrates the sample and moves through a cell, the value of D in the cell changes from D_s to D_l . The material in all cells to the left of the melt front is molten, and diffusion occurs very rapidly within that region. When the melt front reaches its maximum penetration and begins to recede back to the surface, solidification occurs and the value of D in each cell is changed accordingly. A variety of numerical techniques has been used to solve this rather complicated problem. Preliminary results show that the experimental As profiles can be fit rather well. Although the experimental data is not accurate enough to indicate clearly the superiority of this approach over the Green's function approach outlined above, it would seem to be preferred on the grounds of general applicability.

The third model is very similar to the second but employs analytical techniques to solve the diffusion equation in a slab of molten material whose right boundary is defined by the moving melt front. A comparison of the results of the three models is now underway.

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ROLE OF THE REFLECTIVITY AND ABSORPTION COEFFICIENT IN LASER ANNEALING

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In laser annealing and laser-induced diffusion, the reflectivity and absorption coefficient of the material

and the power density in the laser pulse largely determine the heat generation rate at each point in the sample. We have done computer calculations to study the role of the reflectivity and absorption coefficient in determining temperature profiles and melt-front motion in Si samples.

In undoped, perfect, single-crystal Si, the absorption coefficient k at a wavelength of $\lambda = 0.694$ μ m (ruby laser) and at low light intensities is approximately 4×10^3 cm⁻¹. Under the same conditions, in amorphous Si, k increases to a value of 5×10^4 cm⁻¹ (ref. 2). In ion-implanted Si, the lattice damage created by implantation depends on the dopant, the implantation energy, and the dose. In many cases, the Si is driven completely amorphous by the implantation process. Although significant lattice damage extends well beyond the peak of the implanted profile, it is likely that for most implantation conditions and wavelengths of laser radiation the energy will be absorbed in both the damaged and the undamaged regions of the sample. From these considerations alone, it can be seen that the absorption coefficient may frequently be a strongly varying function of the distance from the front surface of the sample. However, the absorption process during laser annealing of ion-implanted material is much more complex than this. It is well known that the absorption coefficient in heavily doped semiconductors depends on the doping level and that the contributions from free-carrier absorption and band-to-band transitions are difficult to disentangle,³ even at low light intensities. When very intense laser radiation is used, yet another effect can enter because the probability of pseudo-two-photon processes may become significant.⁴ Also, after ion implantation the implanted dopants are not in substitutional sites and are not electrically active; the absorption in such cases is likely to be quite different than it is after the dopants have been electrically activated.

Although experimental data is sparse for the dependence of the absorption coefficient on position in the sample and on light intensity in circumstances approximating those encountered in laser annealing, computer programs such as we have been using can easily handle spatial- and intensity-dependent absorption. At low light levels, for example, the change in light intensity dI due to absorption in a differential element of the sample is

$$dI = -k(x)I dx, \quad (1)$$

which integrates to

$$I(x) = I_0 \exp \left(- \int_0^x k(x_0) dx_0 \right). \quad (2)$$

We have carried out temperature and melt-front motion calculations with a variety of assumptions about the spatial dependence of k . It is clear from the results that the spatial dependence of k on the lattice damage and on the dopant profile must be included in a number of cases to obtain satisfactory agreement between theory and experiment. Unfortunately, this dependence is not easily determined experimentally, and assumptions about it must often be made.

The reflectivity is somewhat easier to deal with than is the absorption coefficient because the main change in it occurs when the surface melts. For pulses of low energy, melting may not occur until the pulse is nearly over, but for high-energy pulses it occurs much earlier in the pulse-duration time.⁵ This temperature dependence of the reflectivity is also easily handled within our computer codes.

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MULTIPULSE LASER ANNEALING OF B-IMPLANTED Si

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The redistribution of the dopant profile in B-implanted Si under laser annealing with successive laser pulses has been calculated by methods explained elsewhere.² Figure 1.19 shows a comparison of the theoretical and experimental (from secondary ion mass spectroscopy) results for one, two, and three pulses and the theoretical results for six pulses. The disagreement for the two-pulse profiles is probably due to inhomogeneities in the laser beam and/or lack of satisfactory reproducibility of the energy and duration of successive pulses. It is interesting to note, however, in connection with discussions of the role of the absorption coefficient in laser annealing,³ that the lattice damage due to ion implantation in this sample was entirely annealed and the dopant electrically activated after the first pulse. Thus, the absorption coefficient may very well have changed from one pulse to another, particularly from the first to the second pulse. A more detailed

Fig. 1.19. Dopant concentration after annealing with successive laser pulses. The points give the experimental data, and the lines give the theoretical results.

experimental study of profile redistribution after successive, highly reproducible pulses would be of great help in further understanding the details of pulsed laser annealing.

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MODEL OF IMPURITY SEGREGATION DURING PULSED LASER ANNEALING OF ION-IMPLANTED Si

J. C. Wang R. F. Wood

The concentration profiles of Fe and Cu implanted into Si show that significant segregation to the surface

occurs as a result of pulsed ruby laser annealing.¹ Although this phenomenon is consistent with laser-induced, near-surface melting and subsequent recrystallization,² together with the observed low segregation coefficients of these impurities in Si, the detailed mechanism seems somewhat more complicated than that normally used to describe solute redistribution during solidification.³ A model with the following assumptions and approximations was constructed to fit the experimental data.

1. As the melt front sweeps back to the surface, it encounters at any point x an impurity distribution $n(x)$ that has two components. The first component $n_0(x)$ is the as-implanted profile as it evolves during the time the near-surface region is molten. The second component $n_s(x)$ consists of the dopant piled up at x due to the segregation process itself.
2. The impurities piled up in the liquid in the immediate vicinity of the advancing melt front are assumed to be redistributed between the surface and the instantaneous melt-front position at $x = x_0$ by diffusion in the approximate form $n(x_0)\exp[-(x_0 - x)/\delta]$.
3. An effective, spatially dependent segregation coefficient $k_e(x)$ is assumed, and therefore the impurity concentration left behind in the solid is $n'(x) = k_e(x) \times n(x)$. The form of $k_e(x)$ is chosen to be

$$k_e(x) = k \left[1 - \frac{1}{2} \operatorname{erfc} \left(\frac{x-c}{b} \right) \right] + (1-k) \exp(-x^2/a^2),$$

and the parameters a , b , and c are determined such that when the impurity concentration at the melt front is small, all impurities are rejected from the solid; when $n(x)$ reaches a certain value (near $x = c$), $k_e(x)$ starts to build up; when the melt front reaches the surface, all impurities stay in the sample.

Under the above assumptions, the function $n(x)$ satisfies the equation

$$\frac{dn(x)}{dx} = \frac{n_0(x)}{[1 - \exp(-x/\delta)]} - \frac{k_e(x)n(x)}{[1 - \exp(-x/\delta)]},$$

which can be integrated numerically. The results for a sample implanted with Fe to a dose of $\sim 4.7 \times 10^{15} \text{ cm}^{-2}$ and laser annealed with a pulse of $\sim 1.5 \text{ J/cm}^2$ are shown in Fig. 1.20. The characteristic width of the impurity layer δ just in front of the liquid-solid interface is about 47 Å. When the impurity concentration in

Fig. 1.20. Comparison of theoretical and experimental Fe profiles in Si after laser annealing. The fitted effective segregation coefficient k_e is also shown.

this layer becomes high enough ($\sim 4 \times 10^{21} \text{ cm}^{-3}$), a segregation coefficient k_e of about 0.1 is reached, and significant amounts of Fe begin to be left behind in the solid. Finally, when the melt front approaches the surface, k_e rises to the limiting value of 1 in order to satisfy the requirement that no impurity atoms leave the sample. The characteristic width of the peak in $k_e(x)$ at the surface is about 33 Å.

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THEORETICAL ANALYSIS OF THERMAL AND MASS TRANSPORT IN ION-IMPLANTED, LASER-ANNEALED Si¹

J. C. Wang R. F. Wood P. P. Pronko²

Profiles of dopants such as B, As, and P in ion-implanted Si change drastically under pulsed ruby laser annealing when the threshold energy is exceeded.³ These changes can be explained in terms of solutions of standard equations for heat and mass diffusion, appropriately modified to include the effects of melting.

The thermal diffusion coefficient used in the diffusion equation is strongly dependent on the temperature,

and other parameters such as the absorption coefficient may depend on both temperature and depth into the surface; furthermore, the crystal may melt during laser annealing. Two approaches were taken to deal with these nonlinearities. In one approach, we simply made the necessary approximations (e.g., constant diffusion coefficient, no melting) to eliminate them, and in the other, we used a general purpose heat transport computer program, HEATING5,⁴ based on finite difference equations, which allows the nonlinearities and melting to be taken into account.

The HEATING5 program allows us to map the motion of the melt front as it progresses into the substrate region and as it is reflected back to the front surface; this is shown in Fig. 1.21. It can be seen that the temperature rises so rapidly in the near-surface region that this part of the crystal is melted during the first 10 to 20 nsec of the laser pulse.

Fig. 1.21. Calculated position of the melt front as a function of time.

A simplified model, in which instantaneous melting and freezing of the implanted region and diffusion of impurities in the liquid state are assumed, yields profile changes for B, As, and P in good agreement with experiment. An example of the fits that can be obtained

between calculated and experimental profiles is given in Fig. 1.22. Calculations in which the melt-front motion is explicitly taken into account show that this motion can have some effects on the profile. For example, we have evidence that the small discrepancies around 0.3 μm in Fig. 1.22 are due to the neglect of melt-front motion. The profiles in ref. 3 for As and P in Si have been fitted with agreement comparable to that shown in Fig. 1.22, although the effects we ascribe to melt-front motion are somewhat larger in the case of P.

Fig. 1.22. Comparison of experimental and theoretical dopant profiles.

The process of pulsed laser annealing under conditions used in most of the experiments described in ref. 3 may be summarized as follows. During the laser pulse, the temperature rises very rapidly in the near-surface region, and melting occurs. The melt front propagates rapidly into the crystal and reaches its maximum penetration of several tenths of a micron in a time only slightly greater than the pulse duration. The melt front then sweeps back to the surface, recrystallizing the material epitaxially as it proceeds. While the crystal is

molten, the dopant atoms have a very high diffusion coefficient and the implanted profile can change markedly. We conclude not only that the crystal melts during laser irradiation but also that normal diffusion processes in the molten state can account for the spreading of the implanted profile.

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TEMPERATURE CALCULATIONS FOR SCANNING cw Ar-ION LASER ANNEALING OF ION-IMPLANTED Si

J. C. Wang

Although it is reasonably clear that near-surface melting and liquid-phase recrystallization occurs during static, pulsed laser annealing (50 nsec, energy density $\sim 1.5 \text{ J/cm}^2$)¹ of Si, the annealing of similar samples with a scanning cw Ar-ion laser emitting radiation of energy density $\sim 1.5 \times 10^3 \text{ J/cm}^2$ did not show any evidence of impurity profile changes.² To resolve this apparent discrepancy, the temperature distribution in the sample during laser scanning has been calculated. The laser beam of power P incident along the z direction is assumed to have a Gaussian spatial distribution with standard deviation R . It is also assumed that the beam is scanned along the x direction with velocity v , beginning at $x = -\infty$. If the time t at which the center of the beam reached the point $x = 0$ is taken to be zero, the temperature distribution at that moment is shown to be

$$T(x, y, z, t=0) = T_0 + \frac{P(1-r)k}{4\pi\rho C} \times \int_{-\infty}^{\infty} \left(\frac{dt'}{R^2 + 2\kappa t'} \exp \left\{ -[(x - vt')^2 + y^2] / 2(R^2 + 2\kappa t') \right\} \right. \\ \left. \times \exp(k^2 \kappa t') \right) \left[\exp(-kz) \operatorname{erfc} \left(k\sqrt{\kappa t'} - \frac{z}{2\sqrt{\kappa t'}} \right) \right. \\ \left. + \exp(kz) \operatorname{erfc} \left(k\sqrt{\kappa t'} + \frac{z}{2\sqrt{\kappa t'}} \right) \right], \quad (1)$$

where T_0 is the starting temperature, k the absorption coefficient, κ the thermal diffusion coefficient, ρ the

density, r the reflectivity, and C the specific heat of the sample. The function $\operatorname{erfc}(x)$ is of the form

$$\operatorname{erfc}(x) = 1 - \frac{2}{\sqrt{\pi}} \int_0^x \exp(-u^2) du. \quad (2)$$

For metals, one can assume that the photon energy is absorbed only at the surface, and let $k \rightarrow \infty$ without introducing any significant error. Equation (1) will then reduce to the form derived by Cline and Anthony.³ However, for semiconductors, the k dependence of T may be important.

Figure 1.23 shows the calculated results corresponding to the annealing conditions used in ref. 2, namely, $P = 7 \text{ W}$; $v = 2.76 \text{ cm/sec}$; $R \approx 11 \times 10^{-4} \text{ cm}$; $r \approx 0.3$; $k \approx 2 \times 10^5 \text{ cm}^{-1}$, $\kappa \approx 0.23 \text{ cm}^2/\text{sec}$; and $C \approx 0.95 \text{ J/(g K)}$. It can be seen from the figure that the temperature of the crystal surface under the laser beam

Fig. 1.23. Temperature distribution of the sample under laser scanning. The function $T(x, y, z, t)$ gives the temperature at the position x, y, z at time t , where z is normal to the sample surface [$T(0, 0, z, 0)$ curve] and x is the direction of laser scanning [$T(x, 0, 0, 0)$ curve]. The $T(0, 0, 0, t)$ curve shows the temperature at $x = y = z = 0$ as a function of time.

may reach the melting point (1683 K), but the laser power is not sufficient to melt the sample (the heat of fusion is equivalent to ≈ 2000 K). The time that any point on the surface remains above 1400 K is of the order of 10^{-3} sec. This time, though apparently long enough to anneal the damage from the ion implantation and to electrically activate the implanted ions, is too short for significant concentration profile changes to occur.

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ELECTRONIC AND MAGNETIC PROPERTIES

SEMILINEAR APPROACH TO METAL HYDRIDES

Mark Rasolt

To describe the interaction of a single H ion with its metal host, account must be taken of the strong proton potential. The usual treatment of such an interaction via linear response theory (and its corresponding pair potentials) is no longer adequate. To treat these systems, we have developed a method that is relatively simple and yet contains the essential physics of the problem.

We first replace the "proton plus lattice" potential by a spherical average. This simplified problem, which neglects the nonspherical contributions of the host, is solved exactly for its ground-state density and energy. The nonspherical contributions are then evaluated as linear order corrections to this spherical model. These corrections involve the construction of linear response functions that depend only on the spherical density and do not change for different nonspherical potentials; thus, once calculated, they can be stored and used for different host configurations. We note that in this method we treat the strong proton potential to all orders, and only the nonspherical part of the host potential is treated to lower order. In Al, such an assumption is likely to be valid, and we are presently applying our method to the construction of a potential surface for a proton in Al.

OPTICAL SPECTRA FOR LARGE AGGREGATES OF CHROMOPHORES¹

R. P. Hemenger² Theodore Kaplan L. J. Gray³

The problem of calculating optical spectra for large aggregates of chromophores interacting through electronic transition dipoles has been studied, with emphasis placed on relating the band shapes of such aggregate spectra to the band shapes for the constituent chromophores for all interchromophore coupling strengths. We argue that, because of the close connection of the degenerate ground state (DGS) model⁴ to an exact formulation, it predicts spectral band shapes much more accurately than other commonly used methods of calculating aggregate spectra. This is particularly true for intermediate or strong coupling, that is, for interchromophore coupling strengths comparable to or greater than the bandwidths for the individual chromophores. A number of calculations of optical absorption and circular dichroism spectra for simple helical polymers have been carried out using the DGS model. These calculations exploit the formal identity of the DGS model to the "cellular disordered" problem of solid state physics. We use the coherent potential approximation^{5,6} and the augmented space formalism⁷ to solve this problem. The theoretical spectra found in this way differ considerably from those found using other methods, especially in the intermediate and strong coupling regimes.

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ELECTRONIC STRUCTURE OF THE F CENTER IN SrO¹

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Absorption and emission states of the F center in SrO have been calculated using a theoretical model emphasizing the importance of (a) electronic structure on the ions neighboring the defect, (b) electronic and ionic polarization of the lattice, and (c) lattice distortion and

its effects on the energy levels and wave functions of the defect. The electron-lattice interaction for A_{1g} , E_g , and T_{2g} displacements of the nearest-neighbor ions has been calculated and used to interpret the absorption and luminescence bands of the F center. The calculated energy-level scheme as a function of lattice relaxation predicts luminescence bands corresponding to the ${}^1T_{1u} \rightarrow {}^1A_{1g}$ transition at 1.5 eV and to the ${}^3T_{1u} \rightarrow {}^1A_{1g}$ transition at 0.56 eV. It also suggests the possibility of observing the excited-state absorption for the ${}^3T_{1u} \rightarrow {}^3A_{1g}$ transition at about 1.9 eV. Calculations of the Jahn-Teller coupling constants indicate that both the ${}^1T_{1u}$ unrelaxed excited absorption and the ${}^3T_{1u}$ relaxed emission states are strongly coupled to the T_{2g} vibrational modes.

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2. Oklahoma State University, Stillwater.

FLUORESCENCE FROM ANION VACANCIES IN SrO^1

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The singly charged anion vacancy (F^+ center) can be introduced into SrO by proton or neutron irradiation. Illumination into the F^+ optical absorption band at 3.1 eV produces a photoluminescence band centered at 2.5 eV, with a half-width of 0.34 eV at 5 K, as shown in Fig. 1.24. The radiative lifetime of the 2.5-eV fluorescence is found to be 0.42 μsec . Calculations have been made of the electronic structure of the F^+ center using a model that emphasizes the importance of (a) electronic structure on the ions neighboring the defect, (b) electronic and ionic polarization of the lattice, and (c) lattice distortion and its effects on the energy levels and wave functions of the defects. The calculation predicts that in absorption the ${}^2T_{1u}$ state, to which the transition takes place, is about 0.25 eV below an excited ${}^2A_{1g}$ state (${}^2A_{1g}^*$), but that after relaxation the ${}^2A_{1g}^*$ state is lowest in energy, making emission to the ground state partially forbidden, as shown in Fig. 1.25. An emission energy for the ${}^2A_{1g}^* \rightarrow {}^2A_{1g}$ transition was calculated to be 2.5 eV, in good agreement with the measured value.

1. Summary of paper: *Solid State Commun.* 25, 839 (1978).
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Fig. 1.24. Photoluminescence spectrum of neutron-irradiated SrO at 5 K. The luminescence was excited with 405-nm light.

Fig. 1.25. Configuration coordinate diagram for the F^+ center in SrO .

ELECTRONIC STRUCTURE OF DILUTE Cu ALLOYS

R. Zeller¹ J. F. Cooke H. L. Davis

The KKR Green's function method² has been used to calculate the electronic structure of impurities in Cu. This method is based on the muffin-tin approximation and, at present, the impurity is represented by a single perturbed potential. The Cu and impurity muffin-tin potentials were calculated using a lattice superposition of atomic charge densities obtained from Herman and Skillman.

In order to evaluate the relevant Green's functions, the electronic energy bands and wave functions must be evaluated at a relatively large number of points in the first Brillouin zone. In the past, we determined the electronic energies and wave functions from interpolation fits to a first-principles band calculation. This was done to reduce computer time and to avoid problems associated with degeneracy at symmetry points. We have recently generalized our KKR band structure programs to overcome these difficulties and now have the capability of calculating Green's functions directly from the KKR band structure without having to carry out any intermediate interpolation fits. The Brillouin zone integration is performed using the tetrahedron method.

Whereas the calculation of the imaginary parts of the Green's functions is straightforward, the real parts are more difficult to obtain. For this calculation, we have used two methods. The first is a Kramers-Kronig integration over the imaginary part,

$$\text{Re } G_{LL}^{mn}(E) = \int_{-\infty}^{+\infty} dE' P \frac{1}{E - E'} \text{Im } G_{LL}^{mn}(E'), \quad (1)$$

where m and n label the atomic positions and L and L' the angular momenta. The lower bound of the integral can be replaced by the bottom of the valence band, but a somewhat arbitrary cutoff at higher energies has to be introduced. The second method is to integrate the inverse of the KKR matrix directly,

$$G_{LL}^{mn}(E) = \int_{V_B} dk \left\{ [1 - \hat{G}(k, E) \hat{\tau}(E)]^{-1} \hat{G}(k, E) \right\}_{LL} \times \exp[i\mathbf{k} \cdot (\mathbf{R}^m - \mathbf{R}^n)]. \quad (2)$$

Here, the $\hat{G}_{LL}(k, E)$ are the KKR structure constants. Because the Brillouin zone integration has to be re-

peated for each energy E , the second method¹ is much more time consuming. We have found that both methods give essentially the same results so that the simpler Kramers-Kronig integration can be used.

Local densities of states for several impurities (Ni, Zn, Ga, and Ge) in Cu have been calculated and are shown in Fig. 1.26. It can be seen that Ni has a 3d virtual

Fig. 1.26. Local densities of states for Ni, Zn, Ga, and Ge impurities in Cu. In each plot, the lowest curve gives the s contribution, the second one the sum of the s and p contributions, and the highest the total density of states as the sum of the s , p , and d contributions. For Zn, Ga, and Ge the scale of the density of states has been enlarged by a factor of 9 compared to Ni.

bound state centered slightly below the Fermi energy E_F of Cu, while for Zn the 3d state is localized below the valence band of Cu. For Ga and Ge this state moves to still lower energies. The arrows indicate the position of the 3d state as obtained by recent photoemission measurements of Norris and Williams³ for Zn, Ga, and Ge and of Durham et al.⁴ for Ni. Clearly, the agreement between theory and experiment is very good. In the sequence Zn, Ga, Ge, the p contribution strongly increases but is essentially unchanged in energy, and the s contribution gradually moves to lower energies. For Ge there is also a localized 4s state below the valence band. These calculations indicate that the KKR Green's function approach is a practical and accurate method for

calculating the electronic structure of impurities in transition metal systems.

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1. Guest scientist from Kernforschungsanlage, Jülich, Germany.
 2. R. H. Lameter and P. Soven, *Phys. Rev. B* **8**, 2476 (1973), and references therein.
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2. Surface and Near-Surface Properties of Solids

The success of initiatives over the past few years to redirect research programs into areas relevant to various energy technologies is clearly demonstrated in this section of the progress report. Although the surface and near-surface properties of solids are important in nearly all of the technologies, such research within the Division has emphasized work in areas relevant to catalysis, magnetic fusion energy, and solar energy conversion. It is significant that approximately one-third of the reports contained in this section pertain to ion implantation and/or laser annealing of semiconductors, a topic that has not appeared in any previous progress report of the Division. Research supportive of the Magnetic Fusion Energy Program at ORNL also has been greatly expanded during the past year. To obtain an overall view of research in these areas, the reader should examine the portion of this report devoted to theoretical solid state physics, for much of the experimental work relies strongly on theoretical support.

Studies in the Surface Physics and Catalysis Program have continued to emphasize investigations of relaxed and reordered surfaces using the combined techniques of LEED, PICS, and theoretical modeling studies. The structure of the reordered Au(001) has been firmly established, but that of the reordered Au(011) remains an enigma. It has been shown that two simple models proposed in the literature for the latter are incorrect, but determination of the true structure has yet to be established by a satisfactorily consistent theoretical interpretation of the experimental data. The exploration of AES also continues because it is a possible means of establishing surface crystallography, especially of adsorbates, and of determining the electronic band structure at the surface by means of Auger line-shape analysis. Initial-state screening effects, as well as final-state effects, introduce difficulties in interpretation of the latter data. However, success has been realized for free-electron-like metals, and a much better understanding of quasi-atomic Auger electron emission has been achieved through cooperative efforts with personnel at Sandia Laboratories.

Ion-solid interactions studies have emphasized analysis of boundary layers of plasmas in the ISX-A tokamak. The energy and intensity distributions of D in the plasma edge region have been measured by exposing amorphous silicon samples to various portions of the plasma and then using ion-scattering and nuclear reaction techniques to establish depth profiles of D in the Si. Impurity profiles in the plasma edge also have been measured. This work, which requires a great deal of basic laboratory research support, has shown that the amounts of D retained in the exposed samples vary as a function of distance behind the limiter and that the ability to differentiate between ion and neutral impingement of D is probably necessary in ISX-B, if the measured D distributions are to be understood. Also, differentiation could possibly contribute to testing recent models of the plasma edge region. In addition, research in channeling phenomena and determination of low-energy ion-sputtering yields has continued, and the effects of Pt ion implantation on the corrosion behavior of Ti have been determined in a cooperative effort with staff members from the ORNL Chemistry Division and from Vanderbilt University.

Outstanding accomplishments in both the ion implantation and photovoltaic conversion programs in the area of pulsed beam annealing reflect the efforts of those directly

involved in that research, as well as broad support of Division staff primarily engaged in other programs. The characterization of the unique materials produced by laser annealing of ion-implanted materials required the individual skills of a large number of staff members during this past year. The power density from a Q-switched ruby laser necessary to anneal the lattice damage in ion-implanted regions in Si has been determined by ion-backscattering and electron microscopy measurements. The results were shown to be consistent with a theoretical model, based on macroscopic diffusion equations for heat and mass transport, which established that the near-surface regions of the samples melted and recrystallized in the order of a few hundred nanoseconds. Changes in implant depth profiles upon pulsed beam annealing were established by ion-backscattering and SIMS techniques, and the changes in lattice parameters and degree of perfection of the regrown regions have been determined by x-ray diffraction, electron microscopy, and ion back-scattering. Profile changes were consistent with the theoretical model for dopant diffusion in the liquid state. Reported here also are studies which demonstrate that implanting Si with either B, P, As, or Sb and then laser annealing produces material with a dopant concentration not readily achieved by normal equilibrium techniques and in which the implant species is >8% substitutional. Theory relevant to the laser annealing process can be found in the theory portion of this report.

This section also describes research on the application of ion-implanted, laser-annealed Si to photovoltaic conversion of solar energy. Solar cells have been fabricated from ion-implanted, laser-annealed Si, and experimental measurements indicate that a good *p-n* junction can be produced by these combined techniques. However, the spectral response of the cells needs to be improved, especially in the short wavelength region. Current research is addressing this problem, as well as the problem of determining the B concentration in B-implanted, laser-annealed Si where the concentrations of B deduced from measured implanted doses, carrier concentrations, x-ray determinations, and Raman scattering are in disagreement. The feasibility of avoiding the expensive ion implantation process by laser-induced diffusion of B and Al deposited on the surface of doped Si has been demonstrated, and solar cells with efficiencies fully comparable to those of ion-implanted, laser-annealed cells have been fabricated from this material. Both the ion implantation, laser annealing, and the laser-induced diffusion techniques have also been applied successfully to GaAs. Research on photovoltaic conversion of solar energy that involves the processing and characterization, in terms of electrical and defect properties, of NTD Si has continued during the period covered by this report. Annealing studies for NTD Czochralski single-crystal Si have shown that some type of defect-oxygen complex that can only be removed by extended high-temperature annealing may exist in Czochralski NTD Si. Similar studies on float-zone NTD Si indicate that the presence of fast-neutron-induced lattice damage may enhance the rate of removal of recombination centers that degrade the minority carrier lifetime. A continuing study comparing the characteristics of NTD and conventionally doped Si for solar cell applications now seems to indicate that the NTD material gives slightly higher efficiencies under one-sun illumination.

SURFACE PHYSICS AND CATALYSIS

INVESTIGATIONS OF REORDERED AND RELAXED Au(011) SURFACES BY PICS, LEED, AND COMPUTER SIMULATIONS

B. R. Appleton J. H. Barrett
D. M. Zehner O. E. Schow III

From previous LEED observations, it is known that the atomic arrangement of atoms in the surface region of a Au(011) crystal is dependent on the state of cleanliness of the surface. A contaminated (C, S, or O) surface has an atomic arrangement in the outermost layer possessing the same lateral periodicity as that of an ideal plane within the bulk. In contrast, LEED observations indicate that a clean surface consists of an atomic arrangement differing from that of a truncated ideal crystal. Specifically, the distance between scattering sites in the $\langle 100 \rangle$ direction in this reordered surface is determined to be twice that in an ideal (011) plane. Several models involving the arrangements of atoms within the outermost layer have been proposed in an attempt to explain these observations. Recently, an investigation of the Au(011) surface using the PICS technique was initiated, and the results obtained provide new information and permit evaluation of these models.

The scattering yields of 1-MeV He ions channeled along $\langle 011 \rangle$ directions as well as angular scans about these directions have been measured on both contaminated and clean surfaces. Results of such measurements on the contaminated surface are plotted in Fig. 2.1. The value of 2.17 atoms per row, which was obtained from computer simulation calculations along a $\langle 011 \rangle$ direction, is plotted as point "C.S." in this figure. An examination of these results shows that the data obtained along the crystal normal, $\langle 011 \rangle_{0^\circ}$, yield a backscatter value close to that obtained by computer simulation and exhibit a symmetric angular dependence about this axis. Thus, these results agree well with previous LEED observations and allow one to conclude that the atoms in the outermost planes on a contaminated surface have the same lateral arrangement as atoms in the bulk. Results of similar measurements made along the $\langle 011 \rangle_{60^\circ}$ show a much higher backscatter yield and asymmetric angular data, as would be expected for experimental conditions producing an increased yield. The direction of the asymmetry indicates an inward relaxation. However, the degree of this relaxation and the number of layers involved are still unknown and await further comparisons with results of model calculations.

Fig. 2.1. Angular scan of surface peak about $\langle 011 \rangle$ axes for contaminated Au(011) surface.

A yield of 1.93 atoms per row, again slightly less than the computer simulation value, is obtained from measurements made along the $\langle 011 \rangle_{0^\circ}$ normal of a clean Au(011) surface. Again, one is able to conclude that the intraplanar spacings in the surface region are either the same or multiples of those in the bulk. Thus, it is possible to rule out the paired-row model, which involves large lateral displacements, previously suggested to explain the LEED observation of a reordered surface structure. Measurements made along the $\langle 011 \rangle_{60^\circ}$ on a clean surface yield a value of 2.68 atoms per row. Because this value is 0.5 atoms per row larger than the computer simulation value, it is possible to rule out the simple missing-row model, for it does not allow for a change in interlayer spacings. However, these latter measurements would be consistent with a missing-row model that included interlayer relaxations or with a rippled surface model. Additional measurements on this surface, including angular scans about major axes, are presently planned, and they should provide further information about this complex atomic arrangement.

STRUCTURE DETERMINATION ON Au(001) SURFACES BY PICS, LEED, AES, AND COMPUTER SIMULATIONS

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In contrast to the simple (1×1) LEED pattern obtained from a contaminated (C, S, or O) Au(001)

surface, complex (5×20) patterns are obtained from the reordered surface subsequent to cleaning by ion bombardment and annealing. Interpretation of the LEED patterns from the contaminated surface indicates that the atomic arrangement within the outermost Au layer(s) has the same configuration as the cube planes in the bulk. The atomic arrangement thought to exist on the reordered surface consists of a top Au layer ordered in a hexagonal array with an intraplanar spacing $\sim 5\%$ smaller than that found in bulk (111) planes. Previously, the PICS technique has been employed to determine that the reordered region on the clean surface contains only one layer of atoms consistent with this model.¹⁻³ Those results were obtained on samples that were cleaned in a UHV chamber and subsequently transferred in a N environment to a second UHV chamber where the PICS measurements were made. Recently, these measurements have been repeated under experimental conditions that permitted cleaning by Ar ion bombardment and annealing in the same UHV chamber where the PICS results are obtained.

Present measurements were made first on the contaminated surface after insertion in the UHV chamber and prior to any surface treatment. The backscatter yield of 1-MeV He particles incident along the (001) surface normal and the (011) together with angular scans about each of these axes were determined. Experimentally measured yields of 1.95 and 2.33 atoms per row along the (001) and (011) directions, respectively, are in good agreement with the computer simulation predictions of 1.89 and 2.17 atoms per row for these two axes. Furthermore, the result obtained for the (011) is in close agreement with the value of 2.2 atoms per row previously measured from a (001) contaminated surface. From these results it is possible to conclude, in agreement with LEED observations, that the atomic arrangement within the outermost Au layer on a contaminated surface is the same as in cube planes in the bulk. Symmetric angular curves were obtained from measurements made about both the (001) and (011) axes. One can infer from these results that the interlayer spacing in the surface region is identical to that existing in the bulk. These combined results indicate that the atomic arrangement of Au atoms in the surface region of a contaminated surface is identical to that of an ideally truncated crystal.

Subsequent to cleaning, measurements were made of the backscatter yields from the reordered surface along the (001) and (011) directions and values of 2.48 and 3.58 atoms per row obtained. These values again are in close agreement with the computer simulation predictions of 2.49 and 3.43 atoms per row. The predictions

are based on the assumption that only one reordered hexagonal layer exists on top of the ideal (001) face, and this agreement provides additional support for this model. In the prior investigation of this surface structure, a backscatter yield of 3.2 atoms per row was measured along the (001). At that time it was suggested that, as a result of small amounts of contamination that occurred during the sample transfer process, domains containing the normal surface atomic arrangement could exist on the surface. This condition would result in measurements being made on a surface that would yield somewhat lower backscatter values. The increased yield obtained in the present investigation and its agreement with computer simulation predictions provide strong support for the validity of the prior suggestion.

Placement of a hexagonal layer on a square array, a model structure proposed for this surface, results in a surface unit cell containing 126 basis sites with respect to the two layers. This condition is expected to produce variations in the interplanar distance from site to site (rumpling effect). As a consequence, angular scans about major axes cannot provide information that will permit any further elucidation of the model. Thus, our conclusions about this surface structure must be limited to the determination of the depth of the reordered region.

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AUGER AND IONIZATION LOSS SPECTRA FROM CLEAN Be SURFACES

D. M. Zehner H. H. Madden¹

The characterization and knowledge of the electronic structure in the surface region of a solid are of fundamental importance in understanding the physical and chemical properties of the surface of a solid. Several spectroscopic techniques that utilize the short mean-free path of low-energy electrons in solids ($\lambda \sim 5-20 \text{ \AA}$) have been developed over the past decade and applied in the investigation of the surface electronic structure. Specifically, an inner electron core level can be used as a window to view the local electronic environment of an atom in the surface region. When valence electrons are involved in the Auger decay of an atom with an inner

core level vacancy, AES provides a way of examining the valence band electronic structure specific to the surface. The CLS provides the complementary view of the electronic structure of the conduction band by examining the energy distribution of electrons that have lost energy in creating an inner core level vacancy, an ionization process. The two techniques together thus provide the experimentalist with methods suitable for examining the filled and unfilled electronic density of states in the surface region.

Although these techniques have been in existence for several years, it is only recently that attempts have been made to utilize their full capabilities. In extracting the desired electronic structural information from the measured electron energy distributions, one must correct for the energy dependence of the analyzer, secondary-electron background, and distortions due to a low-energy tail that results from electrons which have suffered energy losses before leaving the solid. Techniques have been developed to account for these effects.

By employing the much longer mean-free path of x rays ($\lambda \sim 10^3 - 10^4$ Å), similar information about bulk electronic structure can be obtained from soft x-ray emission and soft x-ray absorption spectroscopies. Although different physical processes are involved, these are well understood, and comparisons with results of these techniques should provide useful information about Auger and ionization loss phenomena as well as possible ways of separating bulk and surface effects. Because soft x-ray emission and soft x-ray absorption measurements exist for Be and BeO and because previous AES measurements on free-electron-like materials have suggested the dominance of *p*-like states in the Auger emission process, an investigation of the clean Be surface has been initiated.

The line shape of the *KVV* Auger transition from a clean Be surface subsequent to background correction and loss-deconvolution is plotted in Fig. 2.2. Because two valence band electrons participate in the Auger process, the line shape has a base energy width comparable to twice the energy width of the filled density of states. Also plotted in this figure is the self-fold of the soft x-ray emission data of Aita and Sagawa.² All data in this figure have been normalized to have the same maximum intensity. Contrary to previous observations on other materials, there is an absence of agreement between these two types of data. In particular, note the differing peak positions and FWHM. Because the soft x-ray emission data sample only the *p*-like states in the valence band (a consequence of the optical selection rules) and are in good agreement with the results of calculations of the *p* partial density of states, this lack

Fig. 2.2. Beryllium *KVV* experimental Auger spectrum (solid line), self-fold of soft x-ray emission data (dashed line), and self-fold of the valence band theoretical density of states (dotted line).

of agreement indicates that states with *s*-like character contribute significantly to the Auger transition. However, a comparison with the self-fold of the theoretical total density-of-states results of Loucks and Cutler,³ also shown in Fig. 2.2, reveals disagreement, most notably in the peak position. Consequently, one can deduce that additional factors must be considered to explain the Auger line shape. As discussed in a separate contribution,⁴ better agreement with results of theoretical calculations is achieved when the partial wave character of the screening charge (the response to the initial *K* core hole) is included. Best agreement is obtained when this charge is taken to be entirely *s*-like.

The CLS spectrum below the *K* core level edge obtained on a clean Be surface is shown in Fig. 2.3. Because there is no finite width to the conduction band (in contrast to the valence band), the low-energy tail of the spectrum does not decay to zero intensity at any energy but rather contains a flat region at lower energies. In addition to background removal and loss-deconvolution, plasmon loss structure coupled to the elastic peak and present in this energy range was removed by using a synthesized plasmon spectrum. The initial undershoot is a consequence of the sharpness of the *K* edge and the width of the loss function used in the deconvolution. Also plotted in this figure are the soft x-ray absorption data of Haensel et al.⁵ Close agreement in terms of peak positions is observed within 15 eV of the *K* edge. Moreover, both spectra reproduce the

Fig. 2.3. Beryllium *K* edge CLS spectrum (solid line), soft x-ray absorption data (dashed line), and conduction band theoretical density of states (dotted line).

structure present in the theoretical density-of-states calculations of Nilsson, Arbman, and Gustafsson,⁶ also shown in this figure. The differing widths and relative intensities of these features may be a consequence of the different physical processes involved and deviations from a one-electron density-of-states model, although treatment of the data cannot be ruled out. Additionally, because the final state energy of the detected electron in the CLS technique can be varied, an energy-dependent matrix element effect may be present that has not yet been investigated. Similarities in the two experimental spectra in Fig. 2.3 are observed at lower energies also, in spite of the differing behavior of the low-energy tails. Unfortunately, calculational results are absent in this region.

In addition to providing a data base for comparison with results of model calculations, which have already provided new insight into the solid state Auger process,

these data in conjunction with data to be obtained on the oxide surface will permit an examination of the changes in electronic structure that occur in the surface region as a result of oxidation.

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INITIAL-STATE SCREENING EFFECTS IN METAL AUGER SPECTRA: Be¹

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Valence electron screening of a core-hole in most metals has long been recognized as a local effect due to the short screening length. Recently, AES has been shown to be a local probe of the variation of atomic (as opposed to bonding) charge across the valence bands. Thus, if the screening charge alters the relative atomic valence configuration, it will alter the Auger line shape from that calculated from a band-theory model. By studying deviations from the band-theory line shape, information may be derived as to the initial-state valence configuration and thus the nature of the screening charge.

To facilitate such a comparison, Auger electron spectra were obtained from a clean polycrystalline Be sample. Extraction of the Be *KVV* line shape from the as-measured data involved corrections for secondary-electron background and deconvolution to remove signal distortions related to those Auger electrons that suffer energy losses before leaving the solid.

An LCAO Be band structure was generated using Kohn-Sham exchange and a potential from a superposition of Hartree-Fock atomic charge densities. The basis set employed was the compact (3s, 3p) Slater basis previously used for Li but scaled to the Be nearest-neighbor distance. The density of states was generated using a Gaussian-broadened histogram over 364 points in the irreducible wedge of the Brillouin zone. The same method was used to generate the partial densities of states, and these, together with appropriate atomic-like Auger matrix elements, were used to generate the Auger line shape.

The partial densities of states were used to compute atomic (as opposed to bonding) densities of states via

$$A_l(E) = \sum_{ij} F_{ij}(E) S_{ij},$$

where F_{ij} is a partial density of states, S_{ij} is the overlap matrix between basis functions i and j on the same site, and the sum is restricted to basis functions of the l th angular momentum ($l = s$ or p). Functions A_s and A_p may be integrated to yield the net atomic charges for this basis set. Because this set is compact, little redistribution of bonding charge is needed to find that Be metal has the configuration $s^{0.68}p^{1.32}$.

Due to matrix element effects and the almost 2:1 p/s ratio, the KVV line shape without screening is dominated by the pp portion, as shown in Fig. 2.4a. However, comparison to experiment shows that there is a clear disagreement, strongly implying that the screening charge does not take on the same s/p ratio as the valence band.

For a first approximation to the inclusion of the screening charge, we make use of the following intuitive arguments. The area under the partial density of states is a measure of the amount of charge available for decay, and the shape of the partial density of states indicates how that charge is weighted among the possible final-state holes as a function of energy. Because the

screening charge does not alter the energies of the possible final states, its predominant effect is only to alter the transition probabilities by changing the areas under the partial density of states and thus their relative scaling. A rigorous derivation of this screening charge effect is that each occupied Bloch function polarizes towards the core-hole and changes its local site amplitude by a relative amount that is only a function of the basis function involved. In materials such as Be with considerably less than half-filled shells, this effect is reasonable because only the lower bonding orbitals are filled.

Best agreement with experiment was obtained, as shown in Fig. 2.4b, when the bonding charge was taken to be entirely s -like, thus producing a configuration including screening of $s^{1.68}p^{1.32}$. This configuration increases the ss and sp portions relative to the unscreened case and shifts the Auger peak towards lower energies. The accuracy of the fit indicates >95% s -like screening as determined by comparing the peak position to the high-energy half maximum, the latter being chosen as being largely free from experimental artifacts. Thus, this first determination of the partial wave character of the screening charge indicates that, at least in Be, it does preferentially occupy the lowest available atomic-like levels.

1. Summary of paper to be published.
2. Sandia Laboratories, Albuquerque, N.Mex.

Fig. 2.4. Beryllium KVV experimental and theoretical Auger spectra shown with the contributions from the various final-state hole angular momenta. (a) Without screening effects; (b) with purely s -like screening.

HIGH-RESOLUTION LMM AUGER SPECTRA FROM Ar IMPLANTED IN Be AND Si¹

D. M. Zehner¹ H. H. Madden²

Auger transitions from atoms in solids involving one or more valence band electrons have generally been classified as being either band-like (line shape energy widths directly correlate with the density of states of the material) or quasi-atomic (line shape is controlled by final-state effects, generally resulting in peaks with narrow energy widths). In particular, for atoms adsorbed on or embedded in a material, information about their local environment and thus the extent of bonding or interaction with the host can be acquired from a determination and analysis of Auger line shapes.

Auger spectra have been obtained previously from solid Ar formed by condensation on a metal cold finger at ~ 10 K.³ The spectra could be simulated by using broadened gas-phase data,⁴ restricted to the principal lines, which lead to a quasi-atomic characterization of the transitions from the solid. Argon ions can be easily embedded in a solid and subsequently become neutral implants. Thus, to provide a comparison with both gas-phase and condensed spectra and to examine effects due to the solid environment, a study of the $L_{2,3}M_1M_{2,3}$ and $L_{2,3}M_{2,3}M_{2,3}$ transitions from Ar implanted in both Be (Ar/Be) and Si (Ar/Si) was initiated.

Results of measurements of the high-resolution LMM Auger spectrum of Ar implanted in Be are plotted in Fig. 2.5. Measured emissions from the $L_{2,3}M_1M_{2,3}$ and $L_{2,3}M_{2,3}M_{2,3}$ Auger transitions are shown in the 190- to 205-eV and 205- to 225-eV portions of the spectrum respectively. The relative intensities and energy separations of the gas-phase data are represented by the line spectrum also plotted in this figure and shifted so that the $L_3M_{2,3}M_{2,3}$ (1D_2) component in each spectrum is aligned at the same energy. From a comparison of these spectra, it is apparent that all principal lines present in the gas-phase data and expected to be resolved by the analyzer employed in this investigation are observed in the Auger spectrum from Ar/Be. Using peak J as a reference peak, the measured energy separations for all other peaks in the spectrum are determined to be within 0.5 eV of the energy separations observed in the gas-phase data. The sources responsible for peaks A, F, and K cannot be positively identified at this time.

In contrast to the 0.2- to 0.3-eV FWHM values determined for the principal lines in the Ar gas-phase spectrum,⁴ the smallest FWHM value for Ar/Be was observed to be 1.3 eV. However, it is believed that this value should be considered an upper limit because the determination of the peak widths may be limited by the

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Fig. 2.5. $L_{2,3}M_1M_{2,3}$ and $L_{2,3}M_{2,3}M_{2,3}$ spectra from Ar. (a) Implanted in Be; (b) line diagram of the gas-phase results.

resolution of the analyzer. Nevertheless, this width is smaller than the 2.0-eV FWHM value determined for the Auger spectrum from condensed Ar and may indicate a difference in the processes responsible for the broadening in these two differing solid environments. The observation that the FWHM values for the Auger spectrum from Ar/Si are larger than those for Ar/Be provides additional evidence in support of this concept.

The energies, uncorrected for the work function of the spectrometer, of the peaks determined in the investigation of Ar/Be average 7.6 eV higher than those observed in the gas-phase data. This increase in emission energy can be attributed to electron screening effects that can occur in the host material but which are not possible in the gas-phase. The magnitude of the screening is comparable in both Be and Si.

In conclusion, the Auger transitions from implanted Ar can be characterized as quasi-atomic. Peak broadening, shifts in emission energies, and changes in relative peak intensities are effects that can be attributed to the solid state environment.

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$L_{2,3}VV$ AND MVV AUGER SPECTRA OF Cu^1

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Electron-excited $L_{2,3}VV$ and MVV Auger spectra measured as the number of electrons per volt have been obtained from clean Cu(100) and Cu(110) surfaces using a retarding field analyzer. The deconvoluted spectra are compared with x-ray-excited $L_{2,3}VV$ spectra, with other electron-excited MVV spectra, and with the results of atomic-model and band-theory calculations. Our $L_{2,3}VV$ spectra agree well with the x-ray-excited results in both line shape and L_3VV to L_2VV integrated intensity ratio. Recent atomic-model interpretations of these spectra by McGuire³ are found, especially for the L_3VV spectrum, to provide a very good explanation of the spectra: the multiplet-splitting mechanism is responsible for the major peaks, and satellite intensity contributions resulting from Coster-Kronig L_1L_2V , L_1L_3V , and L_2L_3V transitions give rise to the low-energy portions of the spectrum.

Our MVV spectra also have sharp features with shapes that are in agreement with atomic-model calculations. The experimental $M_{2,3}VV$ to M_1VV integrated intensity ratio is much larger than 3 to 1 and varies with primary electron beam energy, indicating that satellite intensity contributions make up part of the MVV signals. However, the sharp features in these spectra do not change with variations in primary beam energy from 119 to 3000 eV, indicating that they are not dependent upon satellite intensity. The experimental M_3VV to M_2VV integrated intensity ratio also remains unchanged at 1.3 to 1 for the same variation in primary beam energy. This deviation from the expected 2 to 1 ratio could be an indication that the M_2VV and M_3VV line shapes are significantly different. A broad high-energy shoulder forms part of the MVV spectra, especially for the M_1VV signal. This feature of the MVV line shape is not in agreement with the atomic-model calculations. It

is also not simply related to the undistorted total valence band density of states for Cu. However, the width of this feature is roughly consistent with the width of the self-fold of the s or p valence band density of states. Comparison of our M_1VV signal, in particular with recent band-theory arguments of Cini⁴ and of Sawatzky,⁵ indicates that parts of the MVV line shapes are explainable in terms of distortions in the Auger core-valence-valence signals from narrow valence band metals. These distortions are expected to occur as a result of hole-hole interactions in the two-hole final-state configuration. Similar estimates of this hole-hole interaction energy of 5.5 and 5.8 eV are obtained by analysis of our data, using the arguments of Cini and of Sawatzky respectively.

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AN ELS VIBRATIONAL STUDY OF CO ADSORBED ON THE $Cu(110)$ SURFACE¹

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High-resolution electron ELS has emerged as an important tool for the characterization of surface adsorbate geometry and for the chemical analysis of surface species.^{2,3} We report here the use of ELS-observed vibrational energies to determine the site location of a simple molecular adsorbate on a single-crystal surface, CO on Cu(110). All measurements were made using a high-resolution electron spectrometer, which has been fully described previously.⁴ The Cu(110) crystal was grown and prepared in-house, and the surface was oriented to within 0.1° by an x-ray diffraction technique.⁵ The crystal was cleaned in situ in the UHV system by 1000-eV Ne^+ bombardment, followed by annealing for typically 1 hr at 400–450°C.

For comparison with published results that indicate the formation of a (2×1) LEED pattern for CO on Cu(110),⁶ we obtained a limited amount of LEED data by observing the growth in intensity of a single $(\frac{1}{2}, 0)$ beam during CO exposure at 80 K. The intensity maximum of the beam occurred at an exposure of 1.25 L, and the $(\frac{1}{2}, 0)$ beam never developed as a sharp diffraction beam. When first detected at low CO coverage, the beam had an angular spread of about 10° FWHM. When

the beam was most intense, the angular spread was 2° in the $[1, 0]$ direction but still about 10° in the $[0, 1]$ direction.

Electron energy loss profiles were recorded over a range of CO exposures and substrate temperatures. Figure 2.6 summarizes the results obtained at a temperature of 80 K. At very low coverages, loss peaks were observed at 85 and 258 meV. With increasing CO coverage, the 258-meV loss peak grew, and at saturation coverage, the peak shifted upward by about 2 meV, which is consistent with recent infrared results.⁶ The 85-meV peak, on the other hand, disappeared with increasing CO coverage.

Fig. 2.6. Specular beam electron energy loss profiles from Cu(110) as a function of CO exposure at 80 K.

Figure 2.7 illustrates the sequence of events that occurred with low CO coverage as the crystal was heated above 80 K. The 85- and 258-meV peaks remained little changed in intensity until the temperature approached 160 K. At this point the 85-meV peak almost disappeared, and the 258-meV peak decreased slightly in intensity and shifted up in energy nearly 2 meV. At a temperature of 170 K, the CO began to desorb, as detected by the quadrupole mass spectrometer. The loss profile at 200 K shows no trace of the 85-meV loss and only a remnant of the 260-meV loss.

Fig. 2.7. Specular beam electron energy loss profiles from Cu(110) with a low coverage of CO showing dependence on temperature.

Auger spectra obtained after thermal desorption showed no indication of C that would remain if the CO dissociated. However, exposure of a CO-covered surface at 80 K to the AES electron beam (2500 eV, $1 \mu\text{A}/\text{mm}^2$) resulted in both desorption and dissociation.

A troublesome aspect of these data was the general lack of reproducibility of the 85-meV peak intensity because the 85-meV peak reaches its maximum intensity at CO coverages that are not much greater than that resulting from the background partial pressure of CO. The possibility that an impurity might be responsible for the 85-meV peak was tested by increasing the levels of each of the known impurities. No link was found between any impurities and the 85-meV peak.

Although most of the results reported here are based on specular beam energy loss profiles, a few nonspecular beam measurements were made. The 85-meV loss peak was more easily resolved by measuring a few degrees away from the specular direction because of the greater width of the inelastic beam as compared to the elastic beam.² As a result of the recent interest in the use of nonspecular nondipole scattering to observe vibrational modes not perpendicular to the surface,^{7,8} we obtained loss profiles for a variety of incident and nonspecular scattering angles. However, no new peaks were seen to indicate nonperpendicular modes.

The observed vibrations may be interpreted with a simple spring model, if we neglect bending modes and treat the Cu lattice in two approximate limits, that is, either as one or two free Cu atoms or as a rigid wall.⁹ The strong dipole character of the 258–260-meV peak, which is the C-O stretching vibration, implies that the molecule stands almost upright.² Infrared and angle-resolved photoemission studies of metal carbonyls and CO adsorption on metals lead us to expect that the C atom is nearest the substrate.^{10,11} Assuming that the two observed vibrations exhaust the low-energy spectrum would imply that the molecules sit in the “on top” position. However, because of the limited energy resolution of our instrument, additional vibrations occurring at or below ~60 meV cannot be ruled out, and we must also consider bridge and hollow sites.

For the on-top site, the equations to be solved are¹¹

$$\Omega_1^2 + \Omega_3^2 = \frac{k_1}{\mu_1} + \frac{k_2}{\mu_2}, \quad (1)$$

$$\Omega_1^2 \Omega_3^2 = \frac{m_O + m_C + m_{Cu}}{m_O m_C m_{Cu}} k_1 k_2, \quad (2)$$

where Ω_1 and Ω_3 are the observed energies; k_1 (k_2) is the C-O (C-Cu) force constant; m_O , m_C , and m_{Cu} are the particle masses; and μ_1 (μ_2) is the C-O (C-Cu) reduced mass. Assuming an on-top site at low coverage, we assign $\Omega_1 = 258$ meV and $\Omega_3 = 85$ meV. Solving Eqs. (1) and (2) for the force constants indicates an unusually weak C-O bond and a very strong C-Cu bond comparable in strength to the C-O bond. This result is unreasonable, particularly in light of the low thermal desorption temperature we observe for the CO molecule. At higher coverage or temperature, when only a single vibrational peak at 260 meV is observed, reasonable values for the force constants are obtained if we set $\Omega_1 = 260$ and assume $\Omega_3 = 40$ –50 meV. Hence, the on-top site is not acceptable at low coverage but is acceptable at high coverage or temperature.

The low-coverage, low-temperature case may correspond to a bridge or hollow position if the 85-meV vibration is an asymmetric stretching mode similar to the case of CO on Ni(100).⁹ The equations for the bridge configuration are¹¹

$$\Omega_1^2 + \Omega_2^2 = \frac{k_1}{\mu_1} + \frac{k_2(m_{Cu} + 2m_C \cos^2 \alpha)}{m_C m_{Cu}}, \quad (3)$$

$$\Omega_1^2 \Omega_2^2 = \frac{k_1 k_2}{m_{Cu}} \left(\frac{1}{\mu_1} + \frac{2m_{Cu} \cos^2 \alpha}{m_O m_C} \right), \quad (4)$$

$$\Omega_4^2 = \frac{k_2}{m_{Cu}} \left(1 + \frac{2m_{Cu}}{m_C} \sin^2 \alpha \right). \quad (5)$$

The angle α is defined as half of the Cu-C-Cu bond angle. Identifying $\Omega_1 = 258$ meV and $\Omega_4 = 85$ meV and assuming the symmetric stretching vibration $\Omega_2 = 40$ to 60 meV, reasonable values of the force constants are obtained that are consistent with the results for CO on Ni(100) and with the low desorption temperature on Cu(110). Comparing the calculated values of α with a hard sphere calculation in which the sum of atomic radii is 2.2 Å suggests that the CO molecule sits in the long bridge position in the low coverage case.

The diffuse and streaked LEED patterns indicate that the adsorbed CO is not well ordered, particularly in the [0,1] direction, although tilting of the CO axis^{10,12} may be partially responsible for the character of the LEED patterns.^{10,11} Nevertheless, our results do indicate a dependence of the site preference on coverage and temperature.

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ION-SOLID INTERACTIONS

SIMULTANEOUS DETERMINATIONS OF GREATER- AND LESS-THAN-RANDOM ENERGY LOSS RATES FROM PLANAR CHANNELING MEASUREMENTS OF He, B, AND C IONS IN Si(111)

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Measurements of the energy loss rates of well-channelled ions transmitted through thin single crystals have been widely applied to test electronic stopping power theories and concepts.⁴ The basis of these tests is that well-channelled ions sample large, correlated, well-defined impact parameter collision events with the atoms of the solid in contrast to the random sampling experienced by ions in amorphous or polycrystalline targets. The energy loss rates of these well-channelled ions are substantially less than random energy loss rates. Recently, a new channeling phenomenon was identified for 1.0-MeV He ions transmitted parallel to the (111) planar channels in thin (0.23 μm) Si single crystals;⁵ this phenomenon allows simultaneous determinations of well-channelled ions that exhibit both greater-than-random as well as less-than-random energy loss rates.

The origin of this new channeling effect is the unusual nature of the Si(111) planar channels composed of planes of atoms with alternately narrow (0.78 Å) and wide (2.35 Å) spacings. The energy loss spectra of ions transmitted parallel to the [111] direction show two distinct energy loss groups: (1) energy loss rates greater-than-random that can be associated with well-channelled ions in the narrow (111) channels and (2) energy loss rates less-than-random corresponding to well-channelled ions in the wide (111) channels. Measurements of the energy dependence of these two energy loss groups have been made for B and C ions. Beams of B⁵⁺ and C⁶⁺ with energies from about 10 to 50 MeV were obtained from the ORNL Tandem Van de Graaff accelerator and transmitted parallel to the (111) planar channeling direction of a $\sim 0.23\text{-}\mu\text{m}$ Si single crystal. The energy loss spectra of B⁵⁺ and C⁶⁺ ions emerging within $\leq 0.05^\circ$ of the incident beam direction were measured with an Enge magnetic spectrometer. The peak and leading edge extracted from both the greater- and less-than-random energy loss groups at each incident energy for C⁶⁺ ions are shown in Fig. 2.8. The connected points at high and low stopping powers at each energy are peak and leading edge values respectively. The energy dependences of these two groups are

Fig. 2.8. Measured energy loss rates for low- and high-loss groups of C⁶⁺ ions transmitted parallel to Si(111) planar channels as a function of incident energy.

contrasted to measurements for the energy loss of randomly directed ions. The significance of these measurements is that they provide stringent experimental tests of recently developed impact-parameter-dependent stopping power theories,⁶ because a single set of measurements exploiting this channeling effect can provide well-defined energy loss groups that span a wide range of energy loss and that can be associated with an identifiable set of impact parameters.

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2. University of Aarhus, Denmark.
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LOW-ENERGY H SPUTTERING OF METALS¹

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The sputtering of first wall materials by low-energy light ions escaping from the plasma can play a major

role in impurity introduction and wall erosion in proposed fusion devices. Recent extensive measurements of light-ion sputtering yields at Garching using a weight-loss method have significantly increased our understanding of low-energy sputtering processes at high ion doses ($\geq 10^{19} \text{ cm}^{-2}$).^{3,4} In the present work, normal incidence sputtering yields have been measured for doses as low as $\sim 10^{18} \text{ cm}^{-2}$ for 0.2- to 2.0-kV H ions on Au and Ni using a Rutherford backscattering technique.

The sputtering beam was extracted from the Solid State Division's ion implantation accelerator at 35 kV and decelerated to its final energy by an electrostatic lens that focused 10 μA of H^+ in a 1 mm^2 spot on the target. The loss of sputtered material was monitored in situ by changes in the backscattering yield of a 2.5-MV He^+ beam from the Solid State Division's Van de Graaff accelerator, which could also be directed onto the sputter spot. Thin film targets on graphite and Si wafers were used for the Au and Ni measurements. Vacuums of $\sim 10^{-7}$ torr were maintained throughout the sputtering runs.

Some typical experimental curves for total sputtered material as a function of ion dose are shown in Fig. 2.9. The results demonstrate a linear dependence for material erosion vs dose down to fluences as low as $2 \times$

10^{18} cm^{-2} . The slight curvature in the extrapolated curves below $2 \times 10^{18} \text{ cm}^{-2}$ (Fig. 2.9) suggests that initial sputtering rates may be higher than "steady state" rates. This result is significant in the relative sputtering data but not on an absolute basis because absolute yields are only determined to $\pm 30\%$. The energy-dependent results for Au and Ni are compared with the Garching data in Table 2.1. The present results are generally consistent with the higher dose Garching

Table 2.1. Normal incidence sputtering yields for H^+ on Au and Ni

H^+ energy (eV)	Au yields (atoms per ion)		Ni yields (atoms per ion)	
	Present work	Data from ref. 3	Present work	Data from ref. 4
200	^a		3.0×10^{-3}	4.0×10^{-3}
400	8.9×10^{-3}	9.8×10^{-3}	7.7×10^{-3}	9.2×10^{-3}
750	4.1×10^{-2}	3.5×10^{-2}	1.2×10^{-2}	1.3×10^{-2}
1000	7.0×10^{-2}	5.8×10^{-2}	1.1×10^{-2}	1.4×10^{-2}
1500	1.1×10^{-1}	8.9×10^{-2}	1.0×10^{-2}	1.4×10^{-2}
2000	1.3×10^{-1}	1.1×10^{-1}		1.3×10^{-2}

^aBelow threshold for H^+ sputtering of Au.

Fig. 2.9. Total sputtered material vs ion dose for 500- and 1000-eV H^+ on Au. The linear relationship implies a constant sputtering rate over this dose range.

data as well as with recent theoretical work and suggest that high-dose-sputtering data may extrapolate reasonably to the lower doses characteristic of fusion reactor discharges.

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USE OF DEPOSITION PROBES FOR ANALYSIS OF TOKAMAK BOUNDARY-LAYER PLASMAS¹

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The deposition of impurities and plasma ions on probes exposed in plasma devices can be used as a diagnostic method for characterizing boundary-layer plasmas³ (that part of the plasma in the limiter shadow or outside the separatrix in the case of a divertor tokamak). Recent measurements on ISX-A have shown that quantitative measurements of impurity and plasma particle profiles can be obtained from ion scattering and nuclear reaction analysis of samples exposed in the plasma edge.⁴ For such measurements to become meaningful diagnostics, they must be related to the plasma edge behavior. In the present work, a simple analytic model of the boundary-layer plasma is utilized to explore the relationship between the deposition profile on such probes and the particle confinement time and the ionization probability of wall-originated impurities in the boundary layer.

The plasma density in the boundary layer under steady state conditions is derived by equating outward diffusion from the plasma with plasma loss to the limiter. Assuming that ionization of neutrals in the boundary layer can be neglected and that all ions reaching the limiter are trapped or neutralized, one obtains for the deposition density of the k th plasma species on a probe inserted radially in the plasma edge region

$$D_k(x) = \frac{N_k \exp(-x/\delta_k)}{\tau_k \frac{4\pi a \delta_k}{\delta_k}}, \quad (1)$$

where x is the distance from the limiter of major radius a and N_k and τ_k are the density and confinement time of the k th ion species in the plasma respectively. For low-density boundary layers, Eq. (1) can be used to estimate τ for fuel ions because N/r and δ are determined from the profiles and N can be obtained from the electron density profile.

For high-density plasmas, the ionization of impurities originating at the wall as neutrals may largely determine the impurity deposition profiles in the boundary layer. Under these circumstances, deposition profiles similar to those shown for Fe in Fig. 2.10 might be expected. These profiles show a large variation with changes in the electron density in the boundary layer. Although the

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Fig. 2.10. Deposition profiles as a function of distance x from the limiter edge for a probe inserted normal to the toroidal field lines in a tokamak boundary-layer plasma. The curves correspond to 0.1-eV Fe in a 10-eV boundary-layer plasma for several electron densities n_e at the plasma edge.

quantitative application of these techniques will require a more detailed approach, the qualitative trends outlined above should hold, leading to the useful application of deposition probes for boundary-layer diagnostics and measurements of particle confinement times.

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QUANTITATIVE MEASUREMENTS OF ENERGY AND INTENSITY DISTRIBUTIONS OF D IN THE PLASMA EDGE REGION OF ISX-A

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A coordinated surface physics program has been initiated as an integral part of the ISX tokamak project. One goal in this effort to date has been to assess the capabilities of using ion beam analysis to study plasma particle distributions in the scrape-off region (outside the limiter radius) of the tokamak. Information on this region of the plasma, which interacts directly with the limiter and first wall, is of great importance in modeling the plasma and understanding recycling and impurity transport phenomena.

The experimental method used to study D distributions involved exposing *a*-Si samples, via a UHV sample analysis station, to tokamak discharges in which D was puffed into a D plasma. The exposed samples were then transferred to the Solid State Division's positive-ion accelerator facility where they could be analyzed using ion-scattering and nuclear reaction [$D(^3\text{He}, p)^4\text{He}$] techniques. Figure 2.11 shows the energy distribution of ^4He particles detected using a surface barrier detector located at an angle of 60° to the incident beam (700 keV ^3He ions). The detected particles originated in nuclear reactions involving D atoms retained in the Si following exposure in ISX. For this spectrum, the sample was located 2 cm back from the limiter radius perpendicular to the toroidal field in ISX during 17 low-power (200–300 eV central ion energy) discharges. The absolute D concentration corresponding to the spectrum of Fig. 2.11 has been determined to be 4×10^{16} atoms cm^{-2} by detecting protons produced in the reaction. Calibration for this measurement was achieved through comparison of two standards containing a known amount of D. By relating ^4He energy to depth in the sample in Fig. 2.11, the D is seen to be distributed over ~ 500 Å.

Depth profiles and absolute concentrations for D have been obtained as a function of distance from the plasma for Si samples perpendicular to the toroidal field between 2.0 and 4.5 cm back from the limiter radius and for a sample 1.5 cm from the limiter and parallel to the toroidal field. On three samples, the D concentration decreased up to a factor of 10 over the 2.5-cm difference in distance, whereas on one sample the concentration remained constant. The D profile also

Fig. 2.11. Yield of ^4He from the nuclear reaction $D(^3\text{He}, p)^4\text{He}$ for a 700-keV ^3He beam incident on an *a*-Si sample exposed to 17 D discharges in ISX-A. The scattering angle is 60° . The dashed line represents the resolution of the analyzing technique. The depth scale shown has been calculated from the ^4He energy distribution, the geometry, and stopping powers for He in Si.

decreased in width away from the plasma. The sample at 1.5 cm from the plasma had approximately the same D concentration as the sample perpendicular to the toroidal field at 2 cm, but the D was distributed to greater depths.

The measurements on these samples, made only during one series of discharges, were primarily aimed at assessing the feasibility of this experimental approach as a tokamak diagnostic. As such, they should not be generalized. Nonetheless, they indicate that this technique shows great promise as a versatile, quantitative plasma edge probe for future studies on tokamaks. Furthermore, they suggest related laboratory experiments necessary in understanding future exposures. For example, based on plasma parameters for the series of shots in the present analysis, it is not understood how large amounts of D become distributed as deep as 500 Å in the *a*-Si. Consequently, laboratory studies are needed to determine the range, diffusion parameters, trapping, and re-emission of ~ 100 – 1000 -eV D in *a*-Si, as well as the effects of elevated surface temperatures and high surface concentrations of implanted D. In addition, the results of these measurements suggest that experiments planned for ISX-B that distinguish between neutral and

ion impingement may help explain the distributions obtained and also test recent models for the plasma edge region.¹

I. H. Vernick, ORNL report to be issued.

QUANTITATIVE MEASUREMENTS OF IMPURITY PROFILES IN THE PLASMA BOUNDARY LAYER OF ISX-A¹

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Much of the success of the development to date of tokamak plasma confinement and understanding of plasma device operation stems from plasma modeling calculations. In many instances, however, interpretation of experiments and predictive modeling calculations are hampered by inadequate understanding of the role of plasma materials interactions occurring in the plasma device and their effects on machine performance. It is demonstrated that impurities introduced into the plasma can have serious detrimental consequences,² but it is not often clear which introduction mechanisms are the major contributors in a particular machine. This report summarizes an analysis method used to obtain quantitative impurity profiles in the plasma edge region of ISX-A. The method uses ion-scattering and ion-channeling techniques to analyze samples exposed in the plasma edge region.

High-purity single-crystal Si [(100) orientation] samples, which were chosen to take advantage of the reduced background and increased sensitivity attainable through ion-channeling effects in single crystals, were exposed to a series of discharges in ISX-A using the surface analysis station of the surface physics group. Samples were exposed both parallel and perpendicular to the toroidal magnetic field at distances ranging from 1.5 to 4.5 cm behind the limiter radius. After exposure, the samples were transferred in dry air to the Solid State Division's PHISICS facility for analysis by ⁴He backscattering using the 2.5-MeV Van de Graaff. Because the samples were exposed to air during this transfer, interpretation of structure in the backscattering spectra involving C, O, or other atmospheric elements must be limited. An unexposed single-crystal sample was used as a control to assess the effects of the air transfer. A UHV exposure and transfer system is presently being constructed to eliminate this problem in future studies planned on ISX-B.

The samples discussed in this work were exposed to 17 shots in which D₂ was puffed into a D⁺ plasma. For these shots, the line average plasma density ranged from 2.4×10^{13} to 3.1×10^{13} cm⁻³, whereas the toroidal field varied from 10.6 to 15.1 kG, both typical plasma conditions. The plasma current, 64 kA, was approximately half the usual current. Titanium was sublimated prior to the first and eighth shots. During sublimation, the carriage was moved out of the tokamak into the surface analysis station to avoid contamination of the samples.

The backscattering analysis was carried out in a surface analysis chamber at $\sim 10^{-7}$ torr using 2.5-MeV ⁴He ions collimated to give a 1-mm-diam spot at the target. The samples were mounted in a precision goniometer that could orient the single crystals relative to the beam with an accuracy of $\pm 0.01^\circ$ and that could be translated to analyze various areas on the samples. The energy distributions of backscattered ions at 145° were measured using a solid state detector cooled to -20°C and standard pulse height analysis techniques. The energy scale of the detector system was calibrated using a standard target consisting of 300-Å films of Al, V, Cu, Nb, and Au evaporated onto a high-purity C disk. The energy of ions Rutherford scattered from each of these films provided an energy calibration for the scattered ions to within ~ 1 keV. Accurate calibration over the entire range of scattered energies is important both for assuring proper mass identification and for determining the depth distributions of impurities in the sample.

The effectiveness of the Rutherford backscattering and channeling technique for detecting impurities transported from the plasma to the probe sample is illustrated in Fig. 2.12, which shows an expanded region of the backscattered He energy spectrum for elements heavier than Si. This spectrum was taken from a sample exposed perpendicular to the toroidal field, 2 cm back from the limiter radius, and facing into the direction of positive-ion current. During the analysis, the (110) axis of the crystal was aligned with the incident ion beam to give a "channeling" spectrum, as illustrated in Fig. 2.13, which is an expanded scale of backscattering from the surface layers of the Si crystal. Note the marked difference in scattering from Si between the random and the aligned, or "channeling," spectra on the left side of the figure. It is this decrease, caused by shielding of bulk atoms from the incident ion beam by the surface layers, that gives increased sensitivity for impurities in the channeling geometry. Analysis of such measurements provides the following information:

1. The species of each impurity retained on the sample of Fig. 2.12 can be determined from analysis of the peak energies.

Fig. 2.12. Expanded view of aligned (110) ^4He backscattering spectrum from Si exposed in ISX-A showing scattering from elements heavier than Si.

Fig. 2.13. Comparison of Si surface peaks for the exposed and control samples.

2. Absolute quantities can be obtained from the area of each peak compared with the random-scattering spectrum from Si. The results tabulated on the figure indicate a sensitivity of $\lesssim 10^{12}$ atoms cm^{-2} for most impurities.
3. Further analysis of these peaks shows, once the isotopic mass ratios and our experimental conditions are taken into account, that the widths of the impurity peaks are the same as our experimental depth resolution, which is 80 Å, and are thus located within ≈ 80 Å of the surface.
4. This implantation "range" can be used to set limits on the possible energies with which each impurity species bombarded the surface.
5. Impurity concentrations vs distance from the limiter shadow of the ISX were determined by spatial analysis of the exposed samples. The retained impurity concentrations showed a marked decrease as distance behind the limiter increased from 1.5 to 4.5 cm.

We are presently comparing these measured profiles to model calculations in an attempt to deduce impurity introduction mechanisms.³

The surface peak regions of aligned (110) channeling spectra for both control and exposed samples are shown in Fig. 2.13. Using methods previously discussed,⁴ it is possible to extract the number of Si atoms contributing to these surface peaks. The data for the control sample shows a width equal to our experimental resolution, ≈ 80 Å, and indicates that $\sim 1.8 \times 10^{16}$ atoms cm^{-2} are responsible for this scattering from the surface region. This calculation is consistent with a perfect bulk single crystal having SiO_2 on its surface and containing a thin disordered layer at the Si-SiO₂ interface, as hypothesized by Feldman et al.⁵ One would expect this kind of surface for the etched Si samples used in this work. The surface peak of the exposed sample, however, clearly has a much larger area and is broader (175 Å) than the experimental resolution. This increased area and the fact that the height of the surface peak approaches that of the random spectrum indicate that the crystal has been heavily damaged to a depth of ≈ 170 Å. We know from range calculations that heavy impurities would have to be incident on Si at energies of ≈ 10 keV to produce damage to this depth. Furthermore, the measured widths of impurity distributions (Fig. 2.12) indicate that none are implanted as deep as the damaged region. On the other hand, mean ranges for D in Si, as calculated using the MARLOWE binary collision code for the temperatures expected in ISX,⁶ are comparable to the depth of the damage. Experimental

D depth profiles on samples exposed in ISX-A also show a similar depth distribution.⁷ Thus, it appears likely that the near-surface damage has been caused by D. This damage sensor promises to be a useful probe for determining the quantities and energy distributions of plasma particles in the plasma edge region.

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TIME-RESOLVED STUDIES ON ISX-A

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In a recent survey of scientific and technical progress of the tokamak reactor concept during the past few years,² it was concluded that the major questions concerning the feasibility of tokamak fusion power are related to expected plasma physics performance, not to technological or engineering limits. The detrimental effects on performance of heavy impurities introduced to the plasma are well known,³ but the mechanisms that control their introduction and their time evolution during the discharge are not. To improve our understanding of these effects, efforts were initiated to measure heavy impurity profiles as a function of position by using Rutherford backscattering³ and to measure impurity deposition as a function of time during tokamak operation, using a mechanical exposure device in conjunction with Auger analysis and Rutherford backscattering⁴ techniques. By relating the time at which impurities evolve to machine operation, it may be possible to identify and to eliminate the source of impurities.

Serious constraints were imposed on the design of a mechanically operated time-resolved system by the small size of the apertures ($\frac{3}{8}$ -in. square) in the surface

analysis station through which it must pass to enter the tokamak and by the necessity of making the final mechanical connections under UHV after the device was in position. Additionally, the entire assembly had to be capable of being removed from the carriage so that it could be placed at the focus of a cylindrical mirror analyzer and again rotated to carry out the Auger analysis of the surface as a function of position. It was also clear that one shot would not provide sufficient deposition for analysis and that the sample would have to be carefully returned to a zero position and synchronized to the tokamak discharges to collect data over several tens of shots. A 1.2-cm-diam cylinder, to be rotated inside a protective cover and exposed to the plasma only through a 1-mm wide slit, was finally chosen for the sample, giving a maximum time resolution for typical ISX-A discharges of ~ 7 msec. The cylinder was mounted on a bracket that could be attached to and removed from the carriage and transported to the Auger analysis station, all under high-vacuum conditions. The sample was rotated by means of a bevel gear train that was engaged after the carriage was in place and that led through a rotary feedthrough to the exterior of the vacuum chamber where a stepping motor was used to power the system. The stepping motor and its controller provided rapid acceleration to and deceleration from the desired rotational speed and could also be used for consistent indexing of the cylinder position. A start pulse from the controlling computer accurately synchronized the rotation with the plasma discharges. The system was tested for reliability in the laboratory prior to installation on ISX-A.

Shortly before ISX-A shutdown, time-resolved measurements of impurity deposition were made. High-purity Al was used for the sample cylinder so that components of the stainless steel liner and Ti, which had been used as a getter, would be easily detectable. The sample was cleaned by Ar ion bombardment in the surface analysis station prior to insertion into the tokamak, but AES still showed a substantial oxide layer to be present. Thus the results for O will not be indicative of deposition during the discharges, even though O was a major plasma impurity in ISX-A. The sample was exposed to 44 consecutive shots, withdrawn from the tokamak, and moved to the surface chamber under high vacuum where Auger analysis of the surface impurities was carried out. Plasma parameters during the exposure were typical of ISX-A operation. The toroidal magnetic field was 13 kG, the plasma current was 120 kA, and the plasma density varied from 1×10^{13} to $5 \times 10^{13} \text{ cm}^{-3}$. Results of the Auger spectroscopy for Fe and Ti are shown as a function of time in Fig. 2.14. Similar

Fig. 2.14. Time-resolved measurements of impurity deposition in ISX-A. Position is 25 mm behind limiter and perpendicular to the toroidal field.

results were obtained for C and S deposition. The ordinate is expressed in percentage of surface concentration, using the method and sensitivities described by Palmberg.⁵ Although these data represent only impurities retained on the surface, rather than the incident impurity flux that we would like to know to interpret models of impurity introduction, the greatest interaction with the wall, by a factor of ~ 2 , occurs during the first 20 msec and again from 160 to 190 msec. To relate these times to the plasma conditions, we must compare our results with other diagnostics. For the majority of these shots, electron density, as measured with Compton scattering, increased smoothly from 20 to 150 msec when the peak density occurred, then decayed rapidly through the region in which our data show a maximum deposition rate. Likewise, measurements of dynamic variations show activity from 0 to 25 msec, then a flat stable region of 150 msec, and strong activity again from 150 to 200 msec. It is evident that our measured impurity deposition rates reach maxima during periods of plasma instability, such as initial breakdown and plasma formation, and again during the decay of the plasma. During stable operation, plasma fluxes to the wall are minimized. Although many other factors control impurities, these results indicate that long pulse devices, such as future tokamak reactors, may enjoy an advantage in terms of impurity introduction rates.

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ALTERATIONS OF THE SURFACE CORROSION BEHAVIOR OF Ti BY Pt IMPLANTATION

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Corrosion is a serious problem adversely affecting materials and component performance in most technological applications involving metals, particularly in those energy systems that must contend with hostile environments such as high temperature and/or radiation. The physical and chemical mechanisms responsible for corrosion are highly complex. It is established in corrosion technology that small amounts of beneficial dopant atoms can alter corrosion properties, but it is often not clear whether alteration of the chemical interactions (such as oxidation) or of transport mechanisms is responsible for the observed changes. Nevertheless, numerous alloy systems and surface treatments are widely used for their corrosion-resistant properties.

Ion implantation is a promising new technique for (1) creating new corrosion-resistant surfaces by controlled implantation of selected dopant atoms and (2) investigating fundamental mechanisms of corrosion.⁵ Because of the nonequilibrium nature of the ion implantation process, any species of ion can be implanted into any material. This implantation can result not only in the fabrication of conventional surface alloy systems but also in fabrication of unconventional systems not achievable by conventional methods (i.e., doping with a species that does not alloy with the host or to concentration levels exceeding equilibrium solubility limits). Furthermore, because both corrosion and ion implantation are surface-specific processes, the combination is quite often beneficial and competitive as a fabrication process. Finally, the accuracy, control, and versatility inherent in the ion implantation process make it an ideal tool for isolating and identifying the various mechanisms operable in any corrosion process.

A cooperative research program has been initiated between ORNL and Vanderbilt University to study ion implantation effects on the corrosion behavior of the Ti/Pt system. This system was chosen for initial experiments because the electrochemistry of Ti and the bulk

alloy systems of Ti/Pt and Ti/Pd have been investigated previously.⁶⁻⁹ Some preliminary thermal oxidation studies have been made of Ti implanted with Pt;¹⁰ one corrosion study has already been reported for Ti implanted with Pd.¹¹

Cylindrical samples of Ti that would serve as electrodes in the electrochemical measurements were prepared and characterized by anodic polarization in a test solution described previously.⁷ Various Ti samples were then implanted in high vacuum ($\sim 10^{-8}$ torr) with 100-keV Pt ions to doses ranging from 1×10^{12} to 3×10^{16} Pt atoms cm^{-2} . After implantation and characterization by Rutherford backscattering, the samples were placed in a corrosion cell where anodic dissolution measurements were made as a function of time. The quantities and depth distributions of the implanted Pt atoms were determined at various stages of the electrochemical experiments by Rutherford backscattering analysis with 1.0- and 2.5-MeV He ions. Composite results of electrochemical measurements and Rutherford backscattering analysis are shown in Fig. 2.15 for a typical Ti sample implanted with 3.2×10^{14} Pt atoms cm^{-2} . Rutherford

Fig. 2.15. Correlation of electrochemical measurements made on a cylindrical Ti sample implanted with 3.2×10^{14} Pt atoms cm^{-2} (solid curve) and the measured implanted Pt distribution (dashed curve) determined from ion-scattering analysis.

backscattering analysis showed that the implanted Pt distribution was approximately Gaussian in shape, centered at about 300 Å beneath the Ti surface with a peak concentration of ~ 0.10 at. % Pt. This implanted distribution (dashed curve, Fig. 2.15) is shown plotted as concentration vs. depth. The solid curve shows the open circuit corrosion potential vs. time for this sample, and from a comparison of these data with the known

anodic polarization curve for Ti, it is possible to relate the "depth" scale at the top of Fig. 2.15 to the amount of Ti removed at any given time. Correlation of the corrosion behavior of this sample with the implanted Pt depth distribution is typical of the electrochemical measurements made on many of the samples. The initial period of relatively high potential is associated with removal of an air-formed oxide film, followed by dissolution of Ti through the passive layer present on the sample at about -0.300 V. Once corrosion has proceeded to the point that implanted Pt is encountered, a period of passivation persists (at a constant potential of about -0.355 V for this sample) until all the Ti-containing Pt has corroded away, at which time the potential approaches -0.740 V, which is typical of pure Ti. The behavior of the implanted Pt distribution as the Ti corrodes away during this passive period is not known, but it is the subject of part of the continuing study.

Samples implanted to lower doses all showed a similar corrosion behavior when the implanted Pt depth was reached, but the period of passivation and the corrosion potential decreased with decreasing Pt dose. One sample implanted with 2.8×10^{16} Pt atoms cm^{-2} showed complete passivation at a potential of -0.260 V, which corresponds to the reversible H potential in the solution, and the sample remained passive for >200 hr, at which time the experiment was terminated. Rutherford backscattering analysis of this sample showed some redistribution of Pt on the surface but essentially no loss of the implanted Pt.

This high dose case highlights some of the unique aspects of ion implantation for such applications. First, the measured peak concentration of the implanted Pt distribution was ~ 9 at. %, a value which exceeds the equilibrium solubility of Pt in Ti at room temperature by an order of magnitude. Second, implantation of a few monolayers of Pt into the near-surface region of Ti appears to have achieved corrosion results normally associated with a bulk Ti/Pt alloy. In cases where such a system was required, the implantation technique would be very cost effective.

A final example from the present work indicates the usefulness of ion implantation and Rutherford backscattering analysis in identifying specific corrosion mechanisms. A Ti sample was implanted with 5.5×10^{14} Pt atoms cm^{-2} at an energy of 100 keV and placed in the corrosion cell. If measurements like those discussed in Fig. 2.15 were made, one would expect

similar results because the Pt doses are comparable. In contrast to the measurements discussed in connection with Fig. 2.15, however, this sample was polarized and held at a potential of -0.260 V, the reversible H potential, for a period sufficient to corrode away the Ti to a depth well beyond the implanted distribution of Pt. Rutherford backscattering analysis following this treatment indicated that 2.6×10^{14} Pt atoms cm^{-2} remained on the surface of the sample. Previous analysis of the corrosion of Ti suggests that only a monolayer oxide is present on Ti at potentials from -0.740 V to about -0.300 V, but at potentials above -0.300 V the surface oxide film thickens. Thus, from the electrochemical measurements on the sample shown in Fig. 2.15, one could conclude that in that system ion transport occurred in the presence of a monolayer of oxide and that, because the potential eventually reached that characteristic of pure Ti (-0.740 V), all the implanted Pt was lost. For the sample held at static potential, it is reasonable to assume that Ti ion transport occurred through a thick surface oxide film and that nearly one-half of the Pt was retained in the sample. One interpretation of these data is that a thicker surface oxide film seems to retain the Pt. More data are needed to establish this conclusion, but this work serves to illustrate the usefulness of ion implantation in understanding corrosion mechanisms.

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SURFACE SEGREGATION OF Cu AND Fe CAUSED BY PULSED LASER ANNEALING¹

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Laser annealing is a new technique for removing displacement damage and for electrically activating dopants in ion-implanted Si.³ Implanted dopant profiles for B, P, As, and Sb have been shown to undergo substantial redistribution in the absence of surface segregation as a result of pulsed laser annealing.⁴ Calculations,⁵ which compare well with measured profiles,⁴ predict melting of the crystal to a depth of several thousand angstroms and show that dopant redistribution occurs by means of diffusion in the liquid phase where diffusion coefficients are orders of magnitude higher than in the solid.

The behavior of ion-implanted Cu and Fe in Si, which is subsequently annealed using the Q-switched output of a pulsed ruby laser, is radically different than in the case of B, P, As, and Sb. Figure 2.16 shows profiles (measured by 2.5-MeV He⁺ ion backscattering) for Cu and Fe in Si in the as-implanted and laser-annealed conditions.

Annealing was carried out using a pulsed ruby laser with an energy density of 1.4 J/cm² and a pulse duration time of 20×10^{-9} sec. As shown in Fig. 2.16, pulsed laser annealing causes massive segregation of the Cu and Fe to the surface. For Cu, almost all of the impurity is found in the first 200 Å from the surface after laser annealing. The Fe profile is distinctly shifted toward the surface.

The TEM studies of the Cu-implanted, laser-annealed crystal show residual damage in the near-surface region in the form of heavily decorated dislocation tangles and precipitates. Stereomicroscopy indicates that the residual damage is largely contained in the first 200 Å. Precipitates in the regions between dislocations exhibit black-white contrast under bright- or dark-field conditions, and they have been tentatively identified as μ -CuSi precipitates.

Segregation of Cu and Fe toward the surface by pulsed laser annealing is believed to be the result of their very low distribution coefficients (defined as the ratio of concentrations in the solid and liquid phase, $k = C_s/C_l$). For Cu and Fe, the equilibrium distribution coefficients are $\ll 10^{-2}$. This value implies that the

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Fig. 2.16. Profiles for implanted Cu and Fe in Si. (a) ⁶³Cu⁺ (150 keV, 6.9×10^{15} cm⁻²) in (111) Si; (b) ⁵⁶Fe⁺ (150 keV, 4.7×10^{15} cm⁻²) in (111) Si.

dopants will be rejected to the liquid as the melt-front moves toward the surface, thus enhancing the dopant concentration in the liquid over a limited region at the solid-liquid interface. Because the surface is the last region to solidify, the enhanced concentration in the liquid is transported to the surface by the moving melt-front, and segregation occurs. The effective distribution coefficients may be significantly higher than the equilibrium values because the melt-front velocity is predicted to be >1.5 m/sec (ref. 5). Complete segregation to the near-surface region, as is the case for Cu, appears to be possible only if the rejected impurity diffuses away from the liquid-solid interface at a rate comparable to melt-front motion. Further experiments are in progress to distinguish the effects of distribution coefficients and solubility limits on the final profile distribution. In Si, Cu and Fe impurities act as very efficient recombination centers adversely affecting the minority carrier lifetime. Laser irradiation offers attractive possibilities as a rapid purification treatment to segregate these impurities to the surface where they can be removed.

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PULSED BEAM ANNEALING REDISTRIBUTION OF DOPANTS IN ION-IMPLANTED Si BY PULSED LASER ANNEALING¹

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Laser annealing of ion-implanted Si is a new technique for removing displacement damage introduced into the Si lattice by the implanted ions.⁶ The effects of laser annealing on the dopant profile distributions provide fundamental insight into the laser annealing mechanism. We have used SIMS and Rutherford backscattering to study changes in ion-implanted profiles caused by laser annealing in an effort to understand the laser annealing mechanisms.

Single-crystal Si wafers, (001) orientation, were implanted under high-vacuum conditions with ¹¹B,

³¹P, ⁷⁵As, and ¹²¹Sb ions with energies from 35 keV to 100 keV. Laser annealing was carried out in air using the Q-switched output of a pulsed ruby laser (pulse duration time of about 50×10^{-9} sec, energy density about 1.6 J/cm²). Profiles for B and P were measured using SIMS, and those for As and Sb were determined by Rutherford backscattering using 2.5-MeV He⁺ ions. Figure 2.17 compares results for B, P, and As profiles in the as-implanted and laser-annealed conditions. The as-implanted profiles in each case are very nearly Gaussian, as expected. However, laser annealing causes a substantial redistribution of the dopant so that each profile exhibits a region of relatively uniform concentration extending from the surface to a depth of 1000–2000 Å. Other measurements on these crystals by the Hall effect, TEM, and 2.5-MeV He⁺ ion channeling show that complete electrical activity is obtained after laser annealing, that high substitutionality (98–99%) of the dopant is obtained, and that no remaining extended lattice defects are present in the annealed region.

The alteration of the profiles shown in Fig. 2.17 cannot be explained as a result of solid state diffusion. However, comparison of calculations⁷ to the measured profiles⁸ indicates that the laser annealing mechanism is one in which the laser light melts the crystal to a depth of several thousand angstroms. The melted region recrystallizes by means of liquid-phase epitaxial regrowth on the underlying substrate, resulting in damage-free single-crystal material with dopants in electrically active, substitutional lattice sites. During regrowth, dopant redistribution takes place by liquid-phase diffusion. Redistribution of the dopant depends on the diffusivity in the liquid and on the time the implanted region remains in the liquid state. This time is determined primarily by the pulse energy density. In general, the laser annealing mechanism establishes a new method for crystal regrowth and impurity redistribution that can occur in a very short time (≤ 1 μ sec), making it possible to achieve a number of new and unique materials alterations.

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Fig. 2.17. Concentration profiles for implanted B, P, and As in Si.

LATTICE LOCATION OF As AND Sb IN Si AFTER PULSED LASER ANNEALING¹

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Among the most useful materials properties achievable by pulsed laser annealing of ion-implanted Si are perfect single-crystal regrowth in the implanted region and almost complete substitutionality of the dopant after annealing. In the case of As and Sb, we have used 2.5-MeV He^+ ion-channeling and ion-backscattering techniques to make quantitative measurements of the substitutional fractions for these implanted dopants in Si following laser annealing. Our results show that substitutional fractions of 98–99% are achieved for implant doses up to $\sim 1.4 \times 10^{16} \text{ cm}^{-2}$.

Silicon crystals, (001) orientation, were implanted by As or Sb ions (100-keV energy) to doses in the range 10^{15} cm^{-2} to $1.4 \times 10^{16} \text{ cm}^{-2}$. Laser annealing was carried out using a Q-switched ruby laser (pulse duration time of $50 \times 10^{-9} \text{ sec}$, energy density about 1.6 J/cm^2). Ion-channeling measurements were used to investigate the damage distribution and lattice location of the implanted species. Both aligned channeling results and detailed angular scans across the major axial directions were used in determining the substitutional fractions.

Figure 2.18 shows the backscattered energy spectra obtained with the beam aligned along the [110] axial directions of crystals implanted with ^{75}As . Spectra obtained from as-implanted and laser-annealed samples are compared to results from a virgin crystal. The annealed spectrum shown in Fig. 2.18 was from a crystal that had been annealed using two laser pulses, but similar results have been obtained after annealing with one pulse. The Si part of the as-implanted spectrum reaches the random value, showing that the crystal has been made amorphous to a depth of $\sim 1600 \text{ \AA}$ by the implant. After laser annealing, the aligned spectrum changes so that the yield is only slightly greater than that for the virgin crystal, and no evidence remains of a damage distribution. This observation shows directly that long-range single crystal order has been restored to the implanted region by the laser pulse. The low yield of particles scattered from As after laser annealing shows that As is highly substitutional in the lattice.

Angular scans across two of the major axial directions are shown in Fig. 2.19. These results were obtained by plotting the yield of ^4He ions scattered from As (solid circles) and Si (open circles) atoms in the indicated depth intervals. Yields were normalized to the random value and plotted as a function of the angle of the incident beam relative to the axial direction. The yield curves from both Si and As follow each other very

Fig. 2.18. Channeling spectra for ^{75}As -implanted Si. Fig. 2.19. Detailed angular scans for ^{75}As -implanted Si.

closely in both angular scans, again showing that As atoms are highly substitutional in the Si lattice after laser annealing. Angular scan results from crystals implanted by Sb up to doses of $1.4 \times 10^{16} \text{ cm}^{-2}$ show similar close agreement, confirming that Sb is also highly substitutional in the Si lattice.

Quantitative measurements of the substitutional fractions are tabulated in Table 2.2, which summarizes the

Table 2.2. ^{75}As (100 keV, $1.4 \times 10^{16} \text{ cm}^{-2}$) in Si

Axis	$x_{\min}(\text{Si})$ (%)	$x_{\min}(\text{As})$ (%)	Fraction substitutional (%)
[110]	2.41 ± 0.03	2.64 ± 0.15	99.76 ± 0.15
[$\bar{1}\bar{1}0$]	2.64 ± 0.02	4.72 ± 0.16	97.86 ± 0.16
[100]	3.28 ± 0.04	4.37 ± 0.11	98.87 ± 0.11
[111]	3.60 ± 0.02	4.22 ± 0.02	95.36 ± 0.19

aligned spectrum results after laser annealing from the crystal implanted by ^{75}As . Results are tabulated in terms of the minimum yield values $x_{\min}$ associated with scattering from As atoms and Si atoms with the incident beam aligned along three axial directions ([110] and [$\bar{1}\bar{1}0$] are equivalent axial directions). The minimum yield for a given axial direction is the ratio of the yield of scattered particles with the beam in the aligned direction to the yield in a random direction.

Substitutional fractions for As as measured along a given axial direction were calculated in the usual way:⁴

$$\text{fraction substitutional} = \frac{1 - x_{\min}(\text{As})}{1 - x_{\min}(\text{Si})} \times 100.$$

As shown in Table 2.2, the substitutional fractions along either of the three principal axial directions is in the range 98–99%. This value is significantly higher than the value that has been reported after thermal annealing of As-implanted Si(80–90%).⁴

Similar measurements show that Sb is also 98–99% substitutional in the lattice after pulsed laser annealing up to doses of $\sim 1.3 \times 10^{16} \text{ cm}^{-2}$. By contrast, thermal annealing results in <90% substitutionality.⁴ Clearly, a significant increase in the number of these dopant atoms incorporated in substitutional lattice sites can be achieved by using the pulsed laser annealing process. Furthermore, these levels of substitutionality are achieved even when the dopant concentration far exceeds the solid solubility limits.⁵

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RUTHERFORD ION BACKSCATTERING STUDY OF THE EFFECT OF LASER ENERGY DENSITY ON ⁷⁵As-IMPLANTED Si¹

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Pulsed laser annealing of ion-implanted Si has been shown to be capable of recrystallizing amorphous layers and incorporating dopants into solid solution.⁴ We have used 2.5-MeV He⁺ Rutherford ion-backscattering and ion-channeling techniques to investigate the effects of different laser energy densities on the damage distribution and degree of dopant substitutionality for ⁷⁵As-implanted Si crystals. Single-crystal Si, (001) orientation, was implanted by ⁷⁵As (100 keV) to doses of $1.4 \times 10^{16} \text{ cm}^{-2}$. Annealing was accomplished using the Q-switched output of a pulsed ruby laser (pulse duration of $5 \times 10^{-8} \text{ sec}$) with photon energy densities that could be varied between 0.5 and 1.5 J/cm². The damage distributions, degree of dopant substitutionality, and dopant profiles were determined by ion-backscattering and ion-channeling techniques.

Figure 2.20 shows [110] aligned backscattering-channeling results demonstrating the effects of different

Fig. 2.20. Rutherford backscattering analysis of ⁷⁵As-implanted Si (100 keV, $1.4 \times 10^{16} \text{ cm}^{-2}$), laser-annealed with different laser energy densities.

laser energy densities on the damage distribution and the degree of dopant substitutionality for As-implanted crystals. Figure 2.21 gives the dopant profiles in several of those crystals as determined from the random back-scattering spectra. The TEM studies on these same crystals are reported in another paper.⁵ The Si part of the as-implanted [110] channeling spectrum in Fig. 2.20 shows that the crystal has been made amorphous to a depth of ~ 1600 Å by the implant. Laser annealing with 0.63 J/cm^2 has no effect on the Si part of the aligned spectrum; however, a significant redistribution of As is observed in Fig. 2.21, but only in the depth interval extending from the surface to ~ 950 Å. Dopant redistribution has been shown to take place by diffusion in the liquid state,^{6,7} and, therefore, at an energy density of 0.63 J/cm^2 , the melted region appears to penetrate to a depth of only ~ 950 Å. For this sample, the crystal structure in the first 1000 Å was found to be

Fig. 2.21. Concentration profile changes as a function of laser energy density for ^{75}As -implanted Si (100 keV , $1.4 \times 10^{16} \text{ cm}^{-2}$).

small-grain polycrystalline.⁵ The polycrystallites are sufficiently small and/or randomly oriented so that the channeling spectrum appears the same as for an amorphous target. In this case, recrystallization was not epitaxial because the melted region did not penetrate to the underlying substrate. Laser annealing at 0.82 J/cm^2 considerably reduces the peak height because of Si damage distribution, but the peak width indicative of the remaining damage distribution is equivalent to that of the as-implanted spectrum. This result shows that annealing did not take place by solid phase regrowth known to proceed from the amorphous single-crystal

interface toward the surface. The change in the Si damage peak in the channeling spectrum indicates that some recrystallization has occurred over the damaged region. Annealing at both 1.07 J/cm^2 and 1.41 J/cm^2 results in a considerable reduction in the aligned yield (Fig. 2.20), and the substitutional fractions for As are 98–99% over the depth interval 300 – 2500 Å. The concentration profile measurements of Fig. 2.21 show considerably more redistribution at the higher laser energies, consistent with increased time available for diffusion in the liquid phase due to deeper penetration of the melted region. The recrystallized region of these crystals was observed to be single crystal with the same orientation as the underlying substrate,⁵ indicating epitaxial recrystallization, probably by means of liquid-phase epitaxial regrowth. There is, however, a thin layer ~ 200 Å thick with residual damage on the surface of the crystal annealed with 1.07 J/cm^2 . The presence of this damaged layer gives rise to dechanneling of the incident beam, accounting for the slight increase in the aligned yield at 1.07 J/cm^2 compared to 1.41 J/cm^2 .

We have shown that increasing laser energy density leads to deeper melt-front penetration accompanied by increasing dopant redistribution. Incorporation of As into substitutional lattice sites correlates well with the onset of liquid-phase epitaxial regrowth as inferred from channeling measurements combined with results from TEM studies.⁵

1. Summary of paper: *Journal of Applied Physics* (to be published).
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3. Guest scientist from Argonne National Laboratory, Argonne, Ill.
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DEPTH OF MELTING PRODUCED BY PULSED LASER IRRADIATION¹

Jagdish Narayan

The depth of melt-front penetration induced by a Q-switched ruby laser ($\lambda = 0.694 \mu\text{m}$) pulse has been investigated using electron microscopy for laser pulses of different duration and energy density in Si crystals diffused with P. In as-diffused specimens, dislocation loops and precipitates were distributed to a depth of about $1.0 \mu\text{m}$. The precipitates and loops were dissolved by the irradiation with Q-switched ruby laser pulses.

Dissolving of precipitates provides evidence for melting by the laser irradiation, and the depth over which precipitates are dissolved provides a measure of the melt-front penetration depth.

Silicon single crystals of (100) orientation (8 Ω -cm, *p*-type Czochralski, 500 μ m thick) were used in this study. Diffusion of P was carried out in a furnace at 1100°C for 60 min using PH₃ gas, and the crystals were then slowly cooled to room temperature. After thermal diffusion, the specimens were irradiated with Q-switched ruby laser pulses. The energy density of the laser pulse was varied from 1.5 to 3.3 J/cm², and pulse duration times of 20 and 50 nsec were used. Pulse energy density and duration were subject to about 10% error. Specimens for TEM studies were thinned chemically from the back side while masking the front surface. The depths of annealed regions were determined from thickness fringes and stereoscopic techniques.

After the thermal diffusion treatment, the Si wafers contained dislocation loops and P precipitates. Small

clusters with black-white directions always parallel to the diffraction vectors were identified as precipitates; larger images with double-arc contrast corresponded to dislocation loops. The average precipitate size and number density were determined to be 120 Å and 3.0×10^{15} cm⁻³ respectively. The average size of the dislocation loops was found to be 200 Å, and the number density was 1.0×10^{15} cm⁻³; uncertainties in the sizes and number densities were ~10%. From stereomicroscopy it was determined that the loops and precipitates were approximately uniformly distributed from the surface to a depth of about 1.0 μ m. The precipitates exhibited strain contrast corresponding to compression centers, which is expected for P precipitates. The dislocation loops were determined to be of interstitial type.

Figure 2.22 shows results of laser annealing with 50-nsec pulses, and the results are summarized in Table 2.3. One pulse ($\tau = 50$ nsec, $E = 1.5$ J/cm²) produced an annealed, defect-free region 0.29 μ m deep containing no P precipitates or loops. The depth of the annealed

Fig. 2.22. Electron micrographs (bright-field, dynamical diffraction conditions) of P-diffused specimens after irradiation with one pulse of ruby laser ($\lambda = 0.694$ μ m, $\tau = 50$ nsec).

Table 2.3. Ruby laser ($\lambda = 0.694 \mu\text{m}$) annealing parameters

Pulse energy density (J/cm^2)	Pulse duration (nsec)	Number of pulses	Depth of annealing (μm)
1.5	50	1	0.29
1.5	50	2	0.38
1.5	50	5	0.56
1.5	50	7	0.58
2.0	20	1	0.57
2.0	20	3	0.70
2.0	20	5	0.75
2.0	20	14	0.77
3.0	20	1	0.95

region was measured by stereomicroscopy and could also be directly estimated from the number of thickness fringes because the sample was wedge-shaped near the edge. The depth of the defect-free and precipitate-free region was found to be $0.38 \mu\text{m}$ after two such pulses; after seven pulses the depth was determined to be $0.58 \mu\text{m}$, which was only a small change from that observed after five pulses.

The depths of the annealed regions were similarly determined for 1, 3, 5, and 14 laser pulses of energy density $2.0 \text{ J}/\text{cm}^2$ and pulse duration 20 nsec; these results are also summarized in Table 2.3. A saturation in the annealing depth at about $0.75 \mu\text{m}$ was observed after five laser pulses. For 2.0- and $3.0\text{-J}/\text{cm}^2$ (20-nsec) laser pulses, the increase in the annealing depth (from 0.57 to $0.95 \mu\text{m}$) is approximately proportional to the pulse energy density. A complete annealing of defects up to $1 \mu\text{m}$ was possible with a pulse of $E = 3.3 \text{ J}/\text{cm}^2$ and $\tau = 20 \text{ nsec}$. The formation of a melted layer during laser irradiation is the most plausible mechanism to account for the dissolution of precipitates and dislocation loops that we observe. For precipitates with number density $3 \times 10^{15} \text{ cm}^{-3}$ and average size $120 \text{ \AA}$, the time required for dissolution in the solid state (at 1100°C) was calculated to be at least 1 min. The time required for removal of dislocation loops under similar conditions was calculated to be about 6 min. These dissolution times are unrealistically large compared to the laser pulse duration time.

The increase in the defect-free depth with increasing laser energy density is a consequence of the increased melt-front penetration at higher pulse energy densities.

The saturation in the depth of the molten layer with increasing number of laser pulses can be understood if there is a change in the absorption coefficient in the annealed layer produced by the previous laser pulse compared to that in the region containing loops and precipitates. The effect of the change in the absorption coefficient becomes smaller with increasing thickness of the previous layer, and it is negligible when this layer extends up to two to three times the absorption length. The effects of pulse duration time and energy density on molten layer thickness can also be explained by recent calculations of melt-front penetration depth.^{2,3}

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ONE-DIMENSIONAL CONTRACTION IN ION-IMPLANTED, LASER-ANNEALED Si¹

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Lattice dilations in ion-implanted and pulse-laser-annealed Si have been investigated by x-ray Bragg reflection profiles and axial ion-channeling measurements. These studies have shown that following laser annealing of B-implanted Si the lattice contraction was one-dimensional (along the surface normal).

Silicon crystals with [100] surface normals were implanted with 35-keV ^{11}B ions and subsequently laser annealed with a $1.7 \text{ J}/\text{cm}^2$ ruby laser pulse. The lattice strain was measured using the 400, 440, and $\bar{4}\bar{4}0$ x-ray Bragg reflection profiles, and axial ion-channeling (1.25-MeV He^+) measurements were used to determine the orientations of the [110] and [111] crystallographic directions in the implanted layer. The x-ray scattering geometry for crystals with thin, dilated layers is shown in Fig. 2.23. Paying attention to the detailed geometry for the 440 and $\bar{4}\bar{4}0$ reflections from both the B-doped layer and the Si substrate, the following relationships have been obtained for the components $q_{\perp}$ and $q_{\parallel}$ perpendicular and parallel to the 440 reciprocal lattice vectors respectively:

$$q_{\perp} = \frac{1}{2}(h_3 \Delta\theta_3 - h_2 \Delta\theta_2), \quad (1)$$

$$q_{\parallel} = \frac{1}{2}(h_3 \Delta\theta_3 + h_2 \Delta\theta_2) \cot \theta_B. \quad (2)$$

In these expressions, h_3 and h_2 are the reciprocal lattice vectors of the 440 and $\bar{4}\bar{4}0$ reflections as shown in Fig.

CRRM-DWG 78-4530

Fig. 2.23. Scattering geometry for the measurements in Fig. 2.24 showing the incoming and outgoing wave vectors k_0 and k in relation to the Ewald Sphere (E.S.) and indicating the symmetry of the q 's. The doped layer and lattice planes are shown schematically.

2.23, and $\Delta\theta_2$ and $\Delta\theta_3$ refer to the change in the crystal rocking angle required to obtain the Bragg reflection from the B-doped layer relative to that for the pure Si. The angle β between q and h for the 440 reflections is then

$$\beta = \tan^{-1}(q_{\perp}/q_{\parallel}). \quad (3)$$

This angle was determined directly from the x-ray profiles shown in Fig. 2.24. This figure shows the large Bragg reflection peaks from the Si substrates (which define the origin for the $\Delta\theta$ scale) and the weaker but well-resolved Bragg peaks associated with the ~ 2000 Å thick B-doped layer.² Because $\Delta\theta_2 \neq \Delta\theta_3$, it was concluded [using Eq. (3)] that the contraction of the lattice was not three-dimensional, and from the values of $q_{\perp}$ and $q_{\parallel}$ listed in Table 2.4, the angle β was found to be $\approx 45^\circ$ for B implants of 1×10^{16} and 2.5×10^{16}

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Fig. 2.24. Bragg reflection profiles for the 400, 440, and 440 reflections from B-doped Si.

Table 2.4. X-ray parameters measured on the B-doped layers

Dose cm^{-2}	Implants of $1.0 \times 10^{16} \text{ B cm}^{-2}$	Implants of $2.5 \times 10^{16} \text{ B cm}^{-2}$
$q_{\perp}, \text{\AA}^{-1}$	1.73×10^{-2}	4.53×10^{-2}
$q_{\parallel}, \text{\AA}^{-1}$	1.65×10^{-2}	4.47×10^{-2}
β, deg	45.7 ± 1.5	45.2 ± 1.5
$\frac{\Delta d}{d}(400)$	-0.55×10^{-2}	-1.32×10^{-2}

B cm^{-2} . This result indicates the contraction to lie along the [100] surface normal for both the lower and higher doses and demonstrates that the dilatation is only one-dimensional.

The ion-channeling measurements of the crystal directions in the implanted layer provide an independent

method of verifying this conclusion. These measurements, which were made on the higher dose sample, have shown that there are rather large deviations (28) in the angles between opposite [110] and [111] directions in the B-doped layer compared with those for crystals having cubic symmetry. As listed in Table 2.5, these deviations from cubic symmetry agree well with the deviations calculated assuming a one-dimensional contraction. The magnitude of the contraction used in the calculation was taken from the lattice parameter change of the 400 planes determined by the x-ray measurements and listed in Table 2.4. The one-dimensional

Boron-implanted (1×10^{16} B cm $^{-2}$), laser-annealed Si crystals with [100] surface normals were used for this study in which the B-doped (and hence strained) region penetrated ~ 0.3 – 0.4 μ m below the surface as determined by SIMS measurements.² The 400 C α K α Bragg reflection profiles were measured on the B-doped Si, and the data were analyzed using the lattice parameter change in Si per unit concentration of substitutional B and the previously established fact that the lattice strain in the laser-annealed crystals is only one-dimensional.³ This analysis leads to the following relationship between the lattice strain ϵ and the B concentration C :

$$\epsilon = 8.85 \times 10^{-24} C. \quad (1)$$

Table 2.5. Channeling measurements of the angles between crystal axes in the high-dose, B-doped layer

	Angles between crystal axes in the implanted layer	
	(110), (110)	(111), (111)
Measured	90.76°	111.17°
Cubic	90.00°	109.47°
2 ϵ ^a	0.76°	0.70°
2 δ ^b	0.76°	0.72°

^aMeasured.

^bCalculated.

nature of the contraction implies the absence of interfacial dislocations that would degrade the electrical properties of the implanted B.²

Using Eq. (1) and the depth profile of the B concentration as determined by the SIMS technique, the x-ray reflectivities at the 400 reflection were calculated and found to be in disagreement with the measured data. On the other hand, x-ray reflectivities calculated under the assumption that the B concentration was a uniform factor of 1.6 times higher than that reported by the SIMS measurement indicated good agreement with the measured diffraction profiles.

This result indicates that the strain profile has the same shape as the B concentration profile in the laser-annealed specimens, but the 1.6 times higher B concentration required to fit the measurements suggests the need for a closer examination of either the x-ray parameters or the B implant dosimetry. This point could be of some significance in light of the factor of 1.5 higher carrier concentration measured on these samples relative to the B concentrations thought to have been implanted.²

1. Summary paper: *Appl. Phys. Lett.* 32, 801 (1978).
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X-RAY DETERMINATION OF THE STRAIN PROFILE IN ION-IMPLANTED, LASER-ANNEALED Si

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Taupin's dynamical diffraction treatment of the scattering from deformed crystals has been used to analyze quantitatively the strain profile in B-implanted, laser-annealed Si.¹ This theory provides a differential equation through which the x-ray intensity diffracted from a crystal with a varying lattice parameter may be calculated and compared directly with scattering intensities measured on crystals with nonuniform strains.

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ENHANCED SOLUBILITY FOR Sb IN Si BY PULSED LASER ANNEALING¹

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Pulsed laser annealing has been found capable of incorporating dopants into substitutional solid solution at concentrations that far exceed the solubility limit.⁴ We have performed systematic studies of this effect in the Sb-Si system because Sb can readily be detected in

Si by Rutherford backscattering and because the fraction of dopant atoms occupying substitutional lattice sites can be measured by ion-channeling techniques.

Single-crystal Si, (001) orientation, was implanted with ^{121}Sb (100 keV) to doses in the range 10^{15} to $3 \times 10^{16} \text{ cm}^{-2}$. Annealing was accomplished using the Q-switched output of a ruby laser (pulse duration time of $60 \times 10^{-9} \text{ sec}$, energy density about 1.6 J/cm^2). Substitutional fractions were measured by ion-channeling techniques using 2.5-MeV He^+ ions, and dopant profiles were determined using reference random Rutherford backscattering spectra.

Table 2.6 summarizes data used to determine substitutional fractions for Sb in crystals implanted with doses in the range 2×10^{15} to $1.8 \times 10^{16} \text{ cm}^{-2}$.

Table 2.6. ^{121}Sb (100 keV) in Si, $[1\bar{1}0]$ aligned results

Dose (cm^{-2})	$\chi_{\min}(\text{Si})$ (%)	$\chi_{\min}(\text{Sb})$ (%)	Fraction substitutional (%)
Virgin crystal	2.23 ± 0.03		
2.34×10^{15}	2.16 ± 0.05	3.07 ± 0.28	99.07 ± 0.29
7.47×10^{15}	2.41 ± 0.05	3.14 ± 0.14	99.25 ± 0.14
1.34×10^{16}	4.14 ± 0.06	6.04 ± 0.14	98.02 ± 0.15
1.84×10^{16}	10.51 ± 0.17	22.02 ± 0.43	87.20 ± 0.45

Results are tabulated in terms of the $\chi_{\min}$ values associated with scattering from Si and Sb in the depth interval from 400–2500 Å with the incident beam aligned along the $[1\bar{1}0]$ axial direction. The value $\chi_{\min}$ is the ratio of scattered ion yield for the aligned direction to the yield obtained with the beam incident in a random direction. The Sb substitutional fraction for each crystal is tabulated in the last column. Substitutional fractions were calculated in the usual manner:⁵

$$\text{fraction substitutional} = \frac{1 - \chi_{\min}(\text{Sb})}{1 - \chi_{\min}(\text{Si})} \times 100.$$

For doses less than 10^{16} cm^{-2} , the $\chi_{\min}$ values for Si and Sb are low, and the substitutional fractions are very high (~99%). For the two high-dose cases, the $\chi_{\min}$ results are significantly higher, but the substitutional fractions are still reasonable (98% and 87%). The increased $\chi_{\min}$ values are directly related to a damaged

layer that, as observed by TEM, extends from the surface to a depth of ~300 Å and contains precipitates at dislocation loops and dislocation tangles. This damaged layer at the surface causes dechanneling of incident ions that subsequently scatter from greater depths in the crystal.

The very high substitutional fractions of Sb (98–99%) for doses up to $\sim 1 \times 10^{16} \text{ cm}^{-2}$ are achieved even though the Sb concentration far exceeds its limit of solid solubility in Si. Profile measurements^{4,6} on these crystals have shown that the Sb concentration in substitutional lattice sites extends up to $1 \times 10^{21} \text{ cm}^{-3}$ after laser annealing, whereas the limit of solid solubility at the melting point is $\sim 4 \times 10^{19} \text{ cm}^{-3}$. Therefore, laser annealing is capable of incorporating dopants into substitutional lattice sites at concentrations much greater than the solubility limit. The pulsed laser annealing mechanism is pictured as one in which the incident laser light causes the first few thousand angstroms of the crystal to be melted.^{6,7} The melted region then recrystallizes epitaxially from the underlying substrate by means of liquid-phase epitaxial regrowth. During regrowth, dopants are incorporated into the solid at concentrations determined by the concentration in the liquid at the moving liquid-solid interface. This regrowth results in defect-free single-crystal material with dopants in substitutional lattice sites. The time required for recrystallization is of the order of a few hundred nanoseconds,^{6,7} and the surface region then cools rapidly toward ambient temperature in a few microseconds. Presumably this time is too short for the formation of precipitates in the solid phase. Precipitation will occur, however, if the laser-annealed crystals are subjected to subsequent thermal annealing (900°C for 30 min).⁸ At the very high doses, precipitation, which is observed in the near-surface region after laser annealing, may be related to the dopant concentration exceeding the solubility limit in the liquid during annealing. This possibility is currently under further investigation.

1. Summary of paper: *Journal of Applied Physics* (to be published).

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COMPARISON OF LASER AND ELECTRON BEAM ANNEALING OF As-IMPLANTED Si¹

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Recent extensive measurements have shown that pulsed laser annealing is a valuable complement to ion implantation doping of Si and that these combined techniques can achieve a variety of unique materials alterations.³⁻⁷ The advantages of pulsed laser annealing result from the rapid melting and cooling of the near-surface region of the solid.^{3,4} An alternate annealing technique that potentially offers many of the same advantages is pulsed electron beam annealing.⁸ Because it is our intention to extend pulsed, near-surface annealing studies to a variety of materials and because electron beam annealing techniques offer distinct advantages over lasers for some materials applications, an investigation has been initiated to characterize both electron beam and laser annealing on a common system. In this report, we have used ion channeling, ion backscattering, and TEM to compare results of pulsed laser and electron beam annealing of ⁷⁵As-implanted Si single crystals.

Silicon single crystals of (100) orientation were implanted in a random direction with 100-keV ⁷⁵As to a dose $\sim 1 \times 10^{16}$ As cm⁻². Some of the samples were laser annealed in air using the Q-switched output of a ruby laser (0.694- μ m wavelength, pulse duration of 50×10^{-9} sec). The energy densities were varied from 0.6

to 3.0 J/cm², and best annealing results were obtained for laser energy densities between 1.5 and 1.7 J/cm². Companion samples were annealed in a vacuum of 5×10^{-5} torr, using the SPIRE Corporation SPI-PULSE 5000 electron beam generator.⁸ For the lowest electron beam doses, incomplete annealing occurred, and for the highest dose, the surfaces of the silicon crystals were damaged. Best annealing results occurred for electron beam fluences between 1.1 and 1.2 J/cm² (mean energy 12 keV, pulse half-width 50 nsec). Dopant profiles before and after annealing were determined from 2.5-MeV ⁴He⁺ ion-backscattering analysis. Pulsed electron beam annealing caused substantial redistribution of the implanted As with a final distribution essentially the same as obtained from laser annealing.³ (Dopant concentrations are uniform to a depth ~ 1200 Å and then decrease exponentially.) Consequently, the redistribution mechanism (diffusion in the melted surface) is probably the same.^{3,4}

The degree of substitutionality of the implanted As and the amount of residual damage to the Si lattice were determined from ion-channeling measurements and detailed angular scans along the major axial directions ([100], [110], and [111]). Details of the nature of the radiation damage were determined from TEM measurements. Typical backscattering-channeling results for a ⁷⁵As-implanted Si crystal before and after electron beam annealing are compared in Fig. 2.25 to measurements from a virgin Si crystal. These measurements

Fig. 2.25. Comparison of 2.5-MeV He ion scattering-channeling spectra for As-implanted Si (1.1×10^{16} ⁷⁵As atoms cm⁻², 100 keV) electron beam annealed, and a virgin Si single crystal.

were made with 2.5-MeV He⁺ ions incident parallel to the [110] axial directions. They show that the implantation process has damaged the single crystal to a depth ~1400 Å. Following electron beam annealing, the scattering yields are nearly the same as that of the virgin single crystal. TEM studies of the electron-beam-annealed sample show that essentially no damage remained in the implanted region, again analogous to the laser-annealed samples. Results from aligned channeling measurements for the major axes showed that the minimum yields (ratio of scattered ion yield with the beam incident parallel to an axis to the yield for random incidence) for ions scattered from As were nearly the same as for those scattered from Si atoms. Furthermore, detailed angular scans showed that the As and Si yields were nearly identical for all axes, indicating that the As atoms occupied substitutional lattice sites. The substitutional fractions extracted for the electron-beam-annealed sample are tabulated in Table 2.7 along with the measured minimum yields. The results for a comparable laser-annealed sample are included in parentheses for comparison.

Table 2.7. ⁷⁵As (100 keV, $1.1 \times 10^{16} \text{ cm}^{-2}$) in pulsed electron-beam-annealed Si compared to ⁷⁵As (100 keV, $1.4 \times 10^{16} \text{ cm}^{-2}$) in laser-annealed Si

Laser-annealed values designated in parentheses

Axis	$x_{\min}(\text{Si})$ (%)	$x_{\min}(\text{As})$ (%)	Fraction substitutional ^a (%)
[110]	3.6 (2.4)	6.1 (2.6)	97.4 (99.8)
[110]	3.2 (2.5)	5.7 (4.7)	97.4 (97.9)
[100]	3.5 (3.3)	4.8 (4.4)	98.6 (98.9)
[111]	4.1 (3.6)	6.2 (4.2)	97.8 (99.4)

$$^a \text{Fraction substitutional} = \frac{1 - x_{\min}(\text{As})}{1 - x_{\min}(\text{Si})} \times 100.$$

Our conclusions from this preliminary comparison of electron beam annealing to laser annealing are that in the best case the electron beam annealing gave results nearly identical to those of laser annealing. There were some significant deviations for some electron-beam-annealed samples (e.g., incomplete and/or nonuniform annealing and surface cracking), but these may be attributable to experimental difficulties in the early stage of the electron beam annealing studies. Further

work is now in progress to optimize the electron beam technique and to extend it to metals. Overall, the present comparison offers great promise for future use of pulsed annealing techniques in processing Si. Both electron beam and laser annealing achieve desirable end results, and the two technologies should cover processing requirements from rapid microbeam annealing (lasers) to large area array production annealing (electron beam).

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TEM STUDIES OF LASER AND THERMAL ANNEALING OF ION-IMPLANTED Si¹

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Ion implantation offers several advantages over the conventional thermal diffusion method as a means of fabricating junctions. The disadvantage of the ion implantation process is that the high-energy ions create lattice damage in the implanted region, resulting in a low carrier lifetime and high sheet resistance. High-temperature annealing is then used to eliminate the damage and recover lifetime and carrier concentration. During the high-temperature treatment of the specimens, the degradation of electrical properties such as minority carrier diffusion length occurs because of contamination and/or thermally induced generation of defects.

Recent work has established that laser annealing can lead to complete recovery of the electrical properties in the implant region without affecting the underlying substrate material. In this study, microstructural aspects of laser annealing have been investigated using electron microscopy. The present summary principally covers the progression of the research from the initial observations on B-implanted Si and extension to additional ion

implant species and to more detailed studies of the energy density dependence of the laser annealing process in Si.¹

Single crystals of Si with (100) faces were implanted with B ($^{11}\text{B}^+$, 35 keV), P ($^{31}\text{P}^+$, 80 keV), As ($^{75}\text{As}^+$, 100 keV), and Sb ($^{121}\text{Sb}^+$, 100 keV) ions near room temperature; ion doses varied from 10^{15} to 2.5×10^{16} ions cm^{-2} . A vacuum of about 2×10^{-8} torr was maintained in the chamber during the implantation. The implanted specimens were treated with pulses from a ruby laser ($\lambda = 0.694 \mu\text{m}$) operated in the Q-switched mode (pulse duration of 20×10^{-9} to 60×10^{-9} sec) with energy densities from 0.6 to 3.0 J/cm^2 . For these conditions the laser effects were essentially confined to the ion implant layers without adverse effect on the electrical characteristics of the substrate. Isochronal annealing of some ion-implanted specimens was carried out at temperatures from 600 to 1100°C in a flowing purified He atmosphere.

Figure 2.26 shows a comparison of laser and thermal annealing in B-, P-, and As-implanted Si. In this laser annealing, pulses with an energy density of 1.5 J/cm^2 and a duration of $\tau = 50 \times 10^{-9}$ sec were used. No damage in the form of dislocations, dislocation loops, and/or stacking faults was observed in the ion-implanted, laser-annealed specimens. In the thermally annealed specimens (even after annealing at 1100°C for 30 min), a significant amount of damage was observed in the form of dislocation loops in the implanted layer, and in certain cases there was a grid of dislocations near the junction. These microstructural features in laser and thermally treated specimens were reflected in the electrically active carrier concentration. The laser-annealed specimens showed complete recovery of electrical activity, but only partial electrical activity was recovered in thermally annealed specimens. The concentration of dopants in solution, as inferred from electrical measurements, could exceed the equilibrium solubility limits. In laser-treated specimens, whenever the implanted doses were in excess of the equilibrium

solubility limits, precipitation of dopants occurred on subsequent thermal annealing at temperatures above 600°C .

The study of the annealing as a function of the energy density of single laser pulses (50×10^{-9} sec) indicated that there is a threshold value of about 1.1 J/cm^2 above which complete annealing of the damage and recovery of the electrical properties is realized. Below this value, incomplete annealing occurs and only partial recovery of electrical activity is obtained. For the case of As-implanted Si, a 0.63 J/cm^2 pulse led to a polycrystalline layer $1000 \pm 200 \text{ \AA}$ thick with a $400\text{--}600 \text{ \AA}$ amorphous layer (unannealed ion damage) between it and the single-crystal substrate. When the energy density was increased to 0.82 J/cm^2 , the amorphous layer was eliminated and only a polycrystalline layer of larger average grain size was observed. Further increase of the energy density to 1.07 J/cm^2 led to complete return of the implant layer to the substrate crystal orientation but with residual damage in the form of dislocation tangles present in a region about $200 \text{ \AA}$ thick near the free surface. For higher energy density pulses, only complete annealing was observed. These observations correlate well with electrical measurements that indicated partial recovery of the electrical properties below $\sim 1.1 \text{ J/cm}^2$ and complete recovery above this value. The progressive changes of structure with energy density were interpreted as resulting from partial melting of the implant region at the lower energy densities; complete penetration of this region by the melt front was at 1.1 J/cm^2 . A similar threshold for complete annealing was also found for the B, P, and Sb implants.

1. Summary of papers: J. Narayan, R. T. Young, and C. W. White, *J. Appl. Phys.* **49**, 3912 (1978); J. Narayan, R. T. Young, and C. W. White, *J. Electrochem. Soc.* **78**, 466 (1978); and J. Narayan, C. W. White, and R. T. Young, "Proceedings of International Conference on Ion Beam Modification of Materials," *Radiation Effects* (to be published).

Fig. 2.26. Transmission electron micrographs taken after laser (pulse energy density 1.5 J/cm^2 , duration $50 \times 10^{-9} \text{ sec}$) annealing (left row) and thermal annealing (right row) of Si [(001) orientation] implanted with $^{11}\text{B}^+$ (35 keV, $3 \times 10^{15} \text{ cm}^{-2}$), top; $^{31}\text{P}^+$ (30 keV, $1 \times 10^{15} \text{ cm}^{-2}$), middle; and $^{75}\text{As}^+$ (100 keV, $1 \times 10^{16} \text{ cm}^{-2}$), bottom. Thermal annealing conditions for the B- and P-implanted specimens were 30 min at 1100°C and for the As-implanted specimen, 30 min at 900°C .

RAMAN SCATTERING FROM B-IMPLANTED, LASER-ANNEALED Si

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Recent work has demonstrated that annealing of ion-implanted semiconductors by laser irradiation offers a number of advantages over thermal annealing. Among these are the avoidance of heating of the substrate, a greater reduction of lattice damage, and the achievement of a higher concentration of electrically active impurities. Young et al. have examined thermally annealed and laser-annealed B-implanted Si using a variety of experimental techniques.¹ Although their results showed a greater electrical conductivity in the laser-annealed samples, the interpretation of their Hall effect measurements was somewhat ambiguous. They found the utilization coefficient, defined as the ratio of electrically active B, N_s , to the total implanted dose, D , to be greater than one (i.e., $N_s/D = 1.5$). To obtain an additional determination of the B concentration, inelastic light-scattering measurements were undertaken.

Raman spectra were taken using an Ar ion laser as a light source and photon counting electronics. A Hewlett-Packard 9825A programmable calculator was used both for digital data acquisition and for control of the spectrometer. To facilitate comparison with other work in the literature, all data were taken for sample temperatures of about 77 K.

Figure 2.27 shows a comparison of the Raman spectra of ion-implanted samples that were (a) unannealed, (b) thermally annealed, and (c) laser annealed. The Si optic mode is visible as the large peak at 523.5 cm^{-1} . The spectrum of the unannealed sample [Part (a)] shows a rather intense background due to first-order scattering induced by lattice damage. This scattering, which is most intense for energy shifts near 480 cm^{-1} , reflects the peak in the Si phonon density of states. The Si optic mode remains visible because the laser beam samples the undamaged region of the crystal in addition to the damaged region. Parts (b) and (c) of Fig. 2.27 show the spectra of thermally annealed and laser-annealed samples. In both spectra the local vibrational mode of substitutional B atoms is visible at 620 cm^{-1} . Both spectra also show a reduction in background scattering due to lattice damage. However, significant differences between curves (b) and (c) are apparent. The optic mode of the thermally annealed sample is quite broad in comparison to that of either the pure Si or the laser-annealed sample. The optic mode of the laser-annealed sample shows a pronounced shoulder on the low-energy

Fig. 2.27. Raman spectra of ^{11}B -implanted Si (35 keV) at $T \approx 77 \text{ K}$ after (a) no annealing, (b) thermal annealing, and (c) ruby laser annealing. The Si optic mode is at 523.5 cm^{-1} , and the B local mode is at 620 cm^{-1} . Data points were taken every 2 cm^{-1} . The laser output was 620 mW at 488.0 nm .

side. Both of these effects were analyzed assuming a Fano-type interaction between the discrete Si optic mode state and the continuum valence band electronic states.

The presence of B acceptor levels makes possible electronic Raman scattering due to transitions from the light to the heavy-hole valence band. In Si the optic mode energy falls within the allowed range of energies for electronic Raman scattering. The result is an interference between the discrete optic mode state and the continuum heavy-hole band states. Such an interaction is of the type first analyzed by Fano,² and Cerdeira, Fjeldly, and Cardona have adapted the Fano theory to the case of B-doped Si.³ They found that the experimentally observed spectra for B-doped samples are given by

$$I(\omega) = \text{const} \times n(q + \epsilon)^2 / (1 + \epsilon^2). \quad (1)$$

where q is related to the ratio of the strengths of one phonon and electronic Raman scattering and $\epsilon = (\omega - \Omega - \delta\Omega)/\Gamma$. In this equation, ω is the frequency shift of the scattered light, Ω is the optic mode frequency of the pure crystal, and Γ and $\delta\Omega$ are related to the strength of the optic mode, band state interaction.

In the case of ion-implanted Si, Eq. (1) requires modification because the B concentration is not constant as a function of depth. For a laser-annealed sample implanted with a similar dose, a SIMS profile showed that the B concentration was highest at the surface, decreased gradually to a depth of about 0.2 μm , and then decreased more rapidly reaching a negligible value for depths greater than 0.5 μm . The SIMS profile was used to construct a function $v(x)$ so that the concentration as a function of depth x in centimeters was

$$N(x) = n_0 v(x), \quad (2)$$

where $v(x = 0) = 1.00$ and $v(x > 0.5 \mu\text{m}) = 0$. Then the total intensity was found by integrating over the depth of the surface layer:

$$I(\omega) = \text{const} \times n_0 \int_0^\infty v(x) (q + \epsilon)^2 / (1 + \epsilon^2) dx. \quad (3)$$

Figure 2.28 shows the experimental points and fitted curve (solid line) for the laser-annealed sample measured at 75 K using the 457.9-nm Ar laser line. The Fano contribution yielded a value of peak B concentration of

$n_0 = 3.82 \times 10^{20} \text{ cm}^{-3}$. The total surface concentration was calculated by numerically integrating the SIMS profile:

$$N_s = n_0 \int_0^\infty v(x) dx. \quad (4)$$

N_s was found to be $8.92 \times 10^{15} \text{ cm}^{-2}$, in excellent agreement with the total implanted dose of $D = 10^{16} \text{ B cm}^{-2}$, a number thought to be accurate to about 10%. One finds the utilization coefficient to be $N_s/D = 0.89 \pm 0.09$, a more reasonable figure than the anomalously large value of 1.5 found by Young et al. from Hall-effect measurements.¹

Fig. 2.28. Silicon optic mode for laser at 457.9 nm at a power of 300 mW. Solid line shows theoretical fit. Dashed line shows Fano contribution of Eq. (3); dot-dashed line shows Lorentzian contribution due to scattering from regions of the crystal where B concentration is zero.

A similar analysis was attempted for the thermally annealed sample, but good fits were not obtained, and the measured value of the B concentration was too low. These results are probably due to residual lattice damage in the sample. Measurements of the strength of the B local mode at 620 cm^{-1} for various wavelengths

of the laser used to excite the Raman spectrum indicated that more of such damage remains in the thermally annealed sample than in the laser-annealed sample.

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3. F. Cerdeira, T. A. Fjeldly, and M. Cardona, *Phys. Rev. B* 8, 4734 (1973).

LASER ANNEALING OF Mg-ION-IMPLANTED GaAs

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Ion implantation has proved to be a successful technique for doping semiconductors. However, thermal annealing needed to remove displacement damage and electrically activate the dopants presents a more complex problem for GaAs than for Si. On heating above about 200°C, GaAs starts decomposing because of the high vapor pressure of As. Various solutions to this problem such as hot implantation and "capping" (with SiO₂ or Si₃N₄) annealing have been tried. Hot implantation offers only limited success, and encapsulation, besides being cumbersome, causes strains in the GaAs on heating due to differential thermal expansion. In this investigation we have shown that laser pulses obtained from a Q-switched ruby laser ($\lambda = 0.694 \mu\text{m}$) can be used to anneal out the displacement damage and consequently electrically activate the dopant in ion-implanted GaAs.

Gallium arsenide samples (<100> orientation, 0.1 $\Omega\text{-cm}$, *n*-type) were implanted with 35-keV ²⁴Mg⁺ ions to a dose of $1.0 \times 10^{15} \text{ cm}^{-2}$. A vacuum of 2×10^{-8} torr was maintained during the implantation. Laser annealing was accomplished using the single pulse of a Q-switched ruby laser ($\lambda = 0.694 \mu\text{m}$) with a pulse duration of 50×10^{-9} sec. The energy density of the laser pulse was varied from 0.3 to 0.9 J/cm². After the laser annealing, the specimens were divided into three parts for study with electron microscopy, electrical measurements, and SIMS techniques. Samples for TEM were prepared by a chemical polishing from the back side while masking the front side.

Results from TEM are shown in Fig. 2.29. At a laser pulse energy of 0.31 J/cm², residual damage in the form of dislocation loops and tangles is observed as shown in Fig. 2.29a. No polycrystalline regions were found, and the implanted layer had the same <100> orientation as the underlying substrate. When the energy density of

the laser pulse was increased to 0.68 J/cm², no damage in any form (defect clusters, precipitates, or stacking faults) was observed, as shown in Fig. 2.29b. The diffraction pattern of the implanted layer in Fig. 2.29c shows that it has <100> orientation, the same as the substrate. The sharpness and regularity of the diffraction spots in Fig. 2.29c are also indicative of the perfection of the lattice. Electrical measurements² on the specimens irradiated with 0.68 J/cm² indicated a recovery of about 90% and less than 40% recovery for the specimens irradiated with pulses of 0.31 J/cm². These measurements indicate a threshold in the energy density of the laser pulse, above which complete annealing of displacement damage occurs similar to results that have been obtained in Si.

Dopant profiles obtained from SIMS techniques are shown in Fig. 2.30. The as-implanted profile has a Gaussian shape as expected, whereas the Mg ion profile after laser annealing is uniform near the surface. Changes in the dopant profiles cannot be accounted for by diffusion in the solid state but are consistent with diffusion in the liquid phase for time intervals of the order of the laser pulse duration.

1. Analytical Chemistry Division, ORNL.

2. J. Narayan, C. W. White, and R. T. Young, in *Proceedings of the International Conference on Ion Beam Modification of Materials*, Budapest, Hungary, September 4-8, 1978 (in press).

PHOTOVOLTAIC CONVERSION OF SOLAR ENERGY

SOLAR CELLS FROM ION-IMPLANTED, LASER-ANNEALED Si

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Although a number of studies¹ have indicated that ion implantation techniques are potentially economically competitive with conventional diffusion techniques for the automated production of solar cells, important problems associated with the fabrication of implanted cells still remain. The most difficult one is associated with removing the lattice damage that accompanies the implantation process. Conventional one-step furnace annealing, aside from its slow processing, cannot satisfactorily remove the lattice damage, and consequently a low open-circuit voltage (V_{oc}) is

Fig. 2.29. Electron micrographs showing residual damage in GaAs below and above the threshold energy. (a) Bright field at $E = 0.31 \text{ J/cm}^2$, the residual damage in the form of dislocation loops and tangles is observed; (b) bright field at $E = 0.68 \text{ J/cm}^2$, showing a complete annealing of defects; and (c) selected area diffraction pattern corresponding to the area in Part (b).

Fig. 2.30. Magnesium ($^{24}\text{Mg}^+$) concentration as a function of depth.

obtained. Although more complicated multistep annealing improves cell characteristics, it further slows the processing. Also, high-temperature treatments of the cells usually cause reduction of minority carrier diffusion length in the substrate, thus reducing the short-circuit current I_{sc} . Pulsed laser annealing avoids these problems by completely annealing the damaged layer without affecting the minority carrier diffusion length in the substrate. Details of the laser annealing of ion-implanted silicon can be found elsewhere in this report.²

Both n^+pp^+ and p^+nn^+ cells have been fabricated with the emitter regions doped by ion implantation and back-surface fields formed by either electron-beam evaporation of a thin Al film or by ion implantation. Laser annealing of both sides of the cells was performed in air by using a Q-switched ruby laser operating in a multimode condition.

The quality of the junction formed in ion-implanted, laser-annealed Si can be obtained from the dark I-V characteristics of mesa diodes; an example is shown in Fig. 2.31. The forward I-V curve follows closely the

Fig. 2.31. Junction characteristics of a typical laser-annealed, B-implanted mesa diode.

ideal-diode equation with diode-perfection factor $A = 1.22$, which indicates that recombination effects are greatly reduced in the space charge region. The low value of the reverse current measured at -0.5 V reveals a small leakage current. This result indicates that a good junction can be formed by pulsed laser annealing. Spectral response curves of B-implanted, laser- and thermally annealed cells are shown in Fig. 2.32. For comparison, the results for the best cell fabricated from a sophisticated B diffusion process reported by Bae and D'Aiello³ of RCA Laboratory is also included. The quantum efficiency of the laser-annealed cell is consistently higher than that of the thermally annealed cell throughout the entire solar spectrum, which indicates

Fig. 2.32. Comparison of quantum-efficiency spectra of laser-annealed, thermally annealed, and B-diffused (RCA) cells.

that the collection efficiency of the photogenerated minority carriers is better both in the emitter and in the base region of the laser-treated cells. However, the spectral response of the laser-annealed cell is substantially lower than that of the diffused cell from RCA, especially in the short-wavelength region (0.4–0.5 μ), which may be due to two reasons. First, the laser-annealed cell had a deep junction ($\sim 0.7 \mu$), as compared with the shallow junction (0.15μ) in the RCA cell. Second, any laser-induced surface damage in the form of microcraters may give rise to a high surface recombination velocity. The typical AM1 cell parameters of both n^+p and p^+n cells are given in Table 2.8.

The RCA cell is also included for comparison. This table shows that not only is I_{sc} somewhat low but also that V_{oc} has not reached its optimum value. To do research on homogenizing the laser beam and on finding the best annealing and implant parameters to reach the optimum I_{sc} and V_{oc} values is our immediate goal in developing high-efficiency, laser-annealed, ion-implanted solar cells.

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2. R. T. Young et al., "Characteristics of Ion-Implanted, Laser-Annealed Si," and J. C. Wang, R. F. Wood, and P. P. Pronko, "Theoretical Analysis of Thermal and Mass Transport in Ion-Implanted, Laser-Annealed Si," this report.

3. M. S. Bae and R. V. D'Aiello, *Appl. Phys. Lett.* 31, 285 (1977).

CHARACTERISTICS OF ION-IMPLANTED, LASER-ANNEALED Si¹

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Recently, pulsed laser radiation has been explored as an alternative annealing technique to remove the lattice damage from ion-implanted Si. The laser annealing characteristics of B-, As-, P-, and Sb-implanted Si have been studied by electrical measurements (Hall effect and surface photovoltage), TEM, ion channeling, and SIMS. Laser annealing used the Q-switched output of a ruby laser ($\lambda = 0.694 \mu$, pulse duration = 30–50 nsec) with an energy density of 1.2–1.7 J/cm².

Table 2.9 shows results for laser- and thermally annealed, B-implanted samples in terms of carrier concentration (N_s), carrier mobility (μ), and sheet resistivity (ρ_s) in the implanted layer as determined by van der Pauw measurements. The ratio of Hall mobility to drift mobility was taken to be 1.0 in these heavily doped samples. The utilization coefficient, defined as

Table 2.8. Solar cell parameters under AM1 illumination

Cell	Front	Back	ρ_s ($\Omega/\square$)	V_{oc} (mV)	I_{sc} (mA/cm ²)	FF	η (%)
1	As ⁺ (5 keV, 2×10^{15})	Al (100 Å)	60	565	33.0	0.73	13.6
2	B ⁺ (5 keV, 2×10^{15})	None	55	550	31.5	0.72	12.5
RCA	Boron diffusion	p ⁺		600	37.1	0.76	17.0

Table 2.9. Comparative data on electrical parameters of 35-keV B implanted in 80- Ω -cm *n*-type Si

Sample	Implanted dose D (cm^{-2})	Laser annealing					Thermal annealing ^a				
		N_s (cm^{-2})	μ ($\text{cm}^2/\text{V}\cdot\text{sec}$)	ρ_s ($\Omega/\square$)	L (μm)	N_s/D	N_s (cm^{-2})	μ ($\text{cm}^2/\text{V}\cdot\text{sec}$)	ρ_s ($\Omega/\square$)	L (μm)	N_s/D
2	4.2×10^{14}	5.0×10^{14}	54	230	340	1.2	3.3×10^{14}	80	238	45	0.79
3	1.0×10^{15}	1.5×10^{15}	41	102	295	1.5	9.2×10^{14}	59	116	40	0.92
4	5.0×10^{15}	7.5×10^{15}	35	24	275	1.5	4.4×10^{15}	45	31	45	0.88
5	1.0×10^{16}	1.5×10^{16}	31	13	350	1.5	9.5×10^{15}	38	18	35	0.94
6	2.5×10^{16}	3.8×10^{16}	30	4.3		1.5	1.4×10^{16}	40	11	30	0.56

^a1100°C for 30 min.

the ratio of N_s to the implanted dose D , is also given. Table 2.9 shows that laser annealing provides better recovery of the electrical activity with little or no degradation of the minority carrier diffusion length (L). The control samples have L in the range 350–450 μm . Thermal annealing at a temperature of 1100°C reduces L by a factor of 5 or more. The carrier mobilities in the laser-annealed and the thermally annealed layers are in satisfactory agreement, allowing for a decrease of mobility with an increase in ionized-impurity concentration. A surprising result is that the utilization coefficient reaches 1.5 in the higher dose, laser-annealed samples, and this cannot be explained by the non-uniform distribution of carrier densities and mobilities in the implanted layer.

To compare the damage remaining in the B-implanted Si subjected to laser and thermal annealing, studies were made with TEM and ion channeling. Figure 2.33 compares the laser-annealed (*a*, *b*, and *c*) and thermally annealed (*d*) samples. As shown in Fig. 2.33 (*a* and *b*), the implanted, laser-annealed samples have no damage remaining in the form of dislocations, stacking faults, or dislocation loops to a resolution of ~ 10 Å. The regularity of an electron diffraction pattern (Fig. 2.33*c*) further confirms the perfection of the lattice of the implanted layer after laser annealing. In contrast, massive damage remains in the implanted, thermally annealed specimen (Fig. 2.33*d*) in the form of dislocation loops with an average loop size of ~ 250 Å and density of $1.0 \times 10^{16} \text{ cm}^{-3}$. The large loops (>150 Å) that were analyzed were interstitial. These results were also confirmed by ion channeling studies.

The effects of laser annealing on the dopant distribution were studied by the SIMS technique. Figure 2.34 shows the measured B profiles. Laser annealing obviously produces pronounced changes in the implanted

profile distribution. The mechanism by which laser radiation induces the substantial dopant diffusion is discussed elsewhere in this report.⁶

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6. J. C. Wang, R. F. Wood, and P. P. Pronko, "Theoretical Analysis of Thermal and Mass Transport in Ion-Implanted, Laser-Annealed Si," this report.

***p-n* JUNCTION FORMATION AND SOLAR CELLS FROM B-DEPOSITED Si by LASER-INDUCED DIFFUSION¹**

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Conventional thermal diffusion and ion implantation of dopants followed by high-temperature annealing are the two main techniques currently used for forming *p-n* junctions in semiconductors. Both techniques involve high-temperature treatment for sufficiently long times that the degradation of the minority-carrier lifetime in the base region becomes a serious problem. The minority-carrier diffusion length in the substrate was recently reported³ to be virtually unaffected after the pulsed laser annealing of displacement damage in ion-implanted Si. In the present investigation, B was deposited by vacuum evaporation on P-doped Si at room temperature, and the specimens were then irradiated with laser pulses similar to those used in the pulsed laser annealing of ion implantation damage. Microstructures of the as-deposited and laser-annealed layers

Fig. 2.33. Transmission electron micrographs of $^{11}\text{B}^+$ -implanted Si (35 keV , $3 \times 10^{15}\text{ cm}^{-2}$) after laser treatment. (a) Bright field, (b) dark field, (c) (001) diffraction pattern, and (d) thermal annealing at 900°C : weak beam, dark field. The arrows in (b) and (d) are $0.20\text{ }\mu\text{m}$ long.

Fig. 2.34. Depth profiles for $^{11}\text{B}^+$ -implanted Si (35 keV, $1 \times 10^{15} \text{ cm}^{-2}$). Flattening of the profiles at counting rates of up to 600 for 10 sec is believed related to insufficient aperturing and to crater wall effects.

were investigated by TEM; electrical properties were determined by Hall measurements; and dopant profiles were measured by SIMS techniques. In addition, p - n junction diodes and solar cells have been fabricated with very promising results.

Silicon single crystals ($\langle 100 \rangle$ plane, Czochralski, n -type, 2–6 $\Omega\text{-cm}$, 1 by 2 cm, and 0.05 cm thick) used in this investigation were obtained from Monsanto. Boron was deposited by electron beam evaporation in a vacuum of $<10^{-6}$ torr. The thickness of the deposited layers ranged from 75 to 200 Å.

Electron microscopy of as-deposited specimens revealed B primarily in the form of clusters on the surface. After the laser irradiation, no defects (precipitates and/or dislocation loops) were observed in the deposited specimens down to a resolution of 10 Å. Electrical parameters, as determined by Hall measurements for B-deposited specimens, are given in Table 2.10. Concentrations of dopants in solution after the laser treatment exceeded the equilibrium solubility limits.

The concentration profiles of B atoms were investigated with the SIMS technique. For these measurements the primary beam (O_2^+ , 16 keV, 15×10^{-9} A, 5 μm diam) was raster scanned over a large area (about 50 by 40 μm), while $^{11}\text{B}^+$ -sputtered ions were detected from

Table 2.10. Electrical parameters of B-deposited, laser-annealed Si

Sample	N_s (cm^{-2})	ρ_s ($\Omega/\square$)	μ ($\text{cm}^2/\text{V}\cdot\text{sec}$)	Amount of B deposited (nominal $\mu\text{g}/\text{cm}^2$)
BD-10	2.10×10^{15}	80.0	40	1
BD-11	8.62×10^{15}	23.8	31	5
BD-12	9.37×10^{15}	22.0	30	5
BD-13	6.10×10^{15}	32.0	33	1
BD-25	3.13×10^{16}	8.2	24	10

15% of the area scanned with an electronic aperture. The $^{11}\text{B}^+$ -sputtered ion intensities were normalized to the intensity of the $^{30}\text{Si}^+$ -sputtered ions to compensate for any changes in the secondary ion extraction efficiency. The concentration profile of B atoms for a specimen quite similar to BD-12 is shown in Fig. 2.35. Note that the solubility limit of B in Si ($\sim 4 \times 10^{20} \text{ cm}^{-3}$ at 1100°C) has been exceeded in the first 300 Å. These dopant profiles are rather shallow and decrease continuously without any plateau. The total concentration of B atoms obtained by integrating the profile in Fig. 2.35 agreed approximately with the measured electrically active carrier concentrations.

Solar cells and p - n junction diodes have been fabricated with the above technique. From the forward and reverse diode characteristics, the value of the diode-perfection factor (A) of about 1.3 and the reverse saturation current of about $10^{-7} \text{ A cm}^{-2}$ obtained indicate a superior p - n junction that equals or excels values obtained by conventional thermal diffusion techniques. Solar cells from B-deposited Si have been fabricated with efficiencies up to 11% (AM1) without anti-reflection coatings and back-surface-field treatments.

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LASER ANNEALING OF DIFFUSION-INDUCED IMPERFECTIONS IN Si¹

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In conventional high-temperature diffusion processes, the B or P distribution in Si does not follow a complementary error function distribution characteristic of a

Fig. 2.35. Boron (^{11}B) concentration as a function of depth in a B-deposited (at room temperature), laser-treated specimen as measured by SIMS technique.

simple diffusion process. Instead, a dense region of impurity precipitates is formed very near the surface; the extremely short carrier lifetime in this so-called "dead layer" limits the short wavelength photocurrent response. Dislocation and dislocation loops are also generated in the interface during the high-temperature diffusion process, and these influence the junction characteristics. We have found that the dislocation loops can be removed, the precipitates can be dissolved, and the B or P in them can be electrically activated by high-power ruby laser radiation. This treatment serves to reduce the

sheet resistance and improve the junction characteristics and other parameters of solar cells made from the material.

1. Summary of papers: *Appl. Phys. Lett.* 33, 14 (1978); p. 1208 in *Proceedings of the Thirteenth Photovoltaic Specialists Conference - 1978*, IEEE 78CH1319-3 ED, Washington, D.C., 1978.

2. Analytical Chemistry Division, ORNL.

DEFECTS IN LASER-DAMAGED Si OBSERVED BY DLTS¹

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Laser-induced defects in Si were studied by the DLTS technique. Figure 2.36 shows the DLTS spectrum of an unimplanted, B-doped Si control sample irradiated with

Fig. 2.36. DLTS spectrum for B-doped Si irradiated with three laser pulses (1.5 to 1.6 J/cm² per pulse, pulse duration of 30–50 nsec).

three laser pulses ($E = 1.5 \text{ J/cm}^2$). There is a dominant feature in the spectrum associated with an energy level at $E_v + 0.24 \text{ eV}$, where E_v is the energy of the top of the valence band. Depth profile measurements show that the defects are concentrated near the surface but extend into the sample about $10 \mu\text{m}$. A similar, though somewhat broader, peak with an energy level at $E_v + 0.22 \text{ eV}$ was observed in samples irradiated with a single

laser pulse under voltage bias and pulse conditions so that the measured region was from about 1.7 to 2 μm in depth. By selecting a deeper region in the Si (2 to 2.5 μm), an additional peak was observed with an energy level at $E_v + 0.37$ eV. The trap density in these measurements was $\sim 1 \times 10^{14} \text{ cm}^{-3}$. Compared to the doping density in the emitter region of a normal device, the density of these trapping centers is so low that their influence on junction characteristics can be neglected.

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ELECTRICAL PROPERTIES OF Mg-IMPLANTED, LASER-ANNEALED GaAs

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In recent years, much attention has been focused on the formation of a highly doped p - or n -type layer in GaAs by means of ion implantation. It has been shown that hot implantation ($>150^\circ\text{C}$) and postimplant annealing at high temperatures ($>800^\circ\text{C}$) are generally required to eliminate lattice damage and to get reasonable recovery of the electrical activity of the implanted species.^{1,2} However, the annealing results are frequently inconsistent from author to author. It is now widely recognized that protection or encapsulation of the implanted GaAs surface during high-temperature annealing to eliminate out-diffusion of the dopant is a most critical factor. Here, we show that the use of a pulsed laser to anneal the lattice damage of Mg-implanted GaAs can fully eliminate the need for surface protection or encapsulation.

Gallium arsenide substrates used in this work were (100)-oriented, Si-doped, n -type, polished wafers with a carrier concentration of $\sim 1.3 \times 10^{18} \text{ cm}^{-3}$. A Mg dose of $5 \times 10^{15} \text{ cm}^{-2}$ was implanted under high vacuum at 35 keV. Laser annealing was carried out in air by using a Q-switched ruby laser with a pulse duration of 15–30 nsec and an energy density that varied from 0.3 to 0.8 J/cm².

The recovery of the electrical activity after laser irradiation with pulses of increasing energy density was determined by the van der Pauw technique, and the results are given in Table 2.11. For comparison, the results as reported by Benson et al. for a similar sample encapsulated with SiO₂ and thermally annealed at 800°C for 30 min are included in this table. The table shows that the utilization factors for the laser-annealed samples are much higher than those for the thermally annealed sample. However, the fact that the utilization factor of the 0.7 J/cm² laser-annealed sample is higher than that for the 0.8 J/cm² laser-annealed sample is not fully understood. Whether or not the high-energy laser pulse has disturbed the stoichiometry of the GaAs will require further investigation.

In conclusion, these preliminary results have provided evidence that a pulsed laser can be used to anneal the radiation damage and recover the electrical activity in ion-implanted GaAs without any surface protection. This observation may prove to be of great advantage in the fabrication of homojunction GaAs solar cells.

1. J. P. Donnelly, W. T. Lindley, and C. E. Hurwitz, *Appl. Phys. Lett.* 27, 41 (1975).
2. K. Gamo et al., *Solid State Electron.* 20, 213 (1977).

Table 2.11. Electrical properties of Mg-implanted GaAs

Dose	Energy (keV)	Annealing	ρ_s ($\Omega/\square$)	N_s (cm^{-2})	μ ($\text{cm}^2/\text{V}\cdot\text{sec}$)	Utilization factor (%)
5×10^{15}	35	Ruby laser, 0.3 J/cm ²	1500	^a	^a	
5×10^{15}	35	Ruby laser, 0.7 J/cm ²	65	4.0×10^{15}	24	80
5×10^{15}	35	Ruby laser, 0.8 J/cm ²	64	3.0×10^{15}	32	60
1×10^{15b}	60	800°C for 30 min	1030	5.5×10^{13}	100	6

^aNot measurable.

^bR. B. Benson, Jr., et al., p. 131 in *Ion Implantation in Semiconductors*, 1976, ed. by F. Chernow, J. A. Borders, and D. K. Brice, Plenum Press, New York, 1977.

SOLAR CELLS FROM NTD Si

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In the last progress report,² it was stated that essentially no difference could be detected between cells made from NTD and from conventionally doped or standard Si. With the advent of better process control, however, cells made from NTD Si are showing a slight statistical advantage in short-circuit current and in minority carrier diffusion length in the base region. These differences became apparent during several runs designed to examine certain processing variants such as diffusion temperatures, cooling rates, and back-surface fields. Both NTD and standard Si samples were used throughout this work.

Because the initial resistivities of the NTD and standard Si were not equal ($\rho_{\text{NTD}} = 11 \Omega\text{-cm}$, $\rho_{\text{STD}} = 5 \Omega\text{-cm}$), it was difficult to assign any favorable or unfavorable advantage to the NTD silicon regarding open-circuit voltage. The open-circuit voltage of the 5- $\Omega\text{-cm}$ cells was generally a few millivolts higher than that for the 11- $\Omega\text{-cm}$ cells, as would be expected with otherwise similar material. The short-circuit current of the NTD cells was always higher than that for the standard cells, in some cases by as much as 10%. These data correlate well with measurements made on the minority carrier diffusion length in the base region, which gives a qualitative estimate of relative current densities. Diffusion length determinations were made by the surface photovoltage method. However, because the diffusion lengths are comparable to the cell thickness, this method yields only relative numbers. In every case, the ratio of measured diffusion length to cell thickness was larger in the NTD cells, often by as much as 50%. This investigation will continue and be extended to polycrystalline Si and to multiple-sun intensities.

1. 1978 summer research participant from Loomis Laboratory of Physics, University of Illinois, Urbana.

2. R. D. Westbrook et al., *Solid State Div. Annu. Prog. Rep.* April 30, 1977, ORNL-5328, p. 80.

ELECTRICAL PROPERTY STUDIES OF NTD Si

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R. T. Yeung

For float-zone-refined single-crystal Si, we have shown that the donor concentration after NTD is equal

to the concentration of the transmutation product P as computed from the thermal neutron fluence.¹ Of the lattice damage that was also introduced during the irradiation, the recoil defects resulting from thermal neutron capture were removed by annealing at 400°C, and the defects from epithermal neutron collisions were removed by annealing for 30 min at 750°C.

The corresponding annealing requirements have not been clearly established for NTD Czochralski single-crystal Si. Silicon grown by this method contains 5×10^{17} to $5 \times 10^{18} \text{ cm}^{-3}$ O impurities. Most of the O is present as electrically inactive interstitial atoms, but some of it may be present as electrically active clusters that act as *n*-type donors. It is known that a 750°C anneal of such crystals minimizes any donor contribution because of clustered O, but subsequent lower temperature annealing treatments required to remove the lattice damage associated with transmutation doping may form O-cluster donors. We have determined that annealing of unirradiated Czochralski Si at 450°C for 120 hr introduces $\geq 10^{16}$ donors per cubic centimeter, presumably due to O clusters.

Previous investigators² have examined Czochralski Si that was doped by neutron transmutation to introduce $10^{15} \text{ P cm}^{-3}$. From their annealing experiments, they concluded that some type of lattice defect-O complex serving as a donor in Czochralski NTD Si was produced by irradiation and/or annealing and that it was stable against annealing up to at least 950°C.

In the present experiments,³ we have examined the annealing requirements for float-zone and Czochralski NTD Si. Companion samples of float-zone and Czochralski material were irradiated for a series of neutron doses and then given a series of annealing treatments at 750°C and at 950°C. After annealing for 30 min at 750°C, the donor concentration measured in the float-zone samples was equal to the concentration of P as calculated from the thermal neutron dose. These values are listed in Fig. 2.37, and the correspondence between them and the measured values for the Czochralski samples similarly treated is indicated. The measured donor concentration vs time of annealing for the Czochralski samples is shown in Fig. 2.37. Note that this measured concentration for the Czochralski NTD samples was larger than anticipated after the 30-min anneal at 750°C, particularly for the low dose irradiations. Also, the donor concentration was increased by 1×10^{15} to $3 \times 10^{15} \text{ cm}^{-3}$ in each of the Czochralski samples after further annealing at 750°C, even though the initial lattice defect concentration was greater by a factor of 6000 from the lowest to the highest neutron

Fig. 2.57. Carrier concentration vs time of annealing at 750 and 950°C for Czochralski NTD Si samples. The ³¹P concentration obtained from companion float-zone NTD Si samples is also indicated.

dose. This additional donor concentration was decreased substantially by subsequent annealing at 950°C, although some fraction of the excess concentration remained even after this extended annealing treatment. It was also found that subsequent annealing at 450°C of these Czochralski samples resulted in an increase in donor concentration of about $1.5 \times 10^{16} \text{ cm}^{-3}$, irrespective of neutron fluence. We conclude that some type of special defect-O complex may exist in Czochralski NTD Si that can only be removed by extended high-temperature annealing, but the concentration of any such complexes is apparently only a very weak function of the neutron fluence, and the total donor

contribution is small as compared to that which may be introduced by clustered O alone.

1. R. T. Young et al., *J. Appl. Phys.* 49, 4752 (1978).
2. V. N. Mordkovich et al., *Sov. Phys. Semicond.* 8, 139 (1974); H. M. Liaw and C. J. Varker, p. 116 in *Semiconductor Silicon/1977: PV 77-2*, Electrochemical Society, New York, 1977.
3. J. W. Cleland et al., *Proceedings of the Second International Conference on Neutron Transmutation Doping of Semiconductors*, Plenum Press, New York (to be published).

MCL IN NTD Si

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Long MCL is one of the material requirements for certain types of Si devices. Process-induced defects, both chemical and physical, are potential sources of recombination centers and therefore are capable of causing lifetime degradation. Studies of MCL in NTD Si irradiated at this laboratory have led to an annealing cycle,^{1,2} as yet not optimized, that produces lifetimes in the milliseconds for lightly doped Si and in the hundreds of microseconds for doping levels up to about $5 \times 10^{15} \text{ P cm}^{-3}$. The process has been used to increase the MCL in commercially obtained NTD Si over that measured in the as-received material. It also restores lifetimes in samples whose lifetimes have been thermally degraded. In all cases, trapping events are usually non-existent.

The samples ranged in size up to $1 \times 1 \times 5 \text{ cm}$, depending on resistivity and material availability, were cleaned using multiple etches, and were finally immersed in hot HNO_3 and H_2SO_4 to minimize residual metal contamination. The annealing was carried out in a conventional quartz tube production-type diffusion furnace. The samples were heated to 1600°C and held for 1 hr in a furnace atmosphere that contained a small amount of PH_3 and O to promote phosphorus oxide gettering.³ A cooling rate of about 20° hr^{-1} to 650°C was used to allow time for vacancy stabilization.³ The samples were then removed and cooled to room temperature in a minute or less to minimize any resistivity perturbations due to O complexes. In samples annealed

without the gettering atmosphere, the MCL was reduced by a factor of 2 or 3. Rapid cooling to 650° after annealing reduced the MCL in other samples by an average of about a factor of 5. Samples of commercially high-purity float-zone Si with initial lifetimes of milliseconds were heat-treated purposely to degrade the MCL to less than 100 μ sec. Following the above annealing procedure, the lifetime was restored to essentially the initial value. In some cases, the MCL was long enough so that measured recovery time was a function of the sample geometry. A few recent experiments extending the times and temperatures of the annealing cycle have yielded even longer lifetimes in selected samples so that we do not yet know the limits obtainable by this annealing and gettering process.

Figure 2.38 is a graph of the MCL as a function of epithermal neutron fluence for various samples of float-zone NTD Si irradiated in a number of different reactor locales to a fluence as indicated and after the annealing schedule indicated above. Note that the measured value of the MCL after annealing is not dependent on the total fluence or thermal-to-fast neutron ratio (R) in a

manner that might have been anticipated. For each reactor locale, there is an inverse relationship between the measured MCL and neutron fluence, as indicated by the lines in Fig. 2.38, but the results for each reactor locale fall on different lines, and they shift toward increasing fluence for a given MCL as R decreases. All of the samples had an identical annealing sequence, but the neutron fluence for sample No. 12 was 10 times that for No. 8 and 30 times that for No. 6. The fact that the measured value of the MCL was nearly identical in these samples after annealing would seem to indicate that the presence of fast-neutron-induced lattice damage may actually enhance the rate of removal of the recombination centers that degrade the lifetime in NTD Si.

1. R. D. Westbrook et al., *Solid State Div. Annu. Prog. Rep. April 30, 1977*, ORNL-5328, p. 80.
2. R. D. Westbrook and J. W. Cleland, *Extended Abstracts, J. Electrochem. Soc.* 125, 144C (1978).
3. C. T. Sah and C. T. Wang, *J. Appl. Phys.* 46, 1767 (1975); R. N. Ghoshtagore, *J. Electrochem. Soc.* 124, 1449 (1977).

Fig. 2.38. The MCL vs epithermal neutron fluence for selected float-zone NTD Si samples after irradiation and partial annealing.

DEFECT ANNEALING STUDIES IN NTD Si¹

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X-ray and electron microscope measurements have been correlated with electrical and infrared measurements on NTD Si to relate the presence of structural defect clusters to the electrical and optical properties of this material after irradiation doping and after thermal annealing. X-ray diffuse scattering measurements and TEM observations indicated the presence of defect clusters of diameter 20–40 Å after irradiation. These clusters were found to decrease in number but to increase in size (to ~65 Å) upon annealing to 650°C and were seen to disappear more rapidly after annealing to 700°C and above. These results correlate with the recovery of the electrical mobility and the annealing of the near-edge absorption coefficient above 650°C. In addition, the increase in the average size (loss of smaller defects) of the defect clusters as a function of annealing below 650°C supports the proposition that the large infrared absorption annealing stage between 150 and 300°C is related to the disappearance of small defects and defect complexes including divacancies. The electron microscope study indicated that a small number of defect clusters remained even after annealing at 900°C. These clusters may be associated with the requirement of at least 1000°C thermal annealing to recover the MCL in NTD Si. No evidence was found for loops larger than 100 Å in any of the samples, contrary to suggestions by other investigators.²

1. Summary of paper: *Neutron Transmutation Doping in Semiconductors*, Plenum Press, New York, 1979 (in press).

2. M. Bertolotti, p. 311 in *Radiation Effects in Semiconductors*, ed. by F. L. Vook, Plenum Press, New York, 1968.

IMPURITY INTERACTIONS IN NEUTRON-IRRADIATED, B-DOPED Si

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R. T. Young P. H. Fleming

Transmutation doping of epitaxial Si layers deposited on low-resistivity Si substrates has been demonstrated and is of interest because conventional chemical vapor deposition and diffusion techniques do not provide well-controlled and uniform dopant concentrations in large area epitaxial Si layers, especially at low dopant concentrations.¹ Potential defect-impurity interactions between an NTD epitaxial Si layer and the substrate material may be of importance in a number of device applications. One example is that Li can be introduced into Si during crystal growth, by subsequent diffusion or by thermal-neutron-induced fission of ¹⁰B in B-doped samples. Lithium can act as an electrically active donor in Si and can interact with other impurities or lattice defects. One can calculate that the rate of introduction of ³¹P (donor) and the rate of removal of ¹⁰B (acceptor) should be about comparable for NTD Si initially doped with $\sim 5 \times 10^{16}$ ¹⁰B or $\sim 2.5 \times 10^{17}$ normal B cm⁻³. A special Czochralski-grown single-crystal Si ingot doped with $\sim 5.5 \times 10^{16}$ ¹⁰B cm⁻³ from a stable isotopic source in which ¹⁰B was ~94.5% abundant was provided for our experiments.²

Samples of the ¹⁰B-doped Czochralski Si were irradiated with float-zone refined control samples, and the results on the impurity concentrations are given in Table 2.12. One must calculate the amount of ¹⁰B removed by fission because the total concentration is reduced by extended irradiation, but some ¹¹B remains. The ³¹P concentration was determined after annealing the float-zone NTD control samples. The net concentration (line 5) is the anticipated value if the only change is

Table 2.12. Transmutation reactions in isotopic ¹⁰B-doped Si for specific reactors

Except as noted, all data are in units of 10¹⁶ cm⁻³

The minus sign indicates n-type donor concentration

	BSR	BSR	NBSR	NBSR	NBSR
Irradiation, days	20	40	7	21	84
Calculated ¹⁰ B removed	0.34	0.52	1.05	2.57	4.74
Total B remaining	5.16	4.98	4.45	2.93	0.76
Measured ³¹ P added	0.34	0.52	-1.21	-3.66	14.00
Net concentration	4.82	4.46	3.24	-0.73	-13.24
Calculated ⁷ Li added	0.34	0.52	-1.05	-2.57	-4.74
Net concentration	4.48	3.94	2.19	-3.30	-17.98
Measured concentration	4.18	3.14	1.57	-2.35	-14.40

that of addition of ^{31}P donors and removal of ^{10}B acceptors. The calculated concentration of ^7Li (line 6) should be identical with the calculated removal of ^{10}B (line 3), and this value was used to estimate the net concentration (line 8) if ^7Li is active as a donor. The measured concentration was obtained for the Czochralski NTD ^{10}B Si (line 9) after annealing for 30 min at 1000°C to remove lattice damage introduced by irradiation and fission because annealing at 750°C was not sufficient to stabilize the apparent carrier concentration in every sample.

It is evident that ^7Li is present as a donor in the low total dose samples in Table 2.12 that remained *p*-type and in the 21-day NBSR samples converted to *n*-type. The 84-day NBSR samples required six months of radioactive decay, and a major portion of the ^7Li may have precipitated in that time period. In any event, the use of B as a substrate dopant will result in the introduction of ^7Li that may migrate and alter the desired dopant concentration of an NTD epitaxial layer. The ability to add a known concentration of ^7Li in Si by the technique of ^{10}B fission is of potential interest in that further experiments could lead to a better understanding of the interaction between Li and O in Si, if float-zone ^{10}B -doped samples of low or controlled O content can be made available.

1. S. Prussin and J. W. Cleland, *J. Electrochem. Soc.* 125, 350 (1978); C. W. Pearce, private communication.

2. We are indebted to L. E. Katz, Bell Telephone Laboratories, Allentown, Pa., for the careful preparation of this ingot.

SOLAR CELL MODELING

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A computer program has been written to simulate the performance of an abrupt-junction solar cell under AM0, AM1, and AM2 conditions. (The AM notation refers to the sun's spectrum filtered through 0, 1, and 2 atm respectively.) Many of the parameters that affect the performance of solar cells, such as MCL, diffusion constant, surface recombination velocity, junction depth X_j , dopant concentrations, temperature, and series and shunt resistances (R_s , R_{sh}) appear explicitly in the model.

The photocurrent I_{ph} generated in the device comes entirely from minority carrier conduction. The dark

current I_d is just the normal diode current of the device and is dependent upon the voltage V across the device before any series resistance is encountered; it is opposite to I_{ph} . The solar cell can then be modeled as an electrical circuit with a current source (I_{ph}) in parallel with a diode (I_d opposite to I_{ph}) and R_{sh} , and in series with a combination of R_s and a load resistance R_L . Calculations are performed by choosing a value of V , calculating I_{ph} and I_d , and then calculating the load voltage V_L and load current I_L . In this way, an $I_L - V_L$ curve can be calculated numerically by changing V in small increments. The short-circuit current I_{sc} and the open-circuit voltage V_{oc} are calculated as the interpolated intercept between the two points straddling the I_L axis and the V_L axis respectively. The fill factor FF and efficiency η are calculated from the maximum power point on the $I_L - V_L$ curve.

Several runs of the computer program were made to determine how certain variables affect solar cell performance, and the following information was found.

1. Decreasing the junction depth under the approximation that the MCL in the front part of the device is small leads to an increase in I_{sc} and η .
2. Decreasing R_{sh} results in decreases in V_{oc} , FF , and η , but I_{sc} is not changed. For moderate values of R_{sh} ($\sim 300 \Omega$), decreases in FF and η are noted long before the decrease in V_{oc} .
3. Increasing R_s results in decreases in I_{sc} , FF , and η , while V_{oc} is unchanged. Similarly, decreases in FF and η occur before the decrease in I_{sc} .
4. Decreasing the temperature increases V_{oc} , FF , and η considerably, and I_{sc} remains nearly constant.

To make and operate the highest efficiency solar cells, X_j and R_s must be small, R_{sh} must be large, and the temperature must be as low as possible.

Perhaps the worst assumption made in the present computation is that of an abrupt junction. This calculation is normally a good approximation only for epitaxially grown junctions. For diffused or laser-annealed junctions, the approximation is not nearly as good. We therefore plan to incorporate the capability of treating graded junctions into the program. Most solar cells made today have a heavily doped region on the back of the device that gives rise to a back-surface field, which has not been included in the present calculations, but will be added shortly.

3. Defects in Solids

The diversity of programs in the Solid State Division is particularly apparent in this section in which research is reported on radiation effects in metals, on fracture, and on defects and impurities in insulating crystals. This section also reflects the change in the Division's research programs on defects in solids that, up to a few years ago, were almost exclusively concerned with radiation effects. Although the work on radiation effects continues to be an important part of this effort, new or redirected programs studying defects in materials of interest in nonnuclear energy applications now represent the largest fraction of the overall effort on defects in solids.

The research on radiation effects in metals has continued, but at a decreased level relative to the past. This decreased effort reflects in good part an increased involvement of the electron microscope and x-ray diffraction activities in cooperative research with other programs for which information on defect structures is an essential component. The results of this cooperative effort are reported in other sections of this report. In view of the increased activity of the Solid State Division in areas of ion implantation and laser annealing, it is expected that this trend toward increased cooperative efforts will continue.

Since the last report, the x-ray activity has acquired a high-intensity x-ray source that provides the intensity needed to carry out differential diffuse x-ray scattering studies. Preliminary results on defect clusters in Cu have shown the potential of this method for obtaining detailed information on the nature of the defect clusters. In turn, the x-ray diffuse scattering studies of vacancies in quenched Au have shown the power of this technique for studying vacancies in metals.

The emphasis of the effort on low-temperature radiation effects has been directed toward the study of radiation damage problems associated with superconducting magnet materials. The studies of magnetoresistance in Cu and the changes in electrical and mechanical properties of organic insulators due to irradiation provide information necessary for the design of superconducting magnets for fusion reactors. The normalization of ion to neutron damage in Al has been completed with the result that theory and experiment are in excellent agreement.

The electron microscope study of the distribution of dislocations in the plastic zone of propagating cracks in stainless steel has provided the first experimental verification of a fracture theory developed about 15 years ago. Extension of these studies to Mo has been started, and the initial observations have shown that the dislocation structure associated with propagating cracks in this material is more complicated than in stainless steel because of cross slip of the dislocations. Concurrent development of a theoretical method for dealing with dislocation distributions different from those considered in the older theory shows promise of providing a basis for understanding the interrelation of the dislocation structure with crack propagation in Mo.

Studies of defects and impurities in insulating crystals are closely related to the problems of mass and charge transport in these materials at elevated temperatures. Investigations of the diffusion of H in metallic oxides are closely coordinated with related

efforts by staff members in the Metals and Ceramics Division. A mechanism for H diffusion perpendicular to the *c* axis in TiO_2 has been established, and the activation energies for H and T were determined to be equal within experimental accuracy. Similar properties of the H isotopes in Al_2O_3 are currently being investigated. Studies of impurities in MgO have emphasized investigation of Li- and Fe-doped material. Because of differences in valence states of the dopants and host cations, charge compensation would require the cation vacancy concentration change as a function of dopant concentration and charge. It has been established that Fe at higher doping levels aggregates, but large concentrations of Li occupy substitutional sites at elevated temperatures. In impurity-doped MgO, the defect structure is altered by applied electric fields at high temperatures, and TEM studies have identified the nature of these changes and the properties of some of the resultant defect structures. Investigations of the mechanical properties of impurity-doped MgO have recently been initiated.

RADIATION EFFECTS IN METALS

CORRELATION OF ION AND NEUTRON DAMAGE IN Cu

J. Narayan B. C. Larson

For a successful correlation of fission and fusion neutron damage with ion radiation damage, a detailed understanding of the depth distribution of ion damage, the damage rate, and the effects of the irradiation temperature and annealing processes is required. Previous basic studies¹ of ion damage in Cu and other metals have been confined to low ion energies (20–100 keV) where only vacancy clusters were observed as a result of the close proximity (~ 200 Å) of the free surface that acts as a sink for the interstitials. Ion simulations make use of higher energy ions that achieve greater penetration depths and therefore more nearly reproduce the "bulk" damage and annealing processes similar to neutron irradiations. In this investigation, TEM and x-ray diffuse scattering have been used to study defect clusters as a function of depth in self-ion-irradiated Cu, and the results have been compared with those from neutron irradiations.

High-purity Cu ($\sim 99.999\%$ pure) single-crystal plates ($10 \times 10 \times 2$ mm) were used in this study. The specimens were irradiated with ^{63}Cu ions to a dose of 5×10^{12} ions cm^{-2} in the Oak Ridge Tandem Van de Graff accelerator. The ion energies used were 5, 16, 27, and 38 MeV. All the irradiations were performed at a temperature of about 25°C . The temperature rise of the specimens during irradiation was only about 1°C as a result of ion beam heating. The depth distribution of the displacement damage was observed directly in the electron microscope through the use of an electroplating and transverse sectioning technique described earlier.² This process allows a direct determination of

the loop size distributions and defect densities as a function of the ion penetration depth over the entire range of ions.

Figure 3.1 is a bright-field electron micrograph showing the depth distribution of defect clusters in a 27-MeV ion-irradiated specimen. Dynamical diffraction contrast and stereomicroscopy showed the defect clusters to be vacancy and interstitial dislocation loops with approximately two and a half times as many interstitial loops as vacancy loops. Taking into account the fact that the vacancy loops are, on the average, smaller than the interstitial loops, significantly more interstitials than vacancies are contained in these loops. This result implies the existence of vacancies in the form of clusters or uncollapsed aggregates below the resolution of the microscope; however, essentially the same ratio has been observed in both fission and fusion energy neutron damage in Cu. A Burgers vector analysis of the dislocation loops indicated that the nature ($\sim 80\% \frac{a}{3}[111]$, $20\% \frac{a}{2}[110]$) of the loops remained invariant with depth within the $\pm 10\%$ experimental uncertainties. This result is also similar to that found in neutron-irradiated Cu.

Because the primary recoil spectrum near the damage peak corresponds most closely to that for fast-neutron irradiations, a comparison of the loop size distribution (number density vs size) at this position has been carried out using both x-ray and microscope techniques. The number density of small loops induced by the 25°C ion irradiations was significantly higher than that observed in specimens irradiated to fast-neutron doses (10^{19} neutrons/ cm^2 , $E > 0.6$ MeV) with equivalent damage energies. It should be pointed out that the "homologous" temperature for the ion irradiation to correspond to the 43°C neutron irradiation has been

Fig. 3.1. Bright-field electron micrograph showing the damage distribution as a function of depth for 27-MeV ^{63}Cu , dose = $5 \times 10^{12} \text{ cm}^{-2}$. The entrance of ions is indicated by "I."

calculated to be about 220°C . Investigations of the dose rate and temperature dependence of ion damage in Cu are in progress.

1. M. Wilkens, p. 441 in *Applications of Ion Beams to Metals*, ed. by S. T. Piraux, E. P. EerNisse, and F. L. Vook, Plenum Press, New York, 1974.

2. J. Narayan, O. S. Oen, and T. S. Nogge, *J. Nucl. Mater.* 71, 160 (1977).

X-RAY DIFFUSE SCATTERING FROM NEUTRON-IRRADIATED Cu

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Numerical diffuse-scattering calculations have predicted the presence of certain characteristic features in the scattering from small dislocation loops in crystals. These features, involving the angular dependence of the scattering intensities, depend on the elastic anisotropy of the crystal lattice, as well as the size and orientation of the loops, and are therefore important in the analysis of diffuse scattering measurements.

In this work we have compared x-ray diffuse-scattering measurements with detailed scattering calculations. The measurements were made on neutron-irradiated Cu crystals with a 12-kW rotating anode generator and a linear position-sensitive detector system where the sample was held at 10 K during data collection to minimize thermal diffuse scattering. Data were collected over an approximately $0.35\text{-}\text{\AA}^{-1}$ range of q relative to the 222 reciprocal lattice point in the plane

defined by the $[222]$ and $[\bar{2}11]$ reciprocal lattice directions. The net scattering introduced as a result of the neutron irradiation (1.3×10^{18} neutrons/cm 2 ; 4 K, annealed to room temperature) was obtained by comparison with measurements on an unirradiated specimen.

The results of these measurements are shown in Fig. 3.2a, where the scattering intensities (times q^4) are plotted in the form of iso-intensity contours. The notable features of this scattering are the high intensities along the $\pm[\bar{2}11]$ directions and the smaller, relative maxima appearing along $\pm[222]$ directions. The relatively weak q dependence of the intensity (multiplied by q^4) indicates the actual intensity falloff to be essentially q^{-4} in nature. These measurements are in qualitative agreement with scattering calculations for a combination of 10-Å vacancy loops and 20-Å interstitial loops as shown in Fig. 3.2b. These calculations, which took the elastic anisotropy of the Cu lattice into account, in particular correspond to the intensity from an ensemble of four 10-Å vacancy loops and one 20-Å interstitial loop. Frank loops were used, and the relative number of each type loop was chosen to obtain the numbers of vacancies and interstitials.

An analysis of the calculations shows that the two relative maxima, along the $[222]$ and $[\bar{2}2\bar{2}]$ directions, arise from the highly strained region immediately surrounding the interstitial and vacancy loops respectively. Because the distances of these maxima from the reciprocal lattice point are inversely proportional to the loop radii, we can infer that the vacancy loops in the irradiated sample are on the average more than a factor of 2

Fig. 3.2. Comparison of measured and calculated diffuse scattering intensities from Cu. (a) Measured diffuse scattering intensities (times q^4) for neutron-irradiated Cu. (b) calculated diffuse-scattering intensities (times q^4) for vacancy and interstitial loops in Cu. The scales are arbitrary.

smaller than the interstitial loops. The high intensities along the $\pm[211]$ directions have not been identified with defect-specific parameters, but in calculations assuming an isotropic elastic medium the intensities in these directions were found to be lower than along the $\pm[222]$ directions and not in agreement with the measured data.

The general agreement between the measured and calculated intensity contours gives a rough overall view of the nature of the defects in the crystal and provides the framework for the extension of this work to detailed fitting of the data along specific directions to obtain more precise information. It is expected, for instance, that a distribution of sizes of both vacancy

and interstitial types will be required to accurately fit the measured data.

X-RAY DIFFUSE SCATTERING FROM LOOPS IN AN ANISOTROPIC MATERIAL

B. C. Larson P. Ehrhart¹ S. M. Ohr

It has been known for some time that the elastic anisotropy of crystal lattices has a substantial effect on the intensity and angular distribution of x-ray diffuse scattering generated by dislocation loops in crystals. Unfortunately, detailed calculations of the scattering cross sections for loops in highly anisotropic materials such as Cu have not been available until now, and the analysis of diffuse-scattering data has had to rely on extrapolations from isotropic calculations.² However, methods for obtaining accurate displacement field data for dislocation loops in anisotropic materials have been developed,³ and these have made it possible to pursue numerical diffuse-scattering calculations in anisotropic as well as isotropic materials.

In this work we have used displacement fields for prismatic dislocation loops in an elastically anisotropic medium to calculate the x-ray diffuse scattering from loops in Cu and have compared these with similar calculations for an isotropic material. The rather sizeable differences in the magnitude of the lattice displacements in an anisotropic material such as Cu compared with those for an isotropic material are illustrated in Fig. 3.3.

Fig. 3.3. Displacement field normal to a prismatic loop in Cu and in an isotropic material.

Fig. 3.4. Reduced diffuse-scattering cross sections calculated for loops on $\{111\}$ planes in Cu and in an isotropic material at the $[222]$ reflection. "A" is the scattering amplitude. (a) q along $[222]$ and $[222]$ directions; (b) q along the $[211]$ direction.

In this figure the displacement S_z normal to the loop (at its center) is plotted in units of the Burgers vector b as a function of the distance Z from the loop in units of the radius R . The direction of Z corresponds to the $[111]$ direction. The diffuse-scattering calculations were carried out under the elastic continuum approximation and employed Gaussian damping to terminate spatial integrations and efficient trigonometric transform algorithms⁴ to minimize computation time.

The results of these calculations are shown in Fig. 3.4 in the form of reduced scattering cross sections as a function of the distance from the 222 reciprocal lattice point. Loops of radius 20 Å on $\{111\}$ planes were used for these calculations, which show that the general form of the scattering is quite similar for the anisotropic (Cu) and isotropic cases. Significant differences do, however, appear in the intensities at small values of qR and in the value of qR at which the shoulders appear in Fig. 3.4a. These shoulders are of particular interest here because they can be identified with "Bragg-like" scattering coming directly from the highly strained region in the immediate vicinity of the loop. As such, they are defect-specific features and the position of these shoulders relative to the reciprocal lattice point is related directly to the magnitude (and sign) of the strain near the loop. The smaller qR for the shoulder in the anisotropic Cu calculation compared with the isotropic case implies a smaller strain normal to $\{111\}$ loops in Cu than in isotropic materials. This is borne out through the smaller gradient in the displacement field for Cu compared to the isotropic lattice as can be seen in Fig. 3.3.

The variations in the x-ray scattering cross sections caused by the elastic anisotropy for these scattering directions, therefore, consist of both intensity and range modifications and as such will affect analyses of diffuse scattering measurements both in the form of the loop sizes and in the number densities inferred. These effects will be especially pronounced when ensembles of loops of varying sizes and number densities, which contain both vacancy and interstitial loops, as encountered in radiation damage investigations, are studied.

1. Guest scientist from Kernforschungsanlage, Jülich, Germany.
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4. D. T. Keating and A. N. Goland, *Phys. Rev. B* 4, 1816 (1971).

INTERSTITIAL CLUSTERING IN ELECTRON-IRRADIATED Al¹

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The clustering of interstitials in irradiated metals is an important consideration in the overall description of radiation damage. For small defect clusters, the most direct information on the symmetry and the size of the clusters is obtained from diffuse-scattering experiments.⁴ The Huang diffuse scattering of x rays from interstitial clusters has been investigated recently in a variety of metals.⁴ In the present work, the results of a detailed Huang scattering study of interstitial clustering in Al are reported. In the experiment, an Al single crystal was irradiated at 5 K with 3-MeV electrons at the Jülich low-temperature irradiation facility to a defect concentration of $\sim 4 \times 10^{-4}$. Huang scattering intensities were measured immediately following the irradiation at 5 K and during an isochronal annealing program from 36 to 190 K. Particular attention was given to the initial stages of the clustering process and the role of the di-interstitial.

In Fig. 3.5, some typical diffuse-scattering curves for measurements in the radial (q parallel to h) direction in the vicinity of the (222) reflection are shown. In this figure, q is the distance from the nearest reciprocal lattice vector h . The curves have been normalized to the same point defect concentration using the electrical resistivity. Following irradiation at 5 K, the Huang scattering (q^{-2}) region extends to quite large values of q as expected for single defects. Upon annealing, the normalized scattering cross section increases and the Huang

Fig. 3.5. Symmetric x-ray diffuse-scattering curves for the radial direction in the vicinity of the (222) reflection at 5 K and after several points in the annealing program. The intensities are normalized to the same Frenkel defect concentration using the electrical resistivity.

region collapses toward the Bragg peak and is replaced at large q by an asymptotic scattering where the cross section varies as q^{-4} . These observations are consistent with the formation of defect clusters in the sample.

For single interstitials at 5 K, the Huang scattering data were combined with measurements of the lattice parameter change $\Delta a/a$ and the electrical resistivity on the same sample to yield values for the interstitial relaxation volume ΔV_i and the Frenkel defect resistivity ρ_F in Al. The present results compare well with previously published data for Frenkel defects in Al (Table 3.1) and establish the presence of a statistical distribution of single defects in the sample before annealing.

For the clustering results, the radial Huang intensities were divided by the corresponding resistivity change to determine the effective number of interstitials per cluster as a function of annealing temperature. These results are shown in Fig. 3.6 along with the resistivity

Table 3.1. Absolute quantities for Frenkel defects in Al

Measurement	Source	Lattice parameter change, $\frac{\Delta a}{a}$ (10^{-3} ; $\Omega\text{-cm}$)	Frenkel defect resistivity, ρ_F ($\mu\Omega\text{-cm/at. \%}$)	$\frac{\Delta V_i}{V_a}$
Huang scattering plus $\Delta a/a$	Present work	1.77 ± 0.17	3.2 ± 0.6	1.7 ± 0.3
	Ehrhart and Schilling ²	1.61 ± 0.10	3.9 ± 0.6	1.9 ± 0.2
Scattering between the Bragg peaks	Humbold ³		4.2 ± 0.8	1.9 ± 0.2

Fig. 3.6. Effective number of interstitials per cluster as a function of annealing temperature. The resistivity recovery with its principal stages is also shown.

recovery. The approximate stage boundary temperatures for the recovery of electron-irradiated Al are also indicated in the figure. Single interstitials survive to ~ 36 K where long-range migration occurs and a distribution of multiple interstitials of effective size ~ 2.5 quickly develops near the end of Stage I (~ 38 K). A second increase in cluster growth rate in the temperature range 44–50 K can be associated with di-interstitial migration. This is consistent with the observed cluster size of about four at 50 K. A maximum cluster size of 12–25 interstitials per cluster is attained at 100–160 K. There is evidence from the distribution of scattering intensity that these larger clusters are dislocation loops.

The effective cluster sizes following single and di-interstitial migration can be correlated with the predictions of a simple kinetic model for diffusion annealing.⁷ On the basis of this model, a statistical distribution of di-, tri-, and tetra-interstitials of effective size 2.6 would be expected upon completion of single interstitial annealing. Di-interstitial annealing would result in a size

distribution of mostly three to six interstitials with an effective size of 4.4. The predicted sizes are consistent with the observed sizes following Stages I_{D,E} and II_I and therefore support the assignment of these stages to single and di-interstitial migration respectively. The overall results establish the usefulness of detailed diffuse-scattering studies of defect clustering and indicate that the initial stages of interstitial clustering in Al can be described by a diffusion-annealing process.

1. Summary of paper: *Phys. Rev. B* 18, 2591 (1978).
2. This author carried out this research while on foreign assignment at Kernforschungsanlage, Jülich, Germany.
3. Kernforschungsanlage, Jülich, Germany.
4. See P. Ehrhart, *J. Nucl. Mater.* 69/70, 200 (1977) for a recent review.
5. P. Ehrhart and W. Shilling, *Phys. Rev. B* 8, 2604 (1973).
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X-RAY DIFFUSE SCATTERING STUDIES OF VACANCIES IN QUENCHED Au¹

P. Ehrhart² H. D. Carstanjen³ J. B. Roberto⁴

Over the past decade, the properties of vacancies in quenched metals have been the subject of numerous investigations that used resistivity, electron microscope, and positron annihilation techniques. Nevertheless, there is little quantitative information about fundamental vacancy parameters such as relaxation volumes or phenomena such as clustering. In the present work, the diffuse-scattering technique,⁵ which has led to a greatly increased understanding of interstitials in metals, is applied for the first time to the study of vacancies in a quenched metal. Although somewhat complicated by the small scattering cross section of the vacancy, the diffuse-scattering method in combination with resistivity and lattice parameter measurements can provide quantitative information on vacancy relaxation volumes, resistivities, and concentrations. In addition, the formation of vacancy clusters can be followed from the beginning to the final form of large clusters and stacking fault tetrahedra that have been studied by electron microscopy.

In the experiment, single crystals of Au (approximately 1 X 2 X 20 mm) were quenched from 900–950°C to –70°C in an HCl and water bath. The quenched samples were electropolished at –30°C in a solution of LiCl and methanol to remove surface

damage and mounted without warming in an x-ray cryostat. X-ray diffuse-scattering measurements were made in the vicinity of the (422) and (400) reflections immediately following the quench and during an isochronal annealing program from 0 to 180°C. Background scattering curves obtained after complete annealing of the vacancies at 900°C returned to the prequench values.

In Fig. 3.7, some typical x-ray diffuse-scattering curves for measurements in the radial direction near the (422) reflection are shown. Following the quench, the vacancy scattering at –25°C varies as q^{-2} where q is the distance from the (422) reciprocal lattice point. This q^{-2} dependence is characteristic of the scattering ex-

Fig. 3.7. Symmetric diffuse-scattering curves for measurements in the radial direction in the vicinity of the (422) reflection in quenched Au. Results following the quench at –25°C and during several steps in an isochronal annealing program are shown.

pected from single defects or small clusters. The increase in diffuse intensity at 0°C indicates an increase in average defect size by a factor 3–4. This observation of vacancy clustering at 0°C agrees with recent positron annihilation studies⁶ of quenched Au but has not been detected by resistivity or electron microscope measurements. Rather large vacancy agglomerates are formed by 80°C, as indicated by the q^{-4} dependence of the scattering at small q . Further annealing at 180°C does not change the scattering but does decrease the resistivity, indicating a decrease in the resistivity per vacancy in the larger clusters.

The diffuse scattering data gathered after the quench were combined with measurements of the lattice parameter change on the sample to determine a vacancy relaxation volume for Au of $\Delta V_v = -0.15 \pm 0.06$ atomic volumes. This value is somewhat smaller than results from other techniques and may suggest a temperature dependence for ΔV_v in Au. Although further studies will be required to fully interpret the present results, the diffuse-scattering technique has been established as a powerful tool for the investigation of vacancy phenomena in metals.

ELECTRON MICROSCOPE STUDIES OF STAGE III RECOVERY IN ELECTRON-IRRADIATED Cu

S. M. Ohr

We have reported previously the results of a study by electron microscopy of the nature of defect clusters in electron-irradiated Cu annealed in the temperature range between Stage III and Stage V. One of the objectives of the study was to identify the defects (either vacancies or interstitials) responsible for Stage III recovery in order to distinguish between two contending models of defect recovery, namely the one-interstitial model and the two-interstitial model. The study showed that all the dislocation loops observed after the Stage III recovery were interstitial. The result, however, could not be taken as evidence against the one-interstitial model because the vacancies could have moved during Stage III, but the clusters they formed were too small to be visible in the electron microscope.

To clarify the situation, we have studied the effect of Stage III recovery on the density of visible defect clusters in pure Cu single crystals electron irradiated at 4 K. Electron microscope specimens were prepared and studied at a temperature below Stage III (200 K). After the specimen was warmed up to above Stage III in thin-foil conditions, additional observations were made to detect possible changes in defect density. Microscope specimens were also prepared from crystals annealed through Stage III as bulk specimens. Figure 3.8a shows the defect structure observed at the onset of Stage III. The loop density is $2.0 \times 10^{16} \text{ cm}^{-2}$, and the average loop diameter is 42 Å. Figure 3.8b shows the same area observed after the specimen was warmed up to a temperature slightly above Stage III. The loop density has

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2. Kernforschungsanlage, Jülich, Germany.
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4. This author carried out this research while on foreign assignment at Kernforschungsanlage, Jülich, Germany.
5. See P. Ehrhart, *J. Nucl. Mater.* 69/70, 200 (1977) for a recent review.
6. S. Mantl and W. Triftshäuser, *Phys. Rev. Lett.* 34, 54 (1975).

Fig. 3.8. Electron micrographs showing the identical area of an electron-irradiated Cu single crystal before and after the Stage III recovery. The density of interstitial loops has decreased by a factor of at least 2 during Stage III.

decreased by a factor of about 2 to $0.8 \times 10^{16} \text{ cm}^{-3}$ with apparently little change in the average size. Nearly identical loop density and size were found in the specimens annealed through Stage III in bulk. Only interstitial loops were observed in these samples, and hence the interstitials in the loops as observed through the microscope decreased by a factor of at least 2 during Stage III. Because the interstitial loops can be annihilated by the arrival of vacancies but not by interstitials, the present result seems to favor the vacancy mechanism of the Stage III recovery. On the other hand, the annihilation of the interstitial loops by glide during Stage III, particularly in thin-foil specimens, cannot be ruled out at present. Further studies are in progress to assess the magnitude of the loss of dislocation loops by the glide mechanism.

IMAGE CONTRAST OF DISLOCATION LOOPS IN ANISOTROPIC CUBIC CRYSTALS¹

S. M. Ohr

The calculations of the image contrast of dislocation loops reported in the past have made use of the displacement fields derived under the assumptions of elastic isotropy. The only exception is the work of Yoffe,² but it is based on the asymptotic field of an infinitesimal loop applied to the first-order analytical theory of image contrast. It is therefore desirable to calculate the image contrast by exact numerical integration of the equations of the dynamical theory of electron diffraction, making use of the displacement field of a finite loop derived from the anisotropic elasticity theory. We have recently presented a scheme by which the displacement field of a circular loop of finite size can be calculated for anisotropic cubic crystals from the Fourier transform of the elastic Green's function.³ In the present study, this numerical scheme has been combined with the image simulation technique developed earlier⁴ to calculate the image contrast of dislocation loops in anisotropic cubic crystals.

Figure 3.9a shows the simulated image of a pure edge faulted loop with Burgers vector $\frac{a}{3} [111]$ calculated using the displacement field of the isotropic elasticity theory. The foil normal is $[110]$, and it is oriented for the exact (002) Bragg reflection ($w = 0$). The foil thickness is 1000 Å, the loop radius is 25 Å, and the loop depth is 150 Å. The Burgers vector b makes an angle of

54.7° counterclockwise from the (002) diffraction vector g . The direction of black-white contrast l is seen to be rotated about 15° away from the direction of b toward g . Figure 3.9b shows the result of the anisotropic calculation for a loop of the same orientation and diffraction condition in Cu. Copper is highly anisotropic and its anisotropy factor $A = 2c_{44}/(c_{11} - c_{12})$ is 3.2. Note that the black-white contrast is stretched considerably in the $[1\bar{1}1]$ direction and the black-white direction l is exactly parallel to the direction of the Burgers vector b . As indicated earlier,³ Cu is elastically soft along the $\langle 111 \rangle$ directions, which is reflected in the predicted image contrast of the dislocation loop. Experimentally, we have observed consistently that the l vectors for the Frank loops in Cu are parallel to the direction of b .

Figure 3.9c shows the result of a similar calculation for Ni for which the anisotropy factor A is 2.4. The black-white direction is nearly parallel to b , but the length of the black-white contrast is somewhat reduced. This is consistent with the fact that Ni is less anisotropic than Cu. Figure 3.9d shows the result for Nb ($A = 0.5$). The loop and the diffraction geometries are the same as before, but the Burgers vector now is $\frac{a}{2} [1\bar{1}1]$, making it a perfect loop. It can be seen that the black-white direction has rotated nearly 25° from the direction of b toward g . Because the anisotropy factor A is 1.0 for an isotropic crystal, Nb is anisotropic in a sense opposite to that of Cu and Ni, and this in turn has influenced the amount of rotation that the black-white direction has suffered in Nb.

The present work clearly shows that the image contrast of dislocation loops in cubic crystals is highly sensitive to the elastic anisotropy. Therefore, the effect of crystal anisotropy must be taken into account to accurately analyze the loop images.

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Fig. 3.9. Computer-simulated image contrast of pure edge dislocation loops 50 Å in diameter imaged under the exact (002) Bragg reflection in various cubic crystals. (a) Isotropic crystal, (b) Cu, (c) Ni, and (d) Nb.

ELASTIC FIELDS OF A DISLOCATION LOOP NEAR A STRESS-FREE SURFACE¹

S. M. Ohr

The displacement field around a finite, circular, edge dislocation loop lying parallel to a stress-free surface has been calculated. The results indicate that when the loop is located close to the free surface the displacement field is extremely asymmetric across the loop plane. The free-surface effect is significant for loops located within about five times the loop radius from the free surface. The effect of a free surface on the interaction between the loop and a point defect has also been examined.

Following the formalism of Eshelby, the size interaction energy is expressed in terms of the transformation strain of the point defect and the sum of the normal stresses of the loop. Near the free surface, the region from which a self-interstitial is attracted to an interstitial loop is considerably reduced. One may conclude, therefore, that near a free surface the interstitial loops are less effective as sinks for self-interstitials than in the bulk.

1. Summary of paper, *J. Appl. Phys.* 49, 4953 (1978).

RESIDUAL IMAGE CONTRAST OF DISLOCATION LOOPS¹

J. Narayan S. M. Ohr

The electron microscope images of large dislocation loops lying perpendicular to the electron beam have been calculated by applying the image simulation technique. It is found that the residual double arc contrast arising from the $g \cdot b \times u$ term exhibits asymmetry which is depth dependent. The predictions of the theory have been verified experimentally for $a[001]$ dislocation loops observed in single crystals of MgO. The depth oscillation of the residual contrast can be used to determine the vacancy or interstitial nature of dislocation loops.

1. Abstract of paper: *Phys. Status Solidi A* 46, 281 (1978).

ION DAMAGE IN Al

T. S. Nogge B. R. Appleton
J. M. Williams G. Vogl¹

Damage production rates of Al ions measured in Al have indicated that experiment and theory generally agree well.^{2,3} To further test the theory, these measurements have been extended to protons, α particles, and ions of each atomic species from Mg to Ar in the third row of the periodic table.

Examples of the comparison of experimental and theoretical damage rates as a function of ion penetration depth are shown in Fig. 3.10a and 3.10b. These examples represent the two extremes studied of the ion sequence in the third row of the periodic table and illustrate the change in the damage curve with increasing ion mass. Similar curves showing similar agreement with

Fig. 3.10. Relative damage rates of heavy ions in Al vs absorber foil thickness. Ions: (a) 4.6-MeV ^{24}Mg and (b) 6.0-MeV ^{40}Ar . Solid curves were calculated using the F-DEP-1 computer code (ref. 4).

the theoretical curves obtained from the E-DEP-1 computer code,⁴ which is based on the LSS theory of the slowing down of charged particles in matter,⁵ were obtained for the other ions in the sequence, and the results of these measurements are summarized in Table 3.2. For this comparison of the experimental results with the E-DEP-1 calculations, the electronic stopping parameter k in the LSS theory was used as an adjustable parameter. The curve in Fig. 3.10b labeled $k = 0.124$ has been calculated using the LSS theoretical value for k and gives a rather poor fit to the experimental data, whereas the curve calculated for $k = 0.137$ gives an excellent fit to the data on the front side of the damage peak. In these experiments, near the end of the range of the ions, multiple scattering in conjunction with the experimental geometry leads to changes in the ion flux and angular distribution at the specimen, which differ from those in a continuous medium, as calculated by E-DEP-1. These changes in the ion beam lead to a reduction in the measured damage rates near the end of the range that is estimated to be less than 3% at the peak of the damage curve, but which increases rapidly with increasing depth. Thus, experimental values on the back side of the damage peak are expected to fall below the theoretical curve as observed. In Fig. 3.11, the values of

k obtained from the best fit to the experimental data are plotted against the atomic number of the ion along with the equivalent LSS theoretical values. The results obtained here are similar to results reported on the Z_1 oscillations in the electronic stopping cross section in which thin C foils were used as the target material.⁶

The experimental results summarized in Table 3.2 compared with the theory as represented by E-DEP-1 show similar agreement between experiment and theory for the sequence of ions from $Z = 12$ to 18. The comparisons of the peak-to-open damage ratios show that in all cases the experimental ratios are somewhat less (10–15%) than the theoretical ratio, with no clear indication of any systematic trend. In addition, the comparison of the normalized damage rates with the normalized damage energy indicates agreement within the estimated experimental accuracy ($\pm 5\%$ for damage rates, $\pm 7\%$ for ratios) except for ^{32}S at 5.9 MeV and ^{40}Ar . In both these cases, the extrapolation to the initial damage rate was subject to a larger error.

In contrast to the generally good agreement found between experiment and theory for the heavy ions, rather large discrepancies are found for the light ions. This discrepancy is observed in the peak-to-open ratio for both the ^1H and ^4He ions listed in Table 3.2 in

Table 3.2. Comparison of experiment and theory for heavy-ion damage in Al

Ion	Run	Energy (MeV)	Resistivity ($10^{-12} \Omega\text{-cm}$)	Initial damage rate ^a ($10^{-22} \Omega\text{-cm/ion}$)	Damage ratio, peak:open		Damage rate normalized to Al	Damage energy normalized to Al
					Experiment	Theory		
^{24}Mg	4A	4.6	3.207	3.921	11.3	12.8	0.76	0.82
^{27}Al	1	4.8	3.193	5.033	10.4	11.9	1.00	1.00
^{27}Al	5	4.8	3.217	5.260				
^{28}Si	2A	5.0	3.196	5.674	9.7	11.3	1.10	1.13
^{31}P	3A	5.3	3.199	6.847	9.5	10.8	1.33	1.31
^{32}S	3B	5.5	3.341	7.731	9.0	10.3	1.43	1.46
^{32}S	3C	5.9	3.472	6.338	9.3	10.9	1.23	1.37
^{35}Cl	2B	5.6	3.431	8.398	8.3	9.5	1.63	1.70
^{40}Ar	4B	6.0	3.367	9.100	8.1	8.9	1.76	1.97
^1H		0.3	3.176	0.0204	19.2	11.8	4.07×10^{-3}	6.02×10^{-3}
						12.2 ^b		$3.92 \times 10^{-3} (b)$
^4He		1.0	3.176	0.0993	31.9	18.8	1.93×10^{-4}	2.70×10^{-3}
						22.0 ^b		$2.11 \times 10^{-3} (b)$

^aOpen-beam (no absorber foils) damage rate extrapolated to zero damage.

^b20-eV threshold energy.

Fig. 3.11. Electronic stopping parameter k vs atomic number. Crosses are theoretical values from the LSS theory (ref. 5), and solid circles are experimentally determined values.

which the experimental results give approximately 50% larger ratios than the theory. On the other hand, the normalized damage rates listed in Table 3.2 for these ions are substantially less than those expected from the theory. This latter result is accounted for by the fact that with the light ions, low-energy recoil events constitute a larger fraction of the primary recoil spectra than is the case for the heavy ions. The use of a 20-eV threshold energy in the E-DEP-I damage energy calculations for both the Al ions and the light ions leads to good agreement between the experimental and theoretical values, as can be seen in Table 3.2. This correction for low-energy recoils also leads to larger peak-to-open ratios; however, the discrepancy between experiment and theory is still about 50%. The reason for this discrepancy has not yet been determined with certainty but is believed to be due to failure of the E-DEP-I code to properly take into account the backscattering that occurs for the light ions but is negligible or not present for the heavy ions.

NORMALIZATION OF FAST-NEUTRON DAMAGE TO SELF-ION DAMAGE IN Al

T. S. Noggle B. R. Appleton J. M. Williams

In the simulation of fast-neutron damage by self-ion irradiations, the equivalence of the damage produced by the different irradiations is obtained from theoretical calculations of the damage energy that is then converted into displacements per atom (dpa) using an appropriate value for the energy required to produce atomic displacements in the material. The theory applied to each type of irradiating particle has a common origin; however, in the case of ion irradiation it must typically deal with a wider range of recoil energies than for neutron irradiation and with additional features associated with the slowing down of the incident ions. Comparison of the damage energy model with experimental damage production rates for thermal- and fission-spectrum neutrons has indicated for a wide range of materials that the theoretical ratio of fission-to-thermal damage energies ranges from 0.75 to 3 times the equivalent ratio of damage rates.¹ A similar comparison of high-energy-neutron damage to fission-neutron damage gave agreement between experiment and theory to within ~10%.¹ To date, similar comparisons of ion damage to fast-neutron damage have not been made, and the present work was carried out to obtain experimental damage rates for such a comparison.

The principal problem in the experimental measurement of ion damage rates is due to the generally very short range of ions in solids, which precludes the use of bulk specimens of the type used in the measurement of neutron damage in metals. We have recently developed and employed thin-film techniques to measure damage production rates as a function of ion penetration depth of MeV Al ions in Al.^{2,3} One of the problems encountered in this work, which makes comparisons with theory of uncertain value, is the scatter in measured ion damage rates. As an example, Table 3.3 lists Al ion damage rates measured in specimens whose thicknesses range from 0.25 to 0.49 μm . On the basis of the estimated experimental errors associated with measurements of specimen thickness, ion dosimetry, and electrical resistance, one would expect that the scatter in the damage rates at a given energy should be within $\pm 10\%$, whereas the results listed in Table 3.3 indicate that the scatter is at least twice as great. On the other hand, the damage rates measured at different times in a given specimen have been found to be reproducible to better than 5%, the estimated experimental uncertainty that is principally due to the ion dosimetry. The reason for the larger data scatter from specimen to specimen has not been identified; however, this is likely due to the uncertainty associated with the size-effect correction in

1. Guest scientist from Hahn-Meitner Institut, Berlin, Germany.

2. T. S. Noggle et al., p. 255 in *Proceedings of Fourth Conference on the Scientific and Industrial Applications of Small Accelerators*, ed. by J. L. Duggan and I. L. Morgan, IEEE 76CH1175-9 NTS, Piscataway, N.J., 1976.

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6. P. Hvelplund and B. Fastrup, *Phys. Rev.* 165, 408 (1968).

Table 3.3. MeV self-ion damage rates in Al

Specimen	Thickness (μm)	Ion energy (MeV)	Damage rate ($10^{22} \Omega\text{-cm ion}^{-1} \text{cm}^{-2}$)
10	0.38	5.0	5.03
9	0.25	5.0	6.95
15	0.49	5.0	6.41
		4.8	6.26
		4.6	6.12
17	0.44	4.6	6.79
25	0.35	4.8	4.53

these thin-film specimens, which ranged from about 10 to 35%, depending on specimen thickness and resistivity. Relating these results to measurements on bulk specimens of the type used for measuring neutron damage rates leads to the result that the theory scales the ion damage to fast-neutron damage to within about $\pm 25\%$. At the ion damage peak position, the difference between experiment and theory increases to about 40%.

The present work was conducted with the goal of further reducing the experimental uncertainties and involved irradiating a thin-film specimen with fission-spectrum neutrons and with Al ions. In view of the reproducibility of ion damage rates measured in a given specimen, we anticipate that the variability of results associated with different specimens will be substantially reduced in this way. To avoid the uncertainties associated with conversion of the electrical measurements of the thin-film specimen into specific resistivities for com-

parison with fast-neutron damage rates measured in bulk specimens, a 0.1-mm wire specimen was placed in close proximity to the thin-film specimen during the irradiation and its damage rate measured along with the thin-film specimen. These measurements provide a direct experimental normalization of the thin-film damage rate to the bulk damage rate.

The results obtained from these measurements and from Al ion damage in the thin-film specimen are tabulated in Table 3.4 along with the damage rate and damage energy ratios. The experimental and theoretical ratios agree to better than the estimated experimental error of $\pm 10\%$ without correction of the ion damage energy calculation for low-energy recoils below the displacement threshold. Using 20 eV for the threshold value leads to essentially identical ratios for experiment and theory. These results, along with the comparison of ion damage rates as a function of ion penetration depth with theoretical damage energy curves,² indicate that the damage energy model scales fast-neutron damage in Al to 4.8-MeV Al ion damage in Al with a maximum error $\sim 15\%$ for ion penetration depths from the entrance surface to the damage peak region.

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2. T. S. Noggle et al., p. 225 in *Proceedings of Fourth Conference on the Scientific and Industrial Applications of Small Accelerators*, ed. by J. L. Duggan and I. L. Morgan, IEEE 76CH1175-9 NTS, Piscataway, N.J., 1976.

3. T. S. Noggle et al., *J. Nucl. Mater.* 69/70, 797 (1978).

Table 3.4. Experimental ion and neutron damage rates in Al compared with damage energy calculations

Specimen	Irradiation	Initial damage rates	Damage rate ratio (ion:neutron)	Damage energy, ratio (ion:neutron)
Wire, 0.1 mm diam	Fission spectrum neutrons	$2.13 \times 10^{-25} \Omega\text{-cm neutron}^{-1} \text{cm}^{-2}$		
Thin film, 0.35 μm thick	Fission spectrum neutrons	$1.39 \times 10^{-26} \Omega \text{neutron}^{-1} \text{cm}^{-2}$		
	4.8-MeV ^{27}Al	$3.27 \times 10^{-16} \Omega \text{ion}^{-1} \text{cm}^{-2}$	2.35×10^6	2.50×10^6
				2.32×10^6 (a)

^a 20-eV threshold.

THE EFFECTS OF IRRADIATION ON THE Cu NORMAL METAL OF A COMPOSITE SUPERCONDUCTOR¹

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C. E. Klabunde R. R. Coltman, Jr.
R. L. Chaplin²

Copper is a candidate material for the stabilizer in composite superconductors to be used in the toroidal and poloidal magnets of the tokamak fusion reactor.³ The anticipated application entails neutron damage to magnet components ranging up to approximately 10^{-2} displacements per atom per year⁴ (dpa/year) at component temperatures of <10 K and magnetic fields up to 110 kOe.³ Therefore, it is of interest to have predictive information on the combined effects of these environmental factors on the electrical resistivity of Cu. This paper combines experimental information that we now have on radiation damage and magnetoresistivity to yield a construction of resistivity vs magnetic field and dpa appropriate to the application.

Magnetoresistivity data were obtained from three Cu stocks in two experiments. One sample was irradiated in the LTIF of the BSR at 4 K with thermal neutrons. The damage produced from the n - γ recoils consists of point defects. About 5% of the total irradiation resistivity, $\Delta\rho_D(0)$, is due to transmutations. Resistivity measurements were made in situ against dose at several fields.

Six other samples, three bare and three Cd shielded (to eliminate thermal-neutron effects), were irradiated at 60°C in CP-15 of the BSR. The neutron spectrum in this facility is typical of core spectra for water-moderated reactors. At this temperature the damage retained has aggregated into dislocation loops. After each increment of radiation, the sample assembly was removed to a shielded dewar containing a superconducting magnet. Measurements were made at seven fields up to 51 kOe.

Kohler plots of the data for all samples are shown in Fig. 3.12. The dispersion in the data is mainly due to different slopes of the Kohler plot for different samples, reflecting deviations from Kohler's rule. The deviations apparently depend on the nature of the electron scattering from different defects, for example, transmutations, dislocation loops, and point defects.

To describe the dispersion, we constructed straight lines that envelop most of the data in the pertinent range of $H/\rho(0)$, that is, to the right of the vertical tic at $H/\rho(0) = 110$ kOe per 430 nΩ-cm. These lines correspond to solutions of the form

$$\rho(H) = 10^\alpha H^\beta \rho(0)^{1-\beta} + \rho(0). \quad (1)$$

Fig. 3.12. Kohler plot containing all the data for all the samples. The α 's and β 's are the intercepts and slopes of the envelope lines respectively. There are 1218 points on the graph.

where α and β are the intercept and slope, respectively, of one of these lines on the Kohler plot and

$$\rho(0) = \rho_0(0) + \Delta\rho_D(0), \quad (2)$$

where $\rho_0(0)$ is the preirradiation resistivity and

$$\Delta\rho_D(0) = (400 \text{ n}\Omega\text{-cm})[1 - \exp(-162D)]. \quad (3)$$

Equation (3) is the integrated form of a linear damage saturation law.

$$\frac{d\Delta\rho_D}{dD} = \left(\frac{d\Delta\rho}{dH}\right)_0 \left(1 - \frac{\Delta\rho_D}{\Delta\rho_\infty}\right),$$

where $\Delta\rho_D \equiv \Delta\rho_D(0)$ and D is the neutron fluence in dpa.

The dpa values used here are calculated using RECOIL⁵ and assume a displacement threshold energy E_d of 30 eV. The calculations were made for a pure fission spectrum in which the corresponding initial resistivity damage rate was measured.⁶ The result was $(d\Delta\rho_D/dD)_0 = 6.49 \times 10^6$ nΩ-cm per dpa.

For reactor neutron irradiation, Nakagawa et al.⁷ found that the linear saturation law was not precisely obeyed for Cu; they used a cubic fit to obtain a better

description of the data. The corresponding $\Delta\rho_{\infty}$ was 435 n Ω -cm. However, a large fraction of the curve could be approximated by a linear fit with a $\Delta\rho_{\infty}$ of 350 n Ω -cm. For the construction presented below, we chose to use a linear decrement with a $\Delta\rho_{\infty}$ of 400 n Ω -cm. This approximation is justified considering the overall uncertainties in relating existing data to the application.

Figure 3.13 is a construction of $\rho_D(H)$ vs D , which represents simultaneous solutions of Eqs. (1), (2), and (3). The curves are spaced by H as a parameter in the third dimension. For each value of this parameter, a curve is constructed to correspond to each of the two envelope lines in Fig. 3.12. Thus, the bandwidth between the two curves is a measure of the uncertainty in ρ_D vs D due to dispersion in the magnetoresistance data.

Fig. 3.13. A plot of ρ_D vs D for $\rho_s(0) = 30$ n Ω -cm at several H 's.

Since the neutron dosimetry in the above tests was converted to dpa, we can go directly to the application, because Santoro et al.⁴ have calculated the neutron fluxes at several positions in a tokamak toroidal field coil and in turn converted these to dpa rates. Table 3.5 presents a resistivity value for a service time of one year at Santoro et al.'s position 4 for two cases, one with a penetration that is being considered for the neutral beam injector and the other without the penetration. Position 4 is on the plasma side of the winding next to the shield. Resistivity values corresponding to the middle of the magnetoresistance band are given for three representative starting materials.

Table 3.5. Projected Cu resistivities at position 4 in a tokamak

Starting material $[\rho_s(0),$ n Ω -cm]	Total resistivities $[\rho_D(110 \text{ kOe}), \text{n}\Omega\text{-cm}]$		
	Unirradiated	One year, no penetration (6.4×10^{-4} dpa)	One year with penetration (1.3×10^{-2} dpa)
3	62	89	392
10	62	95	399
30	78	114	419

Some uncertainties in the use of the above construction due to the tokamak environment are

1. the influence of neutron spectra that differ from those used here;
2. the influence on the damage resistivity behavior of periodic annealing of superconducting coils during the tokamak lifetime; and
3. the influence of transmutation resistivity that will not be removed by annealing.

The constructions presented in the report are not intended to serve as a base from which precise magnet designs can be developed. The methods formulated here, however, can be used at such time as the necessary data become available.

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IRRADIATION EFFECTS ON ORGANIC INSULATORS AT 4.9 K

R. H. Kermohan R. R. Colman, Jr. C. J. Long¹

During this reporting period, a program was initiated to study the effects of irradiation at liquid-He temperature on the properties of organic insulators. The impetus for the program was derived from the need to understand the irradiation behavior of such materials

that may be used in the construction of large superconducting coils that provide magnetic containment for the plasma in a fusion reactor.

Two experiment assemblies have been irradiated near 4.9 K in the ORNL LTIF, which receives a highly thermalized neutron flux originating in the ORNL BSR. In each case, neutron-capture gamma rays produced in a Cd shield surrounding the assembly added to the ambient gamma level to provide an intense gamma-ray flux that was by far the principal damaging radiation received by the samples within. The specimens were arranged in two groups in each assembly: one for the in situ measurement of resistance changes during the irradiation and annealing program and the other for postirradiation measurement of mechanical and electrical properties after warm-up to room temperature. Measurements after warm-up are considered appropriate, since periodic annealing is expected during the operating life of a fusion reactor. The measurements and observations included lap shear, three-point bending and compression strength, voltage breakdown, weight loss, and changes in color and surface features.

The materials tested were

1. Stycast 2850 Blue Epoxy, with 7% 24 LV hardener, Emerson and Cuming, Inc., an inorganically filled room-temperature-curing epoxy;
2. Epon 828 epoxy, 70% Epon 871 flexibilizer, 13-phph Z curing agent, 0.5% Z6020 Silane couplant, Shell Chemical Company (good strength but requires 68°C cure);
3. EF-527 B-stage, Synthene-Taylor Corporation, a partially cured glass cloth-epoxy composite (good mechanical properties but requires curing at 175°C under pressure);
4. NEMA G-10 high-pressure glass-epoxy laminate;
5. NEMA FR-5 - like G-10, but with resin modified for temperature resistance and lower flammability;
6. Nomex paper, type 410, DuPont, aromatic polyamide sheet;
7. Kapton film, DuPont, polyimide film frequently used in magnets;
8. Formvar insulating varnish on Cu wire; and
9. Aluminized Mylar.

Specimens in the first experiment received a dose of 2×10^9 rads at 4.7 K. While some decreases in resistivity were apparent, the materials remained excellent insulators relative to their intended usage. Mechanical-properties changes were small enough to be

within the scatter of the data. A more complete report of the first experiment has been given elsewhere.²

In the second experiment, the dose was increased to 2×10^9 rads. The in situ resistivity specimens showed decreases to as little as one-third the starting value, but all values remained in the usable range. In both experiments, the apparent resistance of the in situ resistivity specimens dropped by a factor of 2 to 50 on warm-up above 200 K after irradiation. The original resistance was restored by purging the sample chamber with clean He gas. This result could be explained by electrical leakage due to contamination of the chamber atmosphere by a species that is immobile at 4 K. Its identity and source are presently unknown but will be investigated.

In contrast to the first experiment, the higher dose in the second produced significant changes in some mechanical properties. One example shown in Table 3.6 is the lap shear strength of materials bonded to Cu and tested at 77 K after irradiation at 4.7 K and warm-up to 300 K. This property is particularly important in magnet design.

Table 3.6. Lap shear strength at 77 K with Cu

	2759 FT Blue Epoxy	Epon 828 epoxy	B-stage glass cloth, EF-527
Control			
Shear stress, psi	6790	7570	9960
Average deviation, %	36	6	25
Irradiated to 2×10^9 rads			
Shear stress, psi	2790	4880	1760 ^a
Average deviation, %	3	21	25

^aFractured at interface.

Analyses of sample-chamber gas taken immediately after the postirradiation warm-up to 305 K and then 35 days later are shown in Table 3.7. The reduced percentage composition of H₂ in the later sample suggests that this decomposition product diffuses out of the irradiated material at a faster rate than the other products shown.

Further testing of these materials to higher doses is anticipated.

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Table 3.7. Percentage composition of gaseous breakdown products present at 305 K after irradiation to 2×10^9 rads at 4.7 K

O ₂ and A barely detected							
	H ₂	CH ₄	H ₂ O	N ₂ + CO ₂	CO ₂	Hydrocarbons	Fluorocarbons
Immediately after warm-up	93.7	0.3	3.2	1.4	0.7	~0.2	~0.5
After 35 days	35.8	29.9	3.1	18.2	8.9	1.8	2.0

ENHANCEMENT OF THE LTIF CAPABILITIES

R. R. Coltman, Jr. C. E. Klabunde J. M. Williams

During this reporting period, three significant advances were made in the capabilities of the ORNL LTIF.

A new high-flux mode

To permit operation of the LTIF with much higher fluxes, the D₂O tank previously mounted on the grid plate of the BSR between the core and the LTIF has been remounted on a movable stand. There it can either be interposed between the LTIF and the reactor as before, or it can be omitted and the core brought directly against the facility, resulting in a high-flux mode. Operation of the cryostat below 4.8 K in this mode has been verified, and calibrations of the thermal- and fast-neutron fluxes and gamma heating have been completed and are tabulated in Table 3.8. The gain in neutron flux carries with it a restriction to low-mass, easily cooled sample assemblies because of the increased gamma heat.

LTIF ozone hazard test

The explosion hazard of cryogenically irradiated air (the "cryogenic ozone hazard") in the LTIF was successfully tested. A charge equivalent to 7 g of TNT,

simulating the maximum credible explosion from the buildup of ozone, was set off in a mock-up of the LTIF cryostat and housing under realistic ambient conditions. The test results showed that such an explosion would not be a hazard to the reactor or to personnel. This test was part of a comprehensive review of the LTIF by the ORNL Reactor Experimental Review Committee and reconfirmed by experiment the earlier conclusions reached by calculation that the LTIF could operate safely in all its normal modes -- including irradiation with the sample chamber below atmospheric pressure, which had been restricted pending satisfactory outcome of the review.

Improved data acquisition and processing capabilities

A resolution as fine as 10^{-8} V of changes in signals as large as 10^{-3} to 10^{-2} V remains the mainstay of studies of radiation damage in metals by means of resistivity effects. Although much of the work is done with state-of-the-art digital voltmeters, which can handle either the high resolution or the large signal, but not both at once, the low-thermal-emf six-dial potentiometer is still the only instrument capable of fully meeting these demands. The calculator-based data-acquisition-and-analysis system was improved by addition of an interface, custom designed and built by the Instruments and Controls Division, which permits direct recording of the

Table 3.8 Low-Temperature Irradiation Facility

Cooling capacity about 40 W

Radiation	Flux mode		Ratio of high to low
	High	Low	
Thermal, ϕ_T , neutrons cm ⁻² sec ⁻¹	8.5×10^{11}	2.13×10^{11}	4.0
Fast, $\phi_F > 0.1$ MeV, neutrons cm ⁻² sec ⁻¹	$\sim 2 \times 10^{11}$	$\sim 2 \times 10^9$	~ 100
ϕ_T/ϕ_F	~ 42	~ 1000	
Gamma-ray heating, mW/g	99	21	4.7

potentiometer reading. Other additions to this system include a 7½-digit digital voltmeter (with 0.3-μV resolution), more low-thermal-emf input scanning channels, more advanced programming capability for the calculator and a tripling of its memory, and an X, Y plotter.

We wish to acknowledge the valuable assistance of J. F. Emery of the Analytical Chemistry Division for the neutron-flux measurements and C. R. Mitchell of Instrumentation and Controls Division for the design and debugging of the potentiometer interface.

FRACTURE

ELECTRON MICROSCOPE STUDIES OF SHEAR CRACKS IN STAINLESS STEEL SINGLE CRYSTALS

S. M. Ohr J. Narayan

Electron microscope studies have been made of the distribution of dislocations in the plastic zone of propagating cracks during *in situ* tensile deformation of thin foil specimens of stainless steel single crystals. In these specimens under plane stress conditions, the plane of maximum shear stress makes an angle of 45° with the tensile axis, and both the fracture and the plastic deformation ahead of the crack are expected to occur in this plane. Figure 3.14 shows an electron micrograph taken from an (001) single-crystal specimen of stainless steel. The micrograph was taken in the stressed condition using the diffraction vector of (020). The crack that was initiated at the edge of the foil has propagated into the crystal, and the plastic zone that is coplanar with the crack has formed in front of the crack tip. The dislocations in the plastic zone are in the form of an inverse pileup. From the stereoscopic analysis, the slip plane was identified as the (111) plane. The dislocations lie nearly along the [011] direction and are split into partial dislocations.

Figure 3.15a shows a close-up view of the plastic zone. Under the operating reflection of (020), the stacking fault fringes and the leading partial dislocations are visible. In Fig. 3.15b the same area is imaged using the (200) reflection. In this micrograph, the stacking fault fringes are still present, but none of the partial dislocations are visible. From this contrast behavior, it was possible to identify the reaction at the dislocations as

$$\frac{a}{2}[011] \rightarrow \frac{a}{6}[121] + \frac{a}{6}[\bar{1}12] ;$$

that is, the dislocations have split into two Shockley partial dislocations. Because the dislocations lie along the [011] direction, the dislocations in the plastic zone

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Fig. 3.14. Electron micrograph showing a shear crack and its plastic zone in a (001) thin foil, stainless steel, single-crystal specimen. The plastic zone is coplanar with the crack, and the dislocations are in the form of an inverse pileup.

Fig. 3.15. Dislocation structure in the plastic zone of a shear crack observed in a stainless steel single crystal imaged with the (a) (020) reflection and (b) (200) reflection. These dislocations, identified as pure screw dislocations, are extended into Shockley partial dislocations.

are an extended form of pure screw dislocations. The plastic zone, therefore, represents pure shear deformation, and the crack is an antiplane strain shear crack of Mode-III type.

These observations are in excellent agreement with the theory proposed by Bilby, Cottrell, and Swinden,¹ known as the BCS theory of fracture. By considering the equilibrium configuration of dislocations in the plastic zone of a shear crack, they have predicted an inverse pileup of screw dislocations coplanar with the crack for the antiplane strain fracture. We have determined the crack opening displacement (COD) of the shear crack directly by counting the number of screw dislocations in the plastic zone. The results show that the value of COD is roughly equal to the thickness of the foil. It is in agreement with the contention that the COD should be greater than the specimen thickness for a propagating crack. The value of COD was also determined from the relative size of the crack and the plastic zone based on the BCS theory. The value was about an order of magnitude lower than that obtained from the number of dislocations in the plastic zone.

The present work is believed to be the first experimental verification of the BCS theory concerning the

dislocation model of a plastic zone associated with a shear crack. However, the details of the theory may have to be modified before it can be applied directly to our thin foil experiments.

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IN SITU ELECTRON MICROSCOPE OBSERVATION OF FRACTURE IN Mo

S. Kobayashi S. M. Ohr

In situ electron microscope studies of fracture in thin foils of stainless steel have shown that the plastic zone at the crack tip, consisting of an inverse pileup of screw dislocations, was extended in the direction of crack propagation. These observations were in good agreement with the theoretical predictions of Bilby, Cottrell, and Swinden.¹ To investigate the role of crystal structure on the microscopic aspect of fracture, we have made similar observations on single-crystal as well as polycrystalline specimens of Mo, a bcc metal representing semibrittle solids.

In single crystals of Mo, the dislocations cross-slipped readily from their slip planes and rarely formed well-developed pileups. In polycrystalline specimens, the cracks tended to propagate along the grain boundaries. In some cases, however, the cracks did propagate inside the grain. Figure 3.16 shows a micrograph taken from a polycrystalline specimen of Mo that was deformed in the electron microscope. As the stress was applied, the crack was initiated at the edge of the hole and propagated rapidly into the specimen. It can be seen that the plastic zone is somewhat broad and is made up of inverse pileups of dislocations extended in the direction of crack propagation. A number of dislocation arrays branch out from the main pileup. From the contrast analysis, it was found that these dislocations represented slip along the $[111]$ direction on various $\{112\}$ and $\{1\bar{1}0\}$ planes. Some of the dislocation arrays terminate at grain boundaries, indicating that a boundary is an effective barrier to crack propagation. These studies have shown that the microscopic processes occurring at the crack tip in Mo are qualitatively similar to those observed in stainless steel. Further experiments involving high-voltage electron microscope observations of crack propagation in thick samples are under preparation.

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FORCE ON A DISLOCATION

S.-J. Chang¹

Stress concentration around a crack tip in metals often causes plastic deformation that introduces on a microscopic scale a continuous distribution of dislocations. The equilibrium configuration of the dislocations is closely related to the phenomenon of fracture initiation. The calculation of forces on the dislocations is required in determining the equilibrium configuration and therefore is essential for the understanding of the phenomenon of fracture initiation.

In the present study, the energy-momentum tensor of Eshelby is used in the calculation of the forces.² A modified form has been derived by Budiansky and Rice in terms of a complex variable.³ The method of complex variables in elasticity can, therefore, be used in the calculation of the forces on defects. The force on an edge dislocation in a two-dimensional elastic medium assumes the following form:

$$J_1 + iJ_2 = -\frac{2i}{F} \left[\oint (\phi'^2) dZ - 2 \oint \phi' \bar{\psi}' dZ \right],$$

Fig. 3.16. Electron micrograph showing the dislocation structure in the plastic zone of a propagating crack in polycrystalline sample of Mo. Some of the dislocations are piled up at the grain boundaries.

where E is the elastic constant and J_1 and J_2 are the x_1 and x_2 components of the force respectively. In the above equation, ϕ and ψ are the stress functions of a complex variable Z where $Z = x_1 + ix_2$. There are two advantages of using this complex representation of force. Because the stress functions for the dislocation are logarithmic functions, the complex integration around a dislocation reduces conveniently to the calculation of residues. Also, because the formula is expressed in terms of a complex variable, it can be transformed readily to other geometries by conformal mapping. Therefore, it provides a simple way to calculate the force on a dislocation in materials of various geometrical shapes. The effect of crack tip geometries, for example, can be treated quite conveniently in this way.

Numerical results have been obtained for an edge dislocation located near a crack. In Fig. 3.17, the contours of constant J_1 are plotted to indicate the magnitudes and the directions of the force. The effect of stress concentration near the crack tip and the effect of an image dislocation can be seen from the curves. The effect of root radius has also been calculated.

Fig. 3.17. Contour plots of the x_1 component of force on an edge dislocation located near a crack of half length $2R$ subjected to a uniaxial stress σ perpendicular to the crack.

The force on a screw dislocation, located close to a crack and subjected to an antiplane shear, can be represented simply by

$$J_1 - iJ_2 = -\frac{i}{2G} \oint (w)^2 dZ,$$

where w is the displacement function of the complex variable Z and G is the shear modulus. If a transformation is made from the Z plane to the ζ plane, the force in the Z plane can be related to the force in the ζ plane as

$$J_1 - iJ_2 = (J_1' - iJ_2') \left(\frac{d\zeta}{dZ} \right)_{Z=Z_0},$$

where Z_0 is the location of the dislocation in the Z plane. For a half plane with a dislocation subjected to an antiplane shear of magnitude σ , it can be shown that

$$J_1' - iJ_2' = i \frac{Gb^2}{4\pi} \frac{1}{\text{Im}(\zeta_0)} - i\sigma b,$$

where b is the Burgers vector, ζ_0 is the location of the dislocation in the ζ plane, and $\text{Im}(\zeta_0)$ is the imaginary part of ζ_0 . For a half plane with a crack of length l , the force can be shown as

$$J_1 - iJ_2 = (J_1' - iJ_2') \frac{Z_0}{\zeta_0}.$$

The effect of root radius can also be treated by a transformation of the crack into an elliptical shape. The result is

$$J_1 - iJ_2 = (J_1' - iJ_2') \frac{1 - a_1^2/Z_1^2}{1 + a_2^2/Z_1^2},$$

where $\zeta = Z_1 + a_1^2/Z_1$ and $Z = Z_1 - a_2^2/Z_1$ with $a_1 > a_2$. Other geometries can be studied similarly.

It is seen from the above consideration that the complex representation of J_1 and J_2 provides a convenient method of calculating the force on a dislocation near the crack. It has an advantage of being able to study the problems of various crack orientations and geometries.

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DEFECTS AND IMPURITIES IN INSULATING CRYSTALS

MECHANISM FOR H DIFFUSION IN TiO_2 ¹

J. B. Bates J. C. Wang R. A. Perkins²

Rutile has a tetragonal structure that is characterized by large open channels parallel to the crystallographic c

axis. This characteristic accounts for the fact that light ions, such as protons, diffuse much more rapidly parallel to the c axis than perpendicular to it. Measurements of the infrared absorption spectra of H and its isotopes³ in TiO_2 have shown that most of the H that enters the lattice on heating rutile in an environment of H_2 or H_2O is bound in the form of OH^- ions.

The activation energies and preexponential factors for the diffusion of H parallel and perpendicular to the c axis in TiO_2 have been reported,⁴ and those for T diffusion were determined in this Laboratory.⁵ The goal of the present work was to develop a model for OH^- in TiO_2 that would provide calculated activation energies for H diffusion in good agreement with the observed values and also give an equilibrium orientation and stretching frequency consistent with experimental results.

It was assumed that the O atom of the hydroxyl ion occupies an O^{2-} site of the rutile lattice. Because of the strong bond between the proton and the O ion in OH^- , we found that it was necessary to represent the O-H interaction by means of a Morse potential. The function we found to give acceptable results is given by

$$V = \sum_i D_e \left\{ 1 - \exp \left[-a(r_{ih} - r_e) \right] \right\}^2 - \sum_{i \neq \text{O}_H} \frac{q_h r_{ih} p_i}{r_{ih}^3} + \sum_j \frac{q_h q_j}{r_{jh}} + \sum_j b \epsilon \exp \left[-\frac{1}{\rho} (r_{jh} - R_h - R_j) \right] \quad (1)$$

The index i labels O^{2-} ions only, and the index j labels only Ti^{4+} ions. The distance between the proton and the k th ion is denoted by r_{kh} , with $r_{kh} = |\mathbf{r}_{kh}| = |\mathbf{r}_k - \mathbf{r}_h|$, where $\mathbf{r}_k$ and $\mathbf{r}_h$ are the position vectors of the k th ion and the proton respectively.

The first term in Eq. (1) is the Morse function, which represents the major part of the O-H potential. The second term arises from the interaction of the charge on the proton q_h with the induced dipole moments on the O^{2-} ions p_i . The net dipole moment at the O^{2-} ion is induced by the electric field due to point charges of all the other ions E_0 and by the electric field due to induced dipole moments on all the other O^{2-} ions. Thus,

$$\mathbf{p} = \alpha_0 \left[\mathbf{E}_0 + \frac{1}{\rho_0} (\rho_x \mathbf{E}_1 + \rho_y \mathbf{E}_2 + \rho_z \mathbf{E}_3) \right], \quad (2)$$

where $\alpha_0 = 2.22 \text{ \AA}^3$ is the polarizability of O^{2-} in TiO_2 . The vector $\mathbf{E}_i$ ($i = 1, 2$, and 3) in Eq. (2) is the electric field at the test O^{2-} ion due to unit dipoles at all other O^{2-} ions. The orientations of these fields are determined

by applying crystal symmetry to the unit vector along the i th ($i = x, y$, and z) coordinate at the test ion. A set of three simultaneous equations are given by the x, y , and z components of $\mathbf{p}$ in Eq. (2), and these were solved self-consistently for the values of p_x, p_y , and p_z .

The third term in Eq. (1) arises from the Coulomb interaction between the charge on the proton $q_h = +0.56$ and the charge on the Ti ions $q_j = +4$. The Coulomb interaction between the charge on the O^{2-} ions and the Ti^{4+} ions was not included because this interaction contributes only a constant energy term under the assumption that the O^{2-} and Ti^{4+} ions remain fixed. The last term in Eq. (1) accounts for the short-range repulsive interaction between the OH^- and the Ti ions. The terms due to O-O, O-Ti, and Ti-Ti contacts were omitted because these contribute a constant energy when only the proton is allowed to move. With the exception of the constant b in the repulsive term, the parameters in Eq. (1) were taken from theoretical or experimental studies of OH^- ions in the free state. The b parameter was adjusted so that the O^{2-} ions remained in their equilibrium position in the perfect (H-free) crystal subject to a potential that included the charge-induced dipole, Coulomb, and repulsive energy terms. The model of OH^- represented by Eq. (1) gave calculated values for (a) the orientation of the proton, (b) equilibrium O-H bond length, and (c) O-H stretching frequency in good agreement with the experimental values.

The mechanism proposed for H diffusion parallel to the c axis consists of proton jumps from one O^{2-} ion to another along the channel. The minimum energy path for this mechanism as determined by Eq. (1) is illustrated in Fig. 3.18. The activation energy for diffusion is given by

$$E_a = E_b - \sum_{k=1}^N G_{e,k}(0) + \sum_{k=1}^{N-1} G'_{e,k}(0), \quad (3)$$

where E_b is the barrier height (difference between the energy at the midpoint of the path and the energy at equilibrium), $G_{e,k}(0)$ is the zero point energy of the k th mode in the equilibrium state, $G'_{e,k}(0)$ is the zero point energy of the k th mode at the saddle point, and N is the number of modes. In our approximation, only the proton is allowed to move so that $N = 3$. Values for $G_{e,k}(0)$ and $G'_{e,k}(0)$ were taken to be $\omega_{e,k}/2$ and $\omega'_{e,k}/2$, respectively, where $\omega_{e,k}$ is the calculated frequency of the k th mode. The barrier height for diffusion parallel to c was calculated to be $E_b = 0.824 \text{ eV}$.

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Fig. 3.18. Calculated path for diffusion of H parallel to the c axis. The equilibrium H positions are indicated by shaded circles with a bond drawn to the appropriate O^{2-} ion. The direction of proton diffusion is indicated by the arrows along the path. The orientations of the dipole moments on the O^{2-} ions are indicated by the arrows within the large open circles.

The activation energies calculated from Eq. (2) are compared with the experimental values in Table 3.9a. The energies listed under (1) in this table were determined from $E_a = E_b - E_0$, where E_0 is the experimental zero point energy for the stretching mode.¹

The mechanism proposed for diffusion perpendicular to the c axis involves a rotation or flip-over of the proton from one channel to an adjacent channel as the rate limiting step. The calculated diffusion path is illustrated in Fig. 3.19. It was found that the difference in zero point energies between the equilibrium and saddle

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Fig. 3.19. Calculated path for the flip-over or rotation mechanism for diffusion of H perpendicular to the c axis.

Table 3.9. Observed and calculated activation energies for diffusion of H, D, and T, parallel and perpendicular to the c axis in TiO_2 .

a. Diffusion parallel to c				b. Diffusion perpendicular to c			
Parameter	Activation energy (eV)			Parameter	Activation energy (eV)		
	Observed	Calculated ^a			Observed	Calculated ^b	
		(1)	(2)				
H	0.59 ^c	0.60	0.64	H	1.28 ^c	1.23	
D	0.59 ^c	0.66	0.69	D	1.28 ^c		
T	0.72 ^d	0.69	0.71	T	1.14 ^d		

^aValues under (1) calculated from $E_a = E_b - E_0$ using experimental zero point energies of the stretching mode. Values under (2) calculated from Eq. (2) using calculated frequencies at the equilibrium and saddle point positions.

^bActivation energies equal to barrier height within 0.001 eV.

^cReported in ref. 4.

^dReported in ref. 5.

point states amounted to only 0.001 eV so that $E_a \approx E_b \approx 1.23$ eV. This calculated value is compared to the experimental results in Table 3.9b. The experimental activation energies for H and T may be considered to be equal to within their relative errors.

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5. J. V. Cathcart et al., *Journal of Applied Physics* (to be published).

H DIFFUSION IN Al_2O_3

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The transport properties of H and its isotopes in Al_2O_3 are largely unknown. We have initiated an investigation of the optical and magnetic properties and diffusion coefficients of H, D, and T in Al_2O_3 with the objective of determining the mechanisms by which H enters into and is transported through the lattice. In this report, we summarize the results of some initial optical studies aimed at characterizing the defect associated with H and the conditions that control its solubility in Al_2O_3 .

Commercially available single crystals of Al_2O_3 were cut and polished into rectangular slabs about 0.3 cm thick with the large faces (1 by 2 cm) parallel to either the (001) or (010) planes.² The infrared absorption in the regions from 3300 to 3270 cm^{-1} and from 2450 to 2430 cm^{-1} observed from measurements of an as-received (001) sample at 77 K is shown in Fig. 3.20a. The band at 3283 cm^{-1} is assigned to the stretching mode of OH^- ions. Using the absorption strength per ion of OH^- in TiO_2 (ref. 3) and the integrated intensity

of this band, we estimate that the crystal initially contained about $5 \times 10^{15} \text{ cm}^{-3}$ of OH^- .

The infrared absorption observed after heating the sample at 1620 K for 24 hr in a dry atmosphere of D_2 is shown in Fig. 3.20b. The intensity of the 3283 cm^{-1} band has decreased, and a new band has appeared at 2441 cm^{-1} . The latter peak is assigned to the stretching mode of OD^- . A comparison of the integrated intensities of the bands in Fig. 3.20a and 3.20b suggests that the treatment of Al_2O_3 with dry D_2 resulted in isotopic exchange of D for H with no change in total H content (H + D) of the sample.

The observed OH^- and OD^- frequencies were used to calculate the harmonic and anharmonic coefficients of the term value equation for OT^- using the method described previously.³ This equation gives a calculated value of 2067 cm^{-1} for the stretching frequency of OT^- in Al_2O_3 at 77 K. Based on the results obtained for H and its isotopes in TiO_2 , we expect this calculated value to be within $\sim 2 \text{ cm}^{-1}$ of the real value. However, infrared measurements of Al_2O_3 treated with dry T_2 or with T_2O vapor at 1000°C have failed to show a band that could be attributed to OT^- , although the presence of T in the sample has been confirmed by liquid scintillation counting. Exploratory searches for T in Al_2O_3 using the ENDOR technique have been initiated.

Fig. 3.20. Infrared absorption of Al_2O_3 at 77 K (a) before treatment and (b) after treatment with dry D_2 . The infrared beam was incident on the (001) face.

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2. Union Carbide Corporation (Crystal Products Division), San Diego, Calif.

3. J. B. Bates and R. A. Perkins, *Phys. Rev. B* 16, 3713 (1977).

KINETICS OF Fe^{2+} OXIDATION AND Fe^{3+} REDUCTION IN MgO SINGLE CRYSTALS¹

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Measurements from EPR have been used to determine the rate of change of the Fe^{3+} concentration in $\text{MgO}:\text{Fe}$ crystals due to reduction and oxidation with ambient gases at temperatures between 900 and 1200°C. The increase or decrease of the Fe^{3+} concentration with time followed a $t^{1/2}$ law where t is the treatment time. Moreover, sectioning of a sample yielded a concentration profile indicative of a diffusion-controlled process. Application of a diffusion formalism allowed determination of diffusion coefficients and the activation energy for diffusion. Figure 3.21 is a summary of these results. It shows that reduction occurs approximately a factor of 4 faster than oxidation, but the activation energy for both oxidation and reduction is the same value, 3.23

Fig. 3.21. Temperature dependence of the oxidation and reduction rate of Fe in MgO. The diffusion coefficient scale shown on the right is derived on the basis of a bulk diffusion model.

eV. These results are consistent with a model in which Fe^{3+} is compensated by vacant cation sites, and reduction and oxidation are rate-limited by the diffusion of cation vacancies to (or from) the surface. There they are annihilated (created) via the reaction $V + \text{O}^{2-} + 2h^+ \rightarrow \frac{1}{2}\text{O}_2$ (gas). In this reaction, V represents cation vacancy, O^{2-} and O_2 represent O in the form of crystal ions and gas, respectively, and h^+ represents a positive electronic charge. The identity of the activation energy determined for the present experiment and that found for bulk self diffusion of Mg ions in MgO (ref. 3) is consistent with a bulk diffusion process. We have found, however, that a diffusion coefficient obtained from a concentration profile contains a small contribution due to an anomalously high mobility, presumably due to diffusion along dislocations.

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2. ORAU undergraduate research trainee from Concordia College, Moorhead, Minn.

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THE DISTRIBUTION OF Fe^{3+} AND Fe^{2+} AT LOW CONCENTRATIONS IN MgO SINGLE CRYSTALS¹

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E. Sonder W. H. Gourdin²

We have utilized EPR and optical techniques to determine the degree of association of Fe ions in MgO single

crystals as a function of the Fe concentration. The EPR measurements were used to obtain information on the aggregation of the Fe^{3+} in the samples. The measurements are especially appropriate because the EPR spectrum of Fe^{3+} in sites of octahedral symmetry in MgO is known,³ and spectral components due to Fe^{3+} in two different sites with noncubic symmetry have been attributed to Fe^{3+} -vacancy pairs.⁴ Optical techniques were used to determine the concentrations of Fe in the Fe^{2+} and Fe^{3+} valence states.^{5,6}

The concentrations of Fe^{3+} in octahedral and orthorhombic sites, as obtained from the intensities of the EPR spectra, are plotted vs total Fe concentration in Fig. 3.22. Data are included for both oxidized and reduced samples. Two aspects of Fig. 3.22 are especially significant. First, the Fe^{3+} concentration in octahedral sites is not proportional to the total Fe content; in fact,

Fig. 3.22. The concentrations of Fe^{3+} in isolated sites of octahedral and orthorhombic symmetries vs total Fe. Data are shown for oxidized samples heated at 1400°C for 48 hr in atmospheres having () partial pressures of 1 and 10^{-5} atm.

it saturates at less than 200 ppm in the oxidized samples. Second, the Fe^{3+} in sites of orthorhombic symmetry saturates and then decreases as the total concentration of Fe exceeds 330 ppm and is <0.1 the concentration of Fe^{3+} in octahedral sites. The spectra attributed to Fe^{3+} in sites of tetragonal symmetry reveal an almost identical behavior to that observed for the orthorhombic sites.

A large number of additional EPR lines with considerable intensity appeared in a sample containing 300 ppm Fe. We attribute these lines to pairs of Fe^{3+} ions associated with single cation vacancies (i.e., trimers). The variations of the intensities of these lines with total Fe are similar to those attributed to Fe^{3+} -vacancy pairs, with the difference that the maximum intensity was observed in a sample that contained 3250 ppm Fe.

A broad resonance line with a g value ≈ 2 was observed in samples containing at least 3250 ppm of Fe. The intensity of the broad line is approximately proportional to the total Fe. This behavior is in definite contrast to that of the Fe^{3+} , which is octahedrally coordinated or associated as dimers and trimers.

The significant finding of the study is that the total concentration of Fe^{3+} in the form of monomers, dimers, and trimers did not exceed 500 ppm even when the total Fe concentration was more than ten times greater. The EPR measurements reveal that the amount of Fe^{3+} in octahedral sites saturates at a concentration of less than 200 ppm. Similarly, one can infer from the EPR spectra of Fe^{3+} dimers and trimers that these species are formed only in low concentrations which reach a maximum value when the total Fe concentration is approximately 300 and 3000 ppm respectively. Only the EPR intensity of a broad resonance continued to increase up to the maximum total Fe concentration studied (7400 ppm). This broad resonance is attributed to clusters larger than trimers. When the total Fe concentration exceeds about 3000 ppm, the Fe is predominantly in such clusters. The temperature-dependent behavior of the resonance line width is that anticipated for clusters of magnesio-ferrite precipitates. In any case, it has been established that clusters larger than trimers are important in the aggregation and charge-state equilibrium of Fe in MgO when the total Fe concentration exceeds a few thousand parts per million.

HIGH-TEMPERATURE AND IONIZATION-INDUCED EFFECTS IN LI-DOPED MgO SINGLE CRYSTALS¹

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H. T. Töhrer² M. M. Abraham

Quenching Li-doped MgO crystals from high temperatures, or performing a high-dose electron irradiation, produces $[\text{Li}]^0$ defects (substitutional Li ions each with a trapped hole).³ In contrast to the $[\text{Li}]^0$ defects formed by low-temperature ionizing radiation, the hole is tightly bound to the aliovalent Li^+ ion in the quenched and electron-irradiated crystals. Investigations using EPR and ENDOR techniques have established that both the stable and unstable $[\text{Li}]^0$ centers have the same local electronic configuration.

An as-grown Li-doped crystal was used to study the thermal generation of $[\text{Li}]^0$ defects. The sample was heated at different temperatures for 10 min in air followed by quenching into a liquid N bath. The defects were generated thermally, without subsequent irradiations of any form. The absorption coefficient of the $[\text{Li}]^0$ band after each heat treatment is plotted as a function of the annealing temperature in Fig. 3.23.

Fig. 3.23. Production of $[\text{Li}]^0$ centers by quenching.

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$[\text{Li}]^0$ defects began to form at 1300 K, and the number rapidly increased until 1500 K; above this temperature, saturation began to take place.

Virgin samples of MgO:Li were also irradiated with 2-MeV electrons at $T = 90$ and 290 K to doses of $\sim 3 \times 10^{17}$ electrons/cm². The cross section for the production rate of stable $[\text{Li}]^0$ defects was $\sim 10^5$ b at room

temperature and 10^3 b at low temperature. This temperature dependence of the cross sections resembles that for the radiation-induced displacement of substitutional H in MgO.⁴

To determine the stability of the $[\text{Li}]^0$ defects, we performed isochronal annealing on samples in which the defects were produced by three methods. Figure 3.24a illustrates the annealing behavior of the $[\text{Li}]^0$ defect in a crystal that was γ -irradiated at 77 K. Curve (b) represents the annealing data of the $[\text{Li}]^0$ band in a crystal irradiated at 290 K to a dose of 5×10^{18} electrons/cm². Curve (c) illustrates the stability of $[\text{Li}]^0$ centers generated by thermal quenching from 1450 K. The temperatures at which half of the defects have been annealed for low-temperature ionizing irradiation, high-dose electron irradiation, and thermal quenching were about 210, 450, and 830 K respectively.

Fig. 3.24. Annealing of $[\text{Li}]^0$ centers in MgO:Li crystals. (a) Slow-cooled and γ -irradiated at 77 K, (b) electron irradiated to 5×10^{18} electrons/cm², and (c) quenched from 1450 K.

To explain the unexpected stability of the $[\text{Li}]^0$ defects, we propose that in slow-cooled (or as-grown) crystals, the Li impurities are concentrated in precipitates. At high temperatures, each precipitate gives rise to a localized Li-rich environment surrounding the precipitate. The precipitate would, of course, diminish in size as a result. Within this "microgalaxy" of abundant substitutional Li^+ ions, charge neutrality requires that the natural state of the impurity be an Li^+ ion with a trapped hole, which is the neutral $[\text{Li}]^0$ center.

TEM STUDIES OF LI-DOPED MgO^1

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A recent study has shown that thermal quenching from high temperatures, or a high-dose electron irradiation at ambient temperature, of Li-doped MgO crystals results in substitutional Li ions, each with a tightly bound hole, forming the stable $[\text{Li}]^0$ defects. The stability of these $[\text{Li}]^0$ defects is an anomaly and appears to be inconsistent with previously held concepts of production and stability of the entire class of hole defects in oxides. Y. Chen et al. proposed that there exist in these crystals precipitates containing Li, that substitutional Li^+ ions form a localized Li-rich environment surrounding these precipitates, and that these ions trap holes to form the $[\text{Li}]^0$ centers.³ We report here the results of TEM studies of precipitates in as-grown MgO:Li and the effects of high-temperature quenching and ionizing radiation on these precipitates.

Figure 3.25a shows an electron micrograph of an as-grown MgO:Li crystal. The black spots are precipitates, with an average precipitate size of 220 Å and a density of 2.5×10^{13} cm⁻³. From stereomicroscopy and tilting experiments, the shape of these precipitates was determined to be a cube with truncated corners. These precipitates and the matrix have $[110]_p/[110]_m$ orientation relationship. Detailed microdiffraction studies made on individual precipitates clearly identified them as Li_2O with the cubic fluorite structure. On annealing the same microscope sample for 12 min in air and quenching from 1200°C, the average size of the precipitate was reduced to 150 Å, and the cluster density remained approximately the same (Fig. 3.25b). The effect of electron irradiation was studied by irradiating the as-grown thin samples in situ in a 200-keV electron microscope (flux = 2×10^{18} electrons/cm²·sec). A reduction in precipitate size of about 15% was observed after an estimated electron dose of 5×10^{20} electrons/cm². From this result the effective cross section was estimated to be $\sim 10^3$ b. This cross section is too large to be associated with a knock-on displacement of Li^+ ions from the precipitate and implies an ionization process.

In as-grown crystals, a significant amount of the Li impurities is concentrated in precipitates, with some soluble Li^+ ions randomly distributed in the crystal. (The randomly distributed Li^+ ions would be responsible for the unstable $[\text{Li}]^0$ defects following ionizing irradiation at low temperature.) At elevated temperatures or upon extensive electron irradiation, the Li ions from each precipitate diffuse out and form a localized Li-rich microgalaxy surrounding the precipitate. Within the

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Fig. 3.25. Bright-field electron micrographs under kinematical diffraction conditions. (a) Li_2O precipitates in as-grown MgO-Li ; (b) Li_2O precipitates after quenching from high temperature. The same microscope sample is used in (a) as in (b) though not the same area.

microgalaxy of abundant substitutional Li^+ ions, charge neutrality requires that the natural state of the impurity be a Li^+ ion with a trapped hole, which is the neutral $[\text{Li}]^0$ center. That is, unlike the soluble Li^+ ions that are charge-compensated primarily by impurities, the substitutional Li^+ ion in the microgalaxy must in itself maintain charge neutrality. Hence, this model requires that the precipitate diminish in size at high temperatures or upon intense irradiation.

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PROPERTIES OF $a\langle 100 \rangle$ DISLOCATIONS IN MgO

Jagdish Narayan

A recent report states that high-temperature electrical conduction for a long period of time (≥ 100 hr) induced a thermal breakdown in MgO crystals.¹ Investigation of

these samples by TEM just before the thermal breakdown revealed the presence of a type of loop not previously observed in this material with $a\langle 100 \rangle$ Burgers vectors lying in $\{100\}$ planes.² In this report, we present results on glide and climb behavior of these loops. Also, $a\langle 100 \rangle$ dislocations can split into or be formed from normally observed $\frac{a}{2}\langle 110 \rangle$ dislocations under the presence of small interaction forces.

Magnesium oxide single crystals (total impurity content < 500 ppm), which were used in this investigation, were supplied by Norton Company. High-temperature electric-field treatment (details are described elsewhere¹) for long period of times leads to a large current through the samples, resulting in catastrophic breakdown of the material. Samples examined in the present work were cooled to room temperature before the breakdown, and the electric field was applied during cooling. Samples for TEM (~ 0.05 -cm thickness) were obtained by cleaving normal to the current direction, then thinned by chemical polishing in a hot (413 K) phosphoric acid jet. To study the glide and climb behavior of $a\langle 100 \rangle$ loops, thinned microscope samples were subjected to high-temperature isochronal annealing for 30-min periods, and the same area was imaged under identical diffraction conditions. The changes in the positions of dislocation loops along their glide cylinders give information about the glide, and changes in the size of loops give information about the climb of dislocation loops.

A sequence of electron micrographs of the same area after successive annealing treatments at 1200°C is shown in Fig. 3.26. It was determined that the loop labeled "1" had an $a[001]$ Burgers vector; measurements of the distance of the loop from the surface as determined by stereomicroscopy indicated that this loop moved toward the surface along its glide cylinder as a result of the annealing treatment. Because the lattice frictional stress decreases at high temperatures, it is expected that the loop will start to move toward the surface when the interaction force between the loop and the surface just exceeds the lattice frictional stress. Using this criterion, the lattice frictional stress for an $a[001]$ loop at 1200°C was estimated to be 1.5×10^9 dynes cm^{-2} , which is about three times the lattice frictional stress for the $\frac{a}{2}\langle 110 \rangle$ dislocations in $\{110\}$ planes.³ Because the glide of an $a[001]$ dislocation along the $[001]$ direction leads to overlapping of like ions creating large repulsive forces, it is estimated that the frictional stress of $a[001]$ loops along the $[001]$ direction should be at least an order of magnitude more than that for $\frac{a}{2}\langle 110 \rangle$ loops along the $\frac{a}{2}\langle 110 \rangle$ direction.

Fig. 3.26. A sequence of electron micrographs showing the glide of loop I and dislocations A, B, C, and D along their Burgers vector direction $[001]$ due to an interaction with the free surface. Micrograph sequence a, b, c, and d correspond to successive 30-min anneals at 1200°C .

The experimental value of the frictional stress determined here can be accounted for if the core of the $a[001]$ dislocation is split into $\frac{a}{2}[011]$ and $\frac{a}{2}[0\bar{1}1]$ dislocations in the (100) plane so that the $a[100]$ glide in the $[001]$ direction consists of glide in the (100) plane of a pair of dislocations with $\frac{a}{2}[011]$ and $\frac{a}{2}[0\bar{1}1]$ Burgers vectors. Glide of $\frac{a}{2}(011)$ dislocations in the $\langle 100 \rangle$ planes has been observed during high-temperature deformation of MgO (ref. 4). Direct evidence for the splitting of an $a[001]$ dislocation into $\frac{a}{2}[011]$ and $\frac{a}{2}[0\bar{1}1]$ has also been obtained, as shown in Fig. 3.27. In this case, only a small segment of the $a[001]$ dislocation was split, and upon annealing the two $\frac{a}{2}(110)$ segments combined into $a[001]$. Splitting of $a[001]$ dislocations at a free surface also occurs, as can be seen in Fig. 3.26.

Fig. 3.27. Splitting of $a[001]$ dislocation according to the following dislocation reaction $a[001] \rightarrow \frac{a}{2}[011] + \frac{a}{2}[0\bar{1}1]$. The arrow indicates the direction of diffraction vector $[220]$ and is $0.7 \mu\text{m}$ long.

Vacancy-type dislocation loops shrink as a result of annealing at high temperatures by emitting vacancies of both positive and negative ions. By measuring the shrinkage rate of loops at different temperatures, an activation energy for self diffusion was determined to be 5.2 eV, which is in agreement with the values determined by tracer techniques.

In summary, the present observations have shown that $a[001]$ dislocations can glide along an $\langle 001 \rangle$ direc-

tion and can climb by emitting vacancies of both positive and negative ions (loop shrinkage). In addition, it is shown that $a(001)$ dislocations can split into or be formed from the more commonly observed $\frac{a}{2}(110)$ dislocations. In view of this behavior, it seems likely that these $a(001)$ dislocations play an important role in determining some of the physical properties of MgO and, perhaps more generally, in materials with the NaCl structure.

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MECHANICAL PROPERTIES OF LI-DOPED MgO CRYSTALS OXIDIZED AT HIGH TEMPERATURES

V. M. Orera¹ Y. Chen M. M. Abraham

Studies show that Li_2O precipitates are present in MgO crystals doped with Li (ref. 2). Heat treatments in an oxidizing atmosphere produce stable $[\text{Li}]^0$ defects, and it has been proposed that the Li^+ ions are concentrated in a spatial region around the precipitates.³ Both the precipitates and the dissolved Li^+ ions can have a profound effect on the flow stress of MgO crystals.

MgO and MgO:Li crystals have been deformed at room temperature in an Instron testing machine. Figure 3.28 illustrates typical stress vs strain curves for three crystals: nominally pure MgO, "as-grown" Li-doped MgO, and an Li-doped MgO that had been heated for 5 min at 1625 K in O. The flow stress values determined are 2, 4, and 10 kg/mm² respectively. These results suggest that both precipitates and substitutional Li^+ impurities contribute to the hardening of MgO.

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LI DECORATION OF SLIP PLANES IN MECHANICALLY DEFORMED MgO DUE TO OXIDATION AND REDUCTION AT HIGH TEMPERATURES

V. M. Orera¹ Y. Chen M. M. Abraham

This study demonstrates that stable $[\text{Li}]^0$ defects can be used to "decorate" regions of high dislocation

Fig. 3.28. Applied stress in [100] direction vs compression for three samples: nominally pure MgO, as-grown (virgin) MgO:Li, and a MgO:Li crystal oxidized at 1550 K.

density. The formation of stable $[\text{Li}]^0$ defects, which yield a blue coloration corresponding to optical absorption at 1.8 eV, requires heating in an oxidizing atmosphere;² heating in an inert or reducing atmosphere does not produce the blue coloration. Both positive (dark-on-light background) and negative (light-on-dark background) patterns of slip planes, produced by mechanical deformation, can be produced using $[\text{Li}]^0$ defects to produce contrast. A positive pattern of slip planes can be obtained by first deforming a crystal and then heating it at 1200 K in O for 5 min. (Fig. 3.29). The slip plane areas are clearly decorated with coloration of $[\text{Li}]^0$ defects. Thus, the preferential production of $[\text{Li}]^0$ defects in regions of high dislocation density must be related to an enhanced oxidation process in the region. Negative patterns of slip planes can be achieved by first providing a dark background and then deforming. A subsequent 2-min heat treatment at 1120 K enhances the contrast.

Etch-pit density was also analyzed on deformed Li-doped samples, both before and after oxidation at 1200 K. Etch-pit patterns were found to be similar to those published earlier,³ and the pit densities were greater in regions of dark blue coloration. The enhancement of oxidation and reduction is not confined to slip systems; it is a general phenomenon observed in any deformed

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Fig. 3.29. Positive pattern of slip planes from a MgO:Li crystal with a 2% deformation.

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Fig. 3.30. A negative pattern of inscribed letters obtained from a MgO:Li crystal.

region. Letters were inscribed with a diamond-tipped pen on Li-doped MgO crystals, and both positive and negative patterns were obtained. Figure 3.30 illustrates a negative pattern formed by writing on an oxidized crystal subsequently reduced at 1120 K for 2 min.

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STRESS-INDUCED OPTICAL DICHOISM OF V^- CENTERS IN MgO

F. A. Modine

The V^- center consists of a cation vacancy that has trapped an electron hole. The center belongs to the large class of trapped-hole defects created by irradiation of oxide materials. To assess models of the electronic structure of such defects, a study was made of the optical absorption and the stress-induced optical dichroism of the V^- center in MgO . The dichroism spectrum supplies information about the symmetries and energies of excited-state levels that are unresolved in the absorption spectrum. Also, the temperature dependence of the dichroism yields information about crystal fields that perturb the centers.

The measured spectra are shown in Fig. 3.31. Similar measurements have been reported previously,^{2,3} but the new measurements extend over a wider range of energy, and they more precisely relate the dichroism to the absorption, the stress, and the temperature. The shape of the dichroism changes somewhat with temperature. However, the shape changes are mostly localized near 5 eV and can be discounted because they are due to the F and F^* bands. These bands give the absorption peak at 5 eV and contribute a temperature-independent dichroism in this region. Most of the dichroism is associated with the V^- band, which peaks near 2.3 eV in absorption. The dichroism is inversely proportional to temperature at high temperatures and is proportional to the applied stress at all measurement temperatures. This behavior indicates that the dichroism results predominantly from a paraelastic alignment of inherently dichroic defects. The saturation of the dichroism can be attributed to crystal fields that tend to pin the defects into random orientations at low temperatures. The mixed absorption-like and absorption-derivative-like shape of the dichroism spectrum reveals that the optically excited state contains levels that differ in their symmetry. Because the electronic ground state of the center is known from magnetic resonance experiments to be an A_1 state of the C_{4v} point group, it can be deduced from optical selection rules and the known positive value for the elastic dipole moment that excited levels of A_1 and E symmetry give the positive and negative contributions to the dichroism respectively. Hence, the lowest excited level has E symmetry and the higher energy levels are predominantly of A_1 symmetry. The indications of structure near 3 eV and the extensive high-energy tails suggest that several levels may contribute to the V^- band.

Different interpretations of the V^- center have been given, but the polaron model,^{3,4} with possible elabo-

Fig. 3.31. Optical spectra of an electron-irradiated MgO crystal. The dichroism is the difference between the absorption of light polarized parallel to and perpendicular to the stress axis. The units are base 10 absorbance. The temperature dependence of the peak dichroism is shown in the inset.

ration,⁵ appears to give the most complete account of the known properties of the center. The model predicts that the center's optical spectra derive from two nearly superimposed, but differently polarized, Gaussian bands, which result from polaron transitions between the σ orbitals on the O^{2-} ions surrounding the vacancy. It is expected that the bands will contribute equally to the intensity of absorption but in a 2:1 intensity ratio to the dichroism. To check these predictions of the polaron model, a curve-fit analysis of the lower energy portions of the spectra was made. Some of the results are shown in Fig. 3.32. Gaussian bands give a qualitative description of the spectra at lower energies, but the quantitative agreement is not good. The problem with the fit is apparent. Because only two bands are used, the near coincidence of the peak absorption and peak dichroism is inconsistent

Fig. 3.32. A comparison of the lower energy portions of the dichroism and absorption spectra with theory and with previous experimental results. To facilitate the comparison, all results are scaled to a complete alignment of the defects and a peak absorption of unity. The measured spectra are indicated by solid curves. The electrically induced dichroism reported by Rose and Cowan (ref. 2) is denoted by open circles. The long-dash curves are based upon Schirmer's parameters (ref. 4): $E_1 = 2.3$ eV, $E_1 - E_2 = 1.94$ eV, $D_{\parallel}/D_{\perp} = 2.0$, and $\sigma^2 = 0.126$ (eV)². The short-dash curve represents an improved fit to the dichroism. The parameters for this curve are $E_1 = 2.23$ eV, $E_1 - E_2 = 2.04$ eV, $D_{\parallel}/D_{\perp} = 1.55$, and $\sigma^2 = 0.15$ (eV)².

with the significant negative dichroism. The best fit is obtained for parameter values that correspond to a ratio of the transition dipole strengths $D_{\parallel}/D_{\perp} = 1.55 \pm 0.20$ and an energy splitting $E_{\parallel} - E_{\perp} = 0.22 \pm 0.07$ eV for the bands polarized parallel ($\parallel$) and perpendicular ($\perp$) to the defect symmetry axis. These values are significantly smaller than the values $D_{\parallel}/D_{\perp} \approx 2.0$ and $E_{\parallel} - E_{\perp} = 0.36$ eV that have been given as the model

parameters by Schirmer.⁴ The analysis implies that more than two Gaussian bands are required to explain the V^- optical spectra, even at low energies. The spectra may reveal the presence of optical transitions to O^{2-} π orbital levels. Electronic structure calculations have predicted an additional transition to a low-energy π orbital level.⁵ The presence of such an additional transition would explain the problem of fitting the spectra at low energies. The high-energy tails of the spectra might also be attributed to transitions to π orbital levels. The π orbitals on the O^{2-} ions surrounding the vacancy can be expected to give both an A_1 and an E symmetry level with a hole-transfer transition moment. In conclusion, the electronic structure of the V^- center may be more complicated than has been generally recognized.

1. Summary of paper: *Journal of Physics and Chemistry of Solids* (in press).

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INFRARED ABSORPTION FROM THE EXCITED STATE OF THE F CENTER IN CaO

Herbert Engstrom F. A. Modine

The optical properties and lower-lying electronic structure of the F center in CaO (two electrons trapped at an O^{2-} vacancy) have been well characterized in previous studies.¹⁻³ The absorption band of this defect, centered at 3.1 eV, arises from a transition from the ground $^1A_{1g}$ level to an excited $^1T_{1u}$ level. Optical excitation in this band causes luminescence at 2.0 eV, which has been assigned³ to a transition from a $^3T_{1u}$ level to the ground $^1A_{1g}$ level. Calculations by Wood and Wilson¹ of the electronic structure of this defect indicate that an optical absorption band due to an allowed transition from this $^3T_{1u}$ level to a higher $^3A_{1g}$ level may be observable at about 0.7 eV.

We have observed the infrared absorption from the $^3T_{1u}$ level in the range 0.5–1.2 eV. The spectrum was obtained using a double modulation and sideband detection technique in which the intensities of both the pump light and the infrared probe light were modulated. The results, shown in Fig. 3.33, indicate that the spectrum is essentially flat between 0.5 and 1.2 eV. Rather than revealing a $^3T_{1u} \rightarrow ^3A_{1g}$ absorption band,

Fig. 3.33. Excited-state absorption (solid line) of the F center in CsO. The dashed line shows the optical system response. Vertical lines at 1.7 and 2.1 μm indicate where changes in optical filters and/or monochromator gratings and in amplifier gain were made to improve sensitivity.

such a spectrum suggests the occurrence of transitions from the $^3T_{1u}$ level to the conduction band, where the electronic density of states is thought to be flat in the region about 7.1 eV from the top of the valence band.⁵ Evidently, either the $^3A_{1g}$ level lies within the conduction band and the $^3T_{1u} \rightarrow ^3A_{1g}$ oscillator strength is very small or the $^3T_{1u} \rightarrow ^3A_{1g}$ transition lies at lower energy than 0.5 eV.

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MAGNETO-OPTICAL PROPERTIES OF METALLIC COLLOIDS IN INSULATORS

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Metallic colloids in insulators are of interest in connection with the applications of high-temperature ceramics because they are associated with material degradation. Colloids are a radiation-damage end product, especially at elevated temperatures; also, they are produced by electrolysis in high-temperature electrical insulators.² Recently, it was found that magneto-optical techniques are very appropriate for identifying and studying metallic colloids. The instrumental sensitivity is high, and information is obtained about the magnetic properties of specific colloids, rather than about the material as a whole. Diamagnetic, paramagnetic, superparamagnetic, or ferromagnetic properties of the colloids can be readily identified and measured.

To obtain more understanding of the magneto-optical measurements, a study of some metallic colloids with well-known magnetic and optical properties has been initiated. The MCD spectra of Ca and Na colloids in CaF_2 and NaCl , respectively, have been measured, and an interpretation of these measurements based upon Mie theory computations has been undertaken.

1. Guest scientist from University of Zaragoza, Spain.

2. F. A. Modine et al., "Dark Streaks Produced by Electrical Conduction in MgO ," this report.

MODE COUPLING AND ISOTOPIC SPLITTING IN THE RAMAN SPECTRA OF NaClO_3 - NaBrO_3 MIXED CRYSTALS¹

Herbert Engstrom Roger French² J. B. Bates

Reports of previous investigations of inelastic light scattering^{3,4} from pure NaBrO_3 have described the ^{79}Br - ^{81}Br isotopic splitting of the ν_1 mode of bromate ions containing a substitutional ^{17}O or ^{18}O , but the splitting for the major isotopic species $\text{Br}^{16}\text{O}_3^-$ was not observed. Using force constants obtained from fitting all observed frequencies for the $\text{Br}^{16}\text{O}_3^-$ ion, the ^{79}Br - ^{81}Br splitting was predicted to be about 0.6 cm^{-1} . The failure to observe such splitting could be attributed neither to inadequate instrumental resolution nor to excessive widths of the lines. In the present work, inter-ionic coupling was found to cause mixing of the ν_1 and

Fig. 3.34. Raman spectra of NaBrO_3 in NaClO_3 , showing ^{79}Br - ^{81}Br splitting of the ν_1 mode. The compositions are given in mole percent.

ν_3 vibrational modes of the bromate ions. By diluting NaBrO_3 in NaClO_3 to sufficiently low concentration (≤ 1 mole %), it is possible to reduce this interionic coupling to a value small enough to permit the observation of the $^{79}\text{Br}^{16}\text{O}_3^-$ - $^{81}\text{Br}^{16}\text{O}_3^-$ isotopic splitting.

Raman spectra were taken in a 90° geometry from powdered samples mounted on a liquid N_2 cold finger.

The light source was the 488-nm line of an Ar ion laser operated at a power of 800 mW. The large dilution of the BrO_3^- ions resulted in such a weak signal that signal averaging techniques were essential. Photon generated pulses were accumulated in a PAR 1112 photon counter/processor. The data acquisition system was under the control of a Hewlett-Packard 9825A programmable calculator into which the total photon counts for each value of energy were read.

The spectra so obtained in the ν_1 region of BrO_3^- in powdered samples of NaClO_3 containing 1% and 0.1% bromate are shown in Fig. 3.34. The two peaks of each curve are separated by about 1 cm^{-1} , and their relative intensities are consistent with the natural isotopic ratio of ^{79}Br and ^{81}Br (i.e., 51/49). Therefore, the two peaks of each sample are assigned to the ν_1 mode of the respective isotopes, $^{79}\text{Br}^{16}\text{O}_3^-$ and $^{81}\text{Br}^{16}\text{O}_3^-$. At 5% BrO_3^- in NaClO_3 , no isotopic splitting was observed. This disappearance of the isotopic splitting in crystals of 5% or higher concentration of NaBrO_3 is indicative of the importance of interactions between neighboring ions. The neglect of this interionic coupling in the force constant calculations is probably responsible for the failure to achieve exact agreement between the observed isotopic splitting (1 cm^{-1}) and the calculated splitting (0.6 cm^{-1}).

1. Summary of paper: *Journal of Chemical Physics* (to be published).
2. ORAU faculty research participant from University of Oklahoma, Norman.
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4. Transport Properties of Solids

Although transport properties are of importance in broad areas of solid state physics, investigations of these phenomena within the Division are emphasized in research programs studying the behavior of ceramic materials in harsh environments, fast-ion conductors, and superconductors. The high-temperature ceramics program seeks primarily to determine how charge and mass transport processes affect electric insulating properties when an electric field is applied at high temperatures. Impurities in such materials are of obvious importance, and some of the research relevant to this problem is described in another section of this report. Fast-ion conduction research seeks to understand the lattice dynamics of mobile cations in various beta-aluminas, to understand differences in conductivities attributable to compositional changes, and to contribute through model calculations to the development of theories for fast-ion conduction. The program is greatly strengthened by cooperative research with staff members of General Electric Laboratories and Purdue University. Research in superconductivity is primarily directed towards gaining an understanding of the properties of fluxoids in type-II superconductors. The anisotropy of equilibrium properties of the fluxoid lattice, fluxoid motion, and flux-pinning interactions constitute current major areas of interest. A cryostat permitting low-temperature ion implantation has been developed, and it is anticipated that new and possibly exotic materials may be produced and characterized in terms of their superconducting properties in the near future.

High-temperature ceramics research during this reporting period emphasized extensive examination of thermal-electric breakdown phenomena in impurity-doped MgO. Observed changes in the conductivity of MgO under applied electric fields at temperatures ~ 1300 K have been correlated with valence changes of the impurities. Many of the consequences of breakdown such as catastrophic failure of insulating properties, transport of impurities, phase transitions, and changes in defect structure have been clearly identified. However, detailed knowledge of the many processes occurring prior to failure has not been achieved as yet. Current research efforts are directed toward acquiring this important information.

A persistent problem in $\beta\text{-Al}_2\text{O}_3$ systems has been the lack of understanding why both the ionic conductivity and diffusivity of Li ions are smaller than those of Na or Ag ions. Raman scattering data, combined with model calculations, have led to a proposed model in which Li ions form two layers about the mirror plane, and the extra Coulombic repulsive force between these two layers can account for the differences mentioned above. Also, the correlated motion of paired ions sharing a Beavers-Ross site has been investigated, and a study of the beta"-aluminas (obtained through the Research Materials Program) has been initiated.

Precision measurements of fluxoid lattices in a high-quality sphere of superconducting Nb using small-angle neutron scattering have shown the correlation between the fluxoid lattice symmetry and the crystalline lattice symmetry. These studies, coupled with concurrent bulk magnetization measurements, have provided a detailed description of the anisotropic behavior of critical superconducting parameters of Nb. They also contribute new information on the intermediate mixed state, a regime of attractive fluxoid interactions that has previously not been explored in great depth.

HIGH-TEMPERATURE CONDUCTIVITY OF INSULATING MATERIALS

THE EFFECT OF ELECTRIC CURRENT ON THE CONDUCTIVITY OF MgO SINGLE CRYSTALS AT TEMPERATURES ABOVE 1300 K¹

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Changes in electrical conductivity over the temperature range 1000 to 1400 K due to treatment of nominally pure MgO crystals with moderate (1000 V cm^{-1}) electric fields at 1300 or 1400 K have been measured. Although different samples of MgO have different initial conductivities, changes produced by the electric fields are qualitatively similar. After treatments for times on the order of 20 hr, the temperature dependence changes and the conductivity decreases by a factor ≤ 4 at about 1273 K. This decrease correlates with the electrolytic reduction of impurities in the MgO. More lengthy treatment (>100 hr) causes the samples to become progressively more conducting until catastrophic failure of the electrical insulating properties occurs. The electric current passed as such failure is approached is more than two orders of magnitude greater than at the beginning of treatment. If the temperature is lowered just before failure with the 1000 V cm^{-1} still applied and the temperature dependence of the conductivity subsequently measured, a large excess conductivity is present. However, the temperature dependence (slope of $\ln \sigma$ vs T^{-1}) remains unchanged. The results are discussed in terms of identity of current carriers and conduction mechanisms.

1. Summary of paper: *J. Appl. Phys.* 49, 5971 (1978).
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AGGREGATION OF DEFECTS AND THERMAL-ELECTRIC BREAKDOWN IN MgO¹

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Transmission electron microscopy has been used to study defects in as-grown MgO single crystals and in crystals that had undergone high-temperature electrical conduction for long periods of time. Besides dislocation loops of $\frac{a}{2}\langle 110 \rangle$ Burgers vector, a new type of defect, dislocation loops of $a\langle 100 \rangle$ Burgers vector lying in $\{100\}$ planes, has been observed in electric-field-treated specimens. The nature of both $\frac{a}{2}\langle 110 \rangle$ and $a\langle 100 \rangle$ loops was

determined to be a vacancy type. The relation of this microstructure to the observed increase in electrical conductivity, which results ultimately in thermal-electric breakdown of the samples, is being investigated.

1. Summary of paper: *J. Appl. Phys.* 49, 5977 (1978).

MODELS OF THE ELECTRICAL BREAKDOWN OF MgO AT HIGH TEMPERATURES

F. A. Modine

Simple mathematical models of the thermal runaway of the electrical conductivity of MgO were investigated, and their predictions were compared with the experimentally observed breakdown behavior. The comparison suggests that electrically driven changes in both the thermal and electrical conductivities of MgO may contribute to the observed breakdown. The models are based upon approximate solutions of the equations for heat and electrical conduction in a solid:

$$C_v \frac{dT}{dt} = K \nabla^2 T + EJ, \quad (1)$$

where T is temperature, t is time, C_v is the heat capacity, K is the thermal conductivity, E is the electric field, and J is the current density. The current density and electric field are related by

$$J = \sigma E, \quad (2)$$

where σ is the conductivity,

$$\sigma(T) = \sigma_0 \exp(-Q/T), \quad (3)$$

with an activation energy of Q . Difficult boundary conditions were avoided by assuming an infinitely long cylindrical MgO sample that was subjected to a coaxial electric field. Although this assumption represents a departure from reality, it yields a qualitative interpretation of the breakdown behavior that reveals relationships between material parameters and thermal stability.

The limits of thermal stability were found from the conditions for thermal equilibrium at the verge of thermal instability:

$$\frac{dT}{dt} = 0, \quad (4a)$$

$$\dot{H}_{in} = \dot{H}_{out}, \quad (4b)$$

$$\frac{dT_B}{dT_C} = 0, \quad (5a)$$

$$\frac{d\dot{H}_{in}}{dT_C} = \frac{d\dot{H}_{out}}{dT_C}, \quad (5b)$$

where T_B and T_C denote the temperature at the boundary and center of the cylinder and $\dot{H}_{in}$ and $\dot{H}_{out}$ denote the rates of heat flow into and out of the cylinder respectively. Equations (1-5) were solved by an iterative method employing a fourth-order Runge-Kutta numerical solution of the differential equation. The resulting thermal-stability boundaries are shown in Fig. 4.1 where T_B is plotted vs θ . The parameter θ , defined by $\theta = \sigma_0 E^2 a^2 / K$ (where a is the cylinder radius), is essentially a product of input power and thermal resistance. The curves specify the temperature of the cylindrical boundary that leads to thermal runaway as a function of θ , for a constant activation energy Q . Alternatively, any point on the graph may be regarded as specifying those values of the parameters T_B , θ , and Q that define a point on the stability boundary. Over the studied range of parameter values, the breakdown temperature, roughly proportional to Q , has a nearly logarithmic dependence upon the other parameters. The predictions are not expected to be precise, but the nature of the relationships and the sensitivity of stability to parameter changes are thought to be significant.

Fig. 4.1. The thermal-stability boundary for electrical conduction in MgO. The curves specify the sample temperature, which will lead to thermal runaway, as a function of sample parameters and applied electric field.

The parameter values believed to correspond to MgO under experimental conditions are $Q \approx 2.9 \times 10^4$ K (i.e., 2.5 eV) and $\theta \approx 1.7 \times 10^9$ K.¹ These values predict breakdown near 1850 K, but the observed breakdown is at temperatures as low as 1300 K. Moreover, the predicted breakdown current is at least an order of magnitude larger than the actual measured current. This discrepancy supports the contention that there are parameter value changes which cause a lower-temperature breakdown. There is experimental evidence for an incubation period during which the crystal properties change slowly at a fixed furnace temperature and a constant applied field and ultimately lead to breakdown.¹ The argument for parameter changes was further supported by a rough calculation of the breakdown time, which predicted only a fast breakdown transient for fixed parameters. Parameter changes could be associated with either the electrical or the thermal properties of the material. The thermal stability is most sensitive to Q , but there is no evidence for a change in Q . There is experimental evidence that σ_0 may increase by a factor of ≈ 5 before breakdown. It is also possible that a decrease in the thermal conductivity contributes to the breakdown process, for there is some evidence for such a change. Crystals that have been heated in an electric field develop localized dark streaks and dislocation loops which can be expected to suppress, respectively, the photon and phonon contributions to the thermal conductivity. Both of these contributions to the thermal conductivity are significant at breakdown temperatures.

The filamentary pathway model¹ of conduction and breakdown was also examined under the simplifying assumption that the current is confined to a filament at the center of the cylinder. For this case, Eqs. (1-5) have closed-form solutions that can be solved for the experimental values $E \approx 10^5$ per meter, $a \approx 10^{-2}$ m, $T_B \approx 1300$ K, $l \approx 3 \times 10^{-3}$ Å, $Q = 2.5$ eV, and $K = 7$ W/(m·K) to obtain $T_C \approx 1475$ K, $b \approx 10^{-7}$, and $\sigma \approx 10^5$ per ohm-meter. The results appear to imply metallic conduction by an extremely small filament.

The calculations suggest a need for additional experimental measurements. It would be useful to establish the breakdown temperature as a function of electric field. The temperature of the sample boundary should be measured directly because it may be at a higher temperature than the furnace. A detailed study of changes in the electrical and thermal properties of the sample as breakdown is approached might also be revealing.

1. E. Sonder et al., *J. Appl. Phys.* 49, 5971 (1978).

DARK STREAKS PRODUCED BY ELECTRICAL CONDUCTION IN MgO

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Measurements of the high-temperature electrical conductivity of MgO have disclosed a breakdown of single crystals subjected to electric field $\geq 1000 \text{ V cm}^{-1}$ and temperatures $\geq 1000^\circ\text{C}$ for times $\geq 100 \text{ hr}$.⁴ This breakdown, which is characterized by a catastrophic increase in the electrical conductivity, has been observed in crystals that developed visible dark streaks between the sample electrodes. These findings have prompted an investigation of the dark streaks that has established their identity, revealed their production mechanism, and connected more directly their production to the breakdown process.

A definite connection between the dark streaks and metallic impurities was established by studying their production in samples that differed in their impurity content. Crystals, which were nominally pure or intentionally doped with various impurities, were placed between a broad, flat Pt anode and a pointed single-contact Pt cathode in a furnace that permitted direct visual observation of the streak development (Fig. 4.2).

Fig. 4.2. Diagrams of the apparatus and a photograph of a dark streak. (a) Apparatus permitting the visual observation of the development of dark streaks; (b) a sketch of the sample and electrodes giving a qualitative description of the E -field flux lines in the sample; (c) a photograph of a dark streak.

The high E field associated with the pointed cathode produced streaks in crystals doped with transition metal impurities, but it did not produce streaks in the purest samples or in Li-doped samples. At furnace temperatures of 1050°C , the application of $\approx 1300 \text{ V}$ to crystals that were $\approx 2 \text{ mm}$ thick produced dark streaks in times

that varied from less than 2 hr for samples containing V, Co, or Mn to more than 24 hr for samples doped with Cr or Fe. In many cases, the growth of the streak, which always progressed from the cathode to the anode, was accompanied by a large increase in the conductivity of the sample. It was confirmed that the streak itself was conducting by simply moving the pointed contact to a new location. This movement reduced the current until another streak was formed.

Optical experiments were performed that directly associated the dark streaks (brown under an optical microscope) with an electrolytically reduced state of the impurities. The MCD measurements of crystals containing ferromagnetic impurities were especially revealing. Figure 4.3 shows MCD spectra of Ni-doped samples. When a dark streak is produced, the MCD spectrum of Ni^{2+} is replaced by the broad, rather featureless spectrum of the streak. The streak spectrum exhibits the hysteresis associated with ferromagnetism. A similar spectrum was observed in MgO:Ni crystals that became dark when they were reduced at high temperatures in H_2 . Although the Ni^{2+} spectrum in these crystals did not completely vanish, it decreased, and an MCD spectrum exhibiting ferromagnetism appeared. From this evidence, it is concluded that the dark streaks are due, at least in part, to impurities that have been electrolytically reduced to form metallic precipitates. In some cases, a part of the coloration may be contributed by lower valence states of the impurities that are produced by the electrolytic reduction. The MCD spectra of several different samples have shown variations that can be attributed to particle-size effects, adding to the evidence for precipitate formation. The spectra of samples that were rapidly cooled are somewhat shifted in comparison with the spectra of slowly cooled samples, and they are relatively less ferromagnetic and more superparamagnetic. This effect is attributed to a ripening of the precipitates during slow cooling. The presence of precipitates in the dark streaks has been verified by Mie light-scattering experiments. Measurements of the angular distribution of scattered laser light reveal that the streaks contain a broad distribution of particle sizes that peaks in the vicinity of $4000 \text{ \AA}$.

Analyses of the composition of the dark streaks were made by SIMS and by XFS. The SIMS disclosed that formation of a dark streak produces no significant gradient in the impurity concentration. Thus, it appears that there is little impurity migration over large distances and that the streaks are produced by chemical changes which occur without compositional changes on a macroscopic scale. Nevertheless, the XFS does show some alloying of impurities with the electrodes. This

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Fig. 4.3. MCD spectra of crystals of MgO doped with Ni. (a) Spectrum of a dark streak produced by passing an electric current through a crystal at 1050°C for 2 hr; (b) spectrum of an as-grown crystal attributable to Ni^{2+} ; (c) spectrum of a crystal that was darkened by reduction in H_2 at 1050°C for 48 hr. The spectra represented by dashed curves were measured at zero field after being magnetized by a 10-kG field. The inset shows a hysteresis typical of the samples that were electrically treated or reduced in H_2 .

observation is also illustrated by the fact that the cathode often welded to the samples during streak formation.

1. Analytical Chemistry Division, ORNL.
2. National Bureau of Standards, Washington, D.C.
3. University of Kansas, Lawrence.
4. E. Sonder et al., *J. Appl. Phys.* 49, 5971 (1978).

ELECTRON MICROSCOPE STUDY OF DEFECT SUBSTRUCTURES RESULTING FROM THERMAL-ELECTRIC BREAKDOWN

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It has been shown^{1,2} that high-temperature electric-field treatment of MgO for long periods of time increases electrical conductivity which ultimately results in catastrophic breakdown of the material. The details of the experimental set-up are described elsewhere.¹ In general, the following behavior is observed in pure as well as in doped MgO crystals. After a relatively small change in electrical conductivity in Stage I, conductivity begins to increase. Stage I varies from about 100 hr for pure crystals (impurity content ~ 300 ppm) to about 20 hr for Fe-doped (~ 1500 ppm) crystals. The increase in conductivity after Stage I is approximately linear for a period of a few hours, and then it accelerates.

In this regime of increasing conductivity, the samples develop dark regions or streaks extending from one electrode (usually the cathode) to the other, more or less parallel to the direction of current flow. The darkness of these regions is related to the impurity content of the crystals; the streaks are very faint (almost invisible to naked eye) in the purest crystals (impurity content ~ 100 ppm) to completely dark in Fe-doped crystals. It should be mentioned that during the period of increasing conductivity, if the voltage applied or the temperature of the specimen is not decreased, the breakdown occurs, sometimes creating a channel (actual hole) extending between the electrodes. The samples that were treated for various times in the regime of increasing conductivity were cooled slowly or quenched to room temperature with or without applied field. Samples for electron microscopy were prepared by cleaving the specimens normal to the direction of current flow, and the areas with and without streaks were selectively thinned by a chemical polishing technique.

In the dark region, dislocation loops of $\frac{a}{2}\langle 110 \rangle$ Burgers vector (denoted as "n" in Fig. 4.4a) and $a\langle 100 \rangle$ Burgers vector (denoted as "s") are observed. Loops with Burgers vector $\frac{a}{2}\langle 110 \rangle$ are those normally observed in MgO; loops with Burgers vector $a\langle 100 \rangle$ have only been observed in material that has been subjected to the high-temperature electric-field treatment.³ Also in the dark region, precipitates are observed that are usually associated with voids, as shown in Fig. 4.4b. The precipitate and void substructure were found to be near subboundaries (Fig. 4.4b), near dislocations, and in the form of colonies, as shown in Fig. 4.4b.

Fig. 4.4. Bright-field electron micrographs from a dark streak. (a) $\frac{a}{2}\langle 110 \rangle$ dislocation loops denoted as "n" and $a\langle 100 \rangle$ dislocation loops denoted as "s" and (b) colonies of voids that are decorated with precipitates.

In Fe-doped crystals, the dark regions contain a high density of precipitates and dislocations that are primarily generated by misfit strains around the precipitates. The dislocation loop density in these specimens was found to be very low. Diffraction and moiré pattern

analyses indicate the presence of FeO, MgFe_2O_4 , polycrystalline MgO, and Fe in these specimens. The average density of Fe atoms contained in the precipitates in the dark region was approximately equal to the original doping concentration, indicating that migration of Fe from areas outside the dark regions is very small. Microstructural changes outside the dark regions in both pure and doped crystals were negligible.

In some pure and Fe-doped samples, the polarity of the applied voltage was reversed before the breakdown. This reversal not only produced a reversal of the current flow but also caused a time-dependent decrease in the current that in about 4 hr gave currents close to the original value for pure samples and slightly higher than its original value for Fe-doped samples. Electron microscope study of pure specimens, which had undergone reverse applied voltage treatment, revealed that the number densities of dislocation loops and voids had decreased significantly, whereas in doped specimens the precipitate substructure remained almost unchanged.

The $\frac{a}{2}\langle 110 \rangle$ dislocation loop density increased primarily through helical climb of dislocations.

The current reversal results suggest that Fe impurities do not contribute significantly to the high-temperature electrical breakdown in MgO. In particular, these observations substantially rule out the speculation that metallic impurity precipitates, particularly on dislocations, provide low-resistance current paths in the material. Among other possible mechanisms for electrical conduction in MgO, conduction via Mg^{2+} and O^{2-} interstitials looks most promising, and a detailed model involving self-interstitials is currently under development for explaining the observed stages of electrical breakdown in pure and doped crystals.

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CONDUCTIVITY AND EPR IN ELECTRIC-FIELD-TREATED MgO:Fe SINGLE CRYSTALS

R. A. Weeks J. Narayan E. Sonder

Electric fields of moderate strength ($\sim 1000 \text{ V cm}^{-1}$) applied to nominally pure MgO single crystals at a temperature of 1200°C increase their conductivity and, after sufficient time ($\sim 150 \text{ hr}$), produce thermal-electric

breakdown. During the period of increasing conductivity, dark streaks develop in crystals that contain ~ 200 ppm of Fe; in crystals containing < 50 ppm of Fe, no streaks are observed, although breakdown paths are observed. A high density of $a(100)$ vacancy loops present within the dark streaks has been shown using TEM.¹ These vacancy loops are also present outside the dark streaks with densities that are < 0.01 the density within the dark streaks. We have suggested² that low-resistance filamentary paths develop in the crystals and that these paths attain continuity between cathode and anode as thermal breakdown occurs. The role of the dark streaks in the development of these paths has not been established. In the following, we describe experiments on crystals doped with 2500 ppm Fe.

An electric field of 1000 V cm^{-1} was applied at 1200°C to samples containing 150 and 2500 ppm Fe. After ~ 150 hr, the conductivity of samples containing 150 ppm Fe increased more than two orders of magnitude. For one sample containing 2500 ppm Fe, a 100-fold increase in conductivity occurred in 18 hr; for another sample a similar increase occurred in 30 hr. Examination of these crystals after removal from the furnace showed that the density of dark streaks was much greater (~ 20 times) in the crystals containing 2500 ppm Fe than in crystals containing ~ 200 ppm Fe.

One set of EPR samples, obtained from treated crystals containing 150 and 2500 ppm Fe, contained dark-streak material, and the other set, cut adjacent to the dark-streak areas, was colorless. The resonance spectra showed that intense, very broad (~ 1000 G in width) spectral components were present in the spectra of dark-streak material but not in the spectra of treated or untreated colorless material. The widths of the components were unaffected by decreasing the sample temperature, but intensities increased slightly. The intensity of these spectral components in material containing ~ 2500 ppm Fe was approximately ten times greater than in the material containing ~ 200 ppm Fe. For rotation of the applied magnetic field in a $[110]$ plane, the orientation dependence of the components could be fitted to a $\cos \theta$ function with a minimum value of 5500 G and a maximum $> 18,000$ G at 35 GHz.

The fact that a significant decrease in the time required for thermal-electric breakdown is correlated with an increase in Fe concentration implies that Fe (and possibly other impurities) influences the breakdown process. The large increase in the density of dark streaks at the higher Fe concentration and the increase in the intensity of the EPR spectrum in the dark-streak areas also indicate that Fe (and possibly other impurities) may play a role in some of the mechanisms that

result in breakdown. It is probable that the visible color and the EPR absorption observed in dark-streak material are due to Fe. However, the orientation dependence and widths of the EPR components do not correspond to any of the spectra normally found in Fe-doped MgO .³

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ENHANCED ELECTRICAL CONDUCTIVITY OF MgO CAUSED BY LI IMPURITY

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Oxidation of Li-doped MgO at $T > 1300$ K generates stable $[\text{Li}]^0$ defects, which are believed to originate from the formation of microgalaxies of Li^+ ion surrounding Li_2O precipitates.² Charge neutrality requires that the monovalent Li ions become neutral $[\text{Li}]^0$ defects within the microgalaxies by capturing holes. Although the holes are bound within a microgalaxy, they are not bound to specific $[\text{Li}]^0$ defects. Each hole hops between different $[\text{Li}]^0$ sites via the valence band.

A representation of the above process is shown in Fig. 4.5. In the as-grown state (top illustration) the Fermi level (ξ) is illustrated as being halfway between the conduction band and the valence band, which are separated by about 8 eV. The Li impurities are primarily in Li_2O precipitate form, and no stable $[\text{Li}]^0$ defects are present. Upon heating to a sufficiently high temperature (T_2), microgalaxies of $[\text{Li}]^0$ defects of average diameter d are formed; the valence band in this region bends to within ΔE of ξ , forming a p -type semiconducting domain. To first approximation, ΔE would be ~ 0.3 eV, a value corresponding to half the activation energy for hole release at each $[\text{Li}]^0$ site, that is, ≈ 0.6 eV. At a higher temperature (T_3), the average diameter of the microgalaxy can be expected to increase. At a still higher temperature (T_4), overlapping of microgalaxies might occur and create a more uniform p -type semiconductor throughout the crystal.

The creation of p -type regions in the crystal should appreciably enhance the electrical conductivity of $\text{MgO}:\text{Li}$ oxidized at high temperature. To determine whether such regions were formed, samples were heated at different temperatures for 10-min periods in flowing oxygen. The samples were then cooled rapidly to room

Fig. 4.5. Energy levels of MgO:Li oxidized at high temperatures. CB = conduction band; VB = valence band.

temperature. The absorption coefficients of the resulting $[\text{Li}]^0$ band are shown in Fig. 4.6a as a function of the treatment temperature. The absorption coefficient increased linearly with treatment temperature up to 1600 K and then decreased. The room-temperature electrical conductivity (Fig. 4.6b) behaved in a corresponding manner. Because the conductivity of undoped MgO crystals $\ll 10^{-16} (\Omega\text{-cm})^{-1}$ (ref. 3), the formation of stable $[\text{Li}]^0$ defects enhances the electrical conductivity of MgO by several orders of magnitude.

Fig. 4.6. Anneal temperature in O atmosphere vs (a) absorption coefficient of $[\text{Li}]^0$ band and (b) electrical conductivity.

ELECTRICAL CONDUCTIVITY AND THERMOPOWER OF MgAl_2O_3 SPINEL AT HIGH TEMPERATURE

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It is known that polaron conduction predominates² in transition metal oxides with the spinel structure. We are studying the conductivity and thermoelectric power of MgAl_2O_3 at high temperatures to determine whether the same mechanism applies. Figure 4.7, representing conductivity data from one nominally pure sample, shows that the conductivity varies over nine orders of magnitude between 500 and 1700°C. The curve can be interpreted as consisting of three straight portions due to thermally activated processes having activation energies of approximately 2.2, 1.5, and 2.7 eV, respectively, for the high, intermediate, and low ranges of temperature. The conductivities of a variety of other

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Fig. 4.7. Electrical conductivity of MgAl_2O_4 spinel.

samples have also been measured. The results indicate that conductivity is neither a function of crystal orientation nor a function of Fe impurity up to 900 ppm. This last result rules out the possibility of Fe^{2+} ions acting as donors of current carriers.

Measurements of the Seebeck Coefficient on a number of nominally pure spinel samples have yielded values of the thermoelectric power between 2 and 8 mV/deg. Data from one particular determination are given as an example in Fig. 4.8. The consistent appearance of a negative thermopower indicates that the charge carriers throughout the temperature range of measurement, 400–1000°C, are negative. We tentatively interpret the results as indicating that current flow throughout the temperature range of measurement is by cation vacancies.

Fig. 4.8. Voltage produced by temperature gradients in spinel.

FAST-ION CONDUCTORS

RAMAN SCATTERING FROM ALKALI-METAL AND Ag IONS IN $\beta''\text{-Al}_2\text{O}_3$ ¹

J. B. Bates W. E. Brundage
T. Kaneda² J. C. Wang

Many of the physical and chemical properties of the $\beta''\text{-Al}_2\text{O}_3$ family of solid electrolytes have remained unexplored because of the lack of single crystals of sufficient size and quality for experimental purposes. Recently, however, we have been able to grow comparatively large single crystals of $\text{Na}\beta''\text{-Al}_2\text{O}_3$. In this report we describe for the first time Raman scattering from the vibrational modes of Na^+ and of $^6\text{Li}^+$, $^7\text{Li}^+$, K^+ , Rb^+ , and Ag^+ ions when these are substituted for Na in this material.

Beta''-alumina has a rhombohedral structure with an ideal composition³ of $\text{Na}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$. This compound can only be formed by reaction of Na₂O and Al_2O_3 powders in a dry state, thereby limiting the growth of

1. 1978 summer research participant from Northern Illinois University, Dekalb.

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single crystals. In a molten mixture of Na_2O and Al_2O_3 , β' either decomposes or is converted to $\beta\text{-Al}_2\text{O}_3$. However, the β' form can be grown from a melt of Na_2O and Al_2O_3 containing either MgO or Li_2O . The crystals used in our measurements have the approximate composition, $0.9\text{Na}_2\text{O} \cdot 0.6\text{MgO} \cdot 5\text{Al}_2\text{O}_3$. Details of the crystal growth are described elsewhere in this report.⁴

Raman scattering measurements were made at 300 and 12 K using either the 476.5 or 488.0 nm lines of an Ar ion laser as the excitation source. The scattering geometry was defined by a set of three orthogonal axes, x , y , and z , where z is parallel to the crystallographic c -axis. The polarized Raman spectra in the region of the mobile cation vibrational mode frequencies were recorded at 2-cm^{-1} increments under computer control, with a counting time of 20 sec at each point.

Examples of the spectra observed for $y(xx)z$ scattering are shown in Fig. 4.9. The sharp peak at 110 cm^{-1} in the $\text{Na}\beta'\text{-Al}_2\text{O}_3$ spectrum is due to a mode of the spinel block. Small changes in the peak position and width of this band are observed when Na is replaced by other cations. Most of the remaining features in the curves of Fig. 4.9 are attributed to modes involving displacements of the mobile cations parallel to the conducting plane.

In $\beta'\text{-Al}_2\text{O}_3$, most of the Na^+ ions occupy the rhombohedral $2c$ (C_{3v}) sites alone. The remaining ions share a vacant cation site and are located at positions along the line connecting the $2c$ sites, that is, along the conducting path. These ions may give rise to two distinct in-plane modes with different frequencies corresponding to displacement parallel and perpendicular to the conducting path. Preliminary calculations suggest that the frequency of the in-plane mode of the Na^+ ions occupying the $2c$ sites alone is much higher ($>100\text{ cm}^{-1}$) than that of the parallel displacement mode of the ions near a vacancy ($\sim 40\text{ cm}^{-1}$). The peak at 140 cm^{-1} in the $\text{Na}\beta'\text{-Al}_2\text{O}_3$ spectrum of Fig. 4.9 is assigned to the in-plane mode of cations at the singly occupied site. Tentatively, the broad band centered near 85 cm^{-1} is assigned to the perpendicular displacement mode and a weak band at $\sim 35\text{ cm}^{-1}$ is assigned to the parallel displacement mode of the ions near a cation vacancy. Our assignment is supported by the observation that on replacement of Na^+ by Li^+ these bands disappear. The large width of these bands compared to that of the 140 cm^{-1} band is also consistent with this assignment.

The bands due to in-plane modes of K^+ , Rb^+ , or Ag^+ ions can be seen from the spectra of the respective $\beta'\text{-Al}_2\text{O}_3$ shown in Fig. 4.9. The frequencies of these modes do not simply scale with cation mass because the

Fig. 4.9. Raman spectra of Na, K, Rb, and Ag in $\beta'\text{-Al}_2\text{O}_3$ for $y(xx)z$ scattering measured at 12 K.

effective force constant is different for each cation. Tentatively, however, we associate the bands at 30 cm^{-1} in $\text{Ag}\beta'\text{-Al}_2\text{O}_3$, at 52 cm^{-1} in $\text{Rb}\beta'\text{-Al}_2\text{O}_3$, and at 73 cm^{-1} in $\text{K}\beta'\text{-Al}_2\text{O}_3$ with the displacements of the cations near a vacancy along the conducting path (attempt mode). The bands due to displacements of $^6\text{Li}^+$ and $^7\text{Li}^+$ ions are not shown in Fig. 4.9. These were found in the region between 475 and $3/5\text{ cm}^{-1}$. Compared with the other cations, the Li^+ frequencies are

nearly a factor of 2 higher than predicted from scaling the Na^+ ion frequencies with the change in mass. A similar situation was also found for Li^+ ions in $\beta\text{-Al}_2\text{O}_3$.⁵

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RAMAN SCATTERING FROM $^6\text{Li}^+$ AND $^7\text{Li}^+$ IONS IN $\text{Li}\beta\text{-Al}_2\text{O}_3$ ¹

T. Kaneda² J. B. Bates J. C. Wang

In spite of its small radius, the ionic conductivity and diffusivity of Li^+ in $\beta\text{-Al}_2\text{O}_3$ are much smaller than those of Na^+ or Ag^+ ions.^{3,4} As a basis for developing a model to understand this phenomenon, Raman scattering from $^6\text{Li}^+$ and $^7\text{Li}^+$ ions in $\beta\text{-Al}_2\text{O}_3$ was investigated. Low-frequency bands originating from the motion of mobile-conducting cations in the region between 20 and 200 cm^{-1} have been reported from studies of Raman and infrared spectra of $\beta\text{-Al}_2\text{O}_3$ containing Na^+ , Ag^+ , K^+ , Rb^+ , or NH_4^+ ions.⁵⁻⁷ However, the corresponding bands due to Li^+ ions have not been previously identified.

Samples containing $^7\text{Li}^+$ or $^6\text{Li}^+$ ions were prepared by heating single crystals of $\text{Na}\beta\text{-Al}_2\text{O}_3$ in molten $^7\text{LiCl}$ (99% ^7Li) or $^6\text{LiCl}$ (98% ^6Li) at 650 to 670°C. Assuming a formula unit of $\text{Na}_{2.3}\text{O} \cdot 11\text{Al}_2\text{O}_3$ for the starting crystals, a chemical analysis of the Li^+ samples heated for 16 hr showed that 82% substitution of Na by Li was achieved. The only bands that could be associated with scattering from Li ion vibrations were found in the region from 300 to 500 cm^{-1} . Figure 4.10 shows the spectra obtained for $a(cc)a'$ polarization in this region. The bands observed here are due to A_{1g} modes. The two peaks at 323 and 424 cm^{-1} in the spectrum of the Na compound are due to modes of the spinel block. The latter peak shifts to $\sim 428 \text{ cm}^{-1}$ in the spectra of the Li compounds, and the frequency of the former remains unchanged within experimental error. The frequency ratio of the broad features centered at 393 and 370 cm^{-1} in spectra of the respective $^6\text{Li}^+$ and $^7\text{Li}^+$ crystals, $393/370 = 1.06$, agrees closely with the value expected for a Li ion translational mode [i.e., $(7/6)^{1/2} = 1.08$].

Fig. 4.10. Raman spectra of $\text{Li}\beta\text{-Al}_2\text{O}_3$ showing the bands due to vibrations of $^7\text{Li}^+$ and $^6\text{Li}^+$ ions parallel to the c axis. The same region of pure $\text{Na}\beta\text{-Al}_2\text{O}_3$ is shown for comparison.

The polarization characteristics of the 393- and 370- cm^{-1} bands show that they are due to displacements of $^6\text{Li}^+$ and $^7\text{Li}^+$, respectively, parallel to the c axis, that is, perpendicular to the conducting plane. The bands that could be assigned to Li^+ displacements parallel to the conducting plane [$a(a'a')c$ polarization] were observed at about the same frequencies (390 and 370 cm^{-1}), but their intensities were much lower.

Because of its small ionic radius, a Li^+ ion near a Beevers-Ross (BR) site may deviate away from the mirror plane. To find by model calculations the equilibrium position, a Li^+ ion was first moved in small steps away from the BR site along the c direction in the ideal structure, $\text{Li}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$. At each point, the Coulombic, short-range repulsive, and polarization energy of the system was calculated. The calculated potential energy curve is shown in Fig. 4.11. It was found that the equilibrium position is about 0.8 Å away from the BR site (note the dashed line in Fig. 4.11). Near this position, the vibrational frequency along the c -direction was estimated to be 265 cm^{-1} , which is too small compared to the value of 370 cm^{-1} shown in Fig. 4.10 for $^7\text{Li}^+$ ions. Next, other Li^+ ions were allowed to deviate from the mirror plane. Because a Li^+ ion can deviate toward

either side of the plane, the net result is to form two Li^+ ion layers separated by 1.6 Å. The extra Coulombic repulsive force between the two Li^+ ion layers along the c direction pushes each Li^+ ion against a spinel block and keeps it in the "pocket site" formed by three O^{2-} ions of the block. The configuration of the Li^+ ions near a mirror plane was simulated by using 11×11 planar unit cells with periodic boundary conditions, and the Li^+ ions were allowed to deviate from the mirror plane by ~ 0.8 Å under Coulombic interaction. The solid line in Fig. 4.11 shows the averaged potential seen by a Li^+ ion when the mutual Coulombic repulsive potential between the two Li^+ layers was included.

Fig. 4.11. Potential energy of the system when a Li^+ ion is moved along the c direction. BR = Beavers-Ross.

Notice that the potential curve is no longer symmetric about the mirror plane because of this repulsive potential. The frequency along the c direction for the $^7\text{Li}^+$ ion is now calculated to be 370 cm^{-1} , in good agreement with the observed value.

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RECENT DEVELOPMENTS OF MODEL CALCULATION ON $\text{Li}\beta\text{-Al}_2\text{O}_3$

J. C. Wang, J. B. Bates, T. Kaneda¹

Deviations of Li^+ ions from BR sites along the c direction and from mid-oxygen sites perpendicular to the conducting paths in the mirror plane of $\text{Li}\beta\text{-Al}_2\text{O}_3$ have been studied by model calculations using a potential that includes Coulombic, short-range repulsive, and polarization energy terms. Because of their small radius, Li^+ ions near a mirror plane tend to move into the "pocket sites" formed by O^{2-} ions of the neighboring spinel blocks. This movement results in the formation of two ion layers about 0.8 Å from the mirror plane. The Coulombic repulsive force between the two Li^+ ion layers pushes the ions against the spinel blocks, results in unusually high Raman frequencies,² and may also be responsible for the greater c lattice constant than that of the $\text{Na}\beta\text{-Al}_2\text{O}_3$.

The Li^+ ion pairs formed from the excess Li^+ ions also have a different configuration from that calculated for Na pairs in $\beta\text{-Al}_2\text{O}_3$ (ref. 3). As shown in Fig. 4.12, paired Li^+ ions tend to deviate toward the O^{2-} ions in

ORNL-DWG 78-4847

MINIMUM POTENTIAL ENERGY CONFIGURATION: BR - BEEVERS-ROSS SITE; oBR - ANTI-BR SITE

- * - PAIRED Li^+ IONS IN THE M.P.
- - Li^+ IONS 0.8 Å BELOW THE M.P.
- - Li^+ IONS 0.8 Å ABOVE THE M.P.

Fig. 4.12. Calculated minimum potential energy configuration of paired Li^+ ions in $\text{Li}\beta\text{-Al}_2\text{O}_3$.

with the accelerator are minimal. Final wiring and testing of the dewar are in progress, and installation in the accelerator facility will begin shortly.

1. 1978 summer faculty research participant from the University of Tennessee, Knoxville.

THE INFLUENCE OF THERMALLY ACTIVATED FLUX CREEP ON THE AC RESPONSE OF A HARD SUPERCONDUCTOR¹

H. R. Kerchner

A theoretical and experimental study of the influence of thermally activated flux creep on the ac response of a hard superconductor in the mixed state was completed. The sample was placed in an axial dc magnetic field and a superposed parallel ac field of low amplitude and low frequency. The magnetic moment of such a sample varies with time in a manner that is largely described by a critical-state model of the form first suggested by Bean.² The current density in the critical-state model depends solely upon the magnetic-flux density B (and is independent of $\dot{B}$). It follows that the magnetic flux in the sample should be maximum or minimum exactly at times corresponding to the maxima or minima of the ac-applied magnetic field. Thus, for sinusoidal excitation, the time rate of flux change in the sample (as can be measured by the voltage induced in a pickup coil wound around a cylindrical sample) should cross zero exactly at the peaks and valleys of the ac-applied field.

We found experimentally in studying a cold-worked Nb-5 at. % Zr cylinder that the induced voltage in the pickup coil crossed zero at times slightly later than expected on the basis of the critical-state model. The phase angle of the shift of the zero crossing was independent of the frequency of the ac-applied field in the low-frequency range. To account for these observations, we examined our results in terms of the thermal-activation model of flux motion.

Thermal activation of flux motion leads to an expression for the electric field E of the form

$$E = E_c \exp\left[\frac{U}{kT}(J - J_c)/J_c\right], \quad (1)$$

for current density J less than the critical-current density J_c in the absence of thermal activation. Here U is the potential barrier to flux-line motion, k is Boltzmann's constant, and T is the absolute temperature. One always finds that $kT \ll U$ so that $J_c - J \ll J_c$ for experimentally accessible values of E . The thermal-activation model was invoked originally to explain the

previously observed logarithmic creep of magnetic flux in superconducting samples.³ Although both logarithmic flux creep and exponential $E(J)$ relations were observed repeatedly,^{4,5} the inverse linear temperature dependence of the exponent in Eq. (1) was never clearly observed in bulk samples. As a result, the validity of the thermal-activation model has been questioned.^{4,5} We have shown theoretically that an exponential $E(J)$ relation leads to a frequency-independent phase shift of the zero crossing of the ac voltage waveform, such as we observe. Moreover, detailed measurements of the instantaneous value of the voltage waveform at the peak of the ac-applied field are consistent with the thermal-activation model in regard to magnitude, field dependence, and temperature dependence.

We measured the ac response by using a Hartshorn mutual-inductance bridge. When the sample was in the mixed state, the signal across the secondary of the bridge was proportional to the time derivative of the magnetic flux in the sample and to the electric field at the sample surface, $E(a, t)$. A narrow-band lock-in amplifier and a boxcar integrator produced dc output voltages in proportion to the real or imaginary part of the ac permeability $\mu' + i\mu''$ and $E(a, t)$ respectively. A typical plot of $E(a, t)$, shown in Fig. 4.14, is compared with the sinusoidal voltage observed when the sample is removed from the pickup coil. Note that the scales for the two waveforms in Fig. 4.14 differ by a factor of 10. E_0 is the peak sample-out $E(a, t)$. The phase shift and

Fig. 4.14. The ac voltage waveforms $E(a, t)$ in a static and in an increasing dc field are compared with the function $\sin \omega t$, which is obtained experimentally by removing the sample from inside the pickup coil. There is a scale difference of a factor of 10 between the two curves. The rate of increase of the swept field is $800 \text{ Oe/sec} = 0.004 \omega H_0$.

rounding of the waveform near the zero crossing are small, but clearly observable, effects. A dip appears near $t = 0$ when the "dc" field increases with time. This dip depends strongly on the rate of increase of the "dc" field, and it disappears entirely when the field sweep is stopped. Both the phase shift and the dip are essentially dynamic effects that cannot be understood on the basis of any quasi-static model.

Measurements of μ'' and $E(a, 0)/E_0$ as functions of dc field H were carried out at seven temperatures between 1.6 and 4.2 K. The critical-current density J_c and pinning-energy barrier U were deduced from the data by using the theoretical relations

$$\mu'' = (4/3\pi)\mu'_0\alpha(1 - \frac{1}{2}\alpha), \quad (2)$$

$$U/kT = (3\pi\mu'_0\mu''/4)[E(a, 0)/E_0]^{-2} \times (1 - 27\pi\mu''/40\mu'_0), \quad (3)$$

where $\alpha = ch_0/4\pi J_c a$, h_0 is the ac field amplitude, and a is the sample radius. The differential permeability $\mu'_0 = dB/dH$ was deduced from dc magnetization data for an annealed sample of the same material. At all temperatures, U was found to be proportional to $1 - H/H_{c2}$ for H near H_{c2} . We obtained H_{c2} and the constant of proportionality by fitting measured values

$$U/\mu'_0 kT = (3\pi\mu''/4)[E(a, 0)/E_0]^{-2} (1 - 27\pi\mu''/40)$$

to the function $A - BH$ at each temperature. The parameter $A^{-1} = \mu'_0(1 - H/H_{c2})kT/U$ is plotted in Fig. 4.15. The linear temperature dependence that is associated with thermal activation clearly dominates these data. In our opinion, this evidence provides the strongest experimental support obtained to date for the concept of thermal activation of flux-line motion.

Fig. 4.15. The temperature dependence of $\mu'_0(1 - H/H_{c2})kT/U$ obtained for $H \approx H_{c2}(T)$ by a least-squares-fitting procedure.

AC PERMEABILITY OF DEFECT-FREE TYPE-II SUPERCONDUCTORS

H. R. Kerciner S. T. Sekřila

The magnetocaloric behavior was taken into account in a new theoretical calculation of the ac permeability of a defect-free type-II superconductor. The results appear to account for discrepancies found previously between an isothermal theory and measurements made on dilute NbTa alloys.¹ In the experiment envisioned, a cylindrical superconducting sample is placed in a large, axial dc magnetic field and a small, superposed, parallel ac field. The sample is assumed to be free of flux-pinning defects.

Whenever the magnetic susceptibility of a material depends on temperature, changes in entropy are coupled to changes in field. As a result, an ac field produces temperature oscillations and heat flow as well as oscillations of the magnetization and eddy currents. The ac response of a superconducting sample in contact with an isothermal bath depends on both the flux-flow skin depth,

$$\delta_f = (\rho_0 c^2 / 4\pi\mu'_0 \omega)^{1/2},$$

and the heat-flow skin depth,

$$\delta_Q = (K_0 / \omega C_0)^{1/2},$$

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where

$$\mu_0' = \left(\frac{\partial B}{\partial H} \right)_T$$

is the isothermal differential permeability,

$$C_0 = T \left(\frac{\partial S}{\partial T} \right)_H$$

is the specific heat (per unit volume), ω is the angular frequency of the ac field, ρ_0 is the flux-flow resistivity, and K_0 is the thermal conductivity. Heat flow and flux flow obey coupled diffusion equations. The strength of the coupling term depends on the parameter

$$\nu_0 = \left(\frac{\partial B}{\partial T} \right)_H = 4\pi \left(\frac{\partial S}{\partial H} \right)_T$$

Although an accurate determination of δ_Q , δ_f , and ν_0 for any one sample would require at least four experiments, those parameters can easily be estimated. For most alloys, $\delta_Q \ll \delta_f$ throughout the mixed state. In pure and nearly pure materials, $\delta_f \ll \delta_Q$ at the upper critical field H_{c2} , but $\delta_f \approx \delta_Q$ at some field in the mixed state. The coupling parameter ν_0 is largest for nearly pure superconductors. It follows that, under the conditions studied in ref. 1 (i.e., $\delta_f \lesssim a$, the sample radius), the ac response of an alloy is an adiabatic process, but the temperature oscillations are small. For a nearly pure material, the ac response is neither adiabatic nor isothermal but depends critically on the magnitude of all the parameters.

The diffusion equations were solved for the general case, and estimates of the effect were made for the samples studied in ref. 1. Sample 1 falls in the "nearly pure material" class, while sample 2 should show adiabatic response. Detailed measurements of at least three of the five parameters ρ_0 , μ_0' , ν_0 , K_0 , and C_0 are planned to check quantitatively the theory against measurements of the ac response.

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ANISOTROPY OF THE MAGNETIZATION OF SUPERCONDUCTING Nb

H. R. Kerchner D. K. Christen S. T. Sekula

The magnetization of a single-crystal sphere of Nb in the mixed state was measured as a function of applied field and temperature for applied fields oriented parallel

to each of the high-symmetry crystal axes. The measurement technique and some early results were described previously.¹ The data have been analyzed and compared with available theoretical results. In addition, direct comparisons have been made with neutron-diffraction measurements of the flux-line lattice in the same sample.²

The measurements obtained at the upper critical field H_{c2} are summarized in Fig. 4.16, where the temperature dependences of the parameters

$$\kappa_1 = H_{c2}/\sqrt{2} H_c$$

and

$$\kappa_2 = \left\{ \frac{1}{2} \left[1 + (4\pi\beta dM/dH)_{H_{c2}}^{-1} \right] \right\}^{1/2}$$

are plotted (see also refs. 3, 4, 5, and 6). Here H_c is the thermodynamic critical field and $\beta = 1.16$ is the value of

Fig. 4.16. Temperature dependences of the generalized Ginzburg-Landau parameters κ_1 and κ_2 .

a lattice sum. Near the critical temperature T_c , both κ_1 and κ_2 approach the same isotropic value κ . The results of the isotropic, weak-coupling microscopic theory (Gorkov theory)³ and the semiphenomenological boson theory⁴ are shown for comparison. A zero-temperature calculation of H_{c2} that takes into account the effect of an anisotropic Fermi surface (real-metal theory)⁵ is in good agreement with the experimental results. Real-metal effects have also been included in a recent calculation of the temperature dependence of H_{c2} .⁶ Our data also support those results in detail. Except for κ_2 at low temperature, our spatially averaged results are indistinguishable from the experimental results of ref. 7 (line FSS on Fig. 4.16) for polycrystalline Nb.

Because real-metal effects have not been included in theoretical calculations of the magnetization in the mixed state or of the low-field critical parameters, agreement between theory and experiment is correspondingly modest. However, the experimental results are now firmly established because we have been able to measure the lower critical field H_{c1} and the equilibrium flux density B_0 at H_{c1} by two experiments with substantial agreement.² The relative anisotropy of H_{c1} determined from the magnetization measurements is compared with the neutron-diffraction determination in ref. 2. Our data should provide a sensitive test of more realistic theories of the mixed state as they become available.

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FLUXOID PINNING BY SMALL Nb_2N PRECIPITATES IN Nb

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Despite an intense research effort since the early 1960s, the fundamental understanding of fluxoid pinning by crystal defects in type-II superconductors

remains incomplete. Although a number of attempts have been made to characterize the defect structure of a material and calculate its critical-current density, in most cases the theoretical value differs from the measured one by several orders of magnitude. In addition, the theoretical models imply a threshold effect, suggesting that many small defects should not contribute to the critical-current density. Experimentally, the threshold effect has never been observed.

Recently, attempts have been made to ascertain at what stage our understanding of fluxoid pinning breaks down.^{1,2} The absence of an experimental observation of the threshold effect strongly implies that the theory of the statistical summation of the elementary interactions is at fault. We have recently observed the threshold effect but have not obtained quantitative agreement with the statistical-summation theory.

The statistical-summation theory as developed by Labusch applies rigorously only to a dilute system of small, weak-pinning defects.³ It is formulated in terms of the elastic response of the lattice of fluxoids in response to randomly distributed point forces. Schmucker and Brandt recently corrected Labusch's original calculations to account for nonlocal elasticity effects.⁴ When the elastic response is linear, no critical-current density can result from randomly distributed defects. However, an elastic instability occurs when the fluxoid lattice is deformed sufficiently to move the fluxoid nearest the defect about one-sixth of a lattice parameter from its equilibrium position.² Defects whose interaction with a fluxoid is strong enough to create an elastic instability will contribute to the critical-current density; weaker ones will not. Schmucker and Brandt showed that small defects will satisfy the threshold criterion when the applied field is very close to the upper critical field H_{c2} ;⁴ that is, a critical-current density will appear only near H_{c2} .

We have loaded single crystals of Nb with N to concentrations up to 0.1 at. %. The samples were heated to 1800°C in a dynamic pressure of N in the range 10^{-7} – 10^{-5} torr. In the two most heavily doped samples, a portion of the interstitial N absorbed at high temperature apparently formed Nb_2N precipitates upon cooling. Because of the high rate of cooling and the low concentration of N, the precipitates were much smaller than in previous studies of fluxoid pinning. For each N concentration, a prolate spheroid sample and a rod of similar size were prepared by identical procedures. The prolate spheroid was used for magnetic measurements, and the rod was sliced to obtain a specimen for electron microscopy.

Precipitates in the N-doped Nb specimens were investigated using TEM techniques. Images of these precipitates were obtained under dynamical bright- and dark-field conditions. From the image properties under different diffraction conditions, the strain distribution was determined to be three-dimensional, corresponding to a precipitate. Size distribution (number density vs third moment of a diameter) was determined by counting the precipitates in a given volume, and the results are plotted in Fig. 4.17.

Fig. 4.17. The size distribution of precipitates observed in a Nb sample doped with 0.05 at. % N.

Throughout most of the mixed state, dc and ac magnetization measurements showed that the critical-current density was comparable to the most reversible samples ever investigated. Most likely, the small hysteresis observed was mainly due to surface sheath currents. However, the dc magnetization measurements revealed that flux was trapped in the samples when the applied field was reduced to zero, and the ac measurements revealed a peak in the critical-current density within 2% of H_{c2} . When the applied field H reaches $0.98 H_{c2}$, the critical-current density rises abruptly by at least a factor of 50. Data are shown in Fig. 4.18. It is difficult to understand this behavior even qualitatively in the absence of a threshold effect, but the statistical-summation theory predicts what we observe.

The elementary pinning interaction can easily be estimated by using Ginzburg-Landau theory, and the fluxoid-lattice deformation may then be calculated by

Fig. 4.18. Field dependence of the critical-current density J_c at 4.2 K and near the upper critical field H_{c2} for a Nb sample doped with 0.05 at. % N.

using the result of Schmucker and Brandt. The calculated fluxoid-lattice deformation is about a factor of 5 too small to produce the instability required to produce the observed onset of a critical-current density at $0.98 H_{c2}$. Although it is possible that refinement of our calculation will improve the agreement between theory and experiment, our results appear to support the speculation that the fluxoid lattice is really much softer than has been calculated, perhaps because of the presence of fluxoid-lattice dislocations.¹ Aside from the question of magnitude of the elastic response of the fluxoid lattice, the fundamental premises of the statistical-summation theory appear to be sound.

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DEGRADATION OF THE SUPERCONDUCTING TRANSITION TEMPERATURE BY FAST-NEUTRON DAMAGE IN V-Ga COMPOUNDS

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The dependence of the degradation of the superconducting transition temperature on the stoichiometric composition of V-Ga compounds with the A15 crystal structure has been investigated. Vanadium-gallium compounds containing 27 at. % Ga, 25 at. % Ga, and 23 at. % Ga, respectively, were prepared by arc casting. Samples cut from these ingots were then homogenized at 1400°C in the bcc phase field for 4 hr followed by an annealing treatment at 1150°C for 7 hr within the A15 phase field. Measurements were then made of the superconducting transition temperature prior to irradiation. The largest value of T_{c0} , the transition temperature before irradiation, was found for the V-25 at. % Ga sample (Fig. 4.19). At this composition, a maximum in the crystallographic long-range order can be attained.

Fig. 4.19. Normalized superconducting transition temperature T/T_{c0} for several V-Ga compounds with A15 crystal structure vs fast-neutron fluence ($E > 1$ MeV).

The samples were then simultaneously irradiated in the BSR at a temperature of 60°C to a series of fast-neutron fluences. The normalized transition temperature T_c/T_{c0} vs the fast-neutron fluence for these samples is plotted in Fig. 4.19. The results indicate that the degradation of T_c with fast-neutron fluence increases with increasing Ga content. This observation is difficult to reconcile with the mechanism of the depression of T_c as being due solely to the destruction of long-range order by

neutron damage. These results are also at variance with the observations of Sweedler, Cox, and Moehlecke,² who carried out similar measurements in Nb-Pt and Nb-Al systems. Further work on systems having sufficiently wide A15 phase fields is planned to understand these discrepancies.

1. U.S. Naval Research Laboratory, Washington, D.C.

2. A. R. Sweedler, D. E. Cox, and S. Moehlecke, p. 50 in *Radiation Effects in Superconductivity*, ed. by B. S. Brown, H. C. Freyhardt, and T. H. Blewitt, North Holland Publishing Company, New York, 1978.

LOW-FIELD CRITICAL PARAMETERS OF SUPERCONDUCTING Nb BY SMALL-ANGLE NEUTRON DIFFRACTION¹

D. K. Christen P. Thorel³

S. Spooner² H. R. Kerchner

The double-perfect-crystal, small-angle neutron diffraction technique has been used to study the anisotropic behavior of the critical parameters B_0 and H_{c1} , characteristic of the first-order magnetic phase transition that occurs in low- x type-II superconductors. Magnetic fields were applied parallel to several crystal axes in the (110) and (100) planes of a large single-crystal sphere of pure Nb. At a given orientation, this procedure results in a well-defined, two-dimensional flux-line lattice (FLL), and measurement of the FLL basic cell area in the intermediate-mixed-state (IMS) field region yields the equilibrium flux density $B_0 = \phi_0/A_c$, which is due to the attractive interaction between fluxoids. Here, ϕ_0 is the magnetic flux quantum and A_c the FLL basic cell area determined by the small-angle scattering vectors.

In conjunction with the cell-area measurements, the field variation of the scattered neutron intensity allows determination of the transition field between the mixed state and the IMS. This transition field $H_p = \frac{2}{3}H_{c1} + \frac{1}{3}B_0$, together with the independent B_0 measurements, enables determination of the lower critical field H_{c1} to a precision of 0.2%. Data at 4.30 K, shown in Fig. 4.20, display a small anisotropic effect of about 2% in B_0 and 1% in H_{c1} . These results are being compared with current theoretical results in low-field anisotropic effects.⁴

1. Summary of paper: *J. Appl. Crystallogr.* 11, 650 (1978).

2. Consultant from Georgia Institute of Technology, Atlanta.

3. Guest scientist from DRF-CEN, Grenoble, France.

4. M. Tachiki and H. Umezawa, private communication.

Fig. 4.20. Experimental data at $T = 4.300$ K for the anisotropy of $H_2 = \frac{2}{3}H_{c1} + \frac{1}{3}B_0$, B_0 , and H_{c1} , for applied fields in the $(1\bar{1}0)$ and (100) Nb crystal planes. Solid curves are derived from Cubic Harmonic fits to the $(1\bar{1}0)$ data.

DIRECT OBSERVATION OF THE EQUILIBRIUM MISALIGNMENT BETWEEN FLUXOIDS AND AN APPLIED MAGNETIC FIELD DUE TO ANISOTROPY EFFECTS IN A TYPE-II SUPERCONDUCTOR

D. K. Christen P. Thorel¹

The macroscopic properties of a single-crystal type-II superconductor in the mixed state are influenced by the crystal lattice (CL) direction along which the applied field is directed. These effects are due to the microscopic anisotropies of the superconducting electronic system.

Because of both experimental and theoretical difficulties, scant information has been acquired in the past regarding anisotropy in the low-field critical parameters H_{c1} and B_0 (for type-II/1 materials). Recently, however, theoretical models have been proposed to describe the fluxoid system at low flux density,² and we have reported reliable measurements of the anisotropy in B_0 and H_{c1} for pure Nb in which we employed double-perfect-crystal small-angle neutron diffraction and magnetization techniques.³ We describe here neutron-diffraction studies showing in a direct way that the FLL in equilibrium may be nonparallel to the applied magnetic field when the field is aligned along low-symmetry crystal directions.

For applied fields that lie in the IMS range of a finite, type-II/1 superconductor, this misalignment effect is related directly to the anisotropy in H_{c1} . In the following, this relationship is presented and tested for independent experimental determinations of the misalignment angle and H_{c1} anisotropy.

For the applied field H_a parallel to a given CL axis, the equilibrium misalignment angle $\Delta\psi$ is that which minimizes the Gibbs free energy of the system. For a spherical sample, such as the one used for these studies, the Gibbs potential (relative to the sample in the normal state) is given by

$$G(H_a) - G(0) = V_s \left[\frac{3}{2} H_a^2 + \frac{B}{4\pi} \cdot \left(H_{c1} - \frac{3}{2} H_a \right) + \frac{B^2}{16\pi} \right] + \Delta U. \quad (1)$$

Here, $B = B_0\eta$ is the macroscopic flux density in the IMS, given in terms of B_0 and the volume fraction η of the sample that is occupied by domains of FLL having flux density B_0 . The quantity ΔU is a small positive energy due to the existence of the domains, which

necessarily possess a positive surface wall energy and which make the external field slightly inhomogeneous, thus increasing its magnetic energy. This small correction has been neglected in the result that follows.

Minimization of G yields for the equilibrium misalignment angle

$$\sin \Delta\psi \simeq \frac{-2dH_{c1}/d\alpha}{3H_a}. \quad (2)$$

Here, α is an angle that describes the applied-field direction with respect to the CL in a reflection plane of the CL. It is seen that $\Delta\psi$ is related to the anisotropy in H_{c1} and is inversely proportional to the applied field in the IMS.

The sample used for these studies was a high-purity Nb single-crystal sphere, approximately 13.6 mm in diameter, with measured deviations in the diameter of only $\pm 7 \mu$. The sample was surface-oxidized at 400°C for 5 min to minimize surface pinning, and the Ginzburg-Landau parameter was determined from bulk magnetization measurements to be $\kappa = 0.774 \pm 0.003$.

The SANS techniques used to measure the anisotropies in H_{c1} and the misalignment angle are described elsewhere.⁴

In Fig. 4.21 are experimental data of FLL misalignments for applied-field directions in a (110) and (100) CL symmetry plane. In addition to the gross orientation dependence, a small systematic dependence of $\Delta\psi$ on the history of the FLL was observed, with the largest disparity occurring for histories of opposite rotation of the sample in the fixed applied field. This effect is most likely due to small remnant bulk or surface flux pinning, which tends to "drag" the fluxoids with the sample when it is in rotational motion. Consequently, the FLL is left with a "memory" of the rotational history after the sample is stopped. This small effect was compensated by averaging the $\Delta\psi$ values for equivalent orientations symmetric about high-symmetry directions. These mean values were then least-squares-fit to an expansion in the angular derivatives of orthonormal Kubic Harmonic functions, H_i .

This type of fit was made in view of the relation in Eq. (2) and the fact that H_{c1} is directly expressed in terms of Kubic Harmonics according to

$$H_{c1} = 1429.5 + 2.931H_4 - 0.285H_6.$$

The above result was derived from fits to independent experimental H_{c1} data for field directions in both the

Fig. 4.21. The misalignment angle $\Delta\psi$ at a constant applied-field magnitude 1175 Oe in the IMS, for various field directions in (110) and (100) CL planes. The field direction α is measured relative to [001] CL axis. The systematic dependence on the FLL history was averaged out using the results at equivalent CL directions for the decrease α cycle. The solid curve shows the best fit of these data to a series expansion in the angular derivatives of orthonormal cubic harmonic functions.

(110) and (100) planes. From Eq. (2) and the H_{c1} measurements, one obtains

$$\Delta\psi H_a = -1'2.0dH_a/d\alpha + 10.9dH_a/d\alpha$$

in units of degrees-oersted. For the case of Fig. 4.21, where $H_a = 1175$ Oe in the IMS, the predicted misalignment angle is $\Delta\psi$ (deg) = $-0.095dH_a/d\alpha + 0.009dH_a/d\alpha$. This relation is to be compared with the expansion coefficients found by fitting the $\Delta\psi$ of Fig. 4.21. This comparison reveals that the $\Delta\psi$ values predicted by Eq. (2) are approximately 18% smaller than the actual measured values, although the functional dependence of the anisotropy agrees to within 3%. This prediction is not unreasonable when one realizes that the $\Delta\psi$ measurements are a sensitive indication of the relative anisotropy of H_{c1} , which is itself only 1% of H_{c1} (i.e., we observe an 18% inconsistency in the magnitude of a 1% effect).

As a verification of the applied-field dependence predicted by Eq. (2), the misalignment angle was measured for fields aligned along the [113] CL axis, a direction which is near to that of maximum misalignment. These results, shown in Fig. 4.22, are compared with the relation $\Delta\psi H_a = 863$ deg-Oe, which is obtained from $\Delta\psi$ fit of Fig. 4.21. The expected result lies between the experimental data for different field histories. Again, the hysteretic effect is probably due to weak pinning and the tendency of the equilibrium FLL to rotate within the sample when the field is swept, because of the field dependence of the equilibrium misalignment angle. This latter fact is verified by the experimental data in the mixed state, where both the misalignment angle and the hysteresis decrease as the field increases.

It has been shown above that simple quantitative relationships can be found among some low-field macroscopic anisotropies of the superconducting Nb system. These relationships are verified qualitatively by com-

Fig. 4.22. The magnetic-field-intensity dependence of the misalignment angle for the field parallel to a $[113]$ CL axis. The heavy solid line represents the expected value of $\Delta\phi H_0$ in the IMS. The curve in the mixed state is drawn as a guide for the eye.

parison of data obtained from quite different experimental techniques, among which are the first direct observations of the equilibrium fluxoid applied-field misalignment. These types of measurements should help provide a definitive test for recent microscopic theories relating the fluxoid-CL anisotropies.⁵

1. Guest scientist from DRF-CEN, Grenoble, France.
2. E. H. Brandt, *Phys. Status Solidi B* 77, 105 (1976); F. Mancini, M. Tachiki, and H. Umezawa, *Physica* 94B, 1 (1978).
3. D. K. Christen et al., *J. Appl. Crystallogr.* 11, 650 (1978).
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5. H. Tachiki and H. Umezawa, private communication.

ANISOTROPY IN THE FLL SYMMETRY OF SUPERCONDUCTING Nb¹

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Small-angle neutron diffraction has been used to study the correlation between the symmetry of the two-dimensional FLL and the real CL in a superconducting Nb sphere. The systematic dependence was investigated as a function of temperature and magnetic-field intensity for fields parallel to a few high-symmetry CL axes in the $(1\bar{1}0)$ plane. In addition, at $T = 4.30$ K the progressive deformation of the FLL was studied as the sample was rotated in the $(1\bar{1}0)$ and (100) planes. The FLL is perfectly hexagonal only for fields parallel to the (111) CL axes. Two-fold symmetry prevailed for other CL directions in these planes except for those near the four-fold axis where either of two distorted triangular lattices existed, preserving the reflection symmetry as a total system, but not as individual domains.

When compared to current theoretical models for fluxoid-CL interactions, the present results show that no theory predicts the observed behavior quantitatively under general conditions, but some models agree well for certain high-symmetry directions. A pictorial comparison is shown in Fig. 4.23.

1. Summary of paper: *J. Appl. Crystallogr.* 11, 654 (1978).
2. Guest scientist from DRF-CEN, Grenoble, France.

Fig. 4.23. Pictorial summary of the FLL symmetry according to the theoretical models and the present experimental results.

5. Neutron Scattering

The Neutron Scattering Program of the Solid State Division is dedicated to obtaining fundamental microscopic information on condensed matter. Such information is essential for increasing our knowledge of solid state science and in providing insight to, and guidance for, the solution of the long-range, energy-related materials problems of the nation. To these ends, the neutron beams of the HFIR and ORR are exploited.

During the past year, the Neutron Scattering Program of the Division has been strengthened and augmented in several significant aspects. In January 1978, a National Center for Small-Angle Scattering Research was created at the Laboratory under an interagency agreement between the DOE and the NSF. As part of the center, the construction and operation of a national user-oriented SANS facility was authorized for an initial period of three years. This SANS facility, now under construction at the HFIR, is expected to be ready for test experiments in June or July 1979 and for full-scale user operation in November 1979.

The ORR has been found to be ideally suited for radiation damage simulation studies required by the Magnetic Fusion Energy Program, and this reactor is again being operated full time. As a consequence, the SANS studies and the magnetic diffuse scattering studies previously carried out with instruments at HB-6 and HB-3 have been resumed. In addition, three instruments from the Ames Laboratory Reactor, decommissioned in January 1978, have been installed at the ORR. These are used in part by Ames Laboratory staff in residence at Oak Ridge and in part by Solid State Division staff and guests. The new units are (1) a triple-axis spectrometer (HB-4), (2) a polarized-beam spectrometer (HB-2), and (3) a multipurpose double-axis diffractometer (HB-1).

The beams at the HFIR are the most intense thermal-neutron beams for research in the world, and the experimental facilities associated with them provide powerful and, in some cases, unique tools for materials science research. The new instruments at the ORR will be used for those problems for which the high flux of the HFIR is not required, or for preliminary or set-up experiments, and will thus make possible a more efficient use of the HFIR instrumentation.

As in past years, because of the properties (energy, momentum, and magnetic moment) of neutrons that are exploited in scattering experiments, the neutron scattering research of the Division falls generally into the areas of lattice dynamics and magnetic properties. For convenience, the research results that appear in this section have been divided into these two areas and a third area containing results from SANS experiments; the latter division reflects the growing emphasis of the program in exploiting the small-angle scattering technique to obtain information about long-range scattering density fluctuations. Other equally good divisions could be made that would reflect the concentration of the research into specific problem areas. Many of the problems investigated have as a primary aim the acquisition of fundamental information related to energy production, storage, and transmission, a trend that was already marked last year and that no doubt will continue in future years. As an illustration, examples may be cited of the several types of investigations already carried out to study superconductivity.

It is generally accepted that a knowledge of the electron-phonon interaction is an important datum for the understanding of superconductivity on a quantitative level. One of the most important tools for obtaining such knowledge is that of inelastic neutron scattering. Important information can be obtained from the phonon-dispersion curves and from phonon line-broadening measurements. The technique has been applied during the past year to α -U, Nb and Mo, Hg, and several A15 compounds. Particularly gratifying is the excellent agreement between experiment and theory in the case of the electron-phonon contribution to the phonon line width in Nb. The SANS technique (last three research summaries of Sect. 4) has been used to study the low-field critical parameters of superconducting Nb, and the extremely high resolution of the double-perfect-crystal, small-angle neutron diffraction instrument at the HFIR has been employed to investigate the anisotropy in the fluorine lattice symmetry of superconducting Nb. Application of the method has permitted the direct observation of the equilibrium misalignment between fluxoids and an applied magnetic field due to anisotropy effects in single-crystal Nb. Inelastic scattering measurements have been made on examples of two classes of materials that are both magnetic and superconducting, the RRh_4B_4 compounds and the chevre phase RMo_6S_8 compounds, with R a rare-earth element. Searches have been made for magnetic excitations and crystal-field level splittings and measurements of the phonon densities of states have been made to correlate the lattice dynamics with the magnetic and superconducting properties of these materials. Some of the chevre phase compounds have very high critical fields and may be of interest in the construction of high-field superconducting magnets.

The solution to a given problem is sought by all possible means and with all experimental tools available to Division members. A very close and important interaction exists among members of the Neutron Scattering Program, the Solid State Theory Program, and the Superconductivity Program. An equally close relationship exists with members of the Research Materials Program, who have provided well-characterized single-crystal specimens for many of the neutron scattering investigations reported here.

SMALL-ANGLE NEUTRON SCATTERING

THE NATIONAL SMALL-ANGLE NEUTRON SCATTERING FACILITY¹

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Small-angle neutron scattering (SANS), an important research tool for the characterization of long-range fluctuations in scattering density, has found important applications in materials science and engineering, solid state physics, polymer research, and the biological sciences. In recent years, the technique has gained considerable importance because of the invention of two-dimensional position-sensitive detectors.

The development of SANS to its present high level has taken place primarily in Europe, especially at the KFA in Jülich, Germany, the CENS in Saclay, France, and the ILL in Grenoble, France. Although the facilities at the KFA and the CENS were constructed for the research programs of these centers, they are made available to a number of external investigators for

research of mutual interest. On the other hand, the D-11 facility at the ILL was conceived as a user-oriented facility operating under the guidance of a multinational (France and Germany initially and England participating later) scientific council that selects research of the highest merit.

Since it was commissioned in 1973, the small-angle scattering camera D-11 at the ILL has been heavily oversubscribed. A very large fraction of the research proposals submitted to the ILL have been in the SANS area. To alleviate this overload, a second camera D-17 has been constructed and is now working routinely.

A need for national user-oriented small-angle scattering facilities in the United States, with which U.S. scientists can exploit this important structural tool, has been evident for some time. Neutron small-angle scattering programs do exist at several reactor centers. Biological investigations are being carried out at BNL, for instance, and experimentation on DOE-related problems is going on at two installations at ORNL. These facilities are dedicated to specific research programs for the most part, and they cannot adequately fill the needs of the large number of potential users in

university and industrial communities. The solution to this problem is the creation of user-dedicated facilities at one or more of the existing reactor centers.

To that end, the NSF has made an award to ORNL for the construction and operation of a general purpose instrument designed to meet the needs of as broad a group of users as possible. This facility, now under construction at the HFIR, will be operated under an interagency agreement between the DOE and the NSF. It will provide (1) an intense beam of 4.74-Å neutrons collimated by apertures up to $2 \times 2 \text{ cm}^2$ separated by up to 10 m and (2) a large ($\sim 60 \times 60 \text{ cm}^2$) moveable two-dimensional position-sensitive detector (approximately 128×128 resolution elements) mounted on rails inside a vacuum flight path 20 m long. Angular resolutions of < 2 milliradians ($k < 3 \times 10^{-3} \text{ Å}^{-1}$) will be achievable. A data acquisition system identical to that already in use on the ORNL 10-m small-angle x-ray camera will be provided. This system provides for both high-speed memory switching to permit time-slice experimentation and for more routine on-line data visualization and analysis. When it is completed in late 1979, this instrument will be available to scientists from university, industrial, and other research laboratories.

The original proposal to the NSF, with approval of DOE and ORNL management, has been broadened to form the National Center for Small-Angle Scattering Research. In the program for the center, the 10-m small-angle x-ray scattering camera, a newly developed Kratky camera with linear position-sensitive detector, a 5-m SANS facility located at the ORR, and a high-resolution double-perfect-crystal SANS facility located at the HFIR all are available, part-time, to external users in the same manner established for the large 30-m SANS facility.

1. W. C. Koehler and R. W. Hendricks, *Journal of Applied Physics* (to be published).

2. Metals and Ceramics Division, ORNL.

NEUTRON SMALL-ANGLE SCATTERING FACILITY AT ORR

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This instrument, which was first described in the last progress report,² has undergone extensive testing during the intervening period. Several problem areas have been identified, and corrective measures have been proposed.

The two-dimensional detector appears to be undergoing a continuous deterioration of its energy resolution capability, which gradually decreases the effectiveness of the electronic discrimination used to eliminate unwanted gamma-ray counts. The detector gas was cleaned in the Instrumentation and Controls Division, which greatly helped the resolution, but within a few months, the degradation was again visible. The long-term solution is to replace this detector (one of the first of its type constructed though not initially designed for neutron use) with a new one that will be identical to the detector to be used in the ORNL-NSF SANS facility at the HFIR. In the short term, a rise-time discrimination has been incorporated into the electronic system so that gamma counts are eliminated by using double discrimination of energy and rise time simultaneously. This method helps but has not solved the problem, and cleaning of the gas will need to be done again shortly.

An instability in the electronics has also been detected in the system, which causes a gradual shift in apparent position of the detected neutrons. This shift is intermittent and gradual so that data can still be used, but it clearly needs to be eliminated. Various components of the system are being checked systematically.

While a good deal of this reporting period has been spent in measuring the characteristics of the facility and in detecting its problem areas, some experiments have been carried out which, while preliminary, indicate the future possibilities inherent in SANS, particularly in this instrument. Some of these experiments are described in other contributions to this report. This facility will probably be capable of handling a portion of the load of experiments proposed for the ORNL-NSF National Center for Small-Angle Scattering Research now under construction at ORNL. In view of this possibility, some preliminary experiments have been done in collaboration with outside users who have expressed a desire for feasibility studies to be done at the ORR. Experiments on polymers, solutions, coal swelling, irradiation damage, phase changes, and metallurgical deformation have been or are being conducted. Although many of these cannot be considered completed experiments, they nevertheless yield some data that show the wide range of possible use and serve as a feasibility test for future, more detailed, studies.

1. Consultant from Georgia Institute of Technology, Atlanta.

2. H. R. Child and S. Spooner, *Solid State Div. Annu. Prog. Rep. April 30, 1977*, ORNL-5328, p. 118.

SMALL-ANGLE NEUTRON SCATTERING OF REACTOR-IRRADIATED Nb

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Analysis of neutron-irradiated Nb and Nb-1% Zr specimens was undertaken with SANS to assess the feasibility of using the technique to supplement methods of TEM analysis of void structure. The neutron scattering experiment was difficult because the scattering from the small sample volume was not far above background. Nevertheless, measurable scattering was obtained by utilizing the advantages of the Borkowski-Kopp two-dimensional position-sensitive detector, and comparisons between data from the SANS method and TEM method can be made.

Three neutron-irradiated samples having the largest swelling (determined by immersion density) were chosen from a larger group of polycrystalline samples irradiated in the core of EBR-II. Each sample was irradiated to a fluence of 2.5×10^{22} neutrons/cm². An Nb-1% Zr alloy was irradiated at 790°C, and two unalloyed Nb specimens were irradiated at 790 and 585°C respectively. Electron microscopy was performed with an Hitachi HU-200 microscope,³ and the structures of voids, precipitates, and dislocations were investigated by standard techniques. TEM structure investigations of samples of this group have been reported previously.⁴ The neutron scattering specimens were coupons of approximately 8 × 12 × 0.5 mm in size. The neutron transmission was 0.998. SANS experiments were performed with 4.82-Å wavelength neutrons with the 20- by 20-cm Borkowski-Kopp detector set at 120 cm from the specimen position. Recording times of approximately 10 hr were used to collect the scattering data. The area detector data were radially averaged to give a scalar intensity function, $I(\kappa)$, ($\kappa = 4\pi(\sin \theta)/\lambda$).

The scattering data are shown in Fig. 5.1 as Guinier plots in which the logarithm of intensity is plotted vs κ^2 . The κ -range over which acceptable data could be measured was $0.0212 (\text{\AA})^{-1}$ to $0.1000 (\text{\AA})^{-1}$. The scattering from the Nb-1% Zr alloys shows two linear regions in this plot. The Guinier plot of scattering intensity from pure Nb irradiated at 790°C shows a linear region merging with a second, less well defined, linear region. The Guinier plot of intensity from the Nb irradiated at 585°C shows one linear region with low scattering statistics. A least squares fitting of the data to a sum of two Gaussian functions yielded the void radii of gyration shown on the plot. The radius of gyration is an average void radius defined by the square root of the fourth moment of radius over the void size distribution divided by the second moment of radius.

Fig. 5.1. Radially averaged SANS intensity for three neutron-irradiated Nb samples vs κ^2 .

Electron microscopy revealed void size populations in each sample that were consistent with the SANS from the inner angles but not with SANS at the higher angles

from the 1% Zr alloy and the Nb irradiated at 790°C. Void concentration histograms were obtained by analyzing photographs of representative void structures taken under absorption contrast conditions. Figure 5.2 shows the percentage of voids in the indicated size intervals vs the log of their diameters. There were several sources of variation in number density that included grain-boundary denudation, size enlargement, and number density reduction near precipitates in the 1% Zr alloy and near dislocations in all specimens. An imperfectly ordered structure of voids was found in the Nb specimen irradiated at 790°C. The larger voids in the 1% Zr alloy were clearly faceted, and the form of the polyhedra is probably a dodecahedron formed by (110) faces with truncation by (100) planes. Precipitates found in the alloy were often found to be rod-like with the small dimension on the order of 50 Å.

Fig. 5.2. Size classification of voids revealed by TEM of Nb alloys irradiated to 2.5×10^{22} neutrons/cm² (>0.1 MeV) at indicated temperatures.

Some of the discrepancies between the TEM and SANS analyses can be partially explained. The lack of evidence for the void lattice in SANS is due to the occurrence of the first void lattice Bragg peak at a scattering angle smaller than the SANS lower detection limit. Because the lattice has limited perfection, the void interference pattern at high angles would be liquid-like at best. There is a problem in explaining the small-angle scattering at higher angles in the two samples irradiated at 790°C. It is not reasonable to

expect that a population of approximately 70-Å-diam voids would have been missed in both TEM examinations of these samples.^{3,4} The Guinier radius of the large voids calculated from SANS in the 1% Zr alloy represents a minimum size because scattering at both lower angles and higher angular resolution is required to avoid intensity-smearing due to finite scattering resolution. To this extent the TEM and SANS results are compatible. Size distribution analysis of the SANS measurements was not useful because the resulting number distribution curves were heavily weighted by small nonvoid effects.

In summary, the SANS method gives an average of void structures over actual variations in the void population shown in TEM. Void ordering was not seen in the SANS experiment because data were not taken at a sufficiently low angle. Agreement between the two methods is best if the intensity from the largest scattering objects is taken to be void scattering.

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NEUTRON SCATTERING FROM COAL AT SMALL ANGLES

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The use of SANS for preliminary investigation of samples of coal treated with pyridine to see if the observations from this technique can be usefully correlated with chemical results has been attempted only very recently. These studies, therefore, are not complete.

Figure 5.3 shows data taken on three different samples of powdered Illinois No. 6 coal chemically treated with (1) deuterated pyridine to cause swelling, (2) hydrogenated pyridine, and (3) untreated. The figure shows the radially averaged intensity, divided by the sample attenuation, vs $\kappa = 4\pi/\lambda \sin \theta$ for these samples. The treatment of coal by pyridine swells the coal, and about 20% of the pyridine hydrogen is retained in the material. We looked for SANS evidence of this swelling and retention, particularly in the case of deuterated pyridine, because of the high scattering amplitude of D compared to H. The data do indeed show an increase in the scattering intensity from the deuterated sample (No. 1) compared to samples 2 and

Fig. 5.3. Neutron small-angle scattering intensity, corrected for sample attenuation, vs κ for three samples of Illinois No. 6 powdered coal. The curves are merely guides for the eye.

3, but the increase is small and may not be conclusive. The radii of gyration R_g , determined from the smallest angle data, are 400 Å, 480 Å, and 480 Å, respectively, for samples 1, 2, and 3. The difference for sample 1 is just on the borderline of significance, and further work would be necessary before a real difference in R_g could be established. Chemical measurements on these same samples give molecular dimensions from 400 to 500 Å, which are consistent with these R_g values. Thus, the results of these preliminary measurements are encouraging and provide hope for the future usefulness of this technique in coal studies.

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SMALL-ANGLE NEUTRON SCATTERING FROM VOIDS IN NEUTRON-IRRADIATED TYPE-304 STAINLESS STEEL

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Preliminary SANS results designed to investigate the structure of voids in neutron-irradiated, polycrystalline, type-304 stainless steel have been obtained from the new SANS instrument at HB-6, ORR. Two specimens of this material, which were cut from a control rod thimble in the EBR-II, were supplied by the Metals and Ceramics Division at ORNL. The specimens taken from

the reactor midplane position were irradiated at 400°C to a fluence of 1.6×10^{23} neutrons/cm² ($E > 0.1$ meV). The samples were 1 mm thick and had a radiation level (principally ⁶⁰Co gamma) of 2 R at contact. The Borkowski-Kopp position-sensitive proportional counter was set at 5 m from the specimen position. The specimen was surrounded on the top, bottom, and sides by 2 in. of Pb. There was no perceptible background contribution from the radioactive sample in this arrangement. The range in $\kappa(4\pi\theta/\lambda)$ for these experiments was 8×10^{-3} (Å)⁻¹ to 60×10^{-3} (Å)⁻¹ and was achieved by letting the incident beam impinge on the corner of the area detector. The data for each specimen, collected in 6 hr, were corrected for instrumental background. Because the data were spherically symmetric, a radial averaging of the data was carried out that yielded scalar scattering curves of good statistical precision; these curves are shown in Fig. 5.4 for both samples. The curves show an interference maximum indicating spatial correlations between voids of large size. In addition, there is an intensity tail characterized by a Gaussian curve.

A curve-fitting analysis was based on a scattering intensity model in which larger voids were distributed as a gas of hard spheres^{2,3} and smaller voids were taken to be randomly dispersed. The intensity is given by

$$I(\kappa) = I_0(1)\exp[-R(1)^2\kappa^2/3] [1 - F\phi(\kappa D_x)] + I_0(2)\exp[-R(2)^2\kappa^2/3],$$

where $R(1)$ and $R(2)$ are Guinier radii of gyration, F is a space-filling correlation number varying between 0 and 1, D_x is an exclusion distance, $I_0(1)$ and $I_0(2)$ are the zero angle intensities for the scattering from each void population, and $\phi(\kappa D_x)$ is an interference function tabulated by James.² The results of the curve-fitting analysis are given in Table 5.1. The goodness of fit measured by χ^2 was approximately 2.4 for both data sets.

Bloom et al.⁴ have reported on electron microscopy analyses of similarly irradiated stainless steel. They found a void population centered around a diameter of 300 Å for a specimen irradiated at 590°C to 3.5×10^{22} neutrons/cm² with no indication of void sizes less than about 100 Å. Although our samples do not duplicate these irradiation conditions (lower temperature, but higher fluence), our larger radius of gyration $R(1)$ would correspond to a diameter of 290 Å ($D = 2\sqrt{5/3} R_g$) in agreement with their value. However, they see no evidence for the second distribution corresponding to $R(2) = 48$ Å. At present, no explanation is offered for

Fig. 5.4. Radially averaged intensity from two samples of neutron-irradiated, type-304 stainless steel vs $\kappa = 4\pi(\sin \theta)/\lambda$.

Table 5.1. Structural parameters derived from curve-fitting analysis

Parameter	Sample 1	Sample 2
Guinier radii		
$R(1)$	$110 \pm 3 \text{ \AA}$	$118 \pm 3 \text{ \AA}$
$R(2)$	$47 \pm 5 \text{ \AA}$	$49 \pm 3 \text{ \AA}$
Exclusion distance, D_x	$307 \pm 12 \text{ \AA}$	$307 \pm 12 \text{ \AA}$
Correlation factor, F	0.99 ± 0.002	0.99 ± 0.01
Relative intensity factors		
$I_0(1)$	366 ± 20	482 ± 27
$I_0(2)$	17 ± 2	23 ± 5

the same geometry. This intensity is proportional to the average number of voids per cubic centimeter, $\bar{N}$. From such comparisons, $\bar{N}$ was $9 \times 10^{15} \text{ cm}^{-3}$ for voids with $R = 115 \text{ \AA}$ and an accuracy estimated to be 50%.

1. Consultant from Georgia Institute of Technology, Atlanta.
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this discrepancy, although several nonvoid artifacts could be responsible. Precipitates, grain boundary effects, or void shape features might be invoked. This discrepancy forces us to the position that void size distribution analyses by scattering intensity inversion, or curve-fitting with number density function coefficients as suggested by Vonk,⁵ may not be valid because such analyses are weighted by the scattering at large angles.

Despite our inability to analyze for void number density, we have estimated the number density by comparing the zero angle intensity, $I_0(1)$, from the stainless steel samples and that from a well-characterized sample of irradiated Al, measured with

SANS STUDY OF DEFORMED AUSTENITIC STAINLESS STEEL

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Plastic deformation partially transforms fcc austenitic stainless steel to hexagonal and bcc phases. Martensite is ferromagnetic and thereby is distinguishable from the paramagnetic fcc and hcp phases. The amount of deformation-induced martensite can be measured in magnetization experiments. A series of hydrogen-annealed type-304 stainless steel strips were rolled to various thicknesses that gave reductions from 12 to 80%. Initially, a transmitted neutron beam depolarization experiment was done at HB-1 of the HFIR to

explore a nondestructive determination of the magnetic phase fraction. Qualitative correspondence between beam depolarization and deformation was established and is shown in Fig. 5.5. However, the method was only qualitative because stray magnetic fields exerted a perturbing and nonreproducible depolarization effect. Later, when this same set of samples was investigated with SANS at the ORR, scattering effects were readily measured in a reproducible way and found to correlate with the degree of deformation and the probable martensite phase shape. Furthermore, an applied magnetic field-dependence in the scattering was found that confirmed the magnetic origin of scattering and, more importantly, suggested magnetic domain structure effects. The SANS investigation of deformed austenitic stainless steel appears to afford a quantitative non-destructive test of material that can yield magnetic

Fig. 5.5. Polarization ratio for neutrons transmitted through rolled stainless steel sample vs thickness of sample. The neutrons were polarized parallel to the rolling directions and the sample thickness.

structural details of use in analysis of deformation effects.

The SANS experiments were done using several beam path and collimator geometries to cover as wide a range in scattering angle as possible. Figure 5.6a shows the scattering data from deformed stainless steel for several deformation levels. On the log-log plot, the scattering follows a κ^{-4} -dependence, where κ is $4\pi\theta/\lambda$ with θ the diffraction angle and λ the neutron wavelength (4.82 Å). Although scattering at small angles tends to fall off more slowly than the κ^{-4} -dependence, even at the smallest angles measured, there is no apparent Guinier regime (linear $\ln I$ vs κ^2). A measurement of scattering from the 80%-deformed material, which was made on the double-crystal small-angle scattering apparatus at the HFIR, indicated that the scattering angle range is much closer to zero angle and the intensity decrease favors a κ^{-2} -dependence suggestive of scattering from a disc-like object. Because slit-height distortion of scattering occurs, this conclusion is tentative.

The applied field-dependence in the scattering was explored in 80%-deformed material with the use of a permanent magnet applying approximately 7500 G parallel to the rolling plane and perpendicular to the incident beam. Figure 5.6b shows the large suppression of smallest angle scattering. The scattering pattern obtained by the area detector showed the anticipated distortion from circular to cylindrical symmetry. This distortion is given by $\sin^2\alpha$, where α is the angle between magnetization vector μ and the diffraction vector κ . As expected, a circular average of the scattering in the outer scattering angle range for the magnetized sample data was found to be reduced to three-fourths of the circular average of the unmagnetized sample. At present, no model of magnetic domain structure in the deformation-induced martensite has been suggested to explain the magnetic field-dependence in the deformed stainless steel scattering.

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Fig. 5.6. Neutron small-angle scattering from deformed stainless steels. (a) Intensity corrected for thickness and attenuation vs κ for three deformed stainless steel samples; (b) comparison of intensity from the unmagnetized and magnetized 80%-deformed stainless steel samples.

SMALL-ANGLE NEUTRON SCATTERING FROM LOW CONCENTRATIONS OF DEUTERATED POLYSTYRENE IN POLY(ORTHO-CHLOROSTYRENE)

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The polymer blend, polystyrene in poly(ortho-chlorostyrene), is a homogeneously mixed system at the preparation temperature (120–140°C). When it is heated above about 160°C, however, the material exhibits a phase separation.^{2–4} Consequently, several phenomena should be observed as the temperature of the mixture is varied; namely, the radius of gyration,

$\sqrt{\langle S^2 \rangle_w}$, should decrease and the second virial coefficient should change from a slightly positive or zero value to a negative one. Neutron scattering studies were carried out on dilute blends of deuterated polystyrene (dPS) in protonated poly(ortho-chlorostyrene) (PoCIS) in the first phase of a systematic characterization of dPS in the blend.

Seven concentrations of dPS in protonated PoCIS were prepared, and all the concentrations were less than 0.06 g dPS/cm³ of the blend. The purified materials were weighed according to the desired concentration, dissolved in benzene, and freeze-dried to yield a powder of the blend. The powder was melt-pressed at 140°C

under vacuum into disks with a diameter of 1 cm and a thickness of 1 mm. These specimens were then used in the scattering experiments performed at the ORR.

The scattering in excess of that of the matrix was obtained by subtracting the scattering due to PoCIS. The excess scattered intensity was analyzed by a method developed by Benoit:⁵

$$I_{ex}(\kappa) = N_A V \phi_0 t T [K^2 c_A M_w P(\kappa)] , \quad (1)$$

where $P(\kappa)$ is the intramolecular interference function, N_A is Avogadro's number, V is the scattering volume, ϕ_0 is the incident neutron flux, t is the counting time, T is the transmission coefficient, c_A is the concentration (g/cm^3), M_w is the molecular weight of the dPS, and K_0 is the contrast factor given by

$$K_0 = z B_i - B_S V_P / V_S^2 / M_a^2 , \quad (2)$$

where B_i is the coherent scattering length of monomer unit i , V_i is the specific volume of component i , M_a is the monomer molecular weight (112 g for dPS), and z is the degree of deuteration of the dPS.

Using a Guinier analysis,⁶ the radius of gyration of the dPS was found to be constant as a function of concentration (Fig. 5.7). This radius extrapolated to a value at zero concentration of 12.7 nm, which is expanded from the unperturbed value of 9.0 nm.⁷

From the $\kappa = 0$ intercepts, the molecular weight and second virial coefficient, A_2 , were obtained by⁸

$$K_0 c_A / R(0) = (1/M_w) + 2A_2 c_A , \quad (3)$$

where $1/R(0)$ represents the reciprocal of the absolute intensity. Difficulty was experienced in placing the data on an absolute level and, consequently, the analysis was performed so that the $1/M_w$ value at $c = 0$ yielded the correct $M_w = 114,000$. This calculation yielded a value for A_2 equal to zero within experimental error, indicating unperturbed conditions. This result does not, at first, appear to be consistent with the experimentally observed value of $\sqrt{\langle S^2 \rangle_w}$. However, on close examination, there is, in fact, no conflict. The second virial coefficient is given by

$$A_2 = (\frac{1}{2} - \chi) / P_2^2 V_1^0 , \quad (4)$$

where χ is the Flory-Huggin's interaction parameter, P_2 is the density of the dPS ($P_2 \sim 1$), and V_1^0 is the molar volume of the matrix PoCIS. Consequently, the first term on the right-hand side of Eq. (3) is about 10^{-4} and the second term is about 10^{-6} . Therefore, even for very compatible mixtures, A_2 will appear to be zero within experimental error because the first term is dominant.

These experiments have demonstrated the feasibility of neutron experiments on this system, which involve

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Fig. 5.7. Radius of gyration dependence on concentration for dPS in PoCIS.

investigation of dPS in a matrix composed of a blend of protonated PS and PoCTS. They have also indicated that $\sqrt{(S^2)_w}$ and not A_2 will be the most sensitive parameter in these studies.

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DETERMINATION OF THE COHERENT NEUTRON SCATTERING AMPLITUDE OF Cu BY SMALL-ANGLE NEUTRON REFRACTION

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In general, when neutrons pass from one medium into another, their wave vectors are changed as a consequence of interference between the incident and forward-scattered waves. Far from the Bragg condition, this phenomenon results in the refraction of neutrons at a material interface and can be described by an index of refraction $n = 1 - \lambda^2 \bar{b}N/2\pi$ (ref. 2). Here, λ is the neutron wavelength, $\bar{b}$ the coherent scattering amplitude, and N the volume density of scattering sites. In general, n differs from unity by less than one part in 10^5 .

We have used a right parallelepiped of 99.999% pure Cu, with highly polished surfaces, as a neutron prism to ascertain $\bar{b}$ by means of small-angle scattering. The angular deviation 2θ between the refracted beam and incident beam is given by

$$2\theta = (\lambda^2 \bar{b}N/2\pi)[\cot \beta - \cot(\alpha + \beta)] \quad (1)$$

where β is the grazing angle between the neutron beam and the first prism face, and α is the prism apex angle (90° in this case). The angle 2θ was measured as a function of the orientation $\phi = \beta - \beta_0$ of the prism in the beam, using the double-perfect-crystal small-angle neutron diffractometer. These data were then fit by least squares to Eq. (1) to obtain $\lambda^2 \bar{b}N/2\pi$ (as well as the experimentally uncertain angle β_0).

The results yield the preliminary value $\bar{b} = 0.77 \times 10^{-12}$ cm. This value compares to the value for normal

Cu, $\bar{b} = 0.76 \times 10^{-12}$ cm, found in the literature.³ The present determination is considered preliminary pending verification of the neutron wavelength $\lambda = 2.599 \pm 0.006$ Å, which was found by optical measurement of the beam takeoff angle from the perfect silicon monochromator crystal. A corroborating wavelength measurement will be undertaken.

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LATTICE DYNAMICS

NEUTRON SCATTERING AND X-RAY STUDY OF THE 18 K TRANSITION IN MEM(TCNQ)₂

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MEM(TCNQ)₂ is a linear chain compound with one-dimensional TCNQ chains similar to those in TTF-TCNQ. However, MEM(TCNQ)₂ is a much simpler material to study because there is no TTF chain and the electron transfer is an integral value. One expects two phase transitions to occur in a one-dimensional material, and the two phase transitions are clearly separated in MEM(TCNQ)₂. The first of these phase transitions, which occurs at 335 K, involves a dimerization of the TCNQ chain and is an electronic transition. Susceptibility measurements have shown that the second transition is at 18 K, and it has been conjectured that it is a spin-Peierls transition in which the dimerized TCNQ chain dimerizes once again giving an antiferromagnetic spin pairing within the unit cell. The spin-Peierls transition would be expected to be driven by a soft phonon.

Neutron and x-ray studies of single crystals of MEM(TCNQ)₂ have shown that a superlattice develops at the zone boundary along the c^* -direction (the TCNQ chain direction) below 18 K. Diffuse x-ray scattering above the transition shows increasing intensity at the superlattice position as the transition is approached from above, and this intensity is found only in transverse-scattering geometry. This phenomenon suggests that the TA phonon softens as the temperature is lowered and drives the transition at 18 K. The neutron studies show phonon-softening at the zone boundary in the region of the TA phonon, but the measurements are complicated by the appearance of a flat phonon branch at the same energy as that of the TA

branch at the zone boundary where the superlattice occurs. Deuterated crystals may be needed to clarify the nature of the soft phonon. The neutron studies have further shown that the LA phonon branch is unaffected by the transition.

The temperature dependence of the superlattice intensity has been measured for several reflections and is reasonably well given by the BCS gap equation. The superlattice intensity, measured at about 80 points in the b^*-c^* plane, is consistent with a dimerization produced by a transverse motion of the TCNQ molecules with respect to c^* . The neutron and x-ray measurements thus show that the 18 K transition stems from a c^* dimerization of the TCNQ chain, which is the expected behavior for the spin-Peierls type of transition. Further phonon measurements are needed to identify the exact nature of the soft phonon mode.

Figure 5.8 shows how the TCNQ chain dimerizes at the transitions. Above 355 K, the TCNQ chain is regularly spaced. The MEM gives up one electron that is shared by the TCNQs, giving half an electron per TCNQ.

Fig. 5.8. Dimerization of the TCNQ chain at the 355 K and 18 K transitions.

Below 355 K, the TCNQ chain dimerizes so that the chain is split into two TCNQ units per unit cell as shown by the dotted line. This division gives one electron on the TCNQs per unit cell. Below 180 K, the chain further dimerizes by transverse slippage of alternate unit cells of TCNQ molecules, and the unit cell enlarges to contain the four TCNQ molecules. The spins have antiferromagnetic coupling from one unit of TCNQs to the next, reducing the magnetic susceptibility to a small value. It appears that a soft transverse phonon

accompanies the 18 K transition. $\text{MEM}(\text{TCNQ})_2$ is the only known material that displays the electronic and spin-Peierls transitions expected for a one-dimensional chain with antiferromagnetic couplings by simple dimerizations along the chain direction. $\text{MEM}(\text{TCNQ})_2$ is thus an ideal testing ground for theories of one-dimensional systems.

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LATTICE DYNAMICS OF NaO_2 NEAR THE ORDER-DISORDER PHASE TRANSITION

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The cubic-cubic phase transition of NaO_2 near 232 K is associated with the long-range orientational order of the O_2^- molecules that are believed to have equilibrium orientations in the $\langle 111 \rangle$ directions in both phases. The ordered pyrite structure (Pa3) below T_c changes to the disordered pyrite structure (Fm3m) above T_c . A part of the lattice dynamics of NaO_2 has been reported in a recent paper.³ We have carried out more detailed measurements of the transverse and longitudinal acoustic phonons in the $[00\bar{1}]$ and $[\bar{1}\bar{1}0]$ directions of both phases. The dispersion curves for these phonons are shown in Fig. 5.9. The phonons have been found to be rather poorly defined above T_c in comparison with those observed at 216 K (Fig. 5.10). The temperature

Fig. 5.9. Phonon dispersion curves for the acoustic branches of NaO_2 .

Fig. 5.10. Phonon peaks below and above the order-disorder transition ($T_c \approx 232$ K). Those peaks above T_c are poorly defined.

effects are interpreted as due to the coupling with the orientational degree of freedom of the O_2^- molecules.

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2. Institut für Reaktorforschung, Würenlingen, Switzerland.
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PHONON LIFETIME FOR PbF_2

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PbF_2 shows high ionic conductivity at relatively low temperatures (< 700 K), and the conductivity is the highest among the pure fluorite compounds. The ionic conduction is due to the migration of F ions that, at high temperatures, seem to occupy interstitial sites near the center of the fcc lattice formed by Pb atoms. To understand the mechanism of the ionic conduction, it is essential to acquire detailed knowledge of the lattice vibrations in the compound. Measurements of the phonon dispersion curves at 10 K have already been reported.¹ However, a more detailed study of the phonon lifetimes is expected to yield important information about the mechanism of migration. Therefore, measurements of the phonon line widths in PbF_2 have been initiated.

The measurements were carried out for both acoustic and optic branches along the $[100]$ direction of the reciprocal space. As the temperature was raised from 10 K to room temperature, the $LO(\Delta_2^-)$ phonons seemed to have much larger width increases than other phonons. Figure 5.11 shows examples of such a comparison. The Δ_2^- branch involves only the motions of the F atoms for wave vectors in this direction. Although the large

Fig. 5.11. Temperature dependence of phonon peaks from PbF_2 . This LO phonon is associated only with the motions of F atoms.

widths observed for this branch could be due to the large anharmonicity of the motions of F atoms, these widths may not be much larger than those observed in various ionic crystals such as alkali-halides. Measurements for other branches are in progress as well as an attempt to construct a theoretical model for interpreting the experimental data.

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PHONON-DEFECT MODE HYBRIDIZATION IN $KCl_{1-x}(KCN)_x$

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Our investigation of the hybridization between the phonons in KCl and the internal modes of CN^- molecular impurities² has been extended to study the

influence of varying the defect concentration. Measurements of the $[110]$ transverse acoustic phonon branch with $[1\bar{1}0]$ polarization have been obtained as a function of temperature between 10 and 100 K for samples with impurity concentrations in the range 0.4 to 6%. The results obtained for a temperature of 10 K are shown in Fig. 5.12. The splitting of the dispersion curve due to the phonon-defect hybridization, as observed previously for a CN^- concentration of 0.4%,² increases substantially with increasing concentration.

Fig. 5.12. The concentration dependence of the phonon-defect mode hybridization for the $[110]$ transverse phonon in $KCl_{1-x}(KCN)_x$.

The energy widths, or damping, of the hybridized modes also increase measurably with increasing concentration, as shown in Fig. 5.13 for the wave vector $q = (0, 0, 0.08)2\pi/a$. For this wave vector, the lower peak tends to gain intensity relative to that of the upper peak while concentration increases. However as seen in Fig. 5.12, the frequency at which hybridization occurs does not seem to be very sensitive to the concentration. In general, the lower frequency peaks for large wave vectors ($\xi \geq 0.07$) are better defined than are the high frequency peaks at small wave vectors.

Fig. 5.13. The frequency distribution of scattered neutrons for $\xi = 0.08$ in $KCl_{1-x}(KCN)_x$.

Also seen in Fig. 5.13 is the increase in the quasi-elastic scattering ($\nu \approx 0$) intensity with increasing impurity concentration. This intensity decreases strongly with increasing temperature and $|q|$ and is anisotropic with respect to the direction of q . This behavior is suggestive of the existence of lattice distortions, which grow with decreasing temperature as the librational or rotational motions of the CN impurities freeze out.

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2. R. M. Nicklow, *Solid State Div. Annu. Prog. Rep. Apr. 30, 1977*, ORNL-5328, p. 135.

NEUTRON INELASTIC SCATTERING MEASUREMENTS OF PHONON PERTURBATIONS BY DEFECTS IN IRRADIATED Cu

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Theoretical² and experimental^{3,4} studies have provided strong evidence that the split-interstitial of the $\langle 100 \rangle$ dumbbell configuration is the stable form for interstitials in Cu and Al. The theoretical work has also indicated that the dumbbell interstitial possesses a low-frequency librational mode.² Wood and Mostoller⁵ and Shober, Tewary, and Dederichs⁶ have shown that these modes are strongly coupled to the phonons of the host crystal, leading to perturbations of the phonon dispersion relation (i.e., frequency vs q) that could possibly be detected by neutron inelastic scattering. In a previous report,⁷ we described the results of a neutron scattering experiment that was carried out to search for such perturbations in a high-purity, low-dislocation-density Cu crystal which had been irradiated at 4.2 K with thermal neutrons to produce a Frenkel-pair concentration of about 40 ppm. The results of this earlier investigation, although showing phonon perturbation effects, were very difficult to understand. First, the phonon peak shapes showed unusual structure that was not removed by an anneal at 300 K, a temperature well above that thought to correspond to the annealing of split interstitials. Second, other perturbation effects in the form of q -dependent peak shifts, although exceedingly small, were considerably larger than could be accounted for by simplified theoretical results.

In addition, the data were incomplete in several respects. Consequently, we have carried out new experiments on irradiated Cu to extend the previous work and to clarify and confirm the previous results. The new measurements were carried out on the same Cu crystal that was used previously. As before, the crystal was irradiated at 4 K in the low-temperature irradiation facility at the BSR and then transferred, without warming, to a cryostat on the neutron spectrometer. For this experiment, the irradiation facility was modified to increase the irradiation flux and, hence, the concentration of defects. The estimated defect concentration was 120 ppm. Phonon measurements were carried out at 4 K on the irradiated sample before annealing and after anneals at 72 K, 300 K (room temperature), 450 K, and 800 K.

A portion of the experimental results obtained for several phonon wave vectors, $q = (0, 0, \xi)2\pi/a$, is shown in Fig. 5.14. The data points represent the scattered neutron frequency distributions obtained for the as-irradiated sample. The most obvious phonon

Fig. 5.14. Frequency distributions of neutrons scattered from irradiated Cu at 4 K for $q = (0, 0, \xi)2\pi/a$.

perturbation effects are the unusual peak structures observed for $\xi \leq 0.07$. This effect is substantially larger than was observed in the previous experiment as is indicated in Fig. 5.14 by the comparison of data obtained in both experiments for $\xi = 0.06$.

The full lines drawn through the data represent the calculated results of one of several peak shape analyses. For the calculations shown in Fig. 5.14, we assumed that the peaks could be described by the sum of two intensity distribution functions. One is the "main" narrow phonon peak that is broadened asymmetrically by the instrumental resolution (as is observed for an irradiated sample); the second is a broad peak with a

Gaussian shape that describes the excess intensity on the high-frequency side of the measured peaks. The fits to the observed intensity distributions are excellent. The use of a more complicated intensity distribution that includes, for example, an asymmetry in the second peak does not seem warranted at present. The dotted lines shown for each ξ are the results of fits made to the data obtained after the sample was annealed at 72 K.

These fitting calculations have provided a systematic and relatively objective means for comparing quantitatively the q -dependence of the peak shapes and positions before and after the annealing treatments of the sample. One result that is relatively obvious from a casual inspection of the raw data is that the intensity of the "assumed" second peak decreases with increasing ξ . For a given ξ , the intensity also decreases with increasing annealing temperature but remains quite distinct after an anneal at 72 K. This result is consistent with that of the previous experiment and suggests that this portion of the phonon perturbation does not correlate well with the assumed annealing behavior of isolated split-interstitials. The origin of this effect is not understood.

The position of the main phonon peak shows a small q -dependent shift from its position measured after a 72 K anneal (Fig. 5.15). This result is consistent with both the type of resonant perturbation anticipated for split-interstitials and the annealing temperature of isolated interstitials. The position of this peak does not change upon annealing at higher temperatures.

Fig. 5.15. The frequency shifts of phonons in irradiated Cu relative to the values measured after a 72 K anneal.

The magnitudes of these peak shifts, although very small and just on the edge of experimental uncertainty, are more consistent with the magnitude expected theoretically than those observed in our previous experiment.

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4. J. Holder, A. V. Granato, and L. E. Rehe, *Phys. Rev. Lett.* **32**, 1054 (1974); *Phys. Rev. B* **10**, 363 (1974).
5. R. F. Wood and Mark Mostoller, *Phys. Rev. Lett.* **35**, 45 (1975).
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TRANSVERSE OPTIC PHONONS AND THE PHASE TRANSITION IN $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$

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Certain IV-VI compounds such as GeTe and SnTe are semiconductors with narrow band gaps and undergo structural phase transitions from the NaCl structure at high temperatures to rhombohedral structures at low temperatures. This lattice instability is due to the strong coupling between the interband electron transitions and the TO phonon at the Brillouin zone center (Γ). Renormalizations of the electron energies and of the TO phonon frequency occur as the temperature is lowered, and softening of the TO phonon is expected. An indication of a softening in SnTe was found above T_c (98 K) by neutron scattering techniques.² Because of the symmetry of the structure, this mode is Raman inactive above T_c , but the lower symmetry below T_c makes it possible to observe the phonon at low temperatures by Raman scattering techniques. The frequency of this phonon observed by this technique³ shows considerable decrease as the temperature is increased toward T_c .

Although GeTe transforms at $T_c = 670$ K, PbTe is known to remain cubic at low temperatures. However, replacing only 5% of Pb atoms by Ge causes the transition to occur at about 150 K. Thus, T_c can be varied over a wide range by changing the concentration

of Ge. The alloy system $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$ should, therefore, offer the possibility of studying the electron-phonon coupling mechanism and interesting aspects of structural phase transitions associated with low T_c . The softening of the TO phonon for $\text{Pb}_{0.95}\text{Ge}_{0.05}\text{Te}$ was observed below T_c by Raman scattering,⁴ and an anomalous temperature dependence of the elastic constants was also found in the ultrasonic data.⁴

To study in detail the electron-phonon coupling mechanism, neutron scattering measurements of the phonon frequencies in $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$ have been initiated. Measurements on $\text{Pb}_{0.95}\text{Ge}_{0.05}\text{Te}$ have been carried out at various temperatures below room temperature. Special attention was paid to the peak shape of the Γ -TO phonon. Figure 5.16 shows examples of the neutron scattering intensity as a function of energy transfer observed at the (113) reciprocal lattice point. The intensity near $E = 0$ is dominated by that of the (113) Bragg scattering. Corrections for the background, the reflectivity of the pyrolytic graphite analyzer

Fig. 5.16. Neutron scattering intensity at the (113) reciprocal lattice point of $\text{Pb}_{0.95}\text{Ge}_{0.05}\text{Te}$. The Γ -TO phonon is poorly defined near the phase transition ($T_c \approx 150$ K).

crystal, and the phonon population factor were made on the data; the results are summarized in Fig. 5.17. The phonon is very poorly defined near the phase transition. However, the phonon width at each temperature seems to be much larger than that expected from the resolution function of the spectrometer.

Fig. 5.17. Temperature dependence of the scattering due to the Γ -TO phonon after correction for background, population factor, and analyzer reflectivity.

Therefore, a careful analysis of the peak shape should yield information about the lifetimes of the electrons and the phonons arising from the coupling between them. The interesting problem associated with the central peak cannot be studied directly because of the large contribution from the Bragg reflection to the intensity at $E = 0$. Although the measurements at (1.05, 1.05, 2.95) also seem to indicate the softening of the mode, those at (1.1, 1.1, 2.9) did not show significant temperature effects. Thus, the softening appears to be confined near Γ .

Further measurements at Γ and the theoretical interpretation of the peak shapes, as well as detailed measurements of the anomalies expected in the acoustic modes, are planned.

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LATTICE DYNAMICS OF γ -Ce

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Over the last several years there has been considerable interest in Ce and some of its compounds that, under certain conditions, exhibit a nonintegral valence. Of particular interest is the fcc γ -phase of Ce in which, under normal conditions of temperature and pressure, the Ce ion is approximately in the trivalent state. When γ -Ce is compressed to modest pressures (~ 8 kbar at 300 K) or cooled to low temperatures (≤ 100 K at 1 atm), it undergoes a transformation to the collapsed α -phase (also an fcc structure but with a volume smaller by 17%) in which the Ce ions are in a mixed valence state. Clearly, a detailed knowledge of the lattice dynamics of γ and α -Ce is essential for a fundamental understanding of this type of transition. In the present work, inelastic neutron scattering techniques have been used to study the lattice dynamics and the magnetic scattering in fcc γ -Ce.

The experimental dispersion curves are plotted in Fig. 5.18. It would have been instructive to compare the dispersion curves of γ -Ce with those of fcc La because the latter element has the same outer electronic structure and approximately the same mass as Ce. Unfortunately, the dispersion curves of fcc La have not yet been measured. However, several rather unique features of the lattice dynamics of γ -Ce can be revealed by comparing the dispersion curves with those of other fcc elements, particularly those of Th, which is in the same column of the periodic table as Ce. Comparison of the dispersion curves in Fig. 5.18 with those of Th shows that the spectrum of γ -Ce is, in general, softer than one would expect from the Lindemann homology rule, which takes into account the differences in mass, spacing, and melting temperatures of these elements. This relative softening is particularly pronounced for the longitudinal branches as well as for the $T(111)$ and $T_1(110)$ branches. On the other hand, the lowering of

Fig. 5.18. Measured dispersion curves of γ -Ce. The solid lines are a fit to an eighth nearest-neighbor force constant model.

the frequencies with respect to the values obtained from the Th frequencies by application of the Lindemann rule is not as pronounced for the $T(100)$ and $T_2(110)$ branches. Actually, the frequencies of the $T(100)$ branch scale quite well with those of Th. This observation is rather interesting because the $T(100)$ and $T_1(110)$ are the only branches whose slopes in the elastic limit do not involve the elastic constants c_{11} and c_{12} which determine the bulk modulus, B , of the material [$B = \frac{1}{3}(c_{11} + 2c_{12})$]. The bulk modulus of γ -Ce at room temperature decreases with increasing pressure and exhibits a dramatic decrease at the $\gamma \rightarrow \alpha$ transition pressure. Thus, it seems that premonitory effects of the transition are present in the dispersion curves of γ -Ce at room temperature: the relative softening of the frequencies of γ -Ce with respect to those of Th is more pronounced for those branches that are sensitive to a volume change in the elastic limit.

The elastic constants obtained by a conventional Born-von Kármán analysis of the experimental data are $c_{11} = 0.241$, $c_{44} = 0.194$, and $c_{12} = 0.102$ in units of 10^{12} dynes/cm². Notice the small difference between c_{11} and c_{44} , quite extraordinary for an fcc metal. As a result, the shear moduli c_{44} and $\frac{1}{2}(c_{11} - c_{12})$ differ by almost a factor of three, which implies that γ -Ce is highly anisotropic with regard to the propagation of elastic waves.

Previous studies of the magnetic scattering in γ -Ce were performed on polycrystalline samples. In these studies relatively well defined peaks were observed below 2.5 THz that were attributed either to Ce³⁺ crystal-field excitations or to one-phonon scattering.

Our magnetic studies clearly establish that below 12 THz there are no well-defined crystal-field excitations. The spin-fluctuation energy $\hbar\omega = 4.0$ THz deduced from our measurements is in good agreement with those obtained in the $\text{Ce}_{1-x}\text{Th}_x$ and CePd_3 mixed valence systems.

condition of elastic isotropy is satisfied to within experimental error. Temperature-dependent elastic peaks were observed in the vicinity of the reciprocal lattice points of the ω -phase.

1. Ames Laboratory and Iowa State University, Ames.

LATTICE DYNAMICS OF hcp Ti¹

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Inelastic neutron scattering techniques have been used to study the lattice dynamics of hcp Ti. The phonon dispersion curves along the [001], [100], and [110] symmetry directions were determined at 295, 773, and 1054 K. As the temperature decreases, we observe a rather large increase in the frequencies of all but the [001]LO branch. The zone-center mode of the [001]LO branch softens appreciably, and at room temperature the branch exhibits a dip at the zone center. These features of the phonon spectrum of hcp Ti bear a striking resemblance to those of hcp Zr and seem to be characteristic of the transition metals of column IV of the periodic table. The data were used to evaluate the lattice specific heat at constant pressure as a function of temperature. The calculated total specific heat, obtained by taking into account the electronic contribution, was found to agree, within experimental uncertainties, with the results of direct specific heat measurements.

1. Abstract of paper: *Physical Review* (in press).
2. Ames Laboratory and Iowa State University, Ames.

LATTICE DYNAMICS OF bcc Zr¹

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We have studied the lattice dynamics of bcc Zr at 1400 K by inelastic neutron scattering techniques. We find that (a) the L[111] branch plunges rapidly to low frequencies in the vicinity of $q = \frac{2}{3}[111]$, indicating a natural inclination for this metal to undergo a structural transformation to the ω -phase, (b) the L[110] branch is anomalous at the zone boundary, and (c) the

LATTICE DYNAMICS OF CeSn₃

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In recent years there has been considerable interest in rare-earth metals and compounds that, under certain conditions, exhibit a nonintegral valence. Because its physical properties do not conform to the conventional behavior of a mixed valence system, CeSn_3 is of particular interest. The suggestion that CeSn_3 is in a mixed valence state in the 4 to 300 K temperature range is supported by thermal expansion and compressibility measurements. On the other hand, the susceptibility (instead of exhibiting a Pauli-like behavior expected from a mixed valence system) is approximately constant down to 40 K but then increases rapidly with decreasing temperature. Recently, large single crystals of CeSn_3 of sufficient size for inelastic neutron scattering experiments were prepared in the Ames Laboratory, and we initiated a systematic study of the lattice dynamics of this compound.

Preliminary measurements of the phonon dispersion curves along the [100], [110], and [111] symmetry directions were performed at room temperature and at 10 K. The room temperature data taken along the [100] symmetry direction are plotted in Fig. 5.19. No dramatic change in the acoustic and lower two optical branches was observed down to 10 K. This observation is consistent with bulk modulus measurements in which the compressibility was found to be anomalously large, but essentially temperature independent. This result is rather interesting because recent polarized neutron measurements on CeSn_3 show that at low temperatures the induced moment contains a component of e_g electronic character. Because the lobes of an electronic distribution with e_g symmetry are along the cube edges, one would expect rather large temperature effects on the phonon branches along the [100] symmetry direction. A more detailed study of the dispersion curves at low temperatures and possibly measurements

Fig. 5.19. The phonon dispersion relation in the [001] direction for CeSn₃ at room temperature.

with an externally applied magnetic field are necessary to clarify the connection between the results of the two neutron experiments.

1. Ames Laboratory and Iowa State University, Ames.

PHONONS IN INTERMEDIATE VALENCE

Sm_{0.75}Y_{0.25}S

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We have continued our measurements on the fluctuating valence material Sm_{0.75}Y_{0.25}S and have obtained highly accurate data on the phonon dispersion and widths as a function of temperature. The Sm ion in Sm_{0.75}Y_{0.25}S changes valence state as a function of temperature, varying from 40% Sm²⁺ at room temperature to 70% Sm²⁺ at 100 K. The valence transition is centered at around 200 K but is fairly broad in temperature, extending over a region of about 30 K. We have shown previously that the valence fluctuations have a strong effect on the phonons, particularly for the (111) direction.² Figure 5.20 shows a plot of the LA phonon dispersion for the (111) direction measured at three different temperatures. We see that the phonon dispersion is sensitive to the temperature. At low q , the phonon dispersion becomes softest at the valence transition, showing that the phonon softening is a result of valence fluctuations. The zone-boundary frequencies move continuously upward in energy with decreasing temperature, suggesting that the zone-boundary phonon energies are more sensitive to lattice constant changes than to the valence fluctuations. At the lowest temperatures, where the valence of Sm in the alloy is nearest to 2+, the phonon energies approach those of SmS, which is purely in the 2+ state.

Measurements of the phonon widths show that the phonons are broadest at the point of greatest phonon softening and at the valence transition at 200 K. Figure 5.21 shows the LA phonon widths at three temperatures for the (111) direction. The broadening of the phonons at 200 K shows that the phonons must be strongly coupled to the valence fluctuations. Measurements of the phonon widths in other directions showed similar effects although the widths tended to be smaller than for the (111) direction. Large broadening was also found for the longitudinal optic modes, especially for the (111) zone boundary. Temperature-dependent measurements show that the optical phonons tend to shift downward in energy with decreasing temperature and more nearly approach the phonon energies for Sm²⁺S as the valence of Sm in the alloy approaches 2+.

Fig. 5.20. LA phonon dispersion curves for the (111) direction in $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$ for three temperatures.

Clearly, valence fluctuations can strongly affect the phonon energies and lifetimes in intermediate valence materials. Any theoretical or model calculations for the phonons in these materials must take into consideration

Fig. 5.21. Widths of the (111) LA phonons in $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$ at three temperatures.

the strong coupling between the valence fluctuations and the phonons.

1. IBM Thomas J. Watson Research Center, Yorktown Heights, N.Y.

2. H. A. Mook and T. Penney, *Solid State Div. Annu. Prog. Rep. Apr. 30, 1977*, ORNL-5328, p. 137.

CHARGE FLUCTUATION MODEL AND PHONONS IN $\text{Sm}(\text{Y})\text{S}$

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A large number of coupling mechanisms between two physical systems can be represented by interaction Hamiltonians of bilinear form in the variables specifying

the state of each system. The symmetry properties of the interaction term determine the type of renormalization of the ground state as well as the spectra of the elementary excitations of the system.

The charge fluctuation model¹ of lattice dynamics proposed recently describes the coupling between the atomic motions and the charge modulations by a bilinear interaction between the atomic displacements and the charge fluctuations. This model was found to reproduce the rather anomalous phonon dispersion curves in Nb quite satisfactorily.

The model has been extended to represent the coupling between phonons and charge modulations that involve relaxational processes. The equation of motion for the κ th atom in the l th unit cell is given by

$$M_{\kappa} \ddot{u}_{\alpha}^{(l)} = - \sum_{l' \kappa'} \Phi_{\alpha\beta} \left(\frac{l'}{\kappa \kappa'} \right) u_{\beta}^{(l')} + \sum_{l' \kappa'} V_{\alpha}^{(1)} \left(\frac{l'}{\kappa \kappa'} \right) z \left(\frac{l'}{\kappa'} \right), \quad (1)$$

where $\Phi_{\alpha\beta}$ is the conventional interatomic force constant; $\alpha, \beta = x, y, \text{ or } z$; and $V^{(1)}$ is the coupling constant between the atomic displacement $u_{\alpha}^{(l)}$ and the charge fluctuation $z \left(\frac{l}{\kappa} \right)$. The relaxation of the charge system is assumed to be given by

$$\dot{z} \left(\frac{l}{\kappa} \right) = - \frac{1}{\tau_{\kappa}} \left[z \left(\frac{l}{\kappa} \right) - z_0 \left(\frac{l}{\kappa} \right) \right], \quad (2)$$

where z_0 is determined from the adiabatic condition

$$\left. \frac{\partial H}{\partial z} \right|_{z=z_0} = 0,$$

where H = the Hamiltonian of the system, as

$$\sum_{l' \kappa'} V_{\beta}^{(1)} \left(\frac{l'}{\kappa \kappa'} \right) u_{\beta}^{(l')} + \sum_{l' \kappa'} V^{(0)} \left(\frac{l'}{\kappa \kappa'} \right) z_0 \left(\frac{l'}{\kappa'} \right) = 0, \quad (3)$$

where $V^{(0)}$ represents the coupling between the charge fluctuations. In $q - \omega$ space, Eqs. 1, 2, and 3 can be written as

$$\begin{aligned} \omega^2 M_{\kappa} u_{\alpha}(\mathbf{q}|\kappa) &= \sum_{\kappa' \beta} \Phi_{\alpha\beta} \left(\frac{\kappa}{\kappa \kappa'} \right) u_{\beta}(\mathbf{q}|\kappa') \\ &\quad - \sum_{\kappa'} V_{\alpha}^{(1)} \left(\frac{\kappa}{\kappa \kappa'} \right) z(\mathbf{q}|\kappa'), \\ (1 + i\omega\tau_{\kappa}) z(\mathbf{q}|\kappa) &= - \sum_{\beta \kappa' \kappa''} (V^{(0)})_{\kappa \kappa'}^{-1} V_{\beta} \left(\frac{\kappa}{\kappa \kappa'} \right) u_{\beta}(\mathbf{q}|\kappa''). \end{aligned}$$

By eliminating $z(\mathbf{q}|\kappa)$, one obtains

$$\omega^2 u_{\alpha}(\mathbf{q}|\kappa) = \sum_{\kappa' \beta} D_{\alpha\beta} \left(\frac{\kappa}{\kappa \kappa'} \right) u_{\beta}(\mathbf{q}|\kappa'),$$

with

$$D_{\alpha\beta} \left(\frac{\kappa}{\kappa \kappa'} \right) = \frac{1}{\sqrt{M_{\kappa} M_{\kappa'}}} \left\{ \Phi_{\alpha\beta} \left(\frac{\kappa}{\kappa \kappa'} \right) + \sum_{\kappa'' \kappa'''} V_{\alpha}^{(1)} \left(\frac{\kappa}{\kappa \kappa''} \right) \left[\tilde{V}^{(0)} \right]_{\kappa'' \kappa'''}^{-1} V^{(1)} \left(\frac{\kappa}{\kappa'' \kappa'''} \right) \right\},$$

where

$$\tilde{V}^{(0)} \left(\frac{\kappa}{\kappa \kappa'} \right) = V^{(0)} \left(\frac{\kappa}{\kappa \kappa'} \right) (1 + i\omega\tau_{\kappa}).$$

The neutron scattering intensity is proportional to

$$\text{Im} \left\{ \frac{1}{\omega^2 - [e(\mathbf{q}j) \cdot \Gamma(\mathbf{q}, \omega) e(\mathbf{q}j)]} \right\}. \quad (4)$$

where $e(\mathbf{q}j)$ is the eigenvector of the j th phonon mode for the wave vector $\mathbf{q}$, and $\text{Im}(A)$ denotes the imaginary part of A . The model was used to analyze the data on the phonon frequencies and widths of a fluctuating valence compound $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$ obtained by Mook et al.² (Figs. 5.22 and 5.23). The lines in the figures represent the peak positions and widths calculated from Eq. (4). The model parameters were adjusted to give good

Fig. 5.22. Phonon dispersion curves for $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$ at room temperature. Solid lines represent the peak positions in the spectral function given by Eq. (4) calculated on the basis of the charge fluctuation model. Data are those of ref. 2.

Fig. 5.23. Phonon widths at room temperature calculated on the basis of the charge fluctuation model. Data are those of ref. 2.

agreement with the data on the phonon frequencies of the acoustic modes. The relaxation time τ determined mainly from the observed line widths was found to be 3×10^{-14} sec, which is consistent with the estimated $\hbar$ -band width of about 10 meV.

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LATTICE DYNAMICS OF $\alpha\text{-U}$ ¹

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Inelastic neutron scattering measurements of the phonon dispersion curves along the three principal high-symmetry directions have been performed to investigate the lattice dynamics of $\alpha\text{-U}$. The dispersion curves along the $[0\bar{1}0]$ and $[00\bar{1}]$ directions are not too unusual. However, dips and depressions are observed in the $\{\bar{1}00\}$ branches similar to those observed in high- T_c superconductors.

Standard group theoretical techniques have been employed to discern the symmetry properties of the phonon branches and to block diagonalize the dynamical matrix of the various phenomenological models that have been applied to $\alpha\text{-U}$. These phenomenological models include a four-neighbor Born-von Kármán general tensor model, a twelve-neighbor axially symmetric model, and a shell model. None of these models were able to fit the $\{\bar{1}00\}$ data satisfactorily. However, a modified form of the shell model that included axially symmetric interactions to six neighbors was found to reproduce most of the dispersion curves well, including the $\{\bar{1}00\}$ branches. A simple pseudopotential model was less successful. To obtain all real frequencies from this model, it was necessary to include a Born-von Kármán short-range contribution.

These measurements and calculations have implied that the bonding properties of $\alpha\text{-U}$ are particularly dependent upon the details of the electronic system.

1. Abstract of Ph.D. thesis, West Virginia University, Morgantown.
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OBSERVATION OF SUPERSTRUCTURE IN $\alpha\text{-U}$ NEAR 43 K

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Various physical properties of $\alpha\text{-U}$ exhibit anomalous behavior near 43, 37, and 22 K. It has been suggested^{2,3} that subtle electronic and structural transformations occur in the vicinity of 43 K but are not complete until lower temperatures are attained. Previous x-ray^{3,4} and neutron⁵ diffraction studies did not reveal any definite structural transitions. Soft modes are also thought⁶ to exist in $\alpha\text{-U}$ and are, perhaps correlated with its superconducting properties.

A detailed lattice dynamics study⁷ of α -U by inelastic neutron scattering at room temperature has, indeed, revealed a pronounced anomalous dip in the Σ_4 transverse optic mode at a Q-vector of (2.47, 2, 0), as seen in Fig. 5.24. An elastic scan in this region did not reveal any extra scattering at room temperature; however, as the temperature was lowered below 60 K an elastic peak appeared in the vicinity of (2.5, 2, 0). Similar reflections were observed at other equivalent points in the Brillouin zone but not at all equivalent points; for example, no extra scattering was observed near (2.5, 0, 0). The observed extra reflections are extremely weak – of the order of phonon intensities. A study of the temperature dependence of the (2.5, 2, 0) reflection (Fig. 5.25) reveals a small but finite intensity at 60 K, which increases to a maximum at 18 K, the lowest temperature studied. The behavior of this reflection in the vicinity of 37 and 22 K has not been studied at this time. The phonon frequency at the anomalous dip in the Σ_4 transverse optic mode, briefly studied as a

Fig. 5.25. Temperature dependence of the (2.5, 2, 0) superlattice reflection.

Fig. 5.24. Phonon dispersion curves of α -U. The solid lines are calculated from a six-neighbor modified shell model with axially symmetric interactions.

function of temperature, was observed to decrease with decreasing temperature. The resolution was not sufficient to determine if the mode became overdamped or if the Q-position of the dip coincided with the superstructure peak. Further experiments are scheduled for the very near future to clarify the superstructure and dynamics of this low-frequency phase of U.

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PHONON SPECTRA IN A15 SUPERCONDUCTING COMPOUNDS

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The A15 superconductors are the most interesting and widely studied of the high- T_c superconducting materials, but there are very few neutron scattering data available, primarily because of small sample sizes (Nb_3Sn) or poor neutron scattering properties (V_3Si). However, sizable samples of Nb_3Sb (very low T_c) have recently become available, and preliminary neutron scattering experiments are very promising with regard to determining the phonon spectra of a "normal" A15 compound for eventual comparison with Nb_3Sn when larger crystals become available.

A large, good crystal of V_3Si has also been obtained, and an extensive search is underway for some type of modulated structure associated with the tetragonal transformation at 20.5 K. (Not all samples transform.) Although the appearance of forbidden reflections has not been observed as they were for Nb_3Sn ,⁵ the possible internal distortions expected in V_3Si may be of a different nature and much more difficult to detect. This difficulty is partly due to the poor coherent

scattering properties of V and partly to its smaller tetragonal distortion ($c/a = 1.0024$ for V_3Si vs $a/c = 1.006$ for Nb_3Sn). The tetragonal distortion was searched for with high collimation ($1/6^\circ\text{S}-1/3^\circ$), but the splittings of the Bragg reflections were too small to be detected readily. However, the expected change in χ_0 , the reference angle, was observed and attributed to the transformation. It is possible that the appearance of forbidden reflections was overshadowed by simultaneous reflections that were observed. The latter could be controlled somewhat by changing the incoming energy E_0 . Remounting the crystal with the $[112]$ direction vertical minimized, but did not eliminate, possible simultaneous reflections. A limited search for an incommensurate lattice was also made, but to no avail.

The determination of the Γ_{12} and Γ_2 optic modes as well as the detection of any low-lying optic modes would be very beneficial in understanding the role the phonons play in the electron-phonon interaction in this crystal. There are indications that high-energy modes (≈ 14 THz) have been observed at 11 K (Fig. 5.26); however, additional studies will be necessary to confirm their existence and their identification. They were not observed in the numerous neutron scattering studies⁶ of polycrystalline A15 compounds, a possible result of the investigators not having extended their measurements to high enough energies. They are substantially higher than the modes observed in Raman scattering measurements of V_3Si by Wipf et al.⁷ A peak has also been observed at 2.1 THz for numerous values of the wave vector, but it is now believed that the peak may be due to some spurious process as yet unidentified.

Fig. 5.26. Possible observance of high-energy (≈ 14 THz) optic modes in V_3Si .

The transverse acoustic modes in the $[110]$ and $[111]$ directions have been readily observed at room temperature. However, at 11 K they are much more difficult to observe, partly because of the Boltzmann factor and partly because of the dramatic softening of some of the modes. It has recently been observed⁸ that the softening of these modes is suppressed in V_3Si single crystals that have been irradiated to very high neutron fluences with a concurrent reduction in T_c from 17.2 to 7.4 K.

1. University of California, San Diego.
2. Catholic University of Nijmegen, Nijmegen, Holland.
3. Argonne National Laboratory, Argonne, Ill.
4. University of Oregon, Eugene.
5. G. Shirane and J. D. Axe, *Phys. Rev. B* 4, 2957 (1971).
6. B. P. Schweiss et al., p. 189 in *Superconductivity in d- and f-Band Metals*, ed. by D. H. Douglass, Plenum, New York, 1976.
7. H. Wipf et al., private communication.
8. D. E. Cox and J. A. Tarvin, *Phys. Rev. B* 18, 22 (1978).

ELECTRON-PHONON INTERACTIONS IN Nb AND Mo: EXPERIMENT

H. G. Smith N. Wakabayashi

The phonon line widths of selected phonons in Nb and Mo have been measured at 10 K by inelastic neutron scattering techniques under conditions of very high energy resolution utilizing good focusing conditions for both transverse and longitudinal phonons. At these low temperatures, the phonon-phonon contributions to the line widths are minimized, and the qualitative features of the electron-phonon contributions are readily observed under favorable conditions. Preliminary results¹ for Nb showed pronounced electron-phonon contributions for the longitudinal $[110]$ phonons as predicted by theory. Limited results for Mo (Fig. 5.27) reveal substantially narrower line widths for these phonons, again in accord with theory.² The theory also predicts an abrupt increase in width for the transverse $[001]$ phonons at $\xi = 0.5$, also verified in these preliminary experiments (Fig. 5.28), although there appears to be some discrepancy in the magnitudes of the calculated and observed line widths. However, the magnitude of line widths extracted from the

Fig. 5.27. Calculated and experimental LA phonon line widths for Nb and Mo in the $[110]$ direction.

experimental measurements is very dependent on the instrumental parameters that have not yet been fully determined.

1. W. H. Butler, H. G. Smith, and N. Wakabayashi, *Phys. Rev. Lett.* 39, 1004 (1977).
2. W. H. Butler, private communication.

Fig. 5.28. Calculated and experimental phonon line widths for Mo in the [100] direction.

ELECTRON-PHONON CONTRIBUTION TO THE PHONON LINE WIDTH IN Nb: THEORY AND EXPERIMENT¹

W. H. Butler² H. G. Smith N. Wakabayashi

Theoretical calculations and experimental measurements of the phonon line width for Nb have been made. The calculations employ the rigid muffin-tin approximation and a realistic band structure. The measurements were done at low temperature to minimize the contributions to the line width from phonon-phonon interactions. The calculations predict and experiments confirm strong electron-phonon coupling for the longitudinal phonon modes in the [110] direction.

1. Summary of paper: *Phys. Rev. Lett.* 39, 1004 (1977).
2. Metals and Ceramics Division, ORNL.

NEUTRON SPECTROSCOPY OF LOW-FREQUENCY PHONONS IN SOLID Hg¹

W. A. Kamitakahara² H. G. Smith N. Wakabayashi

Extensive measurements of the phonon dispersion curves of trigonal Hg have been carried out by neutron inelastic scattering. Some transverse branches of the phonon spectrum have very low frequencies, as small as 0.9 meV at the zone boundary, compared with a maximum lattice frequency of 15 meV. The data have been accurately fitted with an eight-neighbor Born-von Kármán model, and a reliable phonon density of states $F(\omega)$ has been calculated. Comparison with $\alpha^2(\omega)F(\omega)$ derived from tunneling measurements reveals a substantial increase in $\alpha^2(\omega)$ at low frequencies. Direct calculation of $\alpha^2(\omega)F(\omega)$ from the Born-von Kármán model, assuming a simple form for the electron-phonon matrix element, gives $\lambda = 2.0$ compared with $\lambda = 1.6$ from tunneling.

1. Summary of paper: *Ferroelectrics* 16, 111 (1977).
2. Present address: Ames Laboratory and Iowa State University, Ames.

MAGNETIC PROPERTIES

DETERMINATION OF LATTICE DISTORTIONS AROUND IMPURITIES BY THE POLARIZED NEUTRON METHOD¹

J. W. Cable R. E. Parra² H. R. Child

The static lattice distortions around point defects provide important information regarding the interatomic forces in crystals. Such distortions give rise to the diffuse scattering of x rays and neutrons, but this scattering is difficult to measure because the defect concentration must be kept low to ensure randomness and to avoid overlapping distortion effects. For the case of defects due to substitutional impurities in dilute alloys, neutron methods have been used to obtain information on the PbBi , AlCu , and AlMn systems.³ Such measurements are made by taking intensity differences between alloy and pure host samples; they involve the use of sophisticated time-of-flight methods. Here, we show that conventional polarized-neutron diffuse-scattering methods can be used advantageously for such studies. Although limited in scope to those alloy systems for which at least one constituent has a

spin-dependent scattering amplitude, the method is comparatively simple and requires only one sample and a conventional two-axis polarized diffractometer.

At low impurity content, where second-order concentration terms may be neglected, the differential cross section for diffuse scattering from polycrystalline samples is

$$\frac{d\sigma}{d\Omega}(K) = c(1-c)[(f_i - f_h)^2 S(K) - 2f_h(f_i - f_h)D(K)] \quad (1)$$

with

$$S(K) = \sum_j z_j \alpha_j (\sin KR_j) / KR_j \quad (2)$$

$$D(K) = \sum_j z_j (\delta_j / R_j) \{ (\sin KR_j) / KR_j - \cos KR_j \} \quad (3)$$

Here, c is the fractional impurity content, f_i and f_h are the impurity and host scattering amplitudes, the α_j are positional short-range order (SRO) parameters, and the δ_j are radial displacements from the average lattice of an impurity-host atom pair separated by R_j . The Huang scattering is small in the K region under investigation and has therefore been neglected. At the 1 at. % impurity level and with unpolarized neutrons, such cross sections are typically less than 1 millibarn steradian⁻¹ atom⁻¹, but this value can be enhanced, in favorable cases, by using polarized neutrons. In the polarized neutron method, the incident neutrons are polarized parallel and antiparallel to the sample magnetization and perpendicular to the scattering plane. Under these conditions, the amplitudes in Eq. (1) can be replaced by $f = b \pm p$ where b and p are the nuclear and magnetic scattering amplitudes and the $\pm$ sign refers to the spin state of the incident neutron. The difference between the spin-up and spin-down cross sections is then

$$\Delta \frac{d\sigma}{d\Omega}(K) = 4c(1-c) \{ \Delta b \Delta p S(K) - (b_h \Delta p + p_h \Delta b) D(K) \} \quad (4)$$

in which $\Delta b = b_i - b_h$ and $\Delta p = p_i - p_h$ where p is related to the z -component of the atomic magnetic moment by $p = 0.27\mu_B/f(K)$. Here $f(K)$ is the magnetic form factor. Thus, Eq. (4) indicates an enhancement of the lattice distortion scattering for nonmagnetic hosts when $2\Delta p > \Delta b$.

The neutron measurements were made at 4.2 K in an applied field of 40 kG using 1.08-Å neutrons and a flat plate sample of polycrystalline Pd-1 at. % Gd prepared with the isotope ¹⁶⁰Gd to avoid absorption problems. Absolute cross sections were obtained by calibration with a standard V scatterer, and the difference between the spin-up and spin-down cross section is shown in Fig. 5.29.

The pronounced K dependence exhibited here is caused mostly by the lattice distortions. This fact is illustrated in Fig. 5.30, which shows the observed $D(K)$

Fig. 5.29. Difference cross section for Pd-1 at. % Gd at 4.2 K and 40 kG. The horizontal dashed line is the unmodulated level for 5.3 μ_B /Gd, and the solid curve is a least squares fit with five SRO and five displacement parameters.

Fig. 5.30. Comparison of observed and calculated $D(K)$ for Pd-1 at. % Gd. The open data points are for $S(K) = 1$, and the closed data points are for the maximum SRO out to five shells. The solid curve is obtained from Krivoglaz's lattice distortion calculation (ref. 4).

for two extreme $S(K)$ assumptions. The open data points are for a random alloy [$S(K) = 1$], and the closed data points correspond to the maximum SRO [$\alpha_j = -c/(1 - c)$] out to five shells. The actual situation presumably falls in between these extremes that, in any event, produce significant $D(K)$ differences only inside of $K = 0.6 \text{ \AA}^{-1}$. The experimental $f_{\text{Gd}}(K)$ and the fitted Gd moment of $5.3 \mu_B$ ($\mu_{\text{Pd}} \approx 0$) were used to obtain these $D(K)$.

In least-squares-fitting the data in Fig. 5.29 to Eq. (4), we find that both SRO and distortion are required to describe the data and that the best fits are obtained by including both α_j and δ_j out to four or five shells. The ten-parameter fit is shown as the solid curve in Fig. 5.29, and the corresponding parameters are given in Table 5.2.

Table 5.2. SRO and displacement parameters for Pd-1 at. % Gd

j	α_j	$\delta_j (\text{\AA})$	$\delta_j (\text{calculated})^a$
1	0.002	0.052 ± 0.004	0.076
2	-0.003	0.013 ± 0.024	0.027
3	-0.010	0.018 ± 0.006	0.023
4	0.005	0.008 ± 0.019	0.034
5	0.010	0.009 ± 0.007	0.005
	-0.012		

^aThe values in this column were calculated by Krivoglaz (ref. 4).

The negative α_j parameters indicate a preference for unlike neighbors, and the positive δ_j correspond to an expansion of the lattice around the larger Gd atoms. The spherical averaging required for these polycrystalline data smears out any anisotropic displacement effects. Nevertheless, comparison of the radial displacements obtained from this experiment with those calculated for fcc systems by Krivoglaz⁴ is interesting. He expresses the Fourier coefficients of the impurity-associated displacement waves in terms of macroscopic observables and then transforms them to obtain the real-space displacements. The required observables are the elastic constants and the concentration derivative of the average atomic volume. We take the elastic constants for pure Pd at 4.2 K ($C_{11} = 2.3412$, $C_{12} = 1.7614$, and $C_{44} = 0.7117$)⁵ and obtain $\frac{1}{v} \frac{\partial v}{\partial c} = 0.56$ from the lattice constant of pure Pd (3.884 \AA) and of

Pd-5 at. % Gd (3.92 \AA). These constants in Krivoglaz's expression yield the radial displacements given in the last column of Table 5.2. The corresponding $D(K)$ function is shown as the solid curve in Fig. 5.30. This curve has the correct shape, especially for the SRO case, but apparently overestimates the magnitudes of the displacements.

A more direct comparison between theory and experiment is given in Table 5.2 where the calculated δ_j are seen to be consistently higher than the fitted values. This difference is about 50% at δ_1 , which is the best experimental value. Such a discrepancy is perhaps not surprising because the model includes only nearest-neighbor interactions and because we have used the elastic constants for pure Pd and thus do not allow for changes in the host-host force constants caused by the presence of the impurity. Despite these difficulties, the semiquantitative agreement amply demonstrates the validity and potential usefulness of the polarized neutron method for such lattice distortion studies.

1. Summary of paper: *Solid State Communications* (in press).
2. IVIC graduate laboratory participant from the Georgia Institute of Technology, Atlanta.
3. G. Bauer, E. Seitz, and W. Just, *J. Appl. Crystallogr.* 8, 162 (1975).
4. M. A. Krivoglaz, *Phys. Met. Metallogr.* 10, 9 (1960).
5. J. A. Rayne, *Phys. Rev.* 118, 1545 (1960).

LOCAL ENVIRONMENTAL EFFECTS IN DISORDERED ALLOYS¹

J. W. Cable

The magnetic moment of an atom in a ferromagnetic disordered alloy depends on the local environment of that atom. This dependence is particularly true for Ni- and Pd-based alloys for which neutron diffuse scattering measurements of the range and magnitude of the moment disturbances indicate that both magnetic and chemical environments are important in determining the moment distribution. Neutron scattering studies on Ni-based alloys have been interpreted in terms of a phenomenological model that allows a separation of the total moment disturbance at an Ni site into its chemical and magnetic components.

1. Summary of paper: *J. Appl. Phys.* 49, 1527 (1978).

SPIN WAVES IN $\text{Fe}_{1-x}\text{V}_x$

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Substitutional V atoms in the lattice of bcc Fe have magnetic moments that are aligned antiparallel to those of the host Fe atoms. As the V concentration x is increased, the Curie temperature increases linearly for small x and reaches a maximum for $x \approx 0.18$. The moment on V has been determined² to be about $-0.9 \mu_B$, and the V-Fe exchange interaction is estimated to be about five times as large as that between Fe moments. Strong disturbances on the regular array of Fe magnetic moments should be reflected in the spectrum of magnetic excitations. An investigation of the spin waves in the alloy system may yield detailed information about the exchange interactions and, eventually, lead to the understanding of the mechanism for impurity moment formation in itinerant magnetic systems.

Measurements of the spin-wave dispersion curves have been carried out on samples with $x = 0.0, 0.076, 0.083, 0.135, 0.160$, and 0.187 both at HFIR (ORNL) and at JRR2 (JAERI). Spin waves having energies up to about 70 meV have been studied as a function of wave vector q along the $[100]$ direction. Figure 5.31 shows the spin-wave dispersion curves obtained for $x = 0.0$ and 0.076 . Large shifts in the spin-wave energies for the

Fig. 5.31. Spin-wave dispersion curves for pure Fe (Δ) and $\text{Fe}_{0.924}\text{V}_{0.076}$ ($\circ$) in the $[100]$ direction.

alloy exist in the entire range of q covered in the experiment. The results for different x 's are summarized in Fig. 5.32. In this figure, E/q^2 is plotted against q^2 . If the expansion of the energy in q ,

$$E = Dq^2(1 + \beta q^2), \quad (1)$$

is valid, then E/q^2 should be linear in q^2 . However, large deviations from linear behavior were observed for small q in samples with small x . D and β were estimated from the data obtained for the larger values of q and are given in the figure. The D 's thus determined are in very

Fig. 5.32. E/q^2 vs q^2 for alloys with various V concentrations. D can be determined by extrapolating E/q^2 at large q to $q = 0$; β is the slope. Open and filled circles represent the data obtained at ORNL and JAERI respectively.

good agreement with the previous measurement of Lowde et al.³ performed with a different neutron scattering technique.

These results cannot be explained by conventional theories for spin waves in disordered systems. For example, because of the large Fe-V exchange interaction, simple theories based on the Heisenberg Hamiltonian predict a local mode with an energy above the host energy band, which results in very small disturbances in the energies for small values of q . Thus, the large deviation from Eq. (1) observed for the small q region cannot be accounted for by such theories. The change in the electronic band structure due to the impurities seems to be responsible for this deviation as well as for the strong x -dependence of D and β .

1. Osaka University, Osaka, Japan.
2. H. R. Child and J. W. Cable, *Phys. Rev. B* 13, 227 (1976).
3. R. D. Lowde et al., *Phys. Rev. Lett.* 14, 698 (1965).

HIGH-ENERGY MAGNETIC EXCITATIONS IN Ni

H. A. Mook D. Tochetti¹ W. E. Brundage

Band calculations by Cooke and Davis² for the generalized susceptibility of Ni metal showed good agreement with the measured spin-wave spectra. In addition, the calculations predicted a flat, optical spin-wave mode for the [100] direction that should cross the acoustical mode at about 31 THz. If this mode could be found, it would give additional evidence that the band calculations give a good picture of the electronic structure of Ni. The band formalism could then be applied with more confidence to other materials and used to predict their physical properties.

Unfortunately, the experiments are very difficult because high-energy neutrons are required in the experiment to conserve both neutron energy and momentum and to keep the momentum transfer small so that the magnetic form factor is large. Also, the experiment has to be performed with a crystal of Ni highly enriched in ⁶⁰Ni, because normal nickel has a large, incoherent scattering amplitude that would give such a high background that the experiment would be impossible. A large crystal (400 g) of 99.97% ⁶⁰Ni was grown at ORNL by the Czochralski technique. This crystal was then taken to ILL, Grenoble, France, to perform the experiment on the triple-axis spectrometer at the hot neutron source. Incident neutron energies of around 500 meV were used in the experiment. Intense fluxes of

neutrons in this energy range can only be found at the hot source spectrometer at Grenoble. A measuring time of somewhat longer than two weeks was allocated by their Scientific Council.

Measurements of spin waves propagating along the [100] direction are shown in Fig. 5.33. At an energy of

Fig. 5.33. Spin waves in Ni measured along the [100] direction.

27 THz, we see a well-defined spin wave similar to that seen at lower spin-wave energies. As the energy increases, we find extra scattering visible on the low side of the peaks until at 31 THz there appear to be either two peaks or a very broad, flat-topped peak. As the energy increases further, we find a single, narrow, well-defined peak again at 33 THz. Thus, evidence is found for the predicted branch crossing at 31 THz. Figure 5.34 shows a contour plot of the scattering intensity between the energies of 18 and 35 THz. This plot gives a clear picture of $\chi(q, \omega)$ in the neighborhood of the branch crossing. We see that the acoustical spin-wave mode dies out as the branch crossing is approached but that the intensity increases again above the branch crossing. It appears that the optical spin-wave mode itself does not scatter strongly and mainly serves to smear out the intensity in the neighborhood of the crossing. The neutron scattering results thus confirm the predictions of the band calculations. This is a very sensitive test of the calculations because the spin-wave energies are small compared to the band energies, so the bands must be known very accurately to obtain the correct spin-wave results.

1. Institut Laue-Langevin, Grenoble, France.
2. J. F. Cooke and H. L. Davis, *AIP Conf. Proc.* 10, 1218 (1972).

Fig. 5.34. $\chi(q, \omega)$ for Ni for the (100) direction.

NEUTRON SCATTERING STUDIES OF MAGNETIC SUPERCONDUCTORS

H. A. Mook

Materials have recently been produced that are both magnetic and superconducting. There are two main classes of these materials, the RERh_4B_4 compounds and the chevre phase REMo_6S_8 compounds. (RE is a rare-earth element.) We have made some preliminary neutron scattering measurements on both classes of materials to examine both the magnetic and phonon excitations. It has been suggested by some authors that discrete crystal-field excitations can be observed in the chevre phase materials. We have performed experiments on a number of compounds with particular emphasis on TbMo_6S_8 and have found no sign of discrete magnetic excitations. Apparently, the magnetic scattering is highly damped in these materials so that the crystal-field lines are broadened into the elastic scattering. It is not clear what is responsible for the discrete scattering found earlier by other authors, but perhaps it was due

to impurity phases. A few measurements have been performed on the RERh_4B_4 materials to search for crystal-field levels. These materials do appear to have discrete crystal-field excitations at energies of about 1 meV; however, more work is needed to confirm these results.

Phonon density-of-states measurements have been made on a number of REMo_6S_8 and REMo_6Se_8 compounds and on UMo_6S_8 and UMo_6Se_8 . Some of the chevre phase materials have very high critical fields and thus are of immediate interest for use in high-field magnets. The phonon density-of-states measurements show that the RE or U atom in these materials is very loosely bound and vibrates at low frequencies. This characteristic is particularly true in the U compounds. Nevertheless, this appears to have little to do with superconductivity in the materials because the U compounds are not superconducting. Apparently, the low-frequency phonons are not responsible for the superconductivity, and the usual idea of low-frequency modes being favorable for superconductivity does not apply. Further work is underway in an effort to understand what phonon modes are responsible for the superconductivity.

TEMPERATURE DEPENDENCE OF THE INDUCED PARAMAGNETIC FORM FACTOR OF Sm^{3+} IN SmN

R. M. Moon W. C. Kochler

As part of a study of the induced magnetization in mixed-valence materials, we have calculated the temperature dependence of the induced paramagnetic form factor of Sm^{3+} in a variety of crystal fields.¹ A strong temperature dependence was predicted, and this behavior is sufficiently unusual that we decided to seek some experimental verification. Accordingly, we have measured the magnetic form factor of ^{154}SmN at temperatures of 4.3, 18, and 200 K in an applied field of 42.5 kOe.

As shown in Fig. 5.35, the strong temperature dependence is confirmed. The solid lines are fits to the data of the dipole approximation,

$$f(Q) = \langle j_0(Q) \rangle + c_2 \langle j_2(Q) \rangle, \quad (1)$$

where $\langle j_n(Q) \rangle$ is the integral of the product of the $4f$ radial electron density and the spherical Bessel function of order n . These functions were calculated by C. W. Nestor using relativistic Dirac-Fock wave functions. The

Fig. 5.35. The induced magnetic form factor of ^{154}SmN at various temperatures in an applied field of 42.5 kOe.

experimental points were normalized using susceptibility data on our sample of ^{154}SmN by F. Holtzberg of the IBM Thomas J. Watson Research Center. The coefficient c_2 is approximately given by

$$c_2 \cong \frac{\bar{L}_2}{\bar{L}_2 + 2\bar{S}_2}, \quad (2)$$

where $\bar{L}_2$ and $\bar{S}_2$ denote the thermal average of the angular and spin momenta. The very large value observed for c_2 at the lowest temperature implies that, for the ground state, $\langle \chi_G | L_2 | \chi_G \rangle$ is just slightly greater than $-2\langle \chi_G | S_2 | \chi_G \rangle$. In other words, we are close to the interesting situation discussed in ref. 1 where the crystal field produces a doublet ground state with a nearly vanishing magnetic moment. The unusual temperature dependence comes about because there are both Curie contributions and Van Vleck contributions to L_2 and S_2 . The value of c_2 associated with the Curie contribution is large and positive in this case, and that associated with the Van Vleck contribution is approximately -1 . Because the Curie contribution has a $1/T$ temperature dependence, it is dominant at low temperatures, and as

the temperature is raised, the shape of the form factor gradually evolves toward that associated with the temperature-independent Van Vleck contribution.

If Eq. (2) is valid, the form factor measurement is equivalent to a gyromagnetic ratio measurement,

$$g' = \frac{\bar{L}_2 + 2\bar{S}_2}{\bar{L}_2 + \bar{S}_2} = \frac{2}{1 + c_2}. \quad (3)$$

The data of Fig. 5.35 show that g' goes from 0.0058 at 4.3 K to 2.2 at 200 K.

1. R. M. Moon et al., *J. Appl. Phys.* **49**, 2107 (1978).

NEUTRON-DIFFRACTION OBSERVATIONS ON THE $\text{Cu}(\text{Fe})$ KONDO EFFECT

R. W. Tustison¹ C. G. Shull¹ R. M. Moon

We have extended to lower concentration an earlier study² on the induced magnetization surrounding Fe atoms in dilute $\text{Cu}(\text{Fe})$ alloys. The goal of this work is to provide evidence on the existence of a cloud of oppositely polarized conduction electrons surrounding isolated Fe impurities, which is a key prediction of one theory of the Kondo effect. Using the polarized neutron technique, we have observed the average magnetic scattering amplitude for the (111) reflection in an applied field of 42.5 kOe in the temperature range from 1.6 to 19 K. The conduction polarization cloud, if it exists, is thought to be sufficiently extended in real space that it would make a negligible contribution to the scattering amplitude at the (111) reflection. Thus, our neutron measurement is sensitive to only the local 3d magnetization while the bulk magnetization measurement gives the sum of the 3d and conduction contributions. A lack of agreement between the average moment as determined by neutrons and by bulk magnetization measurements would support the idea of the conduction spin compensation cloud.

Because of interaction between the Fe impurities, it is necessary to measure a series of alloys of varying concentration and then to extrapolate the average moment per Fe atom to zero concentration. The earlier work covered a concentration range between 387 and 1007 ppm. The present work extends this range down to 220 ppm.

The recent data support the major conclusion of the earlier study that below 5 K the isolated Fe moment

seen in the neutron measurement is significantly greater than that seen in the magnetization measurement. Bulk magnetization measurements were performed on the same samples used in the neutron experiments to avoid uncertainties caused by sample differences.

Our results support the idea that a spin compensation cloud forms at low temperatures. No evidence for this behavior is found in NMR observations³ of the temperature dependence of the hyperfine field at Cu sites near Fe impurities. Thus, the range of the spin compensation cloud is smaller than the nearest-neighbor distance, but still significantly larger than the 3d electron distribution. A 4s electron distribution would probably satisfy both observations.

1. Massachusetts Institute of Technology, Cambridge.
2. M. H. Dickens et al., *Phys. Rev. Lett.* 35, 595 (1975).
3. J. B. Boyce and C. P. Slichter, *Phys. Rev. Lett.* 32, 61 (1974).

DIAMAGNETIC MOMENT DISTRIBUTION IN Bi

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Pure Bi is a semimetal with an exceptionally high diamagnetic susceptibility of about -300×10^{-6} emu/mole. The calculated atomic susceptibility is only -58×10^{-6} emu/mole, indicating that the outer electron orbits are substantially modified in the crystalline solid. To gain quantitative information on the spatial distribution of the induced diamagnetic moment, we have measured the magnetic form factor of Bi using the polarized neutron technique.

Single crystals were grown, and their reflecting properties were characterized at MIT. The polarized beam experiments were carried out at a temperature of 300 K and an applied field of 42.5 kOe at the HB-1 instrument at the HFIR. Three pillar-shaped crystals, cut with their axes along orthogonal directions, have been studied. Measurements have been obtained on 20 independent Bragg reflections. These are difficult measurements requiring long counting times. For our most sensitive reflection, we must measure an intensity difference of only seven parts in 10^4 .

Converting our scattering amplitudes into values of $\chi(Q)$, our largest susceptibility was observed for the first Bragg peak, $\chi(111) = (67 \pm 7) \times 10^{-6}$ emu/mole. Only this single Bragg peak showed a susceptibility significantly different from that expected using an atomic model.

These data will ultimately be used to construct maps showing the projection of the induced moment along three orthogonal directions. Very roughly, we can anticipate how these maps will appear. At each lattice site, there will be a small atomic-like hump sitting on top of a relatively high plateau, given by the large (000) contribution, which is modulated with a wave vector corresponding to the (111) rhombohedral reflection.

1. Massachusetts Institute of Technology, Cambridge.

TEMPERATURE DEPENDENCE OF THE FIELD-INDUCED MAGNETIC FORM FACTOR OF CeSn₃¹

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C.-K. Loong² R. M. Moon

Polarized neutron scattering techniques have been used to study the spatial distribution and temperature dependence of the magnetization induced in a single crystal of CeSn₃ by a magnetic field of 42.5 kOe. We found that in the 300–40 K temperature range the measured form factor is in good agreement with the free-ion 4f magnetic form factor of Ce³⁺. Below 40 K, large deviations from a 4f magnetic form factor were observed. A satisfactory fit to the data below 40 K can be obtained by assuming that the induced magnetization contains a large component of 5d electronic character of e_g symmetry.

1. Abstract of paper: *Journal of Applied Physics* (submitted).
2. Ames Laboratory and Iowa State University, Ames.

MAGNETIC ORDERING PHENOMENA IN TmS¹

W. C. Koehler R. M. Moon F. Holtzberg²

Neutron diffraction data have been obtained from powder and single crystal specimens of TmS at temperatures ranging from room temperature to 1.7 K and in applied magnetic fields up to 42.8 kOe. In zero field, TmS undergoes a transition at about 8.9 K to an antiferromagnetic structure that is almost the type-2 fcc structure. In this structure there are four G-type or (π , π , π)-type antiferromagnetic sublattices in which the moments are parallel in (111) planes, alternating in sign from one such plane to the next. Superimposed on the

ordering is a sinusoidal modulation with propagation vectors parallel to $[110]$ directions. The structure is multidomain and gives rise to a very complex diffraction pattern. With polarization analysis, it is possible to determine the moment directions in the domains. For example, in domains with propagation vector parallel to $[1\bar{1}0]$ the moments are parallel to $[11\bar{2}]$. From powder data taken at 1.7 K the maximum value of the Tm moment was estimated to be $4.0 \mu_B$. Diffuse streaks of magnetic origin with temperature and field dependence different from that of the satellites were observed, which may influence our estimate of the magnitude of the ordered moment. The response of the magnetic reflections to applied magnetic fields can be understood, in part, in terms of domain repopulation.

1. Summary of paper: *Journal of Applied Physics* (submitted).

2. IBM Thomas J. Watson Research Center, Yorktown Heights, N.Y.

INDUCED MAGNETIC FORM FACTOR OF $\text{Ce}_{0.736}\text{Th}_{0.264}$ ¹

R. M. Moon W. C. Koehler

The $\gamma \rightarrow \alpha$ phase transition in pure Ce is characterized by a decrease in the lattice constant by about 6% and an apparent change in the Ce valence from 3.0 to 3.67.² Thus, α -Ce is a mixed-valence material in which an electron is believed to fluctuate between the 4f and conduction bands. A similar transition, but with a smaller change in lattice constant, is found in $\text{Ce}_{1-x}\text{Th}_x$ alloys. In an effort to detect a change in the shape of the induced magnetic moment distribution, we have performed elastic polarized beam measurements in both the γ and α phases of polycrystalline $\text{Ce}_{0.736}\text{Th}_{0.264}$. Using the same sample, Shapiro et al.³ found that the inelastic magnetic scattering has a Ce^{3+} form factor in the γ phase, but the intensity was insufficient to establish a form factor for the α phase. The diffuse scattering cross section roughly follows the Ce^{3+} form factor in both phases.⁴

Our measurements were performed in an applied field of 42.5 kOe at temperatures of 180 and 50 K. The transition temperature for this alloy is 150 K. We corrected the data for the diamagnetic contribution for the core electrons in both Ce and Th and expressed the results in terms of a susceptibility per mole of Ce. The resulting $\chi(Q)$ is displayed in Fig. 5.36.

Consider first the 180 K data (γ phase). The solid line represents a fit to the neutron data of the relativistic 4f

Fig. 5.36. $\chi(Q)$ for $\text{Ce}_{0.736}\text{Th}_{0.264}$ in the γ (180 K) phase and in the α (50 K) phase. The solid lines are fitted to the data for $(\sin \theta)/\lambda \neq 0$ using the Ce^{3+} form factor.

form factor for Ce^{3+} . The fit is satisfactory, and the scale factor gives a static susceptibility of $(23.1 \pm 0.6) \times 10^{-4}$ emu per mole of Ce, which is in excellent agreement with the bulk susceptibility data of ref. 3, shown as the data point at $(\sin \theta)/\lambda = 0$. These data give additional weight to the conclusion that in the γ phase Ce behaves like a +3 ion. The good agreement with the measured bulk susceptibility is somewhat surprising because in neutron measurements on pure γ -Ce, Stassis et al.⁵ found a 4f susceptibility that was 12–19% below the measured bulk susceptibility. They attributed this difference to a positive conduction electron polarization, which appears to be absent in this alloy.

The situation is quite different at 50 K (α phase). A very unsatisfactory fit is obtained with the Ce^{3+} form factor (5-point fit). The lower solid line, obtained by fitting the free-ion form factor to the outer three points, suggests that the susceptibility may have two components, one 4f-like and the other more diffuse in real space. However, these α -phase data cannot be interpreted unambiguously. The departure from the free-ion form factor could be due to (1) a change in the Ce 4f electronic wave functions, (2) a contribution from localized electrons at the Th sites, or (3) a contribution from the conduction electrons. We hope that single crystals of this material become available so that more precise measurements of the induced form factor can be performed.

1. Summary of paper: *Journal of Applied Physics* (submitted).

2. K. A. Gschneidner, Jr., and R. Smoluchowski, *J. Less-Common Met.* 5, 324 (1969).

3. S. M. Shapiro et al., *Phys. Rev. B* **16**, 2225 (1977).
4. A. S. Edelstein, H. R. Child, and C. Tranchita, *Phys. Rev. Lett.* **36**, 1332 (1976).
5. C. Stassis et al., *J. Appl. Phys.* **49**, 2113 (1978).

INDUCED MAGNETIC MOMENT DISTRIBUTION IN Zr

C. Stassis¹ W. C. Koehler
G. R. Kline¹ R. M. Moon

As part of a continuing study of the induced magnetization of the paramagnetic transition metals, polarized

neutron work has been initiated on the magnetic form factor of Zr in an applied field of 42.5 kOe. Zirconium has the hcp structure with a large anisotropy in the bulk magnetic susceptibility due to a significant orbital contribution. So far our work has been largely confined to a study of the induced magnetization with H applied perpendicular to the c -axis, but we intend to extend the study to include the case where H is along the c -axis.

1. Ames Laboratory and Iowa State University, Ames.

6. Crystal Growth and Characterization

The primary purposes of the Crystal Growth and Characterization Program are to prepare and to characterize high-quality research specimens (e.g., single crystals, alloys, wire, and foils) of materials pertinent to energy-related research efforts within the Solid State Division and elsewhere, to collaborate with members of the Solid State Division on the resolution of general materials problems as they relate to the advancement of DOE research objectives, and to develop new techniques for the preparation of materials having the potential for future applications in advanced energy systems. The viability of many of the currently proposed energy conversion or production approaches rests strongly on the resolution of materials problems as does the ability to realize increased efficiency from essentially all of the present energy systems. The overall goal of the crystal growth and characterization effort is to contribute to the resolution of some of these materials problems in certain selected areas. The materials of current interest include superconducting alloys and compounds with high critical temperatures (e.g., A15 compounds), fast-ion conductors (e.g., β' -alumina, cubic ZrO_2 , and Li_3N), high-temperature materials (e.g., WC and other carbides and nitrides, MgO , Y_2O_3 , and other refractory oxides), materials for use as electrodes in photoelectrochemical cells (e.g., $KTaO_3$), and photovoltaics as fabricated by rapid processing techniques (e.g., sheet growth of Si). Additionally, a significant effort is currently being directed toward the preparation of high-purity single crystals of stainless steel because of the wide-range technological importance of this material. Many of the single crystals (and other forms of research materials) that are prepared as a result of this effort are the subject of investigations not only by scientists in other divisions of ORNL but in research establishments throughout the world.

The efforts of the crystal growth and characterization group during the reporting period have included the growth of approximately 150 crystals of various types, the arc or induction casting of more than 60 samples, and about 24 annealing runs on different metals and alloys.

The Research Materials Information Center provides a valuable service to materials science in general and in particular to the Solid State Division by maintaining an up-to-date compilation and data base pertaining to the crystal growth, purification, characterization, and availability of research materials. The activities of the center include the publication of directories of crystal growth and solid state materials research, the publication (via Plenum Press) of bibliographies, and the establishment of computerized data bases (e.g., a data base of crystal growth documents covering 5100 references has recently been compiled).

CRYSTAL GROWTH AND CHARACTERIZATION PROGRAM

L. A. Boatner W. E. Brundage
Y. K. Chang H. E. Harmon

The various activities of the crystal growth and characterization group result in the production of a wide variety of research-quality samples whose properties are of interest not only to researchers within the Solid State Division but to scientists in other ORNL divisions, other DOE-supported laboratories, and other research organizations in general. The methods of materials preparation include arc-casting in a high-purity inert atmosphere, induction casting or annealing in a silver boat, zone-refining by the EBFZ technique, grain-growth annealing, induction-heating annealing, quenching in an inert atmosphere, the forming of rod or thin foil forms for basic research purposes, arc-fusion growth of oxides, flux growth, Bridgman growth, etc. Extensive sample characterization is required throughout the preparation

of these materials, and the corresponding characterization techniques include a wide variety of standard and some fairly unique methods.

More than 100 different metals, oxides, alloys, and compounds have been arc-cast, purified, grown into single crystals, and/or annealed for studies involving superconductivity, neutron diffraction, ion channeling, hydrogen diffusion, radiation damage, fracture, ionic conductivity, and ferroelectricity.

To realize the maximum utilization of these often unique specimens, a continuing policy of loaning samples to cooperating research groups for supplementary physical property measurements is maintained. Measurements made on these samples often complement the research efforts of Solid State Division members and, in particular, investigations made by workers in foreign research institutions serve as a means of enhancing exchanges of technical information. Representative examples of some of the research specimens and their utilization are provided in Table 6.1.

Table 6.1. Loan of samples for research outside the Research Materials Program

Material	Type of study	To whom sent	Organization
Nb	Superconductivity	D. Christen R. Kerchner	ORNL
Nb	Nitride precipitation	D. Christen	ORNL
Nb	Ion channeling	B. Appleton	ORNL
Nb	Flux flow resistance	R. Kerchner	ORNL
Nb + 5 at. % Zr	Superconductivity	R. Kerchner	ORNL
Nb + 5 at. % Mo	Superconductivity	R. Kerchner	ORNL
Nb + 10 at. % Mo	Superconductivity	R. Kerchner	ORNL
Nb + 5.4 wt % Mo	Radiation effects	R. Kerchner	ORNL
Nb + 10 at. % Ta	Flux pinning	D. Christen	ORNL
Nb + 15 at. % Ta	Hydrogen diffusion	M. Pick	Brookhaven
Nb + 10 at. % Ta	Superconductivity	R. Kerchner	ORNL
Th + 10 at. % Y	Neutron scattering	H. Mook	ORNL
Zr + 40 at. % Hf	Superconductivity	S. Sekula	ORNL
Mo	Fracture	M. Ohr	ORNL
Mo	Crystal perfection	R. Carpenter	ORNL
Ta	Superconductivity	D. Christen	ORNL
Ta	Photoemission	T. Shaw	Brookhaven
Ti	Resistivity	K. Farrell	ORNL
V	Superconductivity	S. Sekula	ORNL
W	Fracture	S. Kobayashi	ORNL
Ti, Au	Fermi surface	A. Arko	Argonne
MgO	Substrate for epitaxial growth	K. Yagi	Arizona State University
MgO	Oxygen diffusion	Y. Oishi	Kyushu University
MgO	Optical studies	W. Sibley	Oklahoma State University
MgO	Electron microscopy	C. Sun	Cornell University
MgO	Chemical characterization	N. Quinn	W&C Spicer Ltd.
MgO	Positron annihilation	W. Mallard	Georgia State University

Table 6.1(continued)

Material	Type of study	To whom sent	Organization
MgO	Positron annihilation	E. Vance	Georgia State University
MgO	Ion implantation	G. Chassagne	University of Lyon
MgO	Electron paramagnetic resonance	M. Aegerter	University of Neuchâtel
MgO	Radiation damage	R. Murray	University of Delaware
MgO	Dislocation dynamics	R. Clifton	Brown University
MgO	Radiation dosimetry	V. Balla	Canadian Department of Health and Welfare
MgO	Mechanical properties	J. Routbort	Argonne
MgO	Microstructure	M. Reichtin	Argonne
MgO	Ion implantation	G. Krefft	Sandia
MgO	EBR II irradiations	F. Clinard	Los Alamos
MgO	Electron microscopy	R. Barnard	Case Western Reserve University
MgO	Optical studies	W. Yen	University of Wisconsin
MgO	Optical studies	J. Williams	Wake Forest University
MgO:Li	Thermal conductivity	H. Weinstock	Illinois Institute of Technology
MgO:Li	Thermal depolarization	J. Crawford, Jr.	University of North Carolina
MgO:Li	Electron paramagnetic resonance	H. Tohver	University of Alabama
MgO:Li	Tunable laser host	A. Mooradian	Lincoln Laboratories
MgO:Li	Thermal diffusivity	D. Hasselman	Virginia Polytechnic Institute
MgO:Li	Light scattering	W. Unruh	Kansas University
MgO:Li	Scanning electron microscopy	W. Kingery	Massachusetts Institute of Technology
MgO:Li	Electrical conductivity	E. Sonder R. Weeks	ORNL
MgO:Ni	Tunable laser host	A. Mooradian	Lincoln Laboratories
MgO:Ni	Light scattering	W. Unruh	Kansas University
MgO:Ni	Phonon experiments	E. Hahn	University of California, Berkeley
MgO:Ni	Electrical conductivity	E. Sonder	ORNL
MgO:Mg	Tunable laser host	P. Moulton	Lincoln Laboratories
CaO:Ca	Optical studies	B. Evans	Naval Research Labs.
CaO:Ca	Fluorescence	G. Summers	Oklahoma State University
SrO	Fluorescence	G. Summers	Oklahoma State University
KTaO ₃ -Cu	Thermal conductivity	A.-M. de Gøer	Center of Nuclear Studies, Grenoble
KTaO ₃	Ferroelectricity	U. Höchli	IBM Research Laboratory, Zurich
KTaO ₃	Photoconductivity	J. Hodby	Oxford University
KTaO ₃	Raman scattering	L. Chase	Indiana University
KTaO ₃	Superconductivity	J. Thompson	University of Tennessee
KTaO ₃	Photoelectrochemical cells	F. Modine	ORNL
KTaO ₃	Raman scattering	J. Bates	ORNL
KTaO ₃	Electron paramagnetic resonance	D. Olson	St. Olaf's College, Northfield, Minnesota
KTa _{1-x} Nb _x O ₃	Quantum ferroelectricity	U. Höchli	IBM Research Laboratory, Zurich
KTa _{1-x} Nb _x O ₃	Photorefractive effects	E. Krätzig	Philips Research Laboratories, Hamburg

Table 6.1 (continued)

Material	Type of study	To whom sent	Organization
$\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$	Thermal conductivity	A.-M. de G��r	Center of Nuclear Studies, Grenoble
$\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$	Raman scattering	L. Chase	Indiana University
$\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$	Infrared reflectivity	J. Bates	ORNL
$\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$	Neutron scattering	H. Mook	ORNL
$\text{K}_{1-x}\text{Na}_x\text{TaO}_3$	Quantum ferroelectricity	U. H��chli	IBM Research Laboratory, Zurich
$\text{K}_{1-x}\text{Li}_x\text{TaO}_3$	Dielectric effects	U. H��chli	IBM Research Laboratory, Zurich
$\text{K}_{1-x}\text{Li}_x\text{TaO}_3$	Raman scattering	L. Chase	Indiana University
GaAs	Photovoltaic study	R. Young	ORNL
GaAs	Electron microscopy	J. Narayan	ORNL
Y_2O_3	Electrical conductivity	E. Sonder R. Weeks	ORNL
Y_2O_3	Electron paramagnetic resonance	M. Abraham	ORNL
Y_2O_3	Optical absorption	Y. Chen	ORNL
Y_2O_3	Electron nuclear double resonance	H. Stapleton	University of Illinois
SrCl_2	Electron paramagnetic resonance	J. Boldu	UNAM, Mexico
Ferrite crystals	Plastic behavior	P. Veysiere	Laboratory de Metallurgie Poitiers, France
Ni	X-ray	B. Larson	ORNL
^{60}Ni (400 g crystal)	Neutron diffraction	H. Mook	ORNL
$\beta''\text{-Al}_2\text{O}_3$ crystals	Raman scattering	J. Bates	ORNL
Fe-Ni-Cr (70-15-15%)	Radiation damage	A. Marwick	Harwell, England
Fe-Ni-Cr (65-20-15%)	Fracture studies	M. Ohr	ORNL
Fe-Ni-Cr (65-20-15%)	Creep	T. Riley	ORNL

CRYSTAL GROWTH OF REFRACTORY METALS AND ALLOYS BY THE EBFZ TECHNIQUE

Y. K. Chang H. E. Harmon

Single crystals of refractory metals and alloys that are of interest either due to their superconducting properties or their ability to absorb H_2 have been prepared by the EBFZ technique.

Both unseeded and [100] seeded Ta single crystals of 9 mm diam were produced with two float-zone passes at 2.5 cm/hr in a dynamic vacuum of at least 2×10^{-6} torr. A sphere was shaped from the unseeded crystal and then annealed at 2300C in an O_2 pressure of 1×10^{-5} torr for 3 hr. This treatment was followed by an anneal at 2400C for 7 hr under a vacuum of 2.8×10^{-8} torr to remove both the C impurities and any

damage due to shaping which could have deleterious effects on superconducting flux-pinning measurements. Slices were also prepared from the [100] seeded crystal for a photoemission study of Ta and Ta-H.

A number of Mo single crystals of about 5.5 mm diam and 10 to 12 cm long have been grown by making float-zone passes on five 3-mm Mo rods that were bound together with Ta wires. The initial zone pass was carried out in a partial O_2 atmosphere and then followed by a pass under vacuum at a slower rate (7 cm/hr). An O_2 treatment was used to reduce the C content. These crystals were employed as tensile specimens in fracture studies using TEM.

A 13.5-cm-long single crystal of Nb + 15 at. % Ta was successfully prepared by the EBFZ method using two float-zone passes at 5 cm/hr under vacuum. Specimens were sliced from the resulting single crystal and were

then used in the study of elastic constants and precipitation morphology. Single crystals of Nb and Pt were also successfully prepared by the EBFZ method. Most of these specimens were used in superconductivity investigations.

EBFZ GROWTH OF A15 COMPOUNDS

Y. K. Chang and H. E. Harmon

Many A15 compounds are superconductors, which are characterized by high superconducting transition temperatures. Progress in fundamental investigations of these potentially important materials has been limited, however, by the availability of research-quality single crystals. The growth of these materials is notoriously difficult, and only a few of these compounds have been successfully prepared. The EBFZ method has been applied to the growth of crystals of some A15 compounds. Due to the brittleness of these materials, we have experienced spontaneous shattering of the material during cooling in the arc melter. Therefore, a water-cooled "silver boat" system powered by an rf coil was designed and constructed. All of the A15 compounds we have investigated to this point were prepared in this system. The cast rods were melted and crushed several times to ensure thorough mixing. Because the EBFZ technique only operates under vacuum, serious constraints are placed on the materials that can be prepared by this method. With these constraints in mind, we have chosen the compounds Ti_3Au , Ti_3Pt , Nb_3Au , and V_3Si for the initial crystal growth attempts.

A good single crystal of Ti_3Au (3.8 mm diam) had been prepared near the end of the last reporting period. Since that time, another and significantly larger crystal (7 mm diam) has been grown. Preliminary experiments on the crystal growth of Ti_3Pt have yielded large grains with large mosaic spreads. Instead of smooth surfaces, striations have been observed over the entire surface of the zoned rods. Such striations are generally ascribed to temperature oscillations in the molten zone; in this case it is inferred that the oscillation periods were about 30 sec and 0.5 sec. In general, this type of oscillation may

arise from either a temperature or concentration gradient in the melt. From the results of systematic experiments it was found that the oscillation had no connection with the concentration gradient and no apparent link with the temperature gradient. This observation leads to the conjecture that there may be a discontinuity in the physical properties of this material near its melting point. Preliminary results on V_3Si and results on Ti_3Au and Ti_3Pt indicated that the stability of the power supply played an important role in the crystal growth of these A15 compounds, and the system is currently being improved. The Au in Nb_3Au is highly volatile near the melting point of Nb_3Au , and this eliminates the possibility of growing Nb_3Au in the conventional way using the EBFZ method. We have encased the cast substance in an Nb tube and sealed it by melting an Nb plug at the open end of the tube under vacuum in the EBFZ system. A number of hot zone passes were then made; however, the preliminary results indicate that zone passes at higher temperatures and a shorter zone pass duration may be needed because of a slow alloying of Nb_3Au with the Nb tube.

GROWTH OF SINGLE-CRYSTAL ^{60}Ni

W. E. Brundage

A 400-g single crystal of the isotope ^{60}Ni has been grown for neutron diffraction studies of magnetic excitation spectra at high energies. The investigations were subsequently performed, using the hot-source spectrometer at the Centre d'Etudes Nucléaires de Grenoble. The crystal was grown by the Czochralski method using a quartz-lined graphite crucible with a cover gas of 4% H_2 in Ar. Because of the expensive nature of the material, special precautions were taken to prevent its contamination or loss, and all of the available material was incorporated into the crystal. As can be seen in Fig. 6.1, the crystal was pulled in such a manner as to maintain an approximately spherical configuration so that the maximum sample volume could be positioned in the neutron beam.

Fig. 6.1. Single crystal of the isotope ^{60}Ni weighing approximately 400 g.

GROWTH OF AUSTENITIC STAINLESS STEEL AND RELATED PURE TERNARY ALLOYS

W. E. Brundage Y. K. Chang
H. E. Harmon L. A. Boatner

The projected use of stainless steel in breeder and fusion reactors has resulted in demands for austenitic stainless steel single crystals for a variety of fundamental investigations. Although type-304, -316, and -321 stainless steels exhibit an unacceptably high radiation-induced swelling, some studies^{1,2} have demonstrated the existence of a low-swelling Fe-Ni-Cr alloy. It was found that the swelling decreases markedly with increasing Ni content, dropping by a factor of more than 100 in going from 15 wt % Ni to 35 wt % Ni with the Cr content fixed at 15 wt %. We decided initially to grow crystals of a pure ternary Fe-Ni-Cr (65-20-15%) alloy because, although this composition is close to that of type-316 steel, the higher Ni content ensures that the γ phase will be obtained. Because of the volatile nature of the Cr component near the melting temperature, the possibility of preparing this material in an EBF system was ruled out. Therefore, we have attempted to grow stainless steel crystals by a number of techniques including Czochralski growth, float-zone leveling, horizontal boat growth, and grain growth. The initial attempts at grain growth were not successful, due to oxidation problems. Horizontal boat zone growth was attempted in a Au-plated Cu boat that

was slowly pulled through an rf coil. A number of crucible materials were tested, but thus far the most promising results using the boat growth technique were 2–3 cm grains that were obtained using alumina crucibles. Our best results in the growth of pure ternary Fe-Ni-Cr alloys have been obtained via the Czochralski technique, and large single crystals of the alloy Fe-Ni-Cr (65-20-15%) have been produced. An example of one of these specimens is shown in Fig. 6.2. This crystal was pulled in an NRC crystal growth unit employing graphite resistance-heating elements. One advantage of the Czochralski technique in the growth of stainless-steel-related ternary alloys lies in the ability to control the crystal configuration, and it has been possible to grow long, thin (240 mm $\times$ 3.5 mm) single crystals of Fe-Ni-Cr (65-20-15%) for use in investigations of radiation-induced creep.

Fig. 6.2. Czochralski-grown crystal of stainless steel (65% Fe, 20% Ni, 15% Cr).

The vertical rf induction-heated float-zone technique has also been employed successfully in growing single crystals of Fe-Ni-Cr alloys. A slightly reducing atmosphere was used and float-zoned single crystals 6 mm in diameter and approximately 75 mm long were produced. This technique will now be extended to the float-zone growth of larger-diameter single crystals.

1. J. A. Hudson, D. J. Mazey, and R. S. Nelson, p. 213 in *Proceedings of British Nuclear Engineering Society Conference on Voids Formed by Irradiation of Reactor Materials*, ed. by S. F. Pugh, M. K. Lorreto, and D. I. R. Norris, British Nuclear Engineering Society, London, 1971.

2. W. G. Johnston et al., *J. Nucl. Mater.* 54, 24 (1974).

NEW METHOD OF PREPARATION OF Ni-Ni₃B EUTECTIC BY UNIDIRECTIONAL SOLIDIFICATION

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L. A. Boatner C. F. Yen¹

Eutectic alloys formed by interstitial compounds in a metal matrix frequently exhibit the hardness of the interstitial compounds but not their brittleness. A new technique for preparing such a system by unidirectional solidification has been successfully developed. About 300 g of Ni was melted in a 3.1-cm-diam boron nitride tube by heating with an rf induction coil in an Ar + 4% H₂ atmosphere. The crucible and charge were lowered through the induction coil at a rate of 1.3 cm/hr. The Ni gradually reacted with the B contained in the boron

nitride tube with the N being released as bubbles at the top of the melt. The microstructure of the Ni-Ni₃B eutectic is shown in Fig. 6.3 where metallographic specimens have been cut with planes normal and parallel to the direction of solidification. The surfaces of these samples were mechanically polished with 0.3 μ Al₂O₃ powder and then etched for 1 min in a solution consisting of 35 ml acetic acid, 15 ml HNO₃, and a few drops of HCl. The inclusions have been identified by x-ray powder diffraction as Ni₃B which is reported to be orthorhombic² and isostructural with cemetite, Fe₃C.

1. Metals and Ceramics Division, ORNL.
2. S. Rundqvist, *Acta Chem. Scand.* 12, 658 (1958).

Fig. 6.3. Photomicrographs of Ni-Ni₃B alloy for surfaces parallel to (left) and normal to (right) the direction of a solidification.

A dHvA-EFFECT STUDY OF DISLOCATION LOOPS IN Cu

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F. W. Young, Jr. R. J. Higgins²

The anisotropy of conduction electron scattering due to dislocation loops in Cu single crystals irradiated with neutron doses up to 2×10^{18} neutrons/cm² has been

studied by measuring the dHvA Dingle temperatures for a large number of orbits. It was found that the anisotropy was a characteristic of the defects and did not depend on the neutron dose. The scattering rate from the neck region was the strongest and several times stronger than that from any other orbit. For example, the scattering rate ratio of the [111] neck to belly was about 5.5 ± 0.2 , independent of the neutron dose. The

dHvA scattering rate scaled with the sample resistivity by a factor of 3 to 7, depending on the orbit.

1. Argonne National Laboratory, Argonne, Ill.
2. University of Oregon, Eugene.

ARC FUSION GROWTH OF Y_2O_3 SINGLE CRYSTALS

L. A. Boatner M. M. Abraham Y. Chen

The arc fusion technique that has been employed previously in the growth of large, clear single crystals of MgO, CaO, and SrO has been successfully applied to the production of Y_2O_3 single crystals.

Crystals of Y_2O_3 with markedly different characteristics have been grown by using two different growth configurations. When the carbon electrodes were completely immersed in the Y_2O_3 powder and came in direct contact with the molten oxide, the resulting crystals were black in color and nominally $1.5 \times 1.5 \times 1.5$ cm. Three samples that were cut from these crystals for use in high-temperature electrical conductivity measurements are shown in Fig. 6.4. This material is apparently nonstoichiometric, and an examination using EPR revealed the presence of at least two different defect centers in the region of $g = 2$. The observed EPR spectra exhibited a resolved superhyperfine structure, and ENDOR examination indicated that this structure was caused by coupling to Y nuclei.

ORNL-PHOTO 1410-78

Fig. 6.4. Three single crystals of Y_2O_3 cut from material grown with the carbon electrodes in direct contact with the molten oxide.

When the C electrodes were positioned in a non-contact configuration above the Y_2O_3 melt, the resulting crystals were somewhat smaller than those described above but were optically transparent with a slight yellow coloration. The EPR defect-center spectra found for the black crystals were not observed in the clear yellow specimens. Instead, an intense spectrum due to Fe^{3+} was identified. Conversely, this Fe^{3+} spectrum was not observed in the black samples. Both types of material are currently the subject of extended investigations using a variety of techniques.

THE STATIC, QUASI-STATIC, AND QUASI-DYNAMIC J-T EFFECT IN THE EPR SPECTRA OF Ag^{2+} in SrO, CaO, and MgO¹

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R. W. Reynolds² M. M. Abraham

The EPR spectra observed for Ag^{2+} in the alkaline-earth-oxide host crystals SrO, CaO, and MgO provide an exceptionally clear example of the unusual spectral features associated with the transition from a static to a dynamic J-T effect at low temperature. The spectrum observed for Ag^{2+} in SrO exhibits the low-temperature, threefold tetragonal symmetry with symmetric line shapes and averaging at higher temperatures (80 to 200 K) that characterize the static J-T effect. A threefold tetragonally symmetric spectrum is also observed for Ag^{2+} in CaO at 1.3 K, but in this case the line shapes are not symmetric and resemble those observed for systems exhibiting a dynamic J-T effect. Additionally, a complex line shape is observed at 1.3 K for Ag^{2+} in CaO with the orientation $H \parallel [111]$. These line-shape effects are due to a value of the ratio of random strain splitting δ to "tunneling" splitting 3Γ , which is intermediate to those effects associated with either the static or dynamic J-T effect. The complex line shapes observed at 9 GHz with $H \parallel [111]$ have been computed by performing a numerical diagonalization of the matrix of strain and tunneling for the manifold of states consisting of the ground 2E and first excited A_2 vibronic singlet levels. The results of this calculation are shown in Fig. 6.5. From this calculation a value of 1.2 has been determined for the ratio $\delta/3\Gamma$. At a frequency of 23 GHz, the line shapes for Ag^{2+} in CaO exhibit additional effects due to the increased Zeeman interaction, and, by performing a simultaneous diagonalization of the strain, tunneling, and Zeeman matrices, it is possible to independently determine values of 4.7 cm^{-1} and 3.9 cm^{-1} for δ and 3Γ respectively. For Ag^{2+} in MgO, the angular variation of the EPR spectrum at 1.3 K resembles the

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Fig. 6.5. Line shapes typical of the intermediate Jahn-Teller effect. Top: The experimental X-band line shapes of Ag^{2+} in a CaO single crystal shown in the first derivative of absorption form. The applied magnetic field is parallel to the [111] direction. Middle: The first derivative line shapes computed using a value for $\delta/3\Gamma$ of 1.2. The groups of hyperfine lines are separated by the q -value in Gauss. The magnetic field scale is larger than that shown for the experimentally determined line shapes. Bottom: The calculated absorption line shapes whose first derivatives are shown directly above are presented. Both the absorption line shapes and their corresponding first derivatives were computed by a repetitive diagonalization of the matrix of strain and tunneling appropriate to the A_1 , E_{2g} , $E_{g\sigma}$ manifold of states.

type of variation typical of a dynamic J-T system but with one component shifted and broadened by coupling via random strain to a nearby excited A_2 vibronic singlet level. The spectrum obtained at 1.3 K with the applied magnetic field parallel to a [111] direction is shown in Fig. 6.6 where it is apparent that the strong line-shape effects found for the $\text{CaO}:\text{Ag}^{2+}$ system are not in evidence. A value of $\delta/3\Gamma = 0.13$ was determined for Ag^{2+} in MgO by fitting the observed angular variation to a computed angular variation derived from a numerical diagonalization of the matrix of strain and

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Fig. 6.6. The EPR spectrum observed for Ag^{2+} in MgO at $T = 1.3$ K with the applied magnetic field oriented parallel to the [111] direction. At this orientation, the line shapes are similar to those observed for Ag^{2+} in SrO.

tunneling for the ${}^2E-A_2$ manifold. These observed features classify the J-T effect as static, quasi-static, and quasi-dynamic for Ag^{2+} in SrO, CaO, and MgO respectively.

1. Summary of paper: *Phys. Rev. B* 16, 86 (1977).
2. General Research Corporation, Huntsville, Ala.

EPR FROM ACTINIDE ELEMENTS¹

L. A. Boatner M. M. Abraham

Investigations of actinide ions using EPR techniques have resulted in the acquisition of new information pertinent to the electronic and nuclear properties of these synthetically produced elements and their ions. The special experimental problems and concomitant techniques which have been employed in acquiring this new information were reviewed¹ along with more general information regarding those aspects of actinide science that were applicable to disciplines other than electron resonance. The technique of EPR was introduced, and the type of information that can be obtained using EPR techniques was discussed. The terminology particular to research involving the actinides was treated along with the history of the discovery of various actinide elements and the factors affecting their availability.

Complex experimental problems that arise when dealing with actinide ions were summarized, and topics such as the production and separation of radionuclides and containment and handling of actinide-doped single crystals were also discussed. The aspects of crystal field theory pertinent to the actinides were included, and topics such as hyperfine interactions, core polarization, and pseudonuclear g factors were treated. The available EPR results for actinide ions were reviewed with an emphasis on comparisons between these results and those obtained for the rare-earth analogs. The experimental results were tabulated according to the electronic configuration of the various ions. Problems that remain unresolved were presented and suggestions for possible future experiments considered.

1. Summary of review article: *Rep. Prog. Phys.* 41, 87 (1978).

LOCAL POLARIZABILITY OF QUANTUM PARAELECTRICS AND QUANTUM FERROELECTRICS¹

L. A. Boatner U. T. Höchli²

The ability of ferroelectrics to store a homogeneous polarization for an indefinite period of time is now well established. In addition to the homogeneous permanent polarization that may be induced in the ferroelectric phase, an additional polarization residing in a narrow surface layer has also been shown to be present in the paraelectric phase. Switching of this "surface polarization" has so far not been feasible, however. This surface layer consists of a charge which resides within a Debye length of the surface and which is stabilized by an enhanced electron affinity with respect to the surroundings (metal, vacuum). We have shown that it is possible to generate surface polarization not only in incipient ferroelectrics but also in the paraelectric phase of ferroelectrics whose Curie point is in the cryogenic region (i.e., in quantum ferroelectrics). Acoustic flexure resonance and local optical birefringence measurements show that in $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$, polarization can be induced locally in a surface layer and can be stored indefinitely at 4 K.

1. Summary of paper: *Ferroelectrics* 18, 223 (1978).
2. IBM Research Laboratory, Zurich, Switzerland.

QUANTUM LIMIT OF FERROELECTRIC PHASE TRANSITIONS IN $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ ¹

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Almost all of the previous experimental results pertinent to displacive phase transitions have been characterized by the absence of discernible quantum-mechanical effects. Recent theoretical work, however, has indicated that at or near the so-called "displacive limit," quantum-mechanical effects can become extremely important. This "displacive limit" is defined by the set of coupling parameters for which the critical temperature T_c of the phase transition becomes equal to zero. If T_c of a sample is in the region of zero-point lattice motion, the disordered phase may extend below its classical limit, and the quantum-mechanical T_c will be lower than the classical T_c because of the effects of zero-point motion. Dielectric and elastic constants of $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ have been measured as a function of x and of the temperature. For $x = 8 \times 10^{-3}$, the system exhibits the characteristics of a ferroelectric at the displacive limit (i.e., a "quantum ferroelectric") as evidenced by three critical indices and the temperature independence of all responses near $T = 0$.

1. Summary of paper: *Phys. Rev. Lett.* 39, 1158 (1977).
2. IBM Research Laboratory, Zurich, Switzerland.

PHOTOELECTROLYSIS OF WATER USING KTaO_3

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Through the use of devices called "photoelectrochemical cells," it is possible to convert optical energy into either a chemical or electrical form. By irradiating one or both of the electrodes in such a cell, current flow requiring a redox reaction may be induced, and this reaction can, in turn, be used to produce electrolytic products that can be stored and employed as fuels at a later time (e.g., during periods of cloud cover or darkness). The photoelectrolysis of water by means of the reaction $\text{H}_2\text{O} \xrightarrow{\text{light}} \text{H}_2 + \frac{1}{2}\text{O}_2$ represents a particularly interesting method for converting solar energy into a form that can be stored indefinitely.

The use of semiconducting electrodes in driving the electrolysis reaction has proven advantageous since the "band bending" resulting from the difference in the Fermi levels of the semiconductor and electrolyte inhibits the recombination of the photogenerated

electron-hole pairs. Electrode stability for most of the candidate *n*-type materials has proven to be a crucial problem in the realization of workable photoelectrochemical devices, however, and only a few oxide semiconductors have been found to be stable against photoanodic dissolution. One of the more promising stable semiconducting oxides is potassium tantalate (KTaO_3) along with the related solid solution potassium tantalate niobate ($\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$). The known stability of these materials makes them ideal candidates for a systematic study of the effects of other parameters (dopant effects, contact effects, carrier concentration variations, etc.) on photoelectrochemical cell performance.

As the first step in a systematic study of the use of KTaO_3 for the photoelectrolysis of water, techniques have been established for fabricating electrodes and making measurements of their basic electrical characteristics. Single crystals of *n*-type KTaO_3 were produced by a flux-growth technique from material doped with small amounts of Ca, Mn, Ag, or Yb. Techniques were developed for making electrical contact to the crystals by employing a GaIn eutectic coating, in solder, or conducting epoxy, and insulating epoxy. Electrodes have been fabricated from samples (typically, $1 \times 4 \times 8$ mm) with different concentrations of the various dopants. The electrical characteristics of the electrodes were measured to assess the quality of the contacts and to determine the effects of different impurity concentrations on the crystals. The measurements were made in a quartz electrolysis cell filled with a NaOH solution, using uv illumination from a 450-W Xe lamp. The potential of the KTaO_3 anode relative to a saturated calomel electrode and the current, as sensed by a 100- Ω resistor, were recorded as the bias voltage was scanned. Figure 6.7 illustrates the cell operation and shows representative results for an electrode with good characteristics. The characteristics of the different electrodes varied considerably. Without an applied bias, some electrodes produced no photocurrent, while others produced a significant fraction of their saturation current. Some electrodes produced a photocurrent but exhibited no diode rectification. A part of the variability of the electrodes can be traced to imperfect contacts, but the impurity dopant also appears to influence electrode performance. Definitive conclusions will require further study. The efficiency of the conversion of electrode current to H_2 was also measured. The result is shown in Fig. 6.8. To within experimental error, the conversion is 100% efficient.

Fig. 6.7. Electrical characteristics of a KTaO_3 photoelectrolysis cell.

Fig. 6.8. Hydrogen production vs charge flow for a KTaO_3 photoelectrolysis cell. The solid line represents conversion at 100% efficiency.

GROWTH OF β' - Al_2O_3 CRYSTALS

W. E. Brundage J. B. Bates

Optical-quality single crystals of $\text{Na}\beta'$ - Al_2O_3 were grown by heating a mixture of 32 mole % Na_2CO_3 , 8 mole % MgO , and 60 mole % Al_2O_3 in a tightly covered Pt crucible. The temperature was first raised to 1100°C overnight, then raised to 1700°C and held for 80 hr, followed by furnace cooling. Large crystals were formed

1. 1978 summer research participant from University of California, Berkeley.

during the evaporation of the excess Na_2O_3 but some cracking occurred, apparently during cooling. Flat, clear crystals as large as 15 mm across and 2 to 3 mm thick were recovered, one of which is shown in Fig. 6.9. Imperfect crystals with dimensions over 25 mm were also produced.

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Fig. 6.9. Single crystal of β' - Al_2O_3 .

Lattice parameters determined from precession x-ray photographs agreed with those reported by Bettman and Peters¹ for Mg-stabilized crystals. A chemical analysis for Na, Mg, and Al showed that the crystals have the composition $\text{Na}_{1.73}\text{Mg}_{0.58}\text{Al}_{9.52}\text{O}_{17}$, assuming the balance of the sample weight to be O. If these data are normalized to $5\text{Al}_2\text{O}_3$, the formula unit of the crystals is given by $0.91\text{Na}_2\text{O} \cdot 0.61\text{MgO} \cdot 5\text{Al}_2\text{O}_3$.

1. M. Bettman and C. R. Peters, *J. Phys. Chem.* 73, 1774 (1969).

FLUX GROWTH OF TUNGSTEN CARBIDE

W. E. Brundage L. A. Boatner Y. K. Chang

Single crystals of tungsten carbide have been grown by heating mixtures of WC powder and Co in a graphite tube furnace using an Ar atmosphere and Al_2O_3 crucibles. Contrary to the results of Takahashi and Friese,¹ cooling a melt with a WC concentration of 15 mole % (40 wt %) from 1600 to 1400°C did not produce any WC crystals. When, however, the concentration of WC

powder was increased to 33 1/3 mole %, flat hexagonal and triangular crystals several millimeters in size were obtained by this procedure. A representative crystal is shown in Fig. 6.10. Crystals of WC have also been grown by maintaining a constant 1600°C temperature with a WC loading of 40 mole % and with the heater arranged so that one side is open to permit the crucible to radiate to a cooler region. In this case, the crystals were indeed found on the cooler wall of the crucible. In all cases some reaction with the Al_2O_3 crucible and considerable volatilization of the Co was noted. Other

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Fig. 6.10. Tungsten carbide single crystal grown by cooling a Co flux. The crystal is approximately 2.5 mm in diameter.

techniques including rf-heated float zoning and arc melting are to be applied to the growth of carbide and nitride single crystals.

1. T. Takahashi and E. J. Friese, *Philos. Mag.* 12, 1 (1965).

RESEARCH MATERIALS INFORMATION CENTER (RMIC)

T. F. Connolly G. C. Battle

The RMIC has continued to collect, organize, and index the literature and to answer inquiries (see Table 6.2) regarding the preparation, characterization, properties, and availability of both pure and doped inorganic solid state materials.

Table 6.2. Samples of inquiries answered by RMIC

Inquiry	Source	Application or purpose of inquiry
Ca, Al, SiO ₂ , crystal growth	ORNL, Metals and Ceramics Division	To avoid possible duplication of previous work
Extremely low frequency response of pyro- or piezoelectrics	University of California, Berkeley	Questionable effect noted; verification of theory sought
Correlation of ESR and thermoluminescence	American University, Cairo	Theory; contact with other workers
X-ray diffraction data on some ternary fluorides	Clarendon Laboratory, Oxford University	Identification of grown crystals
Metals and alloy hydrides for H storage	Alloy Data Center, NBS	Energy
Refractive index and infrared absorption of MgF ₂	IIT Research Institute	Laser window coating
Compilation of magnetic transition temperatures	University of Sussex, England	For review
Metal crystals	Physik-Institute, Freiburg	Neutron monochromators
Growth of RbAg ₂ I ₃	University of Illinois	Fast ionic conductors
Growth, magnetic properties of oxides	Lincoln Laboratory, MIT	Continuing program
Al ₂ O ₃ and other oxides, availability	Technical University, Munich	Refractory materials
Compilation of magnetic transitions	CNRS, Grenoble	
Survey of properties of GaAs	University of California, Berkeley	Solar cells
Bibliography, preparation and properties of semiconductor materials	NASA Lewis Research Center	Detectors, solar cells
Metal and alloy crystals	McMaster University, Canada	Monochromators
Crystal growth methods	Institute for Materials Research, Stanford University	Wide variety of applications
Optical materials, availability, properties	Naval Research Labs., Washington, D.C.	Detectors, frequency shifters
Bibliography on ferroelectrics	Institute of Materials Research, NBS	Compilation of dielectric properties
Wire of specified tensile and torsional properties	Physikalisch-Technische Bundestaat	Refinement of measurement of the gravitational constant
Crystal growth of CdSe	Los Alamos Scientific Laboratory	Optical parametric oscillator
Temperature dependence of Si optical absorption	Sandia Laboratories	Sensor of solar thermal flux
Survey of groups IV-VI binary transition metal compounds	Kernforschungsanlage, Jülich	Study of properties and preparation
Discs of low refractive index	Lawrence Livermore Laboratory	High-power laser windows
Information on piezoelectric ceramics	Pennsylvania State University	Survey report on preparation and applications
Growth of wide variety of crystals	Purdue University	Continuing program on crystal growth
Survey (growth, properties, rare-earth chalcogenides)	University of California, Los Angeles	Material for graduate program

Table 6.2 (continued)

Inquiry	Source	Application or purpose of inquiry
Infrared materials	Air Force Cambridge Research Laboratories	Laser auxiliary materials
Reviews on ion implantation in superconductors	ORNL	Preparation; effects on T_c
Information on pyroelectrics	McGill University, Canada	For survey and review
Growth of series of oxides	National Physical Laboratories, England	Magnetic properties
Bibliography on transition metal oxides	Data Center for Binary Oxides, NBS	
High-resistivity compound semiconductors	Harvard University	Photoemission studies
Survey of crystal suppliers	U.S. Office of Industrial Mobilization	Congressional report
Review on EXAFS	ORNL, Solid State Division	Surface studies

The computer terminal acquired by RMIC in 1976 for searching non-RMIC data bases has enabled the Center to accelerate an effort, initiated in 1973, to produce and update RMIC bibliographies with computer assistance. During the current reporting period, this effort was expanded into a major and valuable part of the Center's work. The computerized bibliography of crystal growth documents now covers the period from 1972 to date. After documents are added to the collection, the bibliography is automatically re-sorted alphabetically by author and renumbered, and a new permuted title index is created. (Before entry, the titles are expanded if necessary to include information that enhances the value of the permuted title index.) Three smaller data bases have also been computerized; these are limited to reviews, compilations, and bibliographies on superconductors, surfaces, and catalysis. A bibliography of refractive indexes is being prepared for critical review and publication. All of the completed data bases are on-line and can be searched by any ORNL staff member who has access to a computer terminal.

All input and editing of computer-maintained RMIC data bases is now done by a member of the RMIC staff, who is also performing a continually increasing number of job control operations for purposes such as transfer from one computer or storage area to another and trans-

lation from one format to another. To date, this has necessitated learning to use about 20 computer programs and subroutines of various degrees of complexity. Each computer operation added to the RMIC in-office capabilities has decreased our dependence on other organizations and resulted in increased accuracy and more rapid production.

Arrangements have been made with the editors of Plenum Press and the Landolt-Bornstein series for the use of the RMIC collection (now more than 120,000 documents) in the production of critical reviews and critically evaluated data compilations. After agreement between the editors and the RMIC on subject fields, the editors will seek out authors who are recognized authorities, and the Center will provide coverage of the literature. The results of one such mutual effort is already in press and will appear in the next volume of the Landolt-Bornstein series.

The Center will increasingly emphasize coverage of studies of materials for energy applications, which should lead to greater usefulness to the Solid State Division and the DOE.

A new Directory of Crystal Growth and Solid State Materials Research is being compiled, with the format of the 1975 edition changed to include more information.

7. Isotope Research Materials

The preparation of special chemical and physical forms of separated, high-purity isotopes is the task of IRML. Research samples using nearly all stable isotopes and many radioisotopes (especially the actinide elements) are made to customer specifications in support of research programs throughout the United States and in foreign countries. In addition to satisfying isotope research material requirements for DOE programs, IRML provides an international service of sample preparation supplying over 100 universities and commercial firms in more than 30 countries with samples unavailable from commercial sources. During the reporting period, nearly 7000 samples were prepared for the international scientific community. The support for this work comes directly from sales of materials and services; therefore, IRML has an integral sales function with associated inventory and revenue accounting operations. Research and development activities in IRML are funded by DOE through the Office of Basic Energy Sciences and the Office of Nuclear Waste Management.

Technical functions of IRML can be categorized generally into materials research and development, separation systems for tritium, inorganic chemical conversions, preparation of special physical material forms, fixation of high-level radioactive wastes in cermet form, radioisotope source preparations, purifications, single-crystal and epitaxial growth studies, and development of analytical techniques (usually nondestructive methods) compatible with characterization of thin film and other types of samples. From its inception, IRML has prepared particle accelerator targets, utilizing technologies of physical vapor deposition, chemical vapor deposition, mechanical rolling of metals, distillation of metals, metal reductions, arc melting, levitation melting, sintering, and other metallurgical and chemical processes to produce unique isotope-containing samples. Because of present-day interests in high-energy physics research, new technologies have been required to transform large (multigram) quantities of separated isotopes into thick, large-area target samples. In all operations, specific efforts to improve purity and conserve isotope resources are of vital importance because the monetary value of isotopes consumed during a sample preparation may be many times the cost of assigned manpower and ancillary expense.

Procedures developed for handling stable isotope materials are usually equally applicable to radioisotope sample and source preparations. Adaptation of preparative methods to radioisotopes generally implies modification for remote operations (hot-cell enclosure or processing equipment) or at least glove-box operations required for personnel protection. Almost all of the above-noted operations have been adapted for radioisotope processing.

As a result of the technical capabilities developed for isotope sample preparations, research and development programs on tritium concentration by bipolar electrolysis and on ceramic and cermet waste forms are being carried out in IRML. Considerable progress was made during this past year in the measurement of the separation factors of H-D, H-T, and D-T in an aqueous electrolytic system for the purpose of developing a cascaded process to remove tritium from reactor or fuel reprocessing plant effluents. High-level, radioactive waste from the Thorex fuel recovery process used at Nuclear Fuel Services, New York, was successfully converted into a cermet with high thermal conductivity that is apparently compatible with corrosive brine environments.

ELECTROCHEMICAL SEPARATION OF T FROM AQUEOUS EFFLUENT SYSTEMS

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With the increasing number of sources of T associated with nuclear technology, the amount of T being discharged into the environment is a growing problem. Among the several processes that are applicable for T concentration and removal, countercurrent electrolysis with bipolar electrodes appears to be an attractive solution for specific cases. Although bipolar electrolysis has been studied for less than three years, results show the method to have excellent potential as a means of concentrating T from aqueous effluents.

In principle, bipolar electrodes in an electrolytic cell act both as an anode and a cathode (Fig. 7.1). During normal operation, H atoms are produced electrolytically at the bipolar cathode surface, are dissolved immediately into the metal lattice of the electrode, and diffuse to the anode surface (see Fig. 7.2). At the anode surface, the H atoms electrolytically react with hydroxyl ions present in the electrolyte to form water. All three of these mass transfer processes favor transport of the lighter isotope. Therefore, when isotopic mixtures are used, separation of isotopes results.

Fig. 7.1. A simple electrolysis cell containing one bipolar electrode.

Advantages of the bipolar electrolysis separation process are that it consumes less power than conventional electrolysis and that the multistage separation system is more compact, as compared with direct electrolysis or catalytic exchange. Lower power consumption is possible because electrolysis at the bipolar electrode has a

Fig. 7.2. Hydrogen transfer mechanisms that occur at and in the bipolar electrode.

zero net standard potential, whereas conventional electrolysis has a net standard potential of -1.229 V. A multistage separation system utilizing bipolar electrolysis is inherently compact because each electrode compartment (~ 0.3 cm thick) forms a separation stage. A basic study of the bipolar electrode is in progress, as well as a development program to design and operate a multistage separation system of pilot facility size (~ 40 liters per day feed rate).

A single bipolar electrode placed between the terminal electrodes divides the cell into two separation stages. Separation occurs at both the bipolar electrode and the terminal cathode. Addition of n more bipolar electrodes further subdivides the cell into $n + 1$ stages. With this arrangement, a flow of H is established through the system toward the terminal cathode. An enrichment of the heavier isotope occurs in the aqueous phase adjacent to the cathodic side of each bipolar electrode. To gain full advantage of the separation process, the T-enriched aqueous material must be swept away from the cathode surface and circulated countercurrent to the direction of H transport.

In a countercurrent cascade of this type involving an aqueous electrolyte, the electrolyte (NaOH) must not be allowed to concentrate in the terminal-anode compartment of the cascade. Several concepts for removal of electrolyte from the terminal anode compartment are being studied experimentally. One possibility is removal of Na ions using Nafion ion-exchange membranes. Studies to find optimum conditions for minimizing H₂O (and T₂O) transport associated with the Na⁺ transfer are in progress. Another possible method is the distillation of the liquid in the anode compartment using the heat generated from the recombination of the H₂ and O₂ streams evolved in process.

Separation factors, using a cell with one bipolar electrode at room temperature, for H-D, H-T, and D-T isotope pairs have been measured: $S(H-D) \sim 6-8$, $S(H-T) \sim 8-20$, and $S(D-T) \sim 2.5$. These large values indicate that only a few bipolar electrodes in a cascade are needed to achieve very effective isotope separation. These separation factors do not change appreciably with current density or electrode activation techniques. Changes in separation factor with temperature were measured to be of the same magnitude as predicted from data on conventional electrolysis (at 80°C , $\sim 60\%$ reduction in separation factor from the value measured at 25°C).

Countercurrent electrolyte flow using a gravity overflow technique has been successfully demonstrated. This self-regulating interstage flow scheme minimizes external piping and permits small spacing (3 mm) between bipolar electrodes. Several multistage cells (four to five stages) were tested during the period with $\text{H}_2\text{O}-\text{D}_2\text{O}$ and $\text{H}_2\text{O}-\text{T}_2\text{O}$ mixtures. These cells operated with current densities ranging from 250 to 300 mA/cm^2 (2.02 to 2.42 g of H_2O per day per square centimeter throughput) and were constructed from Polysulfone.

Palladium alloys are used as the bipolar membrane, principally Pd-25 wt % Ag in a thickness range of 0.025 to 0.075 mm. Other alloys of Pd (Pd-10% Y and Pd-5% Ru) have been tested with no significant change in throughput. The most promising electrode improvements have been achieved by surface activation procedures. Activation of the electrode by dipping in molten NaOH and cleaning ultrasonically has yielded current densities up to 500 mA/cm^2 at 70°C .

Current density is limited to that value at which gas bubble formation on the bipolar electrode surface is observed; that is, all H generated at the cathode side must be sorbed into the bipolar electrode. Studies of improvement in throughput (mass transport) are continuing; greater throughput is obtained with increasing cell temperature and activation of the electrode surface. Because of the large magnitude of the separation factor, sacrifice of separation efficiency in favor of greater mass transport through the bipolar electrode is warranted. Electrode activation may also serve to reduce the bipolar electrode overvoltage.

One specific application of the bipolar electrolysis separation system is the extraction of T from the D_2O reactor moderator at the Savannah River Plant. A conceptual design study for a detritiation plant for this purpose is in progress. The objective is to reduce T content in the heavy water moderator from three Savannah River Plant reactors to an ultimate equilibrium T concentration one-sixth of its present level of 20 Ci/liter.

CERMETS FOR HIGH-LEVEL RADIOACTIVE WASTE CONTAINMENT

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The first full-year effort on this program culminated in the successful incorporation into an inert cermet waste form of highly radioactive Thorex acid waste that had been stored at NFS. The cermet in this case was composed of micron-size, fission product oxide, titanate, and aluminosilicate particles uniformly dispersed in a corrosion-resistant, Fe-Ni, base-alloy matrix. Waste loadings of up to 70 wt % have been obtained in these experiments, and waste-to-cermet volume reduction factors were between 2 and 200, depending on the composition of the waste. During processing to form the cermet, volatility losses of radioactive species have been very low. Preliminary leach rate studies indicate a leach resistance comparable to or better than other candidate waste forms; more quantitative and complete leach data are currently being generated. These cermets typically have densities of 6.2 to 8.2 g/cm^3 and high thermal conductivity values ($0.02-0.05 \text{ cal sec}^{-1} \text{ cm}^{-1} \text{ }^\circ\text{C}^{-1}$).

Wastes are processed into a cermet by first adding specific cations and anions to the waste to obtain stable, insoluble, crystalline compounds and a chemically inert metal-alloy matrix in the final cermet. The waste and additives are subsequently dissolved in molten urea. During heating of the solution, denitration in the reducing environment takes place, followed by a coprecipitation of all the components at 180°C . The precipitate is calcined to convert all species to oxides, titanates, or aluminosilicates, which are intimately mixed as a result of their coprecipitation. Reduction of the H-reducible oxides in this mixture to yield the metal matrix components is performed either prior to or during densification to obtain the final cermet waste form.

Processing techniques amenable to full-scale operations on actual waste are being developed, and the characteristics of the cermet itself are being tailored to optimize its properties as a primary waste form. Studies are being conducted on simulated wastes, radiotracer-containing simulated wastes, and authentic waste such as NFS Thorex, Savannah River Plant dried sludge, and untreated process wastes. Although more characterization of the cermet waste form and further developments of the process are required, cermets appear to be a very promising alternate waste form for long-term storage.

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RADIOISOTOPE TARGET PREPARATION AND DEVELOPMENT

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The demand for radioactive targets and high-purity radioactive isotope materials has steadily increased during the past review period. These activities occupied approximately 44% of IRML's preparative efforts. Part of this increased demand was generated by physicists involved in accurate neutron cross-section measurements for various actinide isotopes. Actinide deposits used for the neutron cross-section measurements must be accurately characterized and must be prepared by a process that produces an adherent bond between the actinide compound (usually the oxide) and the substrate. In most instances the actinide oxide was vaporized in a vacuum environment by using electron bombardment heating (Fig. 7.3). The electron beam was programmed to sweep over the surface of a pressed pellet (1-5 g) of the actinide oxide; thus, the pellet essentially acted as its own crucible and eliminated interfering impurities. To ensure an adherent bond

Fig. 7.3. Electron bombardment source used for preparation of actinide oxide deposits.

between the oxide deposit and thin Ni, Ti, or Al substrates, the substrates were heated to approximately 250°C during vapor deposition. All evaporants were characterized by spark source mass spectrographic and isotopic analyses. The elemental mass deposited was determined to $\pm 1.5\%$ by 2π or low-geometry alpha counting. During the review period, IRML produced approximately 40 ^{232}Th , 6 ^{241}Am , and 10 ^{233}U fission foils. The fission foil preparations program will continue

into the coming year with approximately 60 ^{233}U and 40 high-purity ^{232}Th fission foils scheduled for fabrication.

During the past year, a small quantity of ^{241}Am metal was prepared by the pyrochemical reduction-distillation technique¹ for use in preparing ^{241}Am foils for physical property and nuclear physics experiments. Approximately 37 g of high-purity ^{241}Am metal containing less than 100 ppm impurities was produced; however, considerable difficulty was encountered when attempting to roll this metal. In the reduction-distillation process the metal was distilled from a Ta reactor into a quartz collector from which it could be easily removed. The as-distilled metal appeared to be very ductile. However, after the material was worked, it became brittle. Apparently the as-distilled material retained the high-temperature fcc structure, which reverted to the more stable, double-hexagonal, close-packed structure during rolling. More study is required to determine the true phase diagram for high-purity Am metal and low-concentration alloys in which the cubic structure is stabilized. IRML is presently assembling an x-ray diffraction system in an Ar glove box where the ^{241}Am metal phase studies can be done. Although difficulties were encountered in rolling the Am, one 2-g sample of metal (about 2 cm X 2 cm) was produced. Measurements of its neutron cross section will be made in a joint experiment between ORNL and the EURATOM community. In addition to fission foil and high-purity ^{241}Am metal preparation, IRML has prepared many (>700) other actinide samples by vacuum evaporation and rolling. The samples had areal densities that ranged from 10^{-6} to 10 mg/cm^2 .

As was reported in the last period, a rolling technique had been developed for preparing uniform, large-area U foils. This development resulted in an order from Argonne National Laboratory for the preparation of 40 kg of 93% ^{235}U metal foils 5 cm X 15 cm X 250 mg/cm^2 for the Zero Power Reactor. Although this order taxed our facilities, the foils were prepared to specifications and on time.

Pyrochemical reduction-distillation development efforts have continued. The process has been extended to the separation of elements by utilizing differences in their vapor pressures. A list of three rare-earth materials, their melting points, and the temperature required for a vapor pressure of 1 torr is shown in Table 7.1. The rare-earth oxides were mixed with Th, and a pyrochemical reduction-distillation of the oxide compounds was made in vacuum. By carefully controlling the distillation temperatures, Dy was separated from the Nd and Sm. The final distilled sample contained 99.55% Dy

Table 7.1. Melting point and vapor pressure data for rare-earth materials used in initial pyrochemical separations by IRML.

Element	Melting point: (°C)	Temperature (°C) at which vapor pressure = 1 torr
Nd	1024	1727
Sm	1072	987
Dy	1407	1437

After the initial success with the rare-earth materials, the process was applied to purify ^{232}Th which was to be used in preparing high-purity fission foils. The main impurities in the ^{232}Th were the daughter products (in particular ^{228}Ac). A 1-g sample of $^{232}\text{ThO}_2$ was pressed into a pellet and gamma-counted prior to the vacuum distillation process. The pellet was then placed into a Ta still and heated, in vacuum, to 1900°C for 30 min. The resulting gamma analysis showed a 98.2% removal of the undesirable ^{228}Ac daughter product.

The pyrochemical process also was used to separate the daughter product ^{241}Am from ^{241}Pu . Because the vapor pressure difference between Am and Pu metals is a factor of 5000 at the melting point of Am (1176°C), very high decontamination factors were obtained. Fractionation of actinides (Pu, Am, and Cm) has been successfully performed as well as separation of fission products from reactor-irradiated samples.

1. E. H. Kobisk and H. L. Adair, *Proceedings of the World Conference of the International Nuclear Target Development Society*, Garching, Germany, September 11-14, 1978 (to be published).

NEUTRON DOSIMETRY MATERIALS

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The demand for high-purity, well-characterized materials that can be used to monitor the neutron energy spectra, flux, and fluence in reactor cores or blanket regions has increased significantly over the past two years. Since IRML initiated its dosimeter program, approximately 4100 V-encapsulated dosimeters have been prepared and shipped. The increased use of the neutron monitors is emphasized by the fact that 2600 monitors were prepared and shipped during this review

period, which represented a revenue of \$350,000 or about 28% of IRML's sample preparation efforts. Development efforts have been concentrated on the fabrication of diluted isotopic materials (0.1 to 1.0 wt %) for use in very long reactor runs, for which the use of pure materials would be prohibitive because of the long decay times required before analyses by direct counting could be performed.

Dilute alloys of ^{235}U , ^{238}U , and ^{233}U were prepared by alloying each element with high-purity V. Samples were arc melted several times to ensure that each alloy was homogeneous before casting the material into a rod form. The rods (~1.27 cm diam) were then swaged to 0.045 cm diam. Approximately 305 m of V-0.8 wt % ^{235}U , 305 m of V-0.8 wt % ^{238}U , and 30 m of V-0.8 wt % ^{233}U were prepared. In addition, dilutions of $^{239}\text{PuO}_2$ in MgO, $^{237}\text{NpO}_2$ in MgO, and $^{232}\text{ThO}_2$ in MgO were prepared by the urea coprecipitation process. This process involved mixing a small quantity (~1 wt %) of either $^{239}\text{PuO}_2$, $^{237}\text{NpO}_2$, or $^{232}\text{ThO}_2$ with MgO and dissolving in HNO_3 . Subsequent addition of urea to the solution followed by digestion destroys the nitrate content and eventually coprecipitation of dissolved components occurs from molten urea at 180°C . The resultant mixture is calcined in air at 900°C for complete compound dehydration and removal of excess urea by thermal decomposition. After calcination the mixed oxides are added to molten wax containing dissolved polyethylene, and the resultant mixture is extruded into "green" wire; subsequent sintering in MgO tubes at 1450°C for 8 hr removes the binder and forms solid, uniform wires. This procedure has been used during the past year to prepare 98 m of 0.7 wt % $^{237}\text{NpO}_2$ in MgO, 110 m of 1.0 wt % $^{232}\text{ThO}_2$ in MgO and 90 m of 1.0 wt % $^{239}\text{PuO}_2$ in MgO. Each dilute material batch was characterized by spark source mass spectrographic and neutron activation analyses. Analysis of the materials showed them to be homogeneous to $\pm 1.0\%$ from the mean value at the 95% confidence level.

In conjunction with the V-encapsulated dosimeter materials, high-purity actinide deposits are being used in fission track recorders to determine precise fission rates for the various actinides. It has been shown that measurements of increased absolute accuracy are necessary for proper analytical interpretation of in-core neutron energy spectra. To obtain the accuracy needed in the fission rate determinations, high-purity actinide deposits have been prepared by the vacuum evaporation of the respective actinide oxide. Approximately 30 actinide deposits, having areal densities from 10^{-6} to $200 \mu\text{g}/\text{cm}^2$, were prepared during the review period.

Dosimeters produced by IRML are compatible with monitoring light-water, fast breeder, and thermonuclear reactor environments. Consequently, it would appear that the demand for the dosimeter materials will steadily increase for the next several years.

WIRE DOSIMETERS FOR WESTINGHOUSE-BETTIS

W. S. Aaron C. A. Culpepper T. C. Quinby

Two major dosimeter wire preparations were completed during the year. Fifty-five assemblies consisting of 270-cm lengths of 0.25-mm-diam Th wire encapsulated in 0.55-mm-diam pure Ti tubing were fabricated. A second set of dosimeters prepared for Westinghouse-Bettis consisted of two capsule-loading schemes for samples of Co-V and Ta-V alloys and $^{233}\text{UO}_2$ or ThO_2 dilutions in a MgO matrix. After the various sample wires were prepared and their compositions accurately assayed, sections of each type of material were obtained by cutting to specific lengths and weighing each piece. Samples were then loaded, together with appropriate Ti spacer wires between each sample, into 36-cm-long Ti tubing and the tubes sealed by welding in an He-Ar atmosphere. At this point, each tube was swaged to seal each internal sample compartment by closing the tube down around the Ti spacers between each isotope sample. This step was required to prevent material transfer between compartments containing the oxide wires and also to position permanently and accurately the samples within the tube. This requirement facilitated postirradiation sectioning and analysis of the dosimeters. After performing He leak testing and other quality assurance measures, the dosimeters were radiographed and mapped to confirm adherence to specifications. Both sets of neutron dosimeter materials have been used in the Shippingport Reactor core characterization program.

Cm_2O_3 SAMPLES FOR COMPATIBILITY STUDIES

T. C. Quinby J. Oxendine

One of the major concerns in the design of radioactive heat sources for the generation of electrical energy is

material compatibility. Because the sources must operate for long periods of time in remote areas where repair is difficult or impossible, it is necessary to determine the best encapsulation materials for the sources. The procedures used in preparing well-defined radioactive samples, normally of actinide compounds, usually require a major capital investment for processing equipment. During the review period, IRML developed a procedure for preparing such samples with a minimum investment in capital equipment and applied this procedure to the preparation of $^{244}\text{Cm}_2\text{O}_3$ bars. The $^{244}\text{Cm}_2\text{O}_3$ bars are currently being used to study the degree of attack and effect on mechanical properties of several alloys considered as potential encapsulants for $^{244}\text{Cm}_2\text{O}_3$ sources.

The procedure involved the mixing of $^{244}\text{Cm}_2\text{O}_3$ powder with a high-temperature wax binder (mp 205°C) and extruding the mixture through a small rectangular orifice. Experimentally it was determined that a maximum of 2-g increments of $^{244}\text{Cm}_2\text{O}_3$ could be used; larger amounts of oxide caused volatilization and decomposition of the binder because of excessive decay heat from the ^{244}Cm (2.832 W/g). Prior to each extrusion, a 2-g sample of oxide was heated to 800°C in Ar to ensure reduction of CmO_2 to Cm_2O_3 . After cooling in Ar, the material was ground, weighed, and mixed with 0.300 g of wax. After extrusion, the $^{244}\text{Cm}_2\text{O}_3$ bars were cut to 1.43-cm lengths for sintering. Each extruded bar was placed between thin Al_2O_3 plates to prevent warping during sintering. Aging the "green" bars for 24 hr before the sintering cycle was begun apparently polymerized the wax and prevented it from melting during the early stages of the sintering cycle. The result was a better dimensionally defined product. "Green" bars were sintered in a tube furnace at 1450°C for 8 hr. During 2 hr of the 8-hr cycle, the glove-box atmosphere was changed from Ar to air to burn off residual carbonaceous material. A total of 22 Cm_2O_3 bars were extruded and sintered according to the above procedures and are being used to irradiate alloys of Ta, Mo, Pt, and Ir. One such bar is shown in Fig. 7.4. Each of the sintered samples was flat to $1.39 \text{ mm} \pm 0.13 \text{ mm}$, was rectangular in shape ($2.7 \text{ mm} \times 11.0 \text{ mm}$), contained $0.300 \pm 0.008 \text{ g } ^{244}\text{Cm}_2\text{O}_3$, and had 52% theoretical density.

Fig. 7.4. Extruded $^{244}\text{Cm}, \text{O}_2$ bar before cutting and mounting. Also shown are Ta-10 wt % W tensile specimens.

TRITIUM TARGETS USED AS NEUTRON SOURCES

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For many years the IRML has been preparing T targets by reacting various vapor-deposited metal layers with T in a high-temperature environment. Initially most of the T targets prepared by IRML were small in size (area), but as the need for more intense monoenergetic neutron sources increased, the requested targets also increased in size and in T content. Many of the more recent T target preparations have been used at the Rotating Target Neutron Source (RTNS-I) at Lawrence Livermore Laboratory. The RTNS-I target design resulted from a development effort to increase the neutron yield and target lifetime in the deuteron beam beyond those of conventional systems. One of the major changes incorporated in the use of the RTNS-I target was rotation of the target at high speed (~ 1100 rpm), which would reduce the dwell time of the deuteron beam at any one location on the target. Subsequent reduction of the T desorption caused by beam heating resulted from this rotation. A neutron yield of 6×10^{12} neutrons/sec has been produced from the 23-cm-diam RTNS-I target using a 400-keV, 20-mA D^+ beam.

A new deuteron accelerator (RTNS-II) has been built to generate much higher neutron yields for evaluation of component materials exposed to thermonuclear environments. Design goals for the RTNS-II targets are shown in Table 7.2 along with present operational parameters of the RTNS-I targets. The RTNS-II targets will be made of a Cu alloy that will be coated with a layer of Ti in an ion-pumped system capable of maintaining a vacuum of $<10^{-7}$ torr during deposition. A 2000 liter/sec Ti sublimator cryopump supplements the 500 liter/sec ion-pumping capacity. To evaporate the Ti, a rod-fed electron beam gun (Fig. 7.5) will be used, with the source 36 cm from the target. The target substrate will be heated to 450°C prior to and during Ti deposition to assure an adherent Ti-to-Cu alloy bond; the substrate will be rotated to provide the desired Ti thickness uniformity.

Subsequent to preparation, each target will be removed from the deposition system in an Ar atmosphere and transferred to the T sorption system. An exterior view of the T sorption chamber, T storage traps, and appropriate electronic components are shown in Fig. 7.6. The T sorption system is pumped with two 270-liter/sec ion pumps and will maintain a vacuum level of $<10^{-8}$ torr during the heating cycle before T is expanded into the chamber.

Table 7.2. Operational and designed parameters for high-intensity rotating neutron sources

Parameter	RTNS-I	RTNS-II
Beam energy, keV	400	400
High voltage supply current, mA	60	300
Target current, mA	22	150
Spot size, mm	6	10
Target diameter, cm	23	46
Target speed, rpm	1100	5000
Source strength, neutrons/sec	6×10^{12}	4×10^{13}
Maximum flux, neutrons/cm ² -sec	1.7×10^{13}	1.2×10^{13}
Target lifetime, h	100	100

During Ti vapor deposition, film thickness will be determined with a resonating quartz crystal monitor and an electrical resistance monitor. Change in electrical resistance of thin films has been used satisfactorily to determine film thicknesses of Ti up to 1.0 mg/cm². In addition, we hope that the electrical resistance measurement procedure can be used also during T sorption into the Ti layer to monitor this process. Conductance of the Ti-H layer passes through a minimum value and then steadily increases until H saturation is achieved. Uniformity of the T content over the active area will be measured using a small ionization detector. Each target will contain 3000–4000 Ci of T.

During the review period, the systems shown in Figs. 7.5 and 7.6 were purchased, assembled, and tested. The two systems will be moved to our T facility and become

Fig. 7.5. Interior view of Ti evaporation system showing the electron beam gun, quartz iodide heat lamps, and substrate location.

Fig. 7.6. Exterior view of T sorption system showing sorption chamber, T storage traps, and associated electronic components.

operational as soon as the RTNS-II accelerator is completed. Twenty-four 23-cm-diam T targets have been prepared during the past year, some of which were prototypes of the new 46-cm-diam target being designed by Lawrence Livermore.

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STABLE ISOTOPE TARGETS AND RESEARCH MATERIALS

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B. F. Early	C. A. Culpepper
P. R. Kuehn	W. B. Grisham

Stable isotope (or normal assay element) samples prepared to customer specification accounted for 28% of the revenues to IRML during this period. The volume of activity was the largest ever recorded in the 18 years of IRML existence. Many of the more difficult and costly

preparations were the large-area samples required for experiments at the Los Alamos Meson Production Facility and the geometric shapes used in producing heavy-ion beams at the Super HILAC at Lawrence Berkeley Laboratory.

As reported in past years, chemical conversion from inventory compound forms of the isotopes to elemental forms has been one of our major efforts. In this work we have had to expand our capabilities in pyrochemical reduction-distillation to convert larger quantities of isotopes to metal. For example, 59 g of ^{42}Ca was produced by reduction-distillation (La being the reductant) and finally formed into strips of 7 cm $\times$ 20 cm and 5 cm $\times$ 10 cm having thicknesses from 40 mg/cm² to 250 mg/cm². Total loss recorded for this entire fabrication was only 109 mg. Until this year the largest sample of Cr isotope ever reduced to metal from the oxide at ORNL was $\sim$ 200 mg. In increments of 10 g, a total of 50 g of ^{52}Cr was prepared by Ca reduction using a pyrochemical method employing compaction of the oxide with Ca in a thin Ca foil wrap. Yield of $>95\%$ conversion was achieved with a residual oxide content

of <1%. In this reporting period, 23 reduction-distillation conversions contained more than 10 g of element per reduction. The reduction-distillation method we developed has produced increased metal yields.

In many cases, chemical reactivity of elemental samples (e.g., Ca and Eu) precludes their being handled, especially when the experimenters mount them in scattering chambers with extended exposure to the atmosphere. Encapsulation of such samples in other metals either under vacuum or in Ar can protect the sample from deterioration; however, wall thickness of the encapsulating material frequently interferes with or completely nullifies an intended experiment. Recent success with sputter-deposition of Au, Al, or other protective metals to thicknesses of 200–500 $\mu\text{g}/\text{cm}^2$ has permitted handling of the reactive metals for days without deleterious effects. The use of sputter-deposition as compared with vapor deposition significantly improves the adherence of and protection by the deposited layer.

Although thin samples of deuterated polyethylene have been prepared routinely by warm rolling of polymerized bulk material, large losses (~50%) of material have prevented the preparation of thick samples of large area. A method of successive warm pressing of such samples, using incremental reduction in thickness inside fixed metal frames of decreasing thickness, has been developed to control loss of material to within 5%. Uniformity of thickness of samples 10 cm X 20 cm X 0.05 cm has been measured to be ± 0.001 cm or less when this method is used.

As in the past, rolling of thin metal foils (200 mg/cm² to 200 $\mu\text{g}/\text{cm}^2$) continues to be the most conservative and successful method of target preparation. In the past 17 months, more than 1400 rolled isotope samples have been produced. Because of the ever-increasing development of this technology, it is used for the fabrication of most of the metal samples having film thicker than 500 $\mu\text{g}/\text{cm}^2$.

An expansion of stable isotope chemistry facilities has been initiated. One of the reasons for this expansion is the attenuation of production of isotopes and related chemical recovery operations at Y-12. Isotope residuals must be reclaimed from sample preparations whenever possible. Also, chemistry services previously available in other laboratories, for example, conversion of one compound form to another, have been curtailed, and these services are frequently requested by our customers. Finally, the volume of general inorganic chemistry activity normally performed by IRML has increased significantly so that present facilities are marginal at best.

BASIC CHEMICAL COMPATIBILITY OF THORIUM CARBIDES WITH Cr-Fe-Ni ALLOYS

E. C. Beahm¹ C. A. Culpepper

Chemical compatibility of alloy and compound structures formed in mixed fuel systems is being investigated in a cooperative effort with the Chemical Technology Division. Thermodynamic modeling of the fuel-cladding interface is being used to determine the phases present in the interface, or reaction area, between bulk fuel and bulk clad alloy. The result will be a profile of phases expected at equilibrium and the maximum limit of reaction products. This technique allows a screening of a large number of potential cladding alloys and permits an evaluation of maximum cladding carburization.

Thermodynamic calculations of the fuel-cladding interface for the thorium carbides ThC_{0.97}, ThC_{0.90}, and 90% ThC_{0.97} + 10% ThC_{1.94} with the Cr-Fe-Ni compositions of seven alloys have been made. The alloys considered were 316 stainless steel, 330 stainless steel, A286, M813, PE-16, Inconel 706, and Inconel 718. The species considered included all binary compounds in the Th-C-Cr-Fe-Ni system.

To determine if ternary compounds (complex carbides) exist in these systems, alloys of Th-Cr-C and Th-Fe-C were prepared and examined. Six arc-melted samples were prepared containing 25 at. % Th, 42–60 at. % C, and 15–34 at. % Cr or Fe. The samples were characterized by x-ray diffraction and metallography. There was no evidence of ternary compounds in any of the specimens. X-ray diffraction lines indicated the presence of only thorium carbides, chromium carbides, and Fe. These findings substantiate the assumption that only the binary compounds need be considered in the thermodynamic calculation.

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IMPROVED ANALYTICAL CAPABILITIES

W. S. Aaron C. A. Culpepper

During the reporting period, important additions to IRML's analytical capabilities have been secured. An x-ray fluorescence unit is being used to routinely analyze compositions and impurity concentrations of a large variety of base materials and finished products. In particular, it has been used to evaluate pyrochemical separation schemes for both stable and radioactive material mixtures. An electron microprobe was acquired

and will be used for examination of radioactive samples. In addition to IRML programs, the microprobe will be used to examine phases present in fuel-cladding interfaces in support of the reactor fuel compatibility program being conducted jointly by IRML and the Chemical Technology Division. A new SEM equipped with dispersive XFS is being used to provide valuable analytical information needed in both the cermet and T separation development programs. In the cermet program, the SEM/XFS system is used to examine particle size, oxide

dispersion, as well as chemical composition and distribution in the cermets. It is also used to examine bipolar electrodes in the T separation program. The effects of electrode surface structures, reaction products, and impurities on cell performance can be determined with the SEM/XFS system. The additional analytical equipment provides IRML with more nondestructive analytical techniques to characterize both production and research samples.

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PATENTS

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- C. W. White, D. L. Sims, and P. K. Skurkiss, *Patterned Chromate Film Process*, U.S. patent No. 4,077,851 (March 7, 1978).

PAPERS PRESENTED AT TECHNICAL MEETINGS

American Vacuum Symposium, Detroit, Michigan, May 17, 1977:

- D. M. Zehner, "Recent and Possible Applications of Auger Electron Spectroscopy" (invited paper)

International Conference on Borate Glasses, Alfred, New York, June 5-8, 1977:

- R. A. Weeks, "Future Directions of Research in Borate Glasses" (invited paper)

International Discussion Meeting on Radiation Effects on Superconductivity, Argonne National Laboratory, June 13-16, 1977:

- T. L. Francavilla, B. N. Das, D. U. Gubser, R. A. Meussner, and S. T. Sekula, "Neutron Irradiation and Annealing Studies of V₃Ga"

- H. R. Kerchner, R. R. Colman, Jr., C. E. Klabunde, and S. T. Sekula, "Low-Temperature Irradiation of Niobium with 15-MeV Neutrons"

- J. M. Poate, L. R. Testardi, W. Weber, W. M. Augustyniak, and J. H. Barrett, "Temperature Dependence of Atomic Displacements in V₃Si"

- S. T. Sekula, "Effect of Irradiation on the Critical Currents of Alloy and Compound Superconductors" (invited paper)

Third International Conference on Ion Beam Analysis, Washington, D.C., June 27-July 1, 1977:

- John H. Barrett, "Studies of Defects and Surfaces by Channeling" (invited paper)

- G. J. Clark, C. W. White, D. D. Allred, B. R. Appleton, F. B. Koch, and C. W. Magee, "The Application of Nuclear Reactions for Quantitative Hydrogen Analysis in a Variety of Different Materials Problems"

- C. W. White, "Ion-Induced Optical Emission for Surface and Depth Profile Analysis" (invited paper)

J. F. Ziegler, C. P. Wu, P. Williams, C. W. White, B. Terreault, B. M. U. Scherzer, R. L. Schulte, E. J. Schneid, C. W. Magee, E. Ligeon, J. L'Ecuier, W. A. Lanford, F. J. Kuchne, E. A. Kamykowski, W. O. Hofer, A. Guivarch, C. H. Filleux, V. R. Deline, C. A. Evans, Jr., B. L. Cohen, G. J. Clark, W. K. Chu, C. Brassard, R. S. Blewer, R. Behrisch, B. R. Appleton, and D. D. Allred, "Profiling Hydrogen in Materials Using Ion Beams"

R. A. Zuhr, L. C. Feldman, R. L. Kauffman, and P. J. Silverman, "Surface Scattering from W Single Crystals by MeV He"

European Physical Society Meeting, Leeds, England, July 26-29, 1977:

L. A. Boatner and U. T. Höchli, "Local Charge Compensation and Electronic Transport in $\text{KTaO}_3:\text{Cu}^{2+}$ and $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3:\text{Cu}^{2+}$ "

International Conference on the Physics of Transition Metals, Toronto, Canada, August 15-19, 1977:

H. A. Mook, "Panel Discussion: Fundamental Problems of Itinerant Electron Magnetism"

H. G. Smith, "Panel Discussion: Soft Modes, Lattice Instabilities, and High T_c Superconductivity"

Thirty-Fifth Annual Meeting of the Electron Microscopy Society of America, Boston, Massachusetts, August 22-26, 1977:

J. Narayan and S. M. Ohr, " $\alpha(100)$ Dislocation Loops in MgO"

S. M. Ohr, "Image Contrast of Dislocation Loops near a Free Surface"

International Conference on Lattice Dynamics, Paris, France, September 5-10, 1977:

Shashikala G. Das, S. K. Sinha, and N. Wakabayashi, "Microscopic Theory of Charge Density Wave Instability in NbSe_2 "

Seventh International Vacuum Congress and Third International Conference on Solid Surfaces, Vienna, Austria, September 12-16, 1977:

D. M. Zehner and J. F. Wendelken, "Anomalous Au(111) Surfaces Studied by LEED, AES and Oxygen Chemisorption"

Seventh International Conference on Atomic Collisions in Solids, Moscow, USSR, September 19-23, 1977:

B. R. Appleton, "Applications of Channeling to Surface Studies" (invited paper)

B. R. Appleton, O. W. Holland, and J. H. Barrett, "Well-Channelled Ions with Greater-Than-Random Energy Loss Rates"

R. Behrisch, G. Maderlechner, B. M. U. Scherzer, and M. F. Robinson, "The Sputtering Mechanism for Low-Energy Light Ions"

Marc Hou and Mark T. Robinson, "Computer Simulation of the Grazing Incidence Backscattering of Protons from a (110) Nickel Surface"

O. S. Oen, "Some Analytical Solutions to the Two-Atom Blocking Model"

J. B. Roberto and Mark T. Robinson, "A Measurement of the Transverse Range of $(n,2n)$ Recoils in Au"

1977 Joint Fall Meeting of the Nuclear and Basic Science Division, The American Ceramic Society, Hyannis, Massachusetts, September 25-28, 1977:

H. L. Adair, E. H. Kobink, and T. C. Quinby, "Preparation and Characterization of Fissile and Fertile Nuclide Forms for Use as Neutron Dosimeters"

International Photovoltaic Solar Energy Conference, Luxembourg, September 27-30, 1977:

R. T. Young, C. W. White, G. J. Clark, J. Narayan, R. D. Westbrook, and W. H. Christie, "Laser-Annealed Boron-Implanted Silicon Solar Cells"

Fourth International Conference on Small-Angle Scattering of X-Rays and Neutrons, Gatlinburg, Tennessee, October 3-7, 1977:

H. R. Child and S. Spooner, "New Small-Angle Neutron Scattering (SANS) Instrument at ORNL Using a Position-Sensitive Area Detector"

H. R. Child and S. Spooner, "Small-Angle Neutron Scattering from Voids in Neutron-Irradiated Type 304 Stainless Steel"

D. K. Christen, S. Spooner, P. Thorel, and H. R. Kerkner, "Determination of Low-Field Critical Parameters of Superconducting Niobium by Small-Angle Neutron Diffraction"

S. Spooner and H. R. Child, "Small-Angle Neutron Scattering Study of Faceted Voids with the Borkowski-Kopp Area-Sensitive Proportional Counter"

S. Spooner, H. R. Child, and F. W. Wiffen, "Small-Angle Neutron Scattering of Reactor-Irradiated Niobium"

P. Thorel and D. K. Christen, "Anisotropy in the Flux Line Lattice Symmetry of a Low- κ Type-II Superconductor"

Second ASTM-EURATOM Symposium on Reactor Dosimetry: Dosimetry Methods for Fuels, Cladding, and Structural Materials, Palo Alto, California, October 3-7, 1977:

H. L. Adair, F. H. Kobisk, J. A. Setaro, T. C. Quinby, and J. M. Dailey, "Dosimeter Sample Preparation, Quality Assurance, and Materials Development for the ILRk, FRMDC, and FFTF Dosimetry Programs"

DOE Photovoltaics Advanced Materials Review Meeting, Denver, Colorado, October 4-6, 1977:

J. W. Cleland, J. Narayan, R. D. Westbrook, C. W. White, and R. T. Young, "Solar Cells from Ion-Implanted, Laser-Annealed Silicon"

Ninth Southeastern Magnetic Resonance Conference, Atlanta, Georgia, October 5-7, 1977:

J. L. Boldu, H. J. Stapleton, Y. Chen, and M. M. Abraham, "ENDOR of V_{OD} Defects in SrO "

International Conference on Defects in Insulating Crystals, Gatlinburg, Tennessee, October 9-14, 1977:

J. B. Bates, "Resonance Raman Scattering from Metastable Oxygen Species in Irradiated $NaClO_3$ "

J. B. Bates and R. F. Wood, "Raman Scattering from F Centers in CaO "

J. L. Boldu, H. J. Stapleton, Y. Chen, and M. M. Abraham, "ENDOR of V_{OD} Defects in SrO "

Y. Chen, "Radiation Effects in MgO " (invited paper)

Y. Chen, H. T. Tohver, J. Narayan, and M. M. Abraham, "Production and Stability of $[Li]^0$ Defects in MgO Single Crystals"

Herbert Engstrom, "Intensity of Polarized Raman Scattering from Metastable O_2^* in Gamma-Irradiated Sodium Chlorate"

F. A. Modine, "Optical Dichroisms of $[Li]^0$ Defects in MgO "

J. Narayan, M. M. Abraham, Y. Chen, and H. T. Tohver, "Transmission Electron Microscope Studies of Li-Doped MgO "

J. Narayan, R. A. Weeks, and E. Sonder, "Electrical Conduction-Induced Aggregation of Defects and Thermal Breakdown in MgO "

R. M. Nicklow and W. P. Crummett, "The Temperature Dependence of Phonon-Defect Mode Hybridization in $KCl(CN)$ "

M. Rappaz, C. Solliard, L. A. Boatner, and A. Châtelain, "EPR Observation of Size Effects in Small Dielectric Particles of $SrCl_2:Gd^{3+}$ "

E. Sonder, F. A. Modine, and R. A. Weeks, "Determination of Fe^{2+} and Fe^{3+} Concentration in MgO "

J. C. Wang, "Locations of the Conducting-Ion Site Near the Mid-Oxygen Position in Beta-Aluminas"

R. A. Weeks, E. Sonder, J. C. Pigg, and K. F. Kelton, "Electric Field-Induced Changes in Conductivity of MgO at High Temperature"

T. M. Wilson and R. F. Wood, "Electronic Structure of the F^+ Center in Alkaline Earth Oxides"

Sixth Annual Conference of the International Target Development Society, Berkeley, California, October 19-21, 1977:

H. L. Adair, "Preparation and Characterization of ^{241}Am and ^3H Targets"

Twenty-third Annual Conference on Magnetism and Magnetic Materials, Minneapolis, Minnesota, November 8-11, 1977:

J. W. Cable, "Local Environment Effects in Disordered Alloys" (invited paper)

J. F. Cooke and P. A. Lindgard, "Canonical Transform Theory of Spin-Waves in Strongly Anisotropic Magnets"

H. A. Mook, "Magnetic Excitations in Amorphous Ferromagnets" (invited paper)

R. M. Moon, W. C. Koehler, D. B. McWhan, and F. Holtzberg, "Induced Magnetic Form Factor of Sm in Mixed-Valence Compounds" (invited paper)

N. Wakabayashi, R. M. Nicklow, and H. R. Child, "Spin Waves in Ferromagnetic $\text{Tb}_{0.78}\text{Y}_{0.24}$ "

Twenty-fourth National Vacuum Symposium of the American Vacuum Society, Boston, Massachusetts, November 8-11, 1977:

H. H. Madden, D. M. Zehner, and J. R. Noonan, "Atomic-Model and Valence-Band Features in the MVV Auger Spectra of Copper"

J. R. Noonan, H. L. Davis, and L. H. Jenkins, "LEED Analysis of a Cu(110) Surface"

M. V. K. Ulehla and H. L. Davis, "Some Effects of Anisotropic Vibrations in LEED"

Southeastern Section Meeting, American Physical Society, Miami, Florida, November 21-23, 1977:

R. L. Chaplin, R. R. Coltman, Jr., and J. K. Redman, "The Contribution of Damage and Transmutations to the Resistivity of Reactor-Irradiated Copper" [*Bull. Am. Phys. Soc.* 22, 1255 (1977)]

Y. Chen, "Radiation Damage in Magnesium Oxide" [*Bull. Am. Phys. Soc.* 22, 1245 (1977)] (invited paper)

R. R. Coltman, Jr., J. K. Redman, and R. L. Chaplin, "Fast-Neutron Damage Rates in Copper Near Room Temperature" [*Bull. Am. Phys. Soc.* 22, 1255 (1977)]

J. B. Lacy, H. T. Tohver, M. M. Abraham, J. L. Boldu, Y. Chen, and J. Narayan, "Atmospheric Dependence of Stable $[\text{Li}]^0$ -Center Formation in MgO at High Temperatures" [*Bull. Am. Phys. Soc.* 22, 1256 (1977)]

Radioactive Effluents from Nuclear Fuel Reprocessing Plants Seminar, Karlsruhe, Germany, November 22-25, 1977:

E. H. Kobisk, "Separation of Tritium from Gaseous and Aqueous Effluent Systems" (invited paper)

Winter Meeting, American Nuclear Society, San Francisco, California, November 29, 1977:

T. J. Hoffman, H. L. Dodds, Jr., M. T. Robinson, and D. K. Holmes, "Sputtering Calculations with the Discrete Ordinates Method"

Materials Sciences Program Solar Energy Workshop, Ames, Iowa, November 29-30, 1977:

J. W. Cleland, "Neutron Transmutation Doped Silicon and Its Use in Photovoltaic Devices"

R. F. Wood, "Overview of Solid State Division, ORNL, Photovoltaic Program"

R. T. Young, "Solar Cells from Boron-Implanted, Laser-Annealed Silicon"

Annual Meeting, American Mathematical Society, Atlanta, Georgia, January 5-8, 1978:

L. J. Gray and Theodore Kaplan, "Elementary Excitations in Disordered Alloys" [*Notes Am. Math. Soc.* 25, A165 (1978)] (invited paper)

Union Carbide Corporation Nuclear Division Conference on Waste Management, Oak Ridge, Tennessee, January 25-26, 1978:

E. H. Kobisk, "Tritium Concentration by Bipolar Electrolysis"

Symposium on Atomic Surface Physics (SASP), Innsbruck, Austria, February 20-22, 1978:

R. Behrisch, G. Maderlechner, B. M. U. Scherzer, and M. T. Robinson, "Sputtering Calculations for Low-Energy Light Ions"

O. S. Oen and M. T. Robinson, "Computer Simulation of the Reflection of Hydrogen and Tritium from Solid Surfaces"

Annual AIME Meeting, Denver, Colorado, February 27-March 1, 1978:

R. W. Hendricks and W. C. Koehler, "The National Small-Angle Neutron Scattering Facility" (invited paper)

J. Narayan and S. M. Ohr, "In-Situ Observation of Crack Propagation by Transmission Electron Microscopy"

S. Spooner, H. R. Child, and D. K. Christen, "Metals Studied at the Oak Ridge National Laboratory Small-Angle Neutron Scattering Facilities"

Workshop on Surface Analysis Held at the Pittsburgh Conference on Analytical and Applied Spectroscopy, Cleveland, Ohio, February 28, 1978:

D. M. Zehner, "Angular Emission Effect in Auger-Electron Spectroscopy" (invited paper)

Waste Management and Fuel Cycles 1978 Symposium, Tucson, Arizona, March 7-9, 1978:

D. W. Ramey, E. H. Kobisk, and M. Petek, "Tritium Extraction from Aqueous Systems"

International Topical Conference on the Physics of SiO₂ and Its Interfaces, Yorktown Heights, New York, March 22-24, 1978:

D. D. Allred, C. W. White, G. J. Clark, B. R. Appleton, and I. S. T. Tsong, "Measurements of Hydrogen Profiles in SiO₂ by a Nuclear Reaction Technique" [*Bull. Am. Phys. Soc.* 23, 456 (1978)]

Joint March Meeting of the American Physical Society and the Biophysical Society, Washington, D.C., March 27-30, 1978:

B. Alefeld, N. Wakabayashi, H. G. Smith, and W. Bührer, "Lattice Dynamics Near the Order-Disorder Phase Transition of NaO₂" [*Bull. Am. Phys. Soc.* 23, 237 (1978)]

B. R. Appleton, O. E. Schow III, and D. M. Zehner, "Investigations of Reordered and Relaxed Au(001) Surfaces by PICS, LEED, and Computer Simulations" [*Bull. Am. Phys. Soc.* 23, 389 (1978)]

John H. Barrett, "Analysis of Measurements of Ion Scattering from Surfaces" [*Bull. Am. Phys. Soc.* 23, 389 (1978)]

J. B. Bates, T. Kaneda, and J. C. Wang, "Raman Scattering from NH₄⁺ and ND₄⁺ Ions in Beta-Alumina" [*Bull. Am. Phys. Soc.* 23, 243 (1978)]

J. B. Bates, R. A. Perkins, and J. C. Wang, "Mechanism for Hydrogen Diffusion in TiO₂ (Rutile)" [*Bull. Am. Phys. Soc.* 23, 212 (1978)]

L. A. Boatner and U. T. Höchli, "Phase Diagrams and Dipolar Interaction in Mixed-Crystal KTaO₃-Type Ferroelectrics" [*Bull. Am. Phys. Soc.* 23, 197 (1978)]

J. L. Boldu, M. M. Abraham, and Y. Chen, "Valence Compensation of Thermally Generated [Li]⁰ Defects in MgO" [*Bull. Am. Phys. Soc.* 23, 255 (1978)]

R. L. Cappelletti, W. A. Kamitakahara, and N. Wakabayashi, "Phonon Dispersion and Specific Heat Measurements in a Superconducting Zr-Nb-Mo Alloy" [*Bull. Am. Phys. Soc.* 23, 276 (1978)]

Y. K. Chang, F. W. Young, Jr., G. W. Crabtree, and R. J. Higgins, "A de Haas-van Alphen Effect Study of Dislocation Loops in Copper" [*Bull. Am. Phys. Soc.* 23, 256 (1978)]

Y. Chen, M. M. Abraham, J. Narayan, and H. T. Tolver, "A Model to Account for the High Stability of the [Li]⁺ Defect in MgO" [*Bull. Am. Phys. Soc.* 23, 255 (1978)]

D. K. Christen and P. Thorel, "Direct Observation of the Equilibrium Misalignment between Fluxoids and an Applied Magnetic Field Due to Anisotropic Effects in Superconducting Niobium" [*Bull. Am. Phys. Soc.* 23, 229 (1978)]

J. W. Cleland, R. T. Young, R. D. Westbrook, R. F. Wood, and P. H. Fleming, "Impurity Interactions in Neutron-Irradiated Boron-Doped Silicon" [*Bull. Am. Phys. Soc.* 23, 289 (1978)]

J. F. Cooke, "Dielectric Response Theory and the Phonon Spectra of Niobium" [*Bull. Am. Phys. Soc.* 23, 276 (1978)]

W. P. Crummett, H. G. Smith, R. M. Nicklow, and N. Wakabayashi, "Lattice Dynamics of Alpha-Uranium" [*Bull. Am. Phys. Soc.* 23, 275 (1978)]

H. Engstrom and J. B. Bates, "Raman and Infrared Investigation of Boron-Implanted, Laser-Annealed Silicon" [*Bull. Am. Phys. Soc.* 23, 393 (1978)]

J. M. Fournier, A. Delapalme, G. H. Lander, R. Pynn, N. Wakabayashi, and R. M. Nicklow, "Low-Temperature Phonon Measurements in Alpha Uranium" [*Bull. Am. Phys. Soc.* 23, 275 (1978)]

T. Gould, C. Stassis, and R. Nicklow, "Lattice Dynamics of γ -Ce" [*Bull. Am. Phys. Soc.* 23, 275 (1978)]

L. E. Halliburton, M. C. Wintersgill, J. J. Martin, W. A. Sibley, and R. A. Weeks, "The E_4' Center in Quartz" [*Bull. Am. Phys. Soc.* 23, 254 (1978)]

R. W. Hendricks and W. C. Koehler, "The National Small-Angle Neutron Scattering Facility" [*Bull. Am. Phys. Soc.* 23, 371 (1978)]

T. Kaneda, J. B. Bates, and J. C. Wang, "Raman Scattering from Li⁺ Ions in Beta-Alumina" [*Bull. Am. Phys. Soc.* 23, 243 (1978)]

Theodore Kaplan, Mark Mostoller, and L. J. Gray, "A Calculation of Neutron Scattering Cross Sections for Rb_{1-x}K_x Alloys Using the Augmented Space Formalism" [*Bull. Am. Phys. Soc.* 23, 236 (1978)]

H. R. Kerchner and S. T. Sekula, "AC Response of a Hard Superconductor in the Presence of Flux Creep" [*Bull. Am. Phys. Soc.* 23, 230 (1978)]

C. E. Klabunde, R. R. Coltman, Jr., J. K. Redman, and J. M. Williams, "Fission Neutron Damage Rates in Metals at 4.7 K" [*Bull. Am. Phys. Soc.* 23, 288 (1978)]

B. C. Larson, C. W. White, and B. R. Appleton, "Lattice Contraction in Boron-Implanted, Laser-Annealed Silicon" [*Bull. Am. Phys. Soc.* 23, 393 (1978)]

H. H. Madden and D. M. Zehner, "The KVV Auger Lineshape of Beryllium" [*Bull. Am. Phys. Soc.* 23, 335 (1978)]

D. B. McWhan, S. M. Shapiro, J. Eckert, H. A. Mook, and R. J. Birgeneau, "Pressure Dependence of Magnetic Excitations in SmS" [*Bull. Am. Phys. Soc.* 23, 231 (1978)]

J. Narayan, "A New Defect (Dislocations of $a(100)$ Burgers vector) in MgO" [*Bull. Am. Phys. Soc.* 23, 199 (1978)]

J. Narayan, R. T. Young, and C. W. White, "A Comparative Study of Laser and Thermal Annealing of Boron-Implanted Silicon" [*Bull. Am. Phys. Soc.* 23, 392 (1978)]

R. M. Nicklow, W. P. Crummett, and J. M. Williams, "Phonon Perturbations in Irradiated Copper" [*Bull. Am. Phys. Soc.* 23, 236 (1978)]

T. S. Noggle, J. M. Williams, B. R. Appleton, and G. Vogl, "Damage Production Rates Versus Ion Penetration Depth in Al" [*Bull. Am. Phys. Soc.* 23, 287 (1978)]

J. R. Noonan, H. L. Davis, and L. H. Jenkins, "Six-Beam LEED Analysis of the Cu(110) Surface" [*Bull. Am. Phys. Soc.* 23, 391 (1978)]

S. M. Ohr, "Electron Microscope Studies of Stage III Recovery of Electron-Irradiated Copper" [*Bull. Am. Phys. Soc.* 23, 288 (1978)]

J. B. Roberto, B. Schönfeld, and P. Ehrhart, "Investigation of Interstitial Clustering in Electron-Irradiated Al" [*Bull. Am. Phys. Soc.* 23, 288 (1978)]

H. G. Smith and N. Wakabayashi, "Electron-Phonon Interactions in Nb and Mo: Experiment" [*Bull. Am. Phys. Soc.* 23, 277 (1978)]

E. Sonder and R. A. Weeks, "Electrical Conduction in Iron-Doped MgO at Elevated Temperature" [*Bull. Am. Phys. Soc.* 23, 210 (1978)]

M. V. K. Ukhla and H. L. Davis, "A Method for Including Anisotropic Vibrations in LEED Calculations" [*Bull. Am. Phys. Soc.* 23, 391 (1978)]

N. Wakabayashi, H. G. Smith, K. C. Woo, and F. C. Brown, "Phonon Spectra in $I-T\text{TiSe}_2$ " [*Bull. Am. Phys. Soc.* 23, 245 (1978)]

J. C. Wang, J. B. Bates, and T. Kaneda, "Recent Developments of Model Calculations on Li Beta-Alumina" [*Bull. Am. Phys. Soc.* 23, 241 (1978)]

J. C. Wang and R. F. Wood, "Theoretical Investigation of Laser Annealing of Ion-Implanted Silicon" [*Bull. Am. Phys. Soc.* 23, 393 (1978)]

R. A. Weeks, E. Sonder, and W. H. Gourdin, "Aggregations of Fe^{3+} in MgO Single Crystals" [*Bull. Am. Phys. Soc.* 23, 245 (1978)]

J. M. Williams, T. S. Noggle, B. R. Appleton, O. E. Schow III, and G. Vogl, "Annealing of Ion Radiation Damage in Thin Films of Al" [*Bull. Am. Phys. Soc.* 23, 287 (1978)]

C. Wood, J. Woosley, E. Sonder, and R. A. Weeks, "Photoconductivity in Spinel" [*Bull. Am. Phys. Soc.* 23, 413 (1978)]

Rosa T. Young, "Laser Annealing of Ion-Implanted Silicon" [*Bull. Am. Phys. Soc.* 23, 264 (1978)] (invited paper)

R. T. Young, J. N. Nayan, C. W. White, and R. F. Wood, "Dissolution of Boron Precipitates in Boron-Diffused Silicon by Laser Irradiation" [*Bull. Am. Phys. Soc.* 23, 392 (1978)]

D. M. Zehner, B. R. Appleton, and O. E. Schow III, "Structure Determination of Au(001) Surfaces by PICS, LEED, AES, and Computer Simulations" [*Bull. Am. Phys. Soc.* 23, 389 (1978)]

Swiss Physical Society Meeting, Neuchatel, Switzerland, March 30-31, 1978:

D. Rytz, L. A. Boatner, A. Châtelain, U. T. Höchli, and K. A. Mueller, "Octahedral Potential in $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ for a $^{56}\text{Fe}^{3+}$ Ion"

Workshop in Polymer Physics, Washington, D.C., March 31-April 1, 1978:

W. C. Koehler, "Plans for NSF-ORNL National Small-Angle Scattering Facility" (invited paper)

Third International Conference on Plasma Surface Interactions in Controlled Fusion Devices, Abingdon, Oxfordshire, United Kingdom, April 3-7, 1978:

O. S. Oen and M. T. Robinson, "Computer Simulation of the Reflection of Hydrogen and the Sputtering of Hydrogen from Metal Hydrides"

First Annual Symposium on Materials Problems Associated with Solar Energy, Tempe, Arizona, April 12-14, 1978:

F. W. Young, Jr., "Solar Cells from Ion-Implanted and Laser-Annealed Silicon" (invited paper)

American Geophysical Union Annual Meeting, Miami, Florida, April 17-21, 1978:

R. A. Weeks and E. Sonder, "Effect of Electric Fields on Electrical Conductivity in Mg and Aluminum Oxide Systems" [EOS 59, 397 (1978)]

ORNL-Osaka University Cooperative Science Program Meeting, Osaka, Japan, April 18-27, 1978:

W. C. Koehler, "Brief Description of the Small-Angle Scattering Center" (invited paper)

W. C. Koehler, "Recent Magnetic Scattering Experiments at ORNL" (invited paper)

R. M. Nicklow, "Hybridization of Phonons and the Internal Modes of Complex Impurities" (invited paper)

H. G. Smith, "Phonon Spectra, Lattice Instabilities, and Superconductivity" (invited paper)

N. Wakabayashi, "Charge Fluctuation Model of Lattice Vibrations" (invited paper)

Second International Conference on Neutron Transmutation Doping of Semiconductors, Columbus, Missouri, April 23-26, 1978:

J. W. Cleland, P. H. Fleming, B. C. Larson, J. Narayan, R. D. Westbrook, R. F. Wood, and R. T. Young, "Studies of Neutron-Transmutation-Doped Silicon at the Oak Ridge National Laboratory"

R. F. Wood, R. D. Westbrook, R. T. Young, and J. W. Cleland, "Solar Cell Applications of NTD Silicon"

American Ceramic Society Meeting, Detroit, Michigan, May 6-11, 1978:

R. H. Kernohan, "Radiation Effects on Insulators for Superconducting Magnets" [Am. Ceram. Soc. Bull. 57, 355 (1978)]

J. Narayan, M. M. Abraham, Y. Chen, and H. T. Tohver, "Precipitates in Li-Doped MgO" [Am. Ceram. Soc. Bull. 57, 305 (1978)]

H. T. Tohver, J. B. Lacy, M. M. Abraham, J. L. Boldu, Y. Chen, and J. Narayan, "Atmospheric Dependence of Stable [Li]⁰ Defect Formation in MgO:Li Crystals at High Temperatures" [Am. Ceram. Soc. Bull. 57, 314 (1978)]

R. A. Weeks, E. Sonder, and J. Narayan, "Thermal-Electric Breakdown Processes in Crystals of the Mg-Al Oxide System" [Am. Ceram. Soc. Bull. 57, 316 (1978)]

United States-Japan Seminar on Fundamentals and Applications of Particle Channeling, Tokai, Japan, May 8-13, 1978:

B. R. Appleton, "PICS Investigations of Reordered and Relaxed Au Single-Crystal Surfaces" (invited paper)

B. R. Appleton, "Well-Channeled Ions with Greater-Than-Random Energy Loss Rates" (invited paper)

Third ANS Topical Meeting on the Technology of Controlled Nuclear Fusion, Santa Fe, New Mexico, May 9-11, 1978:

B. R. Appleton, W. Bauer, S. A. Cohen, R. W. Conn, and M. J. Davis, "The Role of Plasma Material Interaction in the Magnetic Fusion Program"

D. G. Doran, N. Farrar, IV, A. N. Goland, L. R. Greenwood, R. R. Heinrich, F. V. Nolfi, G. R. Odette, D. M. Parkin, T. C. Reuther, M. T. Robinson, F. A. Smidt, J. A. Sprague, R. R. Vandervoort, and P. Wilkes, "The Damage Analysis and Fundamental Studies Program"

Eighth Conference on Surface Studies, Aiken, South Carolina, May 9-11, 1978:

J. F. Wendelken, "ELS Vibrational Studies of Simple Adsorbates on Cu(110) and Al(100)"

D. M. Zehner, "Investigations of Normal and Reordered Au(001) Surfaces by PICS, LEED, AES, and Computer Simulations"

Symposium on Application of Ion Beams to Materials Science, Wakoh-shi, Japan, May 15-16, 1978:

B. R. Appleton, "Surface Structure Studies with Ion Beams" (invited paper)

Electrochemical Society Meeting, Seattle, Washington, May 21-26, 1978:

R. D. Westbrook and J. W. Cleland, "Lifetime Control in Silicon" [*J. Electrochem. Soc.* 125, 144C (1978)]

Electrochemical Society Meeting, Strategies for Environmental Planning Symposium, Seattle, Washington, May 21-26, 1978:

D. W. Ramey, M. Petek, E. H. Kobisk, and S. D. Nelson, "Electrochemical Separation of Tritium from Aqueous Effluent Systems"

Electrochemical Society Topical Conference on Characterization Techniques for Semiconductor Materials and Devices, Seattle, Washington, May 21-26, 1978:

J. Narayan, R. T. Young, and C. W. White, "Transmission Electron Microscope Studies of Laser- and Thermally Annealed Ion-Implanted Silicon"

C. W. White, W. H. Christie, R. E. Eby, J. C. Wang, R. T. Young, and G. J. Clark, "Redistribution of Ion-Implanted Boron Induced by Pulsed Laser Annealing"

R. T. Young, C. W. White, J. Narayan, G. J. Clark, and W. H. Christie, "Characterization of Boron-Implanted, Laser-Annealed Silicon"

National Research Council Solid State Sciences Committee and Panel Spring Meeting, Oak Ridge, Tennessee, June 1-2, 1978:

B. R. Appleton, "Use of Ion Beams for Materials Analysis" (invited paper)

J. F. Cooke, "Excitations in Superconductors and Ferromagnets" (invited paper)

H. L. Davis, "Geometric and Electronic Structures of Surfaces" (invited paper)

R. M. Moon, "Solid State Research with High-Intensity Neutron Beams" (invited paper)

M. T. Robinson, "Radiation Effects in Metals" (invited paper)

C. W. White, "Laser Annealing of Ion-Implanted Silicon" (invited paper)

Thirteenth IEEE Photovoltaic Specialists Conference, Washington, D.C., June 5-8, 1978:

R. T. Young, J. Narayan, C. W. White, J. W. Cleland, W. H. Christie, and R. F. Wood, "Effects of Laser irradiation on a Diffused Layer in Silicon"

R. T. Young, C. W. White, J. Narayan, R. D. Westbrook, R. F. Wood, and W. H. Christie, "Solar Cells from Laser-Annealed Ion-Implanted Silicon"

Thirty-eighth Annual Conference on Physical Electronics, Gatlinburg, Tennessee, June 19-21, 1978:

H. H. Madden and D. M. Zehner, "Analysis of Electron Energy-Loss Spectra from Beryllium"

International Cryogenic Materials Conference: Special Seminar on Nonmetallic Materials and Composites at Low Temperatures, Munich, Germany, July 10-11, 1978:

C. J. Long, R. H. Kernohan, and R. R. Colman, Jr., "Radiation Effects on Insulators for Superconducting Magnets"

Fourth American Conference on Crystal Growth, Gaithersburg, Maryland, July 16-19, 1978:

L. A. Boatner, M. M. Abraham, and Y. Chen, "Arc Fusion Growth of Y_2O_3 Single Crystals"

Y. K. Chang, "Crystal Growth of A-15 Compounds by Electron Beam Float Zone Method"

J. Narayan, "Investigation of Defects in Crystals by Electron Microscopy" (invited paper)

J. Narayan and F. W. Young, Jr., "Dislocation Near the Interface of Electrodeposited Copper and Nickel Single Crystals"

Gordon Conference on Electron Spectroscopy, Wolfeboro, New Hampshire, July 17-21, 1978:

H. L. Davis, "Aspects of Angular Resolved Auger Spectroscopy" (invited paper)

NATO Advanced Studies Institute, Albany, New York, July 24-August 5, 1978:

S. R. Wilson, C. W. White, P. P. Pronko, and B. R. Appleton, "Profile Changes and Lattice Locations of Ion-Implanted As and Sb in Silicon After Pulsed Laser Annealing"

Ninth International Congress on Electron Microscopy, Toronto, Canada, August 1-9, 1978:

J. Narayan and S. M. Ohr, "In Situ Studies of Fracture in Solids"

S. M. Ohr, "Image Contrast of Dislocation Loops in Anisotropic Cubic Crystals"

Eleventh International Congress of Crystallography, Warsaw, Poland, August 3-11, 1978:

M. K. Wilkinson, "Crystallographic Contributions to the Energy Problem" (invited paper)

Gordon Conference on Particle-Solid Interactions, Andover, New Hampshire, August 7-11, 1978:

John H. Barrett, "Interpretation of MeV Ion Scattering Measurements from Gold Surfaces"

IPNS Radiation Effects Workshop, Argonne, Illinois, August 17-18, 1978:

R. R. Colman, Jr., "Neutron Irradiation Facilities at the ORNL Bulk Shielding Reactor"

Fifteenth International Conference on Low Temperature Physics, Grenoble, France, August 23-29, 1978:

H. A. Mook, T. Penney, F. Holtzberg, and M. W. Shafer, "Magnetic Excitations in the Intermediate Valence System $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$ "

International Workshop on Laser Effects in Ion-Implanted Semiconductors, Catania, Italy, August 31-September 2, 1978:

J. Narayan, C. W. White, and R. T. Young, "Electron Microscope Studies of Ion-Implanted, Laser-Annealed Silicon"

J. Narayan, R. T. Young, R. F. Wood, C. W. White, and W. H. Christie, "p-n Junction Formation by Laser-Induced Diffusion"

C. W. White, "Properties of Laser-Irradiated Layers (Summary)" (invited paper)

C. W. White, W. H. Christie, P. P. Pronko, B. R. Appleton, S. R. Wilson, J. C. Wang, R. F. Wood, and C. W. Magee, "Changes in Dopant Profiles by Pulsed Laser Annealing of Ion-Implanted Silicon"

C. W. White, J. Narayan, B. R. Appleton, P. P. Pronko, S. R. Wilson, B. C. Larson, and R. T. Young, "Characterization of Ion-Implanted, Laser-Annealed Silicon"

International Conference on Ion Beam Modification of Materials, Budapest, Hungary, September 4-8, 1978:

J. Narayan, R. T. Young, and C. W. White, "Laser and Thermal Annealing of Boron, Phosphorus, Arsenic, and Antimony-Implanted Silicon"

C. W. White, W. H. Christie, P. P. Pronko, B. R. Appleton, S. R. Wilson, R. T. Young, J. C. Wang, R. F. Wood, and C. W. Magee, "Dopant Profile Changes Induced by Pulsed Laser Annealing of Ion-Implanted Silicon"

C. W. White, P. P. Pronko, B. R. Appleton, and S. R. Wilson, "Lattice Location of Ion-Implanted As and Sb in Silicon after Pulsed Laser Annealing"

R. T. Young, J. Narayan, C. W. White, P. P. Pronko, B. R. Appleton, S. R. Wilson, and P. M. Mooney, "Characterization of Ion-Implanted, Laser-Annealed Silicon"

World Conference of the International Nuclear Target Development Society, Munich, Germany, September 11-14, 1978:

H. L. Adair, "Preparation and Characterization of Radioactive Targets for Various Areas of Research" (invited paper)

E. H. Kobisk and H. L. Adair, "Conversion of Isotope Compounds to Metals by Reduction-Distillation Methods" (invited paper)

International Conference on Solids and Plasmas in High Magnetic Fields, Cambridge, Massachusetts, September 15-21, 1978:

R. M. Moon, "Polarized Neutron Diffraction in High Magnetic Fields" (invited paper)

1978 Applied Superconductivity Conference, Pittsburgh, Pennsylvania, September 25-28, 1978:

J. M. Williams, C. E. Klabunde, J. K. Redman, P. R. Coltman, Jr., and R. L. Chaplin, "The Effects of Irradiation on the Copper Normal Metal of a Composite Superconductor"

Seminars

SOLID STATE DIVISION SEMINARS AT ORNL

J. F. Cooke served as Seminar Chairman during the period covered by this report. The following seminars were held:

- "A New Theory of Phonon Dispersion and Electron-Phonon Coupling,"¹ W. Weber, Bell Laboratories, Murray Hill, New Jersey
- "Photoemission and Energy Loss Spectroscopy of Surface States on Metal Oxides," V. E. Henrich, Lincoln Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts
- "Aggregation and Mobility of Defects in the Silver Halides," L. M. Slifkin, University of North Carolina, Chapel Hill, North Carolina
- "Dynamics of Radiation Damage in Metals," W. F. Schilling, Kernforschungsanlage, Jülich, Germany
- "Positive Ion Radiation Damage and Radiation Annealing in MgO," R. B. Murray, University of Delaware, Newark, Delaware
- "Heterogeneous Catalysts: CO Oxidation on Ir(111)," S. P. Withrow, California Institute of Technology, Pasadena, California
- "Photoemission from Clean and Overlayered Metal Surfaces," J. B. Danese, University of Pennsylvania, Philadelphia, Pennsylvania
- "Flux Pinning in Selected Type-II Superconducting Model Systems," H. W. Weber, Atomic Institute of the Austrian Universities, Vienna, Austria
- "Neutron Scattering Investigation of the Mixed Valence System Thulium Selenide," H. B. Möller, Research Establishment Risø, Roskilde, Denmark
- "Radiation Damage Studies by Mössbauer Spectroscopy," G. Vogl, Hahn-Meitner Institut, Berlin, Germany
- "Surface Scattering from W Single Crystals by MeV He⁺ Ions," R. A. Zuhr, State University of New York, Albany, New York
- "Theoretical Studies of Chemisorption on Nickel Oxide Surfaces," G. T. Surratt, University of Illinois, Urbana, Illinois
- "The Okorokov Effect?" Y. H. Otsuki, Waseda University, Tokyo, Japan
- "Exchange and Correlation Contributions to the Ground-State Properties of Solids," M. Rasolt, Battelle-Columbus Laboratories, Columbus, Ohio
- "Agglomeration of Point Defects Observed by Diffuse X-ray Scattering," P. Ehrhart, Kernforschungsanlage, Jülich, Germany
- "Superconductivity in Ti₃P Type Compounds," J. O. Willis, Naval Research Laboratory, Washington, D.C.
- "Radiation Damage Threshold Studies by Electron Microscopy," M. Loretto, University of Birmingham, Birmingham, England

- "Recent and Possible Applications of Auger Spectroscopy," D. M. Zehrer, Solid State Division ORNL
- "Inelastic Electron Tunneling: Surface Chemistry at an Interface," S. L. Cunningham, California Institute of Technology, Pasadena, California
- "Ductile Fracture Initiation in Pure Alpha Iron," R. N. Gardner, University of Virginia, Charlottesville, Virginia
- "The Effect of Fluctuations on the Nature of Phase Transitions," S. W. Lovesey, Institut Laue-Langevin, Grenoble, France
- "Local Susceptibilities in Dilute PdNi Alloys Investigated by ^{61}Ni Mössbauer Spectroscopy," J. Fink, Kernforschungszentrum, Karlsruhe, Germany
- "Can Tunneling Levels Explain the Low-Temperature Anomaly in Glasses," J. L. Black, Harvard University, Cambridge, Massachusetts
- "Inelastic Scattering of Ions by Polyatomic Molecules," D. Micha, University of Florida, Gainesville, Florida
- "Ion Bombardment of Sapphire and Rutile," B. Siskind, Argonne National Laboratory, Argonne, Illinois
- "Order-Disorder in the System $\text{SrNd}_2\text{F}_4\text{-Nd}_2\text{S}_3$ by Raman Spectroscopy," P. L. Provenzano, Pennsylvania State University, University Park, Pennsylvania
- "A de Haas-van Alphen (dHvA) Effect Investigation of the Electronic Structure of the Noble Metals and their Dilute Alloys," B. Lengeler, Kernforschungsanlage, Jülich, Germany
- "Surface Studies of Photoelectrolysis and Related Properties of TiO_2 ,"² M. Knotek, Sandia Laboratories, Albuquerque, New Mexico
- "Soft X-ray Spectroscopy of Random Alloys,"³ B. Gyorffy, University of Bristol, Bristol, England
- "Phase-Equilibria in the Binary System Gadolinium-Boron and Extracted Thermochemical Properties," J. H. Blanks, Pennsylvania State University, University Park, Pennsylvania
- "How Neutrons See the Structure of Physisorbed Layers," P. C. Thorel, C.E.N., Grenoble, France
- "Neutron Scattering: A Probe of the Solid State," W. C. Koehler, Solid State Division, ORNL
- "Experimental Evidence for Magnetic Ordering in a Literally Two-Dimensional Monatomic Magnetic Layer," M. Pomerantz, IBM Research Center, Yorktown Heights, New York
- "Some Aspects of the Physics and Technology of Small Clusters of Atoms," A. Châtelain, Ecole Polytechnique, Lausanne, Switzerland
- "Chemical Aspects of Ion Implantation in Solids,"⁴ K. Rössler, Kernforschungsanlage, Jülich, Germany
- "New Heterodiode Solar Energy Converters," S. Wagner, Bell Laboratories, Holmdel, New Jersey
- "Elastic Properties of the Flux Line Lattice in Type-II Superconductors," E. H. Brandt, Max-Planck-Institut für Metallforschung, Stuttgart, Germany, and Ames Laboratory, Ames, Iowa
- "Recent Advances in Secondary Ion Mass Spectrometry," P. Williams, University of Illinois, Urbana, Illinois
- "Dielectric Response of Heterogeneous Solids,"⁵ J. Koringa, Ohio State University, Columbus, Ohio
- "Dielectric Measurements on a New Superionic Conductor Li_3N ," J. Wahl, Max-Planck-Institut für Metallforschung, Stuttgart, Germany
- "Application of Atom Probe to the Radiation Damage Problem," A. Wagner, Cornell University, Ithaca, New York
- "Electron Microscope Studies of Point Defect Clusters in Ion-Irradiated fcc Metals," R. Schindler, Cornell University, Ithaca, New York
- "Solid Phase Epitaxial Growth of Silicon and Germanium," S. S. Lau, California Institute of Technology, Pasadena, California

- "Deformation and Interface Fracture of a Directionally Solidified Eutectic," M. G. Stout, Michigan Technical University, Houghton, Michigan
- "Physical Probes of Cation Diffusion in β -Al Compounds," S. J. Allen, Bell Laboratories, Murray Hill, New Jersey
- "The Pulsed Neutron Source Program at Argonne National Laboratory," J. M. Carpenter, Argonne National Laboratory, Argonne, Illinois
- "Cleavage Studies in the Molybdenum-Niobium System," A. T. Pucino, State University of New York, Stony Brook, New York
- "Microsyntactic Intergrowth in β -Alumina and Related Compounds," H. Sato, Purdue University, West Lafayette, Indiana
- "High Electric Field Transport in Lead Telluride," J. Rozenbergs, University of Linz, Linz, Austria
- "Buckling of Membrane of Human Red Blood Cells: Biological Phenomenon Susceptible to Mathematical Analysis,"³ F. R. N. Nabarro, University of the Witwatersrand, South Africa
- "Electronic States in Random Substitutional Alloys: Theory and Experiment for Cu-Ni and Mo-Nb,"³ G. M. Stocks, Metals and Ceramics Division, ORNL
- "Local Exchange Model of Ferromagnetism,"³ J. Callaway, Louisiana State University, Baton Rouge, Louisiana
- "The Electronic Structure and Chemisorption on d -Band Metal Surfaces,"³ J. R. Smith, General Motors Research Laboratories, Detroit, Michigan
- "Critical Behavior of Percolation Threshold,"³ P. L. Leath, Rutgers University, Piscataway, New Jersey
- "Itinerant Electron Magnetism in Transition Metals,"³ J. F. Cooke, Solid State Division, ORNL
- "The Mixed Valence State,"³ C. M. Varma, Bell Laboratories, Murray Hill, New Jersey
- "The Calculation of Electronic States Near Surfaces,"³ A. R. Williams, IBM Research Center, Yorktown Heights, New York
- "A Summary of Fracture Mechanics Concepts,"³ R. deWit, National Bureau of Standards, Washington, D.C.
- "A Brief Description of the New Heavy-Ion Accelerator Facility," J. B. Ball, Physics Division, ORNL
- "Effect of Pressure and Temperature on Positron Annihilation in Metals and Alloys," J. D. McGervey, Case Western Reserve University, Cleveland Ohio
- "Laser Annealing of Ion-Implanted Silicon," C. W. White, Solid State Division, ORNL
- "Anisotropic Behavior and Magnetoelastic Interactions in Cerium and Actinide Intermetallics," B. R. Cooper, University of West Virginia, Morgantown, West Virginia
- "The Electronic Structure of Actinide Systems as Seen by Neutron Scattering," G. H. Lander, Argonne National Laboratory, Argonne, Illinois
- "New Developments in the Science and Applications of Glass," N. Kriedl, University of Missouri, Rolla, Missouri
- "First Principles Phonon Calculations in Transition Metal Superconductors,"⁵ J. F. Cooke, Solid State Division, ORNL
- "Hybridization Between Phonons and the Internal Modes of CN Impurities in KCl,"⁵ R. M. Nicklow, Solid State Division, ORNL
- "Mixed Valence SmB_6 and Golden SmS , Metals or Insulators," J. W. Allen, Xerox Palo Alto Research Center, Palo Alto, California
- "Electromagnetic Wave Propagation in Small-Particle Composites,"³ D. G. Stroud, Ohio State University, Columbus, Ohio

- "Configurational Thermodynamics of Order-Disorder Reactions,"³ D. de Fontaine, University of California, Los Angeles, California
- "Surface Physics,"³ J. W. Gadzuk, National Bureau of Standards, Washington, D.C.
- "Band Theory,"³ A. C. Switendick, Sandia Laboratories, Albuquerque, New Mexico
- "Theory of Radiation-Induced Swelling in Metals and Alloys,"³ L. K. Mansur, Metals and Ceramics Division, ORNL
- "Fast Interstitial Diffusion,"³ C. P. Flynn, University of Illinois, Urbana, Illinois
- "Critical Point Phenomena,"³ J. Sak, Rutgers University, New Brunswick, New Jersey
- "Light Scattering from Guided Wave Polaritons," K. R. Subbaswamy, University of California, Irvine, California
- "Effect of Surface Film on the Low-Temperature Deformation of Iron Single Crystals," S. Kobayashi, Northwestern University, Evanston, Illinois
- "Equilibrium Misalignment of Fluxoids with an Applied Magnetic Field Due to Anisotropy Effects in Superconducting Niobium,"⁵ D. K. Christen, Solid State Division, ORNL
- "Mechanisms for Diffusion of Hydrogen in Rutile (TiO_2),"⁵ J. B. Bates, Solid State Division, ORNL
- "Surface Structure Studies on Platinum Using MeV Ion Channeling," N. Matsunami, Chalk River Nuclear Laboratories, Chalk River, Ontario, Canada
- "Atomic Profiles of Ion-Implanted Impurities," G. T. Marcyk, University of Illinois, Urbana, Illinois
- "Fracture Mechanics: A Unified View for Griffith-Irwin-Orowan Cracks," J. Weertman, Northwestern University, Evanston, Illinois
- "Studies on Conduction Electron Scattering," R. G. Goodrich, Louisiana State University, Baton Rouge, Louisiana
- "Hydronium and Ammonium Isomorphs of Beta-Alumina," W. L. Roth, General Electric Research and Development Laboratory, Schenectady, New York
- "Inelastic Relaxation of Hydrogen in Niobium Below 10 K," D. B. Pokr, University of Illinois, Urbana, Illinois
- "Light Scattering Study of the RbAg_4I_2 Family of Solid Electrolytes," M. V. Klein, University of Illinois, Urbana, Illinois
- "Experimentation in the Condensed Permanent Gases at High Pressure," W. B. Daniels, University of Delaware, Newark, Delaware
- "Thermal Electric Breakdown in Magnesium-Aluminum Oxides,"⁵ R. A. Weeks, Solid State Division, ORNL
- "Equilibria and Reaction Kinetics of Iron in MgO ,"⁵ E. Sonder, Solid State Division, ORNL
- "Hydrogen in Metals," S. Prakash, C.N.R.S., Université Paris, Orsay, France
- "Recent Results in Low-Energy Ion Sputtering," J. Bohdansky, Max-Planck-Institut für Plasmaphysik, Garching, Germany
- "Nuclear Spin-Lattice Relaxation in Thallium-Containing Chalcogenide Glasses," G. E. Jellison, Jr., Naval Research Laboratory, Washington, D.C.
- "Calculations to Interpret MeV Ion Scattering from Surfaces,"⁵ J. H. Barrett, Solid State Division, ORNL
- "An Attempt to Understand the Annealing Process in fcc Metals,"⁵ N. Wakabayashi, Solid State Division, ORNL
- "Preparation of Fine Powders by Evaporative Decomposition of Solution," T. P. O'Halloran, Pennsylvania State University, University Park, Pennsylvania
- "Surface Structure Analysis of Platinum and Tungsten by MeV Ion Scattering," I. Stensgaard, Bell Laboratories, Murray Hill, New Jersey

- "Charge Fluctuations and Conductivity in Mixed-Valence Systems," R. M. Martin, Xerox Research Laboratory, Palo Alto, California
- "Calculation of Electronic Properties of Point Defects in Metals," R. G. Zeier, Kernforschungsanlage, Jülich, Germany
- "Stoichiometry Structure and Superconductivity in Niobium and Sulfide," W. Fisher, Cornell University, Ithaca, New York
- "Quantum Beats from Nuclei Excited by Synchrotron Radiation Pulses," G. Trammell, Rice University, Houston, Texas
- "Neutron Studies of NaO_2 ," B. Aefeld, Kernforschungsanlage, Jülich, Germany
- "The Dynamic Properties of Normal ^3He : A Review of Neutron Scattering Data and Theory," Stephen Lovesey, Institut Laue-Langevin, Grenoble, France
- "Computer Simulation of Martensitic Transformation Based on Microscopic Elastic Theory," S. Chen, University of California, Berkeley, California
- "Correlation Studies of Ions in Solids and Solutions by EXAFS," D. E. Sayers, Washington State University, Pullman, Washington
- "Two-Level Tunneling States in Metallic Glasses,"³ B. L. Gyorfy, University of Bristol, Bristol, England
- "Complex Potentials in Atomic Scattering," E. D. Thompson, Case Western Reserve University, Cleveland, Ohio
- "Backscattering of Hydrogen and Helium from Metal Surfaces," W. Eckstein, Max-Planck-Institut für Plasmaphysik, Garching, Germany
- "Defect and Transmutation Production in Reactor-Irradiated Copper,"⁵ R. R. Colman, Jr., Solid State Division, ORNL
- "Enhanced Electrical Conductivity of Lithium-Doped MgO by Oxidation at High Temperatures,"⁵ Y. Chen, Solid State Division, ORNL
- "Hydrogen Trapping to Vacancies, Dislocations, and Stress Fields Near a Crack Tip in fcc Metals: A Quantum-Chemical-Lattice Defect-Finite Element Hybrid Approach,"¹ W. D. Wilson and M. Baskes, Sandia Laboratories, Albuquerque, New Mexico
- "Application of Solar Energy: An Experiment in an Egyptian Village," S. Arafa, American University in Cairo, Cairo, Egypt
- "Small-Angle Neutron Scattering from Biological Systems,"⁶ G. Zaccai, Institut Laue-Langevin, Grenoble, France
- "Dissociation and Desorption of Adsorbates: Thermal Reactions," U. Landman, Georgia Institute of Technology, Atlanta, Georgia
- "Computer Simulation Studies of Structure and Interaction of Defects in Crystals,"³ K. W. Ingle, University of Surrey, Surrey, England
- "Anomalous Scaling Properties of Models of Nonequilibrium Phenomena,"³ S. W. Lovesey, Institut Laue-Langevin, Grenoble, France
- "Excitations in Amorphous Solids,"³ L. Roth, State University of New York, Albany, New York
- "What's Interesting about 415s in 1978?" F. M. Mueller, University of Nijmegen, The Netherlands
- "Phase Transitions in $\text{MEM}(\text{TCNQ})_2$," L. Van Bodegom, University of Groningen, Holland
- "Radiation Annealing in Al_2O_3 and MgO," G. Krefft, Sandia Laboratories, Albuquerque, New Mexico
- "Mode Coupling in Low-Dimensional Magnetic Systems," A. Lagendijk, Universiteit Antwerpen, Belgium

- "Theory of the Electron Microscope Image Contrast of Lattice Defects," K. H. Katerbau, Max-Planck-Institut, Stuttgart, Germany
- "Resonant Coherent Excitation of Channeled Ions," O. Crawford, Chemistry Division, ORNL
- "The Electronic and Ionic Conductivity of Nonstoichiometric Uranium Dioxide," N. J. Dudney, Massachusetts Institute of Technology, Cambridge, Massachusetts
- "Computer Simulation of Displacement Cascades,"⁵ M. T. Robinson, Solid State Division, ORNL
- "Diffuse Scattering Studies of Defect Clustering in Metals,"⁵ J. B. Roberto, Solid State Division, ORNL
- "Faces of Self-Consistent Phonons," H. Glyde, University of Ottawa, Ottawa, Canada

¹ Sponsored jointly by Metals and Ceramics Division and Solid State Division.

² Sponsored jointly by Fusion Energy Division and Solid State Division.

³ Joint Metals and Ceramics Division and Solid State Division Theoretical Seminar.

⁴ Sponsored jointly by Chemistry Division and Solid State Division.

⁵ Solid State Division Research in Progress Seminar Series.

⁶ Joint National Center for Small-Angle Scattering Research and Solid State Division Seminar.

LECTURES AND SEMINARS

Lectures and seminars presented by Division members during the period covered by this report included the following:

- M. M. Abraham – University of Alabama, Birmingham, Alabama, "Electron Paramagnetic Resonance"
- B. R. Appleton – University of Aarhus, Aarhus, Denmark, "PICS Investigations of Reordered and Relaxed Au Single-Crystal Surfaces"; Max-Planck-Institut für Plasmaphysik, Garching, Germany, "First Wall Studies Using Ion Beam Techniques"; University of Tsukuba, Ibaraki, Japan, "Ion Implantation and Laser Annealing"; University of Nagoya, Nagoya, Japan, "PICS for Surface Studies"
- J. B. Bates – University of Kentucky, Lexington, Kentucky, "Infrared Spectral Properties and Diffusion Mechanisms of Hydrogen in Rutile"
- J. W. Cable – Venezuelan Institute of Scientific Investigations, Caracas, Venezuela, "Local Environment Effects in Disordered Alloys"
- Y. Chen – Argonne National Laboratory, Argonne, Illinois, "The Effect of High Temperature and Ionizing Radiation on Lithium-Doped MgO"; Illinois Institute of Technology, Chicago, Illinois, "Oxidation and Reduction of Lithium-Doped MgO"; Sandia Laboratories, Albuquerque, New Mexico, "Electrical Conductivity of Li-Doped MgO Oxidized at High Temperatures"
- D. K. Christen – University of Cincinnati, Cincinnati, Ohio, "Fluxoid Lattices in Type-II Superconductors"; University of Alberta, Edmonton, Alberta, Canada, "Anisotropy Effects in the Low-Field Superconducting Properties of Niobium"
- H. L. Davis – Kernforschungsanlage, Jülich, Germany, "Some Current Surface Research at Oak Ridge National Laboratory"
- E. H. Kobisk – Georgia Institute of Technology, Atlanta, Georgia, "Preparation of Isotope Research Materials"
- W. C. Koehler – University of Missouri, Columbia, Missouri, "The NSF-ORNL Small-Angle Scattering Facility"; Tohoku University, Sendai, Japan, "Neutron Scattering from Sm Compounds"; Institut Laue-Langevin, Grenoble, France, "Recent Neutron Scattering Experiments at ORNL"; Kernforschungsanlage Jülich, Germany, "Neutron Scattering from Mixed Valent Systems"; Venezuelan Institute of Scientific Investigations, Caracas, Venezuela, "Magnetic Scattering Experiments at ORNL"

- R. M. Moon – Rice University, Houston, Texas, "Neutron Scattering by Mixed Valence Materials"
- J. Narayan – Metals and Ceramics Division, ORNL, "Laser Annealing Effects in Silicon"
- R. M. Nicklow – University of Tokyo, Tokyo, Japan, "Hybridization of Phonons and the Internal Modes of Complex Imperities"
- J. R. Noonan – Auburn University, Auburn, Alabama, "Analysis of Low-Energy Electron Scattering from Cu Surfaces"
- O. S. Oen – FOM Institute for Atomic and Molecular Physics, Amsterdam, The Netherlands, and University of Munich, Munich, Germany, "The Two-Atom Blocking Model for Analyzing Results of Ion Backscattering from Surfaces"; Hahn-Meitner Institut für Kernforschung, Berlin, Germany, Kernforschungsanlage, Jülich, Germany, and University of Aarhus, Aarhus, Denmark, "Computer Studies of the Reflection of Hydrogen and the Sputtering of Hydrogen from Metal Hydrides"; Frankfurt American High School Visitation Group, Garching, Germany, "Plasma Wall Interaction Program at Garching"; Fusion Energy Division, ORNL, "Results of Reflection of Light Ions from Surfaces for Use in Plasma Simulation Computer Codes"
- S. M. Ohr – Kernforschungsanlage, Jülich, Germany, "Electron Microscope Studies of Radiation Damage and Fracture of Solids"; Max-Planck-Institut für Metallforschung, Stuttgart, Germany, "Image Simulation of Dislocation Loops in Thin Foils"; Auburn University, Auburn, Alabama, "Electron Microscope Studies of Radiation Damage"
- R. A. Parra – Georgia Institute of Technology, Atlanta, Georgia, "Neutron Study of Magnetic Moments of Ni-Pt Alloys"
- M. Petek – State University of New York, Buffalo, New York, "Electrochemical Separation of Tritium from Aqueous Effluent Systems"
- Mark Rasolt – Dalhousie University, Halifax, Nova Scotia, "Effects of Electron-Electron Interactions on Properties of Metals"
- J. B. Roberto – Max-Planck-Institut für Plasmaphysik, Garching, Germany, and University of Aarhus, Aarhus, Denmark, "High-Energy *d*-Be Neutron Interactions in Metals"; EURATOM, Ispra, Italy, and Technical University of Darmstadt, Darmstadt, Germany, "Fusion Energy Neutron Damage in Metals"; Brookhaven National Laboratory, Upton, New York, "Diffuse Scattering Studies of Defect Clustering in Metals"
- M. T. Robinson – Cornell University, Ithaca, New York, "Single-Crystal Sputtering Theory"
- S. T. Sekula – Clemson University, Clemson, South Carolina, "Fluxoids in Type-II Superconductors"
- H. G. Smith – Tohoku University, Sendai, Japan, "Phonon Spectra, Lattice Instabilities, and Superconductivity"
- E. Sonder – University of Kansas, Lawrence, Kansas, "High-Temperature Insulating Solids"
- M. V. K. Uehla – Chemistry Division, ORNL, "Electron Scattering from Oriented Molecules"
- N. Wakabayashi – Argonne National Laboratory, Argonne, Illinois, and Ohio University, Athens, Ohio, "Charge Fluctuation Model of Lattice Vibrations"; Hiroshima University, Hiroshima, Japan, "Models for Lattice Dynamics"
- R. A. Weeks – Vanderbilt University, Nashville, Tennessee, "Effect of an Electric Field on the Valence State of Impurities in MgO Single Crystals"; University of Newcastle, Newcastle, England, and Royal Society Subcommittee, London, England, "Redox Equilibria in Libyan Desert Silica Glass"; American University in Cairo, Cairo, Egypt, "Thermal Electric Breakdown in MgO Single Crystals"; Naval Research Laboratory, Washington, D.C., "Distribution of Fe³⁺ and Fe²⁺ in MgO Single Crystals"
- J. F. Wendelken – University of Texas, Arlington, Texas, and University of Alabama, University, Alabama, "High-Resolution Inelastic Low-Energy Electron Diffraction Applied to Single-Crystal Metal Surfaces"

- C. W. White – Max-Planck-Institut für Plasmaphysik, Garching, Germany, Institut für Angewandte Kernphysik, Karlsruhe, Germany, Centre de Recherches Nucléaires, Strasbourg, France, and Atomic Energy Research Establishment, Harwell, England, "Laser Annealing of Ion-Implanted Silicon"; Bell Laboratories, Murray Hill, New Jersey, "Pulsed Annealing of Ion-Implanted Silicon"
- S. P. Withrow – University of Tennessee, Knoxville, Tennessee, "A Physicist's View of Heterogeneous Catalysis Under High Vacuum"
- R. F. Wood – McGill University, Montreal, Canada, "Mixing of Localized Modes with Phonons"; Oak Ridge Associated Universities, Oak Ridge, Tennessee, "Photovoltaic Energy Conversion"
- R. T. Young – Bell Laboratories, Murray Hill, New Jersey, "Laser Annealing of Ion-Implanted Silicon"
- D. M. Zehner – University of Warwick, Coventry, England, "Surface Structure Determination by Positive Ion Channeling Spectroscopy"; University of York, Heslington, England, Max-Planck-Institut für Plasmaphysik, Garching, Germany, and Institut für Grenzflächenforschung und Vakuumphysik, Jülich, Germany, "Angular-Resolved Auger Emission from Cu Single Crystals"

Scientific Professional Activities

- M. M. Abraham** Member, Organizing Committee, International Conference on Defects in Insulating Crystals, Gatlinburg, Tennessee, 1977
Member, Ph.D. Thesis Committee, Institute of Physics, U.N.A.M., Mexico City, D.F.
Adjunct Professor, Institute of Physics, U.N.A.M., Mexico, Occupying the Elena Aizen de Moshinsky Chair of Physics
Lecturer, ORAU Traveling Lecture Program, 1976-1977
- B. R. Appleton** Member, Graduate School Doctoral Committee, Department of Physics and Astronomy, University of South Carolina, Columbia, South Carolina
Member, Fusion Program Committee, ORNL
Member, Ph.D. Thesis Committee, Department of Physics, North Texas State University, Denton, Texas
Member, Program Committee, Third International Conference on Ion Beam Analysis, Washington, D.C., 1977
Vice-Chairman, Particle-Solid Interactions Gordon Conference, Andover, New Hampshire, 1978
Member, DOE/OFE Plasma Materials Interaction Task Group
Chairman, DOE/OFE Subtask Group on Physical Sputtering, Reflection, and Neutron Effects
Participant, DOE Workshop on Engineering Materials Science, Oak Ridge, Tennessee, 1977
Member, DOE/OFE USA-USSR Fusion Energy Scientific Exchange Program
Participant, USA-USSR Workshop on Surface Radiation Effects in Fusion Devices, Moscow, USSR, 1977
Chairman, Particle-Solid Interactions Gordon Conference (to be held in 1980)
Consultant, National Research Council Panel on Ion Implantation and Competing New Surface Technologies, 1978
Participant, DOE/OFE Materials and Radiation Effects Program Workshop, Washington, D.C., 1978
Participant, DOE/OFE First Wall Coatings Workshop, Albuquerque, New Mexico, 1978
Member, Organizing Committee, Fifth Conference on Application of Small Accelerators (to be held in 1978)
Chapter and Contributing Editor, *Ion Beam Handbook for Materials Analysis*, Academic Press, New York, 1977
Lecturer, ORNL In-House Continuous Education Program Course on Surface Physics, 1978
- J. H. Barrett** Lecturer, ORAU Traveling Lecture Program, 1976-1977
Lecturer, ORNL In-House Continuous Education Program Course on Surface Physics, 1978
- J. B. Bates** Member, Steering Committee, Fourier Transform Technical Group
Member, Organizing Committee, International Conference on Defects in Insulating Crystals, Gatlinburg, Tennessee, 1977
Member, Program Advisory Committee, International Conference on Fast-Ion Transport in Solids - Electrolytes and Electrodes (to be held in 1979)
Coordinator and Lecturer, ORNL In-House Continuous Education Program Course on Laser Applications in Physical and Life Sciences
- L. A. Boatner** Member, Thesis Examining Committee, The University of Geneva, Geneva, Switzerland
- J. W. Cable** Member, Program Committee, 24th Annual Conference on Magnetism and Magnetic Materials
Member, Ph.D. Thesis Committee, Department of Physics, Georgia Institute of Technology, Atlanta, Georgia
- Y. K. Chang** Guest Scientist, Argonne National Laboratory, Argonne, Illinois, September 1977
- Y. Chen** Conference Secretary, International Conference on Defects in Insulating Crystals, Gatlinburg, Tennessee, 1977
Member, Advisory Panel on Publishing, American Institute of Physics
- D. K. Christen** Lecturer, ORAU Traveling Lecture Program, 1977-1978
- J. W. Cleland** Member, Advisory Committee, International Conference on Neutron Transmutation Doping of Semiconductors, Columbia, Missouri, 1978

- H. L. Davis** Lecturer, ORNL In-House Continuous Education Program Course on Surface Physics, 1978
Participant, Study of the Metrek Division of Mitre Corporation (for the NSF) to analyze the effectiveness of Materials Research Laboratory Funding, 1978
Member, Local Committee, Paper Selection Committee and the Nottingham Prize Committee of the 38th Annual Conference on Physical Electronics, Gatlinburg, Tennessee, 1978
- L. H. Jenkins** Co-Chairman, 38th Annual Conference on Physical Electronics, Gatlinburg, Tennessee, 1978
Member, Advisory Committee, Department of Physics, University of Missouri, Columbia, Missouri
Member, ORNL Wigner Fellowship Committee
Member, ORNL Exploratory Studies Review Committee
Member, ORNL-ORAU Graduate Selection Panel
Member, ORNL Ph.D. Recruiting Program
Advisory Member, Physical Electronics Conference Committee
- Theodore Kaplan** Lecturer, ORAU Traveling Lecture Program, 1977-1978
- E. H. Kobisk** Member, Research Materials Committee, Division of Nuclear Sciences, DOE
Member, Board of Directors, International Target Development Society
- W. C. Koehler** Director, National Center for Small-Angle Scattering Research
Member, Editorial Advisory Board, *Journal of Magnetism and Magnetic Materials*
Member, Editorial Advisory Board, *Magnetism Letters*
Member, ORNL Neutron Beam Users' Organizing Committee
Editor, Magnetic Form Factor Data Sheets, International Union of Crystallography
Member, Ph.D. Thesis Committee, Department of Physics, Georgia Institute of Technology, Atlanta, Georgia
Member, International Advisory Committee, Conference on the Physics of Rare Earths
Member, International Advisory Committee, Conference on Neutron Scattering and Magnetism (to be held in 1979)
Participant, U.S.-Japan Cooperative Science Program
Member, Subpanel on Structures, National Research Council Panel on Research Facilities and Scientific Opportunities in the Use of Low-Energy Neutrons
- B. C. Larson** Member, ORNL X-Ray Planning Committee
Lecturer, ORAU Traveling Lecture Program, 1976-1977
Lecturer, ORNL In-House Continuous Education Program Course on Surface Physics, 1978
- F. A. Modine** Member, Organizing Committee, International Conference on Defects in Insulating Crystals, Gatlinburg, Tennessee, 1977
- H. A. Mook** Member, ORNL Ph.D. Recruiting Program
Member, Program Committee, 25th Annual Conference on Magnetism and Magnetic Materials (to be held in 1979)
Member, Program Committee, International Conference on the Physics of Transition Metals, Toronto, Canada, 1977
Member, Subpanel on Dynamics of Solids and Liquids, National Research Council Panel on Research Facilities and Scientific Opportunities in the Use of Low-Energy Neutrons
- R. M. Moon** Chairman, ORNL Neutron Beam Users' Organizing Committee
Member, Commission on Electron Charge, Spin, and Momentum Densities of the International Union of Crystallography
Consultant, National Research Council Panel on Research Facilities and Scientific Opportunities in the Use of Low-Energy Neutrons
Member, Subpanel on Facilities and Instrumentation, National Research Council Panel on Research Facilities and Scientific Opportunities in the Use of Low-Energy Neutrons
Member, ORNL Ph.D. Recruiting Program
Lecturer, ORAU Traveling Lecture Program, 1976-1977
- Mark Mostoller** Member, Organizing Committee, and Editor, *Abstract Book, International Conference on Defects in Insulating Crystals*, Gatlinburg, Tennessee, 1977
- R. M. Nicklow** Member, Ph.D. Thesis Committee, Department of Physics, West Virginia University, Morgantown, West Virginia
Member, Subpanel on Radiation Damage, National Research Council Panel on Research Facilities and Scientific Opportunities in the Use of Low-Energy Neutrons
Member, Subpanel on Dynamics of Solids and Liquids, National Research Council Panel on Research Facilities and Scientific Opportunities in the Use of Low-Energy Neutrons
Member, ORNL Neutron Beam Users' Organizing Committee
Participant, U.S.-Japan Cooperative Science Program

- J. R. Noonan Lecturer, ORAU Traveling Lecture Program, 1976-1977
Lecturer, ORNL In-House Continuous Education Program Course on Surface Physics, 1978
- O. S. Oen Guest Scientist, Max-Planck-Institut für Plasmaphysik, EURATOM-Association, Garching bei München, Germany, 1977-1978
- S. M. Ohr Guest Scientist, Institut für Physik, Max-Planck-Institut für Metallforschung, Stuttgart, Germany, June-July, 1977
Member, Chemistry and Physics of Metals Committee, the Metallurgical Society of AIME
Member, Nuclear Metallurgy Committee, the Metallurgical Society of AIME
Member, Nuclear Metallurgy Committee, Materials Science Division of ASM
Member, ASTM E-10 Task Group on Description of Radiation Damage in Metals Using Electron Microscopy
Lecturer, ORAU Traveling Lecture Program, 1977-1978
- J. B. Roberto Guest Scientist, Kernforschungsanlage, Jülich, Germany, 1977-1978
Member, ORNL Exploratory Studies Review Committee
Member, ORNL Ph.D. Recruiting Program
- M. T. Robinson Member, Editorial Advisory Board, *Journal of Nuclear Materials*
Member, DOE/OFE Task Group on Damage Analysis and Fundamental Studies
Chairman, DOE/OFE Subtask Group B: Damage Production
Member, ad hoc Advisory Committee on Fusion Materials Program, Lawrence Livermore Laboratory, Livermore, California, 1978
- S. T. Sekula Member, Advisory Committee, International Discussion Meeting on Radiation Effects on Superconductivity, Argonne, Illinois, 1977
- H. G. Smith Member, Ph.D. Thesis Committee, Department of Physics, West Virginia University, Morgantown, West Virginia
Participant, U.S.-Japan Cooperative Science Program
- E. Sonder Program Chairman, International Conference on Defects in Insulating Crystals, Gatlinburg, Tennessee, 1977
Member, Advisory Board, *Diffusion and Diffusion Data Journal*
- M. V. K. Uehla Recipient, Eugene P. Wigner Fellowship
Participant, NATO Advanced Study Institute on Electrons in Disordered Metals and at Metallic Surfaces, Gent, Belgium, 1978
- N. Wakabayashi Participant, U.S.-Japan Cooperative Science Program
Lecturer, ORAU Traveling Lecture Program, 1977-1978
- R. A. Weeks Member, Editorial Committee, *Journal of the American Ceramic Society*
Member, Thesis Committee, Department of Mechanical Engineering and Materials Science, Vanderbilt University, Nashville, Tennessee
Adjunct Professor, Department of Geology, University of Pennsylvania, Philadelphia, Pennsylvania
Member, Organizing Committee, International Conference on Defects in Insulating Crystals, Gatlinburg, Tennessee, 1977
- J. F. Wendelken Member, ORNL Ph.D. Recruiting Program
Lecturer, ORAU Traveling Lecture Program, 1977-1978
Lecturer, ORNL In-House Continuous Education Program Course on Surface Physics, 1978
- R. D. Westbrook Member, ASTM Committee F-1
- C. W. White Member, Organizing Committee, International Workshop on Inelastic Ion Surface Collisions, Hamilton, Ontario, Canada, 1978
Member, Organizing Committee, Symposium on Laser-Solid Interactions and Laser Processing, Boston, Massachusetts, 1978
Member, Ph.D. Thesis Committee, Department of Physics, North Texas State University, Denton, Texas
Editor, *Inelastic Ion-Surface Collisions*, Academic Press, New York, 1977
Lecturer, ORNL In-House Continuous Education Program Course on Surface Physics, 1978
- M. K. Wilkinson Adjunct Professor, Department of Physics, Georgia Institute of Technology, Atlanta, Georgia
Member, Advisory Panel of the Solid State Sciences Committee of the National Research Council
Chairman, Organizing Committee, Meeting of Solid State Sciences Committee and Panel, Oak Ridge, Tennessee, 1978
Member, Evaluation Panel for Reactor Radiation Division, National Bureau of Standards
Member, Evaluation Panel for Materials Science, National Bureau of Standards
Secretary, Advisory Committee, Conference on Magnetism and Magnetic Materials
Member, Executive Committee, Southeastern Section of American Physical Society

- Member, Program Committee, Meeting of Southeastern Section of American Physical Society, Blacksburg, Virginia, 1978
- Member, National Research Council Panel on Research Facilities and Scientific Opportunities in the Use of Low-Energy Neutrons
- Member, Subpanel on Users and Education, National Research Council Panel on Research Facilities and Scientific Opportunities in the Use of Low-Energy Neutrons
- Member, Screening Panel for the 1978 E. O. Lawrence Award
- Participant, Summary Meeting of DOE Workshops on Materials Science, Washington, D.C., 1977
- R. F. Wood**
- Chairman, International Conference on Defects in Insulating Crystals, Gatlinburg, Tennessee, 1977
- Chairman, Interim Steering Committee for the International Conference on Defects in Insulating Crystals (to be held in 1980)
- Member, International Advisory Committee, Third Europhysics Topical Conference on Lattice Defects in Ionic Crystals (to be held in 1979)
- Editor, Solid State Physics, *Computer Physics Communications*, North-Holland Publishing Company
- Technical Consultant, National Research Council ad hoc Committee on Microstructure Fabrication
- Member, Advisory Committee, International Conference on Neutron Transmutation Doping of Semiconductors, Columbia, Missouri, 1978
- F. W. Young, Jr.**
- Member, Executive Committee, American Association of Crystal Growth
- Member, Editorial Board, *Topics in Crystal Growth*
- Member, Editorial Board, *Journal of Applied Physics*
- Member, Editorial Board, *Applied Physics Letters*
- Participant, Summary Meeting of DOE Workshops on Materials Science, Washington, D.C., 1977
- D. M. Zehner**
- Member, Steering Committee, Eighth Surface Conference, Savannah River Laboratory, Aiken, South Carolina, 1978
- Advisory Member, Physical Electronics Conference Committee
- Co-Chairman, 38th Annual Conference on Physical Electronics, Gatlinburg, Tennessee, 1978
- Lecturer, ORNL In-House Continuous Education Program Course on Surface Physics, 1978

Personnel Changes

New Staff Members

A. Scientific Staff

J. F. Barforst, Argonne National Laboratory, Argonne, Illinois
L. A. Boatner, Federal Institute of Technology, Lausanne, Switzerland
H. L. Engstrom, Brookhaven National Laboratory, Upton, New York
O. W. Holland, North Texas State University, Denton, Texas
G. E. Jellison, Jr., Naval Research Laboratory, Washington, D.C.
S. P. King, Change from Consultant Status
S. Kobayashi, Northwestern University, Evanston, Illinois
M. Petek, Allied Chemical Corporation, Buffalo, New York
M. Rasolt, Battelle Columbus Laboratories, Columbus, Ohio
R. D. Taylor, Georgia Institute of Technology, Atlanta, Georgia
J. C. Wang, Wright-Patterson Air Force Base, Dayton, Ohio
S. P. Withrow, California Institute of Technology, Pasadena, California
R. A. Zular, State University of New York, Albany, New York

B. Administrative and Technical Staff

B. R. Brown, Laboratory Technician
M. A. Gillespie, Secretary
J. T. Luck, Secretary
G. W. Ownby, Laboratory Aide
C. A. Sampson, Jr., Laboratory Technician (transferred from Analytical Chemistry Division)
D. K. Thomas, Laboratory Technician (transferred from Industrial Safety and Applied Health Physics Division)
L. A. Zevenbergen, Laboratory Technician

Staff Transfers and Terminations

B. R. Brown, Laboratory Technician (voluntary resignation)
G. J. Clark, Research Staff Member (completion of temporary assignment)
D. K. Holmes, Research Staff Member (retirement)
S. D. Nelson, Laboratory Technician (voluntary resignation)
J. C. Pigg, Research Staff Member (retirement)
T. L. Polgreen, Research Staff Member (completion of temporary assignment)
F. A. Sherrill, Research Staff Member (deceased)

Guest Assignments

A. Scientific Staff

B. Alefeld, Kernforschungsanlage, Jülich, Germany
P. H. Dederichs, Kernforschungsanlage, Jülich, Germany
P. Ehrhart, Kernforschungsanlage, Jülich, Germany
T. Kaneda, Fuji Photo Film Company, Tokyo, Japan
D. L. Knaer, Vanderbilt University, Nashville, Tennessee

- N. Kunitomi, Osaka University, Osaka, Japan
 E. F. Montesa, Philippine Atomic Energy Commission, Quezon City, Philippines
 Y. Nakai, Osaka University, Osaka, Japan
 V. M. Orea, University of Zaragoza, Zaragoza, Spain
 P. P. Pronko, Argonne National Laboratory, Argonne, Illinois
 J. P. Riviere, University of Poitiers, Poitiers, France
 H. J. Stapleton, University of Illinois, Urbana, Illinois
 P. C. Thorel, Centre d'Etudes Nucléaires de Grenoble, France
 L. Van Bodegom, Netherlands Organization for the Advancement of Pure Research, Zuidhorn, The Netherlands
 G. W. Vogl, Hahn-Meitner Institut, Berlin, Germany
 R. G. Zeller, Kernforschungsanlage, Jülich, Germany
- B. National Science Foundation Postdoctoral Energy-Related Fellowship
 D. D. Allred, Princeton University, Princeton, New Jersey
- C. Great Lakes College Association Science Program
 D. N. Olson, St. Olaf College, Northfield, Minnesota
 K. E. Sickafus, Ohio Wesleyan University, Delaware, Ohio
- D. Graduate Students
 J. L. Boidin, National University of Mexico, Mexico, D.F.
 W. P. Crummett, West Virginia University, Morgantown, West Virginia
 Q. C. Murphree, University of South Carolina, Columbia, South Carolina
 K. E. Parra, Georgia Institute of Technology, Atlanta, Georgia
 S. R. Wilson, North Texas State University, Denton, Texas

Summer Assignments

- A. Scientific Staff
 R. L. Cappelletti, Ohio University, Athens, Ohio
 E. D. Feldman, Stanford University, Stanford, California
 J. S. Koehler, University of Illinois, Urbana, Illinois
 R. D. Licher, Vanderbilt University, Nashville, Tennessee
 M. L. Linvill, University of California, Berkeley, California
 S. W. Lovesey, Institut Laue-Langevin, Grenoble, France
 F. M. Mueller, University of Nijmegen, The Netherlands
 T. L. Polgreen, University of Illinois, Urbana, Illinois
 O. A. Stringle, University of Missouri, Columbia, Missouri
 H. Sato, Purdue University, West Lafayette, Indiana
 J. R. Thompson, University of Tennessee, Knoxville, Tennessee
 K. G. Thompson, Vanderbilt University, Nashville, Tennessee
 H. Vornickel, Max-Planck-Institut für Plasmaphysik, Garching, Germany
 D. E. Weber, Washington University, St. Louis, Missouri
 C. Wood, Northern Illinois University, DeKalb, Illinois
- B. Clerical Staff
 D. M. Smalley, University of Tennessee, Knoxville, Tennessee
 L. A. Smalley, University of Tennessee, Knoxville, Tennessee
 K. P. Wynn, Tennessee Technological University, Cookeville, Tennessee
- C. CRAU - University Faculty
 J. W. Garland, University of Illinois at Chicago Circle, Chicago, Illinois

D. ORAU – Undergraduate Research Trainees

J. D. Brown, Oklahoma State University, Stillwater, Oklahoma

J. B. Lacy, University College, Birmingham, Alabama

K. E. Sickafus, Ohio Wesleyan University, Delaware, Ohio

T. A. Stephenson, Iowa State University, Ames, Iowa

I. G. Stratton, Concordia College, St. Paul, Minnesota

R. E. Thomas, George Washington University, Washington, D.C.

J. D. Woosley, Northern Illinois University, DeKalb, Illinois

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235. Dr. F. Brown, Solid State Science Branch, Chemistry and Materials Division, Chalk River Nuclear Laboratories, Chalk River, Ontario, Canada

236. Dr. Fred C. Brown, Department of Physics, University of Illinois, Urbana, IL 61801
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242. Dr. Andre Châtelain, Lab. Phys. Exp., Federal Institute of Technology, 33 av. Cour, 1007 Lausanne, Switzerland
243. Dr. Mui Fatt Chung, Physics Department, University of Singapore, Bukit Timah Road, Singapore 10
244. Dr. C. B. Clark, Department of Physics, University of North Carolina, Greensboro, NC 27412
245. Dr. G. J. Clark, Mineral Physics Division, Commonwealth Scientific and Industrial Research Organization, P.O. Box 136, North Ryde, N.S.W. 2113, Australia
246. Dr. W. Dale Compton, Vice-President-Research, Ford Motor Company, P.O. Box 1603, Dearborn, MI 48121
247. Dr. J. H. Crawford, Jr., Department of Physics and Astronomy, University of North Carolina, Chapel Hill, NC 27514
248. Dr. W. L. Crummett, Department of Physics, Montana State University, Bozeman, MT 59715
249. Dr. J. C. Crump, III, 2206 Essex Road, Richmond, VA 23228
250. Mr. Floyd L. Culler, Jr., Electric Power Research Institute, 3412 Hillview Avenue, Palo Alto, CA 94303
251. Dr. G. Czjzek, Kernforschungszentrum Karlsruhe, Institut für Angewandte Kernphysik, Postfach 3640, D-7500 Karlsruhe, Germany
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