SOLID STATE DIVISION

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MASTER

ANNUAL PROGRESS REPORT

Period Ending December 31, 1973

OAK RIDGE NATIONAL LABORATORY

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**SOLID STATE DIVISION
ANNUAL PROGRESS REPORT
For Period Ending December 31, 1973**

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

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MAY 1974

**OAK RIDGE NATIONAL LABORATORY
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Introduction

For several years the Annual Report of the Solid State Division has consisted of abstracts of papers on completed research investigations and very brief summaries of research in progress. In an effort to present a more complete picture of the various activities of the Division, the articles in this Annual Report are slightly longer summaries which include some of the most important data in appropriate figures and tables.

The arrangement of the Annual Report has been chosen to emphasize the major areas of solid state science in which the Division conducts research. These areas are Theoretical Solid State Physics, Neutron Scattering, Radiation Damage in Metals, Physics of Insulators and Semiconductors, and the Research Materials Program. Each of them constitutes a main section of the report, and additional subdivisions are included within the sections. Since many changes are taking place within the programs of the Laboratory and the AEC, it seemed desirable to indicate the scope and goals of each major research area, and to this end each section of the Report has a brief introduction concerning the research in that section. Perhaps these introductions will give a clearer picture of the manner in which the individual research programs are interrelated and also show how the research activities of the Solid State Division contribute to various programs of the Laboratory and the Atomic Energy Commission.

1. Theoretical Solid State Physics

The theoretical and computational work in the Solid State Division is generally planned to complement the various experimental programs of this Division and others throughout ORNL doing related work. A continuous effort is made to foster a close working relationship between the theorists and the experimentalists. Although the emphasis of the work varies with the experimental programs, the research can usually be grouped loosely into the three categories of particle-solid interactions, electronic and magnetic properties, and lattice dynamics.

The research on particle-solid interactions deals with a number of problems which are related through their dependence on atomic collisions in solids. Some of these topics, such as radiation damage in metals and sputtering of solid surfaces, are of direct relevance to technical problems in the development of fission and fusion power reactors. Others, such as channeling, are primarily of interest either to fundamental studies of solids or to detailed studies of the atomic collisions themselves. The theoretical investigations are associated with experimental investigations of radiation damage and of channeling in the Solid State Division, with experimental studies of channeling and of atomic collision phenomena in collaboration with the Physics and Chemistry Divisions, and with reactor-oriented radiation damage studies in the Metals and Ceramics Division. The principal objectives of the research are to understand the details of the interactions of energetic ions and atoms with crystalline solids and to provide calculations and technical consultations in support of the various reactor development projects.

The work on the electronic properties of materials is presently concerned primarily with the computation of the electronic band structures of both metals and insulators and with the study of the dependence of the optical properties of point defects in ionic crystals on their calculated electronic energy level schemes. The results of the band calculations not only give important direct information about the electronic structures and optical properties of perfect crystals, but they also are used as part of the initial input data for calculations on the magnetic properties of materials studied in the experimental neutron-scattering program. An example of these calculations is the work on the magnetic properties of nickel and iron, which is, for the first time, permitting detailed numerical testing of certain predictions of various theories of ferromagnetism.

The theoretical research on defects in ionic crystals is directed toward the acquisition of a basic understanding of the electronic and vibrational structures of radiation damage products in insulators. Although the results of this work are most directly related to the experimentally observed optical properties of the defects in the visible region of the spectrum, they also supply valuable data for the interpretation of infrared and Raman experiments. The work on lattice dynamics encompasses a wide variety of calculations on the vibrational properties of perfect crystals, random alloys, and crystals with isolated impurities. Recently, two areas have been emphasized because of their immediate practical importance. One area concerns the lattice dynamics of high T_c superconductors, which is being emphasized because evidence is growing that a deeper understanding of certain anomalies in the phonon dispersion curves of these materials may lead to greater

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insight into the mechanisms of superconductivity. The other area deals with recent advances in the theory of random alloys. The predictions of this theory can be tested by a combined theoretical and experimental program involving neutron scattering, infrared absorption, and Raman scattering. Since an isolated substitutional impurity in a crystal can be viewed as the limiting case of a dilute alloy, this program also has relevance to radiation damage processes in both metals and insulators.

A common feature of many of the theoretical calculations in the Solid State Division is the extensive use of digital computers. The use of computers leads naturally to a type of work that is not feasible at many universities but is ideally suited for the large-scale computational facilities at ORNL.

PARTICLE-SOLID INTERACTIONS

COMPUTER SIMULATION OF ATOMIC DISPLACEMENT CASCADES IN SOLIDS IN THE BINARY COLLISION APPROXIMATION

M. T. Robinson I. M. Torrens¹

The theoretical description of radiation damage in solids requires a detailed analysis of the dependence of the number of point defects produced and their spatial distribution on the energy of the primary recoil atoms. These atoms, originally set into motion by interactions with incident electrons, neutrons, or ions, dissipate their initial kinetic energies in a series of inelastic encounters with other atoms of the solid, displacing some of these to slow down by similar series of collisions. The resulting cascade of displaced atoms and their accompanying vacancies are eventually responsible for the changes which occur in the properties of the irradiated solid. The object of the present work was to develop a comprehensive computational model, including as many elements of the physical situation as seemed possible, so that fairly realistic computer simulations of displacement cascade production could be carried out for a variety of crystalline solids.

The program is described in detail elsewhere.² The projectile trajectories are constructed as a series of isolated classical binary collisions, using the Molière potential to describe the atomic interactions. Impact-parameter-dependent inelastic (electronic) losses are described by a model due to Firsov. Simple uncorrelated Gaussian displacements of the lattice atoms may be included to simulate temperature effects. The target crystal may be unbounded, may have a surface of specified crystallographic orientation, or may have two parallel surfaces a specified distance apart. The crystal may have any structure describable by orthorhombic coordinates and may contain several kinds of atoms.

The permanent displacement of lattice atoms may be based on an energy threshold, E_d , commonly taken as about 25 eV. Alternatively, a capture radius, r_c , may be assigned to each vacancy. An interstitial lying within the capture volume of a vacancy is regarded as being unstable and annihilating the vacancy.

This program, designated MARLOWE, has been applied to a number of related problems. A comparison of the energy dependence of the Frenkel pair production according to the different threshold models will be given briefly; more detail is given elsewhere.² Continuing studies of the low-energy properties of the model are described below.³ The program has been applied to a problem in hot-atom chemistry⁴ and to a study of ion sputtering.⁵ Current investigations include the scattering of low-energy hydrogen atoms from metal surfaces, an activity in support of controlled thermonuclear reactor (CTR) development.

The initial kinetic energy of the primary recoil, E_0 , is ultimately divided between the kinetic energies of slowly moving atomic systems and the energies of excited electrons. The latter energy, $\bar{Q}$, is the sum of all the inelastic energy losses in the development of a cascade and, in metals, plays little part in radiation damage. The former energy, $\bar{E}$, is termed the damage energy. Of course, $\bar{E} + \bar{Q} = E_0$. Previous investigations⁶ have shown that when an energy threshold is used to describe the permanent displacement of atoms from lattice sites, ν , the number of Frenkel pairs produced, is a linear function of the damage energy. The dependence of ν upon $\bar{E}$ has been studied using three different threshold models for copper. The first is the familiar threshold-energy model in which atoms are displaced if they receive energy in excess of E_d , taken here as 25 eV; the cascade is followed until all atoms have energies less than $E_r = E_d$, and no recombination of nascent defects is allowed. In the second model, $E_d = 25$ eV, but atoms are followed until they slow down to 5 eV, allowing the interstitials to reach more realistic dis-

Fig. 1.1. Comparison of high-energy cascades in copper for three different displacement models.

tances from the vacancies than in the first case. Because fewer replacement collisions occur in this model, some close pair recombination is called for. In the third model, $E_d = E_c = 5$ eV was selected, the use of a threshold being essentially a convenience in terminating the calculation. A value of the vacancy capture radius r_v was chosen to define the stability of close Frenkel pairs. The values of r_v in the second and third models were chosen by matching these calculations to the threshold model in the low-energy region $50 \text{ eV} < E_0 < 100 \text{ eV}$, with the results $r_v/a_0 = 0.75$ and 2.50 , respectively, where a_0 is the lattice constant of the target. Figure 1.1 shows values of $\bar{E}/\nu$ as a function of $\bar{E}$ for these three models. The linear dependence of ν on $\bar{E}$ in model 1 is shown. In the other models, however, ν rises less rapidly than linearly as $\bar{E}$ increases. This reflects increased recombination in the highly disturbed tracks of the high-energy recoils, an effect which may be significant in accounting for the long standing discrepancy between theory and observation in this area. Our results are in general agreement with earlier work of Beeler,⁷ although our explanation of the origin of the effect is somewhat different and quantitative differences remain.

1. Centre d'Etudes Nucléaires de Saclay, France. Present address: Energy Division, O.E.C.D., Paris, France.

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3. D. K. Holmes and M. T. Robinson, "Low-Energy Radiation Damage Events in the Binary Collision Approximation," this report.

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6. I. M. Torrens and M. T. Robinson, p. 739 in *Radiation Induced Voids in Metals*, ed. by J. W. Corbett and L. C. Lanniello, USAEC CONF-710601, 1972.

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LOW-ENERGY RADIATION DAMAGE EVENTS IN THE BINARY COLLISION APPROXIMATION

D. K. Holmes M. T. Robinson

In the development of radiation damage cascades in solids, even those resulting from high-energy primaries, the low-energy dynamic events (involving energies below, say, 100 eV) are important, since all atoms in motion must eventually come to rest. The calculation of such events, however, is difficult because they involve many-body interactions. The use of computer simulation of radiation damage events in lattices has had considerable success in this area, since it is possible to follow in detail the motion of hundreds of atoms interacting through two-body interatomic potentials for adequate lengths of time. However, the large amount of computer capacity and time required makes it difficult to obtain statistically significant samples of initial primary directions and energies. This has led to the present work in which low-energy events are treated in the binary collision approximation, using the computer program MARLOWE.¹ The program fails to treat some aspects of the cascade correctly, but it is hoped that most are adequately treated and that statistically significant information can be obtained by averaging the results over large samples.

Recent theoretical work using MARLOWE has been concerned with isolated replacement collisions and replacement-collision sequences. In a replacement collision, a moving atom (usually having a kinetic energy of a few tens of electron volts) makes a very close encounter with a lattice atom at rest, such that the struck atom is given sufficient energy to escape from the lattice site and its immediate surroundings, while the incident atom is left with an energy low enough that it is trapped onto the lattice site in question. Clearly, at such low energies, a replacement collision involves the simultaneous interaction of many atoms neighboring the particular lattice site as well as the two principal atoms.

It has been shown that if the directions of motion are nearly parallel to a close-packed row of lattice atoms, such replacement collisions may occur in sequence down the close-packed row until the energy available has fallen so low that neither the incident nor the struck atom can escape from the vicinity of the final lattice site. Such replacement-collision sequences in a cascade have two observable consequences: (1) in any solid the interstitial atom formed at the end of the sequence is farther from the original vacant lattice site than would be the case if only uncorrelated collisions occurred; and (2) in an ordered polyatomic solid much

more disorder results from the enhanced number of atomic replacements. These two aspects have been studied experimentally so that it was felt worth while to perform pertinent simulation calculations using MARLOWE.² Theory and experiment seem to agree that replacement-collision sequences increase the average vacancy-interstitial pair separation (10 to 50 eV primaries in copper); however, the disordering phenomenon is less clear. Theory and experiment agree that there is not much contribution to the disordering from replacement sequences generated by 50-eV primaries in Ni₃Al. However, for 400-eV primaries, experiment gives much more disordering than would be predicted from the computer results. The origin of this discrepancy is not known.

It is possible that isolated replacement collisions by the primary atom may be observable. For example, if the primary atom (in a monatomic lattice) is made radioactive by the same interaction which produces the initial recoil, its final resting place, as an interstitial atom or on a lattice site as a result of a replacement collision, can influence the angular distribution of the products of the subsequent radioactive decay. While the relevant experiments have not yet been performed, it is of interest for the future to study, theoretically, the fraction of all primaries (having different initial directions in the lattice) which finally make replacement collisions. For a random solid this has been done,³ with certain limitations on the scattering law for the atomic collisions. The rather interesting result is that this fraction rises from zero for a primary energy equal to the displacement threshold energy, E_d , to a value near $\ln 2$ at $2E_d$, then remains constant for higher primary energies.

This probability has also been investigated for the full lattice geometry MARLOWE. The results are shown in Fig. 1.2. The computer results are given both for the perfect lattice⁴ (in this case, copper) and for a randomized lattice. They are to be compared with the analytical results for a hard-sphere interaction, also shown. The paper by Dederichs et al.³ showed that, in general, more realistic scattering laws reduce the probability for energies above $2E_d$ below the hard-sphere value of $\ln 2$. Thus the curve shown for the random model agrees well with their results. The structure shown by the lattice model at low energies seems to be real, at least insofar as the binary collision model is valid. However, the trend of the results for the lattice model to be above $\ln 2$ at higher energies is to be taken less seriously, since modification of the assumptions in the calculation can change these values considerably.

Fig. 1.2. The fraction of primary recoil atoms making replacement collisions in a copper crystal.

The results shown for the lattice model have not yet been explained quantitatively. Close inspection of the details of the collisions made by the primary on the way to its final collision has indicated, in general, that the primary tends to be "steered" towards a final replacement collision by glancing collisions with other atoms. This is similar to so-called "assisted focusing" and also results from the ordered arrangement of atoms in the lattice. Further study is needed to achieve a deeper understanding of these results and to determine whether at least the qualitative trends can be confirmed by a more realistic treatment of the low-energy events than the binary collision model affords.

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BREAKDOWN OF THE STATISTICAL EQUILIBRIUM HYPOTHESIS IN CHANNELING¹

J. H. Barrett

When the direction of a beam of high-energy ions is near a major crystallographic axis in a solid, the ions are steered by the rows of atoms parallel to the axis into the regions between the rows and have a reduced probability of making close nuclear encounters. For

exact alignment with the axis, the steering or channeling effect is strongest and the yield of close encounters is a minimum. The value of this minimum yield has been calculated previously using computer simulation methods and found to be about three times as large as that calculated by analytical methods. Further computer simulations now show the principal reason for this difference to be a breakdown of the so-called statistical equilibrium hypothesis on which the analytical calculations are based. The important consequence of this hypothesis is that the probability of finding an ion at a given position in the plane perpendicular to the crystallographic axis is the same everywhere within the area over which it is energetically allowed to move.

The simulation calculations show a depth dependence of the minimum yield with a peak at the surface and two subsurface peaks, the deeper being the larger. Beyond these peaks, there is a gradual increase of the yield with depth. In the simulation calculation as in an actual crystal, the yield in the surface and near-surface region is entirely due to ions striking the crystal very near row ends exposed at the surface. As expected, the simulations show that the surface peak comes from the originally struck row and the first subsurface peak from the ring of nearest-neighbor rows. However, the second subsurface peak comes not from the ring of second nearest-neighbor rows, as one might anticipate, but instead from the fourth ring of neighbors, with a smaller contribution from the seventh ring.

The reason for the unexpected order of neighbor rows associated with the second peak as well as its high intensity is the focusing effect shown by detailed plots of trajectories in Fig. 1.3. The important point in this figure is the focusing at transverse energies around 400 and 900 eV onto rows in the fourth and seventh neighbor rings respectively. An essential factor in the prominence of the second subsurface peak is that 400 eV is low enough for many ions to possess such an energy yet high enough to allow the close encounters that give a large probability of interaction.

After an ion has come close enough to a row to make an appreciable contribution to the yield, it will be moving very nearly in a radial direction as it moves away so that it will again be subject to the focusing influences shown in Fig. 1.3, and the enhancement of yield will persist as the ion moves deeper into the crystal. The higher probability of finding an ion of a given transverse energy near a row in the simulation calculation is at variance with the hypothesis of statistical equilibrium. Because the simulation is inherently closer to experiment than the analytical calculation and would automatically produce statistical

Fig. 1.3. Projection onto (111) of trajectories of 3-MeV protons traveling nearly parallel to [111] in tungsten at 1200°K. Each group of ions starts radially outward from a row with a specified value of the energy ϵ associated with the transverse components of motion; the value is shown at the upper left of each portion of the figure. The various rings of neighboring rows to the starting row are labeled in the upper right portion of the figure.

equilibrium if it were supposed to be present, it must be concluded that the analytical calculation is in error in assuming that statistical equilibrium exists and that it needs to be modified to take nonequilibrium behavior into account.

In addition to the effect on minimum yield near the surface, the focusing effect described above will have important consequences on many other channeling calculations such as dechanneling rates, half angles, atom location, and nuclear lifetime calculations.

HYPERCHANNELING THEORY¹

J. H. Barrett

The theoretical model already developed for hyperchanneling² has continued to be applied to analysis of experiments. The parameters inferred from the latest experiments³ on the basis of this model are less than those inferred from earlier experiments but still not as low as the values estimated on a theoretical basis. The reduction in the difference between inferred and theoretical values is believed to be due to elimination of experimental sources of error. Although the source of the remaining difference is not understood, efforts at understanding it will continue since the source appears to involve such factors as ion-atom potentials, multiple scattering, and sensitivity of hyperchanneling to radiation damage.

Extensions to the theory have been and are being made to allow determination of stopping power as a function of transverse energy and to allow analysis of experiments in which the detector rather than the goniometer is used to scan the hyperchanneling pattern. Results obtained to date with the first of these extensions indicate that the stopping power varies linearly with the square root of the transverse energy. In addition to these extensions of the existing theory, computer simulation of ion trajectories is being undertaken to seek an understanding of features of the experimental results that appear to stem from a breakdown of the hypothesis of statistical equilibrium on which the present theoretical model is based.

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THEORETICAL STUDIES OF RADIATION DAMAGE BY FAST-ION BOMBARDMENT

O. S. Oen

The use of fast ions and electrons to simulate neutron damage in reactor materials has stimulated investigations of the many factors that enter into the calculations by which the different irradiations are intercompared. The calculational programs discussed here have been designed to provide information and guidance to several experimental investigations at

ORNL: (1) the simulation of high-dose neutron damage by fast heavy ions; (2) the depth dependence of damage produced in copper by irradiation with 1-MeV protons; and (3) bombardment of the first wall of the proposed controlled thermonuclear reactor (CTR) by low-energy hydrogen, helium, and plasma contaminants. A fourth program, which made extensive calculations of the atomic displacement cross sections by fast electrons, has been outlined before.¹ A report describing these calculations has been published.²

Simulation of fast-neutron bombardment by heavy ions has been motivated mainly by the large "equivalent" doses one can achieve in a relatively short time using accelerators rather than existing neutron sources. The correlation of ion damage with equivalent neutron damage depends on the theory of primary production of displaced atoms. The theory used is based largely on the slowing down of energetic ions developed by Lindhard et al.³ (LSS). The analytical approximation to atomic scattering from the Thomas-Fermi potential found by Winterbon et al.⁴ was used to describe the interaction between the moving ion and the target atoms. The electronic energy losses were accounted for by the LSS theory when applicable or by the empirical tables of Northcliffe and Schilling.⁵ Since the damage produced by fast ions is nonuniform over the ion depth, it is necessary to calculate such quantities as the nuclear energy loss and the damage energy deposited by the bombarding ion as a function of ion penetration, taking straggling into account. The specific calculations investigated in detail are for those ion-target combinations currently under experimental study in the Metals and Ceramics Division. These include MeV aluminum ions bombarding aluminum, niobium ions bombarding niobium, and carbon ions bombarding nickel. Penetration profiles of light ions such as hydrogen and helium bombarding the above targets were also calculated.

The second program has calculated the depth dependence of displaced atoms in copper produced by 1-MeV protons. The treatment for energetic light ions bombarding heavy targets is basically similar to heavy ions, but differs in some aspects. Whereas the straggling of heavy ions is due primarily to nuclear collisions, the straggling of MeV protons is due mainly to electronic collisions. The work of Sternheimer⁶ was used to estimate the straggling. The penetration depth and the average cosine of the deflection angle of the proton were calculated as a function of the residual energy of the proton by the method of Lewis.⁷ This method lent itself more readily to the calculations and differed by only a few percent from the LSS theory. The following three quantities were evaluated as functions of the

proton penetration depth: the nuclear energy loss, the damage energy deposited, and the number of atoms displaced according to the Kinchin and Pease model. A displacement threshold energy of 25 eV was used. A comparison of the calculations with the corresponding experimental work is shown in another section⁸ of this annual report.

The third program is closely related to the problems associated with the bombardment and penetration of keV ions such as hydrogen or helium which hit the inner wall of the proposed CTR. The present theoretical studies have developed an improved method for calculating the average ion penetration depth. It has been shown by Schjøtt⁹ that the average calculated penetration depth (projected range) of low-energy light ions moving in a heavy target material may be several times smaller than the total path. He also predicted for such cases that the penetration straggling is so large that the width of the distribution at half maximum may exceed the average penetration depth. The calculations of Schjøtt are based on the LSS formalism, which assumes an infinite homogeneous target having no surface. His method of calculating the average penetration depth automatically counts negative as well as positive values of the penetration depths from the distribution. Thus, comparing average penetration depths calculated by his method with experimentally determined depths in which a surface is present is not strictly correct and may be expected to lead to considerable differences. The method proposed here allows for a surface by counting *only* those projectiles in the penetration distribution that have positive ranges, but in other respects is similar to that of Schjøtt. To calculate the average penetration depth by this alternative method, it is necessary to evaluate higher moments of the penetration distribution in order to renormalize the distribution to account for only that fraction of the projectiles that remains in the target. Calculations have

been made using second moments to describe the distribution (Gaussian), and it is found that the average penetration depth may be a factor of 2 larger than that calculated by the method of Schjøtt (see Fig. 1.4). Recent experimental values of the average penetration depth found by Roth, Behrisch, and Scherzer¹⁰ for 4-keV helium ions in niobium were twice the value predicted by Schjøtt. For this case, the alternative method presented here increases the values of Schjøtt by about 45% and would partly explain the difference found between theory and experiment.

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THEORY OF THE PRODUCTION OF RADIATION DISPLACEMENT DAMAGE¹

O. S. Oen

The basis for the modern method of characterizing nascent displacement damage in solids by the damage energy is reviewed. The damage energy makes it possible to intercompare in a unique way the damage introduced by energetic ion irradiation with that of fast neutrons. The damage energy of a single cascade initiated by a primary recoil atom is the kinetic energy of the primary minus the electronic losses of it and all the other atoms comprising the cascade. The number of displaced atoms in a cascade is directly proportional to the damage energy, and the proportionality constant is the displacement efficiency divided by twice the mean displacement threshold. Torrens and Robinson have found that the displacement efficiency has a value of approximately 0.8 and is independent of primary energy except for energies near twice the threshold. It is

Fig. 1.4. The ratio, R , of the average penetration depth calculated by renormalizing the distribution to account for projectiles "reflected" to the penetration depth calculated by the Schjøtt method for helium ions into niobium as a function of energy.

necessary to use a mean value of the atomic displacement threshold energy, as it has been experimentally found that the threshold is frequently a strong function of crystallographic direction. In neutron irradiation the damage energy averaged over the spectrum of primary energies is a convenient measure of displacement damage as a function of neutron energy. In contrast, for ion irradiation the damage energy is a strong function of ion penetration depth, which needs to be taken into account explicitly.

1. Summary of paper to be published.

DETERMINATION OF COMPOUND NUCLEAR LIFETIMES BY THE BLOCKING TECHNIQUE¹

Y. Hashimoto² J. H. Barrett
W. M. Gibson³

We report the results of a comprehensive computer simulation of angular distributions of 4.0-MeV protons scattered by a 3- μ m-thick germanium crystal and emerging near a $\langle 110 \rangle$ direction. They show that interpretation of measured blocking distributions to obtain short nuclear lifetimes is strongly dependent on the recoil direction and depth distribution of the recoiling compound nuclei in the crystal. This dependence is explained in terms of the associated flux-peaking effect in particle channeling.

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2. Rutgers University, New Brunswick, N.J., on leave from the University of Tokyo.

3. Bell Laboratories, Murray Hill, N.J.

ELECTRONIC AND MAGNETIC PROPERTIES

THEORY OF MAGNETISM IN TRANSITION METALS

J. F. Cooke

The dynamic susceptibility is a quantity of fundamental importance in magnetic systems. Recently, a low-temperature generalized random phase approximation expression for the susceptibility was derived for itinerant electron systems, which included multiband and Coulomb matrix element effects.¹ In order to simplify the calculation, the spin dependence of the Bloch functions was neglected. Because of the multiband character of the problem, the expression for the

susceptibility was cumbersome, primarily because of the appearance of the inverse of a 5 by 5 complex matrix.

This calculation has since been generalized to include the spin-dependent character of the Bloch functions without destroying the property that the spin-wave energy must go to zero at zero wave vector. In addition, a trick involving the use of group theory has been used to reduce the susceptibility expression to a form which is comparable in complexity with that obtained in the single-band limit.

As a result of neutron scattering measurements made at temperatures up to $1.5T_c$ in nickel and iron, it appears that the traditional view of spin-polarized energy bands collapsing into paramagnetic bands as the temperature approaches the Curie temperature is not correct. At present an investigation is in progress into possible mechanisms which might explain the neutron data at finite temperatures.

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NUMERICAL INVESTIGATION OF THE MAGNETIC PROPERTIES OF IRON AND NICKEL

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J. Lynn¹

Neutron scattering experiments performed at ORNL during the past few years have yielded a considerable amount of information about magnetic excitations in nickel and iron. The results obtained from these experiments are to a certain extent in general qualitative agreement with the behavior expected from an itinerant electron model of ferromagnetism. In order to perform calculations based on this model for materials like nickel and iron, an extension of the theory to include multiband and Coulomb matrix element effects and the development of numerical integration techniques were required. An extensive series of calculations has been carried out on nickel.² In particular, calculations of the dynamic susceptibility based on what is thought to be a realistic set of energy bands for nickel provided excellent agreement with the measured spin-wave dispersion curve. Predictions regarding the disappearance of spin waves are not in complete agreement with the experiments, but it is not clear at the present time whether this is due to numerical difficulties in the calculation or to an inadequate theory.

Similar calculations are now under way for iron. Thus far we have been primarily concerned with obtaining a

realistic set of energy bands. In order to do this we have generated a series of paramagnetic crystal potentials from the atomic configurations $3d^7 4s^1$ and $3d^8$ by using a heuristic prescription outlined by Mattheiss.³ Crystal potentials developed by Mattheiss⁴ and by Wood⁵ have also been considered. The ferromagnetic band structure is generated according to the self-consistent procedure developed by Hodges, Ehrenreich, and Lang.⁶ Spin splittings on the order of 2 eV are required to produce the observed moment of $2.2\mu_B$. This value of the spin splitting is roughly one-half of the value determined from first-principles self-consistent spin-polarized calculations. A similar discrepancy was found in the nickel calculations.

Preliminary calculations of the Stoner band density of states along the (100) direction have been performed, and the general features are similar to those found in nickel except that the region of high density of Stoner excitations occurs at a much higher energy in iron due to the larger spin splitting. This would in turn indicate that the spin waves should disappear at a much higher energy in iron than they do in nickel, which does not agree with the experimental findings.

We intend to proceed to a calculation of the dynamic susceptibility in iron to determine the behavior of the spin waves given by our theoretical model. It is hoped that such calculations will indicate what sort of changes are needed in the theory to adequately describe the neutron scattering results.

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INTERPOLATED BAND STRUCTURE MODELS AND INTEGRATION SCHEMES

J. F. Cooke H. L. Davis
Mark Mostoller

The calculation of many of the electronic properties of interest in solid state physics is, in general, difficult to carry out because of the complicated nature of the electronic energy band structure. Since first-principles band-structure calculations require relatively large amounts of computer time, various interpolation schemes have been developed which provide a fast and reasonably accurate procedure for generating the entire

band structure from a relatively small number of first-principles points. In the past we have used the Hodges-Ehrenreich-Lang (HEL) interpolation procedure for calculations in face-centered-cubic materials such as nickel, palladium, and copper. During the past year, computer codes based on a second-neighbor *s-p-d* Slater-Koster (SK) interpolation scheme have been developed for treating body-centered-cubic materials. The 27 parameters of the Slater-Koster model were determined from a least-squares fit of first-principles band-structure calculations. For most bcc transition metals, rms deviations in the range of 0.001 to 0.004 Ry were achieved. In contrast to this, the niobium band structure was found to be harder to fit, since an rms deviation of no better than 0.007 Ry could be achieved. This kind of accuracy is, however, good enough for most types of calculations.

Many of the quantities of interest in electronic systems involve Brillouin zone integrals of functions of the electronic energy. In order to obtain these quantities, some means of generating the band structure must be coupled with a numerical procedure for doing the integrals. A very efficient method for calculating Brillouin zone integrals was developed at ORNL by Gilat and Raubenheimer (GR).¹ In order to use this linear integration procedure, electronic energies and gradients of the electronic energy with respect to the wave vector must be supplied on a fine mesh of evenly spaced k points. The ideal situation would be to calculate this information directly from the first-principles band-structure equations, but unfortunately this would require many hours of computer time. In order to circumvent this problem, Cooke and Wood² suggested using a quadratic interpolation scheme developed by Mueller et al.³ In this approach the first-principles band-structure equations are solved at a relatively small number of k points (about 1000). An irreducible section of the Brillouin zone is then subdivided into small cubes. In each cube the energy bands are approximated by an analytic expression which contains terms up to second order in the wave vector. This quadratic expression can then be differentiated to obtain the energy gradients. When this procedure is combined with the GR linear integration scheme it provides a reasonably accurate and fast method of calculating Brillouin zone integrals, and it has been called the combined linear-quadratic (CLQ) method.

It has been pointed out by Gilat et al.⁴ that quadratic interpolation might introduce errors in numerical calculations of quantities, such as the electronic density of states, because of its inability properly to describe regions where bands either cross or almost cross. In

order to investigate this possible source of error a new method has been proposed which, in the final analysis, appears to be more accurate than the CLQ scheme with relatively little increase in computer time.

This method is based on the fact that the SK, HEL, and other similar interpolation schemes provide much more accurate fits to energy bands than the quadratic interpolation procedure described above. This is especially true around band crossings. However, even though these schemes are much faster than the first-principles method, the overall time required to generate the energies and gradients at enough points to ensure convergence of the GR integration procedure would be

too large if the gradients are calculated in the conventional numerical manner of evaluating the energy at k and at $k + \delta k$. Instead of doing this, the Hellman-Feynman theorem⁵ is used to calculate the energy gradients. This procedure will be called the direct gradient method. It turns out that the direct gradient method is extremely accurate and much faster than the conventional method for generating energy gradients. The Hellman-Feynman theorem is easiest to apply to the SK scheme because the Slater-Koster matrix elements are simple analytic functions of the wave vector. The application to other interpolation schemes, such as HEL, is more tedious but certainly straightforward.

Fig. 1.5. Computer plot of electronic density of states for niobium. The upper curve is the result based on CLQ, while the lower curve is based on the direct gradient GR result.

Figure 1.5 shows a comparison of electronic density of states calculations for niobium based on a SK fit to the bands. The upper curve was obtained from CLQ and the lower curve from the direct gradient method. Notice that there are some differences in peak heights, which are clearly sensitive to energy gradients. Notice also that the arrow points to a peak in the CLQ result that does not appear in the lower curve. It turns out that this "spurious" peak should be a part of the larger peak to the right of the arrow. It has been moved out of this larger peak because of the inability of the quadratic interpolation scheme properly to describe the energy bands near a band crossing.

The results shown in Fig. 1.5 point out the advantages of using the direct gradient method instead of the CLQ scheme wherever possible. This is especially true for cases where band crossings are known to occur near the Fermi energy. On the basis of this and other calculations that have been performed, it appears that an SK, HEL, or other similar interpolation scheme for fitting first-principles bands, coupled with the Hellman-Feynman theorem for calculating energy gradients and with the GR linear integration procedure, provides the best combination of accuracy and speed for calculating Brillouin zone integrals.

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DETERMINATION OF PARAMETERS FOR BAND STRUCTURE INTERPOLATION

H. L. Davis J. F. Cooke

The use of the Hodges-Ehrenreich-Lang (HEL) interpolation method,¹ as well as other established methods, is by now a well-known calculational convenience for the study of the electronic structure of transition metals. Basically the HEL method relies on the treatment of matrix elements as adjustable parameters for the approximate duplication of a calculated "first-principles" electronic band structure or to generate energy bands having some empirical foundation. Once values for the necessary parameters have been obtained, the method enables the energy bands, $\epsilon(k)$ as a function of wave vector k , to be calculated easily and quickly throughout the entire Brillouin zone (BZ). Although there are many uses of an interpolation method when

investigating the experimental consequences of the electronic structure of a transition metal, one important use is in the Brillouin zone integrations which occur in the calculation of many physical quantities. It is sometimes necessary to perform such integrations over only a limited portion of the BZ or over the entire BZ using only those energy bands within a limited range of energy. Thus, it is desirable to have available those HEL parameters which would best reproduce the band structure for that region of k and/or range of energy of interest in a given application. To do this we have developed a computer code to obtain the HEL parameters by application of detailed least-squares procedures to the fitting of energy bands as a function of k .

Some examples of the results obtained by use of the above code are given in Table 1.1, which is based on fits to $\epsilon(k)$ vs k calculated via the Korringa-Kohn-Rostoker method for the nickel potential tabulated by Hanus.² Each column of Table 1.1 is based on fitting the $\epsilon(k)$ at 152 k points evenly distributed throughout $1/48$ of the BZ, but in any individual column only those $E_{\min} < \epsilon(k) < E_{\max}$ were used in the fit. The six bands of interest all fall within the energy range -0.10 to 1.20 Ry, and the Fermi energy of this band structure is about 0.60 Ry. The quantities A_1 through B_3 of Table 1.1 denote the usual HEL parameters, and χ denotes the rms deviation for the fit. As might be expected, the

Table 1.1. Examples of HEL parameters for conditions explained in the text

Entries are consistent with energies expressed in rydbergs

$E_{\min}$	-0.10	0.20	0.35	0.50
$E_{\max}$	1.20	0.90	0.70	0.70
A_1	0.02947	0.02952	0.03017	0.02784
A_2	0.00749	0.00765	0.00854	0.00364
A_3	0.01212	0.01241	0.01331	0.00750
A_4	0.01901	0.01927	0.01913	0.01786
A_5	0.00363	0.00360	0.00362	0.00356
A_6	0.01402	0.01405	0.01399	0.01480
E_0	0.45912	0.45873	0.45653	0.47060
Δ	-0.00224	-0.00229	-0.00042	-0.01101
α	0.01880	0.01943	0.02089	0.01764
β	-0.08011	-0.09379	-0.21696	-0.13041
V_{111}	0.22804	0.24613	0.19694	0.13608
V_{200}	0.30668	0.34100	0.24752	0.17088
B_1	0.42247	0.42384	0.44076	0.40556
B_2	1.45906	1.45411	1.53641	1.62180
B_3	1.32591	1.33115	1.32585	1.44724
χ	0.005	0.004	0.003	0.001

tabulated results show the rms deviation decreases as the energy range is narrowed to include only those $\epsilon(k)$ within ± 0.10 Ry of the Fermi energy. At the same time, it is seen that some of the parameters (e.g., A_3 , V_{111} , and B_2) undergo relatively large changes as the energy range is narrowed, while others (e.g., A_6 and B_1) show relatively little change. We are investigating whether the use of the different parameter sets of Table 1.1 will significantly affect our present interpretations of some of the properties of transition metals.

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PRECISE DETERMINATION OF THE CRYSTAL FIELD IN TmAl_3

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E. Bucher¹

The intermetallic compound TmAl_3 has the cubic Cu_3Au structure, and susceptibility measurements² have shown it to be a Van Vleck temperature-independent paramagnet below about 20°K. Crucial to understanding this magnetic behavior and some of the compound's other properties is a detailed knowledge of the crystal field present at the thulium sites in the solid. Although the cubic symmetry alone dictates that the 3H_6 multiplet of the free Tm^{3+} ($4f^{12}$) ion will be split into two singlets, Γ_1 and Γ_2 , one doublet, Γ_3 , and three triplets, Γ_4 , $\Gamma_5^{(1)}$, and $\Gamma_5^{(2)}$, by the crystal field, more precise information concerning the compound's electronic structure is required to establish the energetic ordering of the Γ_i . Or, inversely, knowledge of the Γ_i could be used to infer information concerning the compound's electronic structure (e.g., charge transfer).

Although an inspection of the susceptibility data² for TmAl_3 immediately establishes that the ground level is either a singlet (Γ_1 or Γ_2) or a nonmagnetic doublet (Γ_3), attempts to gain more information from a detailed analysis of the susceptibility data have produced conflicting results. For example, an analysis by Buschow³ has implied that the ground level is the Γ_1 , while one by Cooper⁴ has implied it is either the Γ_1 or the Γ_3 . Furthermore, a joint analysis of the susceptibility data and ^{27}Al NMR data by de Wijn et al.⁵ has led to the conclusion that the ground level was the Γ_3 . But, since the authors of each of these papers weighted their inferences by including reasoning based on point-charge models, it could not be concluded that the combined work had definitely excluded the possibility

of a Γ_2 ground level. Therefore, in an attempt to clarify the situation, we decided to apply neutron scattering techniques to an investigation of TmAl_3 , since such techniques coupled with a proper analysis provide the possibility of a direct spectroscopic determination of the energies of the Γ_i crystal-field levels.

Inelastic neutron scattering data from TmAl_3 powder samples were obtained at 4.2, 78, and 293°K with the Oak Ridge magnetically pulsed time-of-flight spectrometer. The data were then analyzed in detail in a manner described elsewhere.⁶ Such analysis has definitely established that the cubic crystal-field parameters have values of $A_4\langle r^4 \rangle = 2.20 \pm 0.10$ meV and $A_6\langle r^6 \rangle = 1.38 \pm 0.10$ meV. Equivalently, the crystal-field levels were determined to be in the order Γ_2 , $\Gamma_5^{(2)}$, Γ_1 , Γ_4 , Γ_3 , and $\Gamma_5^{(1)}$, with energies of 0.00, 3.87, 5.20, 6.31, 14.1, and 17.0 meV respectively. It is perhaps novel that the analysis of the neutron results has definitely established the ground level to be the Γ_2 , since this result was not inferred from any of the detailed analyses of the susceptibility. It is important to note, however, that the crystal field deduced by the present work is entirely consistent with all details of the published susceptibility data.^{2,3} One of the interesting aspects of the present results is the magnitude of the charges which must be used in a first- and second-neighbor point-charge model to reproduce the empirically deduced crystal-field splittings. For example, charges of about $+8|e|$ would have to be placed at the neighboring Al sites in such a model. Such large charge values simply mean point-charge models are completely unrealistic for TmAl_3 , which then explains why the susceptibility analyses³⁻⁵ produced invalid inferences.

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ELECTRONIC STRUCTURE OF POINT DEFECTS IN INSULATORS

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Mark Mostoller

Calculations of the electronic structure of point defects and color centers in insulators, especially ionic crystals, have continued during the past year. The work

on the one- and two-electron color centers in MgO and CaO, which has been going on for several years, is now nearing completion and will be discussed in more detail below. The electronic structure of the F center in KMgF_3 has been calculated, and it has been shown that results consistent with the experimental data can be obtained. However, the complexity of the crystal structure (perovskite) is such that the calculations are unable at this time to give the detailed results possible for the alkali halides and alkaline-earth oxides. This is because the parameters which enter into a Mott-Littleton type of calculation of the energy of lattice relaxation are not well known. Calculations on the absorption band shapes of MgO:Fe and $\text{KMgF}_3\text{:Fe}$ have been initiated. These bands show clearly the presence of a dynamic Jahn-Teller effect; the study of the consequences of this effect is an area of increasing importance in defect work. We hope to be able to modify our present computer programs² to deal with both the static and dynamic Jahn-Teller effect in a consistent and comprehensive manner.

As an example of the results obtained from the MgO and CaO calculations, we will briefly discuss those for the F center. This defect consists of two electrons trapped at an O^{2-} ion vacancy. The two-electron nature of the center gives it some rather interesting properties, but also greatly complicates the calculations. Both singlet and triplet states can occur; the calculations show that the ordering of the first four levels from the ground state up is $^1A_{1g}$, $^3T_{1u}$, $^3A_{1g}$, and $^1T_{1u}$. The absorption band in both crystals is due to the allowed electric dipole transition $^1A_{1g} \rightarrow ^1T_{1u}$, and there seems little doubt that the interpretation of the experimental results on absorption, which have already appeared in the literature, is correct. The same cannot be said of the emission, which is much more complicated. In CaO, measurements of the luminescence spectra by Henderson, Stokowski, and Ensign³ seemed to indicate that perhaps three emission bands were associated with the two-electron F center. One of these, the most intense, is long-lived and was associated with the $^3T_{1u} \rightarrow ^1A_{1g}$ transition. This band lies at approximately 2 eV. Another band at 2.5 eV is very weak, and Henderson et al. suggested that this was due to the $^1T_{1u} \rightarrow ^1A_{1g}$ transition. A third band which appeared just to the low-energy side of the 2-eV peak at room temperature seemed to be entirely absent at 4°K. No attempt was made to explain this peculiar band.

Our calculations confirm that the most intense, orange luminescence is undoubtedly due to the $^3T_{1u} \rightarrow ^1A_{1g}$ transition. However, the calculations strongly suggest that the 2.5-eV band is not due to the $^1T_{1u} \rightarrow$

$^1A_{1g}$ transition. Very recent measurements by J. B. Bates of the Solid State Division at ORNL have confirmed that the 2.5-eV band does not appear in crystals grown and colored at Oak Ridge. B. Henderson of the University of Keele, while on a sabbatical leave at ORNL, collaborated with Y. Chen and W. A. Sibley of the Solid State Division in careful measurements⁴ of the orange luminescence ascribed above to the $^3T_{1u} \rightarrow ^1A_{1g}$ transition. These measurements were carried out primarily at 4°K, but measurements at higher temperatures indicated some peculiarities in the variation of the band shape with temperature. However, these authors did not comment on the band just to the low-energy side of the 2-eV band which Henderson, Stokowski, and Ensign had previously observed. Our calculations in both MgO and CaO strongly suggest that the $^3T_{1u} \rightarrow ^1A_{1g}$ and the $^1T_{1u} \rightarrow ^1A_{1g}$ transitions occur at very nearly the same energy. We are now inclined to believe that the band just to the low-energy side of the 2-eV band in CaO at room temperature is due to the $^1T_{1u} \rightarrow ^1A_{1g}$ transition. As the temperature is lowered the preferential population of the $^3T_{1u}$ state leads to the disappearance of this band. This interpretation again seems to be confirmed by the measurements of Bates and by recent measurements of Chen on the emission band shape of the two-electron center in MgO. Chen's measurements show that even at low temperatures the emission band has a very peculiar shape, which almost certainly must be ascribed to transitions from two different excited states.

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LATTICE DYNAMICS

LATTICE VIBRATIONS IN ALLOYS: THE COHERENT POTENTIAL APPROXIMATION FOR MASS DEFECTS¹

Theodore Kaplan Mark Mostoller

In contrast to pure crystalline materials, alloys are not periodic on a microscopic level, and, as a consequence, it is much more difficult to construct practically applicable theories to describe their properties. In recent years, however, considerable insight into the

behavior of random substitutional alloys has been provided by a mean-field theory called the coherent potential approximation (CPA).^{2,3} In the CPA, the alloy is approximated by a periodic effective medium which is chosen self-consistently, such that the average scattering from a single real solute or solvent atom in the otherwise perfect effective crystal vanishes.

For lattice vibrations, the simplest model for the substitutionally disordered alloy is one in which only the masses of the constituents differ, while the interatomic forces remain periodic and do not depend on the local environment in the crystal. Until very recently, applications of the CPA for this simple mass-defect model were restricted to cubic Bravais lattices, and these applications were typically made with clumsy interactive numerical techniques. We have refined the computational methods to automate the CPA for mass defects in cubic Bravais lattices, and we have developed the numerical techniques needed to extend the CPA to treat mass defects in polyatomic cubic alloys, like mixed alkali halides, and in hcp systems, like mixed rare earths. An extension of the CPA to include force-constant changes as well as mass disorder has also been performed.⁴

We have performed mass defect CPA calculations for a number of alloys studied experimentally by the neutron scattering group in the Solid State Division. The systems studied include the cubic Bravais alloys Al-Cu, Ag-Au, and K-Rb, the mixed halides (NH₄-K)Cl and (Ag-Na)Cl, and the hcp rare earth alloy Y-Tb. The Ag-Au and K-Rb results are described elsewhere in this report;^{5,6} the CPA calculations for these materials, as well as for other monatomic cubic systems, typically take at most a few minutes of computer time on the ORNL IBM 360-91 for a given alloy composition.

Figure 1.6 shows a comparison of calculated⁷ and experimental⁸ results for the inelastic neutron scattering cross section of Al_{0.10}Cu_{0.90} at the zone boundary wave vector $Q = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})(2\pi/a)$. Resolution broadening is included in both curves. Since the outer electronic configurations of aluminum and copper are quite different, the agreement between the CPA and experiment for the local mode peak at roughly 8.8 THz is surprisingly good. However, the CPA does a rather poor job in fitting the sharpness and intensity of the local mode relative to the in-band peak, and it predicts an in-band longitudinal acoustic mode higher in frequency than is observed. Furthermore, the experimental results contain an interesting but barely resolved hint of structure at about 9.2 THz in the local mode region. These discrepancies between theory and experiment indicate that local force-constant changes, and

Fig. 1.6. The calculated and observed inelastic neutron scattering from Al_{0.10}Cu_{0.90} for the scattering wave vector $Q = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})(2\pi/a)$. The experimental points are from Nicklow et al.⁸ with background subtracted, and the horizontal bar shows the experimental resolution; a dashed curve has been drawn through the experimental points.

possibly cluster and correlation effects among the (Al) defects, play an important role in determining the properties of this alloy.

Nicklow and Wakabayashi⁹ have measured the phonon line shifts and widths in the hcp rare earth alloy Y_{0.90}Tb_{0.10} relative to the corresponding quantities in pure yttrium. Figure 1.7 compares the results of hcp and cubic mass defect CPA calculations with their measurements for lattice vibrations polarized along the *c* direction. It should be noted that it is quite difficult to determine the intrinsic line widths in the alloy experimentally, and this accounts for the scatter in the data. Figure 1.7 makes two points. First, even though the *c/a* ratio for this system is close to ideal, the cubic approximation is much less satisfactory at higher phonon frequencies than the hcp theory, which treats the crystal symmetry properly. Second, the relatively good agreement between the hcp mass defect CPA and experiment suggests that some rare earth alloys may realistically be considered to be mass-disordered systems in which force-constant changes play a minor role.

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LATTICE VIBRATIONS IN ALLOYS: FORCE CONSTANT AND MASS DISORDER IN THE COHERENT POTENTIAL APPROXIMATION¹

Theodore Kaplan Mark Mostoller

It is well known that local force-constant changes generally play an important role in determining the behavior of phonons around isolated defects;² force-constant disorder can be expected to have similarly large effects on the properties of lattice vibrations in alloys. For both theoretical and practical reasons, however, it has proven difficult to go beyond the single-site coherent potential approximation (CPA) discussed in the preceding article³ to include randomness in the interatomic forces as well as in the atomic masses of the alloy constituents. We have now overcome these difficulties and extended the CPA to include both force constant and mass disorder for systems in which the force constants superimpose linearly.⁴ In this limit, the effects of each constituent of the alloy can be described in terms of spatially extended, overlapping scattering

matrices. As in the case of mass defects, the CPA effective crystal is then determined by setting the average scattering from the extended space of a single real atom in the effective crystal equal to zero.

One-dimensional systems provide an excellent test for new theories of alloys, because exact results for the density of states of random linear alloys can be calculated relatively easily by using the techniques of Dean.⁵ Figure 1.8 compares exact results with the predictions of the extended CPA for the density of states of a binary one-dimensional alloy, $A_{1-c}B_c$, with nearest-neighbor force constants which superimpose linearly. The masses of the two constituents are $M_A = 1.0$ and $M_B = 0.5$, and the spring constants coupling nearest neighbors are $\gamma_{AA} = 1.0$, $\gamma_{BB} = 1.5$, and $\gamma_{AB} = (\gamma_{AA} + \gamma_{BB})/2 = 1.25$. The maximum frequencies in the pure A and B systems are $\sqrt{4}$ and $\sqrt{12}$ respectively.

For dilute concentrations, c , of B atoms, the mass defect and the force-constant change $\Delta = \gamma_{AB} - \gamma_{AA}$ are such that a local mode band is produced above the pure A spectrum. As the concentration of B atoms is increased to 25%, this band increases in width and merges with the in-band modes. As the concentration increases further, the higher frequency portion of the spectrum is filled in, and the agreement between the CPA and exact results improves as the structure in the exact results diminishes in magnitude. While the extended CPA fails to reproduce the fine structure at higher frequencies, which arises from pair and larger

Fig. 1.8. CPA (smooth curve) and exact results (histogram) for the phonon density of states of a monatomic one-dimensional alloy $A_{1-c}B_c$ with nearest-neighbor force-constant changes and mass differences.

cluster correlations, it does give a good average description of the spectrum and counts the numbers of modes in the different regions correctly.

The extended CPA might be expected to apply best to polyatomic alloys of the form $A_cA'_{1-c}B$, in which the alloyed constituents cannot be nearest neighbors and are to some extent buffered by the intervening stable constituent. One such system studied experimentally by inelastic neutron scattering at ORNL is

Fig. 1.9. Calculated and experimental results for the incoherent neutron scattering cross section of $(\text{NH}_4)_{0.07}\text{K}_{0.93}\text{Cl}$ in the local mode region.

$(\text{NH}_4)_c\text{K}_{1-c}\text{Cl}$, with c in the 7 to 10% range.⁶ A local lattice vibrational mode well above the band modes of pure KCl is observed for this system. When only mass disorder is included in the theory, the CPA predicts a quasi-local resonant mode near the high-frequency end of the KCl spectrum, which is far below the observed local mode peak.⁷ As shown in Fig. 1.9, a nearest-neighbor force-constant change of roughly 23% brings the predictions of the CPA, with force constant as well as mass disorder, into good agreement with the observed local mode peak position and width.

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LATTICE DYNAMICS CALCULATIONS FOR TRANSITION METALS AND TRANSITION METAL COMPOUNDS

Mark Mostoller R. F. Wood

The phonon spectra of the transition metals and their compounds are closely related to other properties of these materials. A particularly striking example is the appearance of characteristic anomalies in the dispersion curves of those elements and compounds which have high superconducting transition temperatures T_c ; these anomalies are not seen for similar materials with low T_c .¹⁻⁴ The relationship between the phonon spectra and the electronic band structures of the transition metals and their compounds remains poorly understood, and, at present, the best theoretical description of the lattice dynamics is provided by the phenomenological double-shell model (DSM) of Weber.⁵⁻⁷ In the DSM, each transition metal ion is surrounded by two rigid electronic shells, one of which is only very loosely coupled to the ion in the materials with high T_c . Long-range Coulomb interactions between the charged components of the model are screened by a free electron gas to avoid unphysical results in the long-wavelength limit.

Computer programs for the double-shell model in the NaCl structure have now been written, and results for the transition metal carbides calculated with these programs agree with those published by Weber. As shown in Fig. 1.10 for TaC, the DSM does give a good fit to the experimental data; no other model advanced thus far is nearly as successful. A modified version of the DSM has also been programmed for hcp crystals to investigate the anomalies observed by H. G. Smith in the phonon dispersion curves of technetium,⁸ which has the highest T_c of the hcp metals.

It is generally thought that the phonon anomalies in the high- T_c materials reflect some special feature or features of the electronic screening function, although the precise connection is not known. The results of accurate numerical calculations of the diagonal part of the electronic susceptibility of several bcc transition metals, which were obtained from their band structures, are described by Cooke, Davis, and Mostoller⁹ elsewhere.

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ELECTRONIC SUSCEPTIBILITIES FOR BCC TRANSITION METALS

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Anomalies occur in the specific heat, phonon dispersion curves, and other physical properties of niobium, and similar anomalies have been observed in other high- T_c superconductors. Several explanations, which involve the electronic screening or dielectric response function $\epsilon(q, \omega)$, have been proposed for these anomalies. One is that they are Kohn anomalies resulting from electronic transitions between parallel portions of the Fermi surface. Another, suggested by Ganguly and Wood¹ at ORNL, is that they reflect a strong frequency dependence of the electronic screening function in the range of the phonon frequencies and might therefore be related to the concept of acoustical plasmons. To test these conjectures, we have undertaken calculations of the random phase approximation electronic screening function of niobium² and other bcc transition metals. In order to calculate $\epsilon(q, \omega)$ it is first written in terms of the susceptibility $\chi(q, \omega)$. The susceptibility is the Brillouin zone integral of a function which depends on the electronic energy bands and matrix elements of $\exp(-iq \cdot r)$. For each material a second-neighbor *s-p-d* Slater-Koster interpolation scheme is used to generate the energy bands. Consistent with the use of the Slater-Koster interpolation scheme for the energy bands, the matrix elements are approximated by a tight-binding approach. The matrix elements are first expressed in terms of orthogonalized Landshoff-Löwdin orbitals, and all but site-diagonal integrals are neglected. An expansion of $\exp(-iq \cdot r)$ in spherical harmonics then gives an expression for the matrix elements in terms of Slater-Koster wave-function expansion coefficients, spherical harmonics for the direction $\hat{q}$, Gaunt factors, which are obtainable from

products of Clebsch-Gordan coefficients, and radial integrals. The radial integrals are numerically calculated using the wave functions from the band calculations to which the Slater-Koster model had previously been fitted. The integration is carried out over the muffin tin for the wave functions at the Fermi level. The Brillouin zone integration was carried out using a variety of methods to check on convergence. All procedures gave values for $\chi(q, \omega)$ which agreed to within a few percent. Also, the identity $\chi(q = 0, \omega = 0) = \rho(E_f)$, where $\rho(E_f)$ is the electronic density of states at the Fermi energy, is satisfied to within a few percent.

Figure 1.11 shows the results for the static susceptibility $\chi(q, \omega = 0)$ along the (100) direction for niobium. The calculation is based on energy bands generated from the muffin-tin potential of Deegan and Twose,³ which is thought to be good for niobium. The open circles represent the results when the matrix element is approximated as outlined above. The solid circles are results from the same calculation but with the matrix element set equal to unity. Both with and without matrix elements, the susceptibility in Fig. 1.11 is relatively smoothly varying. The constant matrix element calculation is rather flat and does not exhibit any of the peaks reported in previous calculations.⁴ The structure reported in these previous calculations is probably related to the use of a rather crude integration scheme based on the trapezoidal rule.

The structure appearing in the calculation that includes matrix elements is due primarily to the fact that the Gaunt factors act like selection rules which weight transitions between bands of the same wave-function character much more heavily than those connecting states of different characters. Notice also that putting the matrix element equal to unity increases $\chi(q, \omega = 0)$ by an order of magnitude. The relatively small peak around $|q| = 0.7$ corresponds well to the position of the observed longitudinal acoustic phonon anomaly, since this peak would correspond to a dip in the phonon dispersion curve at the same $|q|$.

In order to determine whether or not this peak was somehow related to the superconducting behavior of niobium, we repeated this calculation for tungsten, which is not superconducting. The results obtained for tungsten were similar in magnitude and form to those found for niobium for q near the zone boundary. However, instead of increasing with q as $q \rightarrow 0$, the tungsten susceptibility decreases. This is due to the fact that the density of states of tungsten at the Fermi energy, $\rho(E_f)$, is smaller than for niobium, and $\chi(q, \omega = 0)$ must approach $\rho(E_f)$ as $q \rightarrow 0$. There is a broad maximum in the tungsten result around $|q| = 0.7$, but

Fig. 1.11. The static susceptibility for niobium with $\vec{q}$ along (100) and $|\vec{q}|$ in reduced units of $2\pi/a$.

there does not appear to be any structure which is peculiar to this region as there was in the niobium case. The slight differences between the tungsten and the niobium results around $|\vec{q}| \cong 0.7$ might indicate that a calculation of the full dielectric function matrix could lead to a proper description of the phonon anomaly in niobium. Our calculations thus far indicate that the phonon anomaly does not result directly from any peculiar behavior of the diagonal part of the electronic susceptibility.

Calculations of $\chi(\vec{q}, \omega)$ in the phonon frequency range do not show any strong frequency dependence which must be present to predict the occurrence of acoustical plasmons. This is not too surprising, however, since the RPA expression we are using may not be general enough to predict acoustic plasmon behavior. Work is now in progress on extending the present calculations to include off-diagonal terms in the susceptibility and to integrate them into a more general electronic screening calculation of the phonon dispersion curve.

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INFRARED ABSORPTION AND RAMAN SCATTERING BY POINT DEFECTS IN IONIC CRYSTALS

Mark Mostoller R. F. Wood

Some of the most direct information about the effects of substitutional impurities and radiation-induced damage in insulators is given by the techniques of infrared absorption and Raman scattering. The introduction of the impurities and radiation damage may change not only the masses at some of the ion sites of the perfect crystal but also the forces acting among

the ions in the vicinity of the defects. The theoretical interpretation of the infrared and Raman experimental data can give detailed information about these changes if the model on which the theory is based is sufficiently flexible. We have been developing such a model along the following lines

In a simple classical ionic crystal model,^{1,2} the lattice-relaxation and force-constant changes around a substitutional defect can be found by separating the neighboring ions of the defect into two regions. The short-range and Coulomb interactions among region I ions and their interactions with the defect are treated exactly within the framework of the potential energy model used. The displacements and induced dipole moments of more distant neighbors in region II are assumed to be small, so that the forces exerted on region I ions by these more distant neighbors can be determined by first making Taylor series expansions in the region II displacements and moments and then performing the appropriate sums over the ions in region II. Finally, the task of calculating the lattice-relaxation and force-constant changes within region I can be further simplified by working with symmetrized coordinates, which are linear combinations of ionic displacements that transform according to the irreducible representations of the point group of the defect. Once the relaxation and force-constant changes are known, the Raman scattering and far-infrared absorption induced by the defect can be calculated.

We are now able to perform calculations for the lattice-relaxation and force-constant changes around defects in NaCl-type crystals with the four nearest-neighbor shells included in region I. The short-range interactions are treated as the sum of Born-Mayer and van der Waals interactions, and polarization and region II relaxation are included in an internally self-consistent fashion. The computer programs for the Raman scattering and far-infrared absorption calculations are presently being extended to include the second as well as the first and fourth shells; third-shell displacements are very small. A series of calculations have been performed for Ag⁺ impurities in NaCl^{3,4} and for the two-electron O²⁻ vacancy or F[•] center in MgO and CaO. For these cases, some difficulties arise in the choice of Born-Mayer potential parameters, and it is not yet clear whether those discrepancies which remain between calculated and experimental results indicate fundamental limitations in the approach, or, simply, poor selection of parameters.

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AN INTERMOLECULAR POTENTIAL FUNCTION MODEL FOR CRYSTALLINE HEXACHLOROBENZENE¹

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A consistent intermolecular potential-energy function model has been developed for crystalline hexachlorobenzene (HCB). The model assumed consists of rigid molecules in which the effects of internal vibrations are neglected. This approximation is justified by the relatively large separation between the lowest internal mode frequency (79 cm⁻¹) and the highest external mode frequency (56 cm⁻¹).³ It is further assumed that the interaction between these molecules can be represented as the sum of atom-atom terms which depend only on the separation r_{ij} between atoms i and j . The energy contributed by each interaction term is taken as

$$V(r_{ij}) = (q_i q_j / r_{ij}) + V_1(r_{ij}), \quad (1)$$

where

$$V_1(r_{ij}) = \epsilon_{ij} \left[1 - \left(6 \frac{B_i + B_j}{\sigma_{ij}} \right) \right]^{-1} \left[- \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 + 6 \left(\frac{B_i + B_j}{\sigma_{ij}} \right) \exp \left(\frac{\sigma_{ij} - r_{ij}}{B_i + B_j} \right) \right]. \quad (2)$$

The term $q_i q_j / r_{ij}$ describes a Coulomb interaction where q_i and q_j are the charges on atoms i and j respectively. The q_i , q_j , ϵ_{ij} , B_i , and B_j potential-energy parameters in Eqs. (1) and (2) may be treated as variables in obtaining the best fit between observed and calculated properties. Certain constraints were imposed on these parameters. For C-Cl interactions, it was assumed that $\epsilon_{C-Cl} = (\epsilon_{C-C} \cdot \epsilon_{Cl-Cl})^{1/2}$ and that $\sigma_{C-Cl} = \frac{1}{2}(\sigma_{C-C} + \sigma_{Cl-Cl})$; for the charges on carbon and chlorine atoms, $q_C = -q_{Cl}$. The carbon-carbon parameters were fixed at the values equivalent to those determined by Williams,⁴ and the softness parameter of chlorine, B_{Cl} , was fixed at the value equivalent to that reported by Bonadeo and D'Alessio.⁵ With these constraints imposed, there were three energy parameters (q_{Cl} , σ_{Cl-Cl} , and ϵ_{Cl-Cl}) which were varied to achieve agreement between observed and calculated properties.

Fig. 1.12. Two views of the crystal structure of hexachlorobenzene. Two equivalent molecules in the primitive cell are marked with crosses (x) in their centers.

The computer program used for the HCB calculations was briefly described in a previous publication.⁶ To assure convergence of the Coulomb and Van der Waals energies, the program uses Ewald's summation method as extended by Williams.⁷ The energy is obtained by making summations in both direct and reciprocal space. The initial stages of the calculations consisted in obtaining the best least-squares fit between observed and calculated lattice parameters, molecular orientation, and lattice energy. The observed lattice parameters and atom coordinates were taken from a recent refinement of the crystal structure of HCB carried out in this Laboratory by Brown and Strydom.⁸ The crystal structure is monoclinic, space group $P2_1/c$, with two C_6Cl_6 molecules in the unit cell. An illustration showing the contents and surroundings of a unit cell is presented in Fig. 1.12. The molecular planes are inclined by about 23° to the crystallographic ac plane. The structural parameters, which were employed as observed quantities in the least-squares procedure, included a , b_0 , c_0 , $\cos \beta$, R_x , R_y , and R_z , where R_x ,

R_y , and R_z represent rotations (in radians) about orthogonal axes and are taken as zero for the experimental structure.

Crystal structure parameters calculated by minimizing the lattice energies for two sets of potential-energy parameters of HCB are listed in Table 1.2. Set A includes only Van der Waals and repulsion terms; set B includes Coulomb terms as well. Inclusion of the Coulomb terms appears to be necessary to obtain good agreement between the observed and calculated structures. The contributions of the various terms to the lattice energies are also listed in Table 1.2; these show that, in spite of their apparent importance, the Coulomb terms add only about 13% to the total energy. Note that this is a positive term and therefore represents a net repulsion between molecules. The external optical ($k = 0$) mode frequencies calculated using the energy and structural parameters of sets A and B, Table 1.2, are given in Table 1.3. The agreement between observed and calculated external mode frequencies and their assignments for set B provides strong confirmation of

our proposed model for HCB. In particular, the observed reversal in the sequence for the 21- and 25-cm⁻¹ pair of librational modes,³ that is, $\nu(A_g) < \nu(E_g)$, was reproduced in the calculations. The calculated eigenvectors in terms of Cartesian displacement vectors of the atoms are presented in Fig. 1.13. A scaling factor was applied such that the length of the largest vector for each mode corresponds to 1 Å.

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Table 1.2. Calculated crystal structures and lattice energies for hexachlorobenzene based on energy parameter set A, which excludes Coulomb terms, and energy parameter set B, which includes Coulomb terms

Energy parameters					
Energy parameter ^a		Set A		Set B	
$q_{Cl} (= -q_C)$		0.0		-0.1058	
ϵ_{Cl-Cl}		0.2245		0.2658	
ϵ_{C-C}		0.0945		0.0945	
σ_{Cl-Cl}		3.9479		3.9367	
σ_{C-C}		3.8850		3.8850	
B_{Cl}		0.1420		0.1420	
B_C		0.1390		0.1390	
Structural parameters					
Structural parameter ^b	Observed ^c	Set A		Set B	
		Calculated ^d	Observed-calculated	Calculated ^d	Observed-calculated
a	8.048	8.242	-0.194	7.974	0.074
b	3.836	3.679	0.157	3.806	0.030
c	16.599	17.124	-0.525	16.711	-0.112
$\cos \beta$	-0.452	-0.514	0.062	-0.449	-0.003
(β)	(116.9°)	(120.9°)	(-4.0)	(116.7°)	(0.2)
R_x	0.0	0.237		-0.003	
R_y	0.0	-0.007		0.027	
R_z	0.0	0.006		0.004	
Lattice energy ^e					
	Observed	Set A		Set B	
		Calculated	Obs-calc	Calculated	Obs-calc
Coulomb		0.0		2.43	
Van der Waals		-36.96		-39.31	
Repulsion		14.64		14.85	
Total	-23.6	-22.31	-1.3	-22.03	-1.6

^a q_{Cl} in electron units; ϵ_{ij} in kcal/mole; σ_{ij} in Å; B_i in Å.

^b a , b , and c in Å. R_x , R_y , and R_z represent rotations (in radians) about orthogonal axes centered in a molecule. These axes are defined so that x is parallel to a , y is parallel to b , and z is perpendicular to x and y to form a right-handed system. A positive value of R_i ($i = x, y$, or z) denotes a clockwise rotation of the molecule with the i axis pointing toward the viewer.

^cG. M. Brown and O. A. W. Strydom, "Hexachlorobenzene, C₆Cl₆: Crystal and Molecular Structure from Least Squares Refinements with New X-Ray Data," *Acta Crystallogr.*, in press.

^dCalculated from energy minimization procedure.

^eLattice energy and contributions in kcal/mole.

Table 1.3. Calculated external optical ($k = 0$) mode frequencies (cm^{-1}) of hexachlorobenzene using the energy parameters of sets A and B in Table 1.2

Assignment ^a	Observed ^b	Calculated	
		Set A	Set B
A_g	56	51.4	59.4
B_g	54	48.7	57.7
A_g	45	44.0	46.1
B_g	38	40.3	41.1
A_g	21	21.2	22.4
B_g	25	25.7	28.5
A_u	51	49.5	52.0
A_u	c	40.5	40.4
B_u		27.0	22.8

^aAssignment based on symmetry species of C_{2h} factor group [J. B. Bates et al., *Spectrochim. Acta* 27A, 637 (1971)].

^bFrequencies measured at 300° K from J. B. Bates et al., *ibid.*

^cNot identified.

Fig. 1.13. Calculated eigenvectors for the $k = 0$ modes of hexachlorobenzene. The maximum displacement of a given chlorine atom was scaled to have a length of 1 Å for each mode. Each block shows two views of the two molecules in the unit cell corresponding to those marked x in Fig. 1.12.

2. Radiation Damage in Metals

The effect of radiation on the properties of metals is an important aspect of the development of both fission and fusion power reactors. The timely and orderly study of radiation effects in metals under technologically relevant conditions requires the development of new or improved tools for the study of defects and for the study of solid surfaces, as well as the acquisition of a fundamental understanding of the basic processes involved in the production and annealing of radiation damage. The experimental studies reported in this section are designed to acquire the information necessary for developing and testing the investigative tools required and the theoretical understanding of the processes involved. These investigations deal with various aspects of radiation damage in metals which are identified as critical areas and assigned priorities in the AEC report, *Critical Questions in Fundamental Radiation Effects Research*, WASH 1240-73, U.S. Atomic Energy Commission, Washington, D.C., April 1973.

The production of damage in metals is investigated using the channeling of ions in crystals as a means of effectively separating the energy loss due to electron excitation and ionization from the energy loss due to nuclear collisions which cause the damage. These studies improve the understanding of the basic interactions of charged particles in solids and provide information for better calculations of the damage production. Channeling is also employed as a method for locating and identifying defects in a lattice. In other experiments the amount and type of damage are being measured directly as a function of the ion penetration depth. The production of damage by irradiation with neutrons of thermal and fission energies, with ions and with electrons, is determined by measuring changes in electrical resistivity. Particular emphasis is placed on determining the number and nature of the defects produced by the different types of irradiation; in subsequent annealing experiments, the mechanisms of defect motion, aggregation, and annihilation are studied. Principal attention is now being given to the body-centered cubic transition metals. A program has been initiated for the direct comparison of the damage rates produced in niobium, molybdenum, and vanadium by fission neutrons, 14-MeV neutrons, protons, and electrons.

Clusters of point defects, which are formed both directly by the irradiations and during postirradiation annealing, are of technological importance in structural metals, because clustering of defects is the mechanism by which damage is retained in metals at reactor ambient temperatures. The clustering processes and the quantitative characterization of these clusters are being investigated by x-ray scattering and electron microscopy techniques. Since both of these methods sense the clusters through the strains produced in the lattice, more precise calculations are being made of the displacements associated with small dislocation loops in isotropic and anisotropic lattices. The interaction of these loops with dislocation lines is studied by transmission electron microscopy.

The program on the effects of irradiation on the properties of superconductors has the goal of understanding the interactions of radiation-produced defects with magnetic fluxoids. Investigation of these effects is now possible in magnetic fields up to 50 kOe at

4°K in the BSR irradiation facility. Magnetoresistance and Hall effect measurements on irradiated metals are also performed in this facility.

In proposed thermonuclear reactors the surfaces of the containment vessel will be subjected to large doses of many types of irradiations. The damage effects produced in the surface by such irradiation, the energy-loss mechanisms of the various types of radiation, and the characterization of that radiation reflected back to the plasma from the containment vessel are very imperfectly understood. Investigations by low-voltage electron diffraction and by Auger spectroscopy have been initiated to provide information on these problems.

LOW-TEMPERATURE RADIATION EFFECTS

INTERSTITIAL MIGRATION IN MOLYBDENUM

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Although there is general agreement as to the temperatures at which recovery processes occur in the range below 55°K in molybdenum, there is not agreement as to which of these is related to long-range interstitial migration. (Two recent reports^{1,2} give broad results and a discussion of damage in molybdenum.) This preliminary report gives results which indicate that the onset of long-range interstitial migration in molybdenum occurs at 40°K. In addition, results have been obtained from which a close comparison between the recovery of thermal and fission neutron damage can be made. Each type of neutron damage is produced by primary knock-on atoms having greatly different energies.

Two methods can be used to demonstrate the presence of long-range interstitial migration, commonly called Stage I-E in the fcc recovery scheme. These are a study of the effect of initial dose and the effect of irradiation doping upon recovery.

In the first method, isochronal recovery is observed for two different doses in which the defect concentration in the smaller is sufficiently dilute that impurities are expected to play an important trapping role during free interstitial migration. When the small-dose results are compared with the large-dose results, the latter should begin to show greater damage recovery at the point where free interstitial migration begins. In the higher dose, the competition of impurities for trapping is weaker, which allows more free interstitial-vacancy recombination.

Figure 2.1 shows the isochronal recovery of thermal neutron damage in molybdenum after irradiation at 4.9°K. The two doses indicated here differ by a factor

of 4.5. Below 35°K the recovery of the two doses is virtually identical, but beyond 40°K the high-dose recovery exceeds that of the low dose, consistent with the idea that free interstitial migration begins near 40°K. Recovery by recombination resulting from freely migrating interstitials is a non-first-order process, and annealing kinetic theory predicts a dependence of the recovery rate structure between dose and temperature. The recovery rate data have been examined, and it is found that near 40°K a subpeak moves downward in temperature with increasing dose.

In the second method, isochronal recovery is compared between two equal doses, one of which has been doped by partially annealed damage from a previous 4.9°K irradiation, sometimes called the doping dose. If the damage produced in the doping dose is annealed to well above the temperature at which free interstitial migration occurs, but below that at which vacancy

Fig. 2.1. The isochronal recovery of two thermal neutron irradiations of molybdenum after irradiation at 4.9°K. The fluences were 1.38×10^{17} and 6.36×10^{17} neutrons/cm², and the corresponding damage resistivity changes were 0.55 and 2.42×10^{-9} Ω-cm. Initial resistance ratio ($R_{300}/R_{3.6}$) of the specimen was ~1800.

clustering can occur, the retained damage will be in the form of interstitial clusters and isolated vacancies. During annealing of additional damage, the migrating interstitials will find themselves in what is effectively a vacancy-rich environment. Thus, during free interstitial migration the recovery of a small dose in an irradiation-doped sample will be greater than that in an undoped sample.

Following the low-dose study, the sample was given a dose six times as large and then annealed to 200°K, giving a doping damage 2.5 times the original low dose. The sample was then given a second low dose very nearly equal to the first, and a comparison of the resulting two low-dose recovery studies was made. The recovery results appear nearly identical to those seen in Fig. 2.1, with virtually identical recovery up to 40°K and enhanced recovery in the doped specimen above this temperature. This result is additional evidence that the onset of free interstitial migration occurs near 40°K in molybdenum.

We conclude that in molybdenum, free interstitial migration begins near 40°K, and, in combination with the first-order recovery preceding this, the low-temperature recovery scheme in bcc molybdenum strongly resembles that found for stage I in several fcc metals. From internal friction measurements, Okuda¹ has suggested there are two kinds of interstitials: one which migrates freely at 22°K and the other at 40°K. The present data show no evidence for a freely migrating interstitial at 22°K.

A second molybdenum wire was mounted inside of a small tubular ²³⁵U converter located in the same irradiation capsule as the thermal neutron sample. The converter, which was lined inside with gadolinium to absorb thermal neutrons, produced a nearly pure fission neutron flux in the sample. A close comparison of the two types of damage could be made, since both specimens received identical treatment except for neutron flux.

In the case of the thermal neutrons, the mean primary atom recoil energy is about 160 eV, while a typical primary energy from a fission neutron hit is about 35 keV. Comparing damage resistivity values, the number of Frenkel pairs produced is estimated at 100 for a fission hit and 2 for a thermal neutron capture event. The fission neutron damage also showed the same enhanced recovery effect at 40°K due to irradiation doping as that seen for thermal neutrons. This result is in agreement with similar results obtained by Hanada et al.³ for fast neutron damage. Another feature was the loss of recovery rate peak resolution of the fission compared with the thermal neutron damage. This is

accounted for by the localized high defect concentration present in the displacement cascades produced by the fission neutrons. The high concentration leads to defect interactions which tend to smear the otherwise unique activation energy of recovery processes.

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THERMAL AND FISSION NEUTRON DAMAGE IN VANADIUM¹

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Damage production and annealing recovery results for thermal and fission neutron damage have been obtained on 0.25-mm-diam vanadium wires having measured resistance ratios $R_{303}/R_{5.5} = 360$.

Two specimens were mounted in a thin-walled copper irradiation capsule which was filled with liquid helium during irradiation at 4.9°K and contained 3 atm of helium exchange gas pressure during postirradiation pulse annealing. One specimen was located inside a miniature ²³⁵U tubular neutron converter lined with gadolinium to absorb thermal neutrons. This arrangement produced very pure fission neutron damage. The calculated fission neutron flux was 5.1×10^{10} neutrons $\text{cm}^{-2} \text{sec}^{-1}$. The other sample was in a thermal neutron flux of 1.4×10^{12} neutrons $\text{cm}^{-2} \text{sec}^{-1}$ and a negligible fission neutron flux. Two irradiation doses differing by a factor of 4.3 were studied (low dose first) for each type of damage.

From the measured damage resistivity values, $\Delta\rho$, and the neutron fluences, Φ , the specific resistivity related to each type of neutron-atom event can be calculated by $\delta\rho = \Delta\rho/\sigma\Phi$, where σ is either the thermal neutron capture or the average fission-neutron-vanadium-atom scattering cross section. Using $\sigma_t = 5.1$ and $\sigma_f = 3$ b (ref. 2) gives $\delta\rho_t = 51 \times 10^{-4}$ and $\delta\rho_f = 2680 \times 10^{-4} \Omega\text{-cm}$ per unit concentration of primary events. Since the specific resistivity of Frenkel pairs, $\rho_{F.P.}$, in vanadium is not known, we estimate a value using an empirical rule good for some elements that $\rho_{F.P.}$ is 1.5 times the room temperature resistivity, or $33 \times 10^{-4} \Omega\text{-cm}$ per unit concentration of F.P. for vanadium. This gives an estimate of 1.5 F.P. per neutron capture and 81 F.P. per primary knock-on event from fission neutrons.

Fig. 2.2. The isochronal recovery rates of thermal and fission neutron damage in vanadium after irradiation at 4.9°K. An isochronal program of 5-min pulses and $\Delta T = 0.055T$ was used for both doses. The thermal and fission neutron fluences were 6.4×10^{17} and 2.2×10^{16} , respectively, for the high dose and less by a factor of 4.3 for the low dose. For the low dose the data between 16 and 20°K were lost. We have no reason to believe that the subpeak at 18°K would not be present in the low dose.

Figure 2.2 shows the isochronal recovery rates of each type of damage. One striking feature of these results is that for equal damage concentrations there is a close similarity in the recovery of the damage produced by two drastically different mechanisms. This similarity suggests that the defect distributions differ little between the two types of damage. Since the defect concentrations studied in each case are small (5×10^{-6} estimated), irradiation annealing or the overlap of displacement cascades can in no way be responsible for the similarity. We conclude that, although the localized defect concentration within a displacement cascade is almost certainly greater than the more or less uniform thermal neutron damage, it is sufficiently dilute to produce the same recovery behavior.

Another notable feature is the almost structureless recovery (except for a small peak at 18°K) between 6 and 40°K. In most metals the onset of recovery at low defect concentrations occurs by recombination of close Frenkel pairs, giving rise to discrete annealing peaks. At high damage concentrations the interactions between defects tend to smear these discrete processes, giving nearly continuous recovery. The low defect concentrations studied in the vanadium are believed to be too small for this smearing to occur, and accordingly the recovery below 40°K is probably not associated with close-pair processes. The continuous nature of this

recovery could be accounted for by the long-range migration of an interstitial having a very small activation energy which is trapped at relatively large distances by impurities and other defects. The annealing of such an interstitial would be governed mainly by the nearly continuous spectrum of detrapping energies.

Above 40°K there is substantial alteration of the recovery behavior with irradiation dose. The recovery peak at 46°K indicates a first-order process on the basis of the dose dependence, while the peak at 72°K appears to move slightly toward lower temperature with increasing dose, as expected of non-first-order processes. The recovery in this region appears to be complicated by the presence of more than one process. Identification of non-first-order processes is important, since they frequently provide the key to understanding other regions of the recovery behavior such as, for example, the recovery above 100°K in Fig. 2.2. The changes in the recovery behavior are suggestive that one is dealing with processes in which defects have moved large distances, either as a result of the primary recoil event or because of long-range migration in the low-temperature recovery. In either case, impurities would be expected to play an important role, and higher-purity material would be helpful in sorting out the basic processes.

The data presented in this report are not sufficient to formulate a model of the low-temperature recovery processes in vanadium, and we know of no other low-temperature recovery studies. It seems clear that for vanadium further study is needed, particularly on the recovery below 40°K, before a firm recovery model can be formulated.

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DAMAGE RECOVERY IN VANADIUM BETWEEN 3.8 AND 6.0°K

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The isochronal recovery of thermal neutron damage in vanadium has recently been studied¹ from 6 to 320°K by means of resistivity changes. One interesting result was the observation of continuous recovery from 6 to 40°K in contrast to the spectra of discrete recovery

rate peaks seen for thermal neutron damage in nearly all other metals studied. The absence of recovery rate peaks in this low-temperature range of recovery led to the speculation that the onset of recovery in vanadium may occur by means of long-range interstitial migration rather than the collapse of close Frenkel pairs, which are believed to initiate the recovery in most other metals. Another possibility is that close-pair recovery in vanadium occurs below 6°K . This speculation is not unreasonable, since recovery below 6°K has been observed in Au, Cd, In, and Zn.² In the case of cadmium a large recovery rate peak occurs at 5.2°K , with a subpeak at 3.6°K .³

Because vanadium is a superconductor and a magnetic field for driving the sample normal was not available in the experiment mentioned above, useful recovery results could not be obtained below about 6°K . Through the use of a superconducting magnet described elsewhere in this report,⁴ the isochronal recovery of vanadium was studied after irradiation at 3.8°K by thermal neutrons in another more recent experiment. Figure 2.3 shows both the recovery and recovery rate results. From these results, we conclude that the continuous recovery found earlier extends downward in temperature to at least 4.7°K and probably to 4.3°K . The approach to the continuous recovery behavior seen between 4.0 and 4.7°K is what might reasonably be expected if the continuous recovery extended even

below 4.7°K and thermal annealing of the damage occurred at the irradiation temperature of 3.8°K . For this reason we believe that 3.8°K may not be cold enough to stabilize all damage in vanadium. The absence of close-pair peaks at low temperatures during the recovery of vanadium suggests that vanadium resembles gold, which has recently been studied by Gwozdz and Koehler⁵ using electron irradiation on samples as low as 1.55°K . They concluded that long-range defect migration occurs in gold below 2°K .

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THE ELASTIC CONSTANTS OF THERMAL-NEUTRON-IRRADIATED COPPER¹

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Fig. 2.3. Isochronal recovery and recovery rates of vanadium irradiated at 3.8°K to a thermal neutron fluence of 4.0×10^{17} neutrons/cm². The capture event concentration was 2.0×10^{-6} , and the Frenkel pair concentration is estimated at 3.0×10^{-6} . The damage resistivity was $9.0 \times 10^{-9} \Omega\text{-cm}$. The initial residual resistance ratio of the 0.25-mm-diam wire was 387. All measurements were made at 3.8°K in a transverse magnetic field of 2.3 kOe, which was found by a separate test to drive the sample normal while producing negligible magnetoresistance. The isochronal program was $\Delta T = 0.05^\circ\text{K}$.

The three independent elastic constants of copper irradiated with thermal neutrons below 4°K have been measured. Simultaneous measurements of attenuation and resistivity were used to monitor the defect density. The elastic constant changes during irradiation per unit concentration γ of defects, $d \ln C/d\gamma$, are -2 , -15.8 , and -18.1 for the bulk modulus, C_{44} , and $C' = (C_{11} - C_{12})/2$ respectively. The percentage elastic constant changes measured at 3.6°K after pulse annealing to different temperatures are different for different elastic constants in the same annealing range. Also, the elastic constant changes are strongly temperature dependent. The results show that there are five different types of elastic constant effects, each of which depends upon the type of defect involved. This also helps to account for the wide variation of results found previously for measurements using different types of irradiation at different temperatures.

1. Abstract of paper to be published.
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INTERLABORATORY PROGRAM TO STUDY LOW-TEMPERATURE DAMAGE RATES IN DILUTE VANADIUM, NIOBIUM, AND MOLYBDENUM ALLOYS

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As a part of our program to investigate 14-MeV neutron radiation damage and to provide more exact normalization standards for simulation of neutron damage with energetic heavy ions, a cooperative program has been initiated by this division in which the special capabilities of a number of laboratories will be used for the measurement of damage production rates for electron, proton, fission neutron, and 14-MeV neutron irradiation of dilute alloys of vanadium, niobium, and molybdenum. In order to measure damage production rates to better than 10%, the various experimenters must coordinate their experiments to reproduce accurately at the various laboratories all experimental conditions other than the bombarding species. The production rates will be measured by the change in resistivity accompanying irradiation near 4°K. Dilute alloys were chosen for this study to suppress a transient variation in the apparent damage rate that is observed at low dose in high-purity materials. The limited maximum dose available in the 14-MeV neutron irradiations ($\sim 10^{17}$ neutrons/cm²) makes it necessary that all the measurements be made at low dose levels so that damage production rates will be obtained at comparable damage concentrations. For electron irradiations, damage production rates will be carried out by W. Schilling of the KFA, Jülich, Germany, and displacement threshold measurements will be made by R. Chaplin of Clemson University. Damage rates will be measured by H. H. Andersen of Aarhus University, Denmark, for proton irradiations, by R. R. Coltman, Jr., of ORNL for pure fission neutron irradiations, and by R. Borg of Lawrence Livermore Laboratory for the 14-MeV neutron irradiations.

R. E. Reed of this division has prepared 0.025-mm-thick foils of nominally 0.03 at. % zirconium in vanadium, niobium, and molybdenum. The purification of the solvent metals was done by electron-beam float-zone melting (EBFZM). Niobium was first purified using the EBFZM oxygen treatment and subsequent outgassing techniques developed previously.¹ High-purity dendritic vanadium pieces were first melted in a special arc-casting facility and then melted by EBFZM in ultrahigh vacuum as described in earlier work.² Molybdenum was melted by EBFZM in an oxidizing atmosphere, producing material with a resistance ratio of about 7000.³

A slot was then milled along the length of each solvent metal rod, and the appropriate amount of zirconium foil was pressed into the slot. The alloy rod was then made by electron-beam float-zone leveling by making an EBFZM pass up and then down the rod. The rods were extensively analyzed for impurities and zirconium content prior to rolling. The rolling was done at room temperature. After rolling to a 0.125-mm thickness, the foils were flash annealed by passing an ac current through the foils for pulsed intervals of time so as not to allow the pressure in the system to go above a chosen level. The temperature of the foils was kept below the recrystallization temperature for the particular alloy being annealed in order to prevent zirconium loss. The foils were given a metallographic examination to verify the annealing temperatures. After this strain-relief anneal, the metals were rolled to 0.025 mm thickness. The width varied from 13 to 16 mm. Another flash annealing treatment was given to each alloy, and chemical analysis by spark source mass spectrometry was performed prior to distribution. Sample material has recently been sent to the various experimenters.

The resistance of several samples of each alloy was measured at 4.2°K. In the case of vanadium and niobium, which are superconductors, curves of resistance vs transverse magnetic field strength were obtained. From these curves, transverse field strength values of 1.8 kOe for vanadium and 10 kOe for niobium were chosen as the best compromise between driving the material fully normal and minimizing magneto-resistance effects. These values will be used by all experimenters. Resistance ratios found for the various alloys are between 70 and 130, which are consistent with the alloy content necessary to suppress the transient damage rate variations mentioned above. These values also confirm that sample uniformity is satisfactory.

To meet the ORNL commitment to this program (fission neutron damage rates), it will be necessary to use a ²³⁵U converter located in the sample chamber of the ORNL Low-Temperature Irradiation Facility (LTIF), which has a highly thermalized neutron flux. Somewhat similar converters have been used in the past.⁴ In this experiment, the converter design is dictated in part by the need to locate it inside a superconducting magnet situated in the sample chamber of the LTIF. (A superconducting magnet intended for this use has been designed by S. T. Sekula of ORNL and is presently being constructed. Except for length and mass, it is similar to one described elsewhere in this report.)⁵ A further limitation is the need to orient the ribbon-shaped samples transverse to the magnetic field.

To meet these requirements, the converter will be in the form of a pure ^{235}U ribbon about 3 mm wide by 0.125 mm thick and shaped to form a ring 10 mm in diameter. The sample will also be a ring inside and as close as possible (~ 0.2 mm) to the surface of the converter. Gadolinium foil will be used to shield appropriately the sample from thermal neutrons. Detailed computer calculations of the fission neutron flux produced by this ring configuration have been made, including variations of ^{235}U thickness and converter-sample separation. These will be used to determine the final design of the converter-heat exchanger and the sample holder, which will be separate devices keyed together. One converter and its integral heat exchanger will be used for all specimens. Preliminary estimates are that a fission neutron flux of 6×10^{11} can be produced at a heat power output within the capacity of the LTIF. The flux estimate is 50% greater than the highest previous value obtained⁴ with such in-cryostat converters.

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THE MAGNETORESISTANCE OF IRRADIATED PLATINUM, VANADIUM, AND COPPER

R. R. Colman, Jr. J. K. Redman
C. E. Klabunde J. M. Williams

Electrical resistivity has long been used as a sensitive and easily applied detector of irradiation defects in metals. It is generally agreed that, except for small deviations in Matthiessen's rule which can occur in some cases, electrical resistivity responds linearly with a high degree of accuracy to the presence of unclustered defects. In small defect clusters (two to a few), the resistivity per defect is not changed significantly, which precludes the use of this property for detecting the nucleation of clusters during annealing. Since defect-cluster nucleation is a very important aspect of radiation damage recovery, there is a need for a property which is responsive not only to defect concentration but also in some way to defect configuration. It has long been speculated that magnetoresistance might

show such a response in some metals, but very few studies have been made. Böning¹ et al. have studied the effect of a large fast neutron dose (20% irradiation annealing) upon the magnetoresistance of copper and aluminum. They found effects during postirradiation annealing that could be attributed to defect agglomeration. We know of no other similar work.

To look for possible magnetoresistance effects due to simple point defects at smaller concentrations than Böning et al., we are studying the effect of thermal neutron damage on the transverse-field magnetoresistance of vanadium, copper, and platinum. Some of the preliminary results obtained for platinum during irradiation at 4.91°K to a thermal neutron fluence of 1.8×10^{18} neutrons/cm², and during subsequent annealing, are shown in Fig. 2.4. These results are presented here as a plot of the measured resistivity at several field strengths, $\rho(H)$, vs the resistivity in zero field, $\rho(0)$. Since $\rho(0)$ increased nearly linearly with neutron fluence, the abscissa is also a measure of the dose for the damage production points. The most important and unexpected finding of this study is the very close superposition of the annealing curves on the damage production curves. This result is observed for all

Fig. 2.4. Resistivity of thermal-neutron-irradiated platinum (4.91°K) measured in various transverse magnetic fields, $\rho(H)$, vs resistivity in zero field, $\rho(0)$. Annealing pulses were 5 min, except 420°K was 20 min. The initial resistance ratio ($R_{300}/R_{3.6}$) of the specimen was 7300.

field-strength values shown in Fig. 2.4, and similar results were obtained for copper and vanadium.

In platinum the thermal neutron damage is in the form of a more or less random distribution of vacancy-interstitial pairs. During annealing up to 30°K, recovery proceeds by the recombination of close and correlated Frenkel pairs. Above this temperature, long-range interstitial migration leads to uncorrelated recombination, which removes damage, and to trapping and clustering of interstitials, which retain damage. Between 35 and 420°K, detrapping of interstitials and growth of interstitial clusters occur. Thus the superposition of the annealing curves on the damage production curves at all temperatures above 35°K indicates that the magnetoresistance does not distinguish between isolated defects and defects in the clusters present in this experiment. In the study of Böning¹ et al., large clusters and possibly other defect agglomerates are expected to form as a result of their high-dose fast neutron irradiation. At the moment, we are led to speculate that significant sensitivity of magnetoresistivity to defect configuration is found only with large defect clusters.

It can be noted on the high-field curve that the slope at low defect concentrations, although negative, has a much greater magnitude than at zero field. This suggests that under proper conditions of H and ρ_0 , such as those seen here, magnetoresistivity could be used to increase the sensitivity for measuring defects at low concentrations. The shape of the high-field curve seen in Fig. 2.4 is one that can reasonably be expected for some metals in terms of Kohler's rule.

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A CRYOSTAT FOR ELECTRON IRRADIATION

C. E. Klabunde J. M. Williams

Construction and initial testing have been completed on a cryostat for low-temperature studies of electron irradiation damage. The initial impetus for this project is an experiment to obtain a definitive answer to the question of what defect is migrating in the stage III recovery of irradiated copper. The experiment requires irradiation of samples near 4.2°K, as well as between 150 and 300°K, and postirradiation annealing up to 470°K.

The cryostat is designed for use with the Division's electron accelerator and utilizes either a conventional 50-liter nitrogen-shielded helium dewar or a commercial superinsulated 30-liter dewar. A continuous small stream of helium is transferred from the dewar through the window-frame-style sample-mounting block. To minimize the ambient radiant heat load on the helium-cooled system, it is surrounded by a metal-conduction-cooled shield dipping into a 25-liter nitrogen dewar. One common vacuum jacket houses the nitrogen and helium dewar dip tubes, the sample chamber, and the horizontal line connecting all three. The jacket may share the accelerator vacuum or be isolated from it by an aluminum-foil window in the beam tube. Both dewars may be refilled in place.

Thin foil samples (such as 12.5 μ thick by 0.75 mm wide by 5 mm between potential probes) will reach across the window opening of the refrigerated mounting block through the path of the beam. Metallized sapphire plates soldered onto the block provide thermal conduction and electrical insulation for the samples. Thermometry at the 150 to 300°K irradiation temperatures is no problem. To assure a reproducible liquid-helium temperature for measurements of the sample electrical resistivity, a carbon resistor thermometer, mounted rather like a sample, will monitor the low temperatures.

Once the entire nitrogen-cooled shield has reached equilibrium, which takes a few hours, the helium-system cooldown is completed in a few minutes with very modest flows. Liquid helium consumption rates range from 0.05 to 0.4 liter/hr for stable maintenance of sample-block temperatures from 200°K down to about 4.3°K. At the elevated temperatures, an electric heater built into the block provides fine control and may be used for sample annealing as high as 470°K. The thermal conductivity of the sample itself will set the limits of electron beam current because the temperature gradient within the sample must be kept acceptably small. The beam will place a negligible heat load on the refrigeration system compared with the main residual heat leak (through the leads). Even at this limited beam current, the anticipated irradiation times for the initial experiment will not be unduly long, ranging from a few minutes to a couple of hours. Remote monitoring of flows and temperatures with automated controls has been set up to facilitate continuous operation. Extended irradiations to a few days appear practical.

The sample-mounting block is easily modified or replaced, and the whole system is compatible with other accelerators for studies of charged-particle damage.

SUPERCONDUCTIVITY

FAST NEUTRON DAMAGE IN A SUPERCONDUCTING Nb-Ti ALLOY

S. T. Sekula

Nb-Ti alloys are currently being used in the fabrication of wire suitable for the construction of superconducting solenoids, and a number of investigations have studied the effect of energetic particle irradiation on these materials. A decrease in the transport critical current, I_c , of a cold-worked Nb-Ti wire irradiated with 5-MeV deuterons at 30°K was observed by Coffey et al.,¹ and Brechna and Maure.² report a reduction in I_c after room-temperature irradiation with 50-MeV deuterons of commercial stabilized Nb-Ti multicore wires. Soell et al.³ observed a reduction of a factor of 2 of I_c in a commercial Nb-Ti filament 1.1×10^{-3} cm in diameter after fast neutron irradiation at 5°K to a fluence of 7.5×10^{18} neutrons/cm² ($E > 0.1$ MeV), while Sugisaki et al.⁴ found that the critical current in a commercial cold-drawn niobium-50 at. % titanium wire 1.5×10^{-2} cm in diameter was increased by a factor of 2 after fast neutron irradiation at ambient temperatures to a fluence of 3.5×10^{18} neutrons/cm². It was therefore decided to study the effect of fast neutron irradiation at 40°C on the superconducting properties of a cold-drawn sample of similar composition (niobium-52 at. % titanium), as well as a sample that had been partially annealed by heat treatment at 1100°C for 1 hr in a vacuum of 10^{-6} torr.

The samples consisted of cylinders 0.32 cm in diameter and approximately 2.5 cm in length. These samples were irradiated in the Oak Ridge Research Reactor at 40°C to a fast neutron fluence of 4.8×10^{19} neutrons/cm² ($E > 1$ MeV). Prior to and after the irradiation, measurements were carried out at 4.2°K in a Hartshorn mutual-inductance bridge employing a lock-in amplifier at the bridge output.⁵ In these experiments, the ac (350 Hz) magnetic permeability is measured as a steady magnetic field H is slowly increased or decreased (5 Oe/sec) in a superposed sinusoidally varying field of amplitude h_0 and frequency 350 Hz. As previously described in detail,⁵ one can resolve the fundamental component of the generally nonlinear response of the sample to the sinusoidal field to obtain a signal V_L , which is proportional to the imaginary component of the ac permeability and is simply related to the power dissipation in the sample. Moreover, it has been observed⁶ that a modified version of the Bean-London critical state model can adequately describe the flux-pinning effects in these measurements

so that one can deduce values of the superconducting critical current density $J_c(H)$, which is inversely proportional to the experimental values $V_L(H)$.

Values of the deduced values of $J_c(H)$ plotted against the magnetic field H for fields of up to 7 kOe and at a temperature of 4.2°K are shown in Fig. 2.5 for the cold-drawn and the partially annealed samples. Also shown in Fig. 2.5 are values of $J_c(H)$ for these alloys after fast neutron irradiation. The ac field amplitude in these measurements was 72 Oe. Prior to irradiation, it is seen that for the cold-worked sample, $J_c(H)$ decreases monotonically from values of about 10^5 A/cm² to approximately 1.5×10^3 A/cm² as the field is increased from $H = 0$ to 7 kOe. Partially annealing an identical sample as previously specified leads to a drastic reduction in $J_c(H)$, so that at a field of 2 kOe, J_c is only of the order of 10^3 A/cm². This reduction by annealing can be interpreted as being due to a removal of rather effective flux-pinning defects thought to be for the most part dislocation cell structures.³

Fig. 2.5. The superconducting critical current density J_c vs the applied field H for cold-worked and annealed samples of a niobium-52 at. % titanium alloy prior to and after fast neutron irradiation at 40°C.

Following irradiation, the critical current density, $J_c(H)$, of the cold-worked sample shows an overall decrease with about a 50% reduction at higher field values in comparison with the preirradiation results, as can be seen in Fig. 2.5. On the other hand, irradiation of the partially annealed sample leads to an increase in $J_c(H)$ by about 30% at a field of 2 kOe, although the magnitude is still considerably less than in the cold-worked case.

The increase in $J_c(H)$ of the annealed sample by irradiation can be qualitatively understood as resulting from the production of radiation defect aggregates that can pin magnetic fluxoids. In the case of the cold-worked sample, the experimental observations suggest a decrease in the pinning strength of the existing defects after irradiation over and above the production of flux-pinning defect aggregates. Thus, if dislocation cell walls in the cold-worked material are the dominant flux-pinning mechanism, one tentative explanation of the experimental results is that the production of radiation defect aggregates in the relatively defect-free region surrounded by dislocation cell walls leads to a homogenization of the sample from the aspect of magnetic-fluxoid-defect interactions. This increase in matching of the defect structure in the matrix and in the original pinning centers results in a net decrease of the flux-pinning force.³

Further investigations on these samples will be carried out to larger fluences and in larger fields, and additional studies will be made on multiphase Nb-Ti alloys.

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LOW-TEMPERATURE IRRADIATION OF SUPERCONDUCTING VANADIUM

S. T. Sekula J. K. Redman
R. R. Coltman, Jr. J. M. Williams

Vanadium is an elemental type II superconductor¹ which shows substantial increases of flux pinning in the superconducting state due to radiation damage defects

introduced by fast neutron irradiation at 40°C.² It was decided to search for possible effects of thermal neutron damage in this material with irradiation at low temperatures, where defects could be stabilized in their as-produced configuration.

A polycrystalline wire sample of vanadium 0.25 mm in diameter and with resistance ratio $R_{273^\circ\text{K}}/R_{3.6^\circ\text{K}} = 387$ was mounted in a sample can in the bore of a superconducting solenoid and cooled to 3.8°K in the Low-Temperature Irradiation Facility in the BSR. Current and potential leads were attached to the sample, which was positioned so that the current passing through the sample was perpendicular to the magnetic field generated by the solenoid ($H \perp I$). With a constant current passing through the sample, the voltage drop across the gage length of the sample was measured as the magnetic field was increased from zero to values sufficiently large to destroy the superconducting state. The effective resistance, R_e , defined as the ratio of the sample voltage drop to sample current, is plotted vs the magnetic field H . Typical preirradiation results are shown in Fig. 2.6 for a sample current of 0.5 A (solid points). At low values of H the sample is completely superconducting, and $R_e = 0$ until some critical value of the field is reached and the sample begins to show a resistive voltage drop. The critical field H_R is defined to be that field at which a 1-μV signal is obtained. For the case seen in Fig. 2.6, this value is 580 Oe. Above this field, the field dependence of the resistance is characterized by a rapid rise due to the motion of magnetic fluxoids in the mixed state,³ followed by a more gradual rise as bulk superconductivity disappears and only a superconducting sheath remains.⁴ At sufficiently high fields (in this case, about 2000 Oe), all traces of superconductivity vanish, and the sample exhibits normal-state resistivity.

Data for the resistive transition of the sample following thermal neutron irradiation to a fluence of 4×10^{17} neutrons/cm² are also shown in Fig. 2.6 for purposes of comparison. It is observed that there is no noticeable change in H_R , although there is an increase in the normal-state resistance due to thermal neutron damage. From this it is inferred that point defects produced during this irradiation did not appreciably interact with magnetic fluxoids, since one would expect a shift in H_R (towards higher values) in the presence of defect-fluxoid interactions.

Isochronal anneals at temperatures of 60°K, 200°K, and 420°K were also carried out with subsequent measurements of the resistive transition at 3.8°K. No shifts in H_R were noted, although the normal-state resistivity decreased with increasing annealing tempera-

Fig. 2.6. Resistive transition of superconducting vanadium vs the applied magnetic field prior to and after low-temperature irradiation.

ture. This indicates that the concentration of various defect aggregates believed to remain after each anneal and/or the strength of the defect-fluxoid interaction are too small to give rise to observable flux-pinning effects.

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LOW-TEMPERATURE IRRADIATION OF A SUPERCONDUCTING SOLENOID

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R. R. Coltman, Jr. J. M. Williams

A superconducting magnet constructed of multifilamentary Nb-Ti wires embedded in a copper matrix

for stabilization (composite wire diameter 0.008 in.) and previously tested and calibrated¹ was incorporated into the Low-Temperature Irradiation Facility (LTIF) at the BSR. While one purpose of the solenoid was to generate magnetic fields for low-temperature magnetoresistance studies and investigations of superconductivity in irradiated materials as described elsewhere in this report,^{2,3} another objective was the study of an in situ operation and performance of a superconducting magnet in a radiation environment. Some experiences and observations pertinent to this objective are given in the following paragraphs.

Prior to irradiation it was found that at 3.6°K with a sample chamber pressure of 230 torr of helium exchange gas (standard conditions with the reactor off) a maximum field of 50.8 kOe could be attained, corresponding to a critical current of 43.8 A. The abrupt release of energy stored in the magnet (192 Wsec) at this current level had no serious effects on the LTIF cryostat or the helium liquefier system. With liquid helium condensed in the sample chamber (standard condition with the reactor on) and the solenoid immersed in the liquid at 3.6°K, it was found that a field of 42 kOe could be attained without quenching of the magnet. While it is expected that the maximum field of 50.8 kOe could be obtained with operation in the liquid, field collapse tests at lower magnet currents produced abrupt pressure transients in the chamber, and, to prevent possible damage to certain instrumentation, it was decided to limit "in liquid" magnet operation to 25 kOe until additional tests could be made. The time constant of the magnet (wound on an anodized aluminum coil form) was found to be about 1 sec, so that relatively rapid field changes could be made during sample measurements with the reactor on or off.

However, it was observed that the equilibrium temperature of the liquid helium in the sample chamber depended on the power level of the reactor, mainly as a result of gamma-ray heating in the magnet (magnet mass = 161 g). Thus at full reactor power (2 MW) the liquid in the sample chamber was about 5°K. Under these conditions the magnet performed adequately at 7 kOe to a thermal neutron fluence of 1.5×10^{18} neutrons/cm². No attempt was made to quench the magnet in order to avoid undesired heating of the sample can during irradiation. Following an inadvertent electrical power failure and subsequent warm-up, the magnet was operated in a continuous fashion at 25 kOe for three days in a thermal neutron flux of 6.8×10^{11} neutrons cm⁻² sec⁻¹ to a fluence of 2×10^{17} neutrons/cm². In this experiment the reactor was operated at approximately one-fourth of full power with the temperature of the liquid in the chamber

about 3.7°K. Three additional days at this power level gave satisfactory short-term operation up to the 25-kOe level.

Further studies are planned to investigate the influence of thermal neutron damage on the Nb-Ti filaments as well as the copper cladding, both of which may affect the quenching characteristics of a magnet. In addition, an investigation of gamma-ray heating on magnet critical current at a given liquid-bath temperature will be pursued.

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RESISTIVITY MEASUREMENTS OF HIGH-PURITY METALS USING A MUTUAL INDUCTANCE METHOD

S. T. Sekula

Resistivity measurements at 4.2°K, using a dc four-probe technique, are commonly used to evaluate the purity of metal samples. This requires the attachment of electrical leads by soldering or other means, and in many cases the voltage drop across the gage length of the sample (usually in the form of a rod with a circular cross section as obtained by zone refining) can be less than 0.01 μ V, even when using large sample currents. An alternative method of determining the low-temperature resistivity is to measure the complex eddy current susceptibility of the rod when subjected to a sinusoidally varying magnetic field of frequency ω . It can be shown, using classical electrodynamics, that the real and imaginary components of the susceptibility are unique functions of the sample diameter, the excitation frequency ω , and the electrical resistivity of the metal, so that the electrical resistivity can be extracted from such measurements. This technique is limited to non-magnetic metals but has the advantages that leads do not have to be attached to the sample and, also, that the eddy current susceptibility signals do not become vanishingly small with decreasing sample resistivity.

A mutual inductance bridge of the Hartshorn type was constructed similar to that used in other work,¹ employing a lock-in amplifier at the bridge output. With the bridge initially nulled, samples with diameters up to 1.4 cm could be inserted into a sample coil located in a

liquid helium bath. The resultant bridge signal could be decomposed into two signals proportional to the real and imaginary components of the eddy current susceptibility of the sample by suitable phasing of the lock-in amplifier. The classical arguments for the eddy current susceptibility of a metallic cylinder do not apply when the electron mean free path l becomes comparable with the skin depth δ , so to avoid these anomalous skin effect problems, magnetic field excitations of low frequency are required for high-purity sample measurements. It is estimated that at the lowest frequency used in these measurements (20 Hz) the lower limit (the limitation arising from the anomalous skin effect) to the resistivity that can be measured to 3 to 4% is about $2 \times 10^{-9} \Omega\text{-cm}$, although results to within 10% can be obtained for resistivities of the order of $1 \times 10^{-9} \Omega\text{-cm}$. Comparison of the resistivity values of high-purity molybdenum and copper at 4.2°K shows good agreement with values obtained from the same samples using the dc technique.

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X-RAY DIFFRACTION AND ELECTRON MICROSCOPY

CONCENTRATION AND SIZE DISTRIBUTION OF DISLOCATION LOOPS FROM DIFFUSE SCATTERING

B. C. Larson

Integral Huang x-ray diffuse scattering measurements have been analyzed to obtain the concentrations and size distributions of dislocation loops produced by fast neutron irradiation in copper crystals. These measurements were made using a two-axis diffractometer and a wide-open detector, which corresponds to integrating the scattering over the Ewald sphere with data collected as a function of the rocking angle of the sample relative to the Bragg angle.

The analysis of this scattering is based on the dipole-force model for clustered defects with the constraint that the Huang scattering changes from a $1/q^2$ to a $1/q^4$ dependence at $q = 1/R$, as expected from the Stokes-Wilson approximation. For dislocation loops, this scattering can reasonably be approximated by an isotropic average for purposes of integration over the Ewald sphere and in this approximation leads to a closed-form integral diffuse scattering model. The model can then be used to analyze diffuse scattering

data by least-squares-fitting the scattering from a number of loop sizes to the measured data, with the individual concentrations of each size as parameters.

The observed integral diffuse scattering intensity for a copper crystal irradiated for a dose of 7.2×10^{18} neutrons/cm² at 43°C in the BSR is shown in Fig. 2.7 for measurements made near the 111 reciprocal lattice point using copper $K\alpha$ x rays. The solid line represents the fit of the model to the measured data (given as the individual points), and it can be seen that a very good fit can be obtained with this model. The concentration and size distribution of dislocation loops corresponding to this fitting procedure is shown as the solid line in Fig. 2.8 in terms of the concentration (loops/cm³) per angstrom of radius increment of the loops. The hatched area represents the uncertainty in the concentrations as estimated from the uncertainty in the scattered intensities.

The individual points plotted in Fig. 2.8 refer to electron microscopy observations on a similarly irradiated copper crystal, expressed in the same units as the x-ray distribution, and the error bars on these points represent the statistical uncertainty in the measurements. The agreement between the two measurements is quite remarkable considering there are no arbitrarily adjustable parameters involved.

Fig. 2.7. Integral Huang diffuse scattering from 111 reciprocal lattice point in neutron-irradiated copper.

Fig. 2.8. Concentration and size distribution of dislocation loops in neutron-irradiated copper.

The usefulness of x-ray measurements such as these lies in their relative ease of application and in the nondestructive, bulk property nature of the measurements. In addition, these measurements contain an inherently good statistical sampling of the defects. This is in contrast to electron microscopy observations, which must be confined to sampling the order of a few thousand defects because of the tedious nature of the measurements and which as far as further bulk property measurements are concerned are essentially destructive measurements. For systematic studies where subtle changes are expected or investigations where bulk properties are required, such as in step annealing programs, these aspects are particularly important.

HIGH-PRECISION MEASUREMENTS OF LATTICE PARAMETER CHANGES IN NEUTRON-IRRADIATED COPPER¹

B. C. Larson

Measurements have been made of the lattice parameter changes in copper after neutron irradiation at 43°C

in the BSR for doses of 1.0 to 10.8×10^{18} neutrons/cm². These measurements were made using a multiple-reflecting monochromator which made it possible to measure the changes with high precision and eliminate the asymmetric diffuse scattering near Bragg reflections.

The presence of both vacancy- and interstitial-type loops in these samples eliminates the first-order lattice-parameter changes from loops, leaving the smaller, second-order effect only. The two-beam, multiple-reflecting geometry shown in Fig. 2.9 was developed to measure these small changes. The two beams incident on the sample are angularly separated by $2\theta_B$ (θ_B = Bragg angle of monochromator) by respectively diffracting them singly and doubly from the inside surfaces of the boundary-free U-shaped monochromator. As the sample is rotated, the x-ray beams are Bragg-reflected from their respective sides of the sample with an angular separation of $\Delta\alpha = 2 \tan \theta_B \times (\Delta a/a)$, where Δa is the lattice-parameter change relative to that of the monochromator. The lattice-parameter change is therefore measured independent of the lattice parameter itself, and, since only the Bragg peak is used with monochromatic x rays, the rather intense diffuse scattering near the peaks does not affect the measurement.

The results of these measurements are shown in Fig. 2.10 for the doses measured, where the solid line represents a curve of the form $\Delta a/a = B[1 - \exp(-\lambda D)]$ to emphasize the saturation as a function of dose. In this curve, $B = 55 \times 10^{-6}$, $\lambda = 2.2 \times 10^{-17}$ cm²/neutron, and D is the neutron dose. These results were analyzed using second-order elasticity for which, adapting the method of Lomer² for straight dislocations, the lattice-parameter change for a loop of radius

Fig. 2.9. Schematic view of lattice-parameter measurement.

Fig. 2.10. Measured lattice-parameter change as a function of the neutron dose ($E > 0.6$ MeV).

R was found to be

$$\frac{\Delta a}{a} = \frac{\gamma_G K \mu b^2 R}{3 V_c (1 - \nu)} \left[\ln \left(\frac{8R}{b} \right) - 1 \right]. \quad (1)$$

V_c is the atomic volume, γ_G is the Gruneisen parameter, K the compressibility, μ the shear modulus, b the Burgers vector, and ν Poisson's ratio.

Assuming an exponential distribution of loop sizes, the saturation in the concentration of loops as a function of neutron dose was found to agree quite well with results from electron microscopy. However, the absolute value of the concentrations was about a factor of 3 higher than that found with the microscope. The source of this discrepancy is unknown at present, and, until a more complete theory is available, taking the anisotropy of the lattice and the details of the distortion fields around the loops into consideration, the absolute concentrations determined from the lattice parameter must be considered tentative. Nevertheless, the agreement of the dose dependence with electron microscopy and also with more detailed x-ray diffuse scattering measurements seems to imply that qualitative inferences made from the lattice-parameter measurements are reliable when the size distribution is known approximately.

1. Summary of paper: *J. Appl. Phys.* in press.
2. W. M. Lomer, *Phil. Mag.* 2, 1053 (1957).

LOW-TEMPERATURE IRRADIATION DAMAGE IN COPPER

B. C. Larson F. W. Young, Jr.

As part of the program of investigating the temperature dependence of radiation damage in metals, copper crystals were irradiated at liquid helium temperature to doses of 1.3×10^{18} neutrons/cm² (fission) at Argonne National Laboratory and 4.4×10^{18} neutrons/cm² (reactor spectrum) at FRM, Munich. These crystals have been studied by integral diffuse scattering measurements after warming to room temperature, and it has been found that the average size of the dislocation loops formed under these conditions is about a factor of 2 smaller than the size present after irradiations at room temperature. Exponential-like [$C(R) = C(0) \times e^{-R/R_0}$, where C is the concentration, R the loop radius, and R_0 a constant] size distributions are found for both low-temperature and room-temperature irradiations, but the low-temperature distributions were found to be much more sharply peaked at the smaller sizes, and the concentrations are such that two to three times more total point defects are retained (in the form of loops) after the low-temperature irradiations. No significant differences were found in the sizes of loops resulting from fission-spectrum neutrons compared with those of the reactor spectrum for this temperature. A detailed comparison of these data with those of electrical resistivity is in progress and will include the annealing characteristics of these defects above room temperature.

HUANG DIFFUSE SCATTERING FROM DISLOCATION LOOPS AND COBALT PRECIPITATES IN COPPER¹

B. C. Larson W. G. Schmatz²

High-resolution Huang x-ray diffuse scattering measurements have been carried out on neutron-irradiated copper and copper-1% cobalt crystals (aged at 570°C) using a three-axis diffractometer. These measurements were made near the 111 and 200 reciprocal lattice points and have been compared with calculations based on the dipole-force model for dislocation loops and spherical precipitates.

The diffuse scattering close to the reciprocal lattice points is generated mainly by the long-range part of the strain fields surrounding lattice defects, and these long-range strains are related in a straightforward way to the elastic dipole moment of the local force array

required to introduce the defects. This relationship makes it possible to calculate the diffuse scattering cross sections directly in terms of the Fourier transforms of the distortion fields for a variety of defect shapes and symmetries (point, spherical, disk). In addition, this formulation takes the elastic anisotropy of the lattice into account explicitly.

The scattered intensity can be separated into symmetric and antisymmetric parts; the former contains information on the symmetry of the defect, and the latter is dependent only on the sense (inward or outward) of the distortions around the defects. The symmetric part of the scattering near the 111 reciprocal lattice point from the precipitates formed in the copper-1% cobalt is shown in the form of equal-intensity contours in Fig. 2.11. Comparing these contours with those calculated for spherical and platelet-shaped defects, it is clear that the spherical model is the most appropriate and that the crystal anisotropy is quite important. Measurements near the 200 reflection rule out other platelet orientations.

Similar measurements made near the 200 reciprocal lattice point of copper irradiated with 1.08×10^{19} neutrons/cm² at ambient temperature are shown in Fig. 2.12, where the scattering contours favor the case of dislocation loops with {110} Burgers vectors lying on 111 planes. Spherical defect clusters would give a lemniscate (figure 8)-type scattering for this reflection, and from measurements around the 111 reflection, such defects can be ruled out as possibilities.

From the sign of the antisymmetric scattering it was inferred that the cobalt precipitates have inward distortions around them and contract the copper lattice and that the larger dislocation loops (which contribute the largest amount of scattering due to the size dependence of the scattering cross section) are of interstitial type, causing outward distortions around them.

The shapes of both the symmetric and antisymmetric intensity contours were found to be strongly dependent on the anisotropy of the lattice and departed markedly from those calculated using isotropic average elasticity (as demonstrated in Figs. 2.11 and 2.12), indicating that the anisotropy must be considered in detail in analyzing measurements of this type. All of these observations are in agreement with electron microscopy observations on these systems, confirming the reliability of measurements of this type in characterizing defect clusters.

1. Summary of paper to be published.

2. Guest Scientist from Institut für Festkörperforschung der Kernforschungsanlage, Jülich, Germany.

Fig. 2.11. Symmetric Huang scattering contours at 111 reciprocal lattice point. The solid calculated curves – anisotropic; dashed calculated curves – isotropic.

Fig. 2.12. Symmetric Huang scattering contours at the 200 reciprocal lattice point. Solid calculated curves – anisotropic; dashed calculated curves – isotropic.

TEMPERATURE DEPENDENCE OF IRRADIATION DAMAGE IN COPPER

B. C. Larson F. W. Young, Jr.
J. M. Williams

A means of controlling the sample temperature during irradiation was added to the CP-15 facility in the BSR to cover the temperature range of 40 to 300°C. This system makes use of gamma heating for heat input to the samples, with the temperature controlled by varying the conduction of heat away from the samples by a controlled adjustment of the pressure of helium exchange gas in the irradiation vessel. The sample tem-

peratures were monitored by thermocouples on dummy samples, and a control of $\pm 5^\circ\text{C}$ was obtained.

Irradiations of copper specimens have been carried out in this facility and are being studied by integral diffuse scattering, where rather large changes have been found in the sizes and concentrations of defects produced in this temperature range. These changes can be characterized by a tendency toward elimination of the smaller clusters (loops) as the irradiation temperature is increased and a faster rate of increase in loop sizes with increasing dose at the higher temperatures. These changes in the size distribution result in sizable decreases (~ 2 to 6) in the total number of point defects stored in loops, due to the absence of the smaller sizes,

which highly dominated the exponential-like distributions at lower temperatures. A detailed quantitative analysis of these effects is in progress.

NUMERICAL CALCULATIONS OF DIFFUSE SCATTERING CROSS SECTIONS FOR DISLOCATION LOOPS¹

B. C. Larson W. G. Schmatz²

Detailed calculations of the diffuse scattering by prismatic dislocation loops in aluminum have been carried out using numerical displacement fields calculated by S. M. Ohr³ to evaluate second- and higher-order scattering terms. Calculations along and perpendicular to the 200, 400, 220, and 222 reciprocal lattice vectors have shown that the cutoff of the $1/q^2$ dependence is given approximately by $qR \sim 5.5/\sqrt{hb}$, where R is the loop radius and h and b are the reciprocal lattice vector and Burgers vector respectively. In directions, q , perpendicular to h , the cutoffs were consistently higher than those parallel to h . The influence of the second-order (Debye-Waller factor) term was found to cause a sizable asymmetry in the cross sections for $qR < 2$. The higher-order terms not included in the Debye-Waller factor play an important role in determining the $1/q^2$ cutoff and are anticipated to be critical in similar calculations for more anisotropic crystals.

Calculations such as these are in progress for copper crystals using displacements generated for anisotropic media;⁴ however, due to the increased complexity of these calculations, a rather more approximate method will apparently be necessary.

1. Summary of paper to be published.
2. Guest Scientist from Institut für Festkörperforschung der Kernforschungsanlage, Jülich, Germany.
3. S. M. Ohr, *J. Appl. Phys.* 43, 1361 (1972).
4. S. M. Ohr, to be published.

ANISOTROPIC ELASTICITY OF DISLOCATION LOOPS¹

S. M. Ohr

Defect structures in irradiated crystals observed by electron microscopy often consist of small dislocation loops of either vacancy or interstitial type created by the condensation of point-defect clusters. Characterization of these loops as well as the measurement of their true size-density distribution is dependent on knowledge of the strain fields of the loops. Until recently, the displacement fields around the dislocation loops have

been available only for pure prismatic loops in elastically isotropic media. Many dislocation loops, however, have their Burgers vectors inclined to the plane of the loops, and furthermore most crystals are elastically anisotropic. It is, therefore, desirable to have solutions of anisotropic elasticity for dislocation loops whose Burgers vectors have both shear and prismatic components.

In the continuum theory, the components of displacement obey the equation of equilibrium, which is essentially an inhomogeneous partial differential equation of the second order. Following classical field theory, the solution can be expressed in terms of the integral over space of the body force density, f_n , and the Green's tensor function, G_{mn} , that is,

$$u_m(\mathbf{r}) = \int_V G_{mn}(\mathbf{r} - \mathbf{r}') f_n(\mathbf{r}') dV'.$$

In isotropic and hexagonal crystals, elastic Green's functions are available in closed forms; therefore, the displacement field can be obtained explicitly in terms of elliptic integrals. For cubic crystals, only the Fourier transform of the Green's function is available in closed form. By applying the Fourier convolution theorem, the Fourier transform of the displacement component may be written as

$$\tilde{u}_m(\mathbf{k}) = \tilde{G}_{mn}(\mathbf{k}) \tilde{f}_n(\mathbf{k}).$$

Thus, the displacement field in anisotropic cubic crystals can also be obtained by the process of Fourier inverse transformation. With these methods, the displacement fields for both prismatic and shear types of loops can be calculated. By a suitable superposition of the displacement fields arising from the prismatic and shear components, one can obtain solutions for any type of dislocation loop in both isotropic and anisotropic crystals.

Figure 2.13 shows the equidisplacement contours in units of the magnitude of the Burgers vector of the component u_x parallel to the Burgers vector for a pure shear dislocation loop lying in the basal plane of graphite. Compared with an isotropic crystal, the magnitude of u_x is lower by about a factor of 10. On the other hand, the component u_z perpendicular to the basal plane is nearly as great as that found in the isotropic crystal. These characteristics of the displacement field are in accord with the crystal structure of graphite, in which carbon atoms in the basal plane are rigidly bound by a covalent bond, whereas bonding between the basal planes is of the weak van der Waals

type. When a dislocation loop is created, this results in a large displacement of atoms along the c axis, while the dimensional changes in the basal plane remain quite small.

Fig. 2.13. Equidisplacement contour plot in units of the magnitude of Burgers vector of the displacement component u_x parallel to the Burgers vector around a pure shear dislocation loop located in the basal plane of graphite.

Fig. 2.14. Equidisplacement contour plot of u_x for a dislocation loop lying in the (111) plane of copper with Burgers vector $a/2 [110]$.

Figure 2.14 shows a similar contour plot for a dislocation loop lying in the (111) plane of copper with Burgers vector $a/2 [110]$, which makes an angle of $35^\circ 16'$ with the loop normal. Compared with a similar plot for an isotropic crystal, the contour lines for a given displacement extend considerably further from the loop. The magnitude of the displacement at any given point is greater in copper, by a factor of as much as 2, than that predicted in the isotropic crystal. In many cubic crystals, the magnitude of the displacement field relative to the isotropic crystal is proportional to the anisotropy factor $A = 2c_{44}/(c_{11} - c_{12})$.

1. Summary of paper: *Phys. Status Solidi B* 58, 613 (1973); subsequent paper to be published.

ELECTRON MICROSCOPY OF DISLOCATION LOOPS IN IRRADIATED METALS¹

S. M. Ohr

Dislocation loops have been observed in the electron microscope in a number of crystals following irradiation. One objective of radiation damage studies is to characterize these loops in terms of Burgers vector, loop plane, size, and the vacancy or interstitial nature. An accurate determination of these properties is often difficult, especially when loops are too small to be resolved as loops in the microscope. These small loops have been analyzed in the past by examining the black-white contrast behavior predicted under the dynamical diffraction condition,^{2,3} using the displacement fields calculated for prismatic loops from isotropic elasticity theory.⁴ These authors predict that the direction of maximum black-white streaking is parallel to the projected direction of the Burgers vector. Furthermore, the sense of the black-white streaking at a given depth is dictated by the sense of the displacement field, that is, the vacancy-interstitial nature of the loop.

The image contrast of a dislocation loop can be calculated from the equations of the dynamical theory of electron diffraction if the displacement field around the loop is known. Recently, general solutions which take elastic anisotropy into account have been obtained for the displacement field of a dislocation loop having both prismatic and shear components of the Burgers vector.^{5,6} These new displacement fields have been used to calculate the image contrast of dislocation loops for the case of two strong beams under the column approximation to compare directly with the results of the previous authors. By computing the intensities of direct and diffracted beams at points corresponding to a square array, an electron micrograph is simulated by generation of a series of equi-intensity contour lines.

Fig. 2.15. Equi-intensity contour lines corresponding to the bright-field image of a sheared dislocation loop in the (110) plane of niobium with Burgers vector $a[100]$. The loop lies close to the top surface of the crystal, which is oriented for the exact $(12\bar{1})$ Bragg reflection.

Figure 2.15 shows the result obtained for a circular dislocation loop in niobium located at the depth of 30 Å from the top surface of the foil. The Burgers vector of the loop is $a[100]$, and the loop plane is (110). The figure shows the well-defined black-white contrast under the exact $(12\bar{1})$ Bragg reflection. The outermost contour lines correspond to $\pm 5\%$ deviation from the background intensity, and consequently they delineate the actual size of the image expected in the electron microscope. It is noted that, contrary to previous results reported in the literature, the direction of maximum streaking indicated by the vector l is not parallel to the projected direction of the Burgers vector b . In fact, the direction l lies roughly halfway between the projected directions of the Burgers vector b and the loop normal n . Thus, the previous results on the Burgers vectors of the loops determined from the direction of maximum streaking may be in serious error. According to calculations for loops in other crystallographic orientations, some loops exhibit either white-black-white or black-white-black contrast under the dynamical diffraction condition. In contrast to previous calculations, even loops whose Burgers vectors lie in the reflecting plane ($g \cdot b = 0$) exhibit prominent black-white contrast. The rules of black-white depth oscillation, which have been used widely in the past to determine the vacancy-interstitial nature of the loops, will also

have to be modified to take into account these complex contrast behaviors.

1. Summary of paper: p. 62 in *Proceedings of International Conference on Defects and Defect Clusters in BCC Metals and Their Alloys*, National Bureau of Standards, Gaithersburg, Maryland, 1973.
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ION RADIATION DAMAGE¹

O. S. Oen J. Narayan
T. S. Noggle

The relation of ion damage to equivalent reactor neutron damage is dependent on theoretical treatments of the slowing down of energetic (MeV) particles in solids. The theory is largely untested by experiment, particularly with respect to the nuclear collision component of the stopping, which produces the atomic displacements that generate the damage in metals. The present work represents the initial results of a combined theoretical and experimental program to obtain information on the relation between the nuclear collisions and damage retained in a solid. This study at present is concerned with the damage produced in copper irradiated with 1-MeV protons.

Figure 2.16 shows the initial results of this study. A sectioning technique is used which allows the study of the damage over the full range of the ions, from the surface to the end of range. The spot type of damage seen in Fig. 2.16 is resolvable at higher magnifications into dislocation loop structures. Analysis has shown that these loops are due to the clustering of interstitials. Measurements of damage density and the size distribution of the loops as a function of depth from the surface allow estimates of the number of point defects in the loops to be made as a function of depth. The histogram in Fig. 2.16 shows the results of these measurements. The smooth curve is the theoretical curve for the damage energy loss rate. Experiment and theory are in quantitative agreement with respect to the range of the protons and in semiquantitative agreement with respect to the variation of the damage rate as a function of penetration depth. This study has pointed up both qualitative and quantitative differences between proton and fast neutron damage in copper. First, only interstitial-type dislocation loops have been detected here, whereas approximately equal numbers of

Fig. 2.16. Transmission electron micrograph showing the variation in damage density as a function of penetration depth for 10^{16} 1-MeV protons/cm² on copper irradiated at room temperature. Original surface on which the protons are normally incident is at left. Histogram above is experimentally determined damage density, and smooth curve is calculated from theory. Micrograph and graph are to the same scale for penetration depths.

vacancies and interstitials are observed in dislocation loops in fast-neutron irradiated copper. Second, only about 1% of the calculated number of displaced atoms are observed in the proton irradiation, whereas approximately 5 to 10% of the displaced atoms are observed in the neutron irradiations.

1. Summary of paper: *Proceedings of the International Conference on Applications of Ion Beams to Metals*, Plenum Press, in press.

DISLOCATION CHANNELING

J. Narayan T. S. Noggle

The deformation of irradiated or quenched metals is characterized by a low initial rate of work hardening and a very inhomogeneous distribution of deformation within a specimen. The deformation is concentrated in narrow bands separated by relatively thick regions in which there is no detectable deformation. Transmission

electron microscope studies of this type of deformation have shown that the regions of high shear strain no longer contain the dislocation loop structures associated with the irradiated or quenched state of the metal. It is inferred that the passage of the first dislocations through the material has eliminated the dislocation loops in the regions near the path of the dislocations, thereby removing these obstacles to dislocation motion and providing channels through which large numbers of dislocations can move more easily than through the matrix. This behavior is called dislocation channeling and appears to be a general feature of the deformation of metals containing large numbers of small dislocation loops. Several mechanisms for the removal of dislocation loops by cutting dislocations have been proposed;^{1,2} however, there is little direct evidence to support these models, and neither mechanism by itself can account for the clearing of the channels. It is worth noting that virtually all electron microscope studies of this phenomenon have been made on specimens after deformation, and the attempts to relate observed structures to basic mechanisms is inhibited by lack of information on both the number and kinds of dislocations that created a given channel.

A specimen holder has been built which deforms a specimen in the microscope. The velocity of the moving dislocations is too great to study the dynamic interactions with the loops; however, the progressive development of the dislocation channels is being studied in which the changes that occur can be correlated with the number and kinds of dislocations that are associated with the development of a channel. The observations to date have provided evidence that although cutting mechanisms play a role in the clearing of channels, the required conditions for complete clearing by these mechanisms have not been observed and other mechanisms must be an important aspect of the channel development. Figure 2.17 shows the edge of a dislocation channel in a quenched Al + 1.7% Cu alloy. This micrograph shows the essentially complete elimination of the vacancy loops in the channel and several jogs on the dislocations at the edge of the channel. These jogs are the structure expected from the cutting mechanisms; however, to date it has not been possible to determine whether these are formed by the Saada and Washburn mechanism,¹ in which the moving dislocation and the loop have the same Burgers vector, or by the Foreman and Sharp mechanism,² in which the Burgers vectors of the dislocation and the loop before reaction are different. The progressive development of this channel has occurred with only one kind of dislocation, an observation which eliminates the cutting mechanisms

Fig. 2.17. Channel formation in quenched Al + 1.7% Cu alloy. Dislocation-loop interactions and the coarsening of dislocation loops near the edge of the channel are shown.

Fig. 2.18. Dislocation channeling in neutron-irradiated copper (total dose 10^{18} neutrons/cm² at room temperature). All the dislocations in the channel have Burgers vector $a/2$ [110].

as the sole process for the clearing of the channels. It may be noted in Fig. 2.17 that at the channel margin, large loops are present due to loop-loop coalescence in this region. This strongly suggests that prismatic glide of dislocation loops interacting with the moving dislocation changes the local distribution of loops so that

attractive interactions between loops can lead to coalescence. In the case shown in Fig. 2.17, all of the loops are of the vacancy type, and coalescence leads to larger loops. In Fig. 2.18 the irradiated copper contains both vacancy and interstitial loops, and the coalescence of loops of opposite type would remove both types of defects from the material. There is no indication of loop coarsening in this case but simply a reduction in loop density at the channel edge. In both of the cases shown, relatively small numbers of dislocations (~ 10) have passed through the channels. Both of the cutting mechanisms would require much greater numbers of dislocations in order to clear the channels to the extent observed. This in turn is additional evidence that mechanisms other than those involving cutting of the loops are active in the channel-clearing process.

The observations to date have shown that the previously proposed mechanisms for the clearing of dislocation channels do not adequately account for the observations made with in situ deformation. Evidence has been obtained that loop coalescence occurs and could be an important mechanism in the channeling process. This study is continuing with the goal of determining the relative importance of the different mechanisms for the channeling, as well as obtaining firmer evidence on the dislocation interactions and reactions that are associated with the various mechanisms.

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2. A. J. E. Foreman and J. V. Sharp, *Phil. Mag.* 19, 931 (1969).

SUBGRAIN BOUNDARIES AND THEIR JUNCTIONS IN MAGNESIUM OXIDE¹

Jagdish Narayan

Mechanical properties such as fracture strength, toughness, plastic deformation, and high-temperature creep; electrical properties such as conductivity and dielectric losses (in ceramic materials); processes such as sintering, nucleation, and grain growth; and phase transformations are in large part controlled by the behavior of grain boundaries. Better understanding of the structure and properties of boundaries thus contributes directly to better understanding of the behavior of polycrystalline materials.

In the present investigation, transmission electron microscopy was used to study the dislocation substructure and impurity precipitation at small-angle boundaries (subboundaries) in MgO. High-purity

ORNL-grown MgO crystals, as well as relatively less pure as-grown crystals from Muscle Shoals Electrochemical Corporation, were used in this study. Dislocations constituting the subboundaries were characterized, and the various dislocation reactions were analyzed by applying the rules of kinematical theory of electron diffraction.

The following types of small-angle boundaries occur most frequently:

1. Tilt boundaries on (101) consisting of parallel-edge dislocations with Burgers vectors $b = a/2 [101]$ and the axis of rotation $[10\bar{1}]$ (an example is shown in Fig. 2.19a).
2. Tilt boundaries on (121) containing $a/2 [110]$ and $a/2 [011]$ dislocations and the axis of rotation $[1\bar{1}1]$. These boundaries can contain equal numbers of the two types of dislocations which alternate in the boundary, or unequal numbers in which one type of dislocation alternates with two or three of the other type, as shown in Fig. 2.19b.
3. Twist boundaries on (111) consisting of two sets of screw dislocations, with $b = a/2 [101]$ and $b = a/2 [011]$, and having $[1\bar{1}1]$ as the axis of rotation, for example, the boundary in Fig. 2.19c.
4. Mixed boundaries on planes close to (121) with varying combinations of $a/2 [110]$, $a/2 [011]$, and $a/2 [0\bar{1}1]$ dislocations with the axis of rotation $[1\bar{1}1]$. Figure 2.19d shows a typical example of this kind of boundary. The plane of the boundary is determined by the relative abundance of the $a/2 [0\bar{1}1]$ dislocations. This boundary is the same as type 2 when the $a/2 [0\bar{1}1]$ dislocations are absent.

The dislocation structures at the junctions of twist and tilt boundaries have been analyzed; for instance, two twist boundaries consisting of two sets of $a/2 [110]$ dislocations result in another twist boundary with two sets of $a/2 [110]$ dislocations. Similarly, two tilt boundaries give rise to another tilt boundary. The observed angles between boundaries have been rationalized in terms of interactions between subboundary dislocations. The occurrence of the following types of dislocation reactions has been directly confirmed:

$$a/2 [011] + a/2 [10\bar{1}] = a/2 [110],$$

$$a/2 [10\bar{1}] + a/2 [101] = a [100].$$

The first reaction takes place because of reduction of the elastic energy, whereas the second reaction involves

Fig. 2.19. (a) Tilt boundary of parallel $a/2$ [101] dislocations; (b) tilt boundary of two types of $a/2$ [101] dislocations; (c) twist boundary of two types of $a/2$ [101] dislocations; (d) mixed boundary with all three types of $a/2$ [101] dislocations. Arrow in each micrograph indicates the direction of the diffraction vector 200.

no change in elastic energy and must occur because of reduction in core energy.

Impurity precipitation at the subboundaries was observed to be a common phenomenon, both in high-purity and less pure crystals. In general, grain boundaries in oxides have an electronic potential which is of the order of a few tenths of a volt, the sign and magnitude of which depend on the valency of the

solute and its concentration. Boundaries also have an associated space charge. These electrostatic potentials, together with the short-range elastic stress field of the boundary, cause the segregation of impurities leading to precipitation in these regions. Because of the difference in coefficients of thermal expansion, these precipitates develop a stress field around them during cooling from the precipitation temperature. This in turn can lead to

an attractive interaction with the dislocations at the boundary. These precipitates and sessile [100] dislocation segments make subboundaries relatively immobile.

In the case of high-angle boundaries, the direct observation of the dislocation structure of the boundary is not possible. However, from stereomicroscopy together with other geometrical considerations, the probable nature of dislocations present in the boundaries can be described.

1. Summary of paper: *J. Amer. Ceram. Soc.* 56, 33 (1973).

ION BOMBARDMENT AND CHANNELING

HYPERCHANNELING: I. INVESTIGATIONS FOR HIGH-ENERGY HEAVY IONS IN SILVER¹

B. R. Appleton	C. D. Moak ²
J. H. Barrett	Sheldon Datz ³
J. A. Biggerstaff ²	T. S. Noggle

When a beam of energetic ions enters a single crystal parallel to an axial direction, those which enter most nearly the center of the channel receive the smallest deflections. Some small fraction will acquire trajectories which remain within the confines of one particular axis (i.e., the open region surrounded by nearest-neighbor rows), while a larger fraction will be axially channeled, but wander from one particular axis to another. Those ions confined to a particular axial channel will have two distinguishing characteristics: (1) they will be distributed over a much smaller range of angles than in the case of regular axial channeling, and (2) they will have a much lower rate of energy loss. It is this particular axial channeling phenomenon which we call hyperchanneling. Although this effect was recognized to exist in the 1963 paper by Robinson and Oen,⁴ which initiated present-day channeling studies, it was not until 1966 that the first experimental observation was reported by Eisen.⁵ He attributed a high-energy tail for 375-keV protons transmitted through 2.2- μ m-thick silicon crystals along the [110] direction to protons which remained within a single axial channel (hyperchanneling) in traversing the crystals. The effect was not, however, sufficiently prominent to investigate in detail. No further investigations of this phenomenon were reported until 1972, when Appleton et al.^{6,7} observed hyperchanneling for high-energy heavy ions. For

21.6-MeV iodine ions transmitted through thin silver single crystals near the [011] axis, they observed a distinct, hyperchanneled group of ions with much lower energy loss rates than for regular axial channeling and with a characteristic critical angle well within the axial critical angle. Because of the prominence of this effect for high-energy heavy ions, it was possible to study the details of hyperchanneling phenomena.

Recently, the investigations for high-energy heavy ions were extended to include measurements for the [001] directions as well as the [011], and these results were compared with model calculations. Although the main features of the hyperchanneling measurements could be understood in terms of the model, several new and unexpected features appeared. Perhaps the most interesting of these can be understood with the aid of Fig. 2.20. The two sets of data shown in this figure were obtained by measuring the transmitted energy spectra of 21.6-MeV iodine ions incident at various angles, $\Delta\psi$, relative to the [001] (left-hand figure) and [011] (right-hand figure). The spectra were measured by an energy-sensitive detector in line with the incident beams, but with an acceptance angle of only $\pm 0.012^\circ$. Consider first the data for the [011] axis. The features in these spectra are well understood in terms of the hyperchanneling model. The intense peak at lowest energy loss, near $\Delta\psi = 0$, results from hyperchanneled ions; the smaller peak at lower dE/dx , which grows as $|\Delta\psi|$ increases, can be identified as axially channeled ions which are wandering from one particular axis to another. These same two peaks can be identified in the spectra for the [001] axis, but in addition, group structure, which cannot be understood in terms of the model calculations at all, appears at intermediate energy loss values. Although more work is required to identify the nature of this structure, it appears likely that it results from discrete oscillations supported within a [001] hyperchannel. It is clearly a fine-structure effect which will be valuable in studying the ion-solid interaction potential.

1. Summary of paper to be published.

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Fig. 2.20. Comparison of normalized transmitted energy-loss distributions for 21.6-MeV iodine ions incident at various angles to [001] in (100) (path length = 0.835 μm , mosaic spread = 0.055° FWHM) and to [011] in (100) (path length = 1.18 μm , mosaic spread = 0.055°).

HYPERCHANNELING: II. INVESTIGATIONS OF H^+ AND He^+ IONS IN SILVER SINGLE CRYSTALS¹

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One important motivation for pursuing these hyperchanneling studies is to probe the ion-atom interaction potential at large impact parameters (≈ 1 to $2 \text{ \AA}$) where solid-state effects become important.^{4,5} This is complicated when heavy ions are used, because they carry their own electron cloud into the interaction. Conversely, if one understood these interactions for simple light ions, such results would yield information concerning the nature of heavy-ion interactions. For this reason, a program was initiated to see whether hyperchanneling structure could be resolved for low-energy hydrogen and helium ions.

Experiments were performed for 0.30-MeV H^+ and for 0.5-, 1.0-, and 1.5-MeV He^+ ions from the Solid State Division's 2.5-MeV positive-ion accelerator; the ions were transmitted through a $0.45\text{-}\mu\text{m}$ -thick silver single crystal along the $[001]$ and $[011]$ axial channels. Typical results are shown in Fig. 2.21 which contrast

energy loss distributions for 1.0-MeV He^+ transmitted parallel to the $[001]$ axial and (100) planar directions. The entire $[001]$ distribution with energy losses less than $\approx 430 \text{ keV}/\mu\text{m}$ can be identified with hyperchanneling. There is even some evidence of the intermediate group structure observed so clearly when heavier ions are used. The prominence of this effect in these preliminary experiments is encouraging for future studies. Comparison of detailed measurements with model calculations should provide tests of the relative merits of free atom versus solid-state boundary conditions at these large impact parameters, of impact-parameter-dependent stopping-power theories which have been recently developed, and of ion multiple-scattering theories in free-electron gas environments.

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3. ORAU Graduate Laboratory Participant from the University of South Carolina, Columbia.
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1 MeV $\rightarrow$ Ag $[001]_{(100)}$

Ag 28-3, $t = 0.45 \mu\text{m}$, MOSAIC = 0.08° FWHM, 10-73

Fig. 2.21. Transmitted energy loss spectra for 1.0-MeV He^+ ions incident parallel to the $[001]$ axial direction, (100) planar direction, and in a random direction of a $0.45\text{-}\mu\text{m}$ -thick silver single crystal.

VELOCITY DEPENDENCE OF THE STOPPING POWER OF CHANNELLED IODINE IONS¹

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Recent measurements of some uranium ion stopping powers in the energy range 30 to 90 MeV in polycrystalline targets,⁴ together with earlier data for beryllium and iodine ions, have shown that $S_e = a + bE^{1/2}$ in the energy region where the theories of Lindhard, Scharff, and Shioft⁵ and of Firsov⁶ predict that electronic stopping should obey the relation $S_e = KE^{1/2}$. The heavier the ion, the larger the value of a . The important point is that the data cannot be reconciled with theory by a simple change of the value of K .

It was expected that ions moving in crystal channels and having no close collisions with atoms might show the $S_e = KE^{1/2}$ behavior. Some data taken by Eriksson, Davies, and Jespersgaard⁷ with very-low-energy xenon ions in tungsten crystals do appear to follow this relationship. At higher energy, 21.6 to 32.5 MeV, iodine ion stopping powers have been measured for particles hyperchanneled⁸ in the (100) axis of a crystal of silver. The results are shown in Fig. 2.22. Polycrystalline stopping powers measured by Moak and Brown⁹ are shown as measured and, slightly below, after they

were adjusted to remove the estimated contribution of nuclear stopping.¹⁰ Channeling data generally have not been adjusted to remove the estimated contribution of nuclear stopping,¹⁰ because there is strong evidence for the conclusion that nuclear stopping is negligible for channeled ions. The energy loss pattern for iodine ions hyperchanneled in the [100] axis in silver is shown schematically in Fig. 2.22. Beginning with particles showing the least energy loss (and running nearest the center of the channel), including particles which fall in the class of ordinary axially channeled particles, and finally including particles which run in the (100) planar channels, the behavior of the stopping power does not obey the relation $S = KE^{1/2}$. The data given by Eriksson, Davies, and Jespersgaard have been included in the figure, even though both the ion and the stopping medium are different. At higher energies, where the iodine measurements were made, the stopping powers do follow the relation $S_e = a + bE^{1/2}$. The data suggest that below 21.6 MeV (or $\sqrt{E/A} = 0.41$ in Fig. 2.22) there is a velocity region where the stopping-power curve is more complicated and that some additions must be made to the theory for this velocity range. The importance of these conclusions extends beyond improvement of the stopping-power theory in this region. Extensive use is made of these theories in radiation damage calculations, for example, in calculating the

Fig. 2.22. Measured energy loss vs velocity ($\sqrt{E/A}$) for iodine ions in silver. Data include energy loss for polycrystalline silver, for iodine ions randomly directed in a silver single crystal, best channeled along the (100) and (111) planar channels, and hyperchanneled along the [001].

damage distributions resulting from knock-on atoms, and in cases where large amounts of damage are expected, such as a controlled thermonuclear reactor, these differences can be important.

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INFLUENCE OF IONIC CHARGE STATE ON THE STOPPING POWER OF 27.8- AND 40-MeV OXYGEN IONS IN THE [011] CHANNEL OF SILVER¹

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Since the pioneering paper by Bohr⁵ on stopping powers and charge exchange of ions in matter, there has been considerable interest in the influence of the charge of an energetic ion on its stopping power in a solid. In many cases it has been postulated that the stopping power of an ion is not strongly affected by its ionic charge, because electron screening largely masks the effects of charge-state differences. In a recent paper by Brandt et al.,⁶ the concept of dynamic screening was developed to account for their observations that the aluminum *K* x-ray yield was strongly dependent on the incident charge state of 12- to 68-MeV oxygen ions bombarding thin (0.5 to 25 $\mu\text{g}/\text{cm}^2$) aluminum targets. They concluded that oxygen ions in this energy range were screened at a rate $\lambda = 5.5 \times 10^{14} \text{ sec}^{-1}$. Thus, for example, a 40-MeV oxygen ion would become screened by the electrons of the solid within a path length of 0.04 μm . The results reported here utilize the unique constraints imposed on the behavior of well-channeled oxygen ions as a direct test of these screening concepts.

Measurements of the charge-state distributions for 17- to 40-MeV oxygen ions transmitted through 0.80- μm -thick silver single crystals parallel to the [011] axial channel confirmed that oxygen ions in silver, like

channeled oxygen ions in silicon⁷ and gold,⁸ have the unusual property of remaining at one charge state for channeled path lengths $>1 \mu\text{m}$. Both electron capture and loss cross sections are so small ($\sim 10^{-19} \text{ cm}^2$) that, in a channel, the ionic charge state remains "frozen." However, throughout this distance the channeled ions are free to interact with conduction (and weakly bound) electrons. Thus, by measuring the stopping power of well-channeled oxygen ions as a function of input charge state, one might deduce a mean free path for screening. If oxygen ions are screened within 0.04 μm as suggested, then in the crystals available to us (0.8- μm path length) the ionic stopping powers for different input charge states would differ only in the first 5% or so of their total path before screening would equalize their stopping powers. In the absence of any screening the stopping powers would be expected to depend on the input charge as $S = kq_i^2$.

Some results of these studies are presented in Fig. 2.23 for 40-MeV oxygen ions channeled along the [011] direction of silver for various input (q_{in}) and output (q_{out}) charge combinations. These results clearly follow the stopping relation $S = kq_i^2$ and indicate that for oxygen ions at velocities $v/v_0 \sim 10$, where v_0 is the Bohr velocity, dynamic screening has no significant effect on the stopping powers. The ability to

Fig. 2.23. Measurements of the stopping power for 40-MeV oxygen ions, for various charge state combinations q_{in} and q_{out} , channeled along the [011] axis of a silver single crystal.

work with frozen charge states in solids presents a number of other exciting areas of investigation. We observed, for example, that new features appeared in the planar-channeling energy loss distributions for oxygen ions of different charge states which could be associated with charge dependence of the planar continuum potential. This should provide a sensitive new means of extending our previous investigations of ion-atom potential interactions in solids by planar group structure⁹ and hyperchanneling measurements.¹⁰

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RADIATIVE ELECTRON CAPTURE BY CHANNELED OXYGEN IONS¹

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Recently, Schnopper et al.⁷ reported the first observations of the radiative electron capture process (REC) for highly stripped heavy ions incident on a variety of amorphous or polycrystalline targets. In this process a highly stripped heavy ion captures a weakly bound electron from the solid directly into one of its inner shells with the subsequent emission of a photon having a characteristic energy

$$E_{h\gamma} = Z_1^2 Ry + (M_e/M_1) E,$$

where the first term is the binding energy of the ion with charge Z_1 , mass M_1 , and energy E , and the second is the energy equivalent of an electron moving at the same velocity as the ion. The observed REC photons formed a broad line whose width was attributed to the spread in charge states of the heavy-ion beams in solids and to the velocity distribution of the captured electrons.

The work reported here is an investigation of the REC process for 17- to 40-MeV oxygen ions channeled through thin silver single crystals. This arrangement has the following advantages: (1) The attendant "background" due to characteristic x rays excited when the ions approach within $\sim 10^{-12}$ cm of lattice atoms is greatly reduced, since channeled ions never approach closer than $\sim 10^{-9}$ cm to lattice atoms. (2) These channeled ions have frozen charge states, so this contribution to the line width is diminished. (3) The well-channeled ions interact freely with the conduction electrons, so that the measured line width is potentially a new tool for probing the velocity distribution of conduction electrons in solids. (4) The channel provides a unique environment to study the REC process at large impact parameters (~ 1 Å).

The important conclusions from these preliminary investigations are as follows: (1) As shown in Fig. 2.24,

Fig. 2.24. Comparison of measured and calculated radiative electron capture (REC) cross section vs energy. Measurements made for fully stripped oxygen ions channeled along the [011] axis of silver single crystal.

the measured cross section, σ_{KEC} , is larger and has an anomalous energy dependence compared with the calculated cross sections per electron of Bethe-Salpeter, σ_{BS} , or Ritchie-Neelavathi, σ_{RN} . The difference in magnitude could be an indication that the oxygen ions are interacting with more than one silver electron. The energy dependence may signify that an impact parameter correction to the theoretical calculations is needed. (2) The REC lines are wider than calculated, again an indication that weakly bound silver electrons as well as conduction electrons are participating in the REC process. (3) The most probable energy of the REC line appears in the measurements at an energy corresponding to that expected for an O^{7+} ion regardless of whether O^{6+} , O^{7+} , or O^{8+} ions are channeled.

The proliferation of unexplained results in these preliminary measurements indicates that there is much to be understood about the REC process and about the attendant heavy-ion interactions in solids. It also appears that the REC process, in conjunction with channeling, should be a useful tool for sampling the electron momentum distribution of weakly bound electrons in solids.

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SURFACE PROPERTIES

AUGER AND IONIZATION LOSS SPECTRA FROM BERYLLIUM SURFACES¹

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Previous investigations of the KVV Auger spectrum of beryllium conflict in that the twin-peaked spectrum published by Musket and Fortner³ disagrees with the single-peaked spectrum reported by Suleman and Pattinson,⁴ who suggest oxygen contamination as a possible explanation of Musket and Fortner's results. The presence of a peak in the Auger spectrum of Musket and Fortner at the energy associated with the silicon $\text{L}_{2,3}\text{VV}$ Auger transitions suggests that silicon contamination might be responsible for the differences in the above results.

Three polycrystalline beryllium samples having bulk silicon contents of <1, 60, and 600 ppm, respectively, and an amorphous film obtained by evaporating beryllium onto a molybdenum rod were used. The bulk samples were mounted in molybdenum holders and could be heated resistively and bombarded with argon ions in the standard fashion for cleaning. All observations were made in a standard Varian LEED (low-energy electron diffraction) system in which the three-grid LEED optics were employed as a retarding-potential analyzer.

Typical Auger spectra obtained from clean surfaces of both the beryllium crystal with a bulk silicon content of <1 ppm and the evaporated beryllium film are shown in Fig. 2.25a. The minimum observed at 105 eV is due to the KVV Auger transition in beryllium, while subsequent minima near 91, 85, and 67 eV are attributed to surface and to first- and second-order bulk plasmon losses, respectively, by Auger electrons.

Fig. 2.25. Auger electron and ionization loss spectra from (a) clean polycrystalline beryllium surfaces and (b) from silicon-contaminated polycrystalline beryllium surfaces.

Silicon diffused to the surface of each of the beryllium polycrystals upon heating for a time. The minimum temperature required varied with the bulk silicon concentration, being $\sim 800^\circ\text{C}$ for the sample containing 600 ppm Si and $\sim 970^\circ\text{C}$ for the sample containing <1 ppm. After silicon had diffused to the surface, each of these specimens exhibited an Auger spectrum similar to those shown in Fig. 2.25b. In addition to the 105-eV beryllium KVV transition, the silicon L_{23} VV transition at 92 eV is also seen. The maxima near 83 and 67 eV are interpreted as first- and second-order bulk plasmon losses by beryllium Auger electrons, while the minimum at 75 eV might arise from first-order bulk plasmon losses by Auger electrons associated with the silicon L_{23} -shell vacancy.

Positive identification of the elements present on all surfaces is provided by noting that ionization loss events associated with the beryllium K shell (Fig. 2.25a) and with both the beryllium K and silicon L_{23} shells (Fig. 2.25b) are observed. Both events are shown to be coupled to the primary beam energy and indicate electron-level binding energies of 113 and 100 eV respectively. These values are in good agreement with the ESCA (electron spectroscopy for chemical analysis) results of Siegbahn et al.⁵

Exposure of both clean and silicon-contaminated beryllium surfaces to oxygen produced the effects illustrated in Fig. 2.26. The extent of oxygen exposure and the ratios (R) of the oxygen Auger peak height at 512 eV to the sum of the heights of peaks occurring in the energy range 92 to 105 eV are indicated. These ratios are used to indicate the relative amounts of oxygen present and are directly comparable with those of Fortner and Musket.⁶ In the initial stages of oxidation, a minimum appeared at 96 eV on the silicon-free surface, while on the silicon-contaminated surface the 92-eV minimum increased by strength relative to the 105-eV minimum. Additional oxygen exposure to both surfaces continued these trends, with slight shifts in peak energy, and eventually produced Auger spectra on each type of surface which are indistinguishable. After extensive oxidation, only the beryllium K-shell ionization loss at 116 eV below the primary beam energy was detectable on both kinds of surfaces, and measurements indicated a 3-eV difference between the beryllium K-shell binding energy in beryllium and in BeO.

The agreement between data presented here and those of Suleman and Pattinson suggests that a clean beryllium surface exhibits an Auger spectrum containing only one strong minimum at 105 eV and, moreover, implies that the data treated by Musket and Fortner do

Fig. 2.26. Normalized Auger electron spectra following various degrees of oxidation of (a) a clean beryllium surface and (b) a silicon-contaminated beryllium surface. R is the ratio of the oxygen Auger peak height at 512 eV to the sum of the heights of peaks occurring in the energy range 92 to 105 eV. Total oxygen exposure in torr-min: (A) none, (B) 10^{-5} , (C) 10^{-3} , (D) 10^{-1} .

not pertain to a clean beryllium surface. However, notwithstanding similar oxidation results, we would not agree with Suleman and Pattinson's suggestion that oxygen contamination might be responsible for the spectrum observed by Musket and Fortner. The data in Fig. 2.26a indicate that the relative oxygen content (R) on a silicon-free beryllium surface must be about 0.10 in order to exhibit an Auger spectrum similar to that identified in Musket and Fortner's work as being from a clean surface. Since they state that R was <0.002 , and since a relative oxygen content of this amount had no appreciable effect on our beryllium spectra, it would seem most unlikely that their Auger spectra resulted

from oxygen contamination. In view of the data presented here, it seems more plausible to suggest that perhaps silicon contamination was responsible for the large minimum at 92 eV in the spectra measured by Musket and Fortner. Additional evidence to support this hypothesis comes from the more recent observation by Fortner and Musket that exposure of their specimen, with twin Auger peaks at 92 and 104 eV, to oxygen produced material whose Auger spectra are identical with those presented here, that is, spectra which were obtained from a silicon-contaminated beryllium surface after exposure to oxygen. Furthermore, comparison of their data with ours reveals that similar stages of oxidation, as measured by R , correspond to similarly shaped Auger spectra. All data strongly suggest that either silicon or some impurity other than oxygen was responsible for the 92-eV minimum in the Musket and Fortner³ spectrum.

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PLASMON ENERGY GAIN AND DOUBLE IONIZATION SATELLITES IN THE BERYLLIUM AUGER SPECTRUM¹

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In this section we show the beryllium KVV Auger spectrum and two higher energy satellites, one of which is attributed to double ionization in the beryllium K shell, that is, $(K)_2VV$ emission, and the other to plasmon energy gain processes, $KVV + \hbar\omega_p$ events.

The data were obtained in a standard Varian LEED system (base pressure $<10^{-10}$ torr) by employing the three-grid LEED optics as a retarding-potential analyzer. Identical results were obtained from both a bulk beryllium specimen with no surface contaminants detectable by Auger spectroscopy and a film evaporated in situ from which a barely detectable carbon signal was observed. In obtaining the spectra reported here, signal-averaging techniques were used to improve the signal/noise ratio, an improvement necessary to ensure detection of the higher-energy satellites.

Figure 2.27 illustrates the data obtained from these specimens. Curve A, a relatively well-resolved spectrum, shows the main beryllium Auger peak at 105 eV. The first- and second-order volume plasmon losses ($\hbar\omega_p \cong$

Fig. 2.27. Auger and higher-energy satellite spectra of beryllium.

19 eV) can be seen at 86 and 67 eV, respectively, and the shoulder at 91 eV is probably due to the surface plasmon loss. Curves *B* and *C* show the results obtained when the primary electron beam energy was varied and the sensitivity of the detection system was increased by increasing the modulating signal amplitude.

The binding energy of beryllium K-shell electrons is 111 eV with respect to the Fermi level. Therefore, the energy necessary to remove the second K-shell electron can be expected to lie between this value and that for the K-shell binding energy of boron, 188 eV. The mean value of 150 eV suggests that the beryllium $(K)_2VV$ Auger process should be detected at an energy 39 eV (150–111) above the KVV peak. Moreover, our measured value of 38 eV is in agreement with the value of 37.6 eV observed for the separation between the beryllium KV soft-x-ray spectrum and its $(K)_2V$ satellite. Therefore, the event shown at 143 eV in curve *C* is assigned to the Auger process initiated from doubly ionized K shells. The decrease in intensity of this signal with decreasing primary-beam energy as illustrated in curves *B* and *C*, a result generally in keeping with double-ionization phenomena, supports this assignment.

The event at 123 eV, 18 eV above the main Auger peak, as observed under the different detection conditions applying to both curves *B* and *C*, is attributed to the plasmon energy gain process due to the coupling of the energy of a beryllium KVV Auger electron and the decay of a volume plasmon. The 123-eV event could not be detected unambiguously below primary beam energies of about 250 eV because of inelastic losses by the primary electron beam. However, this is a limitation of the experimental system, and no implications regarding energy dependence of the plasmon energy gain process should be inferred from this result.

The two high-energy satellites in the Auger spectra reported here indicate that at a primary electron beam energy of 2.5 keV, $(K)_2VV$ and $KVV + \hbar\omega_p$ events occur in beryllium with about equal probability, since the relative intensities of the two signals ($\approx 0.5\%$ of the amplitude of the 105-eV event) were about equal. It should be recalled that signal-averaging techniques were required to measure these signals, which were approximately a factor of 5 less intense than the single satellites we observed at energies greater than the main $L_{23}VV$ Auger peaks in Mg, Si, and Al. These observations, as well as the energy values estimated for $(L_{23})_2VV$ events, suggest a near coincidence in energy for double-ionization and plasmon-gain satellites in these third-period elements. Consequently, it is believed that the satellites in our Auger spectra from these materials result from both plasmon energy gain and

double-ionization processes, and, in general, the two probably are of comparable importance.

Energy difference data of the type reported here and in previous publications by the authors cannot be used to determine the mechanism of the plasmon energy gain process by Auger electrons, but models for specific energy coupling processes have been proposed by others.^{2,3} However, the data presented here do indicate that, at a primary electron beam energy of 2.5 keV, both double-ionization and plasmon energy gain processes involving Auger electrons are of about equal importance in beryllium and that at lower primary beam energies the plasmon-gain satellite can be detected even after the double-ionization satellite signal is relatively too weak to be observed.

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CHARACTERISTIC ENERGY GAIN AND LOSS, DOUBLE IONIZATION, AND IONIZATION LOSS EVENTS IN BERYLLIUM AND BERYLLIUM OXIDE SECONDARY ELECTRON SPECTRA¹

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Characteristic energy losses by low-energy electrons scattered inelastically from beryllium and BeO surfaces, as well as the "true secondary" spectra of electrons with energies slightly above the vacuum level, have been determined. Figure 2.28 illustrates the former and Fig. 2.29 the latter. These data and ionization loss spectra (not shown) from both types of surfaces are used to construct an electron energy-level diagram for BeO which agrees with a model proposed by Fomichev.³ From the data it is concluded that the "true secondary" spectrum of BeO is probably more representative of the beryllium substrate than of the BeO overlayer. The corresponding spectrum from beryllium can be discussed in terms of characteristic energies related to excited electron states in the solids. However, the data do not permit an unambiguous choice between several possible explanations for structure noted in the spectrum.

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Fig. 2.28. Characteristic loss spectra from clean and oxidized beryllium surfaces.

Fig. 2.29. True secondary spectra from clean and oxidized beryllium surfaces.

AUGER TRANSITIONS INITIATED FROM SINGLY AND DOUBLY IONIZED STATES IN LITHIUM METAL¹

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Satellites, appearing in secondary electron spectra on the high-energy side of events associated with principal Auger transitions, have been attributed both to a plasmon energy gain process and to Auger events initiated from doubly ionized shells. Lithium is a material in which the energies of events produced by both mechanisms should have values which would be easily resolvable. Although lithium has recently been examined by Löfgren and Wallden,⁴ these authors found no evidence for the occurrence of either event.

The Auger spectrum of the lithium material used in this investigation has recently been reported by Clausing et al.⁵ Although the principal lithium KVV Auger event at 52.5 eV was correctly identified, the transitions responsible for several weaker minima in this spectrum were not unambiguously determined.

The Auger spectrum from a freshly scraped lithium sample is shown in Fig. 2.30. Positive identification of all major events in this spectrum can be made with the aid of the characteristic and ionization loss spectra shown in Fig. 2.31. The minimum at 52.5 eV (Fig. 2.30) is ascribed to the lithium KVV Auger transition, while the corresponding lithium K-shell ionization loss signal is shown in Fig. 2.31 at 443 eV, 57 eV below the elastic peak. Ionization loss signals were identified not only by their energy but by noting that they were coupled to and moved with the elastic peak. In Fig. 2.31, losses due to the creation of surface and volume plasmons by incident electrons are illustrated at 4.5 and

Fig. 2.30. Auger spectrum from lithium surfaces containing sodium and potassium.

Fig. 2.31. Ionization and characteristic loss events in the secondary electron spectrum from lithium surfaces containing sodium and potassium.

7.8 eV below the elastic peak. Due to surface roughness the surface loss is the stronger of the two. Similarly, the broad minimum below the lithium KVV Auger transition in Fig. 2.30 is attributed to plasmon losses of both types.

The minimum at 28.5 eV in Fig. 2.30 is identified as the sodium $L_{23}VV$ Auger transition, while the small shoulder on the high-energy side at 31 eV is ascribed to the sodium $L_1L_{23}V$ Auger transition. The presence of sodium was confirmed by the observation of both the L_1 and L_{23} level ionization loss signals at the expected values of 64 and 29 eV, respectively, below the elastic peak and also by detection of a very weak $KL_{23}L_{23}$ sodium Auger transition at 990 eV. Although the small minimum at 40.5 eV occurs at the energy expected for an $(L_{23})_2VV$ process, that is, an Auger decay initiated from a doubly ionized L_{23} level of sodium, it is likely⁵ that this event is due primarily to the oxidation of lithium.

The small minimum at 16.5 eV in Fig. 2.30 is ascribed to the $M_{23}VV$ Auger transition in potassium. Although the M_{23} ionization loss signal from potassium should be observable 18 eV below the elastic peak, its detection is hindered by the presence of multiple plasmon loss events. However, a small $L_{23}M_{23}M_{23}$ Auger transition

attributed to potassium could also be detected at 257 eV, thereby confirming the presence of potassium on the surface.

The minimum at 82 eV in Fig. 2.30 is due to $(K)_2VV$ Auger electrons arising from events initiated in doubly ionized K shells of lithium. The 29.5-eV separation between this event and the lithium KVV event is in excellent agreement with both a calculation based on the atomic approximation and the 28.8-eV value between the parent and satellite bands in the lithium soft-x-ray emission spectrum. Moreover, a weak ionization loss signal from the doubly ionized K shell of lithium could be detected 143 eV below the elastic peak. The minimum immediately below the 82-eV event is due to both surface and bulk plasmon losses by exiting Auger electrons. For incident electron beam energies in the range 0.5 to 3.0 keV, the ratio of the $(K)_2VV$ event to the KVV event for lithium varied between 0.5 and 0.7%. Using signal averaging techniques, the $(K)_2VV$ event could be detected at primary beam energies as low as 200 eV, where the ratio was about 0.2%. This relative intensity of the double-ionization satellite is similar to that observed for beryllium (0.5%).⁶ Moreover, these data are in approximate agreement with results from soft-x-ray emission studies and suggest that the relative cross section for double ionization is larger in the L_{23} shell than in the K shell of the lighter elements.

Although a thorough search was conducted in the energy region immediately above the lithium KVV Auger transition, no event associated with either a surface or volume plasmon gain could be detected. Taking into account the noise background, it was determined that if either event was present, it had to be less than 0.1% as intense as the main lithium Auger transition. The two small minima illustrated in Fig. 2.30 at 62 and 68 eV cannot be associated with a plasmon gain. While the event at 62 eV could be due to a sodium L_1VV Auger transition and the one at 68 eV to a second-order plasmon loss by the lithium $(K)_2VV$ Auger electrons, these assignments can be considered tentative only.

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3. Physics of Insulators and Semiconductors

The general purpose of the research program involving insulating solids is to increase the understanding of the influence of defects, both intrinsic and radiation induced, on the physical properties of such materials. In order to pursue this objective, it is necessary to have available well-documented knowledge of the properties of nominally pure crystals. For new classes of materials, this often entails research on "perfect" crystals and on the effects of small amounts of impurities introduced during the growth process. These growth impurities, which usually have a concentration of the order of 10–100 ppm, often interact with the defects induced in the crystal by irradiation, and the study of these interactions is also an objective of the program. The primary experimental tools employed include electron paramagnetic resonance (EPR), electron-nuclear double resonance (ENDOR), optical absorption and emission, and magnetic circular dichroism (MCD). Also, during the last year the Solid State Division has acquired a well-developed program in Raman scattering and Fourier transform infrared spectroscopy which extends the scope of studies in both perfect and radiation-damaged substances.

The greatest emphasis is presently placed on experimental research into the properties of: (1) the alkali halide; (2) the alkaline-earth oxides possessing the alkali-halide structure; and (3) more complicated halides and oxides including perovskite structures such as RbCaF_3 , polymorphs of SiO_2 , and silicates. The alkali halides are studied primarily because they are the prototype of all ionic crystals. This work relates to the practical problems of radioactive waste storage in natural salt deposits, which have been pursued in cooperation with members of the Chemical Technology Division. High temperature refractory materials such as alkaline-earth oxides are being studied because of their importance as insulators which are relatively resistant to extreme environments and to radiation damage. Specific interest in the oxides arises because of their importance in fission and fusion reactors. Also, the alkaline-earth oxides form very nearly ideal hosts for the rare-earth ions and their transuranic analogs which are produced at the HFIR and processed at the ORNL Transuranium Laboratory. Magnetic resonance studies of these ions in the cubic oxides yield electronic and nuclear properties of transuranic elements and have the advantage that extremely small quantities of these highly radioactive elements are sufficient for the experiments. More complicated halides and oxides are of intrinsic interest and practical importance because of the useful dielectric, optical, piezoelectric, acousto-optic, and structural properties which are associated with phase changes frequently occurring in these materials. All of these studies of the physics of insulators are greatly aided by members of the Research Materials Program and the Metals and Ceramics Division who frequently supply high-purity, well-characterized crystals.

The primary purpose of research in semiconductors is to explore the possibility of producing better radiation-resistant materials. This work involves the study of the influence of the type and concentration of impurities on the production of vacancies and interstitials in germanium by ^{60}Co gamma, high-energy electron, and reactor irradiation.

The data collected tend to support the suggestion that silicon or germanium *p-n* junction-type devices can be made more radiation resistant using oxygen, instead of other conventional elements, as the donor impurity.

During the past year the program on magnetic resonance studies of lunar samples was successfully concluded. One of the interesting discoveries was that ferric oxides are present in some lunar soils despite the extreme environmental reducing conditions.

RADIATION DAMAGE

NEUTRON IRRADIATION EFFECTS AND STRUCTURE OF NONCRYSTALLINE SiO_2 ¹

J. B. Bates¹ R. W. Hendricks² L. B. Shaffer³

The nature of the defects produced in crystalline quartz and noncrystalline SiO_2 by fast-neutron ($E > 0.1$ MeV) irradiation has been investigated by Raman

and infrared spectroscopy, small-angle x-ray scattering, transmission electron microscopy, and electron diffraction. Measurements were made at 25°C on samples irradiated at fluences from 1×10^{18} neutrons/cm² (*nvf*) to $\sim 2 \times 10^{20}$ *nvf*. The changes observed in the Raman spectra of SiO_2 with increasing fluence are shown in Fig. 3.1. The spectra of two high-fluence α -quartz samples are essentially identical to those of the SiO_2 samples irradiated to corresponding fluences. The polarized band at ca. 608 cm^{-1} increases by about a

Fig. 3.1. Raman spectra of unirradiated and irradiated noncrystalline SiO_2 at 25°C for $X(Z_X^X)Y$ scattering geometry. Fluence of fast neutrons in neutrons/cm² (*nvf*). ($E > 0.1$ MeV).

factor of 7 from unirradiated SiO_2 to the 2×10^{20} *nvt* specimen. This band is assigned to a mode of the defect center and may be due to a symmetric bending motion of non-bridged oxygen atoms. A graph of the 608 cm^{-1} Raman band intensity vs fluence for SiO_2 is shown in Fig. 3.2. Infrared absorption spectra were measured in the region from 3900 to 2900 cm^{-1} in order to determine the change in OH^- concentration with increasing fluence. The A/b values, where A is the absorbance and b is the sample thickness, are plotted in Fig. 3.2 vs fluence for the SiO_2 and α -quartz samples. The increase in OH^- concentration is nearly linear with fluence for SiO_2 , but a jump in the OH^- concentration in α -quartz was observed between the 9×10^{19} *nvt* sample and the 2×10^{20} *nvt* sample.

The small-angle x-ray scattering from the SiO_2 samples and from the most heavily irradiated α -quartz specimen showed a monotonic increase from the zero-angle value into the first high-angle Si-O peak. A graph of the scattering intensity at the smallest angle, $I(0)$, as a function of fluence is shown in Fig. 3.3.

The scattering curve of the 2×10^{20} *nvt* α -quartz sample was similar to those of SiO_2 , and $I(0)$ had approximately the same value as $I(0)$ for SiO_2 irradiated to the same fluence. On the other hand, α -quartz irradiated to 9×10^{19} *nvt* showed a strong small-angle maximum superimposed on the monotonic curve. An electron diffraction pattern of this sample showed a glass-like bulk phase and a second crystalline phase in

Fig. 3.2. Graphs of normalized intensity of 608 cm^{-1} Raman band and A/b values of the OH^- band, where A = infrared absorbance and b = sample thickness, for irradiated SiO_2 and α -quartz.

Fig. 3.3. Zero-angle x-ray scattering intensity $I(0)$ for SiO_2 and α -quartz vs fluence.

which the orientation was the same for all particles. The fact that all the individual α -quartz crystallites remaining after irradiation to 9×10^{19} *nvt* have the same crystallographic orientation implies that they are remnants of the original α -quartz crystal and are not a result of devitrification. Assuming a simple two-phase model for this sample, the x-ray scattering curve was separated into two components, and the scattering intensity for the glass-like phase was determined to be approximately the same as that of SiO_2 irradiated to the same fluence (Fig. 3.3). However, the mean density of the glass-like phase is higher than that of a corresponding SiO_2 sample. The radius of gyration and volume fraction of the α -quartz phase were $47 \text{ \AA}$ and 6.7%, respectively.

Comparison of the data of Fig. 3.2 and Fig. 3.3 shows that the mean square density fluctuations, which are proportional to $I(0)$, and the intensity of the 608 cm^{-1} Raman band grow in the ratio 1:2. This suggests that the removal of an SiO_2 unit from the random network creates one unit of density fluctuation as well as two non-bridged oxygen atoms. The OH^- concentration as a function of fluence (Fig. 3.2) appears to be correlated with the density of the glass-like bulk phase into which it is diffusing. The fact that the computed density of the glass phase in α -quartz irradiated to 9×10^{19} *nvt* is well above that of SiO_2 irradiated to the same fluence explains the sudden jump seen in Fig. 3.2.

1. Summary of paper to be published.
2. Metals and Ceramics Division.
3. Anderson College, Anderson, Indiana.

Fig. 3.4. Effect of uv bleaching on the irradiation-induced optical absorption of MgF_2 .

STUDIES OF AGGREGATE CENTERS IN MgF_2 BY OPTICAL BLEACHING¹

Jay Cee Figg

A strong optical absorption band at 2600 Å has been observed by Facey et al.² in electron-irradiated MgF_2 . These workers also observed that neutron irradiation produced a complex absorption band in the same energy region. They concluded that the difference between the two absorption characteristics arose from the fact that neutron irradiation produced a large concentration of damage clusters whereas the electron-irradiation damage consisted predominantly of single fluorine vacancies and a small concentration of di-vacancies.

A simple way of testing the conclusion is to irradiate with gamma rays, which produce isolated vacancies, and then to bleach the sample with ultraviolet light to cause motion of the vacancies and thus allow aggregate centers to form. The sample chosen was one with the face perpendicular to the *c* axis, so as to simplify the structure of the *F*-center absorption band. The resultant spectra are shown in Fig. 3.4.

Irradiation with ^{137}Cs gamma rays produced the characteristic *F*-center absorption at 4.85 eV. There was also a small *M*-center band at 3.8 eV, which implies some vacancy motion during the room-temperature irradiation. After bleaching for 87 hr at room temperature, the spectrum shown was observed. This spectrum

after bleaching shows the essential characteristics of the *F*-center region of the post-neutron-irradiation absorption spectrum.

A second irradiation with ^{137}Cs gamma rays restored the absorption spectrum to that observed before the bleaching. One can conclude from these data that the model proposed by Facey et al. to explain the absorption observed in the *F*-center region after neutron bombardment is essentially correct.

An attempt was also made to find the band edges of MgF_2 absorption. The lower band edge was found to be 0.12 eV. The upper band edge was beyond the range of the present instrumentation, i.e., above 11.5 eV. (However, one can say that the upper band edge is above 11.5 eV.)

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TEMPERATURE DEPENDENCE OF THE PRIMARY PROCESS OF RADIATION DEFECT PRODUCTION IN ALKALI HALIDES¹

E. Sonder

The identity and stability of enough of the radiation-produced defects in alkali halides is now sufficiently known² to permit reliable measurement of the primary Frenkel pair production efficiency as distinct from the

net production rate of F centers. The latter is determined by secondary reactions occurring during and after irradiation and before the defect concentration is measured. The experimental method, which has been tested for KCl in the past,³ involves measuring the rate of radiation destruction of defects or impurity centers that are present in the samples before the irradiations begin. We have been employing this method to investigate the increase with temperature of the primary Frenkel pair production efficiency between 80°K and room temperature. This increase is more than an order of magnitude for the case of KCl, NaCl, and RbCl, and may be characterized by the relation $\dot{F} = A + B \exp(E/kT)$, where $\dot{F}$ is the primary Frenkel pair production rate, A and B are constants, and E in the exponential temperature dependence is 0.06 ± 0.01 eV. A comparable increase occurs in KBr, but the temperature dependence is less, corresponding to an E of 0.03 eV.

Our measurements yield values for the defect production rate after completion of the primary process, but before motion of the interstitials and vacancies takes place. It is of interest to compare these values with results of pulsed radiolysis measurements (done so far⁴ only for KBr), which have indicated a similar temperature dependence for the ratio of the concentration of widely separated Frenkel pairs to close pairs 100 nsec after the radiation pulse.

It appears that the observed temperature dependence of Frenkel defect production in alkali halides stems from a temperature dependence of the average distance of separation between a radiation-produced interstitial and the vacancy it has left behind. Such a temperature dependence connected with the collision process is surprising, and the fact that it occurs may have significance for other materials in addition to alkali halides.

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RADIATION DAMAGE IN BERYLLIUM OXIDE SINGLE CRYSTALS¹

J. C. Figg² A. K. Garrison³ S. B. Austerman³

Radiation damage in single crystal BeO has been studied using ⁶⁰Co gamma, 2-MeV electron, and epithermal-neutron irradiations. The temperature of irradi-

ation and the accumulated dose were kept within the range in which the change in the a lattice parameter has been found to predominate.^{4,5} The observed changes produced by ⁶⁰Co irradiation are attributed to ionization of crystal impurities. Both electron and neutron irradiation produce optical absorption bands at about 5.25 and 6.5 eV. The energy at which the band peak occurs varies slightly with the conditions of irradiation and from sample to sample. No EPR resonance could be correlated with either band. Neither F^+ or V^- centers reported by other investigations^{6,7} were observed. The data from the annealing of these two bands indicate that they arise from different, but related, defects and that they are not due to simple point defects.

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DEFECT-IMPURITY INTERACTIONS IN THERMAL-NEUTRON-IRRADIATED GERMANIUM

J. W. Cleland

The rate of introduction of lattice defects in germanium as a consequence of irradiation is usually estimated from electrical property measurements of the change in the net carrier concentration. There is a general agreement in the published literature that lattice defects are created and that electrons are removed from conduction, but there is no general agreement at present as to the type of defect structure that is responsible for the removal of conduction electrons. The purpose of these experiments, therefore, was to investigate defect-impurity interactions in germanium of known chemical dopant and oxygen concentration in an attempt to understand better the lattice defect structure.

Single-crystal ingots of n -type germanium of known chemical dopant were obtained from commercial sources, and oxygen-doped ingots were produced at this laboratory¹ by the Czochralski process from starting material with $<10^{13}$ cm⁻³ chemical donor- or acceptor-type impurities. Crystals of known chemical dopant and donor concentration were also produced, and oxygen was added during growth to the bottom portion of the ingot.

Infrared absorption band measurements ($11.7\ \mu$) were used to determine the oxygen concentration. Annealing of germanium at 350°C is known to cluster oxygen atoms, which then act as donor-type electrical impurities, and quenching from $>600^\circ\text{C}$ is known to remove the donor contribution, presumably as a consequence of dissociation of oxygen clusters. The IR technique is sensitive to an oxygen concentration of $10^{14}\ \text{cm}^{-3}$, or even less if special care is taken, but IR measurements (at $11.7\ \mu$) do not detect the presence of oxygen clusters in germanium.

Lattice defects are introduced in germanium as a consequence of lattice atom recoil subsequent to thermal-neutron absorption and capture-gamma-ray emission. Irradiations were carried out in the N or S tubes of the D_2O tank attached to the Bulk Shielding Reactor at ORNL. This facility is unique in that the thermal-neutron flux is $\sim 1.5 \times 10^{12}\ \text{cm}^{-2}\ \text{sec}^{-1}$ at 2 MW, whereas the fast-neutron flux ($>0.6\ \text{MeV}$) is $<10^8\ \text{cm}^{-2}\ \text{sec}^{-1}$ at 2 MW. This means that one can study (n, γ) recoil and subsequent transmutation effects in germanium with only a very negligible contribution from any fast-neutron-induced defect clusters or disordered regions.

Neutron-absorption cross section data were used to calculate the initial number of (n, γ) -activated atoms, and isotopic abundance data were used to calculate the final number of donor- or acceptor-type chemical impurities introduced by the transmutation process. Electrical property measurements (at 77°K) were taken ~ 7 – 10 days after each successive irradiation to determine the carrier concentration.

Figure 3.5 is a graph of the rate of removal of conduction electrons per absorbed neutron vs the total (%) decrease in donor concentration. All of the ^{75}As donors, most of the ^{77}Se double donors, and ~ 0.4 of the ^{71}Ga acceptors were present by the time of each measurement; hence the transmutation-induced donor and acceptor contribution tended to balance out, so these data primarily indicate the lattice defect concentration changes from (n, γ) recoil events.

The initial consequence of an (n, γ) event in germanium is expected to result in the formation of a lattice atom vacancy (V) and an interstitial (I), and both can probably migrate. The electrical behavior of (I) is not known, but there must be some type of barrier to (V/I) recombination, since electrically active lattice defects remain as a consequence of irradiation. Annealing (20 hr at 450°C) is known to remove all evidence of lattice defects in germanium as observed by electrical property measurements, presumably as a consequence of (V/I) recombination.

Fig. 3.5. Rate of removal of conduction electrons per absorbed neutron in n-type germanium vs the total (%) decrease in conduction-electron concentration.

Note that the initial removal rate of conduction electrons per neutron absorbed (Fig. 3.5) is ~ 1.5 – 2.0 for phosphorus- or arsenic-doped germanium, ~ 1.0 – 1.5 for antimony-doped germanium, and ~ 0.5 for germanium with a donor concentration as introduced by clustered oxygen. Preliminary data (not shown) indicate an initial removal rate of ~ 1.0 – 1.5 for antimony-doped germanium that also contained up to $\sim 6 \times 10^{17}\ \text{cm}^{-3}$ oxygen, as long as the oxygen was dissociated by quenching; but the initial removal rate was reduced to ~ 0.5 for the same antimony-doped germanium, if the apparent donor concentration was increased to $\sim 5 \times 10^{16}\ \text{cm}^{-3}$ by annealing at 350°C to produce oxygen clusters.

Recent publications have suggested the fabrication of radiation-resistant silicon or germanium p-n junction-type devices by using oxygen to produce donors instead

of using conventional chemical impurities. The present data are in general agreement, but they also indicate that there is no electrical property evidence for a radiation-induced lattice defect structure that consists of a (*V*) and an isolated oxygen atom in the germanium lattice.

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DEFECT-IMPURITY INTERACTIONS IN ELECTRON-IRRADIATED GERMANIUM

J. W. Cleland Floyd James¹

The purpose of these experiments was to use 1.0–2.0-MeV electrons from the Solid State Division Van de Graaff accelerator to investigate defect-impurity interactions in germanium in a similar manner to that utilizing thermal-neutron-induced (*n*, γ) reactions. The experiments and the interpretation are still in progress, but the results to date confirm those indicated in Fig. 3.5 above² as regards a lower removal rate of conduction electrons per incident electron for antimony- or O₄-doped *n*-type germanium. Ambient temperature annealing subsequent to ambient ($\sim 300^\circ\text{K}$) irradiation is much more evident in these samples, since short (10 min to 2 hr) irradiation times were required; hence, it is anticipated that a careful examination of the electrical property changes during annealing will provide a better understanding of any interactions between radiation-produced (*V*), (*I*), and normal chemical impurities or oxygen clusters in germanium.

1. Summer research participant from the University of North Carolina, Chapel Hill.

2. J. W. Cleland, "Defect-Impurity Interactions in Thermal-Neutron-Irradiated Germanium," this report.

DEFECT-IMPURITY INTERACTIONS IN ⁶⁰Co-PHOTON-IRRADIATED GERMANIUM

J. W. Cleland

A prominent lattice defect state has been observed by electrical property measurements at ~ 0.2 eV below the conduction band ($E_c - 0.2$ eV) in *n*-type germanium as a consequence of irradiation with photons, electrons, or neutrons. Goncharov et al.,¹ in some recent ⁶⁰Co-photon-irradiation experiments, did not observe this lattice defect state. They suggested that the germanium used by all previous investigators contained more oxygen than their material, which contained $\sim 3 \times 10^{15}$ cm⁻³ oxygen, and that any observation of a defect

state at $E_c - 0.2$ eV was due to the formation of vacancy oxygen (VO) defect clusters.

Previous experiments² have indicated that the apparent rate of introduction of lattice defects by ⁶⁰Co photons was essentially independent of the oxygen concentration in germanium containing up to $\sim 10^{16}$ dissolved oxygen per cubic centimeter, and formation of a primary defect state at $E_c - 0.2$ eV was observed for all oxygen concentrations. These experiments have been extended to samples of germanium that contained $\leq 10^{14}$ to $\geq 6 \times 10^{17}$ cm⁻³ oxygen, and formation of the $E_c - 0.2$ eV level was observed in every case. The fact that the rate of removal of conduction electrons per incident ⁶⁰Co photon was independent of the oxygen concentration in these experiments also indicates that there is no electrical property evidence for vacancy oxygen (VO) cluster-type defects.

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DISSOLUTION REACTIONS OF IRRADIATED NaCl¹

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J. R. Walton⁴

In connection with a study of energy storage in irradiated NaCl, it was found that heat evolved upon aqueous dissolution was typically only half of the total stored energy. In order to assess whether that discrepancy was a result of radiation activation of the solid salt and consequent side reactions occurring during dissolution, we have conducted a number of measurements to help identify reactions taking place during dissolution of irradiated NaCl. The quantities measured have included identity and amount of gas released, change of pH of solution, change in optical absorption due to OCl⁻ ion in solution, as well as stored energy and heat of solution. A number of solution reactions for the activated species, written as Na⁺e⁻ (electron trapped at a sodium ion) and Cl⁻e⁺ (hole remaining at a chlorine ion) have been analyzed, and the possibility of their occurrence has been tested vs experimental results. Table 3.1 is a list of the considered reactions, which includes normal dissolution to produce Na⁺ and Cl⁻ in solution and reactions involving water or dissolved oxygen to produce hydrogen or oxygen gas or a number of dissolved ions. It is possible to conclude that, in contrast to unirradiated salt which dissolves to produce

Table 3.1. Possible reactions occurring during aqueous dissolution of irradiated NaCl

only Na^+ and Cl^- in solution, irradiated salt dissolves to produce H_2 and OCl^- , indicating that there is a significant contribution of reactions (1) and (4) of Table 3.1.

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1. Summary of paper to be published.
 2. Chemical Technology Division.
 3. University of Kansas, Lawrence.
 4. Analytical Chemistry Division.

OPTICAL PROPERTIES

FORMATION AND STABILITY OF V^- AND V_{Al} CENTERS IN MgO^1

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The exposure of an as-grown MgO crystal to moderate doses of ionizing radiation, such as x, γ , β , or uv rays, produces a broad optical absorption band³ at 2.3 eV which decays at room temperature. This band has been correlated with an axially symmetric defect whose EPR g values have been given³⁻⁵ as $g_{\parallel} = 2.0032$ and $g_{\perp} = 2.0385$. For many years, this center has been accepted as the V^- center, a Mg vacancy with a trapped hole.^{6,7}

Five years ago, it was suspected that more than one type of defect existed with this set of g values and optical absorption band because of both radiation damage and thermal stability data.⁸ Specifically, in some crystals, certain types of irradiation produced a much longer-lived species of V^- center. In a recent letter,⁹ we gave conclusive evidence that (1) in crystals subjected to ionizing radiation an aluminum ENDOR signal was associated with this set of g values, and we named this the V_{Al} center; (2) based upon a detailed EPR and ENDOR survey covering a wide assortment of crystals (from various sources used by past investi-

gators), the center which researchers have previously accepted as the V^- center was primarily this same V_{Al} center; and (3) another center, which we found to be present in crystals irradiated with energetic particles (neutrons or 2-MeV electrons), has the same g values but no aluminum ENDOR signal. We believe this latter center, which is distinguished by being electronically stable at room temperature, to be the V^- center. Optical absorption measurements, supported by ENDOR and EPR, were used to study the formation and annihilation of V^- and V_{Al} centers in MgO . Our studies show that some crystals can harbor either center exclusive of the other, or contain both centers simultaneously. Actually, the simplest and most obvious way to distinguish between the V_{Al} and the V^- centers follows from their different production rates and thermal stabilities.

The formation of the V^- center in single-crystal MgO was found to be strongly sample dependent. In certain crystals, V^- centers could not be produced under electron or neutron irradiations regardless of dose (up to 10^{17} e/cm²). For other crystals, a concentration gradient of the V^- center could be observed visually in various portions of the crystal. Subsequent repeated thermal annihilations and rejuvenations by high-dose electron irradiations at 80°K produced the same concentration gradient, indicating impurity dependence as the cause. Certainly, it cannot be attributed to non-uniform thermal annealing over the crystal, since the temperature of irradiation was well below the annealing temperature of the V^- center and was indeed far below room temperature. Furthermore, the procedure was repeated each time at somewhat different irradiation geometry positions with uniform electron flux.

Investigations are being undertaken to determine the impurity which makes possible the formation of the V^- center. Preliminary results indicate that the V_{OH} (and V_{OH}^-) center is a precursor of the V^- center. It appears that the production of the V^- center is achieved, not by the displacement of the Mg^{2+} ions, but by the removal of the hydrogen ion at a V_{OH} (or V_{OH}^-) site by ionization.

The observed cross section for the production of the V^- center by means of high-energy electron irradiation is inconsistent with the mechanism of knock-on production of Mg^{2+} vacancies. Furthermore, the center can also be produced by ionizing radiation of quite low energy, and the relative ease with which photoelectrons of energy less than 10 keV create V^- centers clearly shows that there is an essentially zero-energy threshold for the production of V^- centers. Therefore, the V^- center is formed by an ionization process and not by a

knock-on process. Furthermore, in view of the apparent lack of energy dependence, we conclude that the ionization process of V^- center production is the dominant one. Certainly, the production of V^- centers by electron or neutron irradiation is the result of the intense ionization accompanying both irradiation methods, rather than a consequence of knock-on processes. In the case of neutron irradiation, the neutron flux of 2.3×10^{13} neutrons $\text{cm}^{-2} \text{sec}^{-1}$ in the Oak Ridge Reactor is accompanied by an overwhelming γ intensity of 2×10^9 R/hr. There is no evidence at this time that V^- centers can be produced by a knock-on process using electrons or neutrons in single-crystal MgO. In fact, while neutrons are conducive to the formation of F -type centers, it appears that the V^- center cannot survive high doses of neutrons. V^- centers can be produced, however, by low doses of neutrons, presumably due to the concomitant large γ fluxes.

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PHASE TRANSITIONS IN RbCaF_3 ¹

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Several properties of crystalline RbCaF_3 have been studied and were found to reveal changes in the crystal structure. The crystals have the cubic perovskite structure at room temperature, but undergo phase transformations and have lower symmetry at temperatures below 198°K.

The polarizing microscope enabled the direct visual observation of a phase transformation and revealed the formation of a domain structure. At higher temperatures the crystals are cubic and hence optically isotropic; however, at 198°K, there is an onset of optical birefringence that is readily observed with polarized light. The crystals became bright when viewed between

crossed polarizers, and a pattern of striations oriented in a [110] direction developed. The striations can be interpreted as 90° domain boundaries of a tetragonal phase. An extinction could be obtained with crossed polarizers oriented in crystallographic [100] directions. This indicates that the optical axis of a tetragonal domain is oriented in a [100] direction lying in the face of the crystal.

Quantitative measurements of the optical birefringence Δn were made by utilizing a high-frequency light modulation method, and some results are shown in Fig. 3.6. The birefringence varies almost linearly with temperature over most of the range of measurements; however, it has an approximate square root dependence on $T_c - T$ in the critical region near the transition. At lower temperatures than the measurements shown, the birefringence saturates. It was found to be well saturated at liquid helium temperature.

The electron paramagnetic resonance of Fe^{3+} in crystalline RbCaF_3 was studied both in the high-temperature cubic phase and in lower-temperature phases. The substitutional site for the Fe^{3+} was determined from the superhyperfine interactions with ^{19}F nuclei to be the Ca^{2+} site. Below 198°K, the paramagnetic resonance spectrum exhibited a large temperature-dependent tetragonal splitting of the fine-structure lines, which when examined in detail also revealed the domain structure. Values for the tetragonal field parameter $b_2^0(T)$ were determined from the measurements and are shown in Fig. 3.6. Like the birefringence, $b_2^0(T)$ has a nominal square-root dependence for about 10° below T_c ; then an apparently linear

Fig. 3.6. The temperature dependence of birefringence (Δn) and the Fe^{3+} fine-structure axial splitting (b_2^0) for RbCaF_3 . The square of the order parameter (ψ) known for some antiferroelectric perovskite crystals is also shown. The curves were normalized to have equal slope in the linear region.

splitting takes over. However, measurements between liquid-nitrogen and liquid-helium temperatures indicate that the crystal field parameters do not continue to have the linear behavior depicted, but undergo abrupt changes at 43°K and near 10°K. These abrupt changes are accompanied by much hysteresis and apparently reflect additional phase changes. This is substantiated by the observation of corresponding changes in the crystal dielectric function and specific heat.

Audio-frequency measurements of dielectric properties were made with an impedance bridge which permitted simultaneous measurement of capacitance and loss. Results are shown in Fig. 3.7. Transitions in the vicinity of 200°K and 40°K are clearly visible, as is a small change in dielectric constant and accompanying loss peak at 10°K.

Heat capacity measurements of a preliminary nature were made on a polycrystalline sample by means of a temperature drift rate method. The results are shown in Fig. 3.8, where temperature differential is plotted against the actual sample temperature. Even with this

crude method, the 198°K and 43°K transitions are evident. The prominent nearly vertical slope at 43°K suggests a first-order transition, and is consistent with the abrupt changes seen in the paramagnetic resonance at this temperature.

Near the 198°K transition, the temperature dependence of the Fe^{3+} fine-structure splitting is in excellent agreement with that of the optical birefringence and is very similar to that observed in some other perovskite crystals, particularly SrTiO_3 (ref. 3) and KMnF_3 (ref. 4). On that basis, it is assumed that the 198°K transition is a similar antiferroelectric phase transition resulting from condensation of a Γ'_{15} phonon mode at the Brillouin zone R corner. The order parameter corresponding to such a transition in RbCaF_3 is a rotation angle of the CaF_3 octahedra around $\langle 100 \rangle$ pseudo-cubic axes. Both the birefringence Δn and the tetragonal field parameter b_2^0 are then necessarily proportional to ψ^2 . If ψ is to be described by a critical exponent β , where $\psi = (1 - T/T_c)^\beta$, three separate temperature regions described by distinctly different values of β are found. For $T/T_c \leq 0.85$, there is a mean field region where $\beta = 0.5$, in correspondence with predictions of Landau theory; for $0.85 < T/T_c \leq 0.95$ there is a critical region where $\beta = 0.33$, in essential agreement with the value $\beta = 0.31$, computed from a three-dimensional Ising model, but for $0.95 < T/T_c$, $\beta = 0.25$, for which we have no explanation.

The paramagnetic resonance and, more conclusively, the dielectric function and specific heat measurements indicate additional transitions at lower temperatures. The form of the dielectric behavior at 43°K is similar in appearance to that of PbZrO_3 (ref. 5) near its antiferroelectric transition at 233°K. However, RbCaF_3 does not exhibit the large dielectric constant found for oxide perovskites nor does it exhibit a Curie-Weiss shape above the phase transition.

Fig. 3.7. Audio-frequency dielectric constant (ϵ) and loss (R_2) of RbCaF_3 vs temperature. Solid lines and points indicate measurements made during cooling; dashed lines and open circles indicate measurements made while the sample warmed.

Fig. 3.8. Specific heat anomalies in RbCaF_3 .

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RESONANCE RAMAN SPECTRA OF O_3^- ION IN γ -IRRADIATED POTASSIUM CHLORATE¹

John B. Bates

The ozonide ion, O_3^- , has been identified as one of the chemical species produced by the action of ionizing

radiation on certain oxygen-containing inorganic salts. From a recent ESR study⁷ of x-irradiated potassium chlorate (KClO_3), it was concluded that O_3^- ions occupy three non-equivalent sites in the crystal lattice. Earlier ESR measurements,³ however, indicated that more than three non-equivalent sites were occupied by ozonide ions. Resonance Raman spectra of irradiated KClO_3 were measured in order to provide additional information regarding structural and dynamical properties of O_3^- in the irradiated crystal. A single crystal of KClO_3 was irradiated with ^{60}Co gamma rays at 35°C for a total absorbed dose of 4×10^{20} eV/g. An optical absorption band of O_3^- in irradiated KClO_3 is centered at ca. $4520 \text{ \AA}$, and the $4880\text{-\AA}$ line of an argon-ion laser

operating at ca. 50 mW was found to be suitable for exciting the resonance Raman spectrum of the ozonide ion. Spectra measured at 195°K for the $a(b_b^a)c'$ and $a(c_b^a)c'$ settings are presented in Fig. 3.9.⁴ In Fig. 3.9b, the ν_1 fundamental and $n\nu_1$ overtones are characterized by two major components, and the two main components of $2\nu_1$ and $3\nu_1$ appear to be split, producing four bands. The splitting between the components of each mode is caused by a difference in static field effects on the O_3^- ions which occupy non-equivalent sites in the KClO_3 lattice. The results for $2\nu_1$ and $3\nu_1$ as well as the large bandwidths observed for ν_1 and $n\nu_1$ indicate occupation of a large number (>4) of non-equivalent lattice sites by O_3^- .

Fig. 3.9. Raman spectra of gamma-irradiated KClO_3 at 198°K . Laser power at 50 mW for *a-d*; power increased to ca. 300 mW in *e*. Instrument settings in *b*: ν_1 - slit = 3 cm^{-1} and sensitivity = 100 counts/sec; $2\nu_1$ - slit = 4, sensitivity = 100; $3\nu_1$ - slit = 8, sensitivity = 500; $4\nu_1$ and $5\nu_1$ - slit = 8 cm^{-1} , sensitivity = 100.

Table 3.2. Observed and calculated frequencies for the ν_1 fundamental and $n\nu_1$ overtones of O_3^- ion in gamma-irradiated KClO_3 .

	Component frequency (cm^{-1})		Splitting (cm^{-1})	
	Observed	Calculated ^a	Observed	Calculated ^c
ν_1	1016	1016		
	(1020) ^b		6	6
$2\nu_1$	1022	1022		
	2022	2022		
	(2028) ^b		11	12
	2033	2034		
$3\nu_1$	(3016) ^b			
	3020	3018		
	3034	3036	14	18
	(3040) ^b			
$4\nu_1$	4007	4004		
	4030	4028	23	24
$5\nu_1$	4986	4980		
	5018	5010	32	30

^aFrequencies calculated from $G(n) = \omega_0 n - \omega_0 X_0 n^2$. For the low-frequency component, $\omega_0 = 1021 \text{ cm}^{-1}$ and $\omega_0 X_0 = 5 \text{ cm}^{-1}$. For the high-frequency component, $\omega_0 X_0$ set at 5 cm^{-1} and $\omega_0 = 1027 \text{ cm}^{-1}$.

^bIdentification of component uncertain.

^cSplitting between pairs of components indicated given by $\Delta (\text{cm}^{-1}) = 6n$ for the n th vibrational level.

The fundamental and first-overtone frequencies of ν_1 given in Table 3.2 were used to compute the coefficients in the term-value equation $G(n) = \omega_0 n - \omega_0 X_0 n^2$, where n is the vibrational quantum number. Subtracting the term-value formulas for the two major series of fundamental and overtone states, the two-site splitting is given by $\Delta = 6n \text{ cm}^{-1}$ for the n th level. In general, the splitting between any pair of two-site components of the n th level will be approximately given by $\Delta = (\omega_0^a - \omega_0^b)n \text{ cm}^{-1}$, where ω_0^a and ω_0^b are the harmonic frequencies for the components at sites a and b , respectively.

The changes in relative band intensities that were observed for the components of ν_1 and $n\nu_1$ as the polarization of the incident light was varied are illustrated in Fig. 3.9c for $2\nu_1$ and in Fig. 3.9d for ν_1 . The polarization results suggest that the O_3^- ions which give rise to the low-frequency components ($\nu_1 = 1016 \text{ cm}^{-1}$, $2\nu_1 = 2022 \text{ cm}^{-1}$) lie nearly in the ab plane, while the molecular planes of the ions which produce the high-frequency components ($\nu_1 = 2033 \text{ cm}^{-1}$) are nearly parallel to the bc' plane.

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4. a and b denote the crystallographic axes of the monoclinic cell, and c' is perpendicular to a and b .

MAGNETO-OPTICAL PROPERTIES OF THE F CENTER IN KMgF_3 ¹

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The compound KMgF_3 crystallizes in a cubic perovskite structure that can be envisaged as a cube with a Mg^{2+} ion at the center surrounded by F^- ions at the face centers and K^+ ions at the cube corners. An optical absorption band at 275 nm and an electron paramagnetic resonance (EPR) spectrum described by $g = 2.00$ and $A = 60 \text{ G}$ have been attributed to an F center.^{2,3} In KMgF_3 , this center has the tetragonal (D_{4h}) symmetry of two nearest-neighbor Mg^{2+} and four next-nearest-neighbor K^+ ions. The study of an F center in such an environment might reveal the perturbing effects of the site symmetry which are not present in alkali halides.

The F centers were produced by electron irradiation at room temperature. Magneto-optical experiments were performed using a combined magnetic circular dichroism (MCD) and EPR spectrometer.² The MCD channel was used to measure the difference in the absorption of left- and right-circularly-polarized light by a sample in a magnetic field oriented parallel to the direction of light propagation. The EPR channel was used to measure microwave power absorption; it consisted of a standard 24-GHz EPR system equipped with a cavity having optical ports. The two-channel spectrometer enabled the optical detection of a microwave resonance, thus giving a direct correlation of optical and paramagnetic resonance spectra associated with the center.

Representative MCD and optical absorption spectra for the F band in KMgF_3 are shown in Fig. 3.10. The MCD spectrum has an absorption-derivative-like shape which indicates that an orbital degeneracy is present. The MCD is quite strongly temperature dependent, varying inversely with temperature; this reveals a ground-state degeneracy. Since the MCD retains its derivative-like shape at low temperature, it is possible to assign the orbital degeneracy to the excited state. The temperature dependence is therefore ascribable to the combination of a spin degeneracy in the ground state and a spin-orbit coupling in the excited state. The tetragonal symmetry of the KMgF_3 anion vacancy site requires that the F -center states be classified according

Fig. 3.10. The MCD and optical absorption spectra. The inset shows the average difference in the absorption energy of left and right circularly polarized light which was calculated using moments of the spectra.

to the D_{4h} point group. Since the MCD indicates both orbital and spin degeneracy in the excited state, its most straightforward classification is as a 2E_u state (E_u' + E_u'' in the spin-orbit double group). The spin-degenerate ground state is classified as a ${}^2A_{1g}$ state (E_u' in the double group). The data do not, however, exclude the possibility that the excited state is an accidentally degenerate level. The present MCD spectra require that the 2E_u and the ${}^2A_{2u}$ states are either distant in energy or so closely degenerate as to be completely unresolved.

The MCD and optical absorption spectra were measured at various temperatures, and the results were analyzed by the method of moments.⁴ The ratio of the first moment of the MCD to the zeroth moment of the optical absorption, $\langle \Delta E \rangle$, is a measure of the average difference in the absorption energy of left- and right-circularly-polarized light and is quite rigorously a measure of the Zeeman splittings in the excited state. The variation of $\langle \Delta E \rangle$ with inverse temperature is shown as an inset of Fig. 3.10. It may be related to parameters g_L and λ which are proportional to the strengths, respectively, of the Zeeman and spin-orbit interactions.

Table 3.3. Excited-state parameters of the F center in KMgF_3 for two assumed site symmetries

Site symmetry	Excited state	g_L	λ (cm^{-1})	Δ (cm^{-1})
D_{4h}	2E_u	1 ± 0.2	-60 ± 12	-60 ± 12
O_h (assumed)	${}^2T_{1u}$	0.5 ± 0.1	-30 ± 6	-45 ± 9

Unfortunately, the quantitative relation between $\langle \Delta E \rangle$ and these parameters depends upon the choice of symmetry of the center, and the experimental results give little basis for making that choice. Table 3.3 lists the values of g_L and λ as well as Δ , the spin-orbit splitting that can be derived from λ , for two sets of assumptions: (1) the tetragonal symmetry causes the excited 2E_u state and the ${}^2A_{2u}$ state to be widely split so that the F band is due solely to the transition to the 2E_u state; (2) the excited state is an accidentally degenerate 2E_u and 2A_u state, which may be treated as a ${}^2T_{1u}$ state of O_h symmetry.

The width of the MCD spectrum is less than the width of the optical absorption band, implying that lattice modes which are not totally symmetric make a significant contribution to the width of the optical band. This was quantitatively checked in two ways. First, the values of $\langle \Delta E \rangle$ determined using the method of moments were compared with values of ΔE estimated by assuming that the MCD is due to a rigid shift of the absorption band. $\langle \Delta E \rangle$ was found to be only about two-thirds of ΔE . Second, the ratio of the third moment of the MCD spectrum to the second moment of the optical band was computed and found to be approximately $2.2\langle \Delta E \rangle$. This implies that totally symmetric (A_{1g}) vibrational modes contribute roughly 60% of the width of the F band, if a 2E_u excited state is assumed, and roughly 50% of its width, if all tetragonality is neglected (assumption 2 of the previous paragraph).

Figure 3.11 illustrates the optically detected EPR which confirms the connection of the optical band with a paramagnetic center having a ground-state g factor of 2.0. In the optically detected EPR, it was possible to resolve five of the nine hyperfine lines, first reported by Hall and Leggett.² The hyperfine structure has been attributed to the nearest eight F^- ions ($I = 1/2$), with an unresolved ${}^{39}\text{K}$ hyperfine contributing most of the width of the lines.

This study corroborates the F center identification and the optical and EPR assignments. The ground state of the center is a spin doublet, and the identified

Fig. 3.11. The microwave resonance spectrum obtained by measuring the reflected microwave power (a) and the corresponding optically detected resonance obtained by monitoring the MCD (b).

excited state is now known to be an orbitally degenerate level. The energy levels of the center exhibit magnetic splittings that are very similar to those found for F centers in alkali halides. However, it is still not clear whether the excited $^3A_{2u}$ state is or is not degenerate with the E_u states.

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THE VACUUM UV ABSORPTION SPECTRUM OF KMgF_3 ¹

J. C. Pig,

The optical absorption spectrum of KMgF_3 , and its modification by irradiation has been extensively studied² at ORNL in the energy range from 2.0 to 5.5 eV. These workers have identified the F , F_2 , F_3 , and V_k centers and observed that the absorption energies of these centers in KMgF_3 corresponded well with the same centers³ in irradiated LiF . Since radiation-induced absorption in LiF has been observed in the vacuum uv region, and since the band edge of KMgF_3 has not been determined, it was decided to extend the study of KMgF_3 into the vacuum uv region.

Fig. 3.12. Irradiation-induced changes in the vacuum uv spectrum of KMgF_3 .

The vacuum uv absorption spectrum of KMgF_3 before and after irradiation with ^{137}Cs gamma radiation is shown in Fig. 3.12. The lower limit of the upper band edge is 10.9 eV. In addition to the previously observed F center absorption at 4.5 eV, another absorption band is observed at 9.25 eV. This band is small but real. Its intensity, like the F center band, grows with irradiation. The new band is not a second-order effect from the F center absorption; order goes with wavelength while energy goes as reciprocal wavelength. The origin of the absorption at 9.25 eV has not yet been identified.

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RAMAN AND INFRARED SPECTRAL STUDIES OF ANHYDROUS POTASSIUM AND RUBIDIUM CARBONATE¹

M. H. Brooker² J. B. Bates

Raman and infrared spectra of anhydrous K_2CO_3 and Rb_2CO_3 were measured at 300 and at 80°K. Infrared transmission, multiple internal reflection, and polarized specular reflection techniques were used to determine transverse optical (TO) and longitudinal optical (LO) mode frequencies. The observed vibrational spectra for both salts were in excellent agreement with a C_{2h} unit cell group analysis, which suggests that the crystal structures of anhydrous K_2CO_3 and Rb_2CO_3 are isomorphous (space group: $P2_1/c$). Unlike Na_2CO_3 , the K_2CO_3 and Rb_2CO_3 structures are not complicated by disordering of CO_3^{2-} groups over two sets of nonequivalent sites. Studies of the isotopically substituted ions $^{13}\text{C}^{16}\text{O}_3^{2-}$ and $^{12}\text{C}^{16}\text{O}_3^{2-}$ were employed to confirm assignments.

1. Abstract of paper to be published.
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VIBRATIONAL SPECTRA OF CRYSTALLINE Li_2ZrF_6 AND Cs_2ZrF_6 ¹

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The infrared and Raman spectra of Li_2ZrF_6 and Cs_2ZrF_6 have been measured, and all active internal vibrational modes, except for the $\nu_6(E_u)$ component of Li_2ZrF_6 , were observed and assigned. Single-crystal Raman measurements on Li_2ZrF_6 have enabled the identification of individual components arising from the

internal degenerate modes of the ZrF_6^{2-} ion having O_h point symmetry. The splittings of these degenerate modes were compared for Li_2ZrF_6 and Cs_2ZrF_6 . Splitting in the Raman arises principally from short-range forces, whereas in the infrared it is attributed mainly to long-range dipolar effects. A normal-coordinate analysis of the O_h modes of the ZrF_6^{2-} ion has been performed to verify the assignments.

1. Abstract of paper to be published.
2. Metals and Ceramics Division.

LUMINESCENCE EFFECT IN DEFORMED CaO ¹

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C. M. Nelson⁴

In examining rare-earth-doped CaO for luminescence resulting from the dopant,⁵ the crystals were excited with uv light from a mineral light source. A brilliant blue emission, whose origin was traced to deformation in undoped, nominally pure crystal, was observed. The effect appears to be independent of the presence of impurities, since it is present in both doped and undoped samples. By simply placing an undeformed single crystal in a vise and illuminating it with uv light, a dramatic increase in the emission intensity can be observed on compression. To our knowledge, this luminescence effect has not been observed previously in

Fig. 3.13. Emission spectrum at 295°K of deformed CaO crystal.

latic crystals. Such an effect permits simple and direct observation of slip bands without the use of artificial decoration techniques, for example, etching.

The crystals used were grown in this laboratory, using an arc-fusion method. Rectangular platelets, obtained

by cleaving the crystals, were compressed along the (100) direction of the greatest crystal dimension in an Instron testing machine with a crosshead speed of 0.005 cm/min. The emission spectra were taken with a Jarrell-Ash scanning monochromator in conjunction

Fig. 3.14. Luminescence of accidentally deformed (during cleavage) CaO crystal on uv excitation. Slip bands are observed in (110) directions.

with a photomultiplier tube. The wavelength response of the detecting system was calibrated using a standard quartz-iodine lamp. The deformation-induced absorption band peaks at ≈ 2.6 eV. Excitation of the crystal with light of this energy yields an intense blue luminescence, whose spectrum is shown in Fig. 3.13. At 295°K, the peak of the emission band occurs at ≈ 2.6 eV and the half-width is ≈ 0.7 eV.

The emission band provides a direct means of studying gross imperfections induced by strain in CaO. Figure 3.14 illustrates the luminescence from a crystal; the film used for these photographs is not sensitive to the exciting uv light. Slip bands along (110) directions can be clearly observed as luminescence. In addition to bulk imperfections, small surface imperfections caused by deformation are readily apparent.

Although this effect was reported previously,⁶ a series of EPR studies were performed on CaO crystals from different growths to determine if impurity effects were involved. There was no indication of any magnetic impurities that could be related directly to this phenomenon.

This behavior in CaO has led to similar studies in other alkaline-earth oxides, and the results will be reported subsequently. Work is also under way to use this technique to obtain quantitative information about dislocation interactions by monitoring the intensity of luminescence as a function of stress applied to the crystal. Thus, emission intensity vs strain curves that would complement stress vs strain curves can be obtained.

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3. Present address: Wake Forest University, Winston-Salem, N.C.
4. Emory and Henry College, Emory, Va.
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VIBRATIONAL SPECTRA OF THE H_3O_2^+ ION IN CRYSTALLINE $\text{YH}_2\text{O}_2(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$

J. B. Bates L. M. Toth²

Polarized Raman and infrared spectra of crystalline $\text{YH}_2\text{O}_2(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$ and its deuterated analogs were measured over the frequency interval from 20 to 4000 cm^{-1} . Primary consideration was given to recording the vibrational spectrum of the diaquated hydrogen ion, H_3O_2^+ , and to correlating the spectral properties of this

species with the results from recent neutron diffraction studies of yttrium oxalate trihydrate. Calculations based on models of H_3O_2^+ produced root-mean-square displacements of the central proton which were compared with the thermal parameters derived from neutron diffraction data. A comparison of calculated and observed properties suggested that H_3O_2^+ may be represented by a model based on a proton trapped between two water molecules.

1. Abstract of paper to be published.
2. Metals and Ceramics Division

ANGLE-DEPENDENT EFFECTS IN POLARIZED SPECULAR REFLECTION INFRARED SPECTROSCOPY¹

J. B. Bates

Polarized specular reflection infrared spectra of crystalline NaNO_3 were measured in the ν_3 region at angles of incidence from 75° to 10°. In addition to the LO component, the TO component of ν_3 appeared in the 65° spectrum and the intensity of $\nu_3(\text{TO})$ increased relative to $\nu_3(\text{LO})$ with decreasing angle. The frequency of $\nu_3(\text{LO})$ shifted from 1460 cm^{-1} at 75° to 1448 cm^{-1} at 10° angle of incidence.

1. Abstract of paper: *Chem. Phys. Lett.* 22, 156 (1973).

THERMAL CONDUCTIVITY OF ADDITIVELY COLORED MgO ¹

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The thermal conductivity of nominally pure MgO , additively colored in magnesium vapor to produce 2×10^{17} anion vacancies/ cm^2 , has been measured in the temperature range 1 to 55°K. These measurements have been compared with those from the same crystal prior to additive coloration. A dip to one-fifth of the initial thermal conductivity, which occurs near 20°K, is attributed to resonant phonon scattering associated with quasi-localized modes of the F center (anion vacancy with two electrons).

After uv irradiation, resulting in partial $F \rightarrow F^+$ conversion, the thermal conductivity dip was found to be much weaker (Fig. 3.15). The increase in thermal conductivity, due to bleaching, is attributed to a relaxation of neighboring ions associated with a different charge state of the defect. The thermal conductivity data have been successfully fitted to the Debye

Fig. 3.15. Thermal conductivity vs temperature of an as-grown high-purity MgO crystal (a) after introducing 2×10^{17} F centers/cm³ by additive coloration at 2100°K in magnesium vapor (b) and subsequently bleached with uv light (c).

model of solids, with the defect scattering rate consisting of a resonance expression plus a Rayleigh scattering term. The post-bleaching data can also be explained by a variation in the parameters associated with F-center concentration.

1. Summary of paper: *J. Low Temp. Phys.*, in press.
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SPIN RESONANCE

ENDOR OF V_F AND V_{OH} CENTERS IN CaO¹

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ENDOR (electron-nuclear double resonance) studies on CaO single crystals have positively identified the V_F center (trapped hole with an associated fluorine impurity) and have resolved a discrepancy in the reported g values of the V_{OH} center (trapped hole associated

Fig. 3.16. Electron paramagnetic resonance of V_{OH} and V_F centers in CaO.

Fig. 3.17. Electron-nuclear double resonance of V_{OH} and V_F centers in CaO at $\theta = 0^\circ$.

with hydrogen). Data for the same two centers in MgO were also obtained, and an analysis of the anisotropic hyperfine coupling constants showed that the relevant lattice expansion due to both centers is approximately the same in these hosts.

The EPR (electron paramagnetic resonance) spectra of the two trapped hole centers in CaO each show resolved splittings consistent with a 100% abundant isotope of spin $i = 1/2$, and each may be distinguished at 4.2°K (Fig. 3.16). However, it is not possible to identify unequivocally which nucleus is related to each line without observing the corresponding ENDOR transitions. The ENDOR technique positively identified which EPR lines are associated with hydrogen and which are associated with fluorine. While the electron resonance is being performed on each line in turn, an additional frequency sweep is made through the region of the nuclear magnetic resonance for the nuclei in

question (Fig. 3.17). The average value of the two ENDOR frequencies, observed when saturating an electron resonance line at a given magnetic field, should be equal to the nuclear magnetic resonance frequency of that nucleus in the same field. Hence, we were able to identify properly the EPR transitions shown in Fig. 3.16.

1. Summary of paper: *J. Chem. Phys.* 59, 3284 (1973).
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ELECTRON PARAMAGNETIC RESONANCE DETERMINATION OF THE NUCLEAR SPINS AND MAGNETIC MOMENTS OF ^{243}Cm AND ^{247}Cm

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W. P. Unruh⁴

We have previously reported EPR investigations of $^{241}\text{Am}^{2+}$, $^{243}\text{Am}^{2+}$, $^{245}\text{Cm}^{3+}$, and (even) Cm^{3+} in single crystals of strontium chloride.⁵ Here we report the nuclear spins of ^{243}Cm and ^{247}Cm in the same host material.

Crystals of SrCl_2 doped with ^{243}Cm were prepared by the method previously described.⁵ EPR experiments were performed at X band with the samples cooled to liquid helium temperatures. Spectroscopic analysis of the actinide dopant containing ^{243}Cm indicated that ^{241}Am , ^{244}Cm , and other (even) Cm isotopes were also present. The EPR spectrum obtained from a SrCl_2 crystal doped with this material is shown in Fig. 3.18a. The spectra associated with $^{241}\text{Am}^{2+}$ and (even) Cm^{3+} were readily identified from their previously determined spectroscopic properties.⁵ EPR spectra observed at X-band frequencies for $5f^7$ configurations in SrCl_2 arise from a ground Γ_6 electronic doublet which is coupled by the applied magnetic field to a nearby Γ_8 quartet level. As a result of this coupling, the spectral line positions exhibit a characteristic variation as a function of magnetic field orientation. This variation has been used to evaluate the energy separation between the Γ_6 and Γ_8 levels.⁵⁻⁷ The six-line pattern, which is approximately centered about the intense (even) Cm line, exhibited an angular variation identical to that observed for the (even) Cm isotopes, and was identified as the spectrum of $^{243}\text{Cm}^{3+}$. This sixfold multiplicity fixes the nuclear spin of ^{243}Cm as $I = \frac{5}{2}$. The hyperfine parameter A was determined to be 20.92 ± 0.04 .

Spectroscopic analysis of the dopant containing ^{247}Cm indicated that ^{243}Am , ^{244}Cm , and other (even) Cm isotopes were also present. The EPR spec-

Fig. 3.18. (a) The first-derivative presentation of the EPR spectrum of ^{243}Cm -doped SrCl_2 with the applied magnetic field oriented near a [111] direction; (b) the EPR spectrum (first-derivative presentation) of ^{247}Cm -doped SrCl_2 with the applied magnetic field oriented near a [111] direction. EPR transitions due to other actinide ions also present are identified in the spectra of both samples. The large transition is primarily due to ^{244}Cm , but includes contributions due to small amounts of the even- A isotopes ^{246}Cm and ^{248}Cm .

trum obtained from the SrCl_2 single crystals doped with this material is shown in Fig. 3.18b. Again, the presence of $^{243}\text{Am}^{2+}$ and (even) Cm^{3+} was easily verified from their previously characterized spectra. A ten-line spectrum, which was centered (to first order) about the single intense (even) Cm^{3+} line and which duplicated its angular variation, was identified as the spectrum of ^{247}Cm . The multiplicity of this spectrum fixes the nuclear spin of ^{247}Cm as $I = \frac{7}{2}$. The hyperfine parameter A was determined to be 10.52 ± 0.07 G for ^{247}Cm .

The three odd- A curium isotopes 243, 245, and 247 have 147, 149, and 151 neutrons respectively. On the

basis of the Nilsson diagram for an odd number of neutrons,⁸ the experimentally determined nuclear spins of $\frac{5}{2}$, $\frac{7}{2}$, and $\frac{9}{2}$ are expected, if the deformed nuclei have eccentricities between 0.2 and 0.3.

The nuclear magnetic moment μ_I is proportional to the product AI , and this proportionality may be used to obtain estimates of the nuclear moments of ^{243}Cm and ^{247}Cm . In the present case, this is accomplished by using a proportionality constant calculated from the known values for A^5 and μ_I^9 of $^{231}\text{Am}^{2+}$ with the assumption that such a proportionality constant will be the same for the isoelectronic Cm^{3+} isotopes. (This procedure has previously been employed to obtain estimates^{5,10} of the nuclear magnetic moments of ^{245}Cm and ^{249}Bk .) From the values of A and I given above for ^{243}Cm and ^{247}Cm , we obtain the values $|\mu_I| = 0.40\mu_N$ for ^{243}Cm and $|\mu_I| = 0.36\mu_N$ for ^{247}Cm . It should be noted that these values have not been corrected for differences in the values of $\langle r^{-3} \rangle$ (the mean inverse cube of the $5f^7$ electron radii) between $^{243}\text{Cm}^{3+}$, $^{247}\text{Cm}^{3+}$, and $^{241}\text{Am}^{2+}$. For the curium isotopes, however, $\langle r^{-3} \rangle$ is the same, and assuming no hyperfine anomaly, the ratios of the magnetic moments are: $^{243}\mu_I/^{247}\mu_I = 1.105 \pm 0.008$, $^{243}\mu_I/^{245}\mu_I = 0.79 \pm 0.01$, and $^{245}\mu_I/^{247}\mu_I = 1.41 \pm 0.01$.

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FERROMAGNETIC RESONANCE PROPERTIES OF LUNAR FINES: APOLLO 16¹

R. A. Weeks

Petrographic data indicate that lunar minerals crystallized under conditions of extremely low oxygen fugacity. Consequently, exsolved metallic iron is observed, but ferric oxide phases are rarely detected, at

least as particles $> 1 \mu\text{m}$ in diameter. Hence, one of the major components of an electron magnetic resonance (EMR) spectrum of lunar samples should be due to the ferromagnetic resonance (FMR) of iron particles. EMR spectra of lunar fines on which measurements have been made from the Apollo sites (11 through 16) are dominated by an intense absorption whose intensity and width have a temperature dependence characteristic of ferro- and/or ferrimagnetic phases. The intensity of this absorption in some Apollo 14 breccias was found to decrease with increasing degree of consolidation and recrystallization.² On the basis of temperature- and frequency-dependent characteristics of Apollo 11 samples, it was suggested³ that submicron iron particles were the source of the absorption. However, the characteristics of the dominant absorption in Apollo 14, 15,^{2,4} and 16 samples deviate considerably from those expected for such particles. On the basis of these deviations, it has been suggested² that ferric oxide phases might be present in the soil samples. Additional and more precise data on these deviations have been obtained and are given below.

The line width, ΔH , and specific intensity, I , of the dominant EMR absorption of Apollo samples of fines $< 0.1 \text{ mm}$ are given in Table 3.4. The range of ΔH is 417 to 950 G, while the intensity ranges from 0.1 to 26 arbitrary units. The Apollo fines samples have average values of ΔH which are ranked $\Delta H(\text{A-11}) > \Delta H(\text{A-12}) > \Delta H(\text{A-15}) > \Delta H(\text{A-14}) > \Delta H(\text{A-16})$, and the ranges of values about each average value overlap in only the Apollo 14 and 16 samples. (The number of Apollo 15 samples measured was only 2.) A second significant difference between the Apollo 11 and 12 samples and the Apollo 14 and 16 samples is the frequency dependence of ΔH which is evident from the ratios $\Delta H(35 \text{ GHz})/\Delta H(9 \text{ GHz}) \approx 1.2$ for the Apollo 11 samples and ≈ 1.5 for the Apollo 16 samples.

The temperature dependence of ΔH for samples from four Apollo sites is given in Fig. 3.19. In the range of temperatures from ≈ 175 to 300°K , $d\Delta H/dT \approx 1.1$ for the Apollo 11 sample, ≈ 1.6 for the Apollo 15 sample, ≈ 1.8 for the Apollo 14 sample, and ≈ 2.0 for the two Apollo 16 samples. A plateau is observed in the increase in H with decreasing temperature between 120 and 175°K . The plateaus and subsequent rapid increase in ΔH at a slightly lower temperature are most clearly evident in data points for the Apollo 11 sample, for which there is very rapid change in ΔH between 140 and 152°K . The plateau occurs at 175°K in the data on the Apollo 15 sample, at 150°K in the two Apollo 16 samples, and is not resolved in the data for the Apollo 14 sample. The solid curve gives calculated values of

Table 3.4. Intensities and line width of a ferromagnetic resonance characteristic of lunar soils and selected fragments from Apollo 11, 12, 14, 15, and 16

Sample (comments)	Line width, ^a ΔH (G)	Relative intensity, ^a I (mg ⁻¹)
A-11	950	
A-12 (average of 4 samples)	750-768-785 ^b	1.5-26
A-12 (magnetic fraction)	791	18
A-14 (average of 5 samples)	600-613-634 ^b	8-18
A-14 (magnetic fraction, average of 4 samples)	692-710-724 ^b	9-18
15271,68	670	5.0
15601,80	734	4.5
A-16 (average of 11 samples)	540-584-640 ^b	4-25
15271,68 (dark red spheroid)	600	0.7
15271,68 (30 green spheroids)	467	~0.3
14003,60 (6 spheroids)	568	~0.1
14003,60 (plagioclase-rich fragments)	510	~0.1
14003,60 (gray and yellow glasses)	750	3.4
14318,36 (glassy layer)	417	1.5

^aThe intensity of the absorption was found from the relation $I = \Delta H^2 A/W$, with $\Delta H = H_{\max} - H_{\min}$ and A = amplitude of the dI/dH curve between the field, $H_{\max}$, at which the maximum amplitude of the curve occurs and the field, $H_{\min}$, at which the minimum amplitude occurs, and W is the sample weight in milligrams. The magnetic field modulation amplitude was constant for all these measurements. These values have all been normalized to a constant amplifier setting.

^bThe first value is the minimum and the third is the maximum observed, while the second value is the average of all values.

Fig. 3.19. Observed temperature dependence of line width, ΔH , of "characteristic" electron magnetic resonance of soil samples and the calculated dependence of spherical iron particles, assuming $\Delta H(300) = 800$ G. This value is assumed in order to illustrate differences between the data and the curve for iron.

$\Delta H(T)$ for iron particles, assuming that $\Delta H = 800$ G at 300°K . The lack of agreement between the curve for iron particles and the data for lunar fines is clearly evident.

The line width, ΔH , of the EMR absorption of an ensemble of noninteracting ferro- or ferrimagnetic particles randomly oriented with respect to an applied field, H , is determined by K_1/M_s , where K_1 and M_s are the crystalline anisotropy energy and saturation magnetization, respectively, and by the demagnetizing fields due to shape anisotropies. For particles of iron and for alloys of iron, K_1/M_s is only weakly dependent upon spectrometer frequency, has a temperature dependence in the 100 to 300°K temperature range that gives $d\Delta H/dT \approx 1$ with no discontinuities,^{3,10} and gives at 300°K $\Delta H \approx 900$ G if the particles are perfect spheres and $900 < \Delta H < 26,000$ G for other shapes.² The data given above are not consistent with an iron particle hypothesis. Due to the relative and absolute magnitudes

of K_1 and M_s for some ferrites, demagnetizing factors due to variations of particle shapes will be less important for these compounds. Ferrites have K_1 values which are a function of composition and which can vary from positive to negative, for example, $X\text{Fe}_2\text{TiO}_4 \cdot (1 - X)\text{Fe}_3\text{O}_4$.¹¹ Since one component of this compound, Fe_2TiO_4 , is a relatively abundant mineral in lunar soils, such a ferrite is a distinct possibility. Petrographic identification of such a compound would be difficult in particles with dimensions $< 1 \mu\text{m}$.

Other observations relevant to the foregoing are: Agrell⁶ has identified goethite in an Apollo 14 sample, ferric oxide⁵ (goethite and hematite) has been observed in Apollo 16 samples,⁷ and Cernan and Schmitt reported⁸ the occurrence of orange soil whose color may be due to ferric oxides at the Apollo 17 site. A sample of Apollo 16 soil (61221-11) has been observed to emit H_2O upon heating.⁹ It was suggested by Weeks et al.² that comet impacts could furnish oxidizing conditions required for the formation of ferric oxide phases, a suggestion now advanced⁹ to explain emission of H_2O from an Apollo 16 sample.

Hence the proposal that at least a portion of the intense EMR absorption observed in all Apollo soils thus far measured is due to ferric oxide phases is not only consistent with all of the EMR parameters but also with these observations.

PARAMAGNETIC STATES OF APOLLO 16 PLAGIOCLASES¹

R. A. Weeks

Lunar plagioclases have electron paramagnetic resonance (EPR) spectral components²⁻⁵ which have been attributed to Fe^{3+} and Ti^{3+} . The relative intensities of these two components in some Apollo 14 and 15 samples are inversely correlated.⁵ Observation of ferric oxides in some Apollo 16 (A-16) samples⁶ indicates that the concentration of Fe^{3+} and Ti^{3+} ions in A-16 plagioclases could be significantly higher and lower, respectively, than in plagioclases from other Apollo sites, if the oxides crystallized at the same time as the plagioclases. If the relative and absolute concentrations of Fe^{3+} and Ti^{3+} ions are of the same order of magnitude as those for other Apollo plagioclases, then it is reasonable to assume that the oxygen partial pressure in the liquid from which the A-16 plagioclases crystallized was of the same order as that in the liquids from which the other plagioclases crystallized, provided the liquids had approximately similar compositions. Hence, the ferric oxides would have to be produced at a later time and by other processes. Other EPR components also have been observed,^{3,7} as have ferromagnetic resonance components due to iron particles.^{4,8}

Spectral components due to Ti^{3+} and Fe^{3+} in two samples at $\approx 93^\circ\text{K}$ are shown in Fig. 3.20. A contribution to the spectrum due to another component (Fig. 3.20a) in the region of the Ti^{3+} component is shown by a dashed line. On the basis of its temperature dependence, this component is due to the resonance of ferromagnetic phases. A third component appears in the spectrum of sample 62242-2-1 and is identified by the symbol I and an arrow. The spectrum of Ti^{3+} in 62242-2-1 has structure which can be resolved into at least two distinct Ti^{3+} spectra. This resolution is shown by the curves that have been drawn between the two traces in Fig. 3.20a. These curves are those that would be obtained from a powdered crystal containing Ti^{3+} in two crystallographically different sites in the unit cell for one of which (site 1) $g_x = 1.98$, $g_y = 1.94$, $g_z = 1.91$ and for the other (site 2) $g_x = 1.96$, $g_y = 1.93$, and $g_z = 1.92$. The sum of these two curves is in reasonable agreement with the observed curve when the background, indicated by the dashed line, is subtracted. A comparison of the curve for 62242-2-1 with that for 67455-16-2 shows that the contributions to the Ti^{3+} component from the two sites are not as well resolved. Hence, the sites occupied by Ti^{3+} in 67455-16-2 are more disordered than they are in 62242-2-1. The

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Fig. 3.20. Electron paramagnetic resonance spectra of Ti^{3+} and Fe^{3+} in lunar plagioclases at 90°K . (a) The dashed curves are estimates of the contribution to the observed curve of other resonance components. The dotted curve between the curves for the two samples illustrates the spectrum expected for Ti^{3+} in a powdered sample in which the ion occupies only one site per unit cell. If a second site is occupied by the ion, the solid curve shows the expected spectrum. The arrows show the correspondences between these curves and the one observed in sample 62242-2-1. (b) The narrow line at 1500 G is the $3 \rightarrow 4$ transition of Fe^{3+} in one crystal site. This ion occupies other crystal sites, but spectral components due to Fe^{3+} in these sites are not well resolved.

67455-16-2 spectrum is altered to that of 62242-2-1 by annealing at 800°C for 30 min. On the basis of this effect, it is tentatively assumed that the 67455-16-2 plagioclase cooled more rapidly than the 62242-2-1 plagioclase.

Relative amplitudes of the derivative of the absorption, A , line width ΔH , and relative intensities of the Ti^{3+} and Fe^{3+} components are given in Table 3.5 for nine A-16 samples and one A-14 sample. (Most A-16 specimens are $>70\%$ plagioclases.⁶) The relative ampli-

Table 3.5. Electron paramagnetic resonance of Fe^{3+} and Ti^{3+} in Apollo 16 plagioclases

Sample	Weight, ω (mg)	Line width, ΔH (G)	Amplitude, A (chart units)	Intensity, ^a I (arbitrary units)
Fe^{3+}				
60015-68-1	43.8	30	146	6
61243-3-2	24.3	40	30	4
62242-2-1	52.5	23	88	2
66095-58-2	32.0	35	156	12
67075-21-1	17.1	24	18	1
67455-16-1	33.1	23	53	2
67701-29-2	12.0	30	19	3
68416-13-1	43.8	27	244	8
14321-166-5	31.9	35	31	2
Ti^{3+}				
60015-68-1		105	75	3
61243-3-1		125	60	5
62242-2-1		120	32	1
66095-58-2		130	50	4
67075-21-1		120	15	2
67455-16-1		133	30	2
68416-13-1		105	52	2

^aIntensity for the Fe^{3+} resonance is $I = \Delta H^2 A / W$ with factors of 10 being dropped, and for the Ti^{3+} resonance is $I = A / W$ with factors of 10 being dropped. As a result, the two sets of I 's are not directly comparable. See R. A. Weeks, p. 2503 in *Proceedings of the Third Lunar Science Conference*, vol. 3, suppl. 3, *Geochim. Cosmochim. Acta*, MIT Press, 1972, for an estimate of absolute concentration.

tudes of the Ti^{3+} and Fe^{3+} component do not show the inverse correlation previously reported⁵ for Apollo 14 plagioclases. If a correlation exists, it appears that Fe^{3+} and Ti^{3+} are approximately proportional; for example, 67076-21-1 and 62242-2-1 have the lowest Fe^{3+} concentration and also the lowest Ti^{3+} concentration, while 66095-58-2 and 60015-68-1 both have relatively high concentrations of Fe^{3+} and Ti^{3+} .

The I component observed in 62242-2-1 is also present in the spectrum of 67455-16-2, but it is less intense.⁷ Irradiation of 67455-16-2 with ^{137}Cs gamma rays increases the intensity of the I component by more than two orders of magnitude and also produces additional components. Hence, the I component can be produced by irradiation in the as-received samples. Tentatively, it is assumed that 62242-2-1 had been irradiated to a higher integrated flux of ionizing particles and photons than had 67455-16-2, provided their thermal histories are the same. The g tensor of the I component has principal values $g_x = 2.016$, $g_y = 2.102$, and $g_z = 2.004$.

As was the case with some lunar plagioclases from A-11 through A-15, components due to Fe^{3+} and Ti^{3+} are present in EPR spectra of several A-16 plagioclases. The concentrations of these ions are of the same order of magnitude as in A-14 and A-15 samples. The order of magnitude variation in concentration does not appear to be correlated with a variation in elemental abundance of these elements in the samples. Hence, the variation possibly is due to variation in conditions of crystallization. Additional EPR components are present as a result of radiation effects. The relative intensity is sample dependent and, hence, may reflect the differing radiation history of the samples.

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4. Neutron Scattering

The principal purpose of the Solid State Division neutron scattering program is to utilize the excellent facilities at the ORNL reactors in obtaining fundamental microscopic information that will contribute to a better understanding of the physical properties of materials. The High Flux Isotope Reactor (HFIR) provides the most intense thermal neutron beams now available for research, and certain experiments performed with the neutron spectrometers at that reactor have provided information which could not be obtained at any other laboratory. Most of the research falls quite naturally within the two broad scientific areas of lattice dynamics and magnetism. However, the scope of the research is not limited to these areas, and investigations are frequently performed that are not concerned with either one; such research investigations have been grouped in this report under a third heading entitled Miscellaneous Applications.

Investigations of the lattice dynamics of solids by measurements of the phonon-dispersion curves provide basic information concerning the vibrational properties of various kinds of solids. These studies have led to an insight into the nature of interatomic and intermolecular forces in ionic, covalent, molecular, and metallic crystals. Important information has also been obtained on isolated defects in solids from neutron-scattering measurements of localized and resonant modes of vibration in crystals that contain dilute concentrations of light- and heavy-atom impurities. These investigations have recently been extended to more concentrated alloy systems in an effort to understand and predict the dynamical behavior of random alloys. Another area of great importance is the study of superconductors with high transition temperatures. The phonon-dispersion curves of these materials exhibit certain anomalies, which could provide significant information concerning the mechanisms and origins of superconductivity. Investigations of the lattice dynamics of molecular crystals by neutron inelastic scattering provide data on the intermolecular potential function and complement results obtained from other types of spectroscopic investigations within the Division.

A large fraction of the research program is devoted to studying the magnetic properties of solids in investigations where the neutron is a powerful and often a unique tool. Analogous to the lattice dynamics investigations, measurements of magnetic excitations as a function of energy and wave vector provide detailed information about the magnetic interactions in solids. Recent measurements of the spin wave dispersion relations as a function of temperature have provided data for a critical test of the theory of ferromagnetism for the transition metals. Measurements and analyses of the magnon dispersion relations for the rare-earth metals have given very important information about the indirect magnetic exchange interactions in these metals; in addition to determinations of the strength, range, and anisotropy of the interactions, the variations in these properties with temperature and alloying have been studied. It is also possible to obtain quantitative data on the strength and temperature dependence of the crystalline-field anisotropy in these metals from measurements of the magnon dispersion relation very close to zero wave vector. Experiments with polarized neutrons have been performed to

obtain precise measurements of magnetic form factors; these experiments are important checks on theory, because they give information on the wave functions of the magnetically active electrons. The polarized neutron technique has recently been extended to magnetic systems that are very weakly paramagnetic by measuring the magnetic-moment distribution induced in these systems with a high-field superconducting magnet. Strongly exchange-enhanced magnetic systems are studied by diffuse scattering experiments with neutrons of long wavelength; these experiments determine the magnitude and range of magnetic disturbances induced in these systems by various ferromagnetic impurities.

Various types of neutron-scattering investigations that have been performed during the past year are included in the third section under Miscellaneous Applications. Direct measurements of the crystal field energy levels in compounds have been measured by neutron inelastic scattering, and the dynamics of phase transitions have been studied by measurements of the critical scattering. Neutron-scattering investigations of liquid ^4He have determined precise momentum distributions above and below the lambda transition: these measurements have confirmed the existence of a condensate state when ^4He becomes a superfluid. Investigations on TTF TCNQ have shown a difference in the phonon spectrum at temperatures above and below the region of anomalously high conductivity. A feasibility experiment has been performed to measure the size distribution of radiation-induced voids in aluminum; this experiment utilizes a new type of small-angle neutron-scattering technique, and the results indicated that the technique has considerable potential for a wide variety of problems.

There is a very close and important interaction between members of the neutron scattering program and the solid state theorists. There is an equally important interaction with members of the Research Materials Program who have provided well-characterized single-crystal specimens, which frequently were grown from isotopically enriched samples. Many of the neutron-scattering investigations included in this report would have been impossible without this close cooperation.

LATTICE DYNAMICS

DYNAMICS OF THE AMMONIUM ION IN NH_4ClO_4

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There have been extensive studies of the dynamics of the ammonium ion in solids, particularly in the ammonium halides, which are perhaps better understood than most ammonium compounds.

There has been much speculation about the dynamical behavior of the NH_4^+ ion in ammonium perchlorate. At room temperature the hydrogen atoms could not be located by neutron diffraction techniques,² indicating that the orientation of the ammonium ion is highly disordered. However, it was not possible to say whether the disorder is static or dynamic (e.g., a rotating ion). Specific-heat measurements by Westrum and Justice³ did not show any evidence of phase transitions above 5°K, so that if there is ordering of the ammonium ion at low temperatures it would have to be a gradual process. Recent neutron crystal-

lographic studies by Prask and Trevino⁴ at 10 and 78°K corroborate this suggestion. Nuclear magnetic resonance (NMR) measurements by Richards and Schaefer⁵ showed a narrow line as low as 20°K, indicating reorientation at frequencies $>10^5$ cps. Recent measurements by Riehl et al.⁶ indicated a second moment of 1.3 G^2 at 20°K, which broadened slightly to 4 G^2 at 2°K. One expects a width of about 45 G^2 for a rigid ion.

Total neutron cross-section measurements of NH_4ClO_4 by Rush et al.⁷ with long-wavelength neutrons yielded a barrier of 0.2 kcal/mole, the lowest of any NH_4 compound reported. Ammonium chloride, by contrast, exhibits a barrier of 4.4 kcal/mole. Earlier neutron measurements on NH_4ClO_4 by other workers⁸ did not reveal a torsional mode at 78°K. They did suggest, however, that fluctuations in the inelastic neutron spectra were due to rotational levels, but this suggestion seems unlikely in view of the present study.

We set out to determine by neutron inelastic scattering measurements whether the ion exhibited torsional oscillations at very low temperatures. Inelastic neutron

spectra of polycrystalline samples were recorded at 4.6°K, 77°K, and room temperature for NH_4ClO_4 , ND_4ClO_4 , RbClO_4 , and KClO_4 on the HB-3 triple-axis neutron spectrometer⁹ and on the HB-4 magnetic chopper,¹⁰ utilizing time-of-flight techniques. In the case of NH_4ClO_4 , spectra were recorded at 2°K for comparison with the 4.6°K data, but there were no observed changes. Some of the data are shown in Fig. 4.1. Except for NH_4ClO_4 , the sample volumes were approximately 25 cm³ of polycrystalline material with packing densities of approximately 0.5. Because of the large incoherent scattering cross section of hydrogen, the volume of the NH_4ClO_4 sample was only ~6 cm³ and in the shape of a flat rectangular plate about 3 mm thick, in order to minimize multiple scattering effects.

The broad band centered about 6.0 THz (200 cm⁻¹) in the 4.6°K spectra of NH_4ClO_4 is interpreted to be due to the torsional modes of the ammonium ions. The shift to lower frequencies upon deuteration and the absence of scattering in this energy region in RbClO_4 and KClO_4 reinforces this interpretation. The observed structure in the band and the shift by less than $\sqrt{2}$ in the deuterated sample, however, is not completely understood at this time. The peaks below 4 THz in NH_4ClO_4 and ND_4ClO_4 are probably associated with the optic and zone boundary acoustic modes. The shift in frequency from about 3.1 THz in NH_4ClO_4 to about 2.7 THz in ND_4ClO_4 is approximately what one expects for the TO modes, with NH_4 replaced by ND_4 . A similar shift is observed in the NH_4Cl and ND_4Cl compounds.^{11,12} The very large scattering intensity between 1 and 2 THz is probably associated with zone boundary acoustic modes. Measurements with large deuterated single crystals will be necessary to determine the dispersion curves in order to positively identify these low-energy peaks.

It is not possible from the data presented here for KClO_4 and RbClO_4 to identify uniquely the torsional frequencies of the ClO_4 groups, but from the relative intensities of the total scattering it is safe to say the perchlorate groups are not contributing appreciably to the observed scattering intensity in the NH_4ClO_4 and ND_4ClO_4 spectra. It is not unreasonable to expect the frequencies of the torsional and translational optic modes in KClO_4 to be of the same order as those in KClO_3 , even though the crystal structures are different. Bates,¹³ from a single-crystal polarized Raman study of KClO_3 , has assigned the torsional modes to peaks observed in the region 2.4–4.5 THz (80–150 cm⁻¹). The structure observed in Fig. 4.1 in this region for KClO_4 and RbClO_4 is likely due to similar modes. The disappearance of structure in the spectra at elevated

Fig. 4.1. Inelastic neutron scattering spectra of polycrystalline NH_4ClO_4 , ND_4ClO_4 , RbClO_4 , and KClO_4 at various temperatures.

temperatures is most likely due to multiphonon scattering effects and is associated with large anharmonic motions of the ammonium ions and probably the perchlorate ions as well.

As mentioned above, the structure observed in the proposed torsional band of NH_4ClO_4 is not completely

understood. It could be due to multiphonon scattering, which is certainly important even in the thin sample used. More than likely, it is due to correlation field splitting and site group splitting, since there are four molecules in the orthorhombic unit. These effects can only be resolved by single-crystal studies on ND_4ClO_4 .

Thorough quasi-elastic neutron scattering and form factor measurements of the ammonium ion as a function of temperature, preferably in single crystals, would provide valuable information concerning the dynamics of the behavior of the ammonium ion in NH_4ClO_4 in particular and ammonium compounds in general. Such experiments are planned in the near future.

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LATTICE DYNAMICS OF IODINE AT 77°K

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There is considerable scientific effort expended in determining intermolecular potential functions in crystals. Inelastic neutron scattering is considered one of the most powerful techniques for studying intermolecular forces in solids; however, phonon dispersion curves have been adequately determined and analyzed in terms of physically meaningful potentials only for several of the rare-gas crystals³ and for hexamethylenetetramine.⁴ In the latter crystal only the acoustic and librational modes were considered – the

internal modes were neglected, experimentally and theoretically.

The dynamics of the halogen crystals are of particular interest, since there is good reason to believe the intermolecular interactions are not negligible, and yet the systems are probably simple enough to make a first-principles analysis of the dispersion curves. Iodine is particularly suitable, since it is a solid at room temperature and crystals can be more readily obtained than for the other halogens. In addition, iodine is known to form complexes with a large number of compounds as well as with itself. It is also believed to be metallic under high pressures. A knowledge of the lattice dynamics of iodine should give some insight into the nature of these intermolecular interactions.

The crystal structure of iodine at 110°K has been determined by van Bolhuis et al.⁵ The space group is *Cmca* with four molecules in the unit cell. (Cl_2 and Br_2 have similar structures.) The molecules lie in the $x = 0$ plane with molecular centers at 000 and 0,1/2,1/2. There is a short I_2 - I_2 distance of 3.496 Å in the plane, which is generally attributed to a strong intermolecular interaction, forming a two-dimensional network of I_2 molecules. The nearest I-I distance between layers is 4.269 Å, the distance generally attributed to van der Waals interaction. Since there are only four atoms in the primitive unit cell, there are 12 modes of vibration, 3 acoustic and 9 optic. In discussing only the $q = 0$ modes (i.e., at the Γ point), it is perhaps more illustrative to describe them in terms of molecular modes of vibration with two molecules in the primitive cell. In this notation there are three acoustic modes, with $\nu = 0$ at $q = 0$, three optic modes with translational motion, four optic modes with librational motion, and two internal modes – the symmetric (SS) and asymmetric (AS) stretching modes. The librational modes consist of symmetric and asymmetric librations about the α and β molecular axes. For a general point in the Brillouin zone it is not usually possible to describe the motions in such simple terms.

The phonon dispersion curves were determined by one-phonon coherent inelastic neutron scattering methods from a large ($\sim 25 \text{ cm}^3$) single crystal of iodine at 77°K on the HB-3 triple-axis neutron spectrometer at the HFIR. Measurements were made in the [100], [010], [001], $[\frac{1}{2}, 0, 0.5]$, and $[0, \frac{1}{2}, 0.5]$ directions with eigenvectors in the xz and yz planes. Most of the branches were identifiable except in the [010] direction, where there may be considerable overlap and mixing of the optical and librational modes.

Although it is true that all modes are "active" in neutron scattering, the observed neutron scattering

intensities depend very sensitively on (1) the orientation of the crystal, (2) the displacements of the atoms (the eigenvectors or polarization vectors of the modes), and (3) the structure factor of the Bragg reflections. This is illustrated in Fig. 4.2 for the internal stretching modes. The intensity of the symmetric stretch is maximum at the (0,0,10) reflection, minimum at the (0,0,11) reflection, and zero at the (6,0,0) reflection. Similarly, the intensity of the asymmetric stretch is minimum at (0,0,10), maximum at (0,0,11), and also zero at (6,0,0). The remaining modes were assigned using similar intensity and polarization-vector considerations.

Table 4.1 lists the $q = 0$ lattice vibrations and their assignments as determined in this study. The TO^b mode was the most difficult to assign, because there were no reciprocal lattice points available for which the mode could be uniquely assigned, as in the case of the stretching modes described above. Nevertheless, the behavior of this mode in the interior of the zone is convincing evidence that it has the proper assignment. It has been studied further with other orientations of the crystal. The frequencies and assignments given in several of the infrared and Raman studies are listed for comparison.

The lattice dynamics calculations are based on rigid diatomic molecules interacting through potential energy functions of the Buckingham-six type ($-A/r^6 + Be^{-\alpha r}$). At present the stretching modes within the diatomic molecules are not included in the dynamical matrix but may be calculated according to various versions of Badger's rule. The initial calculations included only one Buckingham-six function to represent all intermolecular

interactions, but later calculations included a separate Buckingham-six function as a first attempt to treat the short I_2-I_2 interaction separately from the longer-range interactions. Considerable improvement in the agreement between ν_{obs} and ν_{calc} was obtained. The latest results are included in Table 4.1. The observed and calculated phonon dispersion curves in the [001] direction are shown in Fig. 4.3. There is qualitative

Table 4.1. Lattice and molecular frequencies in I_2 at Γ

Symmetry	Observed frequency		Calculated frequency*		Optical studies
	(THz)	(cm^{-1})	(THz)	(cm^{-1})	
SL^b	2.62	(87.4)	2.52	(77.4)	
AL^b	2.26	(75.3)	2.21	(73.8)	
LO^c	1.96	(65.3)	2.09	(69.6)	65 cm^{-1} (IR)
SL^a	1.73	(57.7)	1.75	(58.3)	
AL^a	1.25	(41.7)	1.23	(41.0)	
TO^b	1.20	(40.0)	1.33	(44.5)	41 cm^{-1} (IR)
TO^a	0.92	(30.7)	1.23	(40.1)	
AS	5.68	(189.3)	Not calculated		188 cm^{-1} (R) [†]
SS	5.42	(180.7)	Not calculated		180 cm^{-1} (R) [†]

*Based on one Buckingham-six intermolecular potential for the nearest I_2-I_2 interaction and a separate Buckingham-six potential for all other interactions.

[†]This compares with 213 cm^{-1} in the gas phase. The intramolecular distance is 2.662 Å in the gas phase and 2.715 Å in the solid at 110°K.

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Fig. 4.2. Intensities of the symmetrical and asymmetrical stretching frequencies in iodine at 77°K.

Fig. 4.3. Observed and calculated phonon dispersion curves for iodine in the [001] direction at 77°K.

agreement between the two sets of curves in this direction, but the agreement in the [100] direction is not very good. The frequencies of the LA branch in the [100] direction are much too high. This branch depends very sensitively on the interlayer interactions, and it may be necessary to treat the interlayer interactions separately from those within the layer. The computer program is being modified to represent the nearest intermolecular interactions by a Morse potential and the in-plane and out-of-plane interactions by separate Buckingham-six potentials. The results will be reported at a later date.

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LATTICE DYNAMICS OF GOLD¹

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From the point of view of lattice dynamics, the noble metals are particularly interesting, since they are monovalent metals which form simple face-centered cubic structures, and large, pure single crystals are readily available. They also are well suited to investigations of the effects of impurities on their phonon spectra and

thermodynamic properties, since they readily accept a variety of substitutional impurities over broad concentration ranges, and their simple structures should facilitate comparison between theory and experiment. To determine the effects of impurities, of course, a detailed investigation of the pure host material must first be made. The lattice dynamics of copper and silver have already been studied.³⁻⁷ The force systems of copper and silver were found to be approximately homologous,⁶ that is, the forces have the same form relative to their respective lattices. However, deviations from this simple behavior might be expected for gold, since the temperature and the pressure dependence of the elastic constants indicate that noncentral many-body forces are of rapidly increasing importance in the series Cu, Ag, and Au. Furthermore, measurements of the specific heat of gold⁸ show an anomalous Debye temperature, $\theta_D(T)$, at low temperatures. The lattice dynamics of gold, with its large neutron absorption cross section (~ 100 b) and heavy mass, have not been investigated in detail until now.

The room-temperature phonon dispersion relations for gold in the high-symmetry directions are shown in Fig. 4.4. We found that the forces in gold are indeed not homologous with the other noble metals, the frequencies of gold lying appreciably higher than those "scaled" from copper and silver. An analysis of the data in terms of Born-von Kármán force-constant models reveals that a general tensor force is required for the first-neighbor interaction, whereas for neighbors beyond the first, either general tensor or axially symmetric forces give an excellent fit to the data. These calculations are represented in the figure by the solid lines. In addition, simple screened pseudopotential

Fig. 4.4. The room-temperature phonon-dispersion relations for gold in the principal symmetry directions. The solid curves represent both the fourth-neighbor general-force model and the fifth-neighbor mixed axially symmetric model. The dotted line in the Σ direction is the velocity of sound appropriate to the $T_1 \{ \frac{1}{2} \frac{1}{2} 0 \}$ branch. The reduced wave vector $\xi = aq/2\pi$.

models were fitted to the data, and these results also indicate the need for the first-neig bor interaction to be general.

Phonon frequency distribution functions and related thermodynamic quantities were calculated from the force-constant models. The Debye temperature θ_C vs temperature curves calculated from the neutron data show an anomaly at low temperatures consistent with the $\theta_C(T)$ obtained from specific heat measurements.⁸ This anomaly is directly related to the positive dispersion observed in the low-frequency portion of the T_1 [$\{110\}$] branch.

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IMPURITY PHONON MODES IN Ge-Si¹

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The coherent-potential-approximation (CPA) theory for lattice vibrations of crystals containing substitutional impurity atoms has been used to calculate phonon spectra in germanium with 9.2% silicon, and the results have been compared with experimental data obtained by coherent inelastic neutron scattering techniques. The theory has been found to predict accurately both the position and the width of the impurity band. Line shapes of scattered neutron groups have been calculated for various experimental conditions, and the results are in good agreement with experimental results.

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LATTICE DYNAMICS OF AN $\text{Ag}_{0.53}\text{Au}_{0.47}$ ALLOY

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The room-temperature dispersion relations of an $\text{Ag}_{0.53}\text{Au}_{0.47}$ alloy have been measured by neutron inelastic scattering. The measured frequencies lie above those expected from a simple mean lattice model, which is not unexpected since the frequencies of the pure metals do not "scale."² Comparison of the

measured frequencies and widths with those calculated from a mass defect coherent-potential-approximation (CPA) model indicates that the theory needs to be extended to include force-constant changes. These extensions are now in progress.

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"IN-BAND" MODES OF VIBRATION OF $\text{PdH}_{0.03}$ ¹

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Measurements of the lattice dynamics of palladium^{4,5} and platinum⁶ by other authors have shown the existence of a broad anomaly in one transverse branch (called the T_1 branch) of the dispersion relation in the [110] direction. This anomaly has been attributed by these authors to a large number of Kohn anomalies⁷ arising from various portions of the Fermi surface of these metals. Recent calculations⁸ of the effects of hydrogen on the band structure of palladium have suggested that, contrary to previous speculation, the rigid-band model for the effects of adding hydrogen to palladium is not a good approximation. Thus, although no calculations have been done for the present concentrations, one could expect that small amounts of hydrogen added to palladium might cause significant changes in the Fermi surface. For this reason, assuming the proposed explanation of the anomalous behavior of the [110] branch to be correct, it seemed desirable to study the $\text{PdH}_{0.03}$ lattice vibrations and to compare the results with those for pure palladium, with particular emphasis on the [110] T_1 branch. The specimen used in these measurements was the same single crystal used in the earlier diffusion studies.⁹ The measurements were performed using the triple-axis spectrometer HB-4A at the HFIR.

There is a slight tendency toward lower frequencies in the neutron groups observed in $\text{PdH}_{0.03}$; however, the anomaly in the [110] T_1 branch does not show any change in either shape or strength in the $\text{PdH}_{0.03}$ sample. Several explanations for this negative result are possible; for example, the anomaly is not due to the detailed shape of the Fermi surface, or the shape of the Fermi surface is not sufficiently changed by the addition of this amount of hydrogen. Since the present concentration represents the maximum achievable at room temperature without going into the two-phase region, the latter possibility could not be checked experimentally. As pointed out in ref. 8, a detailed

calculation of the band structure of the $\text{PdH}_{0.63}$ alloy is required to estimate the magnitude of the effect.

Measurement of the complete dispersion relation for a single crystal of the β -phase $\text{PdD}_{0.633}$ is under way.¹⁰

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PHONON SPECTRA IN PALLADIUM DEUTERIDE ($\text{PdD}_{0.63}$)

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J. J. Rush¹ H. G. Smith

It has been known for more than 150 years that palladium metal will absorb large amounts of hydrogen or deuterium. During this period, the macroscopic properties have been studied exhaustively (e.g., P - T phase diagrams, diffusion rates, magnetic susceptibility). There have also been an extensive series of x-ray structure investigations (although the information in the literature is surprisingly incomplete) and several neutron diffraction experiments. Recently, many workers have shown that for Pd/H ratios approaching 1.0, this compound becomes superconducting with transition temperatures of about 9°K, while PdD has a T_c near 11°K. These results have intensified the interest in the Pd-H(D) system generally, and, in particular, there has been much speculation about the phonon spectrum in the high concentration hydrides and its relation to their superconducting properties.

As a first step in a program to study the lattice dynamics of palladium and palladium-silver alloys containing hydrogen, we recently measured³ the phonon frequencies of selected modes in a single crystal of $\text{PdH}_{0.63}$. By utilizing the fact that the phase diagram of PdD_x has no phase boundaries as a function of D concentration for temperatures greater than 300°C, we have since loaded a single crystal of palladium to the approximate composition $\text{PdD}_{0.63}$. The loading was

done at 325°C with a D_2 pressure of between 10 and 200 atm over a period of two days. At this concentration the crystal may be cooled to approximately 100°K without phase segregation. The vapor pressure over the sample is less than 1 bar at 25°C. The resultant specimen has a mosaic spread of approximately 2.5° FWHM. There is evidence that there are two large grains misoriented by about 0.5–1.0°; there is no evidence of a mixed phase in the specimen.

We have completed an extensive study of the frequency-wave vector dispersion relation for phonons propagating in the three major symmetry directions ([100], [110], [111]) at 300°K. The acoustic modes are well-defined, and these branches have been mapped in detail. However, there is a large multiphonon and incoherent background which made it somewhat difficult to observe the optic modes. Thus, the measurements of these branches are less extensive. The results of the measurements are shown in Fig. 4.5 as solid points, while the corresponding frequencies for palladium are shown as open circles. (Pure palladium, of course, has no optic modes.)

Several interesting features are immediately apparent for the results shown in Fig. 4.5. First, it can be seen that all frequencies measured are lower than the corresponding frequencies in palladium, except for the anomalous region of the [110] T_1 branch. This result might be expected, since the lattice expands from $a = 3.89$ Å to $a = 4.05$ Å in going from Pd to $\text{PdD}_{0.63}$. However, it is misleading to assume that the expansion of the lattice is the only effect of importance. Calculations of band structures have shown that the Pd(D) system *cannot* be described by a rigid band picture. Further, the measured temperature dependence of palladium phonon frequencies suggests strongly that simply expanding the lattice by this amount would reduce the frequencies much more than is seen here.

The optic modes measured in the present experiment all lie between 9 and 11 THz, the lowest of any metal hydride that has been investigated. The groups have natural widths of less than 2 THz. Thus, the frequency band for optic modes is at most 3 THz wide, a result in direct conflict with measurements of incoherent scattering from $\text{PdH}_{0.67}$. We believe the discrepancy is connected with the strong multiphonon scattering referred to earlier. This effect would broaden the incoherent peak, leading to the disagreement noted above.

Another feature of interest is the [110] T branch, which is anomalous in pure palladium. As can be seen from Fig. 4.5, this anomaly is completely absent in $\text{PdD}_{0.63}$. As the anomaly in palladium is believed

Fig. 4.5. Phonon dispersion curves in $\text{PdD}_{0.63}$ at room temperature.

related directly to the electronic screening, the present result, in combination with the band structure calculations, should assist in the explanation of this feature.

As a first attempt at interpreting the data in terms of a lattice dynamics model, phonon frequencies were calculated assuming an axially symmetric Born-von Kármán model with interactions limited to Pd-D, Pd-Pd, and D-D and compared with similar calculations for some metal carbides. This simple model fits the data surprisingly well. Significantly, the Pd-Pd force constants are much greater than the Pd-D force constants. The opposite results were obtained for ZrC and TaC where the metal-nonmetal interaction was dominant. For UC the metal-metal interaction was about the same as the metal-nonmetal interaction. The C-C interactions in ZrC and TaC are much larger than the D-D and C-C interactions in $\text{PdD}_{0.63}$ and UC, respectively, and are consistent with the large dispersion of the optic modes in ZrC and TaC and the very small dispersion of these modes in $\text{PdD}_{0.63}$ and UC.

Finally, it should be noted that there are no "dips" in the dispersion relations. Since the T_c of the present specimen is believed to be less than 1°K, this result is in accord with predictions based upon the dispersion curves of the transition metals and transition metal carbides.

We are extending the measurements on this sample to lower temperatures (100°K). We also intend to load the crystal to $\text{PdD}_{0.9}$ by low-temperature electrolysis and

then repeat the measurements at 100°K and lower temperatures. A crystal of $\text{Pd}_{0.75}\text{Ag}_{0.25}$ has been ordered, and the lattice dynamics of this system also will be measured for various D/M ratios.

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CHANGES IN THE PHONON SPECTRA OF Nb WITH OXYGEN IMPURITIES

H. G. Smith

It is well known that surface oxides have a marked influence¹ on the superconducting properties of niobium, which may have adverse effects in its use in applied superconductivity. It is also desirable to know and understand what the effects are on the bulk properties of superconducting niobium. A recent study of the effects of interstitial oxygen on the superconducting properties of bulk specimens of niobium by Koch, Scarbrough, and Kroeger² confirmed the results of Desorbo,³ who found a reduction in T_c with increasing oxygen content. In addition, in contrast to the work of Desorbo, they found that the coefficient of the electronic specific heat γ also decreases with oxygen concentration. From the low-temperature specific heat

studies, Koch et al. found an increasing Debye temperature with an increase in oxygen concentration. An analysis of the McMillan equation in terms of θ_D and T_c yields the electron-phonon coupling parameter λ as a function of oxygen content. As a result of their studies, Koch et al. concluded that both the electronic density of states and the phonon spectra may be affecting the magnitude of T_c in the niobium-oxygen system.

It has been shown that the phonon dispersion curves of moderate-to-high T_c superconductors exhibit anomalous features⁴ which are believed due to the electron-phonon interaction – the generally accepted mechanism for superconductivity. The magnitude of the anomalies appears to be related to the magnitude of T_c and may be associated with lattice instabilities.

The only direct method of measuring the details of the phonon anomalies is the use of inelastic neutron scattering from large single crystals. A single crystal of niobium loaded uniformly with 2.6 at. % oxygen ($T_c = 6.8^\circ\text{K}$ vs $T_c = 9.2^\circ\text{K}$ for pure niobium) was supplied by C. C. Koch of the Metals and Ceramics Division. The

crystal was mounted on the HB-3 triple-axis spectrometer⁵ at the HFIR, and the phonon dispersion curves were determined for the high-symmetry directions at room temperature and compared with those⁶ for pure niobium. The longitudinal and transverse modes in the [001] direction are shown in Fig. 4.6. The most pronounced changes occur in the TA mode for $0.2 < \xi < 0.4$ and in the region of the dip in the LA mode for $0.5 < \xi < 0.9$. For this oxygen concentration the expected change in θ_D is expected to be about 10%. There was no measured change in the maximum lattice frequency as compared with pure niobium. However, the low-frequency TA modes in the [110] and [001] directions increased by about 15%, and it is these modes that would have the greatest effect on the low-temperature specific-heat measurements.

This study confirms the conclusion of Koch et al. that the phonon spectrum of niobium is modified upon addition of interstitial oxygen and may perhaps be correlated with T_c . A study will be made in the near future with a niobium crystal containing 3.6 at. % oxygen, the limit of solid solubility of oxygen in niobium. A lattice dynamical analysis should yield useful information regarding the nature of the force-constant changes in the crystals and perhaps shed some light on the electron-phonon interaction in niobium.

Fig. 4.6. Phonon dispersion curves of Nb(2.6% O) in the [001] direction. LA —○—, TA —○—.

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LATTICE DYNAMICS OF CdTe

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The phonon dispersion relation of CdTe at 300°K has been measured for the $\{100\}$, $\{110\}$, and $\{111\}$ symmetry directions, using neutron inelastic scattering. The CdTe single crystal was grown using ^{114}Cd to reduce the neutron absorption of the specimen. The present results along with earlier measurements⁴ on

Fig. 4.7. Dispersion relation for CdTe at 300°K. Solid lines represent shell-model calculations.

α -Sn and InSb complete our study of the lattice dynamics of these isoelectronic semiconductors. These materials are characterized by an increasing band gap and ionicity, while the structure remains the same (zinc blende), and the lattice spacing and atomic masses change very little; hence, they offer an ideal testing ground for theories of the lattice dynamics of semiconductors.

Lacking a truly fundamental theory for these semiconductors, we have fitted the present results to a phenomenological shell model which has been fully described previously.⁴ The model contains 14 adjustable parameters, and hence the parameters are not expected to have much physical significance. The parameters include: near-neighbor ion-ion (or ion-shell) forces; the ratios of the near-neighbor force constants for ion-ion, ion-shell, and shell-shell forces; z , the charge on the tellurium ion; the atomic and mechanical polarizabilities of both cadmium and tellurium; and four general second-neighbor force constants. The model was fitted to the measured frequencies and to the elastic,⁵ dielectric,⁶ and piezoelectric constants.⁷ An extremely good fit to the data was obtained, as shown in Fig. 4.7, where the data and the model calculations are compared. The neutron results for the frequencies of the longitudinal and transverse optic modes at Γ are 5.08 ± 0.10 and 4.20 ± 0.10 THz, respectively, in good agreement with the infrared⁶ results of 5.03 and 4.22.

The shell models are used to compare the dispersion relations for α -Sn, InSb, and CdTe in Fig. 4.8. The splitting of the LO and TO modes at Γ are larger for CdTe than for InSb, as expected from the larger band gap. A general "softening" of the optic and LA modes in the sequence is also evident, while the transverse acoustic modes are much less affected. It should be noted that the average mass and the lattice constants for the three materials are almost identical. It is hoped that the trends observed in this sequence of materials

Fig. 4.8. Dispersion relation for α -Sn, InSb, and CdTe derived from shell-model calculations.

will help stimulate further theoretical work on the lattice dynamics of semiconductors and lead to models with more physical content than is apparent in the shell model.

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PRESSURE AND TEMPERATURE DEPENDENCE OF PHONON SPECTRA IN Rb

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Anharmonic effects on lattice vibrations have been investigated in many crystals by studying the temperature dependence of the phonon frequencies and their line widths, utilizing inelastic neutron scattering techniques. Part of the shift in normal mode frequencies is due to the change in crystal volume as a function of temperature. It is difficult, if not impossible, to separate these so-called "quasi-harmonic" shifts from the "true" anharmonic shifts, that is, those effects attributed directly to a nonharmonic potential. It is desirable to have experimental data obtained at constant volume as a function of temperature, eliminating effects directly attributed to the quasi-harmonic model. This can only be done by varying both the temperature and the pressure. Except for some of the condensed gases³ at rather low pressures (<1 kilobar) this has not been achieved in neutron scattering experiments. Until

now, the only one-phonon neutron measurements at moderately high pressures (1–10 kilobars) have been made at room temperature with a liquid medium and at pressures less than 4 kilobars (Pb,⁴ Na,⁵ and RbI⁶).

We report here inelastic neutron scattering measurements of selected normal modes of vibration in rubidium under hydrostatic pressures between 0 and 5 kilobars and between 80°K and room temperature. Rubidium is a particularly good choice for these studies, since it undergoes a volume change of about 20% between the extremes of the above conditions, and the shifts in phonon frequencies are expected to be of this order. Such shifts are easily measurable under conditions of good neutron energy resolution. Moreover, the lattice dynamics of rubidium have been extensively studied by one of us⁷ (JRDC) as a function of temperature at atmospheric pressure and have been successfully analyzed in terms of an interatomic potential. In addition, rubidium is a solid at room temperature, and large single crystals of it are easy to grow.

The sample was a single crystal of rubidium, 2 in. long by $\frac{5}{8}$ in. in diameter, which was grown by a modified Bridgman method.⁸ The crystal was contained in a 7075-T6 aluminum pressure vessel, with a minimum OD of 2½ in., which was loaned to us by Professor W. B. Daniels of the University of Delaware. The details of the high-pressure apparatus will be published elsewhere. Briefly, it consists of a two-stage helium gas generating system connected to the pressure vessel (encased in a liquid-nitrogen cryostat) via thin-wall stainless steel capillary tubing. The cryostat is made of ¼-in. aluminum pipe which acts as a containment shield for the high-pressure vessel containing the sample.

The system was assembled at Argonne National Laboratory and transported to the High Flux Isotope Reactor, where it was mounted on a large goniometer on the HB-4A triple-axis spectrometer. Measurements were made under conditions of variable E' and "constant Q ." Fixed incident neutron energies of 6.57 THz [with a beryllium (100) monochromator plane] and 3.3 THz [with a pyrolytic graphite (002) plane] were employed. Analyzer planes employed were (101), (002), and (100) of beryllium and (002) of zinc. A graphite filter was used in the incident beam when the graphite monochromator was employed. This essentially eliminated all $\lambda/2$ and higher-order contaminants. The intense aluminum powder lines from the pressure vessel prevented measurements for some values of q .

Phonon measurements were made at four temperatures: 80, 150, 230, and $295 \pm 1^\circ\text{K}$. At each temperature the pressure was adjusted to yield (approximately) the following values of the lattice parameter a : 5.41,

5.50, and 5.62 Å. At 80°K no results were obtained for $a = 5.62$ Å, since $a = 5.608$ Å at atmospheric pressure. A few measurements were made for other values of a . In each case the lattice parameter was determined by measuring the scattering angles for selected Bragg reflections. A particular determination was considered good to ± 0.005 Å, but the measurements were only reproducible to within ± 0.015 Å. Pressures, read from a Bourdon gage, were considered good to ± 10 bars. From the measurements the isothermal bulk moduli were determined as a function of pressure for each of the above temperatures, and these results together with various derived quantities are given in Table 4.2. Some results of other workers are included for comparison.

The thermodynamic quantities of greatest interest to the theorists have been calculated: $(\partial \nu_i / \partial T)_V$, $(\partial \nu_i / \partial a)_T$, the mode gammas $(-\partial \ln \nu_i / \partial \ln V)_T$, and $(\partial \ln C_i / \partial p)_T$, where C_i are the elastic constants appropriate for a given mode. The change in frequencies with temperature at constant volume for some of the modes (Δ_5 , Σ_1) is clearly illustrated in Fig. 4.9. Interestingly enough, not all the modes (Δ_1 , Σ_4) show this behavior. The branches Δ_1 and Σ_4 are of particular interest in anharmonic calculations on the alkali metals.⁹ Hopefully, this new information will shed light on the discrepancies between experiment and calculation, in the case of the Σ_4 branch in particular. The Grüneisen parameters vary considerably from branch to branch but are substantially independent of temperature. The derivatives $(\partial \ln C_i / \partial p)_T$ were obtained under the assumption that each dispersion curve is linear in the range of phonon wave vectors examined. The results are compared with the measurements of Pauer, and reasonably good agreement is obtained.

This investigation represents a first attempt at a detailed study of the lattice dynamics of an alkali metal as a function of both temperature and pressure. Considerable experimental difficulties remain, in view of the large scattering corrections due to the thick pressure vessel and the demands on instrumental resolution. Nevertheless, these measurements can be done, and they can clearly provide valuable experimental data for comparison with anharmonic theories. We hope to make further measurements on rubidium and to make comparisons with theoretical calculations.

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Table 4.2. P - T - a points at which phonon measurements were made and the resultant bulk modulus, including temperature and pressure derivatives

T ($^{\circ}\text{K}$)	P (kilobars)	a (Å)	B_T (kilobars)	
295	0	5.703		$(\partial B_T / \partial T)_V = -0.0172^{\circ}\text{K}$ ($a = 5.502$ Å)
	0.34	5.675	19.6	$= -0.0278^{\circ}\text{K}$ ($a = 5.410$ Å)
	1.02	5.620	22.1	$(\partial B_T / \partial T)_P = -0.0204^{\circ}\text{K}$ ($a = 5.667$ Å) (ref. 11)
	2.07	5.555	25.8	$(\partial B_T / \partial P)_T = 3.1$ ($T = 295^{\circ}\text{K}$)
	3.07	5.502	27.9	$(\partial B_T / \partial P)_T = 3.14 - 3.49$ ($T = 300^{\circ}\text{K}$) (ref. 10)
	3.75	5.470	30.1	$(\partial B_S / \partial P)_T = 3.63$ ($T = 195^{\circ}\text{K}$) (ref. 12)
	4.75	5.420	31.4	
230	0	5.672		
	0.71	5.620	26.0	
	2.71	5.502	30.2	
	4.61	5.408	33.2	
150	0	5.637		
	0.28	5.622	28.4	
	2.26	5.502	31.4	
	4.43	5.402	35.3	
80	0	5.609		
	1.86	5.502	32.4	
	4.23	5.394	37.2

Fig. 4.9. Temperature dependence of selected phonon modes at constant volume for several values of the lattice constant a .

LOCAL PHONON MODES IN $\text{Rb}_{1-c}\text{K}_c$ ($c = 0.06, 0.18, 0.29$)

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In random alloys, because of the lack of exact translational symmetry, the spectra of elementary excitations (electrons, magnons, phonons) cannot be simply characterized as $E(\mathbf{k})$. Rather, there is a spectral distribution at each wave vector. The structure of these distributions, and of the total density of states, is of particular interest for nondilute alloys whose components differ substantially in their relevant properties, and considerable effort has been expended in recent years to calculate and measure these spectra. The best-known theory, the single-site coherent potential approximation (CPA), has been successfully compared with experiments on the electron density of states² (in transition-metal alloys) and on magnon³ (antiferromagnetic salts) and phonon dispersion curves^{4,5} (metals and semiconductors). Coherent inelastic neutron scattering, which can determine the last two of the three types of spectra, gives the most detailed experimental information presently available.

The purpose of the present experiment on Rb-K alloys is to provide experimental results which might indicate a need for a theory beyond the simplest CPA. The situation in which the CPA is thought to have the least validity occurs when the concentration of one component, which in the dilute limit has an impurity local mode, is increased until the impurities interact strongly and the character of the excitation starts to change from localized to propagating. In such a case the environment of each atom is highly variable, and it is unlikely that the excitations in the local-mode region will be adequately described by a mean-field theory like the CPA.

In our experiment there is an impurity local mode which occurs because a potassium atom is much lighter than a rubidium atom ($M_{\text{Rb}} = 2.18 M_{\text{K}}$) and prefers to vibrate at a frequency higher than any in the rubidium host lattice. Most of the partial phonon density of states for the potassium atoms is contained within a high-frequency local-mode peak. It is also restricted in wave vector to regions near the Brillouin zone boundary, in which a phonon frequency for the rubidium host band is high. That is, the local mode draws its strength from the high-frequency host band modes. This last feature has been observed in relatively dilute Cu(Al) and Ge(Si) alloys,^{6,7} but is much more apparent in the Rb-K experiment, as one can see from Fig. 4.10, which shows neutron groups for longitudinal excitations with wave vector $(2\pi/a)(0.5, 0.5, 0)$. The highest frequency

Fig. 4.10. Neutron scattering from Rb-K alloys. An almost flat background has been subtracted from the scans, which show host band and local mode peaks at the wave vector transfer Q . $1 \text{ THz} = 10^{12} \text{ Hz}$.

in the pure rubidium lattice occurs at this wave vector, and the local-mode strength is thus at its maximum. For $c = 0.06, 0.18$, and 0.29 , respectively, the local-mode peaks occur at $1.70, 1.77$, and 1.87 THz . The band mode peak has a frequency of 1.50 THz at all three concentrations. The local mode dominates in intensity at $c = 0.29$ and is becoming the band mode in the sense that, as $c \rightarrow 1$, it must evolve continuously into the band mode of pure potassium. The local-mode peaks for $c = 0.06$ and 0.18 are not broadened much above resolution, but for $c = 0.29$ the peak has a width of 0.3 THz , compared with a resolution width of 0.1 THz .

The increase in the frequency of the local mode as c is made larger can be qualitatively understood as arising from the increasing probability of finding other potassium atoms near a given potassium atom. Since the frequency of the $(2\pi/a)$ (0.5, 0.5, 0) longitudinal mode in pure potassium is 2.4 THz, it is clear that pairs and larger clusters will tend to vibrate at higher frequencies than those of potassium atoms which are isolated in a rubidium host. The large width at $c = 0.29$ probably comes from the highly variable nearest and next-nearest neighbor environments of the potassium atoms.

The wave-vector dependence of the local-mode intensity is similar for the three concentrations. The frequencies, however, show more dispersion at $c = 0.29$ than at lower c , indicating that the local mode is

starting to acquire a propagating character. Figure 4.11 shows dispersion curves for the [110] longitudinal excitations and the q dependence of the local mode intensity. In the inset, f is the fraction of the integrated intensity in a constant- Q scan contained in the local-mode peak, corrected for the factor $[n(\omega) + 1]/\omega$ in the cross section.

The solid lines in Fig. 4.10 are the results of CPA calculations for mass defects. The CPA peaks are less well defined than the experimental peaks for $c = 0.18$ and 0.29 and are further apart. It is probable, although not certain, that the experimental behavior is characteristic of cluster effects and not of force-constant changes. The latter, if they were significant and tended to shift the calculated local-mode frequency downward, would also make the peaks even more poorly defined, with very shallow or no minima between the peaks.

Fig. 4.11. Dispersion curves for [110] longitudinal vibrations in Rb-K alloys and the q dependence of the local mode strength f .

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MAGNETIC PROPERTIES

POLARIZED NEUTRON STUDY OF EUPOUS OXIDE

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Europous oxide, EuO , is a compound which has been studied rather extensively because of its extremely interesting magnetic, magneto-optical, optical, and transport properties. The stoichiometric or slightly metal-deficient compounds are insulating ferromagnets with a Curie temperature near 70°K , and divalent europium is in an S state for which the theoretical atomic moment is $7.0 \mu_B$. With its simple rock salt structure, this compound provides an ideal case for the experimental study of a Heisenberg ferromagnet. We were interested in studying the spin density in this compound because of its relation to the results of measurements on metallic gadolinium,¹ in which S -state ions are coupled via conduction electrons, and on insulating Gd_2O_3 .¹

Two single-crystal specimens,² one a pillar and one a thin flat plate, were investigated at 4.2°K. In both cases the sample was oriented with a [110] direction vertical, and all accessible reflections were measured at neutron wavelengths of 1.067 and 0.75 Å. Some additional measurements were made as well on the distribution of induced moment at temperatures above the Curie point.

In addition to the usual difficulties of making and interpreting polarization ratio measurements on substances with such large magnetic moments, some additional problems characteristic of EuO had to be overcome. In the first place, the normal isotopic mixture for europium (nearly a 50-50 mixture of ¹⁵¹Eu and ¹⁵³Eu) is highly absorbing. The total cross section goes through a minimum of about 950 b at $\lambda = 0.75$ Å. For shorter wavelengths the cross section increases because of close-lying resonances; for longer wavelengths it increases because of the $1/v$ capture law.

As it turned out, the nuclear scattering amplitude for europium is very close to that of oxygen, and this means that the nuclear structure factor for the odd index reflections, $|b_{Eu} - b_O|^2$, is very small. This in turn means that a number of small effects had to be checked for their influence on the experimental results.

Separate measurements were made to assess the corrections to the data required by nuclear polarization, and corrections for the Schwinger scattering and the Foldy interaction were calculated. In each case the corrections lie just within the range of the uncertainty of our experiments. (We propose to reverse our procedures in later experiments to attempt to characterize some of these weak interactions more fully.) Well outside our experimental uncertainty is the change in scattering amplitude with energy as a result of resonant scattering. We find $b_{Eu} = (0.608 \pm 0.002) \times 10^{-12}$ cm at $\lambda = 0.75$ Å and $b_{Eu} = (0.677 \pm 0.003) \times 10^{-12}$ cm at $\lambda = 1.067$ Å. For comparison we note that $b_O = (0.5803 \pm 0.0006) \times 10^{-12}$ cm.

The magnetic scattering amplitudes deduced from the experiment fall on a smooth curve suggestive of spherical symmetry. The 4f spin distribution is significantly expanded relative to that calculated by Blume, Freeman, and Watson,³ based on nonrelativistic Hartree-Fock wave functions, an effect which we had seen earlier in metallic gadolinium. As shown elsewhere in this report,⁴ the best fit to the gadolinium data is obtained with fully relativistic Dirac-Fock wave functions.⁵ Such wave functions have not yet been calculated for Eu²⁺, but the pertinent codes have now been sent to the Laboratory and the computations will be made.

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POLARIZED NEUTRON MEASUREMENTS ON CoS₂

H. R. Child

In CoS₂ pyrite the seven *d* electrons per Co atom occupy the six *t_{2g}* magnetically compensated band states plus one electron in an uncompensated *e_g* band, which gives rise to the ferromagnetic moment of 0.88 μ_B per Co atom.¹ FeS₂ with one less electron is a temperature-independent paramagnetic semiconductor, and NiS₂ with one more electron is weakly paramagnetic and a semiconductor also. Thus the sequence Fe-Co-Ni shows the occupation of the *e_g* band from empty to half full to full. Various alloys of the three can also be made to study this filling of the *e_g* band and its effect on the magnetic properties.^{1,3} Furthermore, changing the anion by replacement of sulfur with either selenium⁴ or arsenic⁵ changes the system from ferro- to antiferromagnetic. Therefore, this system seems to offer an interesting series of experiments.

Measurements of the flipping ratios of the Bragg peaks of CoS₂ at 4.2°K have been made to determine the form factor of the magnetic electrons. A single crystal² was mounted in the superconducting magnet so that a (110) direction was parallel to an applied field of 15 kOe, and all reflections whose scattering vectors are perpendicular to this direction were measured out to $\sin \theta/\lambda = 0.9$ Å⁻¹.

The four Co atoms per unit cell are in fcc positions and contribute to the fundamental reflections only. However, the superlattice reflections are not forbidden for pyrite, because the S atoms are not at special positions. The flipping ratios of these reflections would show a nonzero magnetic amplitude if the S atoms have any magnetic density on them. Measurements of the (112) and (332) reflections, however, gave magnetic amplitudes of zero within experimental error.

The flipping ratios of the normal lattice reflections showed evidence of strong extinction in this crystal. Consequently, the data were least-squares fitted to the equations used by Lander and Brun⁶ for extinction corrections in flipping ratios measurements. Although fits were tried in which the extinction parameter *g*, the ordered moment μ_0 , and the symmetry parameter were

all allowed to vary, the data were not sufficiently sensitive to μ_0 and the symmetry parameter to obtain significant values for all three parameters simultaneously. If we assume $\mu_0 = 0.88$ and e_g symmetry, we get a value of the extinction parameter $g = (3.0 \pm 0.2) \times 10^4$. This value gave a correction to the observed flipping ratio of 76% for the (002) reflection, which was the reflection most affected by extinction.

A correction this large restricts any quantitative conclusions which can be drawn from the data on this crystal, especially with regard to the symmetry of the form factor. An ordered moment of $0.88 \mu_B$ per Co atom is in agreement with the corrected data if we assume the Co^{2+} form factor, but the small effects of symmetry are masked by the large extinction corrections obtained in the least-squares fits. A measurement of the nuclear intensities from this crystal is planned to determine the extinction parameter independently and also to check on the sulfur position parameter. In addition, other crystals, which hopefully do not have such large extinction, will be studied when they are available.

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SPIN DENSITY OF PARAMAGNETIC Pd

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Many of the unusual features of the electronic and magnetic behavior of palladium are attributed to electronic states near the Fermi energy. The spatial distribution of the electrons in this region can be determined from magnetic form factor measurements on the paramagnetic metal. We report here the results of such measurements made by the polarized neutron method.²

The measurements were made at the HFIR on extinction-free palladium crystals maintained at 4.2°K in an applied field of 57.2 kOe. The observed form factor values are given in Table 4.3. Although data were collected for only ten reflections, the form factor

Table 4.3. Comparison of the observed and calculated form factors

hki	$\sin \theta/\lambda$	f_{obs}	$f_{\text{calc}}^{\text{HF}^a}$	$f_{\text{calc}}^{\text{APW}}$
111	0.2230	0.536	0.553	0.523
200	0.2575	0.433	0.407	0.382
220	0.3641	0.178	0.172	0.165
311	0.4270	0.035	0.053	0.041
222	0.4459	0.070	0.090	0.096
400	0.5149	-0.077	-0.071	-0.105
331	0.5611	0.006	0.013	0.020
422	0.6307	0.035	0.001	0.003
333	0.6689	0.020	0.030	0.046
511	0.6689	-0.043 ± 0.015	-0.059	-0.084

$$^a \alpha = 0.15, \gamma = 0.15, \mu_{\text{Pd}} = 8.9.$$

decreases so rapidly with $\sin \theta/\lambda$ that a Fourier analysis was carried out. The resulting moment-density maps show large positive densities centered at the atomic positions with apparent negative regions at the $\frac{1}{4}, \frac{1}{4}, 0$ positions. The positive contours exhibit a pronounced asymmetry with higher densities in the $\langle 110 \rangle$ directions corresponding to a predominantly T_{2g} character of the magnetic electrons. The integrated moment density around the atomic sites varies with the lattice positions at which the background level is taken. The extremes of this variation are $7.1 \pm 0.6 \text{ m}\mu_B/\text{Pd}$ relative to the background level at $\frac{1}{10}, \frac{1}{10}, 0$ and $8.0 \pm 0.7 \text{ m}\mu_B/\text{Pd}$ relative to $\frac{1}{4}, \frac{1}{4}, 0$. These compare favorably with the magnetization value of $7.73 \text{ m}\mu_B/\text{Pd}$ and indicate the absence of any appreciable negative polarization between atoms such as that observed³⁻⁵ for the ferromagnetic metals. This has an important bearing on the comparison of the observed and calculated form factors.

We first compare the data with an atomic calculation. We assume the same model used so successfully in analyzing the form factors of the ferromagnetic transition metals³⁻⁵ and write the form factor as

$$f(K) = \frac{2}{g}(1 + \alpha) \left[\langle j_0 \rangle + \left(\frac{5}{2} \gamma - 1 \right) A_{hkl} \langle j_4 \rangle \right] + \frac{g-2}{g} f_{\text{orb}} - \frac{2}{g} \alpha \delta(K).$$

The g factor, which determines the fraction of the atomic moment associated with unpaired spins, was taken from gyromagnetic measurements⁶ to be 2.20. The $\langle j_0 \rangle$, $\langle j_4 \rangle$, and f_{orb} functions were taken from a restricted Hartree-Fock (HF) calculation⁷ for Pd^{2+} . The

A_{hkl} is simply a geometrical factor. The two parameters are then α , the fraction of the net spin moment appearing as a uniform negative polarization, and γ , the fractional population of the E_g crystal field sublevels. A least-squares fit of this expression to the observed data yields the parameters $\alpha = 0.15 \pm 0.03$ and $\gamma = 0.15 \pm 0.04$. The corresponding form factor values are listed in column 4 of Table 4.3 and adequately represent the data. However, the α parameter corresponds to a local moment of $8.9 \mu_B/\text{Pd}$ and a negative polarization of $1.2 \mu_B/\text{Pd}$. Since this is inconsistent with the Fourier analysis, we conclude that the free-atom HF wave functions do not apply and need to be contracted by about $7\frac{1}{2}\%$ to describe the metal. The asymmetry parameter is not very sensitive to such changes in the radial properties and should remain valid. The 15% E_g character is nearly the same as that observed⁵ for isoelectronic nickel (19% E_g).

Band structure calculations^{8,9} for palladium show that the Fermi energy falls in a high-state-density region and intersects a nearly pure $4d$ band and a conduction band of hybridized spd character. The $4d$ band contributes about 90% of the density of states at the Fermi energy. Recently, Harmon and Freeman¹⁰ performed an APW calculation of the wave functions at the Fermi energy of palladium. The form factor they obtained from these wave functions, by weighting according to the state densities, was nearly the same as for the free-atom HF calculation. It would appear then that the APW wave functions are also expanded relative to the observed moment distribution. However, this discrepancy may be associated with an inappropriate weighting of the band densities due to the effects of exchange enhancement.¹⁰ The magnetic susceptibility of palladium is a factor of 10 higher than that calculated from the bare density of states.^{8,9} This is generally attributed to a Coulomb interaction, J , which enhances the susceptibility by a factor of $[1 - J\rho_F]^{-1}$, where ρ_F is the density of states at the Fermi energy. Because of their relative ρ_F values, one might expect a greater enhancement for the $4d$ band than for the conduction band. If so, this would shift the weighting closer to the pure $4d$ band and tend to contract the spin density as required by experiment. The form factors corresponding to the pure $4d$ band are given in column 5 of Table 4.3. These are only about 8% below the observed values and can be brought into even better agreement by the inclusion of an orbital moment.

In summary, we have measured the magnetic form factors for the first ten Bragg reflections of paramagnetic palladium. The observed form factor falls rapidly with $\sin \theta/\lambda$, in general agreement with a $4d$ electron

distribution and with an asphericity similar to that of isoelectronic nickel, that is, about 85% T_{2g} character. The spin density is contracted by about 15% relative to the HF Pd^{2+} ion but is somewhat better described by APW wave functions for the $4d$ band in the metal.

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INDUCED MOMENT DENSITY IN METALLIC SCANDIUM

W. C. Koehler R. M. Moon

The polarized beam technique has long been recognized as a powerful tool for the investigation of magnetic moment densities. Its first applications were to the ferromagnetic $3d$ transition metals Fe,¹ Co,² and Ni.³ The main conclusion of these experiments is that the unpaired spin densities in these metals are very similar to the corresponding free-atom $3d$ distribution. These results are not inconsistent with band theory calculations which predict that the wave functions for states near the top of the $3d$ band, with which the unpaired spins in these metals are associated, are just slightly more compact than in the free ion.

Polarized beam techniques, with their inherently high precision, can be applied to the measurement of extremely small magnetic scattering amplitudes and hence to the measurement of magnetic moment densities induced in weakly paramagnetic metals by applied magnetic fields. Such measurements have been reported previously for the $3d$ Pauli paramagnet, V,⁴ and the itinerant-electron antiferromagnet, Cr,⁵ at temperatures above and below its Néel temperature. Measurements are given in another section of this report⁶ for the $4d$ transition metal palladium, which is analogous to nickel with respect to its electronic structure. In each of these three cases it is remarkable that the magnetic diffraction data can be interpreted in terms of free-atom $3d$, or for palladium, $4d$ form factors.

We report here results of measurements which have been made on the distribution of induced-moment density in the element scandium, which has the outer electron contribution $3d^1 4s^2$. This represents a case in which the electronic states near the Fermi surface, which are the states involved in the production of the induced moment, lie near the bottom of the d band. This configuration is similar to the outer electron configurations of most of the rare-earth elements, $5d^1 6s^2$, a measurement of which has been obtained from a study of ferromagnetic gadolinium.⁷

The experiment consists in measuring the polarization ratio, R , which is the ratio of the peak intensities for a series of Bragg reflections for the two neutron spin states (parallel and antiparallel to the inducing field applied to the crystalline specimen). Samples were cut in the form of pillars oriented with the long dimension parallel to a crystallographic a axis. The polarized beam unit at HB-1 of the HFIR, which is now equipped with a split-coil superconducting solenoid capable of the production of 57.2 kOe, was used for the measurements. The quantity of interest in the experiment is the magnetic scattering amplitude, $p(\theta)$, which is related to the residual polarization ratio r by

$$r = R - 1 \cong 4p(\theta)/b,$$

in which b is the known coherent nuclear scattering amplitude of the element under investigation. From measurements of $p(\theta)$ one obtains the moment-form factor product through the relation

$$p(\theta) = 0.269\mu f(\theta) \times 10^{-12} \text{ cm}^{-1},$$

where μ , the induced moment, is expressed in Bohr magnetons and is obtained from the (separately measured) susceptibility and the magnitude of the applied field. For pure scandium at 100°K the susceptibility parallel to the a direction is 361×10^{-6} emu/mole,⁸ corresponding to an induced moment in 57.2 kOe of $3.70 \times 10^{-3} \mu_B$. Thus $p(\theta) = 0.995f(\theta) \times 10^{-15}$ and $r = 0.00337f(\theta)$. The results for five Bragg reflections are shown in Fig. 4.12, where the residual polarization ratios, r , are in units of 10^{-5} . The point for $\sin \theta/\lambda = 0$ has been calculated from the observed susceptibility.

It is striking that the observed form factor falls rapidly to zero, and this suggests that the induced density is extremely diffuse, as was the conduction electron density observed for ferromagnetic gadolinium. The same data, now expressed as normalized form factor data, are shown in Fig. 4.13. Shown also are atomic $3d$ and $4s$ form factor curves calculated by

Fig. 4.12. Residual polarization ratios observed for scandium at 100° K in 57.2 kOe.

Fig. 4.13. Normalized form factor data for scandium at 100° K in 57.2 kOe. Solid curves are $3d$ and $4s$ atomic form factors.

Freeman and Watson with Hartree-Fock free-atom wave functions.⁹ In contrast to other $3d$ metals, the induced-moment density for scandium does not have a typical localized d distribution but is in fact considerably more extended. Such a result is not in conflict with present band theory calculations which suggest that the wave

functions for states near the bottom of the band are more diffuse than for those near the top.

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MAGNETIC PROPERTIES OF Gd_2O_3

R. M. Moon W. C. Koehler

The original motivation for this work was to try to resolve an apparent discrepancy between measurements of the gadolinium magnetic form factor in the metallic state, determined by the polarized neutron technique, and measurements of the paramagnetic diffuse cross section of Gd_2O_3 . Polarized beam measurements on a powder sample of $^{160}Gd_2O_3$ were made at 4.2°K. The sample was mounted in a superconducting magnet to partially align the paramagnetic gadolinium moments, and observations of the ratio of magnetic to nuclear structure factors were obtained for a number of Bragg peaks. The gadolinium ions have two different crystallographic sites, and it was immediately apparent that the induced moments on these sites were quite different. Because Gd^{3+} is an *S*-state ion, this effect was not due to the different crystalline fields at the two sites. However, the exchange interaction between an ion on one site and the rest of the crystal would differ between the two sites, so it seemed likely that we were observing different ionic susceptibilities on the two sites resulting from different net exchange interactions. Another interesting characteristic of the low-temperature diffraction pattern was the appearance of large oscillations in the diffuse scattering, indicating strong short-range magnetic order. Our interest in the problem shifted toward explorations of these two interesting effects.

The Gd_2O_3 has the bixbyite structure¹ with 32 gadolinium ions per unit cell. Eight of these ions are on a site with C_{3i} point symmetry (site 1), and 24 are on

sites with C_2 point symmetry (site 2). In an applied field the magnetic structure factors for two particular Bragg peaks are:

$$F_{211}^M = 0.27f_{211}(2.98\mu_2),$$

$$F_{222}^M = -0.27f_{222}(8\mu_1 + 22.27\mu_2),$$

where μ_1 and μ_2 are the induced moments on the two sites and f is the magnetic form factor. Both peaks come at small scattering angles where there is little uncertainty in the form factor. By measuring these two structure factors at the same temperature, we could deduce the separate ionic moments and hence the susceptibilities. The temperature dependence of these susceptibilities was observed over a range from 1.8 to 20°K. These results are shown in Fig. 4.14, together with the average susceptibility computed from our data,

$$\bar{\chi} = \frac{1}{4}\chi_1 + \frac{3}{4}\chi_2.$$

Fig. 4.14. The temperature dependence of the inverse susceptibilities for gadolinium ions on different sites in Gd_2O_3 . The solid lines are calculated from an approximate theory. The dashed line gives the high-temperature asymptote of the calculation (C is the free-ion Curie constant).

This average is in good agreement with ordinary susceptibility² measurements.

Diffuse scattering observations were made over a temperature range from 1.8 to 400°K with an unpolarized beam in the zero applied field. These data were analyzed in terms of pair correlation functions, defined as

$$\epsilon_l = \frac{1}{N} \frac{\sum_m \langle \mathbf{S}_m \cdot \mathbf{S}_{m+l} \rangle}{S(S+1)},$$

where the brackets denote a thermal average. For this experiment the incident neutron energy was very large ($\sim 1000^\circ\text{K}$) compared with possible energy transfers to the spin system ($\sim 2^\circ\text{K}$), so the quasi-elastic approximation should be valid. For a Heisenberg interaction between spins in a cubic paramagnet, the diffuse cross section can be written in the form

$$\frac{(d\sigma/d\Omega) - (d\sigma/d\Omega)_p}{(d\sigma/d\Omega)_p} = \sum_l N_l \epsilon_l \frac{\sin KR_l}{KR_l},$$

where $(d\sigma/d\Omega)_p$ is the cross section for an ideal paramagnet (no correlation), N_l is the number of neighboring spins at distance R_l , and K is the scattering vector. By fitting this expression to the data, the

temperature dependence of ϵ_l was obtained. Terms out to the sixth neighbor shell were included, but only the first two shells gave correlations significantly different from zero. The second-neighbor correlation was easily interpreted in terms of a propagation of two first-neighbor correlations, indicating that only first-neighbor exchange interactions were important. The temperature dependence of the first-neighbor correlation is shown in Fig. 4.15.

An approximate theory has been developed which gives good agreement with our data on the temperature variation of the spin correlation, the susceptibilities, and the available data on the specific heat.³ This theory is based on the well-known thermodynamics of an isolated pair of spins coupled by a Heisenberg interaction, with approximate corrections to account for interactions with the rest of the crystal. The theory is similar to the constant-coupling approximation,⁴ but tailored to the Gd_2O_3 structure. There are two adjustable parameters in the theory, specifying the magnitude of the near-neighbor exchange interactions between type 1 and type 2 sites and when both members of the pair are on type 2 sites. The solid curves in Figs. 4.14 and 4.15 were calculated for $J_{12}/k = -0.1358^\circ\text{K}$ and $J_{22}/k = -0.1442^\circ\text{K}$. The negative signs indicate antiferromagnetic interactions.

Fig. 4.15. The temperature dependence of the first-neighbor spin correlation in Gd_2O_3 . The dashed lines are for isolated pairs with the indicated exchange interactions. The solid lines are based on our approximate theory for Gd_2O_3 . The experimental points should be compared with the middle solid line representing the average over all near-neighbor pairs.

We feel that this work demonstrates a new application of the polarized neutron technique which can be very valuable in understanding paramagnetic systems with more than one type of magnetic ion. Conventional susceptibility measurements give the response of the average ion to an applied field, while the neutron technique can give the individual responses of each type of ion.

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4f WAVE FUNCTIONS FOR Gd – A COMPARISON BETWEEN THEORY AND EXPERIMENT

R. M. Moon

In the theory of rare-earth metals and compounds, the assumption is made that the 4f radial wave functions in the solid are the same as in the free ion. Our recent experimental work on the magnetic form factor of gadolinium metal¹ probably provides the best available experimental description of 4f electrons in a solid. The disagreement between these data and non-relativistic Hartree-Fock² calculations for the free ion prompted some theoretical activity to improve the ionic calculation. Davis and Cooke³ found good agreement with our data using a relativistic Hartree-Fock-Slater calculation for the 4f wave functions and showed that the previous disagreement was due to the nonrelativistic nature of the Hartree-Fock calculation. Subsequently, Freeman and Desclaux⁴ obtained excellent agreement with our data using a relativistic Dirac-Fock scheme. It seemed worth while to make a detailed comparison of our data with the best theoretical calculation to see if there is any significant difference. Further, in anticipation of additional work on the rare-earth metals, it was of interest to establish whether the more complicated Dirac-Fock-Slater calculations would be needed, or whether the simpler relativistic Hartree-Fock-Slater wave functions would be adequate.

Our data consist of 74 observations, at different values of the scattering vector Q , of the Fourier inversion of the magnetization density. For gadolinium the 4f shell is half full, so there is no orbital moment, and the 4f magnetization density is identical to the spin density and charge density. To test the atomic model, we calculate

$$\mu_i = M(Q_i)/f(Q_i),$$

where $M(Q_i)$ are the set of observations and $f(Q_i)$ are calculated ionic or atomic form factors. For each value of μ_i we assign a weight

$$\omega_i = [f(Q_i)/\Delta M_i]^2,$$

where ΔM_i is the experimental error in $M(Q_i)$. The weighted mean, $\bar{\mu}$, is calculated, and the quantity

$$\sigma = \left[\frac{\sum \omega_i (\mu_i - \bar{\mu})^2}{(n-1) \sum \omega_i} \right]^{1/2}$$

is evaluated as a measure of the goodness of fit. The first two Bragg reflections, which are believed to be influenced by conduction electron polarization, were excluded from the analysis. In comparing the data with various calculated form factors, the criteria for selection of the best fit are: (1) σ should be small, (2) $\bar{\mu}$ should be $6.42 \mu_B$ based on magnetization measurements, and (3) there should be no systematic variation of μ_i with Q .

As shown in Table 4.4, the fit to the Dirac-Fock free-atom calculation gives the best agreement. To make the comparison as accurate as possible, small corrections to account for the core polarization have been made in most cases. These corrections were based on a spin-polarized Hartree-Fock calculation for Eu^{2+} by Watson.⁵ The fits to the Hartree-Fock-Slater calculation showed a systematic decrease in μ_i as Q increased, as evidenced in the higher values for σ . It is interesting that a value for the Slater exchange coefficient of 0.705 gives the correct value for $\bar{\mu}$ of $6.42 \mu_B$. This is in

Table 4.4. Summary of fits to gadolinium form factors

For the Hartree-Fock-Slater comparisons, the numbers in parentheses refer to the coefficient of the Slater exchange term

	Core polarization	$\bar{\mu}$	σ
Hartree-Fock Gd^{3+}	Yes	5.763	0.021
Hartree-Fock-Slater Gd^0 (0.76)	Yes	6.257	0.030
(0.72)	Yes	5.378	0.028
(0.68)	Yes	6.477	0.025
Dirac-Fock Gd^{3+}	Yes	6.350	0.014
Gd^0	No	6.563	0.016
Gd^0	Yes	6.399	0.014

excellent agreement with the "best" value for this coefficient obtained by comparing energies in Hartree-Fock and Hartree-Fock-Slater calculations.

It is concluded that the data support the assumption that the 4f electrons in gadolinium metal have wave functions which are accurately given by atomic Dirac-Fock calculations, and that it would be desirable to have these calculations for the remainder of the rare-earth elements.

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MAGNETIC MOMENT DISTRIBUTION AROUND Fe IMPURITIES IN Ni_3Ga ¹

J. W. Cable H. R. Child

The interatomic compounds of the Ni_3Ga phase behave as nearly ferromagnetic paramagnets, as evidenced by their remarkable susceptibility behavior and their dramatic magnetic response to iron doping.²⁻⁵ The compounds become ferromagnetic with an impurity content of only 500 ppm iron and with giant moments as large as $36 \mu_B/\text{Fe}$. The undoped compounds exhibit a susceptibility divergence as the nickel content approaches the critical concentration for the onset of ferromagnetism at 75.8% nickel. They therefore offer a convenient system for the study of giant moment formation as a function of host matrix susceptibility. According to the exchange-enhanced electron-gas model, the increasing susceptibility corresponds to an increase in the exchange enhancement and should lead to an impurity-induced magnetization larger in both magnitude and spatial extent toward the nickel-rich end of the phase region. The magnitude of the impurity-induced moment as a function of host matrix susceptibility has been determined from bulk magnetization measurements⁶ and does indeed show a linear dependence between 73 and 75% nickel. Neutron diffuse scattering measurements are required to determine the spatial distribution of the magnetization and its dependence on host matrix susceptibility. We report here the results of such measurements for iron-doped compounds with susceptibilities differing by a factor of 2.

The neutron experiment consists of measuring the difference in the diffuse scattering intensity for the magnetized and unmagnetized condition. With the appropriate geometry, the magnetic disorder cross section is⁷

$$(d\sigma/d\Omega)(K) = 48.3c_{\text{Fe}} [\mu_{\text{Fe}} f_{\text{Fe}}(K) + M(K)]^2, \quad (1)$$

in which c_{Fe} is the fractional iron content, μ_{Fe} is the magnetic moment at the iron site, with its associated form factor $f_{\text{Fe}}(K)$, and $M(K)$ is the Fourier transform of the magnetization induced in the host by the impurity. In the itinerant electron model, $M(K)$ is assumed proportional to a generalized K -dependent susceptibility of the electron gas.⁸⁻¹⁰ At small K this becomes

$$M(K) = \frac{M(0)}{1 + K^2/K_1^2}, \quad (2)$$

in which $M(0)$ is the net host magnetization per impurity and K_1 is an inverse range parameter. Away from the impurity site the induced moment density has the form

$$\rho(r) = \frac{M(0) K_1^2}{4\pi r} e^{-K_1 r}. \quad (3)$$

The neutron measurements were made at the ORR using 4.4 Å neutrons and a position-sensitive detector of the resistive wire type.¹¹ Magnetic disorder cross sections were measured at 8°K with a 12 kOe magnetizing field on polycrystalline plate samples of nominal composition $\text{Ni}_{74.9}\text{Fe}_{0.1}\text{Ga}_{25}$ and $\text{Ni}_{75.4}\text{Fe}_{0.1}\text{Ga}_{24.5}$. These cross sections in millibarns steradian⁻¹ atom⁻¹ are shown as a function of scattering vector, $K = 4\pi \sin \theta/\lambda$, in Fig. 4.16. Both show pronounced K dependencies characteristic of spatially extended magnetization regions. The observed cross sections were fitted to Eqs. (1) and (2), assuming the Fe^{2+} form factor and an iron moment of $3 \mu_B$ in accordance with previous measurements¹² on a higher iron content compound. The fitted curves are shown as the solid lines in Fig. 4.16, and these clearly describe the cross sections quite well. The parameters are also given in Fig. 4.16 and describe a widespread moment disturbance around the iron impurities. There is an induced moment of about $30 \mu_B/\text{Fe}$ distributed over several hundred neighbors of the impurity. The moment at nearest-neighbor sites is only about $0.17 \mu_B$ per Ni atom and falls to about 10% of that value at a distance of 10 Å.

Fig. 3.16. Magnetic disorder cross sections for iron-doped Ni_3Ga compounds.

In the itinerant electron model, both $M(0)$ and K_1^{-2} are proportional to the exchange enhancement factor, that is, to the host matrix susceptibility.⁸⁻¹⁰ This is not observed here; the parameters are nearly the same for the two compounds even though their susceptibilities differ by a factor of 2. We conclude that $M(0) \cong 31$ and $K_1 = 0.12$ characterize the maximum response of the Ni_3Ga phase compounds to iron impurities. This casts serious doubt on the interpretation of the observed susceptibility divergence in terms of the exchange-enhanced itinerant-electron model. It might rather be explained by superparamagnetic clusters associated with wrong-sited nickel atoms inevitably present on the nickel-rich side of stoichiometry.

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HOMOGENEITY OF THE MAGNETIZATION IN FERROMAGNETIC Ni_3Al COMPOUNDS

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The intermetallic compounds of the Ni_3Al phase exhibit the magnetization behavior predicted for itinerant electron systems.² However, low-temperature specific-heat data are inconsistent with current paramagnon theories of such systems and suggest that magnetic clusters may have a role in their magnetic and thermal behavior.^{3,4} We report here the results of neutron diffuse scattering measurements carried out on ferromagnetic Ni_3Al compounds in an attempt to detect and characterize such clusters in these materials.

The experiment involves taking the difference between the diffuse scattering cross sections for magnetized and unmagnetized samples. With the magnetization parallel to the scattering vector, this difference cross section is

$$d\sigma/d\Omega = 48.3cM(K)^2 \quad (1)$$

in millibarns steradian⁻¹ atom⁻¹. Here, c is the cluster concentration and $M(K)$ is the Fourier transform of the moment density per cluster, which is assumed to be the same for all clusters. In the small K region appropriate to the neutron measurements, $M(K)$ quite generally assumes the form

$$M(K) = \frac{M(0)}{1 + K^2/K_1^2}, \quad (2)$$

in which $M(0)$ is the net cluster moment and K_1 is an inverse range parameter which defines the radial extent of the cluster. The expected cluster cross section is then of Lorentzian shape with a $K = 0$ intercept proportional to $cM(0)^2$ and a K dependence determined by the physical size of the cluster.

The measurements were made at the long-wavelength spectrometer at the ORR using 4.4-Å neutrons and polycrystalline plate samples of nominal composition $\text{Ni}_{0.75}\text{Al}_{0.25}$ and $\text{Ni}_{0.76}\text{Al}_{0.24}$. Magnetization data² show that these compounds are ferromagnetic, with Curie temperatures of 41.5 and 71.5°K and saturation magnetizations of 0.057 and 0.095 μ_B/atom respectively. The difference cross sections, obtained at 7°K with a magnetizing field of 10 kOe, are shown in Fig. 4.17. These are essentially the same for both samples and quite small even at the lowest observed K value, $K_{\min}$.

Cluster parameters derived from these small cross sections would be defined by only the first two data points and would not be very reliable. We therefore approach the problem from the model viewpoint and attempt to set limits on acceptable models. Two distinct models have been proposed for the Ni_3Al compounds: the itinerant electron model² and one that attributes the entire magnetization to sheets of nickel atoms at antiphase domain boundaries.⁵ The first of these has a completely homogeneous moment distribution which would yield a zero cross section at all K values. Since the observed cross sections differ from zero by a maximum of only 3 to 4 error bars, we cannot safely exclude this model. The second model has a suggested⁵ cluster concentration of 10^{-4} , so that the magnetic nickel sheets have an average separation of about 49 Å. The magnetic cross section would appear as diffuse streaks around each reciprocal lattice point. In the reciprocal space region of this experiment these

streaks would appear inside our $K_{\min}$ at about 0.13 $\text{\AA}^{-1}$. We therefore cannot exclude this model either. However, this model is inconsistent with the high-field magnetization² which does not saturate even at 4.2°K and 200 kOe, under which conditions the large cluster moments associated with this model would readily saturate. Finally, we consider a model in which part of the magnetization is attributed to clusters surrounding β -site nickel atoms. It is known that iron atoms with localized moments of 3 μ_B induce a net cluster moment of about 12 μ_B in Ni_3Al compounds in this composition region.⁶ Although the local moment of a β -site nickel atom is not known, we can safely assume that it is less than 0.6 μ_B and therefore that $M(0) \leq 2.4 \mu_B/\text{cluster}$. At the 1% "impurity" level this corresponds to $(d\sigma/d\Omega)(0) \leq 2.8 \text{ mb}$, and this, too, is consistent with the observed cross sections. We note that, even in this model, the major part of the magnetization is outside of the clusters and spatially homogeneous.

In summary, the magnetic diffuse cross sections of these Ni_3Al compounds are quite low to small K values and do not allow for any gross inhomogeneity in the magnetization. Specifically, they exclude magnetic clusters with diameters less than $2\pi/K_{\min} \sim 43 \text{ \AA}$ for which $c^{1/2} M(0) > 0.24 \mu_B/\text{cluster}$.

Fig. 4.17. Magnetic disorder cross sections of Ni_3Al compounds.

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TEMPERATURE DEPENDENCE OF FERROMAGNETIC DISORDER SCATTERING FROM IMPURITIES IN Fe

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Ferromagnetic disorder scattering of neutrons from alloys has been used extensively to obtain information about the individual magnetic moments of the constituents of the alloy and the effect of the impurities on the host moment. However, these past measurements have been restricted to low temperatures compared with the Curie temperature. In the present work, we have investigated the temperature dependence of this

scattering up to $T/T_C \cong 0.8$ for a series of dilute impurities in iron to (1) determine whether or not the scattering does show a temperature dependence as predicted by Lovesey and Marshall¹⁻³ and (2) if so, to see if new information concerning the magnetic properties of the alloy can be obtained from this temperature dependence.

We have studied 3 at. % V, Ge, Si, Co, Ti, Mn, and Ni in iron using a position-sensitive counter and a 4.4-Å wavelength neutron beam at the ORR. With this arrangement it was possible to measure cross sections as small as 1.0 ± 0.7 mb/atom as a function of $K = 4\pi \sin \theta/\lambda$ for $K < 1.4 \text{ Å}^{-1}$. A polycrystalline slab was mounted in the gap of an electromagnet in a furnace and maintained at a constant temperature. One run with zero applied field and another with an applied field sufficient to magnetically saturate the sample parallel to the scattering vector were made. The difference between these runs gives the intensity of magnetically scattered neutrons, and this intensity was calibrated by comparison with the scattering from a plate of pure vanadium, which has a known differential scattering cross section.

The cross sections vs K obtained at low temperature confirm previous measurements⁴ on these impurities in iron, although there are small differences that apparently are due to sample-dependent effects. As an example, Fig. 4.18 shows Fe + 3% Ge at two values of T/T_C . At low temperature these data agree with ref. 4, but as the temperature is raised toward T_C an increase in scattering is observed at small K . The increase is largest for silicon and germanium, which have nearly zero moment at low temperatures when dissolved in iron, and is least for nickel and cobalt, which have ferromagnetic moments in iron. Titanium and vanadium, which have negative moments, exhibit intermediate effects. Since critical scattering from a pure material should also show an increase in scattering⁵ at small K , a pure iron sample was studied in the same geometry so that a correction could be applied to the alloy data. For $T/T_C > 0.8$ this correction becomes large, so this region was not included in the alloy studies.

The ferromagnetic disorder scattering cross section is given by Marshall⁶ as

$$d\sigma/d\Omega = c(1-c)(e^2\gamma/2mc^2)^2 [\Delta\mu f(K) + M(K)]^2,$$

in which $\Delta\mu = \mu_i - \mu_h$ (μ_i = impurity moment, μ_h = host moment in Bohr magnetons), $M(K)$ is the Fourier transform of the moment deviation on the neighbors of the impurity, c is the concentration of impurities, and

Fig. 4.18. Magnetic disorder cross sections for 3 at. % germanium in iron vs K at two temperatures.

$f(K)$ is the magnetic form factor. The cross section gets most of its K dependence from $M(K)$, because over the small K region with which we are concerned, $f(K)$ decreases by only about 10%. Thus the increase in scattering at small K must be attributed to the change in $M(K)$ with temperature. This is probably due to an increase in range of the magnetic disturbance, since an increase in size of the disturbance on the first few neighbors would not cause such a large increase in $M(K)$ at small values of K without requiring unreasonable magnitudes for the moment of the neighbors. In fact, if the observed data are fitted to the above equation by least squares, the values of the disturbance on the first few neighbors are found to be unreasonable at high T/T_C . An alternate form for $M(K)$ is obtained if one assumes a particular form for the disturbance:

$$M(R) \sim M(0) \exp(-K_1 R)/R.$$

This assumption results in a Lorentzian form for $M(K)$:⁷

$$M(K) = \frac{M(0)}{1 + K^2/K_1^2}.$$

Fitting the observed cross section to this form for the parameters $M(0)$ and K_1 gives agreement for germanium with K_1^{-1} of the order of 15 Å, and $M(0) \cong 18 \mu_B$ at $T/T_C = 0.77$. However, for some of the impurities, these two usual assumptions concerning an analytic form for $M(K)$ are not satisfactory.

The cross-section formula applies only to elastic scattering, but our experiment would also measure inelastically scattered neutrons, since it is a constant-scattering-angle experiment. However, the cutoff angle for spin-wave scattering in this type of experiment is well inside our minimum scattering angle, and measurements of spin-wave dispers on⁸ in iron have shown that the energies do not become low enough for the spin-wave scattering to be visible to us for $T/T_C \leq 0.8$.

The increase in scattering observed in the alloys over and above that seen in pure iron is too large and occurs at too small a K value to be explained by the theory of Lovesey and Marshall. Even an extension of their approximation to the case of eight nearest-neighbor shells (they only included first-neighbor effects) or a separate exact calculation of the effects out to eight neighbors in the molecular-field approximation by computer iteration⁹ does not reproduce the measurements. Thus a more exact theory of temperature effects in magnetic alloys is required to explain our results.

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CRITICAL SCATTERING OF NEUTRONS FROM Gd

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The inelastic scattering of neutrons from a single crystal of ^{160}Gd near its ferromagnetic Curie point has

been measured. The Curie temperature for this crystal was determined to be 291°K in a separate experiment in which the polarization of a beam of polarized neutrons was measured after the beam had been transmitted through the crystal. Far above the Curie point, the transmitted beam is polarized in the same direction as the incident beam, but near T_C the beam is depolarized by the critical fluctuations¹ of the spin correlations in the sample. This effect provided a very sensitive measure of the transition temperature.

Critical scattering² is usually described in terms of two scattering functions, $S_{\parallel}(\mathbf{q}, \omega)$ and $S_{\perp}(\mathbf{q}, \omega)$, which are the Fourier transforms of the correlation functions of the components of the spins parallel and perpendicular to the ordered-moment direction. Since gadolinium has its ordered moment parallel to the c axis from 210°K to its Curie point,³ it is possible to measure both functions by measuring $S_{\parallel}(\mathbf{q}, \omega)$ near the (002) reciprocal lattice point and $S_{\parallel} + S_{\perp}$ near (100).

The scattering functions are usually written² as

$$S(\mathbf{q}, \omega) \propto \chi(\mathbf{q}) F(\mathbf{q}, \omega),$$

with the generalized susceptibilities $\chi_{\parallel}(\mathbf{q})$ and $\chi_{\perp}(\mathbf{q})$ independent of energy. The energy dependence of the scattering is included in the functions $F(\mathbf{q}, \omega)$, which are normalized so that

$$\int_{-\infty}^{\infty} F(\mathbf{q}, \omega) d\omega = 1.$$

The present measurements were made with an energy width of 0.31 meV, which is not sufficiently small to determine the details of the $F(\mathbf{q}, \omega)$ functions in gadolinium, but by integrating the runs over energy at constant $\mathbf{q}$, the susceptibilities $\chi_{\parallel}$ and $\chi_{\perp}$ could be measured. Near T_C , these functions are predicted by theory to be of the form

$$\chi(\mathbf{q}) = \frac{A}{K^2 + q^2},$$

where A and K are temperature-dependent constants. Thus the primary purpose of the present experiments was to determine the temperature dependence of χ and the region of temperature over which this form for χ is valid.

Figure 4.19 shows the intensity integrated over ω at various values of $\mathbf{Q}$ vs temperature near T_C . In the upper portion of the figure the intensity proportional to $\chi_{\parallel} + \chi_{\perp}$ is shown, and the intensity in the lower section is proportional to $2\chi_{\perp}$ only. At small $\mathbf{q}$ near

Fig. 4.19. Intensity integrated over ω at constant q vs temperature for gadolinium.

(100) the intensity peaks sharply at T_C , reflecting the rapid rise of $\chi_{\parallel}$, while near (002) the intensity is rounded and peaks at a temperature 8 or 9° below T_C . Measurement of $\chi_{\perp}$ for MnF_2 (ref. 4) also showed that $\chi_{\perp}$ has its maximum at a temperature somewhat below that for $\chi_{\parallel}$, which peaks at the critical temperature. If the reciprocal intensity is plotted vs q^2 (as in Fig. 4.20), a linear plot is obtained if the form for χ is Lorentzian; K can be determined from the slope of the linear portion. Departures from linearity at large q show the presence of a q^4 term in the denominator.

According to theory,¹ the quantity $K = 2\pi/\xi$, where ξ is the range of the correlation function. Our measurements show that ξ decreases slowly above T_C , which is an indication of the short-range order present in systems with long-range interactions such as the rare earths. Theory predicts that $K_{\parallel} = K_{\perp}$ above T_C since no anisotropy is included, but below T_C they are not expected to be equal even in the simple molecular field theory. Magnetization data show anisotropy in $\chi(q=0)$

Fig. 4.20. Reciprocal integrated intensity from gadolinium vs q^2 for q along the (001) direction at 292.4°K.

for the rare earths even above T_C , so $K_{\parallel}$ may not be equal to $K_{\perp}$, although gadolinium has smaller anisotropy⁵ than the others. If $K_{\parallel} \neq K_{\perp}$ the intensity near (100) will be proportional to the sum of two Lorentzians, both of which contain unknown parameters A and K which are not equal. Under these circumstances the plot of $1/I$ vs q^2 will not be linear, and the only feasible method of determining the parameters is by least-squares fitting of the observed intensity to the calculated cross section folded with the resolution function of the spectrometer. We are carrying out this procedure.

Further experiments are planned with improved energy and q resolution to determine the form of the $F(q, \omega)$ functions and to determine more accurately the form of $\chi(q)$. An independent measurement of $\chi_{\parallel}$ and $\chi_{\perp}$ without energy analysis of the scattered beam should also be made. This type of experiment avoids part of the difficulty due to the correlation between energy and q , which is always present in a finite energy resolution inelastic experiment. If the energy widths of $F(q, \omega)$ are small, the quasi-elastic approximation can be employed to correct for the inelasticity of the scattering.⁶

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CRITICAL NEUTRON SCATTERING IN DYSPROSIUM

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A neutron scattering experiment has been performed to study the way in which magnetic order in dysprosium develops as the Néel temperature ($T_N = 178^\circ\text{K}$) is approached from above. Just below T_N , dysprosium possesses a helical magnetic structure which produces neutron diffraction peaks at satellites displaced in reciprocal space by $\pm k_0$ along the c direction from each nuclear Bragg reflection peak; k_0 is the wave vector giving the periodicity of the helical structure. Above T_N , regions of short-range helical order in the crystal give rise to broader, less-intense satellite peaks, which result from the critical magnetic scattering.

The neutron cross section for critical scattering above T_N by rare-earth metals with helical ordering may be written in the form ²

$$S(Q, \omega) \propto T(\kappa^2 + \bar{q}^2)^{-1} \cdot \Gamma(Q, T) / [\Gamma^2(Q, T) + \omega^2], \quad (1)$$

where κ is the inverse correlation range, $\Gamma(Q, T)$ describes the time decay of correlations with wave vector Q , T is the temperature, and $\bar{q}$ is a normalized wave vector measured with respect to the satellite position with $\bar{q}^2 = q_x^2 + q_y^2 + a^2 q_z^2$, a being an arbitrary anisotropy parameter. To obtain Eq. (1), the transverse and longitudinal components of the spin correlations are assumed to be equal.

The experiments were carried out on the HB-3 triple-axis neutron spectrometer at the High Flux Isotope Reactor. Beryllium crystals were used as monochromator and analyzer, and $10'$ horizontal and 1° vertical beam collimation was used before and after the sample. For most of the measurements the scattered neutron energy was fixed at 13.64 meV, giving an energy resolution of 0.20 meV. For this neutron energy, graphite filters were placed in the scattered beam to remove possible contamination. The temperature was monitored with a copper-constantan thermocouple with liquid nitrogen as the reference temperature. The temperature was stable to better than 0.05°K .

A few measurements were also made with the neutron energy of 82.7 meV, thereby decreasing the energy resolution to achieve an approximate experimental ω integration of Eq. (1) at each $\bar{q}$ when the spectrometer was set for $\omega = 0$. Intensities measured under these conditions should then vary approximately as $(\kappa^2 + \bar{q}^2)^{-1}$ and therefore should provide some information about κ vs T . Examples of such data are shown in Fig. 4.21 which illustrate the way that the neutron intensity increases as the correlation range κ^{-1} increases when the critical temperature, 177.5°K , is approached. However, the "raw" data in Fig. 4.21 do not give accurate values for κ directly because of the finite q resolution of the spectrometer for which corrections must be made at small q_z .

Instead of correcting the data shown in Fig. 4.21 to obtain $\kappa(T)$, the data obtained with the better energy resolution were used for this purpose. The ω scans carried out at each q_z for a given temperature were fitted by a least-squares procedure to a numerical convolution of the scattering function, Eq. (1), and the resolution function of the neutron spectrometer. These fits give directly $\Gamma(Q, T)$ as well as calculated integrated intensities $I_0(q_z)$, which are proportional to $(\kappa^2 + \bar{q}^2)^{-1}$. Plots of $I_0^{-1}(q_z)$ vs $a^2 q_z^2$ should be straight lines with intercepts equal to $-\kappa^2$. The calculations were iterated until the κ values obtained from the plots were the same as those used in the convolution calculations. The initial calculation for each temperature was carried out with a κ obtained from a crude analysis of data such as that in Fig. 4.21. In addition, this procedure was carried out for various values of the anisotropy parameter a . The linearity of the $I_0^{-1}(q_z)$ vs $a^2 q_z^2$ plots was quite dependent on a . Values of a near 0.5 were the

Fig. 4.21. Intensity of neutrons scattered by dysprosium as a function of temperature and Q_z . Satellite position below T_N is marked by the arrow at $Q_z = 2.24$.

Fig. 4.22. Inverse correlation range vs temperature shown in a log-log plot. The straight line shows a power law $\kappa \propto [(T - T_N)/T_N]^\nu$ for $\nu = 0.63$.

best, in agreement with the conclusions reached in a study of terbium.²

The results obtained for $\kappa(T)$ are shown in Fig. 4.22. κ is found to obey the power law

$$\kappa \propto [(T - T_N)/T_N]^\nu,$$

with $\nu = 0.63 \pm 0.03$. This result agrees with those for terbium² and for the antiferromagnet MnF_2 (ref. 3) and can be compared with 0.5 from molecular field theory.

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MAGNON DISPERSION RELATIONS AND EXCHANGE INTERACTIONS IN THE HELICAL MAGNETIC PHASE OF Dy METAL

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Our study of the temperature dependence of the magnon energies in dysprosium metal has been continued to include the temperature interval over which the helical magnetic structure is stable, that is, between 85°K, the Curie temperature T_C , and 178°K, the Néel

temperature T_N . The experiments were carried out on the triple-axis neutron spectrometer at the HB-5 beam hole of the High Flux Isotope Reactor. The main results are summarized in Fig. 4.23.

The magnon dispersion relation $\hbar\omega(q)$ along the c direction (Fig. 4.23) varies with temperature at high q ($\xi > 0.5$) approximately as the magnetization; that is, as expected, the magnon energies are roughly proportional to the ordered magnetic moment at each temperature. However, the shape of the dispersion relation also changes in a manner which reflects primarily the changes in $J(q)$, the Fourier transform of the exchange interaction, although the temperature dependence of the effective crystal-field anisotropy must also be taken into account in the data analysis.

The results deduced for $J(q) - J(0)$ from the data are shown in Fig. 4.24. These curves, which include the temperature variation of the magnetization mentioned above, show a strong temperature dependence of the positive maximum $J(k_0) - J(0)$, where k_0 ($\xi \sim 0.2$) is the wave vector giving the periodicity of the helical structure. For dysprosium, k_0 varies from $(0, 0, 0.16) 2\pi/c$ at 93°K to $(0, 0, 0.25) 2\pi/c$ at 175°K. The temperature dependence of $J(k_0)$ is even more pronounced when the influence of the magnetization is taken into account.

The stability of the helical structure, as compared with the stability of other possible types of magnetic order, is directly proportional to $J(k_0) - J(0)$. Thus the helical structure of dysprosium is most stable just below T_N . As the magnetization increases with decreasing temperature, this structure becomes less stable; then at 85°K the anisotropy forces, which in dysprosium favor ferromagnetism, produce a phase change to a ferromagnetic structure.

For the rare-earth metals, $J(q)$ is thought to be proportional to $\chi(q)$, the static conduction electron susceptibility. Theoretical calculations² based on free electron energy bands have indicated that the perturbation of the energy bands by a helical magnetic structure does tend to reduce $\chi(k_0) - \chi(0)$ as the magnetization increases, in qualitative agreement with these experimental results. Hopefully in the future it will be feasible to carry out band calculations for the rare-earth metals that include the influence of helical magnetic order. Measurements such as these may then provide one of the more sensitive tests of such theoretical work.

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Fig. 4.23. (a) Magnon dispersion relation for c direction of dysprosium metal as a function of temperature (the Néel temperature is 178°K); (b) Fourier transform of the exchange interaction in dysprosium metal as a function of temperature.

Fig. 4.24. Dependence of magnon energy at $q \approx 0$ on applied magnetic field.

ANISOTROPIC EXCHANGE INTERACTIONS IN DYSPROSIUM METAL

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In a previous neutron scattering study of the magnon energies of erbium metal,² we discovered that the measurements could not be explained unless a very large anisotropic exchange was included in the theory. This result was quite surprising since all previous experimental studies of the heavy rare earths had indicated that the magnetic properties of these metals could be understood quite satisfactorily in terms of an isotropic exchange and a relatively small single-ion anisotropy resulting from crystal-field and magneto-elastic effects. The anisotropy in the exchange could be more easily detected in erbium because of its conical magnetic structure. For such a structure the magnon energies $\hbar\omega(q)$ are given by

$$\hbar\omega(q)/J = \frac{1}{2} [J(k_0 + q) - J(k_0 - q)] \\ \times \cos \theta + \sqrt{F_1 F_2}, \quad (1)$$

where

$$F_1 = J(k_0) - \frac{1}{2} J(k_0 + q) - \frac{1}{2} J(k_0 - q),$$

$$F_2 = F_1 \cos^2 \theta + [J(0) - J(q) \\ + K(0) - K(q) + L] \sin^2 \theta,$$

J is the total angular momentum of each ion, $J(q)$ is the Fourier transform of the exchange interaction, $K(q)$ is the Fourier transform of the anisotropic part of the exchange interaction, L is a linear combination of crystal-field anisotropy parameters, and θ is the angle between the magnetic moment and the c axis. The wave vector of the sinusoidal (helical) component of the conical structure is k_0 .

Since the first term on the right side of Eq. (1) changes sign with q , there are two branches, $\hbar\omega(+q)$ and $\hbar\omega(-q)$, to the magnon dispersion relation. The $J(q)$ function can therefore be determined independently of $K(q)$ from an analysis of the difference $\hbar\omega(-q) - \hbar\omega(+q)$. $K(q)$ can then be evaluated from an analysis of $\hbar\omega(-q) + \hbar\omega(+q)$. The previous measurements² on erbium indicated that $K(q) \gg J(q)$.

For the other most common magnetic structures of the rare earths, the plane helical and ferromagnetic structure, the theoretical expressions for the magnon

energies do not contain terms analogous to that in Eq. (1) which depend only on $J(q)$. For a helical structure, $\theta = \pi/2$, $\cos \theta = 0$, there is only one branch to the dispersion relation, and it is not possible to separate $J(q)$ and $K(q)$ unambiguously.

A similar situation exists for the ferromagnetic structure. However, as pointed out by Møller et al.,³ measurement of the magnon energies of a ferromagnet as a function of applied magnetic field does allow a separation of $J(q)$ and $K(q)$. When a magnetic field H is applied along the easy direction, the magnon energies of a ferromagnetic rare earth can be written

$$[\hbar\omega(q)/J]^2 = [K^{cc}(0) - K^{cc}(q) \\ + F_a + g\mu H] [J(0) - J(q) + F_p + g\mu H],$$

where $K^{cc}(q) = J(q) + K(q)$ represents the total c -axis component of the exchange interaction and F_a and F_p represent the total single-ion axial and planar magnetic anisotropy energies. Thus a measurement of both $\hbar\omega(q)$ and $(d/dH)[\hbar\omega(q)]^2$ as a function of q provides enough experimental information to determine $J(q)$ and $K(q)$ separately.

As an initial investigation of the extent of exchange anisotropy in rare-earth metals other than erbium, the magnon energies in the c direction of dysprosium metal have been measured by neutron spectrometry as a function of applied magnetic field. The measurements were made at 58°K in fields up to 57 kOe with a superconducting magnet and the triple-axis neutron spectrometer located at the High Flux Isotope Reactor. The change in the magnon energies with applied field were generally rather large and easily measured for small q as illustrated in Fig. 4.24 for the case $q \cong 0$. The relative changes observed at other q values were not as large as those shown in Fig. 4.24, nor were the peaks as sharp. In addition, during the course of this experiment, some difficulties were encountered in the field stability. Therefore, the present measurements of $d/dH[\hbar\omega(q)]^2$ have much larger errors than we expect for future experiments. Nevertheless, these first measurements, while somewhat preliminary, indicate that the exchange interaction is quite anisotropic in dysprosium, and they also confirm conclusions reached in an earlier study,⁴ that the single-ion planar anisotropy for dysprosium is considerably larger than that deduced from magnetization measurements.

The results obtained for $K^{cc}(q)$ and $J(q)$ along the c direction are given in Fig. 4.25. It is clear that for most q , $|K(q)| \sim 3|J(q)|$. Similar recent measurements for terbium⁵ indicate $K(q) \sim J(q)$, whereas the previous

Fig. 4.25. Fourier transform of the isotropic and the c -axis component of the exchange interaction for the c direction of dysprosium.

results for erbium² give $K(q) > 10 J(q)$. Thus the anisotropy in the exchange interaction appears to increase along the rare-earth series from terbium to erbium.

Future work will be performed to improve the accuracy of the present results as well as to determine the temperature dependence of the exchange anisotropy in dysprosium. Hopefully, such measurements will shed light on the origin of this anisotropy. In addition, similar measurements will be made on gadolinium, which is the most magnetically isotropic of the rare-earth metals.

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EXCHANGE INTERACTIONS IN TERBIUM-YTTRIUM ALLOYS

R. M. Nicklow

The analysis of previous neutron scattering measurements of the magnon dispersion relations in the c direction for Y(10% Tb) and Y(10% Ho) crystals has indicated that the exchange interaction $J(q)$ of these alloys possesses a prominent peak near the wave vector k_0 that gives the periodicity of their helical magnetic structures.¹ This peak is much larger than any measured for the pure rare-earth metals, which may explain why dilution of all rare earths by yttrium greatly enhances the stability of a helical structure in these alloys.² The main point is that $J(q)$ is believed to be proportional to the conduction electron susceptibility $\chi(q)$, and since calculations³ of $\chi(q)$ for yttrium show a very large peak near $q = k_0$, yttrium-rare-earth alloys probably possess concentration-dependent susceptibilities for which $\chi(k_0) - \chi(0)$ grows with yttrium concentration.

One fairly direct examination of this conjecture may be obtained through a study of the magnon dispersion relations for terbium-yttrium alloys which are terbium rich, and hence still possess ferromagnetic structures at low temperatures. A schematic illustration of anticipated results for such alloys is shown in Fig. 4.26. The dispersion relation for all such alloys will possess a concentration-dependent energy gap at zero wave vector, owing to the crystal-field and magnetoelastic anisotropy interactions. However, a peak in $\chi(q)$ and

Fig. 4.26. Schematic illustration of anticipated magnon dispersion for ferromagnetic Tb(Y) alloys.

Fig. 4.27. Magnon dispersion relation measured for c direction of terbium and Tb(15%Y).

hence in $J(q)$ at $q \cong k_0$ will produce a minimum in the dispersion relation near $q = k_0$. This has already been observed previously for dysprosium⁴ but a minimum does not exist for terbium.⁵ Thus, if a peak in $\chi(q)$ grows with yttrium concentration, a minimum in the dispersion relation should grow with yttrium concentration.

To date, only a few preliminary measurements have been carried out on one alloy, Tb(15% Y). The results obtained are shown in Fig. 4.27, where they are compared with results reported for terbium at 134°K.⁵ These terbium results were chosen in order to compare curves with the same energy gap. As anticipated, the results for Tb(Y) do show a broad minimum, and they deviate most from the terbium results near $\zeta \cong 0.25$, the location of the large peak in the $J(q)$ deduced previously from the Y(10% rare earth) measurements.¹ In the near future, measurements for this alloy will be completed, and measurements on two other alloys, Tb(24% Y) and Tb_{0.5}Y_{0.5}, will be carried out to examine in detail the exchange interaction $J(q)$ for this alloy system.

Since $\chi(q)$ and, hence, $J(q)$ are rather directly related to the conduction electron energy bands, the neutron measurements to be carried out will provide a rare opportunity to compare experimental information and

energy band calculations for a disordered metal alloy. It is hoped that systematic measurements on these materials will provide valuable information about $\chi(q)$ for disordered metal alloys and stimulate further theoretical work in this area.

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TEMPERATURE DEPENDENCE OF THE MAGNETIC EXCITATIONS IN IRON AND NICKEL¹

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The magnetic properties of iron and nickel have been under intensive investigation for many years. The experimental evidence strongly favors the view that the d electrons in these metals occupy relatively narrow energy bands which are itinerant in character, although the strong electron correlations present give rise to some properties which appear similar to the behavior of localized moments. The quantity of fundamental importance in understanding these magnetic systems is the generalized magnetic susceptibility $\chi(\mathbf{K}, \omega)$, which is directly related to the neutron inelastic scattering cross section. In fact, neutron scattering is the only method available which can measure the full general wave vector and frequency dependence of $\chi(\mathbf{K}, \omega)$. Thus, neutron scattering gives us fundamental information about the system which can be obtained with no other method.

Calculations of the generalized susceptibility at low temperatures predict a spin-wave mode at low energies, with a dispersion relation which is approximately given by $E = Dq^2$. At higher energies the intensity of this mode should die out if it enters the region of high density of single-particle Stoner excitations. The low-temperature neutron-scattering results³ have confirmed this overall picture while providing details such as the spin-wave dispersion relations and Stoner-mode-spin-wave intersection points. As the temperature is raised, it was expected that the spin waves should broaden, while the region of high density of Stoner states should decrease in energy. Earlier measurements⁴ showed that,

indeed, the long-wavelength (small q) spin waves do broaden with increasing temperature and become overcritically damped just below T_C . In addition, Lowde and Windsor⁵ observed a "hump" of scattering above T_C in nickel, which is indicative of short-range correlations. However, they were not able to employ enough resolution or neutron intensity to get a clear picture of the overall behavior of $\chi(\mathbf{K}, \omega)$, particularly at the higher temperatures and higher energies.

We have made detailed inelastic neutron-scattering measurements of the magnetic excitations in iron and nickel as a function of temperature. The measurements were carried out on the triple-axis spectrometers at the High Flux Isotope Reactor.

Figure 4.28 shows the spin-wave spectra for Fe(Si) at a series of temperatures. As the temperature is increased toward T_C , the spin-wave dispersion relations lower in energy. In marked contrast to earlier investigations, however, the spin waves outside the immediate vicinity of $q = 0, \omega = 0$ do not become overcritically damped but persist as well-defined excitations up to the highest temperature measured ($1.4T_C$). Above T_C , no further renormalization of the spin waves is observed. Similar

Fig. 4.28. Fe(Si) spin-wave dispersion as a function of temperature.

Fig. 4.29. Spin-wave intensity vs energy for the [111] direction in nickel at a series of temperatures. $T_C = 631^\circ\text{K}$.

behavior is found for nickel. The spin-wave stiffness parameter D for nickel is found to renormalize from $555 \text{ meV}/\text{\AA}^2$ at 4.2°K to $280 \text{ meV}/\text{\AA}^2$ at T_C and then shows no further decrease with increasing temperature (up to $2T_C$).

The spin-wave intensity vs energy curves for various temperatures in the (111) direction of nickel are shown in Fig. 4.29. It is seen that the sudden decrease in the spin-wave intensity, interpreted as the intersection of the spin-wave mode with the Stoner continuum, appears to be insensitive to the temperature. Measurements for Fe(Si) also show this temperature-independent behavior, the intensity for the (110) direction falling off at about 120 meV regardless of the temperature. This was an unexpected result since the splitting of the up- and down-spin bands was expected to vary in a manner proportional to the magnetization, and thus the Stoner excitations were expected to decrease in energy at the elevated temperatures. We notice also that the overall spin-wave intensity is reduced at the higher temperatures.

In addition to the spin-wave intensities and energies, the line widths were also measured. Since the dispersion curves are so steep, even above the transition temperatures, constant- Q scans are impractical. The majority of the data was thus obtained with the energy transfer held a constant and varying q , so that the measured widths are in q rather than in energy. However, these q widths are related to the energy widths through the slope of the dispersion curves. The results of these line-width measurements show that the higher-energy spin waves do broaden considerably as the temperature is raised toward T_C . Above T_C , they continue to broaden slowly in nickel, while in iron they show no additional broadening. In the paramagnetic phase, we found that for $E > \sim 8 \text{ meV}$, $\Delta E/E < 1$, which we have

used as a criterion for the definition of a spin-wave excitation. The widths, as well as the spin wave energies, are found to be isotropic in q for all temperatures.

The experimental results at low temperatures are best described by calculations of the generalized susceptibility based on band structures in which the electron correlations are treated as accurately as possible. The overall agreement between theory⁶ and experiment gives us confidence that the description of the excitation spectrum presented by the band calculations is correct. Calculations of the temperature dependence of $\chi(\mathbf{K}, \omega)$ are much more difficult to do accurately. Generally, the low-temperature theory is used, with the band splitting set proportional to the magnetization. The only temperature-dependent calculations available are the RPA calculations of Lowde and Windsor for nickel, which do seem to correctly show that the scattering outside the immediate vicinity of the critical region evolves smoothly through T_C . However, the detailed agreement between these calculations and our results is poor. The electron correlations at elevated temperatures need to be more accurately incorporated into the theory to produce the strong short-range spin correlations necessary to support propagating modes above the ferromagnetic transition. Clearly more theoretical effort will be needed to bring theory into agreement with experiment.

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MAGNONS AND PHONONS IN COBALT FERRITE¹

H. C. Ten² M. F. Collins² H. A. Mook

Magnons and phonons have been observed in a single crystal of cobalt ferrite, CoFe_2O_4 , at room tempera-

ture. Dispersion relations are plotted for the [001] and the [111] directions. The longitudinal acoustic phonon branch has been measured out to the zone boundary in both directions, while the transverse acoustic branch has been completely determined only in the [001] direction. The acoustic magnon branches are well defined at low energies, but they rapidly lose intensity and disappear at around 9 THz. We have not determined uniquely why this happens, but some possibilities are given. Optic branches have been observed at around 11.3 and 14.0 THz. Infrared data indicate that the first branch is probably of phonon character and the second branch of magnon character.

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MISCELLANEOUS APPLICATIONS

A NEUTRON SCATTERING INVESTIGATION OF THE MOMENTUM DISTRIBUTION OF ^4He ¹

H. A. Mook

When neutrons of sufficiently high momentum transfer Q are scattered from materials, the scattering may be thought of as taking place from individual atoms, and collective effects play no role in the scattering. For most materials the value of the momentum transfer Q needed to be in the single-particle regime is prohibitively high; however, for liquid ^4He , a material of extreme interest, the value of Q necessary is about $15 \text{ \AA}^{-1}$, making experiments difficult but possible with neutrons available from a reactor.²

Therefore, for the case of liquid helium, when the neutron can be thought of as only interacting with a single atom, conservation of energy and momentum for the scattering event gives the following relation for the scattering law $S(Q, \omega)$:

$$S(Q, \omega) = \sum_p n_p \delta(\omega - \frac{Q^2}{2m} - Q \cdot p/m), \quad (1)$$

where m is the helium mass, n_p is the momentum distribution, and p is the momentum of the atom before the collision, and we have let $\hbar = 1$. The above equation is known as the impulse approximation.

In reality the neutron will not interact solely with one helium atom, and final-state effects must be considered. $S(Q, \omega)$ then becomes

$$S(Q, \omega) = \sum_p n_p R(Q, \omega - \frac{Q^2}{2m} - Q \cdot p/m),$$

where

$$2\pi R = \int_{-\infty}^{\infty} dt e^{-i(\omega - Q^2/2m - Q \cdot p/m)t} R(Q, t), \quad (2)$$

and $R(Q, t)$ is a complicated function involving the one-particle and two-particle off-diagonal density matrices² of the liquid.

Evaluating n_p using Eq. (2) is essentially equivalent to obtaining n_p from an experiment performed with finite resolution. $R(Q, t)$ has been evaluated for $15 \text{ \AA}^{-1}$, and the effective resolution introduced by Eq. (3) is comparable with the actual experimental resolution. This results in a resolution in n_p somewhat under $0.5 \text{ \AA}^{-1}$, which is narrow enough to observe a great deal of interesting structure. Therefore, since it is extremely difficult to unfold the resolution from an arbitrary scattering function, the most straightforward approach to utilizing the data is to evaluate n_p directly from Eq. (2).

Thus, replacing the sum in Eq. (2) by an integral, we obtain

$$S(Q, \omega) = \frac{m}{4\pi^2 Q \rho} \int_{p_{\min}}^{\infty} p n_p dp, \quad (3)$$

where ρ is the density and $p_{\min}$ is the smallest momentum which will give the energy loss ω , so that

$$p_{\min} = \frac{\omega - \omega_0}{Q/m},$$

ω_0 being the energy of the peak in $S(Q, \omega)$, or

$$p n_p \Big|_{p_{\min}} = \frac{4\pi^2 Q^2}{m^2} \frac{\partial S(Q, \omega)}{\partial \omega}. \quad (4)$$

Thus $p n_p$ may be obtained directly from the derivative of $S(Q, \omega)$.

Unfortunately, an experiment with a momentum transfer of $15 \text{ \AA}^{-1}$ is difficult in that neutrons with energies $\sim 200 \text{ meV}$ must be used, and the resolution must be good since the width of $S(\omega, Q)$ is only about 15 meV . An experiment to examine the top of $S(Q, \omega)$ for evidence of Bose-Einstein condensation was per-

formed with sufficient accuracy to determine $p n_p$ for the small momentum region near the peak, but this experiment took five months on a triple-axis spectrometer.⁴ The cross-correlation time-of-flight technique makes an experiment to determine all of $S(Q, \omega)$ with high accuracy possible if short enough pulses can be produced. The magnetically pulsed spectrometer at the HFIR can produce $4\text{-}\mu\text{sec}$ pulses for a 1- by $1\frac{1}{2}\text{-in.}$ beam, making it possible to determine $S(Q, \omega)$ accurately with a few weeks counting time.

Since the time-of-flight technique takes data at constant angle rather than constant Q , Eq. (5) must be modified in a complicated but uninteresting way. However, $p n_p$ can still be extracted directly from the neutron measurements. Figure 4.30 shows the cross section $d^2\sigma/d\Omega d\omega \cong (k_f/k_i) S(\omega, Q)$ for helium at 1.2 and 4.2°K ; k_f and k_i are the final and incident neutron wave vectors. The measurement was performed with a resolution of $\sim 3 \text{ meV}$ and a statistical accuracy of $\sim 3\%$.

Values of $p n_p$ for the two temperatures are shown in Fig. 4.31. The distributions show some extremely interesting structure and give fundamental information about ^4He never before obtained. The sharp peak at $\sim 0.25 \text{ \AA}^{-1}$ in $p n_p$ for helium at 1.2°K is observed in no calculated result for $p n_p$, but it is certainly a result of Bose-Einstein condensation. The structure of the condensate contribution is of course not given correctly by the impulse approximation; however, the area should be correct, since the final-state effects should only broaden the condensate. Thus, by using the Kalos computed curve⁵ or any reasonable extrapolation to zero, we can separate the condensate part of $p n_p$ from the rest of the momentum distribution in a straightforward way and determine the condensate fraction. This turns out to be about 1.7% , which is in agreement with earlier measurements.⁴ The rest of the distribution shows structure that cannot be reproduced by calculations performed to date relying on the Jastrow wave function and serves to encourage improved calculations. The data at 4.2°K show the remarkable result that as the temperature is increased the roton excitations at $\sim 2.3 \text{ \AA}^{-1}$ are increased dramatically and that a large number of the helium atoms are participating in these excitations even though the temperature is twice the transition temperature $T_\lambda \sim 2.19^\circ\text{K}$. As expected, very few rotons are observed at 1.2°K . Although one might expect that as heat is pumped into the ground-state system, more and more rotons are created until a maximum number is produced at T_λ , it is surprising that at almost twice T_λ the rotons still remain well-defined excitations.

Once one knows $p n_p$, many properties of ^4He can be determined, because the one-particle density matrix is

Fig. 4.30. The neutron-scattering cross section for helium at 1.2 and 4.2°K for an incident energy of 189 mV and 2% energy resolution.

Fig. 4.31. pn_p for helium at 1.2 and 4.2°K. The dashed line is a Monte Carlo calculation by Kalos and represents the best theoretical estimate of pn_p available.

given directly by the Fourier transform of pn_p . Only one easily obtained thermodynamic property, that is, the average kinetic energy per helium atom, will be mentioned. This is a bulk property of the liquid and not particularly sensitive to the detailed structure in pn_p . Previous estimates for this quantity, based on the half width of $S(Q, \omega)$ as determined by Harling for 1.2 and 4.2°K, are $(13.02 \pm 0.5)^\circ\text{K}$ and $(15.71 \pm 0.5)^\circ\text{K}$ respectively.⁶ By evaluating the mean squared momentum from the pn_p curves, we obtain a $\overline{KE}$ of $13.2 \pm 0.1^\circ\text{K}$ and $16.9 \pm 0.1^\circ\text{K}$ from the 1.2 and 4.2°K

data respectively. This result is in good agreement with the early result of the 1.2°K; the slightly higher energy obtained at 4.2°K is probably the result of the earlier authors' underestimating the number of atoms participating in the roton excitations.

To summarize, an experiment has been performed with sufficient accuracy and momentum transfer that pn_p has been obtained for ^4He at two temperatures. The distributions, pn_p , show features not predicted by theoretical calculations, and the distribution at 1.7°K shows direct evidence for a condensate. The one-particle density matrix is directly obtainable from the pn_p data and may be used to obtain any desired property of ^4He for the two temperatures.

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NEUTRON SCATTERING FROM VOIDS IN IRRADIATED MATERIALS

H. A. Mook

It has been found that materials swell appreciably when subjected to large doses of radiation such as that found in the core of a nuclear reactor. It has been shown that this swelling could mean an additional cost of several billions of dollars in the cost of fast breeder reactors planned for the United States alone by the year 2000. The swelling is the result of small voids being formed in the materials, and the voids when large enough may be studied with electron microscopes. It was felt that small-angle neutron scattering could also be used to complement the electron microscope observations. In fact, small-angle scattering has some advantages over the electron microscope in that the sample need not be sectioned into thin slices and very small voids may be observed rather easily. Also, the void size distribution can be obtained rather accurately with small-angle scattering in relatively short times, while a large number of voids must be counted with the microscope to get a size distribution with good statistical accuracy. Small-angle x-ray scattering has been used to measure size distributions for many systems, and techniques for making the measurements are well established. However, there are difficulties associated with using small-angle x-ray scattering for observing voids; the x rays do not penetrate the materials of interest unless short wavelengths are used, and then problems with multiple scattering make interpretation of the results difficult. It was thus decided to undertake a demonstration-type experiment to confirm that neutrons could indeed be used to study the voids and that the necessary mathematical formalism could be developed to interpret the data.

The scattering of neutrons from voids in a material is the same as scattering from small particles of the material of interest, and the scattering strength is proportional to the nuclear-scattering cross section of the material. To begin with, let us assume that the voids are spherical and of radius R . If there are N scattering sites per cubic centimeter, the scattering cross section per unit solid angle from an isolated void is then given by

$$\frac{d\sigma}{d\Omega} = N^2 \frac{\sigma_b}{4\pi} \left| \int e^{i\mathbf{k} \cdot \mathbf{r}} dV \right|^2, \quad (1)$$

where σ_b is the coherent neutron cross section, k is the neutron wave vector, and V is the void volume.

Performing the integration we obtain

$$\frac{d\sigma}{d\Omega} = N^2 \frac{\sigma_b}{4\pi} V^2 G^2(kR), \quad (2)$$

where

$$G^2(kR) = \frac{9\pi}{2} \frac{J_{3/2}^2(kR)}{(kR)^3}.$$

For a distribution of spherical voids of various sizes,

$$\frac{d\sigma}{d\Omega} = N^2 \frac{\sigma_b}{4\pi} \int_0^\infty N_v(R) V^2 G^2(kR) dR, \quad (3)$$

where $N_v(R)$ is the void-size distribution. If we have an incident neutron intensity of I_0 , the number of scattered neutrons is then given by

$$I(k) = I_0 V_s \frac{\sigma_b}{4\pi} \int_0^\infty N_v(R) V^2 G^2(kR) dR, \quad (4)$$

with V_s being the sample volume.

We wish of course to obtain the size distribution $N_v(R)$ for a measured $I(k)$. This can be obtained by taking Mellin transformations of Eq. (4), with the result that

$$N_v(R) = \frac{8}{I_0 V_s \sigma_b 3\sqrt{\pi} d\Omega R^3} \times \int_0^\infty k^3 I(k) \xi(kR) dk, \quad (5)$$

where

$$\xi(kR) = \frac{1}{\sqrt{kR}} \{ [2 - (kR)^2] J_{3/2}(2kR) - 3/2 J_{1/2}(2kR) \}. \quad (6)$$

We thus have a formal solution of the scattering problem and can find the void distribution from a neutron small-angle experiment. It is found in practice in some cases, however, that the voids are elliptical in nature. The scattering problem is more complicated in this case, but nevertheless it is quite solvable. The result for the scattering intensity from a void distribution with voids of major axes R , R , and ηR , assuming a

Maxwellian size distribution

$$M(R) \sim (R/R_0)^n e^{-(R/P_0)^2},$$

is

$$I(k, \eta) \sim \frac{\sum_{m=0}^{\infty} (2)_m [(n+4)/2]_m - (R^2 k^2)^m}{m! (4)_m (5/2)_m} \times {}_2F_1(-m, 1/2, 3/2; 1 - \eta^2), \quad (7)$$

where $(\alpha)_m = \alpha(\alpha+1) \dots (\alpha+m-1)$

and F is a generalized hypergeometric function. In the elliptical void case the distribution of void sizes and shapes must be found numerically, but the required sums of hypergeometric functions are easily performed on a computer.

Since the void distributions can thus be obtained from small-angle scattering results, it is necessary only to find a way to perform the neutron measurement. The scattering distribution from a single void is proportional to $G(kR)$ in Eq. (2) and is at half maximum when $kR \sim 2.5$. Since $k = 4\pi \sin \theta/\lambda$, one needs to use long wavelengths or small scattering angles to resolve large voids. Unfortunately, there is no cold neutron source at the ORNL reactors, so we are forced to find a way to measure very small angles. This, in fact, turns out to be easy if one goes about it correctly. Double reflection from perfect crystals in the parallel geometry can yield line widths of a few seconds of arc yet yield high neutron intensity, since neutrons of different wavelengths all contribute to the reflection. If a sample is placed in between the perfect crystals, the small-angle scattering can be easily observed as a broadening in the line width. To test this idea for measuring small-angle scattering from voids, a small-angle spectrometer utilizing perfect germanium crystals was installed at the ORR. In conjunction with R. W. Hendricks of the Metals and Ceramics Division, a series of aluminum crystals was irradiated in the HFIR with different fluences. The small-angle scattering from these crystals could easily be observed over four orders of magnitude, and void size distributions were determined. The scattering measurements were compared with results obtained with a long-wavelength source at Jülich, and good agreement was obtained. The Jülich results suggested that we should carry our measurements to somewhat smaller k in order to get more accurate distributions. These measurements (in progress) are

easy, because the scattering is large in the forward direction.

We feel the perfect-crystal technique is an excellent method of measuring small-angle scattering distributions, especially where a supply of abundant long-wavelength neutrons is not available. The technique would be ideal for studying radioactive samples, since the crystal need not sit on a spectrometer but only between the perfect crystals, so that shielding could easily be installed around the sample position. The neutron scattering from voids in steel would be ten times as strong as for aluminum, since the coherent cross section is ten times as large; thus the small-angle technique would be even more sensitive for steel than for aluminum.

In summary, both the mathematical techniques and the experimental facilities have been developed to study voids in irradiated materials. Systematic studies of samples with various impurities and radiation doses could thus increase our understanding of void formation in materials of interest.

DETERMINATION OF THE PHONON DENSITY OF STATES FOR POLYCRYSTALLINE OR AMORPHOUS MATERIALS

H. A. Mook

The density of phonon states, $g(\nu)$, can usually be determined for a material by measuring the phonon dispersion curves and fitting a force-constant model to the results. Various mathematical techniques can then be used to extract $g(\nu)$ from the model. In some cases, however, this is impossible because the material cannot be crystallized into a sample large enough to make phonon measurements or the sample is noncrystalline in nature, or amorphous. In this case, $g(\nu)$ can be measured from a polycrystalline sample or an amorphous sample directly by measuring the coherent inelastic scattering for a large number of momentum transfers. This is particularly easy to do with a time-of-flight spectrometer, as a large number of detectors can be used and many different momentum transfers measured simultaneously. A sum over all the detectors then gives a quite accurate picture of $g(\nu)$ if the momentum transfer is sufficiently large. Sometimes it is necessary to cool the sample to avoid multiple-phonon scattering. The phonon density of states is then given by

$$g(\nu) = \alpha(E_0 - E') \frac{k_0}{k'} \frac{1}{e^{-2W}} \nu (e^{h\nu/k_B T} - 1), \quad (1)$$

where $\sigma(E_0 - E')$ is the measured inelastic cross section summed together for all scattering angles, k_0 and k' are the incoming and outgoing neutron wave vectors, respectively, and W is the Debye-Waller factor.

The $\sigma(E_0 - E')$ has been measured for several samples using the magnetically pulsed time-of-flight spectrometer, and the $g(\nu)$ have been determined using Eq. (1). Investigations on only two of these samples will be mentioned, and the results for both of them are preliminary, since we have only recently acquired enough neutron detectors to make the technique worth while. The first of these samples is amorphous germanium and has been worked on in conjunction with John Axe of Brookhaven National Laboratory. Only about 1 cm³ of the material could be obtained, since it is difficult to make the material in the amorphous state. Time-of-flight measurements were made on both polycrystalline and amorphous samples and $g(\nu)$ determined for each. The polycrystalline $g(\nu)$ was compared with results from models obtained from phonon measurements in single crystals, and the agreement was quite good. It was found that the $g(\nu)$ for the amorphous sample looked quite similar to that for the crystalline sample except for small shifts in some of the energies. It had been predicted from heat capacity data that the peak in the density states from the acoustic mode should be 75% lower in the amorphous material. This was confirmed, as this peak came at 13.5 meV in the solid and 10.25 meV in the amorphous material. Further work is under way to compare the measured $g(\nu)$ with various calculations for the frequency distribution of the amorphous material.

Some temperature-dependent data have been taken on the organic material TTF TCNQ. In this case, some of the scattering is incoherent, and Eq. (1) does not strictly apply. However, the result of using Eq. (1) will give a distribution closely related to $g(\nu)$, so that temperature-dependent effects can be studied. Data have been taken at room temperature and at temperatures just above and below the large resistivity anomaly at about 60°K. Little change in $g(\nu)$ was seen between room temperature and 77°K; however, a large change in $g(\nu)$ was observed between 77 and 47°K. This change is in the high-frequency part of $g(\nu)$ and is quite possibly indicative of a phase change. Many studies of TTF TCNQ have been made at various laboratories with x rays in search of a phase change, but none was observed. Perhaps the phase change involves the hydrogen atoms only and is not visible with x rays. A phase change has been suggested as a mechanism for the large conductivity, and thus it would be interesting if such a change could be confirmed. Other small effects have

been seen in $g(\nu)$ at low frequencies, but interpretation of these effects is still in question. Further measurements are in progress at this time.

EXCHANGE-SPLIT CRYSTAL FIELD LEVELS OF Fe²⁺ IN FeCO₃

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Ferrous carbonate is a uniaxial antiferromagnetic material which has been postulated³ to be an ideal Ising system. The strong magnetic anisotropy that the iron ions exhibit arises from a predominately cubic crystal-line electric field with a smaller trigonal component. The magnetic excitations at low temperatures were found to be dispersionless over the entire Brillouin zone, except where magnon-phonon coupling occurred.⁴ The absence of dispersion in the magnon branch is indicative of an Ising excitation and means that the magnons are not really propagating modes but rather single-ion excitations.

We have made neutron time-of-flight measurements of the low-lying crystal field levels above and below the Néel temperature ($T_N = 38.4^\circ\text{K}$) on both a natural single crystal and pure synthetic powder. At 4.2°K the principal allowed excitation was measured to be 13.8 meV, in good agreement with previous neutron⁴ and far-infrared⁵ measurements. A second, much less intense line was observed at 20 meV. This was seen in the infrared measurements but not in the earlier neutron measurements. A third excitation at 3.1 meV was found in the natural crystal only and was attributed to known Mn²⁺ impurities in that sample. Above T_N , only a single excitation at 10.6 meV was observed.

The measured excitation energies and transition probabilities can be understood in terms of a single-ion model. The free-ion Fe²⁺ ground state (⁵D) is first split by the large cubic crystal field into a doublet ⁵E and triplet ⁵T₂, separated by ~1250 meV with the triplet lying lowest. In the 15-fold degenerate ⁵T₂ manifold, the Hamiltonian can then be written as

$$H = \lambda \mathbf{L} \cdot \mathbf{S} + D I_z^2 - H_M \langle S_z \rangle$$

representing the spin-orbit interaction, trigonal distortion, and Ising molecular field, respectively. This can then be solved numerically, yielding a consistent picture of the magnetic excitations in FeCO₃.

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NEUTRON MEASUREMENT OF CRYSTAL-FIELD SPLITTINGS IN TmAs AND TmBi¹

H. L. Davis H. A. Mook

A knowledge of the crystal field acting in a rare-earth-based solid is not only useful in helping to provide a consistent "explanation" for some of the solid's physical properties (e.g., magnetic susceptibility and specific heat) but may also be valuable in determining which fundamental processes dominate in the formation of the solid's electronic structure. For these and other reasons, we have employed inelastic neutron-scattering techniques to determine the crystal-field splittings of the 3H_6 ground multiplet of Tm^{3+} ($4f^7$) in the compounds TmAs and TmBi. Both of these compounds are metallic and have the NaCl-type structure.

Neutron data were obtained using the ORNL magnetically pulsed time-of-flight spectrometer. With this in-

strument, after pulsing and monochromating, the neutron beam is then scattered by the sample and detected by 3He detectors. Cross-correlation techniques are then applied between the time distribution of neutrons arriving at the detectors and the pulsing signal to obtain data in the form of counts vs time-of-flight channel (or energy). Data obtained at 4.2 and 78°K for TmAs and TmBi when employing an incident neutron energy, E_i , of 13.1 meV are displayed in Figs. 4.32 and 4.33. The energies of the data points correspond to the average times of the time channels, with a positive (negative) energy representing neutrons gaining (losing) that amount of kinetic energy. The zero-energy peaks correspond to elastically scattered neutrons due to nuclear elastic scattering processes and to quasi-elastic crystal-field scattering.

At the top of Figs. 4.32 and 4.33 are indicated crystal-field transitions found to be responsible for the features seen in the data. These transitions were determined by a theoretical analysis which fitted the data to a model based on the crystal-field Hamiltonian²

$$H = W \{ [x/F(4)] O_4 + [(1-x)/F(6)] O_6 \} \quad (1)$$

Fig. 4.32. Neutron results for TmAs.

Fig. 4.33. Neutron results for TmBi.

and the cross-section formula³ for the neutron scattering,

$$\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} \sim (k_f/k_i) F^2(Q) \times \sum_{n,m} \rho_n |\langle n | J_1 | m \rangle|^2 \delta(\epsilon_{nm} - \hbar\omega). \quad (2)$$

For a given compound and temperature, fitting the data to the model basically involved varying three parameters until the best fit was obtained. These parameters are the crystal-field parameters W and x and a level-width parameter to introduce the same amount of Gaussian energy smearing of each of the crystal-field levels Γ_i . These procedures have led to fits of the TmAs and TmBi data resulting in "goodness of fit" values of less than 2.5 for all data sets considered in this investigation. Parameters obtained for the 78°K data sets are given in Table 4.5.

The quantities $A_4 \langle r^4 \rangle$ and $A_6 \langle r^6 \rangle$ in Table 4.5 are related to W and x via $A_4 \langle r^4 \rangle \chi_4 F(4) = Wx$ and

Table 4.5. Parameters derived from 78°K neutron data

	TmAs	TmBi
x	-0.79 ± 0.02	-0.81 ± 0.03
W , meV	-0.106 ± 0.002	-0.0736 ± 0.0025
$A_4 \langle r^4 \rangle$, meV	8.55 ± 0.15	6.09 ± 0.15
$A_6 \langle r^6 \rangle$, meV	0.53 ± 0.06	0.33 ± 0.07
a , Å	5.711	6.192
Z_4	2.05	2.19
Z_6	7.01	7.77

$A_6 \langle r^6 \rangle \chi_6 F(6) = W(1 - |x|)$, where χ_4 and χ_6 are reduced matrix elements. The Z_i are effective charges (in units of e) which must be used in a nearest-neighbor point-charge model to reproduce the empirical $A_i \langle r^i \rangle$. It is seen that the charges Z_4 fall in the range 2 to 3, which might be expected from simple chemical-valency

considerations. Thus, a simple point-charge model has some success in accounting for certain features of the crystal fields of these compounds. The reason for this partial success is not understood, and it is indeed puzzling if one considers the many mechanisms which might be expected to make a point-charge model inoperative in metallic compounds. However, the Z_6 values are seen to be considerably larger than expected from valency considerations, which may be a reflection of some of the electronic structure complications expected in these metallic systems. But the large Z_6/Z_4 ratio found for these thulium compounds appears unusual when compared with the approximately unity ratio values observed^{4,5} for PrX (X = N, P, As, Sb, Bi, S, Se, and Te) compounds. This difference in ratio may indicate some significant change in electronic structure between PrX and TmX compounds, and it is of interest to determine whether such a difference exists between the semiconducting PrN and TmN. For this and other reasons, we are presently investigating the crystal-field splittings in TmN.

1. Summary of paper: Proceedings of the 1973 Conference on Magnetism and Magnetic Materials (in press).

2. K. R. Lea, M. J. M. Leask, and W. P. Wolf, *J. Phys. Chem. Solids* 23, 1381 (1962).

3. P. deGennes, p. 115 in *Magnetism*, vol. 3, ed. by G. T. Rado and H. Suhl, Academic Press, New York, 1963.

4. K. C. Turberfield, L. Passell, R. J. Birgeneau, and E. Bucher, *J. Appl. Phys.* 42, 1746 (1971).

5. H. L. Davis and H. A. Mook, *AIP Conf. Proc.* 10, 1548 (1973).

A MAGNETICALLY PULSED NEUTRON TIME-OF-FLIGHT SPECTROMETER FOR INELASTIC SCATTERING¹

H. A. Mook¹ F. W. Snodgrass² D. D. Bates²

A time-of-flight spectrometer utilizing a magnetically pulsed beam has been placed in operation at the High Flux Isotope Reactor at the Oak Ridge National Laboratory. The pulsing is accomplished by rapidly changing the magnetic-moment direction in a ferrite crystal that serves to both monochromate and pulse the beam. Good neutron reflectivity is obtained from the ferrite crystal, and pulse rise times on the order of 1 μ sec are available. The spectrometer is interfaced to a Digital Equipment Corporation PDP-15-30 computer which drives pulsed motors to set up the desired scattering geometry and collects and analyzes the time-of-flight data. The magnetically pulsed beam is ideal for use with the cross-correlation technique, and spectra are presented which show the accuracy of the pulsing technique and the power of the cross-correlation methods in obtaining neutron scattering data.

1. Abstract of paper: *Nuclear Instruments and Methods*, in press.

2. Instrumentation and Controls Division.

5. Research Materials

The purpose of the Research Materials Program is to develop the necessary techniques required for the growth of ultrahigh-purity and controlled-impurity research specimens of immediate and long-range interest to ORNL and to other AEC installations and contractors. Progress in understanding the fundamental properties and the ultimate range of properties in many materials has been severely limited in the past by the lack of pedigreed specimens of high purity and perfection. The use of single crystals is required in many experiments for the unambiguous characterization of various physical phenomena. Since suitable crystals are frequently not available commercially, we are conducting a continuing program both to provide crystals as needed in research and to devise and improve methods for producing better crystals.

The actual choice of materials for crystal growth has been based primarily on the potential gain to a fundamental understanding of solids and on an expressed need by investigators for a specific research material. Certain research materials that have not been investigated previously are now being produced, and new techniques of purification and crystal growth have been applied. As examples, we have produced single crystals of germanium of sufficient purity that lithium-drift compensation was not required to fabricate solid-state radiation detectors. Isotopes of lithium and nickel of low neutron absorption cross section have been utilized in the growth of single crystals of ferrites for magnetic beam pulsing and polarization in a time-of-flight neutron spectrometer. The program on purification of refractory-metal single crystals has been extended to include the preparation of dilute refractory-metal alloy foils as standards for comparative radiation damage experiments for the controlled thermonuclear reactor (CTR) program.

Information concerning the preparation, availability, and physical properties of high quality research materials has always been difficult to obtain; hence, the Research Materials Information Center was established as a part of the Research Materials Program to collect and provide information to both producers and users on the initial purification, crystal growth, characterization, and availability of research-quality materials. The ready availability of an accurate and up-to-date listing of research materials has served to eliminate much duplication of effort by individual research groups in attempting to produce materials that were already available elsewhere. The simultaneous listing of those research materials that are desired but are not available, has served to focus the attention of crystal growers on new areas of investigation.

Perhaps the most important technical accomplishment of the Research Materials Program has been an enhanced cooperation between analytical chemists, neutron activation specialists, mass spectrographers, crystal growers, and crystal property researchers in a continuing exchange of samples and information on improved materials. Any improvement in the technique of one group is reflected in the subsequent data and analyses of the other groups. The presence of unexpected impurities or the pronounced effect of certain impurities has sometimes been revealed only by using various analytical techniques, different procedures in crystal growth, and numerous physical-property measurements on one select group of specimens.

RESEARCH MATERIALS PROGRAM

J. W. Cleland

The purpose of this program is to develop techniques as required for the initial purification, crystal growth, and characterization or analysis of research specimens of a size and quality as required in programs on

materials research of interest to the AEC. The Research Materials Information Center assists in identifying those materials for which a need exists, and in supplying information on materials already available. Selected samples are loaned to cooperating research groups for comparative measurements that aid in characterizing these materials. Examples are listed in Table 5.1.

Table 5.1. Loan of single crystals for research outside the Research Materials Program during 1973

Material	Type of study	To whom sent	Organization
Nb	Plastic deformation	R. J. Arsenault	University of Maryland
Nb	Irradiation damage	C. W. Chen	Iowa State University
Ta	Ultrasonic attenuation	R. W. Reed	Pennsylvania State University
Nb	Plastic deformation	J. P. Hirth	Ohio State University
V	Irradiation damage	G. L. Kulcinsky	University of Wisconsin, Madison
Nb	Superconductivity-flux pinning	M. P. Mathur	Westinghouse R & D Center
V	Superconductivity	R. W. Cernberg	Adelphi University
Nb, Nb-Mo, V	Ultrasonic attenuation	M. Levy	University of Wisconsin, Milwaukee
Al, Cu	Plastic deformation	A. Wolfenden	Physics and Engineering Laboratory, New Zealand
Nb	Irradiation damage	B. S. Brown	Argonne National Laboratory
Nb	Low-temperature specific heat	V. Novotny	University of Toronto
V	Irradiation damage	R. L. Chaplin	Clemson University
Fe	Alloy development	W. D. Grisham	ORNL
Ni, Mo, Zr-B, Ti-B, Nb-B, V-B, Ni-B	Neutron irradiation damage	K. Farrell	ORNL
Nb-V	X-ray diffraction	C. J. Sparks	ORNL
Ni, Fe-Si, Sc, Tb-Sc, Fe	Neutron diffraction	W. C. Koehler	ORNL
Tb-Y	Neutron diffraction	R. M. Nicklow	ORNL
Pb	Mössbauer experiments	F. Obenshain	ORNL
Nb	Superconductivity	S. T. Sekula	ORNL
Ir	Alloy development	A. C. Schaffhauser	ORNL
V-Zr, Nb-Zr, Mo-Zr	Irradiation damage - CTR	V. Schilling	KFA, Jülich, Germany
V-Zr, Nb-Zr, Mo-Zr	Irradiation damage - CTR	H. H. Anderson	Aarhus University, Denmark
V-Zr, Nb-Zr, Mo-Zr	Irradiation damage - CTR	R. Borg	Lawrence Livermore Laboratory
Nb-Zr, V-Zr, Mo-Zr	Irradiation damage - CTR	R. R. Coltman	ORNL
Nb	Charged-particle backscattering	F. W. Young	ORNL
High-purity Ge slices	Experimental purposes	J. H. Crawford	University of North Carolina
High-purity Ge slices	Experimental purposes	J. W. Mayer	University of California
High-purity Ge slices	Experimental purposes	G. Armantrout	Lawrence Livermore Laboratory
Ge slices and crystals	Triple-axis spectrometer application	H. Wenzel	Jülich, Germany
Gallium-doped germanium	Sputtering source for thermometer application	J. E. Simkins	Y-12 Thermonuclear
RbCaF ₃	Color centers and birefringence	E. Sonder	ORNL
RbCaF ₃	Color centers and birefringence	F. A. Modine	ORNL
RbCaF ₃	EPR and dielectric studies	W. P. Unruh	ORNL and University of Kansas
RbCaF ₃	Specific heat	J. Ho	Wichita State University
RbCaF ₃	NMR	P. Mahendroo, N. S. K. Menon	Texas Christian University
KCl	Thermoluminescence	J. Felszerváti	Kossuth University, Hungary
Li _{0.23} Ni _{0.3} Fe _{2.45} O ₄	Elect. microscopy	D. Newbury	NBS
Fe ₃ O ₄ , Fe ₂ O ₃	Elect. resistivity	N. Platakis	IBM Corp.
Li _{0.16} Fe _{2.84} O ₄	Neut. diffr.	N. S. Satya Murthy	Bhabha, India
MgO	Optical	R. B. Murray	University of Delaware
CaO:Cu	EPR	R. W. Reynolds	Advanced Technology Center, Dallas, Texas
CaO:Cu	Raman	L. L. Chase	Indiana University

RESEARCH MATERIALS INFORMATION CENTER

T. F. Connolly

In 1973 the Research Materials Information Center answered 390 inquiries involving about 1000 separate questions. The majority of the questions concerned preparation and properties of solid-state materials rather than the availability of research specimens.

A contract has been received from the Office of Standard Reference Data of the National Bureau of Standards for assistance in the critical evaluation and publication of a compilation of the refractive indices of inorganic solid materials. L. A. Harris¹ is on loan part time to evaluate the optical data.

1. Metals and Ceramics Division.

PURIFICATION OF MOLYBDENUM AND TANTALUM BY USING OXIDIZING ATMOSPHERES DURING ELECTRON BEAM FLOAT ZONE MELTING

R. E. Reed E. D. Bolling

Earlier work on the purification of niobium¹ showed that carbon could be removed during electron beam float zone melting (EBFZM) in a 10^{-5} - to 10^{-6} -torr oxygen pressure. This technique has now been extended to tantalum and molybdenum. In the case of tantalum, as with niobium, this treatment also had to be followed by a high-temperature, ultrahigh-vacuum anneal in order to outgas the oxygen. For molybdenum, it was found that the outgassing anneal was not necessary.

Tantalum dendritic powder obtained from Ciba Corp., Summit, New Jersey, was arc cast into a finger ingot and swaged to 6.35-mm-diam rod about 250 mm long. The rod was then given two EBFZM passes at 100 mm/hr in 7×10^{-9} torr pressure. Carbon was not removed during this treatment, as shown in Table 5.2. However, two passes in 1×10^{-5} torr oxygen pressure reduced the carbon readily but left the material with a high oxygen content. Subsequent outgassing anneals at temperatures over 2000°C and pressures below 10^{-9} torr resulted in 6-mm-diam tantalum single crystals, 5 cm long, with resistance ratios near 4000 and a total impurity content below 50 wt ppm.

The effect of the two-EBFZM-pass oxygen treatment upon molybdenum was the same. The carbon content was reduced to 10–15 wt ppm from starting levels in the 40–50 wt ppm range. Two EBFZM passes at 100 mm/hr in 3×10^{-9} torr pressure did not have such a large effect. Table 5.3 lists the impurity contents

Table 5.2. Effect of thermal treatments upon the interstitial impurity content in tantalum

Treatment	Impurity content (wt ppm)				Resistance ratio
	C	O	N	H	
1. As swaged	66	160	43	4	
2. As EBFZM	66	19	6	4	125
3. As EBFZM in O ₂	13	85	7	8	
4. 3 + outgassed 2000°C, 17 hr, 2×10^{-9} torr	10	39	3	<1	2370
5. 3 + 4 + outgassed 2350°C, 28 hr, 3×10^{-10} torr	12	27	<1	<1	3950

Table 5.3. Effect of thermal treatments upon the impurity content in molybdenum

Treatment	Impurity content (wt ppm)						Resistance ratio
	C	O	N	H	Ta	W	
1. Starting material	47	140	<1	10	1	85	
2. As EBFZM in 3×10^{-9} torr	24	14	<1	<1	2	117	577
3. As EBFZM in 1×10^{-5} torr oxygen	13	17	<1	<1	2	120	7315
4. 3 + annealed at 2100°C, 19 hr, in 5×10^{-10} torr	14	22	2	<1	2	120	6507

resulting from the various treatments. It should be noted that the outgassing anneal had essentially no effect upon the purity of the molybdenum single crystals. Single crystals 3.5 mm in diameter and 200 mm long with resistance ratios about 7000 were readily produced using only the EBFZM oxygen treatment.

1. R. E. Reed, *J. Vac. Sci. Technol.* 9, 1413 (1972).

GROWTH OF ⁵⁷Fe–3 wt % Si SINGLE CRYSTALS

R. E. Reed E. D. Bolling H. E. Harmon

A large single crystal of ⁵⁷Fe–3 wt % Si alloy was obtained by grain growth annealing. The iron metal, 90% enriched in ⁵⁷Fe, was received as a loosely sintered powder. This material was arc melted into fingers about 12 mm in diameter and 120 mm long, which were then swaged to 6-mm-diam rods. Zone-refined silicon was arc melted with the ⁵⁷Fe metal to obtain one 50-g button

Fig. 5.1. Berg-Barrett topograph of a 1% Fe- α silicon alloy single crystal using copper $K\alpha$ radiation from a (310) reflection.

and one 60-g button, approximately 30 mm in diameter and 6 mm thick, of ^{57}Fe 3.0 wt. % Si composition.

The arc cast buttons were sealed in tantalum cans containing an argon atmosphere, and the smaller specimen was then annealed at 1400°C for 140 hr. Although grains on the order of 1 cm in diameter were obtained, the sample was not judged suitable for neutron diffraction studies. Thus the 60-g button was annealed at a higher temperature of 1440°C for 144 hr. The resulting button was essentially one single crystal, although two small surface grains less than 3 mm in diameter were subsequently noted and another grain about 6 mm in diameter was on the edge of the button. The button surface was near to a (001) plane, and this preferred orientation also existed on the smaller sample. Berg-Barrett x-ray reflection topographs taken on the single crystal revealed good perfection, with large subgrains on the order of 1 cm in diameter and a total misorientation of less than $2'$ across the single crystal. The Berg-Barrett topographs also exhibited a fine grid of parallel lines with a spacing of about 0.1 mm which has been attributed to magnetic domain structure. A Berg-Barrett topograph taken using copper $K\alpha$ radiation from a (310) reflection is shown as Fig. 5.1. The scale of this topograph can be determined from the fact that the button was 33 mm in diameter.

This work will continue until enough suitable single crystals are available for use as polarizing neutron monochromators. The ^{57}Fe 3 wt % Si single crystals have the potential of providing more polarized neutron intensity than is presently available from Co 8% Fe monochromators now in use.

THE GROWTH OF RARE-EARTH-METAL ALLOY SINGLE CRYSTALS

R. E. Reed E. D. Bolling H. E. Harmon

The grain growth annealing technique previously developed¹ for the growth of large (2 to 4 cm³) single crystals of rare-earth metals has been extended to rare-earth-metal binary alloy systems. The general method consists in first arc melting in a special ultraclean facility a 40- to 50-g button, approximately 30 mm in diameter and 5 mm thick, of the desired alloy using high-purity distilled metal starting material. The cast button was sealed in a tantalum can filled with argon, which was then heated by induction to a temperature near the solidus temperature, if there was no solid-phase transformation in the binary system. In

general, there was no solid-solid phase transformation; thus the annealing temperature was held below this transition temperature. If the phase diagram was not known, linear interpolation was used to estimate these temperatures. The anneals were maintained for times of about 100 hr.

Single crystals large enough for neutron diffraction studies (volume more than 2 cm³) were successfully grown by this method for the following binary systems: Y-Dy, Y-Er, Tb-Sc, and Tb-Y. As an example, Figs. 5.2 and 5.3 show the front and back side of a Y-1.0 at. % Er alloy button that had been annealed at 1440°C for 96 hr. The resulting sample was a bicrystal with the grain boundary running through the button perpendicular to the large face. Such crystals were suitable for subsequent neutron diffraction studies.

1. R. E. Reed and W. D. Graham, *Nucl. Instrum. Methods* 102, 513 (1972).

Fig. 5.2. A Y-1 at. % Er arc-cast button annealed at 1440°C for 96 hr. Note grain boundary running diagonally across the specimen. Magnification: 2.7x. Reduced 9.5%.

Fig. 5.3. The reverse side of the same specimen shown in Fig. 5.2. Magnification: 2.7X. Reduced 5%.

ELECTRON BEAM FLOAT ZONE MELTING OF IRIIDIUM

R. E. Reed A. C. Schaffhauser¹

Iridium powder that had been electron beam melted and hot rolled into 0.81-mm-thick sheet was further processed by electron beam float zone melting (EBFZM) in order to attain higher purities. Both pure iridium and Ir + 0.3 wt % W materials were treated. Sheared sections of the sheet were tack welded in a glove box to obtain bundles approximately 6.35 mm square by 150 mm long. These specimens were then given 6 to 12 EBFZM passes at 100 mm/hr either in high vacuum or at 1×10^{-5} torr oxygen pressure. The resulting single crystals were evaluated by spark source mass spectrometry for substitutional impurities, vacuum fusion and leco combustion techniques for interstitial impurities, and resistivity measurements for all overall indication of purity.

There was no significant movement of impurities by zone refining. However, there was an overall loss of

impurity elements whose vapor pressure at the melting point of iridium was higher than that of iridium. The concentration of all elements except Mo, Nb, Os, Ta, Re, and W was reduced by both treatments. The oxygen treatment during EBFZM resulted in the same purity levels as EBFZM at pressures as low as 1×10^{-5} torr when the chemical analyses were compared. However, the oxygen treatment improved the resistance ratio of the pure iridium starting material. High-temperature (2150°C) annealing in ultrahigh vacuum (2×10^{-7} torr) subsequent to an EBFZM oxygen treatment lowered the resistance ratio, although chemical analyses showed no significant change. Typical results would be resistance ratios of 27, 51, and 41 for high-vacuum EBFZM, EBFZM oxygen-treated, and EBFZM oxygen-treated plus outgassed material respectively. The interstitial impurity content showed little correlation with thermal treatment. However, there appeared to be an inverse relationship between carbon and oxygen content: the lowest carbon values were always accompanied by the highest oxygen levels. Typical concentration ranges were: carbon, 2 to 8 wt ppm; oxygen, 15 to 40 wt ppm; nitrogen, 1 to 4 wt ppm; and hydrogen, 1 to 7 wt ppm.

Work is continuing on this project with the objective of obtaining iridium metal that can be fabricated at lower temperatures than now used. Iridium metal presently available must be fabricated by hot rolling and swaging at temperatures above 1000°C. This has been attributed to an impurity effect.

¹ Metals and Ceramics Division.

CARRIER MOBILITY IN INHOMOGENEOUS SEMICONDUCTORS¹

R. D. Westbrook

The purpose of this work is to show that the apparent charge carrier mobility measured in a slice of semiconductor material will be anomalously low if certain types of ionized impurity gradients exist. Crystals of high-purity germanium grown by the Czochralski method sometimes show a positive radial gradient in the net concentration of acceptor impurities. In extreme cases the core is *n* type and the outer section is *p* type, with a well-defined radial *n-p* junction separating the two conductivity regions. When an *n*-type core exists, it begins at some point on the crystal axis and expands in the form of an inverted cone until it may reach the surface near the bottom of the crystal. Electrical measurements on whole slices yield a decreasing value

of apparent carrier mobility as a function of distance from the top of the crystal.

We have investigated two cases of radial variation in carrier concentration. The first assumed a circular sample made up of a central disk and surrounding ring, each region being of uniform composition, but of opposite conductivity type, with a radial n - p junction at the discontinuity. It can be shown that the apparent Hall coefficient, R_{app} , is the same as the true Hall coefficient, R , for a uniform disk composed of the outer material, while the apparent resistivity, ρ_{app} , is larger than the true resistivity, ρ , of the outer material by a factor depending upon α , the ratio of the radius of the inner disk to the radius of the sample. Apparent mobilities, therefore, are smaller than the true values. Most of the experimental work was performed on cored samples, that is, slices of material from which central sections were removed. A cored sample was assumed to be the approximate electrical equivalent of a radial n - p junction sample under the condition that current flowing in the outer portion of the latter is large compared with the junction saturation current. That this was a valid assumption was shown by corroborative measurements made at 77°K on two p -type samples into which n -type centers had been diffused.

The second case of interest is one where the carrier concentration increases uniformly from the axis to the circumference of the sample. If the sample contains a radial n - p junction, we consider the increasing concentration to be from the junction to the circumference. In either situation, we expect the apparent mobility to be less than would be observed on a whole disk of uniform composition. We chose high-purity germanium crystals with and without radial junctions for these experiments. Because samples that contained junctions also possessed a positive radial gradient in net acceptor concentration from the junction to the perimeter, the measured quantities were influenced both by the junction diameter and the magnitude of the gradient. The data for μ_{app}/μ as a function of the junction radius are summarized in Fig. 5.4. The solid line is the theoretical curve. Open triangle data points were obtained from slices taken at intervals along the axis of one high-purity crystal containing a radial n - p junction. Filled triangle points were obtained from slices taken from four separate but similar crystals. Points shown on abscissa $1 - \alpha = 1$ represent data obtained from samples taken above the junction. In this case, note the decrease in apparent mobility before onset of the junction, indicating the effect of a positive radial gradient in carrier concentration on measured mobility. Data points designated by filled circles and open circles are the apparent mobilities found for the cored and

Fig. 5.4. Ratio of apparent mobility to true mobility as a function of junction radius. At $1 - \alpha = 1$, there is no junction, but μ_{app}/μ decreases as a function of increasing radial carrier gradient from axis to periphery.

diffused samples, respectively, representing μ_{app}/μ for radial n - p junctions in otherwise uniform material.

From this work, we conclude that erroneously high values of resistivity, and hence erroneously low values of apparent mobility, will be obtained for a sample that contains a radial p - n junction (when the sample current is large compared with the junction saturation current) but is uniform in composition from the junction to the perimeter. If the sample contains a positive radial gradient in the carrier concentration, the apparent mobility will again be low. If both a junction and a positive gradient in the outer region are present, the effects are additive.

CHARACTERIZATION OF OXYGEN-DOPED GERMANIUM CRYSTALS

J. W. Cleland

Germanium single crystals were grown¹ in a quartz Czochralski furnace from starting material that was purposely doped with about 2×10^{15} antimony atoms per cubic centimeter, and controlled amounts of water vapor or oxygen were added to the argon cover gas after about one-third of the initial melt had been pulled and solidified. One would anticipate an initial donor concentration of about 10^{15} cm^{-3} near the top and about 3 to $5 \times 10^{15} \text{ cm}^{-3}$ near the bottom, due to the distribution coefficient of antimony under these growth conditions; but the actual donor concentration, as determined by electrical property measurements at 77°K , was about 10^{15} cm^{-3} near the top and about 2 to $5 \times 10^{16} \text{ cm}^{-3}$ near the bottom. It was necessary to quench the bottom samples from above 600°C to obtain the anticipated donor concentration. Annealing of germanium at 350°C is known to cluster oxygen atoms that act as donors, but these data indicate that the presence of oxygen can mask the presence of a sizable concentration of normal chemical donor- or acceptor-type impurities in germanium under otherwise typical conditions of crystal growth.

1. R. D. Westbrook and C. C. Robinson, "Oxygen-Doped Germanium," this report.

OXYGEN-DOPED GERMANIUM

R. D. Westbrook C. C. Robinson

Single crystals of germanium containing oxygen and in some cases other chemical dopants have been grown by the Czochralski process. By controlling the amount of oxygen or water vapor in the furnace during crystal growth, it is possible to produce germanium containing at least 6 to 8×10^{17} oxygen atoms per cubic centimeter. The amount of oxygen in the crystal is determined by the magnitude of the $11.7\text{-}\mu\text{m}$ Ge-O absorption band. When it is necessary to study properties of a doped or undoped crystal with and without oxygen, it is possible to add oxygen or water vapor to the gas stream after part of the crystal has been grown. As the amount of oxygen dissolved in liquid germanium comes to equilibrium rapidly in this system, the desired oxygen concentration in the crystal is achieved within a millimeter or so of growth.

GROWTH OF PEROVSKITE CRYSTALS

R. D. Westbrook C. C. Robinson

Crystals of the fluoride perovskites KMgF_3 and RbCaF_3 have been grown in a high-pressure Bridgman furnace. The boules were always polycrystalline, and the grain sizes were not always large enough to be useful. In addition, the boules often contained large voids and bubbles, and run-to-run reproducibility was poor. Substantial improvements in gas purification and temperature control did little to reduce these problems, particularly in the case of the relatively high-melting, high-vapor-pressure RbCaF_3 . We had planned to grow these crystals in a new high-pressure Czochralski furnace, but the furnace was damaged in shipment, and this phase of the work had to be postponed. Preliminary experiments with these materials in a horizontal zone-refiner-type furnace indicate the feasibility of this approach. Voids and inclusions are virtually nonexistent, and run time is reduced from several days to a few hours, although as yet the grain sizes are not significantly larger than those produced in the Bridgman furnace.

BRIDGMAN GROWTH OF FERRITE CRYSTALS¹

F. J. Bruni² W. E. Brundage

Large single crystals of some ferrites are required for magnetic beam pulsing and polarization in a time-of-flight neutron spectrometer installed at the High-Flux Isotope Reactor.³ The required size, absence of inclusions, and other considerations dictated that growth be attempted by the Bridgman technique. One desired composition, ${}^7\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$, was found to be impossible to grow in air by the Bridgman technique. A single phase corresponding to $\text{Li}_{0.25}\text{Fe}_{2.75}\text{O}_4$ formed over the first third of the melt to solidify, and then changed to a two-phase region with an average composition of $\text{Li}_{0.6}\text{Fe}_{2.4}\text{O}_4$ over the remainder of the melt. These latter two phases were found to have the spinel structure, with lattice parameters of 8.360 and $8.325 \text{ \AA}$, while the lattice parameter for $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ is $8.331 \text{ \AA}$. It was possible to grow a single crystal from a melt corresponding to the composition of the single-phase region but not from one of the composition $\text{Li}_{0.7}\text{Fe}_{2.3}\text{O}_{3.8}$.

Another ferrite crystal, of the composition $\text{Ni}_{0.2}\text{Fe}_{2.8}\text{O}_4$, desired for the spectrometer, was attempted. It was found that the nickel distribution varied smoothly from twice the average composition in

the first part solidified to nearly zero in the final portion. Slow melting and solidification from the top down before remelting and solidification from the bottom upward, in a technique similar to zone leveling, gave single-crystal samples of reasonably uniform composition. The spectrometer application requires that the lithium and nickel be the mass 7 and mass 62 isotopes, respectively, to reduce nuclear scattering. The scarcity and cost of the ^{52}Ni compared with the low cost and ready availability of ^7Li suggested the substitution of lithium for some of the nickel in the crystal. The nickel content was again found to decrease along the length as the crystal solidified and to remain low until it increased in the two-phase region at the end of the solidification. The zone leveling technique was of no help. A crystal of suitable composition could be cut from a portion of the melt, and a second run was made with feed material of the composition

A single crystal resulted, and a suitably oriented slab, nearly transverse to the growth direction, was cut with dimensions about 25 X 20 X 2.5 mm. This crystal is presently being used in the spectrometer.

Crystals of very high perfection are formed when growth rates under $2\frac{1}{2}$ mm/hr are used, and 0.5-mm-thick samples of the lithium, nickel, and gallium-manganese ferrites have been used to observe the magnetic domains in the crystals by x-ray transmission topography.⁴ Much higher growth rates tend to produce polycrystalline melts. Attempts to deform the crystals to produce mosaic spread of about 0.3° (desired as a compromise between monochromation and beam intensity in the spectrometer) were not successful. The lithium-nickel melt was run at 5 mm/hr, and the final crystal had a mosaic spread of 0.15° .

A $\text{Ga}_{0.3}\text{Mn}_{0.7}\text{Fe}_2\text{O}_4$ melt was run at 2.35 mm/hr, and a crystal with this composition resulted over the first 80% to solidify. This crystal was intended for use as a polarizer for the neutron beam, but the crystal perfection was so high that the beam intensity was too low. A portion of the crystal was cut into ten sheets about 25 mm square and 0.4 mm thick which were then stacked and cemented together. The mechanical errors in alignment during the reassembly, added to any residual strains from the diamond sawing operation, combined to give the effect of a wider mosaic spread,

and the assembly has been suitable for use in the spectrometer.

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HOLMIUM ORTHOFERRITE

F. J. Bruni¹ W. E. Brundage

Holmium orthoferrite crystals of centimeter size are desired for neutron spectroscopy studies. Efforts to grow these by grain growth, flux growth, and pulling from the melt were unsuccessful.² During this reporting period the Bridgman growth technique was tried, and coarse-grained polycrystalline samples were obtained. Some of the grains would have been satisfactory, except that twinning had occurred in parallel bands through the grains.

Another run was made in which the charge material was prepared by making two batches, one iron rich and the other holmium rich, reacting each at 1500°C , and regrinding to 100-mesh powder. Each batch was then analyzed and the two combined to give proper stoichiometry. This run again produced the large-grained polycrystalline material but with the twin bands reduced in size.

Chemical analyses always indicated a trend toward loss of iron from the melt, the crystallized solid ending up holmium rich. To study this effect, two additional melts were made from high-purity feed materials, 99.999% Fe_2O_3 and 99.99% Ho_2O_3 , one adjusted to a 2% excess of iron and the other at a 1:1 iron to holmium ratio. Coarse polycrystalline samples again resulted. The sample with the iron excess was found to have small twin bands in only one of three grains examined. The sample from the stoichiometric starting mixture was quite heavily twinned in all four grains examined. Chemical analyses from these melts have not yet been made.

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- John B. Bates, "Infrared Emission Spectra of Molten Salts" (invited paper)

Fourth Lunar Science Conference, Houston, Texas, March 5-9, 1973

- R. A. Weeks, "Ferromagnetic Resonance Properties of Lunar Fines: Apollo 16"
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Topical Conference on Atomic and Molecular Studies at ORNL, Oak Ridge, Tennessee, March 22-23, 1973

B. R. Appleton, "Channeling in Crystals"

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S. Datz, J. A. Biggs, C. D. Moak, and B. R. Appleton, "Ionizing Collisions of Fast Heavy Ions"

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H. G. Smith and M. Nielsen, "Lattice and Molecular Vibrations in Iodine and of the Ammonium Ion in NH_4ClO_4 "

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W. C. Koehler and R. M. Moon, "Magnetic Properties of ^{147}Pm and ^{147}Pm - ^{147}Sm Alloys" (invited paper)

R. M. Moon, "Spin Densities in Rare-Earth Metals and Compounds" (invited paper)

R. M. Nicklow, "Magnetic Interactions and Spin-Wave Dispersion in Rare Earth Metals" (invited paper)

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Summer Study Group on Practical Application of Accelerators, Los Alamos Scientific Laboratory, Los Alamos, New Mexico, August 27-31, 1973

O. S. Oen, "Theory of the Production of Radiation Displacement Damage" (invited paper)

Europhysics Study Conference on the Physics of the Rare Earth Metals, Esbøerne, Denmark, August 29-September 1, 1973

R. M. Moon, "Magnetic Structures and Conduction Electron Spin Densities" (invited paper)

R. M. Nicklow, "Magnon Dispersion Relations and Exchange in Rare Earth Metals" (invited paper)

Seventh International Hot Atom Chemistry Symposium, Jülich, West Germany, September 10-14, 1973

M. T. Robinson, "Computer Simulation of Atomic Recoil Damage in Inorganic Crystals" (invited paper)

Fifth International Conference on Atomic Collisions in Solids, Gatlinburg, Tennessee, September 23-28, 1973

B. R. Appleton, "Hyperchanneling"

B. R. Appleton, J. A. Biggerstaff, T. S. Noggle, S. Datz, C. D. Moak, M. D. Brown, H. F. Krause, R. H. Ritchie, and V. N. Neelavathi, "Radiative Electron Capture by Channeled Oxygen Ions"

John H. Barrett, "Validity of the Statistical Equilibrium Hypothesis in Channeling"

S. Datz, B. R. Appleton, J. A. Biggerstaff, M. D. Brown, H. F. Krause, C. D. Moak, and T. S. Noggle, "Charge State Dependence of Stopping Power for Oxygen Ions Channeled in Silver"

Y. Hashimoto, J. H. Barrett, and W. M. Gibson, "Analysis of Blocking Lifetime Experiments"

D. K. Holmes and M. T. Robinson, "Computer Studies of Replacement Sequences in Solids Associated with Atomic Displacement Cascades"

American Crystallographic Association Meeting, University of Connecticut, Storrs, Connecticut, June 17-23, 1973

Bennett C. Larson, "Study of Diffuse Scattering from Clustered Defects"

28th Annual Symposium on Molecular Structure, Columbus, Ohio, June 11-15, 1973

John B. Bates, "Intermolecular Potential Function Models of Hexachlorobenzene and Solid Chlorine"

M. Nielsen and H. G. Smith, "Lattice and Molecular Vibrations in Iodine"

H. G. Smith, M. Nielsen, and H. A. Mook, "Dynamics of the Ammonium Ion in NH_4ClO_4 "

Europhysics Topical Conference on Lattice Defects in Ionic Crystals, Marseilles, France, July 2-6, 1973

F. A. Modine and E. Sonder, "Magneto Optical Properties of the F Center in KMgF_3 "

E. Sonder, "Trapping in Mobile Interstitials during Irradiation of Alkali Halides"

Lunar Science Institute Conference, Houston, Texas, July 27, 1973

R. A. Weeks, "Paramagnetic States of Lunar Plagioclases and Ferrimagnetic Phases in Lunar Soils: Electron Magnetic Resonance Spectra"

European Physical Society Study Conference on Metal Surfaces, Hinderås, Sweden, August 13-17, 1973

L. H. Jenkins and D. M. Zehner, "Higher Energy Satellites in Auger Spectra from Metals" (invited paper)

Symposium on Defects and Defect Clusters in BCC Metals and Their Alloys, U.S. National Bureau of Standards, Gaithersburg, Maryland, August 14-16, 1973

S. M. Ohr, "Image Contrast of a Dislocation Loop in BCC Metals"

International Conference on Charge, Spin and Momentum Density, Sagamore IV, Minsk, U.S.S.R., August 14-18, 1973

J. W. Cable, E. O. Wollan, G. P. Felcher, T. O. Brun, and S. P. Hornfeldt, "Magnetic Form Factor of Palladium at 4.2°K"

R. M. Moon, "Measurement of the Magnetic Form Factors at General Positions in Reciprocal Space" (invited paper)

C. D. Moak, B. R. Appleton, J. A. Biggerstaff, S. Datz, and T. S. Noggle, "Velocity Dependence of the Stopping Power of Channeled Iodine Ions"

J. R. Mowat, B. R. Appleton, J. A. Biggerstaff, S. Datz, C. D. Moak, and I. A. Setlin, "Charge State Dependence of Si K X-Ray Production in Solid and Gaseous Targets by 40 MeV Oxygen Ion Impact"

K. Rossler and M. T. Robinson, "Radiation Damage in Transition Metal Hexahalo Complexes: The Application of Atomic Collision Dynamics in Hot Atom Chemistry"

International Conference on Applications of Ion Beams to Metals, Albuquerque, New Mexico, October 2-5, 1973

O. S. Oen, J. Narayan, and T. S. Noggle, "Ion Radiation Damage"

Fifth Southeastern Magnetic Resonance Conference, Tuscaloosa, Alabama, October 11-12, 1973

M. M. Abraham, "Dynamic Nuclear Polarization via Electron Paramagnetic Resonance" (invited paper)

R. A. Weeks, "Geochemical Applications of Electron Magnetic Resonance Spectroscopy: Lunar Materials" (invited paper)

Conference on Radiation Damage Problems in Nuclear Power Development, Central States Universities, Inc., Argonne National Laboratory, Argonne, Illinois, November 2-3, 1973

R. R. Colman, Jr., "Neutron Irradiation Effect Studies" (invited paper)

Southeastern Section Meeting of the American Physical Society, Winston-Salem, North Carolina, November 8-10, 1973

B. R. Appleton, "Characteristic Ion-Atom Interactions Induced by MeV Ions in Solids" (invited paper)

R. R. Colman, Jr., C. E. Klabunde, J. K. Redman, and A. L. Southern, "Interstitial Migration in Molybdenum"

C. B. Finch, F. A. Modine, E. Sonder, W. P. Unruh, and R. D. Westbrook, "Structural Phase Transitions in RbCaF_3 "

Bennett C. Larson, "X-Ray Diffuse Scattering from Clustered Defects" (invited paper)

D. M. Zehner, T. S. Noggle, and L. H. Jenkins, "Contributions of Twins to LEED Patterns from Ag(001) and Au(001) Surfaces"

Nineteenth Annual Conference on Magnetism and Magnetic Materials, Boston, Massachusetts, November 13-16, 1973

J. W. Cable, E. O. Wollan, G. P. Felcher, T. O. Brun, and S. P. Hornfeldt, "Magnetic Form Factor of Palladium at 4.2°K"

H. L. Davis and H. A. Mook, "Neutron Measurement of Crystal Field Splittings in TmAs and TmBi"

H. A. Mook, J. W. Lynn, and R. M. Nicklow, "Magnetic Excitations in Nickel and Iron" (invited paper)

R. M. Nicklow and N. Wakabayashi, "Exchange Interaction in Dilute Yttrium-Rare Earth Alloys" (invited paper)

International Conference on Charge, Spin and Momentum Density, Sagamore IV, Minsk, U.S.S.R., August 14-18, 1973

J. W. Cable, E. O. Wollan, G. P. Felcher, T. O. Brun, and S. P. Hornfeldt, "Magnetic Form Factor of Palladium at 4.2°K"

R. M. Moon, "Measurement of the Magnetic Form Factors at General Positions in Reciprocal Space" (invited paper)

C. D. Moak, B. R. Appleton, J. A. Biggerstaff, S. Datz, and T. S. Noggle, "Velocity Dependence of the Stopping Power of Channeled Iodine Ions"

J. R. Mowat, B. R. Appleton, J. A. Biggerstaff, S. Datz, C. D. Moak, and I. A. Selin, "Charge State Dependence of Si K X-Ray Production in Solid and Gaseous Targets by 40 MeV Oxygen Ion Impact"

K. Rossler and M. T. Robinson, "Radiation Damage in Transition Metal Hexahalo Complexes: The Application of Atomic Collision Dynamics in Hot Atom Chemistry"

International Conference on Applications of Ion Beams to Metals, Albuquerque, New Mexico, October 2-5, 1973

O. S. Oen, J. Narayan, and T. S. Noggle, "Ion Radiation Damage"

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M. M. Abraham, "Dynamic Nuclear Polarization via Electron Paramagnetic Resonance" (invited paper)

R. A. Weeks, "Geochemical Applications of Electron Magnetic Resonance Spectroscopy: Lunar Materials" (invited paper)

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Southeastern Section Meeting of the American Physical Society, Winston-Salem, North Carolina, November 8-10, 1973

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C. B. Finch, F. A. Modine, E. Sonder, W. P. Unruh, and R. D. Westbrook, "Structural Phase Transitions in RbCaF_3 "

Bennett C. Larson, "X-Ray Diffuse Scattering from Clustered Defects" (invited paper)

D. M. Zehner, T. S. Noggle, and L. H. Jenkins, "Contributions of Twins to LEED Patterns from Ag(001) and Au(001) Surfaces"

Nineteenth Annual Conference on Magnetism and Magnetic Materials, Boston, Massachusetts, November 13-16, 1973

J. W. Cable, E. O. Wollan, G. P. Felcher, T. O. Brun, and S. P. Hornfeldt, "Magnetic Form Factor of Palladium at 4.2°K"

H. L. Davis and H. A. Mook, "Neutron Measurement of Crystal Field Splittings in TmAs and TmBi"

H. A. Mook, J. W. Lynn, and R. M. Nicklow, "Magnetic Excitations in Nickel and Iron" (invited paper)

R. M. Nicklow and N. Wakabayashi, "Exchange Interaction in Dilute Yttrium-Rare Earth Alloys" (invited paper)

- "Low Temperature Radiation Effects on the Mechanical Properties of High Purity Iron,"¹ P. Groh, Centre D'Etudes Nucleaires de Grenoble, Grenoble, France
- "Lattice Defects in Niobium, Tantalum, and Tungsten," H. Schultz, Max-Planck-Institut, Stuttgart, Germany
- "One Dimensional and Three Dimensional Migrating Interstitials in FCC Alloys,"¹ W. Schulz, EURATOM, Ispra, Italy
- "Phonons in Solid and Liquid Hydrogen Studied by Inelastic Neutron Scattering," M. Nielsen, Atomic Energy Research Establishment Risø, Roskilde, Denmark
- "Pinning of Flux Lines in NbTa Alloys Due to Normal Conducting Precipitates,"² H. A. Ullmaier, Institut für Festkörperforschung, Jülich, Germany
- "Observation of Magnetically Anisotropic Defects during Stage I Recovery in Nickel after Low Temperature Electron Irradiation," J. Hemmerich, Kernforschungsanlage, Jülich, Germany
- "Calculations of Electronic States and Defects in Ionic Crystals," T. M. Wilson, Oklahoma State University, Stillwater, Oklahoma
- "Structural Investigations of Amorphous Solids Using a Pulsed Neutron Source," Adrian C. Wright, University of Reading, Reading, England
- "U.S. Energy Uses and Resources - Possible Solid State Research Implications," Harold L. Davis, Solid State Division, ORNL
- "Controlling Toxic Materials," William Fulkerson, ORNL-NSF Environmental Program, ORNL
- "Neutron Irradiation Effects and Structure of Noncrystalline SiO₂," John B. Bates, Solid State Division, ORNL
- "Purification and Crystal Growth of High Melting Point Metals," R. E. Reed, Solid State Division, ORNL
- "Neutron Scattering at Institut Laue-Langevin, Grenoble," W. C. Koehler, Solid State Division, ORNL
- "Lattice Statics Calculations for Interstitial Atoms in BCC Metals," Roy Benedict, Cornell University, Ithaca, New York
- "Surface Studies by LEED and AES," D. M. Zehner, Solid State Division, ORNL
- "Fusion Reactor Technology," D. Steiner, Thermonuclear Division, ORNL
- "Optimistic Outlook for Mineral Resources," H. E. Goeller, ORNL-NSF Environmental Program, ORNL
- "Defect-Impurity Interactions in Irradiated Germanium," J. W. Cleland, Solid State Division, ORNL
- "Hydrogen Scattering from Lithium Chloride," Grant Rowe, University of Illinois, Urbana, Illinois
- "Neutron Spin Echo Spectrometry," Ferenc Mezei, Institut Laue-Langevin, Grenoble, France
- "Relationship between Two-Body Interatomic Potentials and Elastic Constants," R. A. Johnson, University of Virginia, Charlottesville, Virginia
- "An Investigation of Electrical and Atomic Properties of Gallium Arsenide," Ying Kuen Shum, Princeton University, Princeton, New Jersey

LECTURES AND SEMINARS

Lectures and seminars presented by Division Members during the year included the following:

- M. M. Abraham - Physics Department, University of Texas at Arlington, "Dynamic Nuclear Polarization via Electron Paramagnetic Resonance"
- John B. Bates - Molecular Structure and Dynamics Colloquium, ORNL, "Intermolecular Potential Function Models of Hexachlorobenzene and Solid Chlorine"
- J. W. Cable - Georgia Institute of Technology, Atlanta, Georgia, "Magnetic Moment Distribution in 3d Transition Metal Alloys"

²Sponsored jointly by Metals and Ceramics Division, Thermonuclear Division, and Solid State Division.

- Y. Chen - Wake Forest University, Winston-Salem, North Carolina. "Trapped-Hole Centers in MgO"; Aerospace Research Laboratory, Wright-Patterson AFB, Ohio. "Radiation Damage in II-VI Oxides"
- J. F. Cooke - University of Louisville, Louisville, Kentucky, University of Puerto Rico, San Juan, Puerto Rico, University of Puerto Rico, Mayaguez, Puerto Rico, and University of Florida, Gainesville, Florida. "Theory of Magnetism in Transition Metals"; University of Puerto Rico, San Juan, Puerto Rico, and Benedictine College, Atchison, Kansas. "Electronic Structure and Elementary Excitations in Solids"
- H. L. Davis - Department of Physics, Bowling Green State University, Bowling Green, Ohio. "Beneath, On, and Above the Fermi Surface of Metallic Copper"
- P. Dederichs - Department of Physics, University of Illinois, Urbana, Illinois, Materials Science Division, Argonne National Laboratory, Argonne, Illinois, Physics Department, Brookhaven National Laboratory, Upton, Long Island, New York, and Bell Telephone Laboratories, Murray Hill, New Jersey. "Resonant Mode of the Split Interstitial"; Department of Physics, Southern Illinois University, Edwardsville, Illinois. "Dynamical Behavior of Interstitials in Metals"
- L. H. Jenkins - Kernforschungsanlage, Jülich, Germany, and Max-Planck-Institut für Plasmaphysik, Garching, Germany. "Higher Energy Satellites in Auger Spectra from Metals"
- W. C. Koehler - Chicago Solid State Colloquium, University of Illinois, Chicago, Illinois. "Neutron Scattering and Rare Earth Magnetism"; Institut Laue-Langevin, Grenoble, France. "Neutron Scattering at the Oak Ridge National Laboratory"; C.E.N.G., Grenoble, France. "Spin Densities and Structures of Rare Earth Metals"; C.N.R.S., Grenoble, France. "Magnetic Properties of Rare Earth Metals, Alloys, and Compounds"
- Bennett C. Larson - Physics Division, Oak Ridge National Laboratory. "Defects in Crystals"
- J. W. Lynn - Brookhaven National Laboratory, Upton, Long Island, New York. "Temperature Dependence of the Magnetic Excitations in Iron and Nickel"
- F. A. Modine - University of Alabama, University, Alabama, and Texas Christian University, Fort Worth, Texas. "Optical Spectroscopy with Polarized Light"
- H. A. Mook - Brookhaven National Laboratory, Upton, Long Island, New York. "A Search for Bose-Einstein Condensation in Superfluid ^4He " and "A Magnetically Pulsed Neutron Time-of-Flight Spectrometer for Inelastic Scattering"
- J. Narayan - Bell Telephone Laboratories, Murray Hill, New Jersey. "Distribution of Defects and Dislocation Channeling in Quenched and Irradiated Metals"; Indian Institute of Technology, Kanpur, India. "Ion Damage in Metals"; University of Delhi, Delhi, India. "Electron Microscope Study of Defects in Solids"
- R. M. Nicklow - Kernforschungsanlage, Jülich, Germany. "Neutron Scattering Study of the Lattice Dynamics of Alloys"; Institute for Atomenergi, Kjeller, Norway. "Spin Wave Energies and Exchange Interactions in Rare-Earth Metals and Yttrium-Rare Earth Alloys"; Iowa State University, Ames, Iowa. "Neutron Scattering Studies of Spin-Wave Energies in Rare-Earth Metals"; University of Southern Illinois, Edwardsville, Illinois. "Inelastic Neutron Scattering Investigations of Magnons and Phonons in Solids"
- T. S. Noggle - Department of Physics, Lenoir Rhyne College, Hickory, North Carolina. "Radiation Damage in Metals"
- R. E. Reed - Department of Metallurgy and Materials Science, Lehigh University, Bethlehem, Pennsylvania. "Purification, Crystal Growth, and Characterization of Refractory Metal Single Crystals"
- M. T. Robinson - Materials Science Division, Argonne National Laboratory, Argonne, Illinois. "Computer Simulation of Radiation Damage in Metals"; Max-Planck-Institut für Plasmaphysik, Garching bei München, Germany. "Neutron Radiation Damage in CTR Systems"
- W. Schilling - Department of Physics, University of North Carolina, Chapel Hill, North Carolina. "Investigations of Point Defects in Metals by Diffuse X-Ray Scattering"; Department of Physics, University of Illinois, Urbana, Illinois. "Investigation of Interstitials by Diffuse X-Ray Scattering"; Materials Science Division, Argonne National Laboratory, Argonne, Illinois, and Physics Department, University of Utah, Salt Lake City, Utah. "Physical Properties of Interstitials in FCC Metals"

- H. G. Smith - Clemson University, Clemson, South Carolina, "The Role of Crystal Diffraction in Solid State Physics"; University of Puerto Rico, Mayaguez, Puerto Rico, Rio Pedras University, San Juan, Puerto Rico, and Virginia Military Institute, Lexington, Virginia, "Crystal Dynamics and Neutron Scattering from Superconductors"; Virginia Military Institute, Lexington, Virginia, "The Role of Neutron Scattering in Solid State Physics"
- E. Sonder - Physics Department, Georgia State University, Atlanta, Georgia, "Production of Defects in Ionic Crystals by Radiation"; Physics Department, CNRS, EURATOM, Ispra, Italy, and University of Neuchâtel, Switzerland, "Trapping of Mobile Interstitials during Irradiation of Alkali Halides"; Ecole Polytechnique, Lausanne, Switzerland, "Magnetic Circular Dichroism of the F Center in KMgF_3 "
- R. A. Weeks - McMaster University, Hamilton, Ontario, Canada, "Geochemical Applications of EPR Spectroscopy: Lunar Samples"; Ecole Polytechnique, Lausanne, Switzerland, "Magnetic Resonance of Defects in Silicates"; University of Marburg, Marburg, West Germany, "Magnetic Resonance of Transition Series Ions in Silicates"; University of Newcastle, Newcastle, Great Britain, "Ferromagnetic Resonance of Ferrite Particles"; Analytical Chemistry Division, ORNL, "West of Suez: Modern Egypt"
- R. F. Wood - University of Turku, Turku, Finland, Danish AEC Research Establishment Risø, Roskilde, Denmark, and Kernforschungsanlage, Jülich, Germany, "Acoustical Plasmons, Phonon Anomalies and Superconductivity in Transition Metal Systems"; University of Turku, Turku, Finland, University of Neuchâtel, Neuchâtel, Switzerland, and University of Aarhus, Aarhus, Denmark, "Vibronic Structure and Optical Properties of Ionic Crystals"; University of Turku, Turku, Finland, "Infrared Absorption and Raman Scattering by Defects in Ionic Crystals"; University of Turku, Turku, Finland, and Technical University, Tampere, Finland, "The Electronic Structure of Color Centers in Ionic Crystals"
- F. W. Young, Jr. - Department of Physics, University of Illinois, Urbana, Illinois, "X-Ray Scattering by Defect Clusters in Crystals"; Department of Physics, Wright State University, Dayton, Ohio, "Size Distribution of Dislocation Loops as Determined by X-Ray Scattering"

Scientific Professional Activities

- M. M. Abraham** Lecturer, ORAU Traveling Lecture Program, 1972-1973
- B. R. Appleton** Member, ORNL Basic Physical Sciences Assessment Council, BAPSAC
Member, Proposal Committee for National Heavy Ion Laboratory
Member, Organizing Committee for Fifth International Conference on Atomic Collisions in Solids
Editor, Proceedings of the Fifth International Conference on Atomic Collisions in Solids
Member, Graduate School Doctoral Committee, Department of Physics and Astronomy, University of South Carolina
- J. H. Barrett** Member, Local Committee for Fifth International Conference on Atomic Collisions in Solids
- J. W. Cleland** Member, Executive Committee, American Association of Crystal Growers
- R. R. Coltman, Jr.** Member, Reactor Experimental Review Committee, ORNL
Member, Radiation Damage Working Group of the Clinton P. Anderson Meson Physics Facility, LASL
- J. F. Cooke** Lecturer, ORAU Traveling Lecture Program, 1972-1973
- H. L. Davis** Lecturer, Academic Year 1972-1973, Physics Department, The University of Tennessee
Participant, Annual "Alumni-Faculty Day" Activities of Bowling Green State University, Ohio
Member, ORNL BAPSAC Committee on Non-nuclear Energy
Lecturer, ORAU Traveling Lecture Program, 1973-1974
- D. K. Holmes** Member, Editorial Advisory Board, *Radiation Effects*
- L. H. Jenkins** Lecturer, ORAU Traveling Lecture Program, 1972-1973
- W. C. Koehler** Member, Neutron Diffraction Commission, International Union of Crystallography
Member, Editorial Advisory Board, *International Journal of Magnetism*
Member, Program Committee, 11th Rare Earth Research Conference
Member, International Advisory Committee, Europhysics Study Conference on the Physics of the Rare Earth Metals, Elsinore, Denmark
Chairman, Thermal Neutron Beam Facilities Committee, ORNL
Research Collaborator, Physics Department, Brookhaven National Laboratory, Upton, New York, June 18-July 20, 1973
Participant, Workshop on Intense Neutron Sources, Brookhaven National Laboratory, Upton, New York
Lecturer, ORAU Traveling Lecture Program, 1973-1974
- B. C. Larson** Lecturer, ORAU Traveling Lecture Program, 1973-1974
- F. A. Modine** Lecturer, ORAU Traveling Lecture Program, 1973-1974
- H. A. Mook** Participant, Workshop for Zero Gradient Intense Neutron Generator, Argonne National Laboratory, Argonne, Illinois
- R. M. Moon** Member, Special Commission on Electron Distributions of the International Union of Crystallography
Member, Advisory Council of International Conference on Charge, Spin, and Momentum Density, Sagamore IV, Minsk, U.S.S.R.
- T. S. Noggle** Member, Editorial Advisory Board, *Thin Films* (Gordon and Breach Science Publishing Co., New York-London)
Member, American Society for Testing and Materials E-10 Task Group on Description of Radiation Damage in Metals Using Electron Microscopy
Member, Local Committee for Fifth International Conference on Atomic Collisions in Solids
Lecturer, ORAU Traveling Lecture Program, 1972-1973

- S. M. Ohr
Member, American Society for Testing and Materials E-10 Task Group on Description of Radiation Damage in Metals Using Electron Microscopy
- R. E. Reed
Secretary, Vacuum Metallurgy Division, American Vacuum Society
- M. T. Robinson
Member, Radiation Damage Subgroup of the IAEA Working Group on Reactor Radiation Measurements
Member, Physics Screening Panel for the 1974 E. O. Lawrence Award
- O. E. Schow
Member, Accelerators and Radiation Sources Review Committee, ORNL
- H. G. Smith
Local Chairman, Organizing Committee for International Conference on Superconductivity and Lattice Instabilities
Lecturer, ORAU Traveling Lecture Program, 1972-1974
Member, Thermal Neutron Beam Facilities Committee, ORNL
- N. Wakabayashi
Guest Scientist, Institut für Festkörperforschung der Kernforschungsanlage Jülich, Germany
- R. A. Weeks
Associate Editor, *Journal of Geophysical Research*
Member, Editorial Committee, *Journal of the American Ceramic Society*
Member, Editorial Board, *Journal of Non-Metallic Solids*
- R. D. Westbrook
Member, ASTM Committee F1, Chairman of Subcommittee on Germanium
- M. K. Wilkinson
Professor (Adjunct), Department of Physics, Georgia Institute of Technology
Member, Advisory Panel of the Solid State Sciences Committee of the National Research Council
Member, Advisory Committee of Conference on Magnetism and Magnetic Materials (term expires 1974)
Secretary, Steering Committee of Conference on Magnetism and Magnetic Materials (term expires 1974)
Member, Ph.D. Thesis Committee, Department of Physics, Georgia Institute of Technology
Member, Organizing Committee for Workshop on Intense Neutron Sources, Brookhaven National Laboratory
Member, Evaluation Panel for Reactor Radiation Division, National Bureau of Standards
Member, ORNL Basic Physical Sciences Assessment Council, BAPSAC
Chairman, ORNL BAPSAC Committee on Non-Nuclear Energy
- R. F. Wood
Editor, Solid State Physics, *Computer Physics Communications* (North-Holland Publishing Company)
Guest Scientist, Institute for Theoretical Physics, Goteborg, Sweden, 1972-1973
- F. W. Young, Jr.
Member, Editorial Advisory Board, *Crystal Synthesis*, published by Springer-Verlag New York, Inc., New York
Chairman, Radiation Damage Session, American Physical Society Meeting, San Diego, California

Personnel Changes

The following personnel changes occurred in the Solid State Division during 1973:

Arrivals

Q. C. Murphree, ORAU Graduate Participant from University of South Carolina, Columbia, South Carolina

Anne M. Keesee, Secretary, transfer from MAN Program, ORNL

J. B. Bates, Research Staff Member, transfer from Chemistry Division, ORNL

Velma G. Yates, Secretary

W. A. Kamitakahara, Research Staff Member, from McMaster University, Hamilton, Ontario, Canada

J. W. Miller, Research Staff Member, from Argonne National Laboratory, Argonne, Illinois

P. H. Dederichs, Foreign Guest, from KFA, Jülich, Germany

G. Leibfried, Consultant from KFA, Jülich, Germany

H. E. Harmon, Technician, transfer from Oak Ridge Gaseous Diffusion Plant

Departures

Betty F. Edwards, Secretary, transferred to Environmental Sciences Information Systems Office, ORNL

V. K. Paré, Research Staff Member, transferred to Instrumentation and Controls Division, ORNL

A. L. Southern, Research Staff Member, transferred to Oak Ridge Gaseous Diffusion Plant

H. D. Guberman, Research Staff Member, resigned to accept position with Westinghouse Electric Corporation, Bettis Atomic Power Laboratory, Pittsburgh, Pennsylvania

W. P. Unruh, Temporary Employee, from University of Kansas, Lawrence, Kansas

W. F. Schilling, Foreign Guest, from KFA, Jülich, Germany

M. Nielsen, Foreign Guest, from Atomic Energy Research Establishment Risø, Roskilde, Denmark

F. J. Bruni, Research Staff Member, resigned to accept position with Texas Instruments, Dallas, Texas

Summer Assignments

Summer Employees:

F. J. James, from University of North Carolina, Chapel Hill, North Carolina

C. A. Rotter, from West Virginia University, Morgantown, West Virginia

T. M. Wilson, from Oklahoma State University, Stillwater, Oklahoma

ORAU Summer Students:

D. J. Prestel, from Northeastern Illinois University, Chicago, Illinois

L. J. Hyslop, from St. Bonaventure University, Bonaventure, New York

N. E. Schlotter, from Carleton College, Northfield, Minnesota

Research Participant:

J. M. Tanner, from Georgia Institute of Technology, Atlanta, Georgia