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Abstract
The optical absorptivities of oriented single crystals of hcp Gd, Tb, Dy, Ho, Er, Tm, and Lu were measured at 4.2 K between 0.2 and 4.4 eV. Polarized radiation was used to reveal the optical anisotropy. Systematic movement of structures in the absorptivity and optical conductivity was observed as a result of trends within sp and d bands. Low-energy structures were related to effects of s–f exchange interaction, but were more complicated than previously thought.

Keywords
Polarized radiation, absorptivity, Ames Laboratory

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Anisotropic Optical Properties of Heavy-Rare-Earth Single Crystals

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The optical absorptivities of oriented single crystals of hcp Gd, Tb, Dy, Ho, Er, Tm, and Lu were measured at 4.2 K between 0.2 and 4.4 eV. Polarized radiation was used to reveal the optical anisotropy. Systematic movement of structures in the absorptivity and optical conductivity was observed as a result of trends within sp and d bands. Low-energy structures were related to effects of s-f exchange interaction, but were more complicated than previously thought.

The heavy-rare-earth metals Gd through Tm have long been known to be paramagnetic near room temperature, but display interesting and diverse magnetic ordering upon cooling. Anisotropic resistivity anomalies have been observed on passing through the Néel and Curie temperatures, and these have been interpreted as due to severe perturbations of Fermi-surface sections normal to the hexagonal axis. It has been shown that, depending on the nature of the magnetic ordering, energy-dependent shifts of the majority-spin bands relative to the minority-spin bands occur, or superzone band gaps develop. In the absence of experimental Fermi-surface studies, calculations of the electronic energy bands have of necessity been more qualitative than quantitative, uncertainties of many tenths of an electron volt being expected in the placement of bands relative to one another and to the Fermi level, and uncertainties of ~ 2 eV for the general features being within calculational uncertainty. Accordingly, systematic experimental information concerning the electronic properties of the heavy rare earths is important. Such data should ease the transition from qualitative to quantitative understanding of the interesting phenomena observed in these materials.

It has been shown that the Fermi surfaces of the rare earths bear no resemblance to those predicted by the nearly-free-electron model. Rather, they can be viewed better from the vantage point of the hexagonal transition metals since they share the common features of d bands which intermingle and hybridize with the sp conduction bands near $E_F$. Hence, one would expect considerable anisotropic optical structure at low energy.

We report the first optical measurements obtained with polarized radiation and oriented single crystals of the heavy-rare-earth metals. At 4.2 K, Gd, Tb, and Dy display simple ferromagnetic spin configurations, Ho and Er have conical ferromagnetic spin structures, Tm orders ferromagnetically, and Lu has a filled 4f shell and is nonmagnetic. The absorptivity ($A = R - 1$, where $R$ is the reflectivity) was measured at near-normal incidence between ~0.2 and 4.4 eV by a calorimetric technique discussed in detail elsewhere. The samples were single crystals grown at the Ames Laboratory and generously made available by K. A. Gschneidner and B. J. Beaudry. The samples were cut to expose the c axis, so that both orientations could be studied with the same sample by rotating the polarizers. The samples were mechanically polished to obtain specular surfaces, and then electropolished to remove work damage. While the heavy rare earths are highly reactive at high temperatures, the reaction rate is slow at room temperature and particularly so for strain-free, single-crystal, electropolished surfaces. The oxide which does form should have little effect on our measurements.

The measured absorptivity spectra are shown in Fig. 1. To determine the dielectric functions, Kramers-Kronig analyses were performed with Drude-like behaviors assumed in the infrared. The reflectivity of Gd served as a prototype in the vacuum ultraviolet to ~40 eV. Above 40 eV, the prototype Gd extrapolation was adjusted to give reasonable agreement with the magnitudes of $\sigma$ of Erskine, Blake, and Flaten at ~2 eV and to satisfy the oscillator-strength sum rule by giving ~3 electrons/atom near 20 eV. The re-
FIG. 1. Optical absorptivity of the heavy-rare-earth metals. Each pair of curves is displaced by \( A = 0.2 \) for clarity.

FIG. 2. Optical conductivity of the heavy-rare-earth metals. Each pair of curves is displaced by \( \sigma = 20 \times 10^{14} \) esu.

resulting conductivities, \( \sigma = \epsilon_\omega / 4\pi \), where \( \epsilon_\omega \) is the imaginary part of the dielectric function, \( \epsilon = \epsilon_1 + i\epsilon_2 \), are shown in Fig. 2; again, each pair is displaced upward by \( \sigma = 20 \times 10^{14} \) esu.

Clear trends can be observed in Figs. 1 and 2. The structure in \( A \) for Gd near 0.52 eV \((\mathbf{E} \perp \mathbf{c})\) shifts steadily to higher energy with movement across the series until it appears at about 1.1 eV in Lu. The feature in Gd for \( \mathbf{E} || \mathbf{c} \) near 0.6 eV similarly shifts, but does so less quickly, and at Lu it appears lower in energy than does the feature for \( \mathbf{E} \perp \mathbf{c} \) (-0.95 eV). Other trends are also clear. The feature in Gd at 1.05 eV \((\mathbf{E} \perp \mathbf{c})\) moves to higher energy with increasing atomic number, while the structures near 2.5 eV \((\mathbf{E} \perp \mathbf{c})\) and 1.6 eV \((\mathbf{E} || \mathbf{c})\) remain nearly stationary. Figure 2 shows the corresponding trends in \( \sigma \). These will be discussed in greater detail in a subsequent paper; at that time, comparisons with previous work will also be made, where applicable. Clearly, the optical features observed in the heavy-rare-earth metals bear considerable resemblance to the transition metals.

In the rare-earth metals, the 4f electrons are highly localized, and, below the ordering temperature, communicate with neighboring atomic sites through the sea of conduction electrons. It has been shown that this indirect-exchange interaction is considerably larger for \( d \) electrons than for \( s \) electrons, and that the wave functions at the Fermi surface are 75-85% \( d \)-like in character. In the simple ferromagnets, Gd, Tb, and Dy, the majority- and minority-spin bands are split with the splitting being energy dependent.
Selection rules forbidding spin-flip transitions may be relaxed by strong spin-orbit splitting.\textsuperscript{2,9} Ho and Er have more complicated spin configurations than the spins ordering in conical arrays. For these metals, band gaps develop. In each case, new optical structures might appear. A calculation \textsuperscript{2} indicated that the magnitude of the ferromagnetic splitting would be approximately 0.6 eV for Gd, and then diminish proportionally to the expectation value of the local spin moment for the heavier elements. Such an interpretation of the structures in Dy, Ho, and Tm below 0.7 eV seems reasonable in first order, but does not account for the absence of structure in Er, and should not be assumed to explain the first feature in Gd or Tb.

It can be seen from Fig. 2 that the features in Gd near 0.7 eV have counterparts in the other metals, and these cannot be related to magnetic ordering. The s-f exchange structure seen in Dy (0.6 eV) might persist in Gd and Tb, but, if so, it is largely masked by the strong interband feature in Gd and Tb at about the same energy. The weakness of the s-f structure relative to the first interband feature in Dy suggests that such a masking is possible.

A slightly different explanation for the lack of unambiguous exchange structure in Gd and Tb calls for the absence of such structure rather than a masking of it, and might be found by analyzing the energy bands of the heavy rare earths. The existing qualitative band calculations\textsuperscript{10} of Gd through Lu indicate that only Gd and Tb do not have the webbing feature of the Fermi surface which accompanies the movement of the fourth band at $M$ below $E_F$. Though the interpretation must be a tentative one, one can imagine that the exchange splitting of the bands at $M$ has little effect on the optical properties of ferromagnetic Gd and Tb (both bands above $E_F$), but has greater effect in Dy since the majority bands near $M$ lie below $E_F$ and the minority bands can protrude above $E_F$. The reason for the polarization dependence of the exchange structure is not clear. (It should be pointed out that our measurements were made without an applied magnetic field. In view of the low magnetic anisotropy of many of these crystals, it is likely that many domains were not magnetized along or about the $c$ axis.) A more detailed picture of the Fermi surface and energy bands is thus fundamental to understanding the strongly anisotropic optical features of the rare earths.

At this point it seems unwise to attempt to assign the other structures in $\sigma$ to parts of the Brillouin zone. Caution has been urged by Freeman\textsuperscript{2} for those seeking to compare detailed experimental results such as ours with the bands as they exist today. The uncertainties involved in the treatment of spin-orbit effects (~0.4 eV), relativistic considerations (~0.4 eV), the atomic configuration, and the exchange potential are of the same order of magnitude as the structure observed here. Though the systematics shown in the figures cannot be reliably related to the existing bands, they should aid appreciably in future calculations.

An important point that can be made from Fig. 2 is that calculations of $\epsilon_\sigma$ or $\sigma$ must include a full treatment of optical matrix elements. A calculation of the joint density of states would be less informative since differentiation between $E \parallel \hat{c}$ and $E \perp \hat{c}$ would not be made. It is clear that symmetry selection rules persist and have dramatic effect on the optical spectra. Good agreement between theory and experiment awaits a detailed, relativistic consideration of wave functions and matrix elements. Such quantitative comparisons requiring wave functions may be fundamental in assessing the limits of the single-particle model and the role of many-body effects.\textsuperscript{8}

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\footnotetext[1]{Work supported under National Science Foundation Grant No. DMR-7415089.}
\footnotetext[2]{See the extensive reviews and bibliographies in Magnetic Properties of the Rare Earth Metals, edited by R. J. Elliott (Plenum, New York, 1972).}
\footnotetext[3]{A. J. Freeman, in Ref. 1, Chap. 6; R. E. Watson, A. J. Freeman, and J. P. Dimmock, Phys. Rev. 167, 497 (1968).}
\footnotetext[5]{K. A. Gschneidner, private communication.}
\footnotetext[6]{Preliminary vacuum-ultraviolet measurements indicate the band gap of the oxide of Gd to be ~6 eV.}
\footnotext[7]{J. H. Weaver, C. G. Olson, and D. W. Lynch, unpublished. The Gd samples were films evaporated at ~10^{-3} Torr and studied \textit{in situ} at room temperature. These studies will be discussed at a later date.}
\footnotetext[8]{J. L. Erskine, G. A. Blake, and C. J. Flaten, J. Opt. Soc. Amer. 64, 1332 (1974), and private communication. Detailed comparisons with this work and other recent studies will be given in a later publication.}
Direct Observation of Superlattice Formation in a Semiconductor Heterostructure

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We demonstrate, via low-temperature optical-absorption measurements on ultrathin, coupled potential wells in molecular-beam-grown Al$_x$Ga$_{1-x}$As-GaAs heterostructures, the evolution of resonantly split discrete well states into the lowest band of a one-dimensional superlattice. Both electron and hole superlattices appear to be practical.

The evolution of molecular-beam epitaxy as a technique for the growth of ultrathin layers of high-quality III-V semiconductor single crystals has allowed access to a new regime of quantum effects in structures approaching atomic dimensions. Quantum states of electrons and holes in single potential wells of GaAs bounded by thick Al$_x$Ga$_{1-x}$As barriers have been observed in tunneling as well as in optical absorption and stimulated emission. Coupling between wells through thin penetrable barriers is expected to split the bound quantum states into symmetrical and anti-symmetrical combinations. In the limit of superlattice formation, multiple energy gaps occur in the Brillouin zone, and new and useful transport properties are anticipated. Tunneling measurements in AlGaAs-GaAs superlattices have been reported, although effects due to the bound-state energy-level splittings caused by the coupling of the wells were not resolved, nor was evidence for tunneling via, or the splitting of, valence-band bound-hole states presented in the tunneling reports.

In this Letter, we report optical-absorption measurements in GaAs-Al$_x$Ga$_{1-x}$As heterostructures that give clear evidence of the coupling of both hole and electron states in closely spaced potential wells, as well as showing a number of hitherto unobserved features of superlattice band formation. This work constitutes the first detailed study of the optical characteristics of a finite superlattice. By monitoring the evolution of the GaAs absorption spectrum as the number of coupled wells is increased from one to ten, we are able to present unequivocal evidence for the tunneling of electrons and holes through the Al$_x$Ga$_{1-x}$As barriers. Structures with ten or more coupled wells appear to approximate the superlattice regime, whereas structures with fewer wells appear to be described in terms of interacting single wells. The experimental data are interpreted with an exact solution of the Schrödinger equation for transmission through multiple rectangular potential barriers.

A series of structures, with GaAs well widths in the range 50 Å < $L_x$ < 200 Å and Al$_x$Ga$_{1-x}$As barrier widths in the range 12 Å < $L_B$ < 18 Å (8–12 monolayers), were grown by molecular-beam epitaxy on GaAs substrates with use of a previously outlined procedure. Al concentrations in the range from $x$ = 0.19 to 0.27 were studied. At our present growth rate, the barriers could be reproducibly grown in 3 or 4 sec. Thick layers grown under identical circumstances on semi-insulating substrates were low-doped $p$ type. Handling subsequent to growth included etching, mounting, cooling (<2 K), and spectral measurements as previously reported. For the absorption measurements the beam passed normal to the layers.

The relevant barrier and well thicknesses were determined by interference-microscope measurement of total growth thickness in combination with Al-content determination by interband-absorption-edge and growth-time details. This Al-content determination was also used to establish...