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displays four major peaks which can be correlated with similar structure
observed for EuS⁽¹⁾ and EuSe.⁽²⁾ The lowest energy peak of this chalcogenide
series increases in energy with increasing chalcogenide atomic
number (increasing lattice constant), whereas the three higher energy
peaks move in the opposite direction. The low energy structure probably
arises from transitions between 4f-levels and the X₃ minimum of the
d-like conduction band derived from the Eu²⁺ ions, while the higher energy
peaks most likely belong to transitions analogous to those observed in
alkaline earth chalcogenides. Assignments for these transitions will be
discussed in terms of recent europium chalcogenide band structure models.⁽³⁾

1. J. Mullen and A. W. Lawson, Phys. Letters 24A, 303 (1967).
2. P. Wachter, Phys. Kondens. Materie 8, 80 (1968).
3. S. J. Cho, Phys. Rev. 157, 632 (1967).

P.M. Grant

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■ SERIES II VOLUME 14 NUMBER 3 ■ PUBLISHED FOR THE AMERICAN PHYSICAL SOCIETY BY THE AMERICAN INSTITUTE OF PHYSICS ■ MARCH 1969 ■ PAGES 293-472 ■

bulletin

OF THE AMERICAN PHYSICAL SOCIETY

INCLUDING THE PROGRAM OF THE
1969 MARCH MEETING IN PHILADELPHIA
24-27 MARCH 1969

965 IBM 101

THURSDAY AFTERNOON, 27 MARCH 1969

WASHINGTON ROOM AT 2:00 P.M.

(S. M. MARCUS presiding)

Metal Oxides and Sulphides

HE1. Energy Band Calculations for NiS.* J. M. TYLER, T. E. NORWOOD, and J. L. FRY, *Louisiana State University*.—NiS, a transition-metal compound with the NiAs structure, is of interest currently because it exhibits a metal-to-semiconductor transition accompanied simultaneously by a paramagnetic-to-antiferromagnetic transition. Preliminary energy band calculations are reported here for a crystal potential based on a spherically averaged potential for a $3d^64s^1$ configuration for a nickel with a $\rho^{1/2}$ approximation for exchange. The NiAs structure will be discussed and the method of calculation using an accurate tight-binding approximation will be presented. Preliminary results for the paramagnetic metal will be presented and modifications being made for the antiferromagnetic, semiconducting phase will be discussed.

*Work supported by the U.S. Air Force Office of Scientific Research.

HE2. Band Structure of TiO as a Function of Composition by the APW-VCA.* J. M. SCHOEN, *Columbia University*.—A new perfect crystal technique that is based upon the augmented plane wave (APW) method and the virtual crystal approximation (VCA) has been developed to treat random, 3-dimensional, substitutional alloys and partially vacant crystals. The APW-VCA is superior to existing perfect crystal techniques and is a degenerate form of the t -matrix approximation of Korringa and Beeby. An average muffin-tin potential model for alloys is proposed and extended to non-stoichiometric compounds. Together with the APW-VCA, this model potential has been employed to compute the band structure and density of states of TiO as a function of composition and total vacancy concentration. TiO is a nonstoichiometric, cubic, refractory metal with an intrinsic vacancy concentration on both sublattices of roughly 15%. The APW-VCA results indicate that the rigid band model is valid only up to vacancy concentrations of 10%. Beyond that point the bands broaden significantly.

*Work supported by the U. S. Atomic Energy Commission under contract AT(30-1)3553.

HE3. Physical Properties and Stability of TiO from the APW-VCA Energy Bands.* S. P. DENKER and J. M. SCHOEN, *Columbia University*.—The effective mass approximation and an experimental estimate of the electron relaxation time have been used together with the APW-VCA energy bands to predict the salient features of the titanium K emission bands and several transport and magnetic properties of TiO as a function of vacancy concentration and composition. Adequacy of the muffin-tin potential model of TiO used in the APW-VCA calculation is examined in light of the experimental properties of the solid. Because this model does not accurately treat the potential between the muffin-tin spheres, good estimates of the transport and magnetic properties can be obtained although cohesion cannot be considered. Nonetheless, if it is assumed that the bottom of the conduction band does not vary appreciably with composition or total vacancy concentration, the average electronic energy is minimum at the observed vacancy concentration.

*Work supported by the U. S. Atomic Energy Commission under contract AT(30-1)3553.

HE4. Spin-Polarized Energy Band Structure of MnO and α -MnS.* TIMOTHY M. WILSON, *Oklahoma State University*.—A study of the electronic and optical properties of the 1st-row transition metal oxides and sulfides is in progress. Recently published experimental data on MnO and NiO clearly indicate that these compounds display a typically bandlike electrical conductivity. An effort is being made to examine these compounds through calculations made using a spin-polarized energy band model. A brief description of this model, in which the local, crystal-field optical transitions are included, will be given. The results of calculations that have been made on MnO and on α -MnS are in agreement with the experimentally obtained optical and electronic data. The extension of this model to the calculation of the electronic structure of other compounds (NiO in particular) will be discussed and some preliminary results will be given.

*Work supported by National Science Foundation Grant No. GP-8074 through the Quantum Theory Project, University of Florida.

¹T. M. Wilson, Bull. Am. Phys. Soc. 13, 413 (1968).

HE5. Magnetothermal Oscillations in ReO₃. J. E. GRAEBNER, *Bell Telephone Laboratories*.—Detailed magnetothermal measurements in ReO₃ show 3 sets of frequencies which are in general agreement with the results of Marcus.¹ The present data are sufficiently precise that the 3 frequencies can be fully separated for all magnetic field directions in the {100} and {110} planes. The data show very good agreement with the recent APW calculations of Mattheiss,² which include {100}-directed open orbits. The disagreement is $\sim 5\%$ at worst, and generally $\sim 2\%$ or better.

¹S. M. Marcus, Phys. Letters 27A, 554 (1968).

²L. F. Mattheiss (to be published).

HE6. Magnetothermal Oscillations in RuO₂. W. D. RYDEN and J. E. GRAEBNER, *Bell Telephone Laboratories*.—Magnetothermal measurements have been made in a single crystal of the rutile-structure transition-metal oxide, RuO₂. Several branches are observed with frequencies in the range $0.07-0.9 \times 10^8$ G. These data are more detailed than the previously reported de Haas-van Alphen data¹ in RuO₂ and include several new branches which complicate the interpretation. A detailed Fermi surface deduced from the data will be discussed and compared with recent magnetoresistance measurements.²

¹S. M. Marcus, Phys. Letters 26A, 518 (1968).

²S. M. Marcus, Phys. Letters 26A, 191 (1968).

HE7. Reflectivity and Band Structure of EuO. C. M. GRANT and J. C. SUITS, *IBM Research Laboratory, San Jose*.—Near-normal incidence reflectivity of single-crystal EuO is reported for the energy range 1-8 eV. The spectrum displays 4 major peaks which can be correlated with similar structure observed for EuS¹ and EuSe². The lowest-energy peak of this chalcogenide series increases in energy with increasing chalcogenide atomic number (increasing lattice constant), whereas the 3 higher-energy peaks move in the opposite direction. The low-energy structure probably arises from transitions between 4f levels and the X₃ minimum of the d-like conduction band derived from the Eu²⁺ ions, while the higher-energy peaks most likely belong

to transitions analogous to those observed in alkaline earth chalcogenides. Assignments for these transitions will be discussed in terms of recent europium chalcogenide band structure models.³

- ¹J. Mullen and A. W. Lawson, Phys. Letters 24A, 303 (1967).
²P. Wachter, Physik Kondensierten Materie 8, 80 (1968).
³S. J. Cho, Phys. Rev. 157, 632 (1967).

HE8. Ellipsometer Measurements of the Optical Constants of Tantalum Oxide Films at High Absorption.* FRANK G. ULLMAN, CLARK D. SPIVEY, RICHARD W. LAWS, and B. J. HOLDEN, University of Nebraska.—The optical constants of tantalum oxide, inside its absorption edge, were required for analysis of electroreflectance measurements.¹ Ellipsometer measurements were made on 2 films approximately 450 and 900 Å in thickness, prepared by anodization of tantalum foil in boric acid. The imaginary part of the refractive index is less than 0.02 at wavelengths longer than about 2800 Å and rises steeply at shorter wavelengths. At wavelengths longer than 2800 Å, the real part exhibits normal dispersion, increasing with slowly increasing slope, and decreases at shorter wavelengths. These results will be compared with previously reported measurements of refractive index and absorption in tantalum oxide films. Our results are as yet only semiquantitative because of an inexact knowledge of film thicknesses and of the optical constants of tantalum over the wavelength range of interest. A new numerical technique for determining film thickness by

combining electroreflectance and ellipsometer data will be described.

*Work supported by a National Science Foundation Undergraduate Research Participation Grant.

¹B. J. Holden and F. G. Ullman, J. Electrochem. Soc. 116, February (1969).

HE9. Optical and EPR Absorption Studies of Deformed CaO and SrO Single Crystals.* THOMAS J. TURNER, Wake Forest University.—Single crystals of CaO and SrO were compressed several percent in an Instron testing machine. As a result of the deformation, optical absorption bands were produced at 276 nm in CaO and 280 nm in SrO whose absorption coefficients were proportional to the degree of deformation. A similar band which has been reported by Sibley *et al.*¹ is MgO at 217 nm. As in MgO no EPR signal was observed as a result of this deformation. However, when the deformed crystals were irradiated with 50-KV x rays a number of bands appeared including the F center. This supports the Seitz prediction that dislocation interactions produce vacancies. As has been observed² these deformation bands are probably due to vacancies (α centers) or interstitials produced by the deformation process. The interstitial appears to be the most likely cause of the absorption because of the deep trap produced by vacancies.

*Work supported in part by the U.S. Atomic Energy Commission.

¹W. A. Sibley, J. L. Kolopus, and W. C. Mallard (to be published).

THURSDAY AFTERNOON, 27 MARCH 1969

JEFFERSON ROOM AT 2:00 P.M.

(W. M. WALSH presiding)

Magneto-Plasmas and Magneto-Optics

HF1. Multiple Scattering Theory of Heliconlike Propagation in Powdered Semiconductors and Semimetals.* FRANK LEE GALEENER and JACEK K. FURDYNA, Purdue University.—In an effort to develop powder transmission as a tool for basic solid-state studies we have solved the problem of multiple scattering of electromagnetic waves by a random distribution of aligned anisotropic scatters, in the point-dipole limit. The resultant formulas for effective permittivity and permeability are used to discuss the transmissivity of powdered samples of InSb, InAs, HgSe, and HgTe measured at 35 GHz in the Faraday configuration. These formulas justify the approximate single scattering model already reported¹ and allow quantitative prediction of many more features, including quantum effects, line shapes, dilution effects, and mixing laws.

- *Work supported by the Advanced Research Projects Agency.
¹F. L. Galeener and J. K. Furdyna, Bull. Am. Phys. Soc. 13, 1454 (1968).

HF2. Magneto-Plasma Effects in the Quantum Limit. D. COHN* and BENJAMIN LAX,* Francis Bitter National Magnet Laboratory,[†] MIT.—Fourier transform interferometric spectroscopy has been employed to measure the far infrared reflectivity of bismuth subjected to high magnetic fields in the Voigt configuration. These reflectivity measurements have resulted in the observation of new dielectric anomalies (i.e., zeros and infinities in the dielectric constant) due to the presence of both electrons and holes. At fields above 120 kG an additional anomaly has been observed. This anomaly is associated with the magneto-plasma effect due to a new transition in the high field quantum

limit and results from the unequal g factor^{1,2} of the 1st 2 Landau levels for a highly nonparabolic set of bands.³

*Also Physics Department, MIT.

[†]Supported by the U. S. Air Force Office of Scientific Research.

¹J. C. Burgiel and L. C. Hebel, Phys. Rev. 140, A925 (1965).

²G. E. Smith, G. A. Baraff, and J. M. Rowell, Phys. Rev. 135, A1118 (1964).

³R. N. Brown, J. G. Mavroides, and B. Lax, Phys. Rev. 129, 2055 (1963).

HF3. Quantum Effects in Cyclotron Resonance in p -Type InSb and Ge. KENNETH J. BUTTON and BENJAMIN LAX,* Francis Bitter National Magnet Laboratory,[†] MIT.—Quantum effects in the degenerate valence bands have been observed over a wide range of temperatures at a wavelength of 0.337 mm by using a continuous-wave HCN laser spectrometer and magnetic field intensities up to 175 kG. A multitude of absorption lines have been recorded for both semiconductors which represent individual transitions among the complicated sets of quantum levels predicted by Luttinger and Kohn.¹ Since the holes were excited thermally from acceptor levels, only the lowest-lying quantum transitions were observed at low temperature and the higher-lying transitions appeared successively as the temperature was increased. At this photon energy, the quantum condition holds up to 43°K. The change of intensity of the transitions with temperature confirms the identity of each of the lines. Spectra will be shown for the 3 principal crystal directions for temperatures between 10 and 200°K. The identification of the individual transitions and the refinement of the Luttinger and Kohn theory will be discussed in the following abstract.

Introduction

Intense technological interest has developed in the family of europium chalcogenides over the past few years. This has been due^{mainly} to the discovery of large magneto-optic activity in the visible region by Suits and co-workers in 1965, thus creating hopes that these materials might provide a basis for optically read magnetic memories. This magnetooptic effect has been described by Methfessel as arising essentially from 4f-5d allowed transitions of the Eu^{2+} ion in the rocksalt structure.

We have extended the optical measurements on EuO up to 9 eV through the use of normal incidence reflectivity and it is these results which we will present in this talk.

Slide 1. EuO Reflectivity 1-9 eV

This slide shows the raw reflectivity data on EuO in that range. The data were taken on an automated spectrometer and represent the average of 9 repetitions over the entire spectrum. The samples were air-cleaned single crystals kept in a vacuum of 10^{-6} Torr for the duration of the experiment. Note the presence of four major peaks located at 1.55, 4.72, 5.73, and 7.30 eV, respectively. and the interesting shoulder on the side of the 4.72 eV peak.

The magneto-optic effects of importance take place in the region of the low energy structure. Note that the shape of this structure resembles the dispersive part of a classical oscillator. This is shown more clearly in the next slide.

(5)

Slide 2. EuO Film R and T

Here we have the reflectivity and transmission from 1-3.5 eV of a 3500 Å epitaxial EuO film on CaF₂ which was grown by Ken Lee of our labs. Note that the peak in absorbance is at a much different energy than the reflectivity peak (the extra reflectivity peak is merely an interference fringe). This suggests the bulk reflectivity in this region is dominated by dispersive, rather than absorptive, behavior, as can be seen from the optical constant results shown on the next slide.

Slide 3. Eu0 ϵ_1 and ϵ_2

In calculating ϵ_1 and ϵ_2 from our ^{bulk} reflectivity data, we have used a rather different technique - that of fitting, in a least squares sense, selected Hilbert transform pairs as optical constants to the reflectance - instead of the usual Kramers-Kronig method. This has recently been applied by Verlaan to VO₂, silicon, and germanium reflectivity. It has the advantage of not relying on extrapolation algorithms and provides a means of judging the validity of the result.

We chose four gaussians for ϵ_2 and their corresponding Dawson's function Hilbert transforms for ϵ_1 . This slide shows the optical constants resulting from a least squares optimization of the gaussian positions, heights, and widths. The important physical point to note is the strong resemblance of ϵ_1 , rather than ϵ_2 , to the reflectivity. Just the opposite is true for most valent semiconductors and is because the optical transitions in those materials are of much greater strength than here.

Slide 4. 6₁, 6₂ Goodness of Fit to Reflectivity

This slide merely shows how well the reflectance calculated from our least-squares adjusted gaussians and shown by the solid line, fits the experimental data, shown by the circled points. We consider the fit quite good.

Slide 5. EuO, EuS, and EuSe Reflectivity

This slide compares our EuO reflectivity with the results of Muller and Dawson on powdered EuS and those of Wachter on crystalline EuSe. There are, of course, great similarities. We have grouped the four main peaks as shown, labelling them E_1 , E_2 , E_3 and E_4 , respectively. Note that the E_1 peak moves to higher energies with increasing anion atomic number and increasing lattice constant, whereas the opposite behavior is observed for the other peaks. The latter is usually the case for interband transitions in isomorphic series of isovalent semiconductors and also for charge transfer transitions in chalcogenides and halides of a given transition metal. In this context, then, what we observe for the E_1 peak is somewhat anomalous. In addition, we see a positive temperature coefficient for the E_1 peak in a temperature range well above the Curie point. We must be careful to point out that we believe the mechanism for this shift to be different from that for the sudden red shift observed by Beach and collaborators at temperatures below the Curie point. The temperature effect is shown on the next slide.

Slide 6. Temperature Dependence of E_I Peak

Here we display the temperature dependence of the E_I structure between 300K and 5°K. In the paramagnetic region, the peak moves with a coefficient of about $4.7 \cdot 10^{-4}$ eV/K. As the Curie temperature is passed, a sudden movement to near its final position is observed. Kasuya and Freiser have treated this ferromagnetic red shift in terms of a 'magnetic exciton' model.

Here we compare the E_I structure at 5°K with the room temperature data. In the paramagnetic region, the peak moves fairly slowly with a coefficient of about 4.7×10^{-4} eV/K. As the Curie temperature is passed, however, more rapid movement to its final position is observed. Kasuya and Freiser have treated this ferromagnetic red shift in terms of a 'magnetic exciton' model.

Slide 7. Band Structure of Eu-chalcogenides

This slide shows our postulated band structure for paramagnetic europium chalcogenides. From their general chemical and crystalline similarity to alkaline earth chalcogenides, we naturally expect there to be a p-derived valence band and a 6s-derived conduction band. In addition, however, we will have bands originating from nearby ^{5d} levels of the Eu^{2+} ion. ^{The splitting of the levels at the P point can be thought of as 10D_{5/2} and 10D_{3/2}.} We show their behavior along the {100} direction ^{in the Brillouin zone}, as determined by simple tight-binding considerations. We must now confess that we have been somewhat cavalier in our placement of the half-filled 4f band. It is highly questionable whether we can represent strongly correlated f electrons in a one electron framework. What we have done is to take the following operational approach: We will place the 4f levels below the lowest, conduction band final state an amount in energy equal to the E_1 peak position and call this the energy necessary to excite a single electron to the conduction band, or an exciton ^{state} associated with it. ^{Because of correlation,} A different amount of energy will be necessary to excite a second electron from the same Eu^{2+} ion but not for ^{a second} one from a different site. On this model, then, the E_1 peak is assigned to a $4f \rightarrow X_3$ transition or to an associated exciton.

This is consistent with our observations. E_1 should move to lower energies with decreasing lattice constant because X_3 will lower with respect to $4f$ due to increased crystal field splitting and increased band broadening arising from ^{greater} [110]-directed nearest neighbor europium $5d$ overlap. This is also consistent with the variation in Curie Temperature observed within the series. Our band diagram, then, is essentially that calculated with APW methods by Cho with two important modifications. We show the $4f$ level above P_{15} in agreement with early arguments by Methfessel and ^{in calculations by Cho.} We also show P_1 below X_3 in view of recent theoretical work by Yanase and Kasuya and recent photoconductivity results. That is, one can explain the persistence of photoconductivity ^{in EuO} to very low temperatures observed by Beckmann and Wachter in terms of a metastable exciton formed from the $4f \rightarrow X_3$ transition which ^{then} decays into a bound $4f$ hole and a mobile P_1 electron.

Attempts to make assignments for the higher energy E_2 , E_3 and E_4 peaks open up a whole Pandora's box of possibilities. Among these are $P_{15} \rightarrow P_1$, $P_{15} \rightarrow P_{25}'$, $P_5 \rightarrow P_{12}$ as well as $4f \rightarrow P_5'$ and $4f \rightarrow P_{12}$. For E_2 , $4f \rightarrow P_{25}'$ is inconsistent with the ^{observed} shift to higher energies with decreasing lattice constant. On the one hand, $P_{15} \rightarrow P_1$ is attractive as it would be analogous to the first strong absorption found in the corresponding alkaline earth chalcogenides; but on the other, so is

$4f \rightarrow P_{1,2}$ for such transitions are observed in EuF_2 .
Perhaps the hump on the low energy side of F_2
~~is broadened multiplet structure?~~ For the time
being, we will tentatively assign $P_{1,5} \rightarrow P_1$ to
 Er with $P_{1,5} \rightarrow P_2$'s and transitions at more
general points of the Brillouin zone as strong
possibilities. Much more data is needed and we
are undertaking a series of modulated reflectance
experiments in the hope of pinning down some
of these assignments in a more satisfactory way.