

²B. C. Deaton and R. B. Graf, *Rev. Sci. Instr.* **34**, 45 (1963).

³B. C. Deaton and D. E. Bowen, *Appl. Phys. Letters* **4**, 97 (1964).

⁴B. P. Pashaev, *Fiz. Tver. Tela* **3**, 416 (1961) [translation: *Soviet Phys. - Solid State* **3**, 303 (1961)].

⁵Kh. I. Amirkhanov, G. B. Bagduev, and M. A. Kazhlaev, *Dokl. Akad. Nauk SSSR* **117**, 953 (1957) [translation: *Soviet Phys. - Doklady* **2**, 556 (1957)].

⁶G. C. Kennedy and R. C. Newton, *Solids Under Pressure*, edited by W. Paul and D. M. Warschauer (McGraw-Hill Book Company, Inc., New York, 1963), pp. 163-174.

⁷F. P. Bundy, *Phys. Rev.* **110**, 314 (1958).

⁸N. A. Tikhomirova and S. M. Stishov, *Zh. Ek-*

sperim. i Teor. Fiz. **43**, 2321 (1962) [translation: *Soviet Phys. - JETP* **16**, 1639 (1963)].

⁹P. W. Bridgman, *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957).

¹⁰H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids* (Oxford University Press, New York, 1959), 2nd ed.

¹¹H. M. Strong, *Modern Very High Pressure Techniques*, edited by R. H. Wentorf (Butterworth, Inc., Washington, 1962), p. 103.

¹²K. M. Taylor, *Ind. Eng. Chem.* **47**, 2506 (1955).

¹³H. T. Hall, *Rev. Sci. Instr.* **31**, 125 (1960).

¹⁴F. R. Boyd and J. L. England, *J. Geophys. Res.* **65**, 741 (1960).

SEMICONDUCTOR-TO-METAL TRANSITION IN V_2O_3 †

David Adler and Julius Feinleib

Gordon McKay Laboratory, Harvard University, Cambridge, Massachusetts

(Received 11 May 1964)

After Morin¹ had shown that several transition metal oxides exhibit an abrupt change with temperature from semiconducting to metallic behavior, Goodenough,² Mott,³ and others⁴ proposed qualitative models to account for the transition. In this Letter we will present the results of a generally applicable quantitative theory of semiconductor-to-metal transitions, and the results of new optical and transport measurements on V_2O_3 which strongly support this theory.

Consider a crystal which at low temperatures is a normal semiconductor with valence and conduction bands separated by an energy gap $E_g(T)$. If this energy gap depends on the concentration of carriers excited into the conduction band, n_i , then, to first order in n_i ,

$$E_g(T) = E_g(0) - \beta n_i, \quad (1)$$

ignoring the explicit temperature dependence of E_g . Such a relation can be shown to be appropriate in an antiferromagnet where the energy gap arises from the difference in exchange potential for an electron of given spin on the sublattices of opposite magnetization. When an electron is excited across this gap, the net magnetization on either sublattice decreases, and thus the energy gap decreases with increasing number of carriers excited. For antiferromagnetism in narrow bands, Eq. (1) is found to hold even as n_i becomes relatively large; in this case, the constant β can be shown to be $4E_g(0)/N$, where N is the concentration of electrons in the valence

band.

However, the existence of antiferromagnetism is not a necessary condition for the applicability of Eq. (1). The relation can also be shown to be appropriate when an energy gap is caused by a crystal structure distortion to lower symmetry. This type of gap may arise from an energy gain due to chemical binding—the lower band can be thought of as a bonding band, the upper an antibonding band. Excitation of an electron across the energy gap decreases the gap because the excited electron no longer contributes to the chemical binding. It is more difficult to evaluate the constant β when the gap is caused by crystalline distortion. For simple one-dimensional models with delta function or with Mathieu potentials, β has been evaluated as a function of the amount of distortion, the bandwidth, and the energy gap. It was found that β is more sensitive to the distortion than to the band parameters; for distortions of the order of 1% (such as is found in V_2O_3), for these two models, β is quite close to the value of $4E_g(0)/N$ obtained for antiferromagnetism.

For situations where Eq. (1) is valid, calculation of E_g as a function of temperature, taking into account Fermi-Dirac statistics, shows that, at a temperature T_t , there is a sharp collapse of the band gap, and therefore a sharp semiconductor-to-metal transition. The transition temperature can be evaluated in terms of $E_g(0)$ and β in the limit where the bands are very narrow. In this case, a reasonable limit for d bands, it

is found that T_t is proportional to $E_g(0)$. For antiferromagnetic crystals, the result is

$$E_g(0)/kT_t = 7.1. \quad (2)$$

Regardless of the actual value of the ratio (2), the theory shows that the logarithmic derivatives of E_g and T_t must be equal:

$$\frac{d \ln E_g(0)}{dX} = \frac{d \ln T_t}{dX} \quad (3)$$

where X is any external parameter, such as pressure or uniaxial stress.

We have made several new measurements on single crystals of V_2O_3 , the results of which test relations (2) and (3). Firstly, the energy gap was determined directly from the optical absorption and the transition temperature was found from electrical conductivity. This gave a numerical value for the ratio (2). Secondly, both E_g and T_t were varied by applying hydrostatic pressure and uniaxial stress and the stress coefficients of both were obtained. This provided a critical test of relation (3).

The following results were obtained. No transmission was observed in the room-temperature metallic region between 0.05 and 6 eV for a sample of 25- μ thickness. In the semiconducting region (at 77°K), transmission was obtained between 0.1 and 0.4 eV. The transmission changed by several orders of magnitude in this range, and clearly indicated the presence of an absorption edge at approximately 0.1 eV.

The semiconductor-to-metal transition temperature was measured to be 152°K on our samples. These single crystals were found to be within 0.3% of the stoichiometric composition and are therefore at least as pure as any of the sintered or single-crystal materials previously used for investigation. From these two results, the ratio (2) is measured as

$$E_g(0)/kT_t \sim 7.6.$$

In the second series of experiments, the relation between transition temperature and pressure was determined to be

$$\frac{d \ln T_t}{dP} = -2.6 \times 10^{-5} \text{ bar}^{-1} \quad (4)$$

where P is the pressure in bars. With uniaxial stress applied parallel to the corundum structure's b axis, the transition temperatures ob-

tained gave

$$\frac{d \ln T_t}{dS} = -2.8 \times 10^{-5} \text{ bar}^{-1} \quad (5)$$

where S is the stress in bars. With stress applied along the c axis, the pressure coefficient was at least an order of magnitude smaller:

$$\frac{d \ln T_t}{dS} < 0.3 \times 10^{-5} \text{ bar}^{-1}.$$

The pressure and uniaxial stress coefficients for the energy gap were determined from the stress dependence of the activation energy for electrical conductivity. These results can be expressed as

$$\frac{d \ln E_g(0)}{dP} = -2.2 \times 10^{-5} \text{ bar}^{-1} \quad (6)$$

$$\frac{d \ln E_g(0)}{dS} = -3.0 \times 10^{-5} \text{ bar}^{-1} \quad (7)$$

The magnitude of the activation energy varied from 0.12 to 0.18 eV, consistent with the range 0.07 to 0.20 eV previously measured by other workers.⁵ It can be shown that the pressure coefficient of contributions to the activation energy from polaron effects and nonstoichiometry are of the order of 10^{-6} bar^{-1} , and thus these contributions do not affect the results (6) and (7).

A comparison of (6) with (4) and (7) with (5) shows that Eq. (3) is indeed satisfied within experimental error. Furthermore, the magnitude of the ratio is quite close to the predicted value in (2). In the event that the energy gap does not arise from antiferromagnetism, but rather from the crystalline distortion referred to above, the constant of proportionality in (2) may well be different. However, as referred to above, for distortions of the order of those in V_2O_3 , two simple models have given constants within 10% of (2).

More generally, a thermodynamic relation for the change in energy gap with carrier concentration can be derived:

$$\beta \equiv \left(\frac{\partial E_g}{\partial n} \right)_{P, T} = -\frac{1}{K} \left(\frac{\partial E_g}{\partial P} \right)_{n, T}^2 + \left(\frac{\partial E_g}{\partial n} \right)_{V, T}$$

where K is the isothermal compressibility. The first term on the right gives the decrease in energy gap due to volume changes and the second term represents the explicit dependence of E_g

on carrier concentration as the volume is held constant. Assuming the energy gap decrease is entirely due to volume changes (i.e., no antiferromagnetism), and using the best value available for the compressibility ($K \sim 0.40 \times 10^{-6} \text{ bar}^{-1}$, the values⁶ for Al_2O_3 and Cr_2O_3), we obtain

$$E_g(0)/kT_t = 7.4.$$

The essential point is that there is no a priori reason for the validity of Eqs. (2) and (3), nor does any other model heretofore considered predict these relations. Therefore the agreement with experiment must be considered as good evidence for the applicability of the model. The thermodynamic argument strongly indicates that it is crystal structure changes which bring about the energy gap, whether or not the crystal is antiferromagnetically ordered. No magnetic ordering has as yet been established in V_2O_3 , although antiferromagnetism has been found in Ti_2O_3 .⁷ This is also consistent with both the observed anisotropy in the stress coefficient of the transition temperature and the latent heat experimentally determined at the transition.⁸ Moreover, until these optical measurements were made, there had never been any direct confirmation of the existence of an energy gap in materials such as V_2O_3 , and indeed most theories of the semiconductor-to-metal transition ascribed the semiconducting properties to thermally activated hopping.⁹

It remains to be shown that a reasonable band model for the V_2O_3 crystal structure results in the energy gap and Fermi level required for the validity of the theory. For the corundum structure the trigonal field will split the t_{2g} band into a t_0 and a t_{\pm} band, assuming that these bands are well separated from the filled oxygen $2p$ band and the empty vanadium e_g and $4s$ bands. At low temperatures, the crystal has a monoclinic structure, with cation pairs along the a and c axes in a manner described by Goodenough.² The t_{\pm} band is split into two, the t_a band and the t_b band. The energy band formed from the basal plane orbitals, which we call the t_a bonding band (see Fig. 1), is just filled, since each a -axis pair contributes one energy state with two electrons in it, one electron from each cation of the pair. The t_0 bonding energy band is, for the same reason, exactly filled, and therefore the crystal is a nonconductor if no other bands overlap these. The bonding t_a band is separated from the antibonding bands by an energy gap, E_{g1} ,

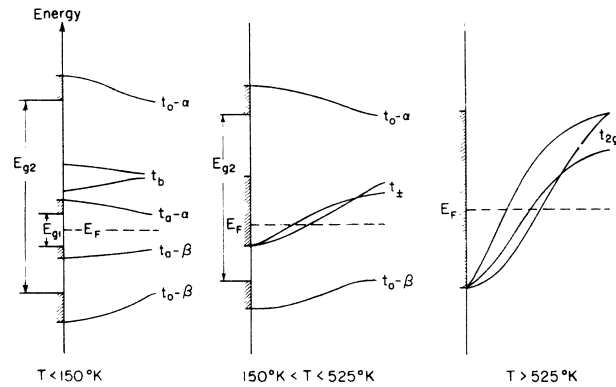


FIG. 1. Possible band scheme for V_2O_3 . The symbol α refers to antibonding, β to bonding bands.

which is of the order of 0.1 eV. This gap is brought about by the monoclinic distortion, and therefore the theory described above applies, and predicts a transition to the metallic state at a temperature $T_t \sim 150^\circ\text{K}$. At the same time a phase transformation occurs because the a -axis pairs break up, changing the crystal structure to the higher symmetry rhombohedral phase.

Similar arguments can be applied to the energy gap E_{g2} between the t_0 bonding and t_0 antibonding bands. The theory predicts another transition at a temperature $T_t' \sim 7E_{g2}/k$, at which point E_{g2} shrinks to zero and leaves one t_{2g} band partially filled. The behavior remains metallic, and no striking change in conductivity will be observed at T_t' . However, this transition changes the shape of the Fermi surface and should give rise to an anomalous resistivity change such as that observed near 525°K in V_2O_3 . In our samples there is an anomalous increase in resistivity in this range, which has the form expected from an atomic order-disorder or spin-disorder scattering.¹⁰ It has been suggested by some workers¹¹ that an antiferromagnetic ordering transition does occur in this temperature range, and this may contribute to the t_0 band splitting. This would also correlate with the situation in Ti_2O_3 , where there is only one $3d$ electron present and the semiconductor-to-metal transition occurs at the Néel temperature, near 500°K .⁷ Since Ti_2O_3 has the same structure as V_2O_3 , we might expect similar band structure, except perhaps wider bands. Figure 1 shows that for one $3d$ electron per cation, it is the high-temperature collapse of E_{g2} which leads to the transition to the metallic state.

The authors wish to thank Professor Harvey

Brooks and Professor William Paul for their helpful guidance of this research.

†Research supported by the Office of Naval Research and the Advanced Projects Research Agency.

¹F. J. Morin, Phys. Rev. Letters 3, 34 (1959).

²J. B. Goodenough, Magnetism and the Chemical Bond (Interscience Publishers, Inc., New York, 1963).

³N. F. Mott, Phil. Mag. 6, 287 (1961).

⁴W. Kohn, Phys. Rev. 133, A171 (1964); J. Callaway, Proceedings of the International Conference on the Physics of Semiconductors, Exeter, July 1962 (The Institute of Physics and The Physical Society, London, 1962), p. 582; J. Hubbard, Proc. Roy. Soc.

(London) A276, 238 (1963).

⁵F. J. Morin, reference 1; A. J. MacMillan, Massachusetts Institute of Technology Report No. 172, 1962 (unpublished); I. G. Austin, Phil. Mag. 7, 961 (1962).

⁶International Critical Tables (McGraw-Hill Book Company, Inc., New York, 1929), Vol. III.

⁷S. C. Abrahams, Phys. Rev. 130, 2230 (1963).

⁸J. Feinleib, Bull. Am. Phys. Soc. 7, 217 (1962).

⁹R. R. Heikes and W. D. Johnson, J. Chem. Phys. 26, 582 (1957); S. van Houten, J. Phys. Chem. Solids 17, 7 (1960); T. Holstein, Ann. Phys. (N.Y.) 8, 343 (1959); F. J. Morin, reference 1.

¹⁰P. G. De Gennes and J. Friedel, J. Phys. Chem. Solids 4, 71 (1958).

¹¹J. Wucher, Compt. Rend. 241, 288 (1955); S. Teranishi and K. Tarama, J. Chem. Phys. 27, 1217 (1957).

SELF-REVERSAL OF RESONANCE LINES AND ENHANCEMENT OF VIBRONICS IN GADOLINIUM IN CRYSTALS*

E. Cohen, U. El-Hanany, and S. Yatsiv

Department of Physics, The Hebrew University, Jerusalem, Israel

(Received 12 May 1964)

The relative intensity of vibronic emission lines in gadolinium chloride¹ varies in different crystalline samples. It also increases sharply upon lowering from liquid nitrogen to liquid hydrogen temperatures. It was suspected that both effects were due to repeated self-trapping of resonance radiation. To elucidate this point the fluorescence of $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ was studied in an unorthodox geometry. The crystal was placed between the source and the entrance slit of a spectrometer. The incident pumping radiation (2750 Å in Fig. 1) penetrated a very thin layer on the surface of the crystal. The emission at 3120 Å and longer wavelengths traversed the width of the crystal before entering the spectrometer. Crystals of 2 to 10 mm thickness were investigated at 77°K and 20°K. The self-trapping of the resonance 3120Å group was manifest in three ways:

(a) In a high-resolution spectrogram, the resonance lines show a well-developed self-reversal [Fig. 2(a)]. This is not observed in the conventional geometry when the incident radiation falls on a surface of the crystal at a right or oblique angle to the direction of observation. The result of front surface emission is reproduced in Fig. 2(b) for comparison. The relative dip in the self-reversed lines, and the separation between the two side peaks, increases with the thickness of the crystal.

(b) The relative intensity of the 3470Å vibronic transition compared with its parent resonance transition increases with self-trapping. This is well known² and is due to the recurrent emission of vibronics in each emission and reabsorption cycle of the resonance radiation.

The vibronic emission is not reabsorbed since the excited vibrational state $v(1)$ of the water molecules is not populated at our working tem-

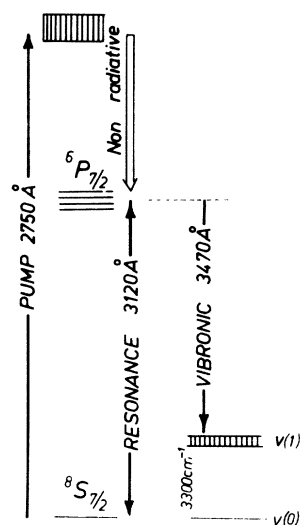


FIG. 1. Schematic energy level diagram for the pump, resonance, and vibronic transitions in gadolinium chloride.