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Nature of the Electrical Transition in Ti₂O₃*

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Data on the electrical, optical, magnetic, and structural properties of Ti₂O₈ are reviewed; the differences between the transition encountered in Ti_2O_3 and V_2O_3 are particularly stressed. Perusal of the available experimental and theoretical work leads to the conclusion that the transition in Ti_sO₈ can be explained without invoking antiferromagnetic ordering. This is of particular relevance in light of recent experimental work which casts serious doubt on the commonly accepted hypothesis that Ti₂O₃ is antiferromagnetic. An alternative interpretation of the transition is offered, according to which a gradual change in the position and width of two close-lying bands results in a change of Ti₂O₃ from a narrow-gap semiconductor to a semimetal. It is pointed out that a simple theory based on this model is in essential accord with the available experimental data, and that it satisfies the requirements imposed by crystal symmetry.

I. INTRODUCTION

In numerous investigations¹⁻⁴ it has been confirmed that the resistivity of Ti₂O₃ drops by a factor of roughly 50 as the temperature is raised from 300° to 750°K. These findings stand in sharp contrast to V_2O_3 ,^{3,5-8} where the resistivity is altered by approximately eight orders of magnitude at the transition temperature $(\sim 150^{\circ} \text{K})$ where the crystal suffers a rhombohedral \rightleftharpoons monoclinic phase change.

Since there is no alteration in the crystal symmetry of Ti₂O₃ in the range for which electrical properties have been measured, the change in resistivity has generally been interpreted as due to the splitting of the conduction band into subbands when antiferromagnetic order sets in.^{3,9-11} The theory for the detailed course of such a transition has been worked out by Adler and Brooks,^{9,10} which involves a catastrophic shrinkage of the gap as electrons are excited across it with rising temperature. The application of this theory to Ti₂O₃ was a natural inference of neutron-diffraction studies of Abrahams,12 according to which Ti₂O₃ exhibits antiferromagnetism below 660°K, with a sublattice magmetization of approximately 0.2 μ_B .

That there are difficulties in the application of the Adler-Brooks model to Ti₂O₃ becomes evident in an examination of various data. In the first place, the change in resistivity with temperature predicted with this theory⁹ is much greater and much more abrupt

- Supported by the NASA Institutional Grant NGR 15-005-021. ¹ M. Foëx and J. Loriers, Compt. Rend. 226, 901 (1948). ² A. D. Pearson, J. Phys. Chem. Solids 5, 316 (1958). ³ F. J. Morin, Phys. Rev. Letters 3, 34 (1959). ⁴ J. Yahia and H. P. R. Frederikse, Phys. Rev. 123, 1257 (1961).
- ⁵S. Kachi, T. Takada, and K. Kosuge, J. Phys. Soc. Japan 18, 1839 (1963).
- ⁶S. Minomura and H. Nagasaki, J. Phys. Soc. Japan 19, 131 (1964).
- ⁷ D. Adler and J. Feinleib, Phys. Rev. Letters 12, 700 (1964).
 ⁸ J. Feinleib and W. Paul, Phys. Rev. 155, 841 (1967).
 ⁹ D. Adler, Phys. Rev. Letters 17, 139 (1966); D. Adler, thesis,
- ¹⁰ D. Adler and H. Brooks, Phys. Rev. 155, 826 (1967).
 ¹¹ D. Adler, J. Feinleib, H. Brooks, and W. Paul, Phys. Rev. 155, 851 (1967).
 ¹² D. Adler, J. Feinleib, H. Brooks, and W. Paul, Phys. Rev. 155, 851 (1967).
- ¹² S. C. Abrahams, Phys. Rev. 130, 2230 (1963).

than the experimental observations of this phenomenon (see Fig. 3). The theory invoking magnetic transitions obviously requires some modifications before it may be considered as having properly explained the experimental observations. In the second place, evidence favoring the existence of antiferromagnetic order in Ti₂O₃ is by no means clearcut, as is indicated in the brief review given below.

A. Magnetic-Susceptibility Measurements

The work of various investigators¹³⁻¹⁷ is reasonably concordant. The magnetic susceptibility χ of Ti₂O₃ in powdered form remains nearly constant up to $\sim 400^{\circ}$ K, then rises sharply by 50% in the range $400^{\circ} < T <$ 600°K, after which there is a further gradual rise of χ with T. These data do not seem to force the conclusion that the material is antiferromagnetic; a small peak in the χ -vs-T plot reported by Adler and Selwood¹³ for a rather impure sample has not been confirmed in later investigations. Measurements taken on single-crystal specimens led Carr and Foner¹⁸ to the conclusion that long-range antiferromagnetic order is absent, since χ values obtained with the magnetic field parallel to the c axis or lying in the basal plane were nearly equal and both small.

B. Neutron-Diffraction Work

Aside from the work by Abrahams, neutron-diffraction experiments have been carried out by Shirane, Pickart, and Newnham¹⁹ and recently, by Kendrick, Arrott, and Werner.²⁰ Neither group detected any superstructure lines indicative of magnetic order;

- ¹⁴ M. Foëx and J. Wucner, Compt. Kend. 241, 104 (1930).
 ¹⁵ J. Wucher, Compt. Rend. 241, 288 (1955).
 ¹⁶ L. K. Keys and L. N. Mulay, Phys. Rev. 154, 453 (1967).
 ¹⁷ V. I. Chirkov, E. E. Vainshtain, and Ya. V. Vasil'ev, Zh. Neorg. Materialy 3, 1017 (1967).
 ¹⁸ P. H. Carr and S. Foner, J. Appl. Phys. 31, 344S (1960).
 ¹⁹ G. Shirane, S. J. Pickart, and R. Newnham, J. Phys. Chem.
- Solids 13, 167 (1960). ²⁰ H. Kendrick, A. Arrott, and S. A. Werner, J. Appl. Phys. 39, 585 (1968).

^{*} Supported by the NASA Institutional Grant NGR 15-005-021.

¹³ S. F. Adler and P. W. Selwood, J. Am. Chem. Soc. 76, 346 (1954). ¹⁴ M. Foëx and J. Wucher, Compt. Rend. **241**, 184 (1955).

according to Ref. 20, any magnetic moment present is less than 0.07 μ_B .

C. X-Ray Emission Spectra

Chirkov, Vainshtain, and Vasil'ev17 have examined the x-ray emission spectrum of Ti_2O_3 at 410° and 560°K. From an analysis of their data they conclude that no long-range magnetic order exists in this material.

D. Negative Magnetoresistance Data

Magnetoresistance measurements²¹ in the range 1.7° to 4.2°K provide further, indirect evidence relating to magnetic ordering. In these experiments Ti₂O₃ was doped with 1-3 at.% V_2O_3 to render the material metallic, thereby suppressing the positive magnetoresistance effects encountered in highly pure crystals (see below). One then observes $\lceil Fig. 1(b) \rceil$ a rather sizable negative magnetoresistance effect, which is interpreted as arising from inelastic scattering of electrons by trace impurities possessing a local magnetic moment. Both from the fact that the effect sets in at the lowest applied magnetic field of 100 G, as well as from a quantitative fit of the experimental observations to the appropriate theory,^{22,23} one is led to the conclusion that in V-doped material there is no molecular exchange field of the magnitude required for the persistence of antiferromagnetic order in Ti₂O₃ into the 500°K range.



FIG. 1. (a) Magnetoresistance of $\mathrm{Ti}_2\mathrm{O}_8$ with impurity content less than .016 at.%. Measurements carried out at 4.2° K. (b) Magnetoresistance of Ti₂O₃ with ~ 3 at.% V₂O₃ added. Measurements carried out at 4.2°K.

²¹ J. M. Honig and T. B. Reed (unpublished).
²² A. R. De Vroomen and M. L. Potters, Physica 27, 657 (1961).

28 L. L. Van Zandt, thesis, Harvard University, 1964.

II. POSITIVE MAGNETORESISTANCE EFFECTS

If one regards the above evidence as conclusive, it is necessary to invoke another mechanism for explaining the electric transition in Ti₂O₃. Here, some magnetoresistance data obtained recently with highly purified single crystals²⁴ provide a clue. For material with a residual total impurity content in the range 0.004 to 0.16 at.% (N is found to be a particularly troublesome impurity) one obtains positive magnetoresistance curves of the type shown in Fig. 1(a). It is seen that in magnetic fields H greater than 200 kG, $\Delta \rho / \rho_0$ exceeds a factor of 4 while still increasing quadratically with applied field. These facts are incompatible with the upper limit of $(\Delta \rho / \rho_0)_{\text{max}} \approx 2.4$ reached asymptotically under neglect of quantization effects in a nondegenerate material with a single band of standard form.²⁵ The data are, however, consistent with a two-band model in which both electrons and holes in nearly equal concentration participate in conduction processes in $\mathrm{Ti}_2\mathrm{O}_3$ at 4.2°K. If this is the case, the material is an intrinsic semiconductor, with a narrow band gap of the order of 0.02-0.06 eV. These conclusions are compatible with (i) the observed $\Delta \rho / \rho_0(H)$ and (ii) the observation that $\rho > 10^5 \Omega \cdot \text{cm}$ at 4.2°K, and (iii) the fact that ρ changes exponentially with 1/T.

III. CHANGE OF LATTICE PARAMETERS WITH TEMPERATURE

The above information is combined below with the known fact that the a, c, and α parameters begin to change rather rapidly above 380°K^{2,26-28} and then settle down to reasonably constant values above 500°K. While the region of marked change is not well delineated from the remainder and appears to depend on sample purity,²⁸ it correlates roughly with the region of rapid change in electrical resistivity. The distension of the unit cell with increasing temperature is such as to bring the anions into closer proximity to the cations, while increasing the spacing between cation pairs along the c axis.

IV. SEMICONDUCTOR SEMIMETAL TRANS-FORMATION AS A MODEL FOR INTERPRETING THE ELECTRICAL TRANSITION IN Ti₂O₃

On the basis of the above evidence, the electrical transition in Ti₂O₃ has recently been reinterpreted²⁹

24 T. B. Reed, R. E. Fahey, and J. M. Honig, Mat. Res. Bull. 2, 561 (1967)

²⁵ A. H. Wilson, The Theory of Metals (Cambridge University Press, London, 1954), 2nd ed., pp. 234–242. ²⁶ R. E. Newnham and Y. M. de Haan, Z. Krist. 117, 235

(1962); Quart. Progr. Rept. No. XXVI, Lab. for Insulation Res. MIT, Cambridge, Mass., January 1960 (unpublished). ²⁷ A. Magnéli *et al.*, U. S. Dept. Comm. Office Tech. Serv., P. B.

Rept. 145,923 (1961 unpublished).

²⁸ P. M. Raccah (private communication).
 ²⁹ L. L. Van Zandt, J. M. Honig, and J. B. Goodenough, J. Appl. Phys. 39, 594 (1968).



FIG. 2. Band structure derived from the d levels, along the Γ - Λ -Z symmetry axis of the first Brillouin zone for the corundum structure.

in terms of a gradual alteration in band structure, such that the material evolves from a semiconductor at low temperature into a semimetal at elevated temperature. A band-structure scheme which satisfies the symmetry requirements³⁰ of the corundum structure along the Γ - Λ -Z symmetry axis of the first Brillouin zone is shown in Fig. 2. The bands are labeled by standard group-theoretical notation according to the symmetry of the five d orbitals with respect to the point group D_{3d} of the crystal structure, which splits the levels into one a_{1g} , two $e_g(\sigma)$, and two $e_g(\pi)$ sublevels. The corresponding orbitals have large lobes directed respectively along the *c* axis, towards the nearest-neighbor cations along the basal plane, and toward the octahedral interstices in the basal plane of the corundum structure. It seems generally agreed^{11,29,30} that the a_{1q} (Γ_1 , $\Gamma_4 \rightarrow Z_1$) bands lie lowest in energy; with a capacity of four electrons per unit cell, these bands are exactly filled by one d electron contributed by each of the four Ti^{3+} ions per unit cell.

From the fact that pure Ti_2O_3 is a high-resistivity semiconductor at 4.2°K, it appears that the next higher-lying bands are separated from the lowest by a band gap; this is of the order of 0.02–0.06 eV. The Fermi level thus lies in the first gap, as shown in Fig. 2, and not in the middle of the a_{1g} band as seems indicated in Ref. 11.

It has recently been conjectured²⁹ that both the e and the a states include an admixture of anionic sp^3 orbitals into the direct cation-cation overlap. In that event, the observed distensions in the unit cell may well lead to a broadening and/or relative shifting of the bands, such that the band-gap energy decreases and becomes negative with rising temperature.

To ascertain whether this explanation is of any relevance to the resistivity data shown in Fig. 3, Van Zandt, Honig, and Goodenough²⁹ adopted a very crude model to simulate the two lowest-lying bands in Fig. 2. They considered two simple bands forming mirror images at 0°K, of structure $\mathcal{E} \sim 6J(\cos k_x a + \cos k_y a +$ $\cos k_z a$, appropriate to a hypothetical simple cubic lattice of unit cell edge length a; here J is a transfer integral and **k**, the wave-number vector. Allowance was made for a variation in band gap with temperature by multiplying J for the conduction band with a temperature function $f(T) \equiv 1 + A [1 + (B/T)^n]^{-1}$. This has the effect (a) of increasing the conduction band width by a factor 1+A as the temperature is raised indefinitely, (b) of having most of the change in band width occur in a narrow temperature range controlled by the exponent n, and (c) of adjusting the narrow temperature range so that it is centered about T=B. Standard transport theory was then used in calculating the total conductivity as $\sigma = \sigma_1 + \sigma_2$, with

$$\sigma_i = - \frac{e^2}{4\pi^3} \int_0^{ku} v^2 \tau \frac{\partial f_0}{\partial \epsilon} d^3 \mathbf{k},$$

where τ is the relaxation time, $\mathbf{\nabla} = \hbar^{-1} \mathbf{\nabla}_k \epsilon$, and f_0 , the Fermi-Dirac distribution function. Aside from the parameters A, B, and n it is necessary to specify J, and the band gap at 0°K. Care was taken to determine the Fermi level as a function of temperature through the requirement p=n.

The fit to the experimental points, obtained with A=2.25, $B=650^{\circ}$ K, n=12, J=0.1 eV, and $\mathcal{E}_{G}=0.06$ eV is shown by the full curve in Fig. 3. Presumably, a



FIG. 3. The electrical transition in Ti_2O_3 . Circles represent experimental data after Abrahams.¹² Dotted line represents the magnetic transition theory after Adler.⁹ Full curve represents the band-broadening theory after Van Zandt, Honig, and Goodenough.²⁹

³⁰ W. Kleiner, MIT Lincoln Laboratory Solid State Res. Rept. 1967, #3, p. 44 (unpublished).

more realistic model with an even greater number of adjustable parameters would fit the data at least as well. It was checked that a band overlap of some 0.3 eV is required in order to reproduce the sharp downturn in ρ , and that a band width 6J of the order of 0.6 eV is needed to provide for an upturn in the resistivity curve above 100°K.

It should be recognized that a magnetic-transition theory involving five parameters might also produce an excellent fit to the data. Hence, the calculations cited above should be interpreted with care. They establish only that it is not necessary to invoke magnetic-ordering effects in an interpretation of the electrical transition in Ti₂O₃. However, they also lend credence to the assertion that a standard theory of two-band conduction processes, which makes allowance for a change in gap energy from positive to negative values, is consistent with all recent experimental findings on Ti₂O₃. If this assertion is correct, Ti₂O₃ represents an example of a semiconductor \Rightarrow semimetal transition.

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Discussion of Honig's Paper

H. BROOKS (Harvard): It seems to me that if you have a model with a very small band gap at low temperatures as you have indicated and if you then assume that carriers are excited as the temperature rises, the entropy gain that you will get by narrowing the gap just because you are bringing states closer together will by itself account for the distortion of the cell which would produce the transition.

J. M. HONIG: Indeed, I would not quarrel with this viewpoint which is precisely why I was careful earlier to explain that the calculations by Van Zandt, Goodenough, and myself are consistent with the experimental data, but are by no means compelling. The suggestion by Professor Brooks may be a good alternative explanation. It seems to me that any mechanism that is ultimately adopted to explain the results would have to lead to band overlap at higher temperatures. For, this feature is needed to obtain the rapid downturn in the plot of log ρ versus 1/T. In the model Professor Brooks suggested it is not immediately evident whether one would indeed encounter electrons and holes in the correct concentration to observe such an effect. Perhaps, I misunderstood you slightly. It is my feeling that we are at much too early a stage to pin the detail down. We now have at hand a good method for growing single-crystal specimens of reasonable perfection, and much more work will have to be done to understand the detailed features of the observations.

D. ADLER (Massachusetts Institute of Technology): An *increase* in the length of the *c* axis surely will not favor a widening of the bands. Consequently, it isn't the c/a ratio that is the critical parameter in determining band width, but rather the length of the *a* axis. The *a* axis only contracts 0.4% over the range of the transition. I don't believe this small a variation could *double* the width of the bands. I would therefore like to suggest that the band gap is always small and negative in Ti₂O₃, and that an excitonic insulator state is formed at low temperature phase without the need for invoking a striking change in band width.

J. M. HONIG: I would label this suggestion as the Adler variant to the interpretation of the experimental data and would by no means discard this as a possibility. Again, at this stage it is much too early to settle on a definite alternative mechanism to replace the antiferromagnetic transition that has been postulated to date. The bands are originally roughly 0.6 eV in width and the overlap beyond 1000°K amounts to roughly 0.3 eV. In the body of the manuscript a statement should have been inserted, as was done in Reference 29, that other types of calculations were also performed. In these both bands were allowed to increase in width to a lesser extent and/or the centers of gravity of the two bands were moved closer together. Any of these alternatives provided as good a fit to the experimental data, as long as the overlap was sufficiently extensive. Thus, the model proposed in the text is not contingent on having an increase in band width which exceeds a factor of 2.

W. PAUL (Harvard): You know your argument is qualitatively different from some of those for VO₂ and V₂O₈. The size of the discontinuity at the transition in these materials increases as we obtain purer and purer materials. In the theories presented for them the size of the discontinuity doesn't matter terribly much yet, but in your case it does, since you are trying to fit the data. I just want to ask whether you are confident enough now of the quality of your Ti₂O₈ that you think this is the final size of the jump in resistivity that has to be fit quantitatively.

J. M. HONIG: The work described earlier was carried out on materials with a total impurity content that was frequently less than 160 atomic parts per million. By many standards this is still rather poor, but it probably represents a significantly lower degree of contamination than the total impurity contents in the samples studied by other investigators.