PHYSICAL REVIEW VOLUME 174, NUMBER 3 15 OCTOBER 1968

Electrical Properties of Ti_2O_3 Single Crystals

J. M. HONIG[*] AND T. B. REED
Lincoln Laboratory,[†] *Massachusetts Institute of Technology, Lexington, Massachusetts 02173*

(Received 27 March 1968)

Crystals of Ti_2O_3 of relatively high purity or doped with various impurities have been grown by the Czochralski method. The semiconductor-metal transition commenced at 435°K with a change of resistivity from 9×10^{-3} to 3×10^{-4} Ω cm. The resistivity at 4.2°K varies between 0.02 and 6×10^{5} Ω cm, depending on purity and stoichiometry. At 77°K and 273°K, the Hall coefficients are positive, small, and independent of magnetic field. At 4.2°K, reliable values could not be obtained. Magnetoresistance was measured in fields up to 220 kG. At 77°K and above, $\Delta\rho/\rho_0$ never exceeds 10^{-3}. At 4.2°K, $\Delta\rho/\rho_0$ for the purest sample rises quadratically with applied magnetic field, reaching a value of about 4 at 220 kG. This result cannot be interpreted in terms of a one-band model. A method has been developed for determining carrier mobilities from magnetoresistance data for an intrinsic semiconductor with mirror-image bands. Application of this method to the data for the purest samples yields carrier mobilities of 500–1000 cm^2/V sec at 4.2°K. The various results have been interpreted in terms of an elementary band-structure model which does not invoke antiferromagnetic ordering effects to explain the semiconductor-semimetal transition observed in Ti_2O_3.

I. INTRODUCTION

THE present investigation was initiated to obtain additional information concerning electrical characteristics of pure and doped single-crystal specimens of Ti_2O_3. Towards this end, a large number of magnetoresistance measurements were carried out at 4.2, 77, and 273°K in magnetic fields up to 220 kG. The variation of resistivity with temperature was also studied to some extent; this makes it possible to check and to elaborate on a band model sensitive to c/a ratio rather than to magnetic order that has been proposed for this material.[1] The work was motivated in part by the observation that commercially available samples are heavily contaminated with both anionic and cationic impurities. Results obtained with such specimens were found to differ significantly from those reported below for purer crystals grown in this laboratory under carefully controlled conditions.

The electrical characteristics of Ti_2O_3 at temperatures above 77°K have been studied repeatedly over the last twenty years.[2–7] There is general agreement among different investigators that the resistivity of this compound first diminishes almost exponentially with rising temperature, then drops rather abruptly, reaches a minimum, and thereafter rises with further increases in temperature. The temperature range over which the relatively sharp change has been found varies rather widely, as does the sharpness of the down-turn. Evidently, these are functions of the purity and the degree of perfection of the specimens.

In what follows, the experimental results will be compared only with those prior investigations that have been carried out on single-crystal specimens.[3,5–7]

II. EXPERIMENTAL

Large single-crystal boules measuring up to $\frac{3}{4}$ in. in diameter and up to 2 in. in length were grown from the melt in a resistance-heated furnace using the Czochralski-Kyropoulos technique. Details of the procedure are described elsewhere.[8] The material was prepared *in situ* by adding appropriate amounts of prepurified titanium metal to high-purity TiO_2. The chemical reaction and crystal growth were carried out under gettered argon in molybdenum crucibles.

Samples were regularly submitted for mass spectrographic analysis; the results are reported in Table I. No contamination by the molybdenum crucibles was observed at the 10 ppm level. The C and N impurity content was also determined by vacuum fusion techniques. The problem of reducing the N contamination

TABLE I. Sample analyses.

Sample designation	O/Ti ratio in TiO_x	Major impurities in ppm relative to Ti			
		N	C	Dopant	Other
(A) Relatively pure, near-stoichiometric samples					
6971	1.504	1800	320		
6368	1.504	1600	400		Mn = 90; Al = 80; Si = 50
142	1.503	270	400		
128	1.501	1500			Mg = 300; Fe = 50
(B) Relatively pure samples with excess oxygen					
562	1.515	250			
115	1.512	450	60		
6365	1.509	580			
123	1.507	210	50		Hf = 110; Fe = 170; Cr = 80
(C) Impure and doped samples					
314 374	1.510	2400		Sc = 1900	
6970	1.506	2300			
496				Cr = 13 000	
329		8000			
314 579	1.510	2200		V = 2600	Fe = 10
4765		5700			
392		1000		Al = 2000	S = 140; Co = 180; In = 150
41 365		10^4			

---

[*] Present address: Department of Chemistry, Purdue University, West Lafayette, Ind. 47907; Guest Scientist, National Magnet Laboratory, Massachusetts Institute of Technology.

[†] Operated with support from the U. S. Air Force.

[1] L. L. Van Zandt, J. M. Honig, and J. B. Goodenough, J. Appl. Phys. **39**, 594 (1968).

[2] M. Foëx and J. Loriers, Compt. Rend. **226**, 901 (1948).

[3] F. J. Morin, Bell System Tech. J. **37**, 1047 (1958); Phys. Rev. Letters **3**, 34 (1959).

[4] D. Pearson, J. Phys. Chem. Solids **5**, 316 (1958).

[5] J. Yahia and H. P. R. Frederikse, Phys. Rev. **123**, 1257 (1961).

[6] S. C. Abrahams, Phys. Rev. **130**, 2230 (1963).

[7] N. G. Anantha, M. S. thesis, MIT, 1960 (unpublished).

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

TABLE II. Summary of data for single-crystal specimens of TiO_x ($1.501<x<1.515$).

Sample designation	O/Ti ratio in TiO_x	Range of mobilities μ (cm^2/V sec)	Range of charge-carrier density ratios (M)	Range of Hall coefficients (cm^3/C)		Range of resistivities[a] (Ω cm)	
		4.2°K	4.2°K	77.7°K	273°K	4.2°K	77.7°K
(A) Relatively pure, near-stoichiometric samples							
6971	1.5038	880–980	~1	0.23–0.46	0.033–0.064	6.0×10^2–3.8×10^3	0.073–0.15
6368	1.504	880–920	~1	0.21–0.49	0.062–0.091	21–4100	0.10–0.21
142[b]	1.5026	840–890	~1	2.07–3.57	0.056–0.12	1.1×10^5–6.0×10^5	0.25–0.63
128	1.501	715–835	~1	0.39–1.47	0.079–0.11	1.3×10^4–18×10^4	0.21–0.82
(B) Relatively pure samples with excess oxygen							
562	1.5151	920	0.40	0.10–0.11	0.028–0.037	0.054	0.040
115	1.512	870–880	0.64–0.77	0.12–0.16	0.019–0.032	22–67	0.044–0.14
6365	1.509	>860	···[c]	0.11–0.12	0.040–0.045	42–79	0.050–0.068
123	1.507	830–880	~1	0.11–0.19	0.027–0.037	19–36	0.055–0.057
(C) Impure or doped samples							
314 374	1.510	870–900	0.50–0.55	0.12–0.19	0.035–0.042	3.2–8.7	0.024–0.061
6970	1.506	770–840	~1	0.049–0.11	0.033	18–36	0.049–0.11
496	···	780	0.047	···	···	0.027	···
329	···	710	0.058	···	···	···	···
314 579	1.510	590–700	0.29–0.42	0.039	···	0.92–1.7	0.031
4765	···	690	0.065	···	···	···	···
392	···	670	0.047	0.0075	0.0066	0.038	0.023
41 365[d]	···	···	···	0.016–0.020	0.0075–0.015	0.017–0.040	0.0090–0.022

[a] Resistivity was a function of sample orientation. See text.

[b] Resistivities in these runs precluded proper analysis of data; for this sample, small negative magnetoresistance effects were observed below 40 kG, which gave way to positive magnetoresistance effects at higher fields.

[c] Data on this sample taken only below 110 kG; no estimate of M could be made.

[d] Magnetoresistivities saturated at approximately $\Delta\rho/\rho_0=0.17$.

below the level of 300 atomic ppm was found to be extremely troublesome. High-purity Ti metal was used as starting material and rigid precautions were taken to exclude N_2 gas at all stages of the reaction and during crystal growth.

After orientation, the single-crystal boules were cut into sections approximately $1\times2\times8$ mm in dimension. The samples were etched and Cu leads were attached with In solder for Hall and for four-probe resistivity measurements. Lastly, the specimens were mounted on holders that could be immersed in liquid helium, liquid nitrogen, or ice baths, or inserted in an evacuated chamber. Magnetoresistance measurements up to 220 kG were carried out at the National Magnet Laboratory at MIT.

The sample stoichiometry was determined by heating a portion of the boule in air or in oxygen. The oxygen/metal ratio x was computed from the mass change, under the assumption that the reaction product was exactly TiO_2.

Altogether, about 20 different samples were used in resistivity and Hall effect studies at 4.2, 77, and 273°K. Some of these specimens were also run between 4.2 and 400°K and between 300 and 1000°K, using a commercial adaptation of the Kelvin bridge, to determine the change in resistivity with temperature.

III. RESULTS

A. Resistivity as a Function of Temperature

The resistivities measured at 4.2 and 77.7°K are shown in Table II. The purest and most nearly stoichiometric samples have resistivities that fall well into the 10^5 Ω cm range at 4.2°K. By contrast, Ti_2O_3 containing 1 at.% N exhibits a resistivity of the order of 10^{-2} Ω cm; samples with the largest ρ values at 4.2°K also exhibit the largest drop in ρ with rising temperature.

In each case there is an anisotropy in resistivity. It is difficult to assess this effect properly since samples of different orientations were cut from different sections of the boule, and thus may contain impurities in variable amounts. However, available data show that the resistivity is generally greatest when the current flow is along the c axis, though sample 142 is a distinct exception to this rule. The degree of anisotropy may be as high as a factor of 10 at 4.2°K and a factor of 2 at 77°K.

A limited number of rapid resistivity measurements with considerable scatter were carried out with sample 6365 in the range 4.2–273°K and with sample 142 in the range 240–950°K. The objectives were to determine the sharpness of the drop in resistivity above 500°K in purified samples and to extend prior measurement to the liquid-helium temperature range. Results are shown in Figs. 1–3.

It is seen from Fig. 1 that the resistivity of sample 6365 varies nearly exponentially with $1/T$ in the range below 20°K. Runs 1 and 2 were carried out in two successive months; the reason for the discrepancies above 16°K is not clear. The activation energy of 0.001 to 0.003 eV observed in various samples is at least one order of magnitude less than those cited in the literature for data obtained between 200°K and the onset of the rapid drop-off to lower ρ_0 values. It is concluded that activation energies exhibited in Fig. 1 for $T < 20$°K characterize the thermal promotion of charge carriers from impurity levels situated some 0.002 to 0.006 eV away from band edges.

Measurements of ρ_0 were carried out between 100 and 300°K on a number of samples; results for a typical run are shown in Fig. 2. The activation energies computed in this temperature range are thought to correspond to band gaps, E_g. In our experiments these varied from 0.027 to 0.050 eV depending on the sample under study. These compare to E_g values of 0.056–0.079 eV obtained by Yahia and Frederikse,[5] 0.079 eV as determined from Morin's data,[3] and 0.14 eV obtained from the data of Abrahams,[6] cited by Adler.[9]

The region in which ρ_0 changes rapidly with T was explored with sample 142, and the results are shown in Fig. 3. Aside from minor cationic impurities, this specimen contained 270 atomic ppm N and 400 atomic ppm C. The temperature range over which ρ_0 diminishes rapidly with increasing T lies between 400 and 500°K; a shallow minimum in ρ_0 is observed at approximately 800°K, before the resistivity rises again with a further increase in temperature.

Both the resistivity range and the temperature interval, over which ρ varies rapidly with T, are consistent with the earlier work by Yahia and Frederikse.[5] However, the resistivities quoted here lie roughly one order of magnitude below those cited by Morin[3] or by Abrahams.[6] Also, the transition range in temperature is considerably smaller than that cited in Ref. 6.

B. Hall-Effect Measurements

Attempts were made to measure the Hall effect of the samples listed in Table I at 4.2, 77.7, and 273°K. Extreme difficulties were encountered in the liquid-helium temperature range for samples in group A or B of Table I. Here the transverse voltages arising from probe misalignment and from the transverse component of the anisotropic resistivity exceeded the Hall voltage by factors of 10^4 to 10^5. The only exception was sample 562 ($x = 1.515$), which showed a noticeable Hall signal and a negative Hall coefficient R, which diminished smoothly from -1.13 to -0.50 cm^2/C as the magnetic field was increased from 0 to 170 kG. It is not possible to decide on the basis of existing data whether this behavior is representative of the Hall effects encountered with samples closer to ideal stoichiometry.

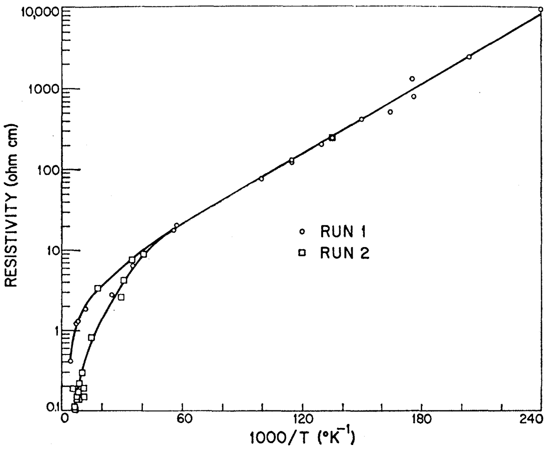

FIG. 1. Variation of resistivity of sample 6365 with temperature at low temperatures.

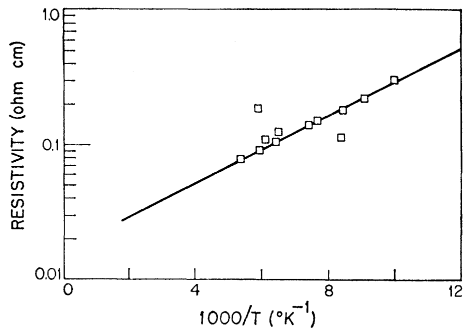

FIG. 2. Variation of resistivity of sample 6365 at intermediate temperatures.

Hall coefficients determined at 77 and 273°K are listed in Table II. Invariably these are positive (including those for sample 562), small, and independent of magnetic field. Both the Hall and the magnetoresistance data taken at or above 77°K are consistent either with a material where carriers in a valence band dominate conduction or with a model involving joint participation of electrons and of holes with comparable effectiveness.

C. Magnetoresistance Effects at and above 77°K

Magnetoresistance data were taken at 77°K on most of the samples listed in Table I; in some instances additional measurements were carried out at 273 and 338°K.

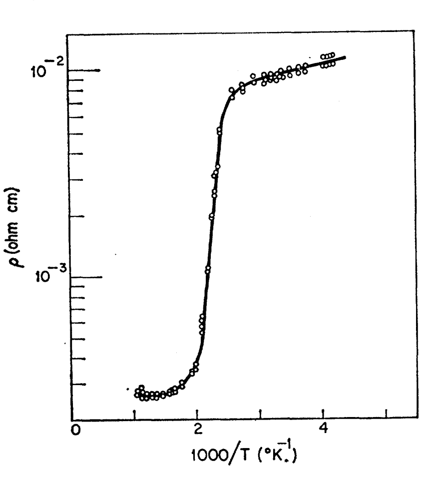

FIG. 3. Variation of resistivity with temperature for sample 142 in the transition region.

---

[9] D. Adler, Phys. Rev. Letters 17, 139 (1966).

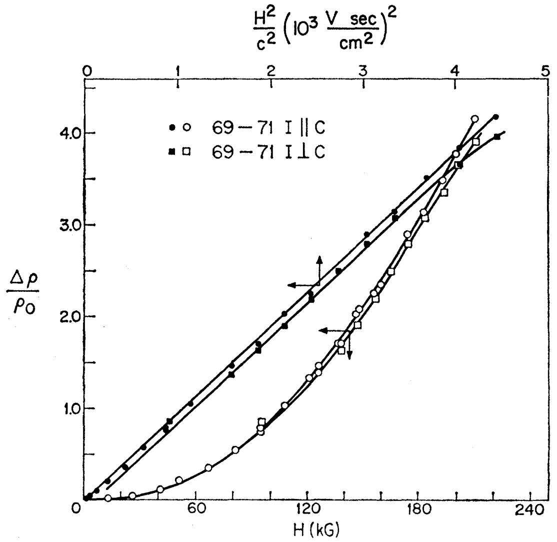

FIG. 4. Magnetoresistance at 4.2°K of Ti_2O_3 plotted as a function of H and of H^2; data representative of samples in group A of Table I.

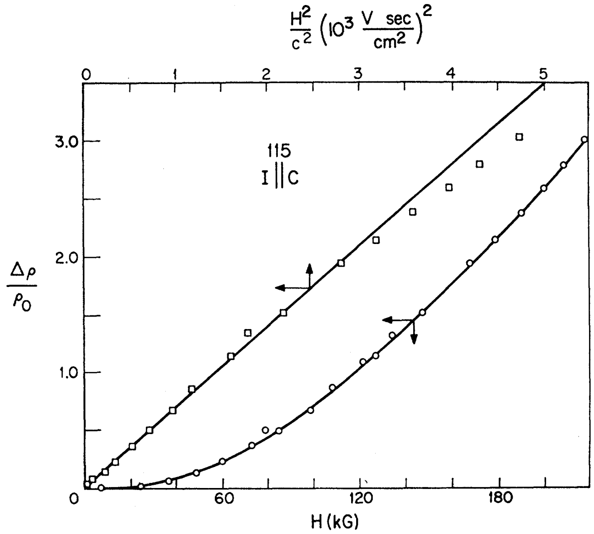

FIG. 5. Magnetoresistance at 4.2°K of Ti_2O_3 plotted as a function of H and of H^2; data representative of samples in group B of Table I.

The magnetoresistance was barely detectable, and in no case did $\Delta\rho/\rho_0$ exceed 10^{-3}. A few samples even exhibited negative magnetoresistance effects.

D. Magnetoresistance at 4.2°K

In Figs. 4–6 are shown the magnetoresistance data at 4.2°K for three representative single crystals of TiO_x with $x=1.504$, 1.512, and 1.515, respectively. These data illustrate the trend, observed in all cases examined in this investigation, according to which $\Delta\rho/\rho_0$ initially rises quadratically with applied magnetic field H. In general, the more nearly stoichiometric and the purer the sample, the greater is the initial slope $S_0\equiv[\partial(\Delta\rho/\rho_0)/\partial(H^2)]_0$, and the larger is the range of magnetic fields over which the quadratic dependence $\Delta\rho/\rho_0\sim H^2$ holds. This trend was further confirmed with numerous observations on samples doped with 0.1 to 0.5 at.% of V, Cr, Mn, or Fe, and on samples that were heavily contaminated (up to 0.8 at.%) with N. All such specimens were characterized by small or near-vanishing values of $\Delta\rho/\rho_0$.

IV. DISCUSSION

A. Magnetoresistance Predictions for a Two-Band Model

For samples that are relatively pure and close to ideal stoichiometry, $\Delta\rho/\rho_0$ at 4.2°K has a value of three to four in magnetic fields above 200 kG. This is considerably above the maximum value of $\Delta\rho/\rho_0\approx 2.4$ predicted for materials characterized by a single band of standard form.[10] Moreover, this maximum ought to be approached asymptotically, whereas for the purer specimens studied here $\Delta\rho/\rho_0$ was increasing linearly with H^2 at the highest available magnetic fields. The conclusion seems inescapable that these magnetoresistance data cannot be interpreted in terms of a one-band model. Therefore, it is concluded that more than one type of charge carrier participates in the conduction process. For two carriers, the resistivity for an isotropic material in a magnetic field is given by[11,12]

$$\rho=\frac{(\sigma_1+\sigma_2)+H^2\sigma_1\sigma_2(\sigma_1R_1{}^2+\sigma_2R_2{}^2)}{(\sigma_1+\sigma_2)^2+H^2\sigma_1{}^2\sigma_2{}^2(R_1+R_2)^2}, \tag{1}$$

where σ_1, σ_2, R_1, R_2 are the one-band electrical conductivities and Hall coefficients. As a first approximation we set $R_j=Z_jn_jec$ and $\sigma_j=n_je\mu_j\approx n_je\mu_j{}^0$, where n_j is the charge carrier density, $Z_j=\pm1$, e is the absolute value of the electronic charge, μ_j and $\mu_j{}^0$ are the charge-carrier mobilities in the magnetic field and for $H=0$, respectively. With these simplifications, Eq. (1), adapted to the case of the two-carrier system involving electrons and holes, becomes

$$\rho=\frac{1}{n_ne\mu_n+n_pe\mu_p}\times\left\{\frac{1+(H^2/c^2)\mu_n\mu_p(n_p\mu_n+n_n\mu_p)/(n_n\mu_n+n_p\mu_p)}{1+(H^2/c^2)\mu_n{}^2\mu_p{}^2(n_p-n_n)^2/(n_n\mu_n+n_p\mu_p)^2}\right\}, \tag{2}$$

---

[10] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, New York, 1954), 2nd ed., pp. 234–242.

[11] E. H. Putley, *The Hall Effect and Related Phenomena* (Butterworths Scientific Publications, Ltd., London, 1960), p. 88.

[12] T. C. Harman and J. M. Honig, *Thermoelectric and Thermomagnetic Effects and Applications* (McGraw-Hill Book Co., New York, 1967), p. 88.

so that with the definition $\rho_0 \equiv (n_n e\mu_n + n_p e\mu_p)^{-1}$ the magnetoresistance reads

$$\frac{\Delta\rho}{\rho_0}=\frac{\rho}{\rho_0}-1=\frac{H^2}{c^2}\mu_n\mu_p\left\{\frac{(n_p\mu_n+n_n\mu_p)/(n_n\mu_n+n_p\mu_p)-\mu_n\mu_p(n_p-n_n)^2/(n_n\mu_n+n_p\mu_p)^2}{1+(H^2/c^2)\mu_n^2\mu_p^2(n_p-n_n)^2/(n_n\mu_n+n_p\mu_p)^2}\right\}. \tag{3}$$

For an intrinsic material $(n_p - n_n) = 0$, so that the expression in braces equals unity, and $\Delta\rho/\rho_0$ should rise indefinitely as H^2. With $|n_p - n_n| \neq 0$, however, saturation effects will occur at values

$$\left(\frac{\Delta\rho}{\rho_0}\right)_{\text{sat}}=\frac{(n_n\mu_n+n_p\mu_p)(n_p\mu_n+n_n\mu_p)}{(n_p-n_n)^2\mu_n\mu_p}-1, \tag{4}$$

which lie considerably above the one-carrier maximum value of 2.4 so long as $|n_n - n_p|$ remains small. [Note that for $n_n \gg n_p$ or for $n_p \gg n_n$, Eq. (4) actually approaches zero. This is so because in setting $\mu_j = \mu_j^0$ we have not taken into account the effect of magnetic field on the charge-carrier mobilities.]

Very considerable simplification is achieved by considering the special case of a solid characterized by mirror-image bands for which $\mu_n = \mu_p \equiv \mu$. In this event, Eq. (3) reduces to

$$\frac{\Delta\rho}{\rho_0}=\frac{H^2}{c^2}\mu^2\frac{1-A^2}{1+H^2\mu^2A^2/c^2}, \tag{5}$$

where

$$A^2 \equiv (n_p - n_n)^2/(n_p + n_n)^2. \tag{6}$$

For a material with mirror-image bands the saturation value of the magnetoresistance is given by

$$\left(\frac{\Delta\rho}{\rho_0}\right)_{\text{sat}}=\frac{1-A^2}{A^2}, \tag{7}$$

which, again, is considerably in excess of the one-band value unless $|n_p - n_n| \gg 0$ giving $A \sim 1$.

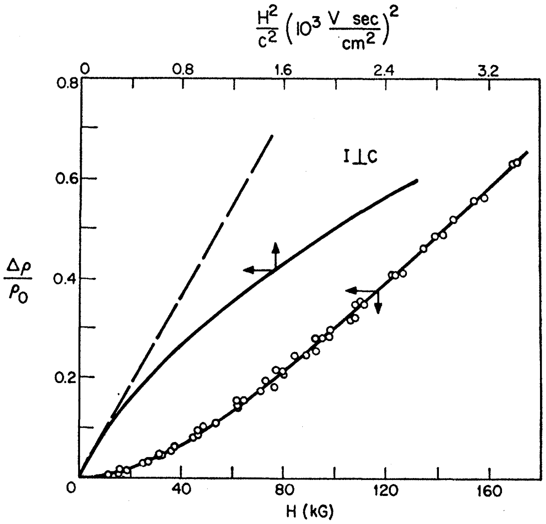

FIG. 6. Magnetoresistance at 4.2°K of Ti_2O_3 plotted as a function of H and of H^2; data representative of samples in group C of Table I.

While the present data indicate that Ti_2O_3 is anisotropic in its electrical properties, the above relations should be useful in a semiquantitative interpretation of the results. Indeed, for a given sample and orientation, it has been found empirically that the results at 4.2°K conform well with Eq. (5). Thus, for the limited objectives of the present discussion we shall adopt the equations based on the mirror-image band model.

According to Eq. (5) the initial slope of a graph of $\Delta\rho/\rho_0$ versus H^2/c^2 is given by $S_0 = \mu^2(1-A^2)$; moreover, a plot of $(S_0H^2/c^2)/(\Delta\rho/\rho_0) \equiv \Delta$ versus H^2/c^2 [suggested by taking the inverse of Eq. (5)] yields a straight line with intercept unity and slope $S_1 = A^2\mu^2$. From the two slopes, S_0 and S_1, one can thus evaluate μ and A separately, to obtain semiquantitative information on the carrier mobility and on the ratio of minority to majority carrier density, according to

$$\mu = (S_0 + S_1)^{1/2} \tag{8}$$

and

$$M \equiv n_{\text{min}}/n_{\text{maj}} = (1-A)/(1+A), \tag{9}$$

where

$$A \equiv [S_1/(S_0+S_1)]^{1/2}. \tag{10}$$

This method of analysis is illustrated by its application to the data shown in Fig. 6. At regularly spaced values of $(H^2/c^2)/10^6$, values of S_0H^2/c^2 and $\Delta\rho/\rho_0$ were read off the dashed straight line and the curve, respectively. The ratio of these values is plotted against H^2/c^2 in Fig. 7, yielding a straight line.

Values of μ and of n at 4.2°K obtained by this type of analysis are collected in Table II. The ranges in μ and n indicate the variation encountered in each sample on changing the crystal orientation relative to the magnetic field and current flow directions. The following trends can be established: (a) The largest carrier mo-

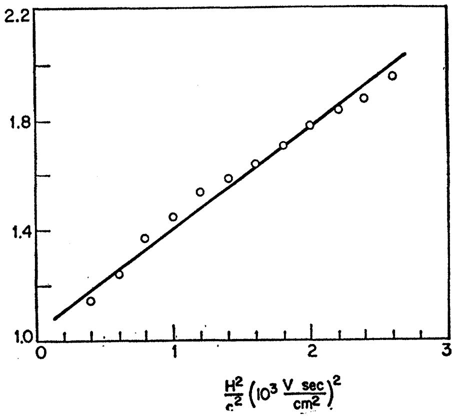

FIG. 7. Graph illustrating data analysis (see text).

bilities were encountered in samples that are both close to ideal stoichiometry and reasonably free of impurities. For the best samples, the mobilities ranged slightly below 1000 cm^2/V sec, and the density of electrons and holes was approximately equal. No deviations from the quadratic dependence $\Delta\rho/\rho_0 \sim H^2$ were observed for magnetic fields up to 220 kG. (b) For materials where $x \geq 1.507$ and which were not heavily doped or contaminated, the mobilities fell in the range 830–920 cm^2/V sec; also, M values were spread over the range 0.40 to 1. Deviations from the quadratic $\Delta\rho/\rho_0 \sim H^2$ law were encountered above 100 kG, and the magnetoresistance of these samples was well below that of the pure materials. (c) For materials which were lightly doped with Sc, V, or Cr, or which were contaminated by nitrogen in amounts exceeding 0.25 at.% relative to Ti, the carrier mobilities varied between 590 and 900 cm^2/V sec. The ratio of minority to majority carrier density fell as low as 0.047 in some instances; this is reflected in a concomitant departure of the magnetoresistance from the H^2 law in fields as low as 20 kG.

B. Band Structure of Ti_2O_3

The rapid change of ρ_0 with T (as in Fig. 3) has generally been regarded as signalling the onset of a semiconductor-metal transition. Since Ti_2O_3 does not exhibit any phase changes below 1000°K, it was suggested that the transition is due to antiferromagnetic ordering below 500°K, with a concomitant splitting of a half-filled band into a filled and an empty subset of band states.[3,9] However, Goodenough[13] recognized that the transition was more probably due to a separation of overlapping of bands as a result of decreasing c/a ratio with lower T. His model was essentially that to be described, except that he implicitly anticipated much smaller valence-band mobilities.

Recent experimental evidence casts serious doubt on the presence of antiferromagnetic ordering in Ti_2O_3.[1,14] Hence it seems desirable to base the interpretation of our data on Goodenough's alternative scheme, which does not have recourse to magnetic ordering effects. Critical to the development of this scheme is the symmetry argument for band splitting in Ti_2O_3 recently discussed by Kleiner.[15] The direction of greatest symmetry in the first Brillouin zone of rhombohedral crystals[16] lies along the Γ-Λ-Z direction. Energy bands along this direction arising primarily from d-type cationic levels are sketched in Fig. 8, together with the orbital degeneracies required by group theory. The band states have been labeled in the standard notation appropriate to the D_{3d} point group.

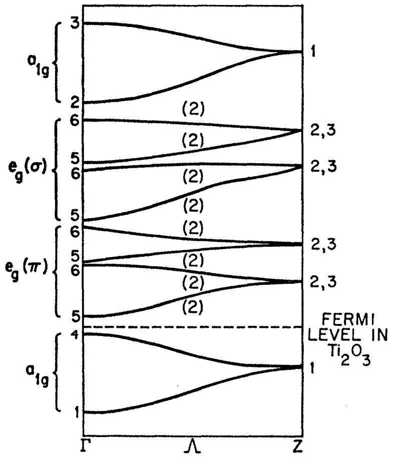

FIG. 8. Energy band scheme for Ti_2O_3, adapted from Ref. 15. Numbers in parentheses indicate degeneracy of levels. The other numbers indicate symmetry character.

There seems general agreement that the Γ_1 and Γ_4 bands lie lowest in energy. The relative positions of all higher-lying bands is quite uncertain. Since the crystal-field splitting parameter $10Dq$ is small in compounds with the corundum structure, the $e_g(\pi)$ and $e_g(\sigma)$ bands may all overlap. However, these details are not important for the general argument here. Consideration of symmetry requirements demands only that, in the absence of spin-orbit coupling, the Γ_5 and Γ_6 bands be doubly degenerate and that there be a double degeneracy at Z_1 and a quadruple degeneracy at Z_2 and Z_3. In a crystal with N unit cells the Γ_1 and Γ_4 bands have a total capacity, including spin degeneracy, for $4N$ electrons. Since the unit cell contains four Ti atoms, each of which contributes one electron to d-like states, the Γ_1 and Γ_4 bands are exactly filled in a pure crystal with the ideal Ti_2O_3 stoichiometry.

The fact that the magnetoresistance at 4.2°K is much larger than can be accounted for on the basis of a one-band model and the fact that the resistivity of the purer Ti_2O_3 specimens exceeds 10^5 Ω cm in the liquid-helium temperature range, show that at 4.2°K there is no overlap between the Γ_1-Γ_4 bands and any higher-lying energy states. In this event, the Fermi level at 0°K would be expected to lie in the band gap bounded by the points Γ_4 and Γ_5, as shown in Fig. 8. The location of the Fermi level with respect to the band-structure scheme drawn here differs nontrivially from that proposed in Ref. 17. From the information given in that publication, it is not possible to ascertain the origin of the discrepancy. One should note that in our scheme it is unnecessary to invoke antiferromagnetic ordering to obtain the band gap that is required to explain the semiconducting properties of Ti_2O_3 at low temperatures.

For the purest samples at 4.2°K, the carrier concentrations (n) are of the order of 10^{10} cm^{-3}, since the mo-

---

[13] J. B. Goodenough, *Magnetism and the Chemical Bond* (Interscience Publishers, Inc., New York, 1963), p. 256.

[14] H. Kendricks, S. Werner, and A. Arrott, J. Appl. Phys. **39**, 585 (1968).

[15] W. Kleiner, MIT Lincoln Laboratory Solid State Research Report No. 4, 1967 (unpublished).

[16] J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Co., New York, 1965), Vol. 2, p. 418.

[17] D. Adler, J. Feinleib, H. Brooks, and W. Paul, Phys. Rev. **155**, 851 (1967).

bilities determined from magnetoresistance data are close to 10^3 cm^2/V sec and the resistivities are 10^5–10^6 Ω cm. If the electron density in the filled valence band is taken to be $n_0 = 3.8\times 10^{22}$ cm^{-3}, the concentration of Ti in Ti_2O_3, then the energy gap (E_g) is found to be $\sim$0.02 eV by solving the equation

$$n = n_0 \exp(-E_g/2kT). \tag{11}$$

These quantities lie towards the lower end of the experimental values reported in Sec. III A and are considerably below those cited in the earlier literature. Further careful experimental work is required to obtain accurate values of E_g; conceivably, this quantity is a function of impurity content. In view of the known impurity content of the Ti_2O_3 samples, carrier concentrations of only about 10^{10} cm^{-3} are somewhat surprising, since in other low-gap semiconductors many impurity donor and acceptor species are fully ionized even at 4.2°K.

The rapid variation of ρ with $T > 300$°K may be explained on the basis of the experimental fact[4,18,19] that the unit cell of Ti_2O_3 is distended in this temperature interval, which results in an increase of the c/a ratio with increasing T. In connection with these findings we adopt the suggestion in Ref. 1 that in addition to the direct cation-cation interaction there is a considerable contribution arising from 90° cation-anion-cation interaction which arises as a result of the participation of the anionic sp^3 states in bonding. The various a and e bands are thus sensitive to the Ti-O distances in the crystal, which are decreased by the distension of the unit cell. This leads to a broadening and shifting in the relative positions of the various bands in such a manner that one would anticipate a diminution of the band gap, and thus a rapid decrease in resistivity with rising temperature. By making allowance both for band broadening and/or for a relative shifting of the bands so as to produce band overlap as a result of the distention in the unit cell, it is possible quantitatively to account for the variation of ρ with T at elevated temperatures, as has been demonstrated in a prior publication.[1] On this model, then, the ρ versus T variation above 300°K results from a shift of the lowest Γ_1, Γ_4, Z_1 band relative to higher-lying bands, in the course of which the material changes from a semiconductor to a semimetal. The increase of ρ with T above 800°K is, in this view, due both to the narrowness of the bands and to the usual temperature effects encountered in a *bona fide* metal.

In conclusion, it appears that the data cited here can be interpreted without the necessity of invoking magnetic ordering effects.

ACKNOWLEDGMENTS

We are pleased to acknowledge the skillful technical assistance of Robert Fahey, Robert Germain, John Roddy, and George Wheatley, Jr., in various phases of the work. We are greatly indebted to Edward Owens for carrying out sample analyses and to Dr. Jerome Sohn for taking resistivity data in the high-temperature range. Finally, we wish to thank Dr. John Goodenough, Dr. Walter Kleiner, and Dr. Lonnie Van Zandt for fruitful discussions pertaining to the interpretation of the data.

---

[18] R. E. Newnham and Y. M. de Haan, Z. Krist. **117**, 235 (1962).

[19] P. Raccah (private communication).