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Electrical Conduction in *p*-Type Titanium Sesquioxide*

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The Hall effect, thermoelectric power, and electrical conductivity have been measured as a function of temperature in crystals of *p*-type titanium sesquioxide. A transition is observed at about 450°K. Below this temperature the crystals behave like semiconductors, while above it the conductivity is apparently metallic. The behavior below 450°K is in line with antiferromagnetic ordering. The effective mass of the holes is found to be about $5m_0$ and the average Hall mobility 5 cm^2/volt-sec at room temperature. It is claimed that these values, combined with the fact that the Hall effect is measurable, support the assumption of conduction in a narrow 3*d* band.

INTRODUCTION

General Remarks

Stoichiometric Oxides

THE electron transport properties of transition metal oxides such as MnO, CoO, and Fe_2O_3 do not fit into the well-known picture of conduction in broad-band semiconductors. From the electronic configuration of the free cation, one would expect these oxides to be metallic in their conduction properties, for when the ions are brought together to form the solid, the cation electrons would only partially fill the resulting band. Experimentally, however, these materials are found to be insulators when in a pure and stoichiometric form. Several attempts have been made to explain this lack of conduction. DeBoer and Verwey[1] retain the band model but believe that the potential barrier between adjacent sites is too high to permit electron motion. Mott[2] asserts that the transition from a nonconducting to a conducting state is sharp. At 0°K there are either no free carriers or a high density of free carriers. A pair of carriers attract each other according to a Coulomb interaction $-e^2/\kappa r$. They can therefore combine to form a bound state and, in consequence, not conduct. However, as the number of carriers becomes larger (of the order of the number of electrons in metals) two carriers attract each other according to a *screened* Coulomb potential $V(r)=(-e^2/r)e^{-r/r_0}$, where r_0 is roughly the spacing between the ionized particles. When r_0 is comparable to the ionic spacing this screened potential is too weak to produce bound states and a sharp increase in the number of free carriers occurs. Slater,[3] considering MnO, has proposed that the antiferromagnetic order in this substance gives rise to two bands (rather than to one unfilled band, as expected when the antiferromagnetic order is absent), the lower band being filled and the upper one empty. This would give rise to the conduction properties actually observed. Zener[4] and Heikes[5] have attempted also to relate the conduction properties to the magnetic properties and have reached the conclusion, based on the Pauli exclusion principle and a model of charge transfer, that insulating behavior is associated with antiferromagnetism while ferromagnetism leads to metallic conduction. This conclusion is in large measure borne out by experiment. Anderson[6] has made a detailed theoretical study of superexchange interactions. He finds that superexchange is closely related to poor conductivity; the *d* electron is characterized mainly by two parameters: its kinetic energy, or its ability to delocalize, and the energy of repulsion of two electrons. Whenever the repulsion energy predominates, preventing metallic conduction, he shows that the opposite tendency to delocalize causes an antiferromagnetic ordering. Thus insulating behavior is linked to antiferromagnetism as is actually observed.

Nonstoichiometric Oxides

Most of the insulating oxides can be made semiconducting by reduction or oxidation or by the introduction of appropriate impurities of a different valency than the cations in the host lattice. The extra electrons or holes produce a mixed valency in the cation lattice, e.g., in Li-doped NiO both Ni^{3+} and Ni^{2+} will be present. An Ni^{3+}-Ni^{2+} pair will be degenerate with a Ni^{2+}-Ni^{3+} pair and hence at sufficiently high temperatures movement of positive charge can take place.[1,7] This mechanism therefore leads to conduction in the cation band. Many investigators[8,9] believe, however, that the overlap of wave function is too small for the formation of bands of appreciable width and that the conduction is better described by a diffusion or jump mechanism. This theory is based on the fact that no Hall effect has been observed in most oxides and that the mobilities deduced from thermoelectric power and conductivity measurements are in the range 10^{-5}–10^{-3} cm^2/volt-sec. A num-

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ber of nonstoichiometric oxides (Cu_2O, ZnO, TiO_2) *do* show a Hall effect; the mobilities are of the order 0.1–10^2 cm^2/volt-sec. There is good reason to believe that the observed conductivity in these substances is due to electrons (holes) in a conventional conduction (valence) band.

Remarks Concerning Titanium Sesquioxide

Stoichiometric Ti_2O_3

The free Ti^{3+} ion is in a ^2D state which is tenfold degenerate if the spin-orbit interaction is neglected. In a hexagonal crystal such as Ti_2O_3 this state is probably split into five doubly degenerate Kramers levels. From these considerations it would appear that stoichiometric Ti_2O_3 would be a good conductor since it would have an incompletely filled 3*d* band. However, the available experimental evidence suggests that the $3d^1$ configuration of the Ti^{3+} ion gives rise to a filled band. It has been pointed out how this apparent inconsistency may be resolved [see General Remarks: Stoichiometric Oxides].

Nonstoichiometric Ti_2O_3

Considering now nonstoichiometric Ti_2O_3 with excess oxygen (actually the case for the samples measured), the following statements may be made. Nonstoichiometric Ti_2O_3 with excess oxygen contains Ti vacancies and Ti^{4+} states; at sufficiently high temperatures the latter will produce holes in the valence band. This prediction is in agreement with the results of Pearson,[10] who measured the conductivity and thermoelectric power of sintered samples. Pearson also investigated the structure, magnetic susceptibility, and optical absorption of the sesquioxide. The lattice parameters and susceptibility showed a discontinuity in the range 400–500°K, while the thermoelectric power changed from positive to negative in this range. Later measurements by Morin[11] on a single crystal showed a similar discontinuity in the conductivity. Early work of Adler and Selwood[12] on the magnetic susceptibility indicated a transition point of 248°K. However, the measurements of Foëx and Wucher[13] are in agreement with Pearson's results: the susceptibility is rather temperature independent up to 400°K, increases rather steeply between 400 and 500°K, and shows a gentle rise above this temperature. Neutron diffraction studies of this oxide recently made by Shirane *et al.*[14] showed the effective magnetic moment of the Ti^{3+} ion to be smaller than 0.5 Bohr magneton. These results, as well as their own magnetic measurements, led Carr and Foner[15] to the conclusion that Ti_2O_3 was *not* antiferromagnetic.

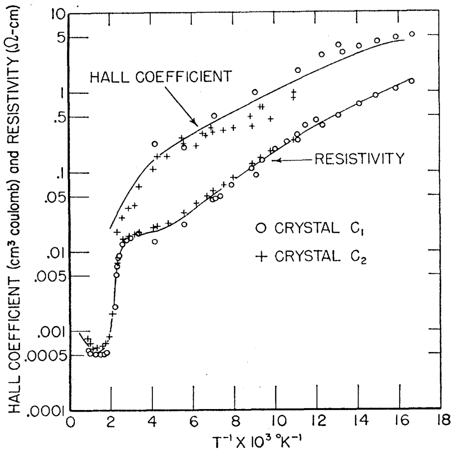

FIG. 1. Temperature dependence of Hall coefficient and resistivity for crystals C_1 and C_2.

In this paper we present results of electrical conductivity, Hall effect, and thermoelectric power measurements for nonstoichiometric Ti_2O_3. These results can be interpreted in terms of the conventional band model and be reconciled with antiferromagnetic behavior below the transition point.

EXPERIMENTAL DETAILS

1. Samples

The samples used in this investigation were in the shape of small parallelepipeds of rectangular cross-section cut from boules provided by the Linde Company. A typical size was 5×1×2 mm^3. Measurements were made on samples from three boules (*A*, *B*, *C*). It was found that the boules were cracked in many places, presumably upon cooling from high temperatures, so that some difficulty was experienced in cutting uncracked samples. No effort was made at orienting the samples; an x-ray investigation of a section from boule *C* showed that it was a single crystal. Measurements of

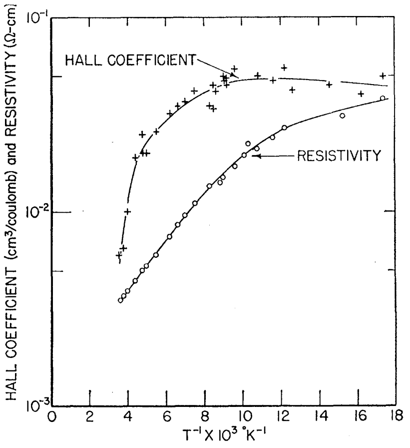

FIG. 2. Temperature dependence of Hall coefficient and resistivity for crystal *A*.

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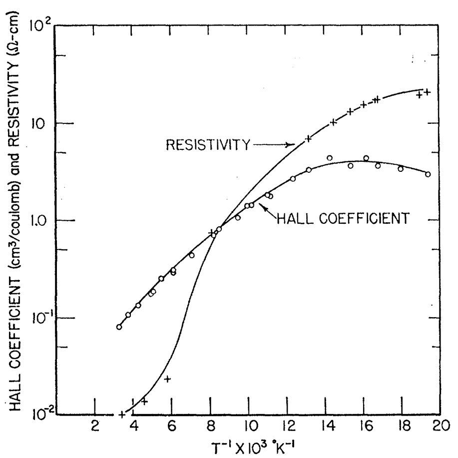

FIG. 3. Temperature dependence of Hall coefficient and resistivity for crystal *B*.

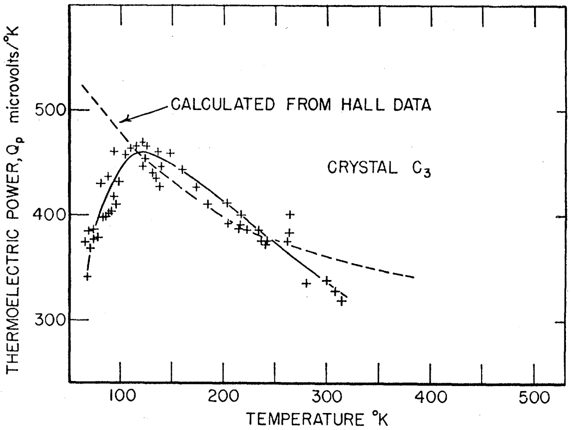

FIG. 4. Temperature dependence of thermoelectric power (low-temperature range) for crystal C_3.

oxygen uptake were made for sections from the different boules in order to determine the degree of stoichiometry; consistent results were obtained for sections from boule *A*, the formula being determined as $TiO_{1.515}$. Assuming three Ti^{4+} sites for each Ti^{3+} vacancy, this formula indicates 11×10^{20} quadrivalent Ti ions per cm³.

2. Measurement Technique

The Hall effect and resistivity were measured using a dc potentiometer method. Small (Hall) voltages were measured with a Rubicon microvolt potentiometer (limit of sensitivity $\sim 0.01\ \mu v$) while a type K-3 Leeds and Northrup potentiometer was used for voltages in the millivolt range. In the low-temperature experiments, wires were soldered to the sample with indium; tungsten pressure contacts were employed in the high-temperature range. Steady temperatures were obtained by conventional means at both high and low temperatures. Below 300°K the temperatures were determined by means of silver vs gold-cobalt thermocouples; in the high-temperature range, platinum vs platinum-rhodium thermocouples were used. Thermoelectric power data in the range 55–300°K were obtained with an apparatus used previously in the work on the thermal conductivity of InSb.[16] Temperature measurements were made by means of copper vs constantan thermocouples affixed to the ends of the crystal with indium; the readings on the thermocouples then determined the temperature gradient across the sample and also its average temperature. The thermoelectric power was measured using the copper arms of the thermocouples. High-temperature thermal emf measurements (300–1250°K) were made by inserting the sample in an oven; Pt-vs-Pt-Rh thermocouples were used as temperature indicators.

RESULTS AND ANALYSIS

The temperature dependence of the Hall coefficient R_H and the resistivity ρ are shown in Figs. 1–3. A sharp drop of ρ at about 450°K (Fig. 1) is connected with the transition also observed in the magnetic susceptibility,[10,13] lattice constants,[10] and coefficient of expansion.[17] The thermoelectric power as a function of temperature is shown in Figs. 4 and 5; here, also, a broad transition range (450–600°K) is observed.

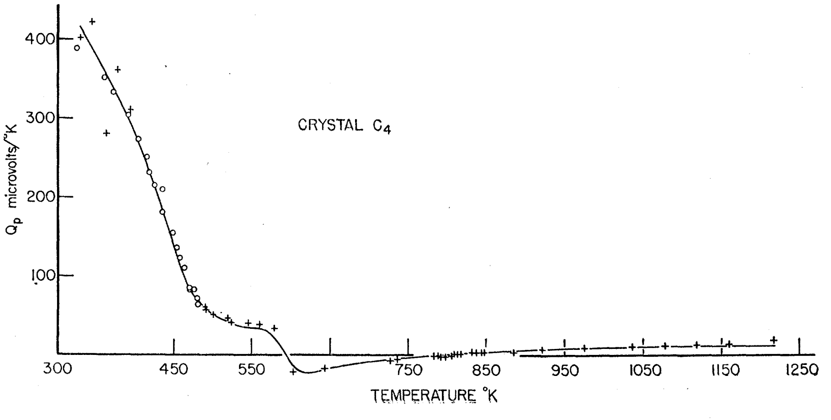

FIG. 5. Temperature dependence of thermoelectric power (high-temperature range) for crystal C_4.

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1. Temperature Range below the Transition Region

From the Hall data, we can calculate activation energies using the formula $R_H = \text{const}e^{\Delta E/kT}$, where ΔE is the activation energy. These are given in Table I. A comparison of these results may be made with the activation energy deduced from Morin's[11] conductivity curve; assuming $\sigma = \text{const}e^{-\Delta E/kT}$, a value of $\Delta E = 0.04$ ev is obtained.

The Hall mobility $\mu_H (=\sigma R_H)$ was found to be of the order of a few cm^2/volt-sec at room temperature. Figure 6 shows the temperature variation of the mobility. The behavior at low temperatures suggests that scattering by ionized impurities is the dominant mechanism. The mobility is then described by the Conwell-Weisskopf formula[18] $\mu_H = \text{const}T^{\frac{3}{2}}/\ln T^2$. This formula appears to fit the data rather well in this range. At the higher temperatures the data indicate that scattering by polar modes predominates. Fröhlich *et al.*[19] have shown that for this case the mobility as a function of temperature may be represented by $\mu_H = \text{const}(e^{\theta/T}-1)$ for $\theta \gg T$, where θ is the Debye temperature. Such a variation is in reasonable agreement with our experimental results. (We use $\theta = 441$°K, a value deduced by Shomate[20] from specific heat measurements).

The effective mass can be calculated from the thermoelectric power data combined with the Hall data by means of the expression[21]

$$Q_p = +(k/e)\left[\ln|R_H|T^{\frac{3}{2}} - \ln r - 7.16 + q + \tfrac{3}{2}\ln(m^*/m_0)\right], \quad (1)$$

where r and q are numerical scattering factors. For impurity scattering $r = 1.93$, $q = 4.00$, and for polar scattering $r = 1.10$, $q = 3.00$. The $Q_p(T)$ curve calculated from the Hall data for crystals C_1 and C_2 is compared with the experimental curve for crystal C_3 using an effective mass $m^* = 5m_0$ (Fig. 4). A puzzling feature is that below 100°K the observed Q_p decreases while that calculated from the Hall data continues to increase.

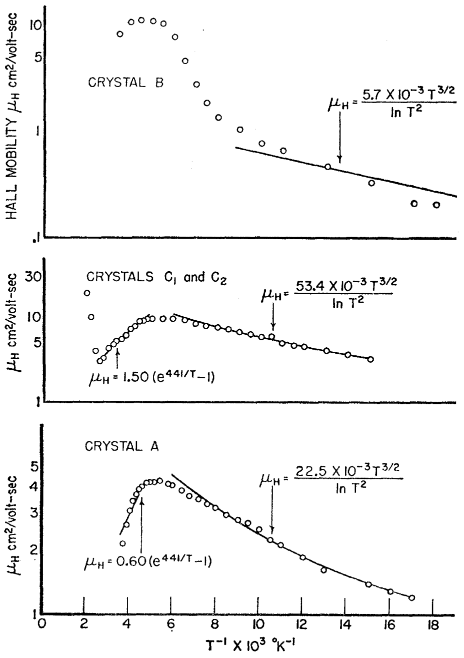

FIG. 6. Temperature dependence of Hall mobility for crystals A, B, C_1, and C_2.

2. Temperature Range above the Transition Region

The resistivity above the transition temperature has decreased by a factor of over 20 from that immediately below it and shows a small *positive* temperature dependence (Fig. 7). The thermoelectric power has dropped by a factor of several hundred and is small and negative immediately above the transition region although at still higher temperatures it reverts to small positive values (Fig. 5).

TABLE I. Activation energies calculated from Hall data for crystals A, B, C_1, and C_2.

Crystal	Temperature range (°K)	ΔE (ev)
A	200–118	0.02
B	330–125	0.04
	125–77	0.03
C_1 (and C_2)	200–87	0.03
	87–63	0.02

DISCUSSION AND CONCLUSIONS

Ti_2O_3 appears to be a *p*-type semiconductor below 450°K. The value of the effective mass of the holes as calculated above is about $5m_0$ and the measured average Hall mobility 5 cm^2/volt-sec at room temperature. These values combined with the fact that the Hall effect is measurable at all are consistent with our assumption of band formation. It is interesting to compare these results with those obtained on reduced TiO_2, where the carriers are electrons with an average effective mass of $25m_0$ and a mobility ~ 1 cm^2/volt-sec (300°K). We believe that the orders of magnitude of all of these values indicate that in *both* materials conduction takes place in a narrow 3*d* band.

It seems to us that the existing data on Ti_2O_3 support the idea of antiferromagnetic ordering below 450°K, in contrast to the conclusions of Carr and Foner.[15] The temperature dependence of the susceptibility measured by Pearson[10] on polycrystalline samples is rather typical

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of antiferromagnets. The small net magnetic moment per site of less than 0.5 μ_B observed in neutron diffraction experiments[14] is quite naturally explained on a collective electron model similar to the one used by Lidiard[22] to interpret the observed small and nonintegral magnetic moment in antiferromagnetic metals and by Stoner[23] to explain the same observations in ferromagnetic materials. The lack of anisotropy observed by Carr and Foner[15] could be due to the heavy strains or polydomain structure of their crystals. It could also be due to a spiral arrangement of moments about the c axis. Another important aspect is the unexpected increase of χ above 450°K; the susceptibility obviously does not follow a Curie-Weiss law in this range. The possibility of a second transition point at the higher temperature should not be excluded.[24]

The conclusion that Ti_2O_3 is antiferromagnetic agrees with the work of Li,[25] who predicts from an analysis of superexchange interactions that this sesquioxide should behave similarly to V_2O_3 and Cr_2O_3, and is in line with the theories of Zener[4] and Heikes[5] mentioned at the beginning of this paper that insulating (or semiconducting) properties of transition metal oxides are associated with antiferromagnetism.

Above the transition point the temperature dependence of the resistivity and the magnitude of the thermal emf suggest metallic conduction. Morin[11,26] explains this behavior by assuming that the two bands produced by antiferromagnetic interaction at low temperatures collapse into a single nonfilled band in the high-temperature range.

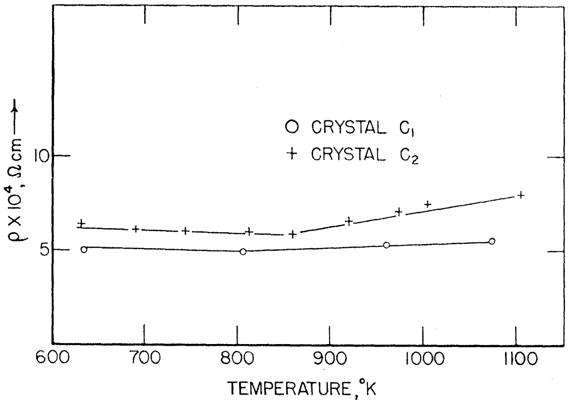

Fig. 7. Temperature dependence of resistivity above the transition temperature for crystals C_1 and C_2.

It would be interesting to test the second half of the theories of Zener and of Heikes, namely, that the metallic bahavior of Ti_2O_3 above 450°K is accompanied by weak ferromagnetism.

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