

## SESSION III—TRANSITION-METAL COMPOUNDS

## Mechanisms for Metal–Nonmetal Transitions in Transition-Metal Oxides and Sulfides

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Transition-metal oxides and sulfides can be insulators, semiconductors, or metals, or undergo metal–nonmetal transitions. The experimental situation in these materials is briefly reviewed. Pure Bloch–Wilson theory predicts that many of the insulators should be metallic, so this class cannot be explained in terms of pure band theory. However, it now appears likely that band theory can be adapted to describe most of the materials that exhibit metal–nonmetal transitions.

### I. INTRODUCTION

Transition-metal oxides and sulfides are ideal subjects for an investigation of insulating and metallic states because of the wide diversity of electrical properties observed in apparently similar materials. *A priori*, there appears to be little difference between MnO and TiO, both of which have the NaCl structure, and yet their room-temperature conductivities differ by a factor of  $10^{20}$ .

The major problem in studying these materials is the difficulty in growing pure, stoichiometric single crystals. Most of the crystals originally investigated contained such large concentrations of random impurities and lattice defects that the results of electrical measurements often had little to do with intrinsic properties of the material. Furthermore, unless special care was taken in sample preparation, grain boundary effects tended to dominate the resistivity. With recent improvements in techniques of crystal growth and the development of more sophisticated equipment, there is now new hope for finding some order in a situation which initially appears to be chaotic.

Most pure, stoichiometric crystalline materials can be classified as either metals or insulators. Metals are characterized by a low resistivity, of the order of  $10^{-2}$ – $10^{-6}$   $\Omega\cdot\text{cm}$  at room temperature, and a linear increase in resistivity as the temperature is raised. Insulators and semiconductors have resistivities of the order of  $10^3$ – $10^{17}$   $\Omega\cdot\text{cm}$  at room temperature, and the resistivity decreases exponentially with increasing temperature. Using these criteria, the largest single group of transition-metal oxides and sulfides can be classified as good insulators. These include NiO, CoO, MnO, Fe<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, MnS, FeS<sub>2</sub>, and MnS<sub>2</sub>. There are also a number of metals, including TiO, CrO<sub>2</sub>, NbO, RuO<sub>2</sub>, ReO<sub>3</sub>, TiS, CoS<sub>2</sub>, and CuS<sub>2</sub>. The situation is not as yet clear for a third class, in which the resistivity has low

magnitude, but a negative temperature coefficient. Of these, FeO seems to be a semiconductor whose conductivity is high due to nonstoichiometry, and MoO<sub>2</sub> is most likely a metal with an inverse temperature dependence of resistivity due to random impurities. In the case of MnO<sub>2</sub>, we cannot as yet make the choice between a nearly degenerate semiconductor and an impure metal.

The materials with which we are most concerned here, however, do not fall into any of the above-mentioned groups. They are semiconducting at low temperatures, but at a given temperature or over a small temperature range their conductivity suddenly jumps by a large factor, as great as  $10^7$ , and at higher temperatures the materials are metallic. Since the transition-metal oxides and sulfides include a large number of pure insulators and a reasonably large number of pure metals, it is perhaps not too surprising to find a few substances which exhibit insulator–metal transitions. However, the number of materials in this class is truly astounding. Such transitions have been observed in V<sub>2</sub>O<sub>3</sub>, VO<sub>2</sub>, VO, V<sub>6</sub>O<sub>13</sub>, Ti<sub>2</sub>O<sub>3</sub>, NbO<sub>2</sub>, Fe<sub>2</sub>O<sub>4</sub>, V<sub>3</sub>O<sub>5</sub>, V<sub>4</sub>O<sub>7</sub>, Ti<sub>3</sub>O<sub>5</sub>, NiS, CrS, and FeS. It seems clear that these transitions cannot merely occur in crystals which, by chance, lie near the borderline between an insulating and a metallic ground state. Before we can consider the problem solved, we must discover the reason why such a vast array of different transition-metal oxides and sulfides fall into this presumably small region, when so few other materials do.

### II. INSULATING MATERIALS

It is worthwhile reviewing the oxides and sulfides which are insulating or semiconducting at all temperatures, in order to gain some insight into those which become metallic above a critical temperature. In particular, we can ask whether all the materials with

insulating ground states should be expected to undergo metallic transitions at some critical temperature  $T_0$  which is above the melting point of some and thus cannot be reached, or whether there is a more fundamental difference between the two classes.

Let us concentrate on the four similar materials, MnO, FeO, CoO, and NiO. All have the cubic NaCl structure, with one molecule per primitive cell. All are antiferromagnetic and are highly insulating both below and above their Néel temperatures,  $T_N$ . Finally, all undergo small distortions from cubic symmetry below  $T_N$ .

In the transition-metal oxides, the only bands in the vicinity of the Fermi energy are made up primarily from the  $d$  orbitals originally associated with the transition-metal ions. The  $s$  band, which in the transition metals overlaps the  $d$  band in both directions, is pushed up in the oxides and begins some 5 eV above the Fermi energy, whereas the highest band originally associated with the oxygen ions, the  $2p$  band, is completely filled, and is depressed about the same amount below  $E_F$ . Thus, the  $d$  band is primarily responsible for the electrical properties of the oxides.

A band theoretic approach to the four materials under consideration must begin with a tenfold-degenerate  $3d$  band. Each cation is in a cubic crystalline field, which is very strong, due to the ionic nature of the nearest-neighbor octahedral array of  $O^{2-}$  ions. This crystalline field can be expected to split the  $3d$  band into a lower sixfold-degenerate ( $t_{2g}$ ) subband and an upper fourfold-degenerate ( $e_g$ ) subband. Although the crystalline field splitting will be large, a real gap in the density of states will occur only if the bandwidth is of the order of the splitting or smaller. However, the  $3d$  band in these oxides can be expected to be extremely narrow compared to that in the metals, since the transition-metal ions are further apart and have smaller spatial extent than the corresponding atoms in the metals. Thus there is most likely a real gap between these bands. However, only FeO, with six  $3d$  electrons per primitive cell can be insulating with this band structure. MnO ( $3d^5$ ), CoO ( $3d^7$ ), and NiO ( $3d^8$ ) should have partially filled bands and be metallic.

If we are concerned only with the ground state, it becomes possible in principle to obtain insulating states for all these oxides. Below  $T_N$ , they are antiferromagnetic, which leads to a doubling of the size of the primitive cell,<sup>1</sup> and consequently an exchange splitting of all the bands. Thus NiO will be an insulator at  $T=0$  if and only if a real gap in the density of states opens up between the exchange-split halves of the  $e_g$  band. MnO will have an insulating ground state provided the exchange splitting exceeds the crystal field splitting, which is possible considering the large sublattice magnetization of  $5 \mu_B$  per cation. But the reverse must

be true to keep FeO insulating at  $T=0$ . Finally, in order to have CoO insulating rather than metallic, we must appeal to the 2% tetragonal distortion which appears below  $T_N$ . This distortion will be sufficiently large to introduce a real gap between the halves of the lower  $e_g$  subband only if the bands are extremely narrow, of the order of tenths of an electron volt,<sup>2</sup> but this may well be the case. However, it is clear that NiO, MnO, and CoO cannot remain insulating in a Hartree-Fock band approximation above  $T_N$ , since the self-consistent gaps introduced by exchange and distortion must vanish.

We are forced to conclude that pure band theory cannot account for the electrical properties of this class of oxides, unless we arbitrarily insist on solutions with lower symmetry than is exhibited by the crystal. The only possible reason for this failure is the neglect of electronic correlations, a necessary consequence of any Hartree-Fock approximation. Correlations must be directly responsible for the energy gap in the many-particle spectrum which leads to the insulating nature of these materials.

With the exception of MnO, CoO, and NiO, it is possible for all of the purely insulating materials to be understood by ordinary band theory. The only other known insulating monoxides are CuO and AgO, which have monoclinic symmetry, and PdO and PtO, which have tetragonal symmetry. The monosulfides are all of sufficiently low symmetry to be nonmetallic in principle. A particularly interesting series is the sesquioxides, most of which have the corundum ( $Al_2O_3$ ) structure. Kleiner<sup>3</sup> has shown that a symmetry analysis of this structure shows that materials with 1, 3, 5, 7, and  $9d$  electrons per cation can, in principle, be insulators, using the most likely ordering of the bands. Thus  $Ti_2O_3$  ( $3d^1$ ),  $Cr_2O_3$  ( $3d^3$ ),  $Fe_2O_3$  ( $3d^5$ ), and  $Ni_2O_3$  ( $3d^7$ ) can be explained by a normal band approach. However,  $V_2O_3$  ( $3d^2$ ),  $Mn_2O_3$  ( $3d^4$ ),  $Co_2O_3$  ( $3d^6$ ), and  $Cu_2O_3$  ( $3d^8$ ), if they existed with corundum symmetry, would most likely be metallic according to the band model. However, of these only  $V_2O_3$  ever occurs with corundum structure, and that phase of  $V_2O_3$  is, indeed, metallic.

As far back as 1949, Mott<sup>4</sup> suggested how an insulating state can be obtained in general for materials in which all the bands in the vicinity of the Fermi energy are extremely narrow. If the total reduction of kinetic energy due to delocalization, a relatively small quantity for electrons in a narrow energy band, does not overcome the total increase of potential energy due to the additional Coulomb repulsion between electrons in the ionized states of a partially filled band, then the ground state of the system should be nonconducting.

<sup>2</sup> D. Adler and H. Brooks, *Phys. Rev.* **155**, 826 (1967).

<sup>3</sup> W. H. Kleiner, M. I. T. Lincoln Laboratory Solid State. Res. Rept. #3, 1967, p. 44 (unpublished).

<sup>4</sup> N. F. Mott, *Proc. Phys. Soc. (London)* **A62**, 416 (1949).

<sup>1</sup> J. C. Slater, *Phys. Rev.* **82**, 538 (1951).

Mott<sup>5</sup> proposed further that the transition between an insulating ground state and the conducting ground state obtained using a band approach occurs sharply at a critical lattice constant for each material. This argument is based on the fact that if an electron is removed from the vicinity of one atom and placed on another atom in the above type of insulator, the free electron and free hole would attract each other via a Coulomb interaction,  $V_c(r) = -e^2/\kappa r$ , and form a bound state or exciton, allowing neither electron nor hole to participate in conduction. However, if many free carriers are present, an electron and a hole attract each other via a screened Coulomb interaction,  $V_s(r) = V_c(r)e^{-\alpha r}$ , where  $\alpha$  is a screening constant. At a sufficiently large value of  $\alpha$ ,  $V_s(r)$  becomes too weak to have bound-state solutions, and a sharp transition from no free carriers to a large number takes place.

Using the concept of these Mott transitions, we can explain the electrical properties of both the purely insulating and the purely metallic classes of the transition-metal oxides and sulfides. However, of all of the materials in the former class, only for MnO, CoO, and NiO was it *necessary* to invoke Mott's ideas to agree with the observations. We must be aware of the possibility that many of the other insulating oxides and sulfides are nonmetallic due to an energy gap between the highest filled and lowest empty band. One prediction of the Mott theory is a nonmetal-metal transition under pressure as the lattice parameter passes through the critical value. Such a transition has not yet been observed,<sup>6,7</sup> although NiO has been subjected to 500 kbar. If a nonmetal-metal transition is found, the sharpness should enable us to distinguish between a Mott insulator and a normal band insulator whose energy gap decreases with pressure. A Mott transition should appear as a sudden jump in conductivity at a given pressure, whereas a transition due to band overlap should lead to a more gradual increase in conductivity as the energy gap is shrinking. However, the analysis could be complicated by an associated symmetry change at a given pressure, since this would lead to a sharp jump in either case.

The main conclusion to draw from this discussion is that band theory fails to account for even the qualitative aspects of the electrical properties of at least three and most likely many more of the insulating materials. In view of this, we should be careful about putting too much faith in a Hartree-Fock approximation for the oxides and sulfides which are not purely insulating. On the other hand, the existence of excellent metals, such as ReO<sub>3</sub> and CrO<sub>2</sub>, can be taken as evidence that a purely localized approach is also inappropriate, and that good *d*-band conduction can indeed occur.

<sup>5</sup> N. F. Mott, *Phil. Mag.* **6**, 287 (1961).

<sup>6</sup> A. P. Young, W. B. Wilson, and C. M. Schwartz, *Phys. Rev.* **121**, 77 (1961).

<sup>7</sup> S. Minomura and H. G. Drickamer, *J. Appl. Phys.* **34**, 3043 (1963).

### III. MODELS FOR NONMETAL-METAL TRANSITIONS

As mentioned above, a large number of the transition-metal oxides and sulfides are semiconducting at low temperatures but are metallic at high temperatures. There are a number of possible mechanisms for these transitions, which are described in detail in this section. We attempt to show how they can be distinguished experimentally and also try to determine if there are any particular reasons why these transitions are so common in the oxides and sulfides, while so rare in general.

#### 1. Band Overlap

The simplest mechanism for a semiconductor-metal transition is ordinary band overlap, without accompanying crystalline symmetry changes. If the material is a normal semiconductor, with a filled valence band separated from an empty conduction band by an energy gap which happens to decrease with increasing temperature, then at a given temperature the gap may vanish. This cannot happen to a direct gap when the bands are the same symmetry, due to the phenomenon of band repulsion. However, bands of different symmetry can cross, and zero-gap semiconductors such as grey tin<sup>8</sup> are well known. A more likely possibility is the vanishing of an indirect gap, in which case the transition is from a semiconductor to a semimetal.

The main experimental consequence of this type of transition is that the increase in conductivity should be gradual. As the gap decreases with temperature, conductivity in the semiconducting state will become relatively large. After the gap passes through zero and becomes negative, the density of states at the Fermi surface will initially be very small, so the conductivity will not increase strikingly. There should, in fact, be no sharp jump in conductivity, but rather a steady increase, and a gradual change from a resistivity which decreases exponentially with increasing temperature to one which increases linearly.

There are two possibilities which could result in a somewhat sharper increase in conductivity in this simple model. First, in this type of a semiconductor-semimetal transition, the gap must pass through a region where its magnitude is extremely small, and the conditions are fulfilled for the formation of an excitonic insulator state.<sup>9</sup> Such a Bose condensation of excitons would reduce the conductivity in the vicinity of the temperature at which the gap vanishes, and lead to a greater increase after the true semimetallic state is reached. However, there still would be no large conductivity discontinuity.<sup>10</sup> Another possibility is that of

<sup>8</sup> S. Groves and W. Paul, *Phys. Rev. Letters* **11**, 194 (1963).

<sup>9</sup> B. I. Halperin and T. M. Rice, *Rev. Mod. Phys.* **40**, 755 (1968), this issue; *Solid State Physics*, F. Seitz, D. Turnbull, and H. Ehrenreich, Eds. (Academic Press Inc., New York, 1968), Vol. 21, p. 115.

<sup>10</sup> D. Jerome, T. M. Rice, and W. Kohn, *Phys. Rev.* **158**, 462 (1967).

a first-order semiconductor–semimetal transition, which indeed could result in a jump in conductivity. Such first-order transitions, without any accompanying symmetry change, should be extremely rare, and have never been observed in ordinary semiconductors.

A major condition which is necessary for a semiconductor–semimetal transition is a negative temperature coefficient of energy gap. In the case we are considering, the energy gap arises from the symmetry of the crystal, and we are assuming that this symmetry does not change with temperature. Thus, the most obvious mechanism for a decreasing energy gap is an increase in valence and conduction bandwidth. Such an increase would be likely to occur if the crystal were contracting with temperature, or at least one crystalline axis had a negative thermal expansion. A second condition for the occurrence of this type of transition is a narrow energy gap in the semiconducting state. There appears to be no *a priori* reason why negative thermal expansion coefficients and narrow gaps should occur *particularly* in the transition-metal oxides and sulfides, so it would indeed be surprising if ordinary band overlap were the cause of a large number of the observed transitions.

## 2. Crystalline Symmetry Changes

A more natural approach to the problem of semiconductor–metal transitions is to consider the metallic state as fundamental, and look for mechanisms which will produce a low temperature semiconductor. The most obvious way of accomplishing this is by means of a crystalline structure distortion. Such a distortion can bring about an insulating ground state in two ways. If the deformation leads to an increase in the number of molecules per primitive cell, as occurs, for example, when ions pair up along a given crystalline axis, extra energy gaps are introduced at the surfaces of the reduced Brillouin zone made necessary by the increase of periodicity. On the other hand, a simple reduction of symmetry, as, for example, the cubic-tetragonal distortion in CoO below 284°K, can also result in additional splittings due to higher-order terms in the crystalline field. A ground-state insulator is obtained, however, only if the Fermi energy is located in a true gap in the density of states.

We begin with a high-symmetry crystal and a partially filled band. A low-temperature distortion will occur only if the total ground-state energy is lowered. Since the strain energy is always increased by structure distortions, the decrease of electronic energy must more than compensate for this increase. A simple model for crystalline distortions has been presented by Adler and Brooks,<sup>2</sup> who assumed that the energy bands were spherical around the valence and conduction band edges, with energies given by

$$\begin{aligned} E_v(k) &= E_0 - [(rE_g)^2 + 4\beta^2 \sin^2(\frac{1}{2}ka)]^{1/2}, \\ E_c(k) &= E_0 + [(1-r)^2 E_g^2 + 4\beta^2 \sin^2(\frac{1}{2}ka)]^{1/2}, \end{aligned} \quad (3.1)$$

where  $E_0$  is the average band energy in the absence of distortion,  $\beta$  is the nearest-neighbor overlap integral,  $E_g$  is the energy gap, and  $r$  is a parameter which depends on the amount of distortion, varying from 0.5 for infinitesimal deformations to very small values for extremely large deformations. This model assumes that the metallic energy band is half full, but this is easily generalized. At zero temperature, the total electronic energy of the crystal is found by summing the energies of the filled valence band. The result is

$$E_{elec} = N E_0 - 3N (rE_g) \int_0^1 dz z^2 \left( 1 + \lambda^2 \frac{\sin^2 \pi z}{z} \right)^{1/2}, \quad (3.2)$$

where  $N$  is the total number of atoms in the crystal, and  $\lambda \equiv 4\beta/E_g$ . The integral in (3.2) can be expressed in terms of elliptic integrals of the second kind, but the two limits of wide bands ( $\lambda^2 \gg 1$ ) and narrow bands ( $\lambda^2 \ll 1$ ) are of particular interest. In the wide-band limit

$$E_{elec} = N \left[ E_0 - \frac{48}{\pi^2} \left( 1 - \frac{2}{\pi} \right) \right] - \frac{K}{\beta} (rE_g)^2 - \frac{\pi^2 (rE_g)}{384\beta^2}, \quad (3.3)$$

where

$$\begin{aligned} K &= \frac{3}{\pi} \sum_{n=1}^{\infty} (-1)^n n^2 \ln \left( 1 - \frac{1}{4n^2} \right) \\ &\approx 0.150. \end{aligned}$$

The wide-band limit is always valid for sufficiently small deformations, in which case the gap will be proportional to the fractional amount of distortion,  $\epsilon$ . On the other hand, the increase in elastic energy must be proportional to the square of  $\epsilon$ . Consequently, the total energy of the crystal for small  $\epsilon$  must be given by

$$E = N \{ E_0 - (48/\pi^2) [1 - (2/\pi)] \} + [B - (KA/4\beta)] \epsilon^2, \quad (3.4)$$

where we have set  $E_g = A\epsilon$ ,  $E_{elas} = B\epsilon^2$ , and  $r = 0.5$ , the appropriate value in this limit. An important result of (3.4) is that there is always a local minimum of energy as a function of  $\epsilon$  at  $\epsilon = 0$ . Thus infinitesimally small distortions cannot occur, and the disappearance of a distortion must be a first-order transition.

Distortions will occur only if there is an absolute minimum of total energy at some finite  $\epsilon$ . When the bands are very narrow, as we might expect is the case in the  $d$  bands of transition-metal oxides and sulfides, the opposite limit,  $\lambda^2 \ll 1$ , becomes appropriate, and the total energy becomes

$$E = N E_0 - N A r \epsilon - (N\beta^2/A) [1 + (6/\pi^2)] \epsilon^{-1} + B \epsilon^2. \quad (3.5)$$

The total energy (3.5) also has a local minimum, at a

finite  $\epsilon$ . The energy at this minimum is

$$E = N[E_0 - \frac{1}{2}rE_0 - (2.4\beta^2/E_0)]. \quad (3.6)$$

From (3.4), we can evaluate the energy at  $\epsilon=0$  as

$$E = N[E_0 - 1.77\beta]. \quad (3.7)$$

Taking values of  $r$  appropriate to distortions of the order of 1%-5%, as are found in the oxides and sulfides, we find that (3.6) is lower than (3.7) if the bandwidth is less than approximately the energy gap introduced by the distortion. This result means that we should expect this type of distortion in materials which otherwise would have a partially filled but very narrow conduction band. In general, clearly the most favorable lowering of electronic energy occurs for a deformation which lowers only the occupied states and raises only the unoccupied states of the partially filled conduction band. This means the distortions which will occur always favor the formation of insulating states. The narrower is the band the higher is the probability that the lowering of electronic energy is greater than the increase in elastic energy. But also, the narrower the band is, the greater the chances are that a real gap is introduced in the density of states, and thus that a ground-state insulator is produced by the distortion. When the gap introduced is larger than the bandwidth, the probability of a true gap is large. This is the great appeal of the crystalline distortion model, for it predicts that these types of distortion occur only for materials such as the oxides and sulfides. Thus it explains why we should not expect to find them, for example, in sodium.

The finite-temperature properties of this model have also been calculated.<sup>2</sup> The important point here is that the energy gap is due entirely to the distortion itself—the lower band may be considered a bonding band, the upper an antibonding band. Thus excitation of an electron across the gap decreases the magnitude of the gap, because the excited electron no longer contributes to the chemical binding. In order to discuss the finite-temperature properties, the free energies of both the semiconducting and metallic states must be calculated and compared. The result is that at a given temperature which depends only on the initial value of the gap and the parameter  $r$  in (3.1), a first-order semiconductor-metal transition occurs. For approximately a 2% distortion, the transition temperature turns out to be

$$T_0 = E_{g0}/10k, \quad (3.8)$$

where  $E_{g0}$  is the gap at  $T=0$ . Thus  $T_0$  will be of the order of room temperature for initial gaps of the order of 0.25 eV.

Experimentally distinguishing this model from the others should be quite simple. In order for the semiconducting properties to be caused by a distortion, the

symmetry below  $T_0$  must be lower than the symmetry in the metallic region. The transition should be of first order, which would lead to a latent heat and most likely a hysteresis between heating and cooling. The only problem is the possibility that a structure distortion could accompany some other mechanism which is primarily responsible for the transition. In this case, we must consider both mechanisms simultaneously.

### 3. Antiferromagnetism

In the same way that a doubling of the number of molecules per primitive cell by means of a pairing of ions in one type of crystalline distortion leads to the introduction of new energy gaps at the surfaces of the reduced Brillouin zone, long-range antiferromagnetic order can produce the same effect by doubling the number of molecules per *magnetic* primitive cell. Thus antiferromagnetism can also bring about an insulating ground state in materials which might otherwise be metallic, as was first pointed out by Slater.<sup>1</sup> However, whereas a crystalline distortion could, in principle, produce an insulator regardless of the fractional population of the original conduction band, antiferromagnetism alone can accomplish this only in the case of a half-filled band.<sup>11</sup>

Quantitative versions of itinerant antiferromagnetism have been presented by Matsubara and Yokota<sup>12</sup> and others.<sup>13-15</sup> The results, as might be expected, are very similar to those obtained from a model of a pairing type of crystalline distortion. However, there are subtle complications.<sup>15,16</sup> It is necessary to introduce explicitly the exchange-energy term in the Hartree-Fock Hamiltonian in order to obtain any long-range magnetic order at all. It is found then that an energy gap appears, self-consistently due only to the sublattice magnetization resulting from the antiferromagnetic alignment. As the temperature is raised, this sublattice magnetization decreases. A self-consistent solution of the Hartree-Fock equations thus must lead to a decrease of the gap. This comes about because the exchange-energy term in the Hamiltonian contains in it a sum over occupied one-electron states, and a change of occupation numbers necessary for a consideration of excited states leads to a new Hamiltonian, and consequently a different one-electron energy spectrum. Discussion of the finite-temperature behavior is further complicated by the necessity to compare the total

<sup>11</sup> A spiral spin arrangement could, in principle, make an insulator out of any partially filled band. However, such spin arrangements appear to be quite rare in these materials, occurring only in  $\text{MnO}_2$ , which is most likely a metal.

<sup>12</sup> T. Matsubara and T. Yokota, Proc. Intern. Conf. Theoret. Phys., Kyoto and Tokyo, September 1953, 693 (1954).

<sup>13</sup> J. des Cloiseaux, J. Phys. Radium **20**, 606, 751 (1959).

<sup>14</sup> A. M. DeGraaf and R. Luzzi, Phys. Letters **18**, 235 (1965).

<sup>15</sup> D. Adler, *Solid State Physics*, F. Seitz, D. Turnbull, and H. Ehrenreich, Eds. (Academic Press Inc., New York, 1968), Vol. 21, p. 1.

<sup>16</sup> D. Adler, Phys. Rev. Letters **17**, 139 (1966).

energies of the ground state and excited states. Since the exchange energy is a pure electronic interaction, we cannot compute total energies by merely summing the filled one-electron energies, but must avoid the double counting of interactions inherent in such an approach.

The result is a catastrophic collapse of energy gap in the vicinity of the Néel temperature. As opposed to the case of a crystalline distortion, an antiferromagnetic-paramagnetic transition can be second order if the bands are extremely narrow. Above a critical bandwidth-to-energy-gap ratio, the transition becomes first order, but the decrease of gap with temperature is not as sharp as in a distorted crystal of comparable bandwidth.

As in the case of a crystalline distortion, experimental identification of antiferromagnetically induced semiconductor-metal transitions should be straightforward. If the semiconducting phase of the material is antiferromagnetic and the Néel temperature is also the transition temperature, this is strong evidence for the applicability of this type of model. An important requirement is that the metallic state must have an exactly half-filled band. However, the possibility exists of the low-temperature phase being both antiferromagnetic and distorted, with a transformation at  $T_0$  to a high-symmetry, paramagnetic metal. Deciding whether the distortion is incidental to the semiconducting properties, as, for example, if it were a consequence of magnetostriction, or whether the distortion is the major effect and the antiferromagnetism is a byproduct of the lower-symmetry phase, becomes akin to the chicken-or-egg problem. An adequate calculation must consider both effects simultaneously.

#### 4. Electronic Correlation and Mott Transitions

All previous models which we have discussed were treated purely within the band approximation. However, as we have seen in Sec. II, correlations between electrons, neglected in any Hartree-Fock approach, were essential in bringing about insulating ground states in at least MnO, NiO, and CoO. As shown by Mott,<sup>4,5</sup> correlations can produce nonconducting states in any material, provided only that the lattice parameter is greater than some critical value. We have indicated that a metallic transition could occur in such a material under very high pressure. We now want to ask whether a Mott insulator could become conducting above a critical temperature.

As Mott<sup>4</sup> has discussed,<sup>5</sup> metallic excited states must always exist in these materials. Above a critical exciton concentration, there is a sudden transition to a large number of carriers. However, it would seem to be unlikely that such a high energy state would be reached at ordinary temperatures, unless the material, by chance, happens to crystallize with a lattice constant

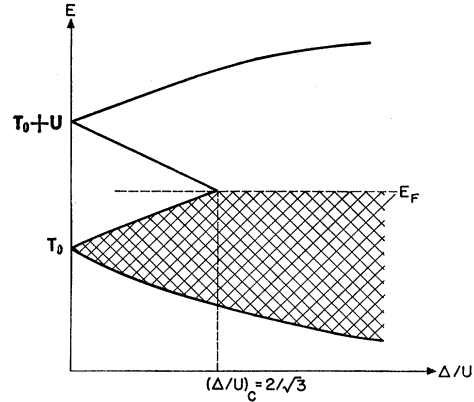


FIG. 1. Pseudoparticle band structure as a function of the ratio of bandwidth  $\Delta$  to intra-atomic Coulomb matrix element  $U$  for the case of a single  $s$  band (Hubbard<sup>19</sup>).

very slightly greater than the critical value. We should not expect this to occur with anywhere near the frequency that semiconductor-metal transitions are observed.

Since Mott's original work, very little has been accomplished quantitatively on Mott transitions.<sup>17</sup> A simple model which introduces the effects of correlation into band theory has been presented by Hubbard,<sup>18-20</sup> based on the Hamiltonian

$$H = \sum_{i,j} \sum_{\sigma} T_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}, \quad (3.9)$$

where  $c_{i\sigma}$  annihilates an electron of spin  $\sigma$  in the Wannier state centered on  $\mathbf{R}_i$ ,  $n_{i\sigma} = c_{i\sigma}^{\dagger} c_{i\sigma}$ ,  $T_{ij}$  is the Fourier transform of the Bloch energies  $\epsilon(\mathbf{k})$ , and  $U$  is the electronic Coulomb repulsion matrix element arising from all four Wannier functions centered on the same site. The fundamental approximation is a massacre of the Coulomb interaction from an infinite range to a delta-function repulsion. However, this has the desired effect of inhibiting the presence of two electrons of opposite spin on the same site.

Hubbard obtained quantitative results only for the case of an  $s$  band,<sup>20</sup> due to the immense complexity involved in applying even this simple model to a  $d$  band.<sup>19</sup> Even for an  $s$  band, it was necessary to make approximations which lead to physical difficulties.<sup>15</sup> Hubbard's result is shown in Fig. 1. For vanishingly small bandwidth (atomic limit), the pseudoparticle  $s$  band is split into two subbands, separated by an energy gap of order  $U$ . Thus, for the case of one electron per atom, the lower band is completely filled and the upper band is empty at  $T=0$ . As the ratio of bandwidth

<sup>17</sup> For a review, see the paper by G. Kemeny and L. G. Caron, *Rev. Mod. Phys.* **40**, 790 (1968), this issue.

<sup>18</sup> J. Hubbard, *Proc. Roy. Soc. (London)* **A276**, 238 (1963).

<sup>19</sup> J. Hubbard, *Proc. Roy. Soc. (London)* **A277**, 237 (1964).

<sup>20</sup> J. Hubbard, *Proc. Roy. Soc. (London)* **A281**, 401 (1964).

to  $U$  is increased, the gap decreases until a critical ratio is reached, at which point the two bands overlap. This disappearance of the gap is much like that already discussed in Sec. III.1. Since the gap decreases slowly to zero, conductivity will increase only gradually as we pass through the critical ratio, unless a first-order transition occurs. This is not a violent transition, as Mott predicted, but the complete neglect of all interatomic Coulomb terms in Hubbard's model eliminates the screening effects invoked by Mott in making a sharp transition plausible.

It is certainly unlikely for a Hubbard model to exhibit a nonmetal-metal transition as the temperature is raised. Neither the bandwidth nor  $U$  should be strong functions of temperature. It is possible that the presence of a large number of free carriers serves to screen  $U$  and effectively reduce its value. However,  $U$  is due to the additional Coulomb repulsion associated with two electrons simultaneously on a single site, and it is doubtful that free carriers could significantly screen such an intra-atomic quantity. Nevertheless, if we assume that the effect of neglecting interatomic Coulomb matrix elements can in some manner be compensated by an effective screening of  $U$ , an insulator-metal transition is obtained. It is difficult to perform a meaningful quantitative calculation, but if a Fermi-Thomas screening is postulated, extremely large values for the transition temperature are obtained, of the order of thousands of degrees for band gaps of tenths of an electron volt.<sup>21</sup>

Since there is no particular reason why such a large number of oxides and sulfides should happen to be Mott insulators with a lattice constant very near the critical value, and since we should expect to observe Mott transitions much more easily as the pressure rather than the temperature is increased, it appears unlikely that this mechanism alone can explain the observed transitions. However, it is quite possible that correlation effects help to open up a real gap in the density of states in the low-temperature phase of crystals which undergo distortions or antiferromagnetic ordering. Formation of a Mott insulator in the non-metallic phase could also serve to lower the conductivity below  $T_0$ , and help to explain the large conductivity discontinuities observed in some of these materials.

### 5. Other Mechanisms

Much work has been carried out on the effect of the electron-phonon interactions on the conductivity.<sup>22</sup> These studies indicate that if the coupling to the lattice is strong, nominally free carriers can become self-trapped in the potential well which arises from the lattice deformation brought about by its own presence

<sup>21</sup> D. Adler (unpublished).

<sup>22</sup> For a review, see J. Appel, *Solid State Physics*, F. Seitz, D. Turnbull, and H. Ehrenreich, Eds. (Academic Press Inc., New York, 1968), Vol. 21, p. 193; and also Ref. 15.

in an ionic crystal. Once the electron is self-trapped, it can participate in conduction only by means of an uncorrelated hopping from its site to a neighboring site which during the course of a thermal fluctuation, momentarily assumes a configuration equivalent to the initial, distorted site. If the strength of the electron-phonon coupling is sufficiently large, it becomes more physical to consider the electron as bound to its associated lattice deformation, a quasiparticle known as a polaron. In a classic study of the polaron in the limit in which the lattice deformation does not extend beyond nearest neighbors (small polaron limit), Holstein<sup>23</sup> found that at low temperatures polaron bands are formed, and metallic conductivity could result. However, above a critical temperature, in the vicinity of half the Debye temperature, Holstein showed that a transition should occur to a state in which conduction takes place only by means of thermally activated polaron hopping. This transition is from a metal to a semiconductor, and is the reverse of what is observed in the oxides and sulfides.

Other models have been presented which exhibit gradual<sup>24</sup> or sharp<sup>25</sup> transitions from states where the carriers are self-trapped to those where they are free. However, these models do not predict temperature-induced transitions, and do not apply to intrinsic material, so are not appropriate to the transition-metal oxides and sulfides under consideration here.

## IV. SUMMARY OF THE EXPERIMENTAL DATA

In this section, we present the experimental results thus far obtained on all of the materials which exhibit nonmetal-metal transitions as the temperature is raised. We treat each material separately, and try to decide which of the mechanisms in Sec. III is most likely to be the major cause of the transition. In many cases, it is impossible to make a choice as yet, since the observations are incomplete. There is a high probability that many of the conclusions which seem obvious at this time will change drastically as new experiments are performed. A case in point is  $Ti_2O_3$ , which was thought to be antiferromagnetic until recently, when the weight of evidence suddenly shifted towards no long-range magnetic order.<sup>26</sup>

### 1. $V_2O_3$

At room temperature,  $V_2O_3$  has the corundum structure, which is of rhombohedral symmetry.<sup>27</sup> It can be considered as a slightly distorted hexagonal lattice, with the metal ions essentially lying in basal planes.

<sup>23</sup> T. Holstein, *Ann. Phys. (N.Y.)* **8**, 325, 343 (1959).

<sup>24</sup> J. Yamashita and T. Kurosawa, *J. Phys. Soc. Japan* **15**, 802 (1960).

<sup>25</sup> Y. Toyozawa, *Progr. Theoret. Phys.* **26**, 29 (1961).

<sup>26</sup> L. L. Van Zandt, J. M. Honig, and J. B. Goodenough, *J. Appl. Phys.* **39**, 594 (1968).

<sup>27</sup> R. E. Newnham and Y. M. de Haan, *Z. Krist.* **117**, 235 (1962).



Along the hexagonal  $c$  axis, normal to these planes, only two of three successive intersections with the basal planes are occupied by  $V^{3+}$  ions. These two ions form the closest cation-cation separation in the structure, and are called  $c$ -axis pairs. The  $O^{2-}$  ions form distorted octahedra around each cation.

Below approximately  $150^\circ\text{K}$ , there is a phase transformation to monoclinic symmetry.<sup>28</sup> The low-temperature structure may be considered as a 2% shifting of pairs of  $V^{3+}$  ions in the corundum basal plane towards one another, parallel to one of the three hexagonal axes in the plane. There is a volume contraction of 3.5% as  $V_2O_3$  is heated through the transition temperature.<sup>29</sup> This indicates that the transition is of first order.

The magnetic properties of  $V_2O_3$  have been investigated numerous times by a large variety of techniques, and it is still difficult to reach a definite conclusion. Magnetic-susceptibility data exhibit anomalies in the vicinity of  $150^\circ\text{K}$ <sup>30</sup> and at an apparent high-temperature transition near  $550^\circ\text{K}$ ,<sup>31</sup> but the temperature dependence of  $\chi_m$  does not have the form characteristically associated with antiferromagnetism. Nuclear magnetic resonance experiments have been interpreted as indicating the presence of antiferromagnetism, since there is a sudden disappearance of the resonance at  $150^\circ\text{K}$ .<sup>32</sup> On the other hand, neutron-diffraction measurements have never given any evidence for long-range magnetic ordering,<sup>33,34</sup> and an upper limit of only  $0.05 \mu_B$  per cation has been placed on a possible antiferromagnetic moment of the  $\text{Fe}_2\text{O}_3$  type (successive ferromagnetic basal planes coupled antiferromagnetically). However, these neutron-diffraction experiments could not detect a possible  $\text{Cr}_2\text{O}_3$ -type antiferromagnetism, with each magnetic ion antiparallel to both its  $c$ -axis partner and one of its basal-plane nearest neighbors. This is the more natural form of antiferromagnetism to be expected in  $V_2O_3$ , considering its low-temperature structure. Finally, the most convincing evidence in favor of antiferromagnetism in  $V_2O_3$  is the Mössbauer results, which exhibit a hyperfine splitting below  $150^\circ\text{K}$  only.<sup>35-37</sup> The sharp decrease of internal field to zero at  $T_0$  is indicative of a first-order antiferromagnet-paramagnetic transition.

Electrical measurements on  $V_2O_3$  have been per-

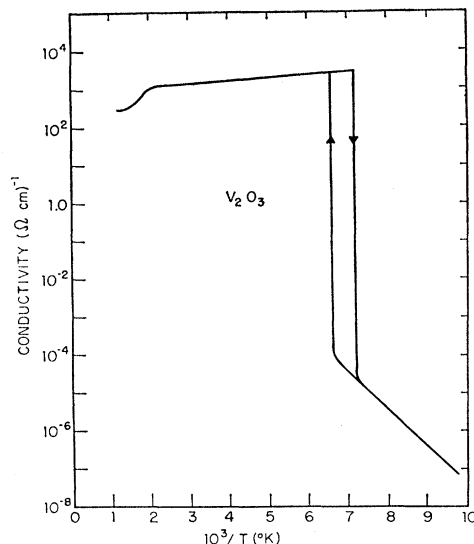


FIG. 2. Conductivity versus temperature for a single-crystal sample of stoichiometric  $V_2O_3$  (Feinleib and Paul<sup>45</sup>).

formed often,<sup>38-45</sup> and are quite consistent. Figure 2 shows the result for a single crystal of stoichiometric material. At low temperatures, conductivity increases exponentially with temperature, with an activation energy of approximately 0.15 eV. At about  $150^\circ\text{K}$ , the conductivity jumps by a factor of  $10^7$  within a few hundredths of a degree to metallic values ( $\sim 2 \times 10^8 \Omega^{-1} \cdot \text{cm}^{-1}$ ). At higher temperatures, resistivity increases linearly with temperature. There is a second resistivity anomaly near  $550^\circ\text{K}$ , where resistivity increases by about a factor of 2 over a 100-deg range. A hysteresis of 10 deg appears between heating and cooling. From the Clausius-Clapeyron equation and their pressure data, Feinleib and Paul<sup>45</sup> evaluated a latent heat associated with the first-order transition of  $1020 \text{ cal/mole}$ .

Feinleib and Paul<sup>45</sup> also performed optical experiments on  $V_2O_3$ . No transmission was found in the metallic region between 0.05 and 6 eV. However, in the semiconducting phase, transmission was found between 0.1 and 0.4 eV. The results are shown in Fig. 3, for  $T = 77^\circ\text{K}$ . There is clear evidence for an absorption edge in the range 0.1-0.4 eV, but it is difficult to decide on an exact value for the gap. The midpoint of the transmission drop is in the vicinity of 0.3 eV, and if this is taken as an approximate value for the gap, it correlates very well with the observed activation energy

<sup>28</sup> E. P. Warekois, *J. Appl. Phys. Suppl.* **31**, 346S (1960).  
<sup>29</sup> S. Minomura and H. Nagasaki, *J. Phys. Soc. Japan* **19**, 131 (1964).  
<sup>30</sup> P. H. Carr and S. Foner, *J. Appl. Phys. Suppl.* **31**, 344S (1960).  
<sup>31</sup> M. Foëx and J. Wucher, *Compt. Rend.* **241**, 184 (1955).  
<sup>32</sup> E. D. Jones, *Phys. Rev.* **137**, A978 (1965).  
<sup>33</sup> A. Paoletti and S. J. Pickart, *J. Chem. Phys.* **32**, 308 (1960).  
<sup>34</sup> H. Kendrick, A. Arrott, and S. A. Werner, *J. Appl. Phys.* **39**, 585 (1968).  
<sup>35</sup> T. Shinjo, K. Kosuge, M. Shiga, Y. Nakamura, S. Kachi, and H. Takaki, *Phys. Letters* **19**, 91 (1965).  
<sup>36</sup> T. Shinjo, K. Kosuge, S. Kachi, H. Takaki, M. Shiga, and Y. Nakamura, *J. Phys. Soc. Japan* **21**, 193 (1966).  
<sup>37</sup> T. Shinjo and K. Kosuge, *J. Phys. Soc. Japan* **21**, 2622 (1966).

<sup>38</sup> M. Foëx, *Compt. Rend.* **223**, 1126 (1946).  
<sup>39</sup> M. Foëx, *Compt. Rend.* **227**, 193 (1948).  
<sup>40</sup> F. J. Morin, *Phys. Rev. Letters* **3**, 34 (1959).  
<sup>41</sup> I. G. Austin, *Phil. Mag.* **7**, 961 (1962).  
<sup>42</sup> A. J. MacMillan, Laboratory for Insulation Research, M. I. T., Tech. Rept. No. 172, 1962 (unpublished).  
<sup>43</sup> G. Goodman, *Phys. Rev. Letters* **9**, 305 (1962).  
<sup>44</sup> G. A. Acket and J. Volger, *Physica* **28**, 277 (1962).  
<sup>45</sup> J. Feinleib and W. Paul, *Phys. Rev.* **155**, 841 (1967).



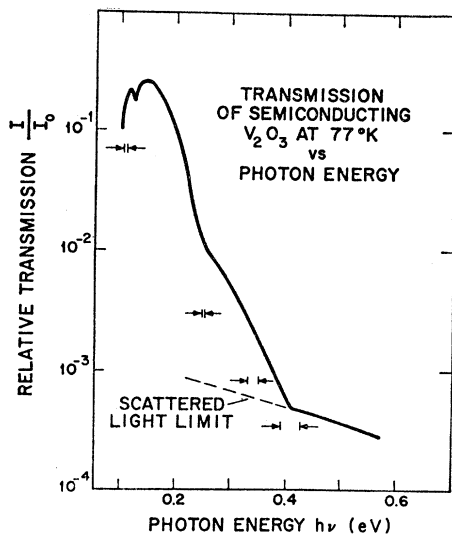


Fig. 3. Relative transmission versus photon energy for  $V_2O_3$  at  $77^\circ K$  (Feinleib and Paul<sup>46</sup>).

( $E_A \sim 0.15$  eV). The optical effective mass was evaluated as  $45m_0$ , consistent with the idea of narrow energy bands.

The crystalline distortion model has been explicitly applied to  $V_2O_3$ .<sup>46</sup> If antiferromagnetism is neglected entirely, the transition temperature of  $150^\circ K$  corresponds to a semiconducting energy gap of 0.1 eV, within the experimental range, but perhaps on the low side. The model quantitatively explains the variation of transition temperature and activation energy with pressure and uniaxial stress measured by Feinleib and Paul.<sup>45</sup> It also successfully predicts a first-order transition, with a latent heat in agreement with the observations. However, the model predicts a jump in carrier concentration at  $T_0$  of the order of a factor of  $10^2$ . Since the conductivity discontinuity is a factor of  $10^7$ , it is necessary to explain a mobility difference of a factor of  $10^5$  between semiconducting and metallic states. The suggestion originally made was that the mobility in the semiconducting state was suppressed by either a large correlation effect or the effect of a self-trapping of free carriers. This was consistent with the observation that the activation energy of 0.15 eV was much greater than  $E_g/2$  ( $\sim 0.05$  eV), and thus the mobility had to be thermally activated as well as the carrier concentration. This interpretation implies that the distortion-induced transition is accompanied by a Mott transition, since the free carriers in the metallic state would have to screen out the correlation effects in order to account for the mobility jump at  $T_0$ .

However, now that it appears likely that antiferromagnetism is also present in the low-temperature phase

of  $V_2O_3$ , a simple model becomes feasible. The simultaneous occurrence of the monoclinic distortion and a  $Cr_2O_3$ -type of antiferromagnetism would combine to reduce the symmetry in exactly the same manner (a doubling of the unit cell along one of the hexagonal axes in the basal plane). Thus this type of antiferromagnetic order would tend to widen the energy gap introduced by the distortion, particularly the true gap which must be smaller than the direct splitting. If we take the value of the gap to be 0.3 eV, as explained above, the mobility will not have any strong temperature dependence. Then the model predicts that a first-order transition at  $150^\circ K$  would be accompanied by a jump in carrier concentration of greater than a factor of  $10^6$ , essentially the entire conductivity discontinuity.

Before this new model can be considered on solid ground, a  $Cr_2O_3$ -type of antiferromagnetism would have to be established for  $V_2O_3$ . However, this approach has great appeal. As has been shown,<sup>2</sup> a narrow-band material with a half-filled conduction band, such as  $V_2O_3$ , could lower its ground-state energy by a pairing of cations. Only an antiferromagnetic ordering which tends to stabilize this distortion would be able to reduce the ground-state energy still further. A different antiferromagnetic arrangement, such as the  $Fe_2O_3$  type, would split the bands in such a manner as to increase just as many of the one-electron energies of states occupied at  $T=0$  as it would decrease. Thus it would lead to no additional lowering of ground-state energy.

A qualitative model to explain the semiconductor-metal transition in  $V_2O_3$  has been proposed by Goodenough,<sup>47</sup> who suggested that in the low-temperature phase, all conduction electrons are trapped in homopolar bonds, and do not participate in conduction. There are two  $3d$  electrons per  $V^{3+}$  ion in  $V_2O_3$ , and two particularly small  $V^{3+}-V^{3+}$  separations in the monoclinic phase, the  $c$ -axis pairs and the basal-plane pairs which arise after the distortion. Thus complete homopolar bonding of all  $3d$  electrons could lead to a low-temperature insulator. Above  $T_0$ , the basal-plane pairs break up, and metallic conductivity should result. This model predicts large anisotropy in conductivity above  $T_0$ , large parallel to the basal planes, but small along the  $c$  axis, where the  $c$ -axis homopolar bonds should inhibit conduction as much as in the monoclinic phase. Such anisotropy is not present, however.<sup>45</sup>

Further evidence in favor of a band model comes from an investigation of the  $Ti_{2x}V_{2(1-x)}O_3$  system, performed by MacMillan.<sup>42</sup> An extension<sup>48</sup> of the crystalline distortion model to include acceptor levels results in three major conclusions. The transition temperature monotonically decreases with increasing acceptor concentration. When this concentration becomes greater

<sup>46</sup> D. Adler, J. Feinleib, H. Brooks, and W. Paul, Phys. Rev. 155, 851 (1967).

<sup>47</sup> J. B. Goodenough, *Magnetism and the Chemical Bond* (Interscience Publishers, Inc., New York, 1963).

<sup>48</sup> D. Adler, Bull. Am. Phys. Soc. 12, 328 (1967).

than  $\sim 3\%$ , the finite bandwidth leads to holes in the valence band becoming degenerate at low temperatures, thus introducing extra structure into the conductivity-vs-temperature curves. Finally, for acceptor concentrations exceeding  $\sim 15\%$ , the criterion for the spontaneous occurrence of the distortion is no longer satisfied, and the conductivity should remain metallic at all temperatures. All three predictions are confirmed by MacMillan's experiments.<sup>42</sup>

## 2. VO<sub>2</sub>

Above 340°K, VO<sub>2</sub> has a structure which is a minor modification of that of rutile, the V<sup>4+</sup> ions forming a body-centered tetragonal lattice.<sup>49,50</sup> Below 340°K, the symmetry becomes monoclinic, closely resembling the MoO<sub>2</sub> structure.<sup>51</sup> The monoclinic phase is a 8% distortion of the tetragonal structure, in which the *c*-axis cations are collinear and equally spaced, 2.87 Å apart. Below *T*<sub>0</sub>, these cations pair up, becoming somewhat noncollinear and spaced alternately 2.65 and 3.12 Å apart.<sup>52</sup>

As opposed to V<sub>2</sub>O<sub>3</sub>, there is still some question about the order of the transition in VO<sub>2</sub>. Minomura and Nagasaki<sup>29</sup> determined that as the temperature is raised through *T*<sub>0</sub>, the monoclinic *b* axis expands, but both the *c* axis and the *a* axis contract, producing no measurable volume change during the transition. The measured pressure coefficient of *T*<sub>0</sub> was an order of magnitude smaller than that in V<sub>2</sub>O<sub>3</sub>. Neuman *et al.*<sup>53</sup> found a still smaller pressure coefficient in VO<sub>2</sub>. Nevertheless, as indicated by Hyland and Taylor,<sup>54</sup> the transition is most likely of first order. A latent heat of 750 cal/mole was measured by Kawakubo and Nakagawa.<sup>55</sup> Since the pressure coefficient of *T*<sub>0</sub> is so small, the Clausius-Clapeyron equation limits the volume contraction to 0.2% or less. Kawakubo and Nakagawa<sup>55</sup> measured an *increase* in volume at *T*<sub>0</sub> of 0.1%, which violates thermodynamics if the sign of the pressure coefficient is negative, as has been observed.<sup>29,53</sup>

The magnetic properties of VO<sub>2</sub> have been studied by means of susceptibility measurements,<sup>55-58</sup> nuclear magnetic resonance experiments,<sup>59</sup> and Mössbauer

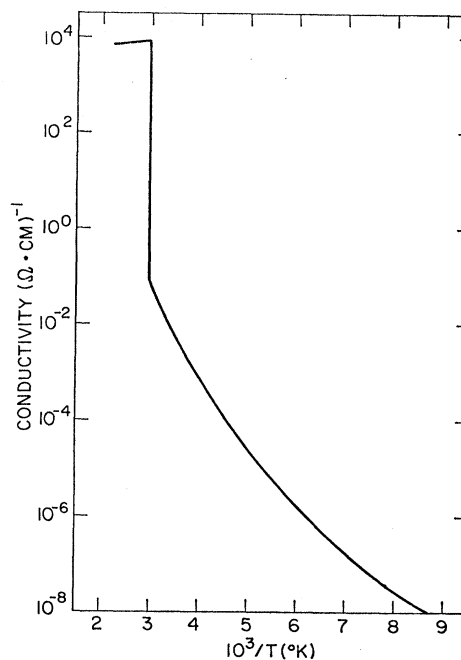


FIG. 4. Conductivity versus temperature for a single crystal of VO<sub>2</sub> (Ladd and Paul<sup>67</sup>).

measurements,<sup>60</sup> and, with rare unanimity, no evidence for any long-range magnetic order has been observed.

Electrical-conductivity experiments<sup>40,53,60-67</sup> show a sharp semiconductor-metal transition at 340°K, with a conductivity discontinuity of a factor of as high as 10<sup>5</sup>.<sup>67</sup> The activation energy in the semiconducting phase increases from the order of 0.15 eV at very low temperatures to the order of 0.5 eV just below *T*<sub>0</sub>. A typical result for conductivity as a function of temperature is shown in Fig. 4.

Hall measurements have been performed by Kitahiro *et al.*,<sup>68</sup> who found a temperature-independent Hall mobility of  $\mu_H = 0.13$  cm<sup>2</sup>/V·sec from 270° to 310°K, then a slight decrease just below *T*<sub>0</sub>. This is strong evidence for a narrow-band model of VO<sub>2</sub>. Kitahiro and Watanabe<sup>69</sup> measured thermoelectric power  $\alpha$  over the same temperature range, and found that  $\alpha$  had the same temperature dependence as the logarithm of the resistivity, also in support of a band model. They

<sup>49</sup> J. Jaffray and A. Dumas, *J. Rech. C.N.R.S.* **27**, 360 (1954).

<sup>50</sup> S. Westman, *Acta Chem. Scand.* **15**, 217 (1961).

<sup>51</sup> G. Andersson, *Acta Chem. Scand.* **10**, 623 (1956).

<sup>52</sup> R. Heckingbottom and J. W. Linnett, *Nature* **194**, 678 (1962).

<sup>53</sup> C. H. Neuman, A. W. Lawson, and R. F. Brown, *J. Chem. Phys.* **41**, 1591 (1964).

<sup>54</sup> G. J. Hyland and A. W. B. Taylor, *J. Phys. Soc. Japan* **21**, 819 (1966).

<sup>55</sup> T. Kawakubo and T. Nakagawa, *J. Phys. Soc. Japan* **19**, 517 (1964).

<sup>56</sup> E. Höschele and W. Klemm, *Z. Anorg. Allgem. Chem.* **242**, 63 (1939).

<sup>57</sup> W. G. Rudorff, G. Walter, and J. Stadler, *Z. Anorg. Allgem. Chem.* **297**, 1 (1958).

<sup>58</sup> K. Kosuge, T. Takada, and S. Kachi, *J. Phys. Soc. Japan* **18**, 318 (1963).

<sup>59</sup> J. Umeda, H. Kusumoto, K. Narita, and E. Yamada, *J. Chem. Phys.* **42**, 1458 (1965).

<sup>60</sup> K. Kosuge, *J. Phys. Soc. Japan* **22**, 551 (1967).

<sup>61</sup> H. Sasaki and A. Watanabe, *J. Phys. Soc. Japan* **19**, 1748 (1964).

<sup>62</sup> P. F. Bongers, *Solid State Commun.* **3**, 275 (1965).

<sup>63</sup> I. Kitahiro, A. Watanabe, and H. Sasaki, *J. Phys. Soc. Japan* **21**, 196 (1966).

<sup>64</sup> T. Ohashi and A. Watanabe, *J. Am. Ceram. Soc.* **49**, 519 (1966).

<sup>65</sup> H. Takei and S. Koide, *J. Phys. Soc. Japan* **21**, 1010 (1966).

<sup>66</sup> S. Koide and H. Takei, *J. Phys. Soc. Japan* **22**, 946 (1967).

<sup>67</sup> L. Ladd and W. Paul (to be published).

<sup>68</sup> I. Kitahiro, T. Ohashi, and A. Watanabe, *J. Phys. Soc. Japan* **21**, 2422 (1966).

<sup>69</sup> I. Kitahiro and A. Watanabe, *J. Phys. Soc. Japan* **21**, 2423 (1966).

determined an effective mass of  $30m_0$ , and a drift mobility approximately equal to the Hall mobility.

Optical measurements have been made by Ladd and Paul<sup>67</sup> and by Barker *et al.*<sup>70,71</sup> In the semiconducting phase only, an absorption edge occurs at approximately 0.8 eV, a value which can be taken as the energy gap.

All the experimental results on VO<sub>2</sub> are entirely consistent with the idea of a low-temperature crystal-line distortion opening up a gap and producing a semi-conducting state below  $T_0$ .

The crystalline-distortion model can be applied to VO<sub>2</sub> without the added complication of antiferromagnetic order. The more pronounced distortion in VO<sub>2</sub> as compared with V<sub>2</sub>O<sub>3</sub> can be expected to lead to a larger energy gap, which is in accordance with observation. In turn, this larger gap should result in a higher transition temperature, provided the bandwidths do not differ by a large factor, and this is also found experimentally. The crystalline-distortion model predicts a jump in carrier concentration at  $T_0$  by a factor of  $4 \times 10^5$ , very close to the largest conductivity discontinuity measured.<sup>67</sup> The observed gap is consistent with the activation energies found in the range 200°–340° K. The activation energy of  $\sim 0.15$  eV at very low temperatures is probably due to a donor level, since semiconduction is *n* type in VO<sub>2</sub>.<sup>70</sup>

Ladd and Paul<sup>67</sup> measured the temperature dependence of the gap and found a decrease from 0.77 eV at 100°K to 0.63 eV just below  $T_0$ . This is quantitatively in agreement with the narrow band limit of the crystalline-distortion model, which predicts a 20% decrease of  $E_g$  from its value at  $T=0$  to its value at  $T_0$ .<sup>2</sup> This decrease in gap will lead to an increase in apparent activation energy from  $\sim 0.4$  to  $\sim 0.5$  eV in the range 300°–340°K, as is observed.<sup>53,60,61</sup>

Goodenough<sup>47,72</sup> has extended his model of direct cation–cation bonding to account for the electrical properties of VO<sub>2</sub>. The monoclinic structure of VO<sub>2</sub> is closely related to the distorted rutile structures found in MoO<sub>2</sub>, WO<sub>2</sub>, and ReO<sub>2</sub>, and Magnéli and Andersson<sup>73</sup> proposed that homopolar bonding between cation pairs could lead directly to such lattice deformations. Goodenough noted that the trapping of one electron per cation in homopolar bonds would be sufficient to bring about insulating VO<sub>2</sub>, which has only one 3*d* electron per V<sup>4+</sup> ion. Above the transition temperature, these bonds break up, and VO<sub>2</sub> will become metallic.

Hyland<sup>74</sup> has proposed essentially the same model, although in order to account for the bandlike semi-

conduction below  $T_0$ , he postulated the existence of an antibonding conduction *band* above localized homopolar bonding *levels*. This approach invokes a recent model due to Fröhlich,<sup>75</sup> in which the Mott transition is treated qualitatively from the point of view of localized multiparticle states splitting off from a band continuum. This model, if investigated quantitatively, should not differ from that of Hubbard<sup>18,20</sup> in the localized or atomic limit where the neglect of interatomic correlations is not serious. Hubbard found that the lower and upper quasiparticle bands were essentially the same width for the case of a ground-state insulator, a result which implies that the assumption of Hyland<sup>74</sup> is inconsistent. Another piece of evidence against this model, which was assumed to hold for V<sub>2</sub>O<sub>3</sub> as well as VO<sub>2</sub>, is that it predicts only *n*-type semiconduction, whereas V<sub>2</sub>O<sub>3</sub> commonly exhibits *p*-type behavior.<sup>42</sup>

### 3. VO

At room temperature, VO has the NaCl structure,<sup>76</sup> and is stable over a composition range from VO<sub>0.80</sub> to VO<sub>1.30</sub>.<sup>77</sup> Stoichiometric samples are highly defective, with about 16% of both cation and anion sites vacant.<sup>78</sup> It has been concluded from an analysis of the infrared spectra that VO consists of alternating regions of composition V<sub>2</sub>O<sub>3</sub> and pure vanadium.<sup>79</sup>

The low-temperature structure is not yet understood. It was initially suggested that VO breaks down below a given temperature to form a mixture of two phases, a body-centered tetragonal structure of approximate composition V<sub>3</sub>O, and a higher oxide, approximately V<sub>3</sub>O<sub>4</sub>.<sup>80</sup> Such a V<sub>3</sub>O<sub>4</sub> phase has been reported to be a body-centered cubic structure<sup>81</sup> or a body-centered tetragonal phase with a *c/a* ratio close to unity.<sup>82</sup> There has also been a report that this phase does not exist.<sup>83</sup>

Electrical conductivity of VO was measured by Morin,<sup>40</sup> who found that the material was semiconducting at low temperatures, with an activation energy of 0.14 eV. At  $T_0=126^\circ\text{K}$ , the conductivity jumped by a factor of  $10^6$ , and above  $T_0$ , the behavior was metallic. Austin<sup>41</sup> studied a sample of approximate composition VO<sub>0.9</sub>, and also found a semiconductor–metal transition

<sup>75</sup> H. Fröhlich, *Quantum Theory of Atoms, Molecules and the Solid State*, P.-O. Löwdin, Ed. (Academic Press Inc., New York, 1966), p. 465.

<sup>76</sup> N. Schonberg, *Acta Chem. Scand.* **8**, 221 (1954).

<sup>77</sup> G. Andersson, *Acta Chem. Scand.* **8**, 1599 (1954).

<sup>78</sup> C. H. Mathewson, E. Spire, and C. H. Samans, *Trans. Am. Soc. Steel Treating* **20**, 357 (1932).

<sup>79</sup> S. M. Ariya and M. V. Golomolozina, *Fiz. Tverd. Tela* **4**, 2921 (1962).

<sup>80</sup> W. Klemm and L. Grimm, *Z. Anorg. Allgem. Chem.* **250**, 42 (1940).

<sup>81</sup> M. A. Gurevich and B. F. Ormont, *Zh. Neorgan. Khim.* **2**, 2581 (1957).

<sup>82</sup> S. Westman and C. Nordmark, *Acta Chem. Scand.* **14**, 465 (1960).

<sup>83</sup> P. V. Geld, S. I. Alyamovskii, and I. I. Matveenko, *Zh. Struct. Khim.* **2**, 301 (1961).

<sup>70</sup> A. S. Barker, H. W. Verleur, and H. J. Guggenheim, *Phys. Rev. Letters* **17**, 1286 (1966).

<sup>71</sup> See also the papers by H. W. Verleur, A. S. Barker, and C. N. Berglund, *Rev. Mod. Phys.* **40**, 737 (1968), this issue; and by R. J. Powell, C. N. Berglund, and W. E. Spicer *ibid.* **40**, 737 (1968), this issue.

<sup>72</sup> J. B. Goodenough, *Bull. Soc. Chim. France* **4**, 1200 (1965).

<sup>73</sup> A. Magnéli and G. Andersson, *Acta Chem. Scand.* **9**, 1378 (1955).

<sup>74</sup> G. J. Hyland, *J. Phys. C. (Proc. Phys. Soc.)* **1**, 189 (1968).

at  $T_0$  with a discontinuity in conductivity of a factor or  $10^6$ . Austin also measured the pressure coefficient of  $T_0$  to be  $d \ln T_0/dP \approx -32 \times 10^{-6} \text{ bar}^{-1}$ , very close to that in  $\text{V}_2\text{O}_3$ .<sup>45</sup>

Kawano *et al.*<sup>84</sup> measured conductivity of samples of VO of several compositions over a temperature range of  $100^\circ\text{--}250^\circ\text{K}$ , and found no transition. The conductivity of nearly stoichiometric VO was  $10^8 \Omega^{-1} \cdot \text{cm}^{-1}$  at  $100^\circ\text{K}$  and rose slowly with temperature. A positive temperature coefficient for nonstoichiometric metals is quite common,<sup>15</sup> and with this large a conductivity, there is no reason to doubt that VO was metallic throughout the temperature range. It is possible that the transition temperature was lowered to below  $100^\circ\text{K}$  because of the presence of random impurities, an effect predicted by the crystalline-distortion model.<sup>48</sup>

Any doubt as to the presence of a semiconductor-metal transition seems to have been dispelled by the recent work of Warren *et al.*,<sup>85</sup> who observed a conductivity discontinuity of greater than a factor of  $10^4$  in the vicinity of  $125^\circ\text{K}$ . They also obtained evidence from magnetic susceptibility, nuclear magnetic resonance, and Knight shift experiments for the presence of antiferromagnetism at low temperatures.

At this point the most striking feature about VO is its resemblance to  $\text{V}_2\text{O}_3$  in both electrical and magnetic behavior. Until the low-temperature structure is clarified, application of any model, even qualitatively, would be a speculation. The presence of a typical NaCl-type antiferromagnetism in VO would precisely split the sixfold-degenerate  $t_{2g}$  band into two threefold-degenerate subbands. Since VO has three  $3d$  electrons per cation, this would explain its semiconducting behavior below the Néel temperature. The antiferromagnetism model would then predict a semiconductor-metal transition at  $T_N$ . In view of the similarity of the electrical properties of VO and  $\text{V}_2\text{O}_3$  and the large conductivity discontinuity, it is reasonable to expect a low-temperature distortion accompanying the magnetic ordering. This distortion should be a rhombohedral pairing of alternate (111) planes. Applying the crystalline distortion model as was done above for  $\text{V}_2\text{O}_3$ , we can predict an energy gap of approximately 0.3 eV for semiconducting VO.

At least two other explanations of the present data on VO are possible. One is that VO is actually metallic at all temperatures, but below a critical  $T_0$ , depending on composition and purity, it decomposes into the two phases suggested by Klemm and Grimm.<sup>80</sup> After decomposition, the material would exhibit very high resistivity, due to phase boundaries. Alternatively, it is possible that nominal samples of VO contain regions of  $\text{V}_2\text{O}_3$  in filamentary form. An analogous phenomenon

has been shown to occur in certain superconductors.<sup>86</sup> In this case, the large number of independent observations of a semiconductor-metal transition at a specific temperature significantly different from the  $T_0$  in  $\text{V}_2\text{O}_3$  makes this possibility rather unlikely. However, VO could decompose into  $\text{V}_2\text{O}_3$  containing a large, but fixed vanadium excess. It is in accordance with the crystalline distortion model for  $\text{V}_2\text{O}_3$  that impurities and lattice defects lower  $T_0$ , and a consistent reduction is not unreasonable. This possibility can be eliminated by an x-ray determination of the structure of a particular crystal for which the transition has been observed.

#### 4. $\text{V}_6\text{O}_{13}$

At room temperature,  $\text{V}_6\text{O}_{13}$  has monoclinic symmetry, with two molecules per unit cell.<sup>87</sup> No low-temperature structure has been reported. Electrical measurements have been performed by Kanazawa,<sup>88</sup> who found a first-order semiconductor-metal transition at  $149^\circ\text{K}$ , with a jump in conductivity of a factor of  $4 \times 10^4$ . The activation energy for semiconduction decreased from 0.12 eV just below  $T_0$  to values as low as 0.044 eV at very low temperatures. The crystalline-distortion model predicts a discontinuity in conductivity of a factor of  $10^4$  and an energy gap of 0.15 eV in the semiconducting region.<sup>89</sup> Preliminary optical reflectivity measurements indicated a peak in this vicinity.<sup>89</sup>

Although these results are good evidence, a low-temperature distortion must be found before this model has any theoretical foundation. However, the fact that a metallic region exists in such a low-symmetry material is significant in itself. The crystalline-distortion model predicts that metallic, narrow-band materials will deform at low temperatures, and thus lower their ground-state total energy, and this appears to be the most reasonable explanation for the electrical behavior of  $\text{V}_6\text{O}_{13}$ .

$\text{V}_6\text{O}_{13}$ , even more so than VO, resembles  $\text{V}_2\text{O}_3$  in its electrical properties. But if  $\text{V}_6\text{O}_{13}$  were unstable, we should expect it would decompose into  $\text{VO}_2$  rather than  $\text{V}_2\text{O}_3$ , and its transition temperature is less than half of that of  $\text{VO}_2$ . This is evidence that the transitions in both  $\text{V}_6\text{O}_{13}$  and VO are intrinsic properties of the materials themselves, and not of  $\text{V}_2\text{O}_3$ . Kanazawa<sup>89</sup> found from x-ray measurements that the sample which exhibited the semiconductor-metal transition was indeed  $\text{V}_6\text{O}_{13}$  and not a two-phase material containing  $\text{V}_2\text{O}_3$ .

#### 5. Other Vanadium Oxides

For the V-O system, there exists a large number of phases between  $\text{V}_2\text{O}_3$  and  $\text{VO}_2$ , of the form  $\text{V}_n\text{O}_{2n-1}$

<sup>84</sup> S. Kawano, K. Kosuge, and S. Kachi, *J. Phys. Soc. Japan* **21**, 2744 (1966).

<sup>85</sup> W. W. Warren, Jr., G. A. Miranda, and W. G. Clark, *Bull. Am. Phys. Soc.* **12**, 1117 (1967).

<sup>86</sup> E. Maxwell and M. Strongin, *Phys. Rev. Letters* **10**, 212 (1963).

<sup>87</sup> F. Aebi, *Helv. Chim. Acta* **31**, 8 (1948).

<sup>88</sup> K. K. Kanazawa, *Bull. Am. Phys. Soc.* **12**, 1120 (1967).

<sup>89</sup> K. K. Kanazawa (private communication).

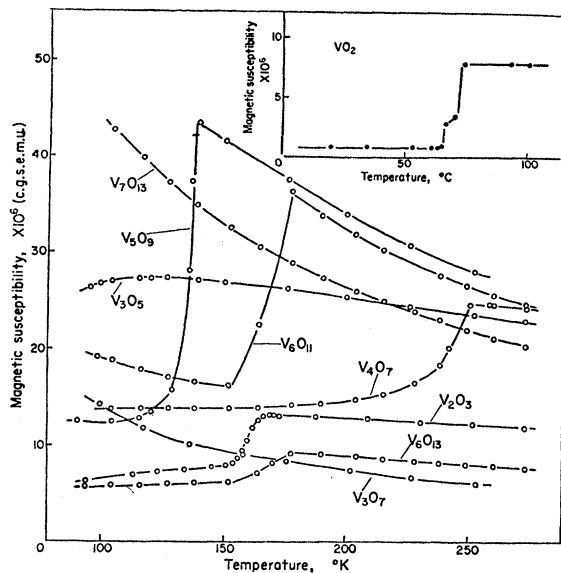


FIG. 5. Magnetic susceptibility versus temperature for several vanadium oxides (Kosuge<sup>93</sup>).

( $n=3, 4, 5, \dots$ ).<sup>90</sup> These phases, known as Magnéli phases, are obtained from the high-temperatures (rutile) form of  $\text{VO}_2$  when periodic stacking faults introduce extra planes of vanadium ions every  $n$  planes in a given crystalline direction.<sup>91</sup>

$\text{V}_3\text{O}_5$  is monoclinic at room temperature, with four molecules per unit cell.<sup>92</sup> Magnetic-susceptibility measurements have been performed by Kosuge,<sup>93</sup> who found that  $\chi$  was essentially independent of temperature from 50° to 300°K. No anomaly was noted, although previous work had shown a jump in  $\chi$  at 235°K.<sup>58</sup> Electrical conductivity was measured by Takei and Koide<sup>66</sup> on single crystals of  $\text{V}_3\text{O}_5$ . Below 150°K, the material was semiconducting, with an activation energy of 0.14 eV. From 150°–180°K, conductivity increased by a factor of  $10^3$ , and the behavior was metallic at higher temperatures. Kachi *et al.*<sup>94</sup> studied polycrystalline  $\text{V}_3\text{O}_5$  from 190° to 270°K and found only semiconducting behavior, with no evidence for a transition. At present, it is impossible to reach a conclusion on  $\text{V}_3\text{O}_5$ .

Kosuge<sup>93</sup> also studied the other Magnéli phases of the V–O system, and found magnetic-susceptibility discontinuities, similar to those of  $\text{VO}_2$  and  $\text{V}_2\text{O}_3$ , at 250°K in  $\text{V}_4\text{O}_7$ , 139°K in  $\text{V}_5\text{O}_9$ , and 177°K in  $\text{V}_6\text{O}_{11}$ . His results are shown in Fig. 5. Mössbauer results<sup>95</sup> on  $\text{V}_4\text{O}_7$  and  $\text{V}_5\text{O}_9$  indicate both are paramagnetic at all temperatures. Electrical measurements<sup>94</sup> on poly-

crystalline  $\text{V}_4\text{O}_7$  showed a sharp increase in conductivity of a factor of  $10^2$  at approximately 130°K. Above this temperature conductivity increased slowly with temperature, a behavior, as we have already noted, characteristic of some impure metallic oxides. On the same sample, a discontinuity in magnetic susceptibility appeared at the same temperature as the conductivity jump. Polycrystalline  $\text{V}_5\text{O}_9$  and  $\text{V}_6\text{O}_{11}$  appeared to be semiconducting at all temperatures. From our past experience with the more well-known vanadium oxides, it appears likely that at least  $\text{V}_4\text{O}_7$  exhibits a semiconductor–metal transition.

## 6. $\text{Ti}_2\text{O}_3$

$\text{Ti}_2\text{O}_3$  has the corundum structure at all temperatures.<sup>96</sup> The only region of unusual behavior is the range 450°–600°K, where the thermal expansion parameters sharply increase.<sup>96</sup> In this region, a specific heat anomaly has been observed.<sup>97</sup> The measured change in specific heat is 36 cal/mole.<sup>98</sup>

The important question of long-range magnetic order in  $\text{Ti}_2\text{O}_3$  has still not been definitely resolved. Magnetic susceptibility, independent of temperature up to 400°K, increases by a factor of a between 450° and 550°K, and then rises slowly at higher temperatures.<sup>30,31,96,99</sup> Neutron-diffraction experiments have been performed three times with conflicting results. Shirane *et al.*<sup>100</sup> found no evidence for antiferromagnetism, and set an upper limit of  $0.5 \mu_B$  per  $\text{Ti}^{3+}$  ion for the antiferromagnetic moment. Abrahams<sup>101</sup> concluded that  $\text{Ti}_2\text{O}_3$  was indeed antiferromagnetic with a small moment of  $0.2 \mu_B$  per  $\text{Ti}^{3+}$  ion and with the  $\text{Fe}_2\text{O}_3$ -type spin alignment. He determined that magnetization decreased slowly with temperature, vanishing at a Néel temperature of 660°K. More recently, Kendrick *et al.*<sup>94</sup> found no evidence for antiferromagnetism, and set an upper limit of  $0.01 \mu_B$  for the moment of an  $\text{Fe}_2\text{O}_3$ -type spin ordering. They suggested that multiple Bragg scattering, which they found to be significant, led to spurious superlattice reflections in the experiments of Abrahams. However, Abrahams rotated his crystal to check for multiple Bragg scattering, and found only small changes in the intensity of the superlattice reflections.<sup>102</sup> Furthermore, the temperature variation of sublattice magnetization obtained by Abrahams was characteristic of a weak antiferromagnet rather than of double Bragg scattering, and it also correlated quantitatively with the resistivity data taken

<sup>95</sup> M. E. Straumanis and T. Ejima, *Acta Cryst.* **15**, 404 (1962).

<sup>96</sup> A. D. Pearson, *J. Phys. Chem. Solids* **5**, 316 (1958).

<sup>97</sup> B. F. Naylor, *J. Am. Chem. Soc.* **68**, 1077 (1946).

<sup>98</sup> S. Nomura, T. Kawakubo, and T. Yanagi, *J. Phys. Soc. Japan* **16**, 706 (1961).

<sup>99</sup> L. K. Keys and L. N. Mulay, *Appl. Phys. Letters* **9**, 248 (1966).

<sup>100</sup> G. Shirane, S. J. Pickart, and R. Newnham, *J. Phys. Chem. Solids* **13**, 167 (1960).

<sup>101</sup> S. C. Abrahams, *Phys. Rev.* **130**, 2230 (1963).

<sup>102</sup> S. C. Abrahams (private communication).

<sup>90</sup> J. Stringer, *J. Less Common Metals* **8**, 1 (1965).

<sup>91</sup> A. Magnéli, *Acta Cryst.* **6**, 495 (1953).

<sup>92</sup> S. Åsbrink, S. Friberg, A. Magnéli, and G. Andersson, *Acta Chem. Scand.* **13**, 603 (1959).

<sup>93</sup> K. Kosuge, *J. Phys. Chem. Solids* **28**, 1613 (1967).

<sup>94</sup> S. Kachi, T. Takada, and K. Kosuge, *J. Phys. Soc. Japan* **18**, 1839 (1963).

on the same crystal.<sup>16</sup> The cause for the discrepancy in the properties of the  $\text{Ti}_2\text{O}_3$  crystals used in these two investigations is still a mystery.

Van Zandt *et al.*<sup>26</sup> measured magnetoresistance of vanadium-doped samples of  $\text{Ti}_2\text{O}_3$ , and found that the best fit to their data was when the magnetoresistance was due to random magnetic trace impurities and the internal magnetic field was essentially just the applied field. This was taken as evidence for the absence of any long-range magnetic order. Two other surprising features of these experiments were that semiconduction was *p* type, despite the vanadium doping which should strongly favor *n*-type conduction, and that the mobility, presumably of the lowest 3*d* band of the  $\text{Ti}^{3+}$  ions, was extremely large, of the order of  $1000 \text{ cm}^2/\text{V}\cdot\text{sec}$  at 4°K. Also, the ascribing of the magnetoresistance to random impurities, rather than to the large amounts of vanadium introduced, seems strange.

No Mössbauer or nuclear magnetic resonance data has been reported on  $\text{Ti}_2\text{O}_3$ . The results of these types of experiments indicated the presence of the magnetic order which is now believed to exist in  $\text{V}_2\text{O}_3$ . The weight of recent evidence is against antiferromagnetism in  $\text{Ti}_2\text{O}_3$ . However, it is clear that any long-range magnetic order is weak, and may easily be destroyed by small impurity concentrations or moderate external fields.

The electrical properties are better understood. Morin<sup>40</sup> found that below 450°K, conductivity was of the order of  $1\text{--}10 \Omega^{-1}\cdot\text{cm}^{-1}$ , and increased with temperature with an activation energy of 0.04 eV. In the vicinity of 450°K, there was an increase in conductivity by a factor of 10, and at higher temperatures, the behavior was metallic. Pearson<sup>96</sup> obtained similar results, although the increase was more gradual, and no metallic region was reached by 650°K. Yahia and Frederikse<sup>103</sup> observed a metallic transition at 450°K, the conductivity jumping by a factor of 40. They measured an activation energy in the semiconducting region of 0.03 eV. Abrahams<sup>101</sup> also obtained a conductivity increase of a factor of 40 and an activation energy of 0.03 eV, but the transition temperature was approximately 660°K, the same temperature as he determined for  $T_N$ . Abrahams' results are shown in Fig. 6.

Yahia and Frederikse<sup>103</sup> measured the Hall effect of  $\text{Ti}_2\text{O}_3$ , and found the same temperature dependence for  $R_H$  as for resistivity, indicating an approximately temperature-independent Hall mobility. At temperatures above 200°K, the Hall mobility decreased with increasing temperature, and it appeared that optical phonon scattering predominated. In this range, thermoelectric power had the temperature dependence of the logarithm of the resistivity, indicating the drift mobility also was essentially independent of temperature.

<sup>103</sup> J. Yahia and H. P. R. Frederikse, *Phys. Rev.* **123**, 1257 (1961).

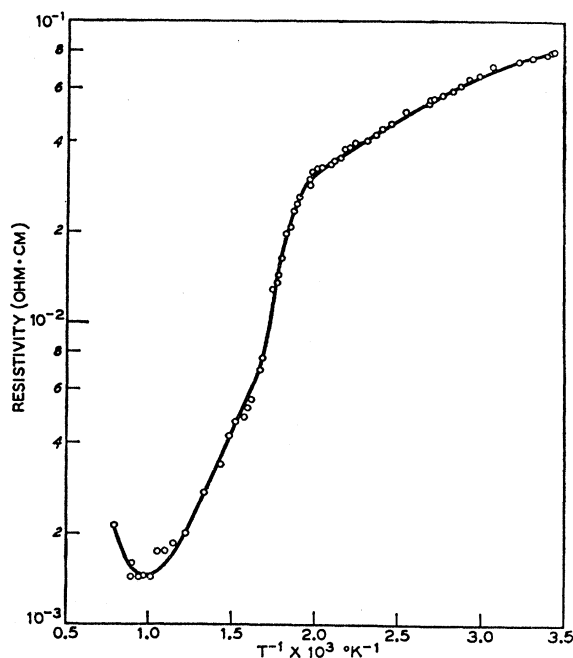


FIG. 6. Conductivity versus temperature for a single crystal of  $\text{Ti}_2\text{O}_3$  (Abrahams<sup>101</sup>).

Choosing an effective mass of  $5m_0$ , the Hall and drift mobilities were the same, of the order of  $5 \text{ cm}^2/\text{V}\cdot\text{sec}$ . Thermoelectric power had a maximum at 130°K, indicating partial compensation occurred at low temperatures. All of these results point to  $\text{Ti}_2\text{O}_3$  being a relatively wide-band semiconductor, with an energy gap of 0.06 eV.

The antiferromagnetism model has been applied explicitly to  $\text{Ti}_2\text{O}_3$ ,<sup>16</sup> assuming Abraham's magnetic data<sup>101</sup> were correct. The sublattice magnetization, the drift mobility, and the activation energy were the only parameters necessary to calculate both magnetization and conductivity as functions of the temperature, and good agreement was obtained with experiment. The effective mass was calculated to be  $4m_0$ , in agreement with the result of Yahia and Frederikse.<sup>103</sup> The transition obtained is first order in this model, which predicts a small latent heat of the order of magnitude of that found from specific-heat experiments.<sup>98</sup> However, this predicts a sharper conductivity increase at  $T_0$  than has been observed. Furthermore, the model clearly breaks down if the gap in  $\text{Ti}_2\text{O}_3$  is not due to antiferromagnetism.

Kleiner<sup>3</sup> has shown that antiferromagnetism is not necessary for obtaining semiconducting  $\text{Ti}_2\text{O}_3$ . The presence of *c*-axis pairs in the corundum structure, together with a strong trigonal component of the crystalline field is sufficient to produce a filled valence band with only one 3*d* electron per cation. Van Zandt *et al.*<sup>26</sup> attributed the semiconductor-metal transition in  $\text{Ti}_2\text{O}_3$  to ordinary band overlap. They presented a

four-parameter calculation which led to a perfect fit with the resistivity data of Abrahams.<sup>101</sup>

The band-overlap model has a great deal of appeal in the case of  $Ti_2O_3$ . There is no crystalline distortion, and perhaps no antiferromagnetism. The valence and conduction bands have all the characteristics of relatively wide bands, despite their  $3d$  nature, so correlation effects do not figure to play a dominant role in creating or stabilizing the energy gap. Thus the band-overlap model may be the only one we have left. Furthermore,  $Ti_2O_3$  has just the characteristics where we should expect band overlap to be a possibility. The energy gap is very small, and one of the corundum axes, the  $a$  axis, has a negative thermal expansion, indicating a widening conduction band. Van Zandt *et al.*,<sup>26</sup> however, had to assume that the conduction bandwidth increased by more than a factor of 2 over a temperature range where the  $a$  axis is contracting only 0.4%,<sup>104,96</sup> a lattice-constant variation less than that of many semiconductors whose bands show no great temperature dependence. A less dramatic bandwidth increase would lead to a conductivity increase of less than that observed. This brings up another possibility. It is not unreasonable that the low-temperature phase of  $Ti_2O_3$  has a negative rather than a positive gap, and that conductivity is inhibited below the transition by the formation of an excitonic insulator state.<sup>9</sup> This would account for the high conductivity (for a semiconductor) in this phase. The transition would then represent an excitonic insulator-semimetal transition, which is qualitatively consistent with the conductivity data.

Another feature of  $Ti_2O_3$  is that, when vanadium is added in relatively small amounts, a sharp increase in the  $c$  axis occurs.<sup>105</sup> The addition of only 2% vanadium leads to a  $c$ -axis expansion of almost 1%, and at 10% vanadium, the  $c$  axis has increased to essentially its pure  $V_2O_3$  value. This is in sharp contrast with the slow  $c$ -axis variation as titanium is introduced into  $V_2O_3$ .<sup>42</sup> Entirely consistent with this, a 2% addition of vanadium to  $Ti_2O_3$  is sufficient to turn the material into a metal at all temperatures.<sup>105</sup> We can conclude that a relatively small impurity concentration can sharply reduce the transition temperature in  $Ti_2O_3$ , even to zero, as 2% vanadium does. It is thus not surprising to find a variation in  $T_0$  for nominally pure  $Ti_2O_3$  from 425° to 660°K. There have also been reports of anomalies in the vicinity of 150°–250°K.<sup>106,107</sup>

## 7. Other Titanium Oxides

As was true for the V–O system, the Ti–O system includes Magnéli phases of the form  $Ti_nO_{2n-1}$  ( $n=3, 4,$

<sup>104</sup> R. E. Newnham and Y. M. de Haan, Quart. Progr. Rept. No. 26, Lab. Insulation Res. M.I.T., 1960, p. 10 (unpublished).

<sup>105</sup> T. Kawakubo, T. Yanagi, and S. Nomura, J. Phys. Soc. Japan 15, 2102 (1960).

<sup>106</sup> S. F. Adler and P. W. Selwood, J. Am. Chem. Soc. 76, 346 (1965).

<sup>107</sup> B. I. Al'shin and D. N. Astrov, Sov. Phys.—JETP 17, 809 (1963).

5, ...).<sup>108,109</sup> At low temperatures  $Ti_3O_5$  has monoclinic symmetry, but near 400°K it transforms to a slightly distorted pseudobrookite (orthorhombic) structure.<sup>110</sup> The magnetic susceptibility has been measured by Keys and Mulay,<sup>99,111</sup> who found a temperature-independent value below 460°K, a sharp jump by a factor of 6 at 460°K, and a temperature-independent value thereafter. The resemblance to the results for  $VO_2$  is striking, and this together with the results of an electron paramagnetic resonance study have been taken as evidence for a first-order semiconductor-metal transition in  $Ti_3O_5$ .<sup>112</sup> The susceptibility results of Keys and Mulay<sup>111</sup> for  $Ti_2O_3$  and the Magnéli phases of the Ti–O system are shown in Fig. 7. The Magnéli phases other than  $Ti_3O_5$  exhibit susceptibility maxima near 130°K. An electron paramagnetic resonance study of Keys<sup>113</sup> has indicated that  $Ti_5O_9$  may undergo a semiconductor-metal transition at this temperature.

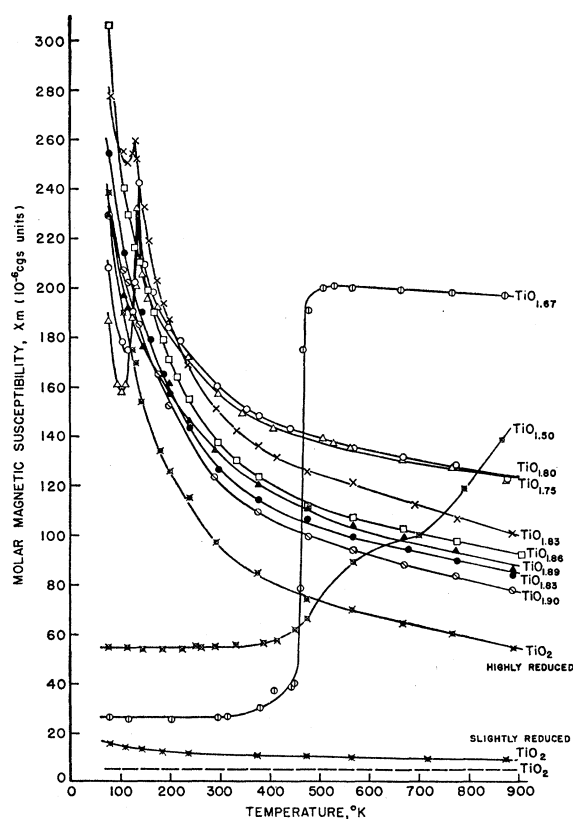


FIG. 7. Magnetic susceptibility versus temperature for several titanium oxides (Keys and Mulay<sup>111</sup>).

<sup>108</sup> B. Marinder and A. Magnéli, Acta Chem. Scand. 11, 1635 (1957).

<sup>109</sup> S. Andersson and A. Magnéli, Naturwiss, 43, 495 (1956).

<sup>110</sup> S. Åsbrink and A. Magnéli, Acta Chem. Scand. 12, 575 (1959).

<sup>111</sup> L. K. Keys and L. N. Mulay, Phys. Rev. 154, 453 (1967).

<sup>112</sup> L. K. Keys, Phys. Letters 24A, 628 (1967).

<sup>113</sup> L. K. Keys, J. Appl. Phys. 39, 598 (1968).



## 8. NbO<sub>2</sub>

NbO<sub>2</sub> is a tetragonal crystal with a distorted rutile structure consisting of 32 molecules per unit cell.<sup>114</sup> Electrical properties have been studied by Janninck and Whitmore,<sup>115</sup> who found that below 1000°K, NbO<sub>2</sub> was semiconducting with a room-temperature conductivity of the order of  $10^{-4} \Omega^{-1}\cdot\text{cm}^{-1}$ , and an activation energy of approximately 0.25 eV. At about 1070°K, the conductivity jumped by a factor of about 10 to  $6 \times 10^2 \Omega^{-1}\cdot\text{cm}^{-1}$ , and above this temperature was independent of  $T$ . The transition was the same for the two samples investigated, although one was NbO<sub>2.003</sub>, containing the maximum possible oxygen, while the other was NbO<sub>1.997</sub>, containing the minimum possible oxygen. Conductivity vs temperature for the former specimen is shown in Fig. 8.

Thermoelectric power was also measured on both samples, and the material was  $n$  type, even with excess oxygen. The thermoelectric power below 1070°K, had the same temperature dependence as the resistivity, implying normal band semiconduction. Above 1070°K, the thermoelectric power was small ( $\sim 70 \mu\text{V}/^\circ\text{K}$ ) and independent of temperature, characteristic of a metallic phase.

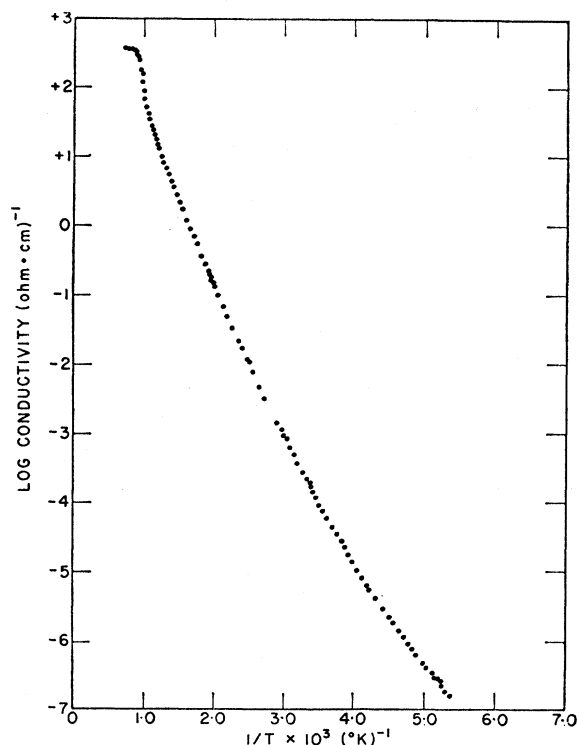


FIG. 8. Conductivity versus temperature for a nonstoichiometric NbO<sub>2</sub> sample of maximum oxygen content (Janninck and Whitmore<sup>115</sup>).

<sup>114</sup> A. Magnéli, G. Andersson, and G. Sundkvist, *Acta Chem. Scand.* **9**, 1402 (1955).

<sup>115</sup> R. F. Janninck and D. H. Whitmore, *J. Phys. Chem. Solids* **27**, 1183 (1966).

No magnetic data have been reported. However, the transition could be explained simply by means of the crystalline distortion model if it were found that a phase transformation occurs at 1070°K to a higher-symmetry structure (e.g., rutile). Stoichiometric NbO<sub>2</sub> may well exhibit a larger conductivity jump, just as the discontinuity in VO<sub>2</sub> increased from a factor of  $10^2$  to one of  $10^5$  as better crystals were obtained. The properties of the isoelectronic materials NbO<sub>2</sub> and VO<sub>2</sub> might be expected to be similar. Consistent with this idea, the distorted rutile structure in NbO<sub>2</sub> can be looked at as an alternate spacing of Nb<sup>4+</sup> ions along the  $c$  axis of 2.80 and 3.20 Å, as compared to a rutile separation of 3.00 Å.<sup>116</sup> In the distorted VO<sub>2</sub> structure, the V<sup>4+</sup> ions are spaced alternately 2.65 and 3.12 Å apart. The distortion is thus slightly less in NbO<sub>2</sub> than in VO<sub>2</sub>, which should favor a smaller gap. The room-temperature activation energy of NbO<sub>2</sub> indicates a gap of the order of 0.5 eV. The crystalline-distortion model would predict a transition temperature of the order of 1070 °K only if the bands were much wider in NbO<sub>2</sub> than in VO<sub>2</sub>, but this is also what we should expect. If this is the case, the gap must decrease significantly just below  $T_0$ , and this would lead to a *larger* apparent activation energy near  $T_0$ .<sup>117</sup> Such an increase, from 0.25 to 0.60 eV, does occur. The crystalline-distortion model then predicts only a jump of a factor of 10 at  $T_0$ , as is also observed.

It would thus be quite pertinent to investigate the structure of NbO<sub>2</sub> above 1070°K. For NbO<sub>2</sub>, neither the antiferromagnetism nor the band-overlap models can be ruled out, especially considering the gradual nature of the transition.

## 9. Fe<sub>3</sub>O<sub>4</sub>

Fe<sub>3</sub>O<sub>4</sub> has the cubic spinel structure at room temperature. Below 119°K, there is a distortion to orthorhombic symmetry.<sup>118</sup> This deformation is very small, of the order of 0.05%,<sup>119</sup> but is accompanied by a large specific-heat anomaly.<sup>120</sup> At all temperatures, Fe<sub>3</sub>O<sub>4</sub> is an inverse spinel,<sup>121</sup> which means that half of its Fe<sup>3+</sup> ions are on tetrahedral spinel sites and half are on octahedral sites, while all of its Fe<sup>2+</sup> ions are on octahedral sites. Above 119°K, the octahedral Fe<sup>3+</sup> ions and the Fe<sup>2+</sup> ions are randomly distributed, but below the transition temperature they align in mutually perpendicular rows.<sup>122</sup> This low-temperature structure

<sup>116</sup> B.-O. Marinder, *Acta. Chem. Scand.* **15**, 707 (1961).

<sup>117</sup> A smaller gap leads to a larger apparent activation energy since conductivity is increasing with temperature faster than when the gap is constant. See Ref. 15 for a proof.

<sup>118</sup> S. C. Abrahams and B. A. Calhoun, *Acta Cryst.* **6**, 105 (1953).

<sup>119</sup> L. R. Bickford, *Rev. Mod. Phys.* **25**, 75 (1953).

<sup>120</sup> B. S. Ellefson and N. W. Taylor, *J. Chem. Phys.* **2**, 58 (1934).

<sup>121</sup> E. J. W. Verwey, P. W. Haayman, and F. C. Romeijn, *J. Chem. Phys.* **15**, 181 (1947).

<sup>122</sup> W. C. Hamilton, *Phys. Rev.* **110**, 1050 (1958).

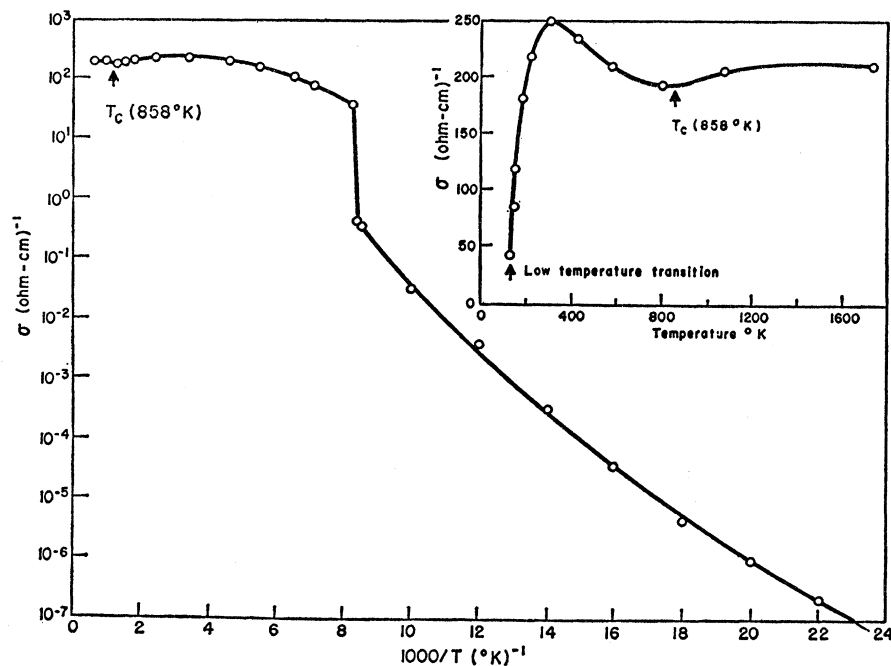


FIG. 9. Conductivity versus temperature for a single crystal of  $\text{Fe}_3\text{O}_4$  (Miles *et al.*<sup>130</sup>).

was first predicted theoretically on the basis of the electrical-conductivity behavior.<sup>123</sup>

The material is a normal ferrimagnet, with a Néel temperature of approximately 850°K.<sup>124</sup> Its magnetic moment is  $4 \mu_B$ , the expected spin-only value.<sup>125</sup> Mössbauer studies have confirmed this model,<sup>126,127</sup> although only two lines appear below 119°K, instead of the expected three. However, this has been explained on the basis that both tetrahedral and octahedral  $\text{Fe}^{3+}$  ions have the same hyperfine field at the nucleus.<sup>128</sup>

Electrical-conductivity measurements have been performed by Calhoun<sup>129</sup> and by Miles *et al.*<sup>130</sup> Both observed semiconduction below 119°K, with a very low-temperature activation energy of the order of 0.03 eV. The activation energy increased to 0.15 eV just below the transition. At 119°K, conductivity sharply jumped by a factor of  $10^2$  to the order of  $10^2 \Omega^{-1} \cdot \text{cm}^{-1}$ , characteristic of some metallic oxides. But as the temperature was raised further, conductivity continued to increase slowly until 250°K. Above this temperature, it remained essentially constant

( $\sigma \sim 250 \Omega^{-1} \cdot \text{cm}^{-1}$ ) through 1700°K. A slight maximum is observed at 350°K, and a minimum near the Néel temperature. This behavior is shown in Fig. 9.

The low-temperature behavior is characteristic of a semiconductor with an energy gap of approximately 0.25 eV, which decreases slightly just below  $T_0$ . The extremely low temperature activation energy is probably related to an impurity level. In a band analysis, the energy gap could arise because of the orthorhombic distortion, which splits all  $t_{2g}$  bands in three. This gap would be stabilized by the ordering of the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions, a further reduction of symmetry.

In such an approach, above 119°K the material should become metallic. The cubic spinel structure has two molecules per primitive cell, resulting in a total of 22  $3d$  electrons per Brillouin zone from the four octahedral sites in the primitive cell. In the absence of long-range magnetic order, these 22 electrons are distributed among four sixfold-degenerate  $t_{2g}$  bands and four fourfold-degenerate  $e_g$  bands. Although we can conceive of an order to the bands which will result in a semiconductor, for example, three  $t_{2g}$  bands as the lowest, followed by one  $e_g$  band, such a situation is unlikely. In the presence of ferrimagnetic ordering, the octahedral sites are aligned mutually parallel. The exchange interaction could then split all of the  $t_{2g}$  and  $e_g$  bands in half, making a semiconducting state somewhat more feasible, but still unlikely. Furthermore, if the magnetic order were responsible for a semiconducting energy gap, we should expect a discontinuity in conductivity at  $T_N$ , which is not observed.

From our discussion of the vanadium oxides, we can

<sup>123</sup> E. J. W. Verwey and P. W. Haayman, *Physica* **8**, 979 (1941).

<sup>124</sup> R. Pauthenet, *Compt. Rend.* **230**, 1842 (1950).

<sup>125</sup> Since  $\text{Fe}_3\text{O}_4$  is an inverse spinel, the contribution from the  $\text{Fe}^{3+}$  ions must vanish, and the net moment is then entirely due to the  $\text{Fe}^{2+}$  ions.

<sup>126</sup> R. Bauminger, S. G. Cohen, A. Marinov, S. Ofer, and E. Segal, *Phys. Rev.* **122**, 1447 (1961).

<sup>127</sup> K. Ono, Y. Ishikawa, A. Ito, and E. Hirahara, *J. Phys. Soc. Japan* **18**, 1465 (1963).

<sup>128</sup> E. Callen, *Phys. Rev.* **150**, 367 (1966).

<sup>129</sup> B. A. Calhoun, *Phys. Rev.* **94**, 1577 (1954).

<sup>130</sup> P. A. Miles, W. B. Westphal, and A. von Hippel, *Rev. Mod. Phys.* **29**, 279 (1957).

conclude that the experimental behavior above 119°K can be considered metallic. If so, the crystalline-distortion model will apply only if a real gap is opened up by an extremely small deformation.

We should not ignore the possibility of a Mott transition in  $\text{Fe}_3\text{O}_4$ .<sup>131</sup> If the distortion and ordering of the cations below 119°K are insufficient to produce a real energy gap, then the low-temperature state must be a Mott insulator. The resulting conductivity jump at 119°K can be explained by the fact that the crystallographic transformation is to a structure where  $\text{Fe}^{3+}$  ions and  $\text{Fe}^{2+}$  ions are on equivalent sites, making a hopping-type conduction very easy. Haubenreisser<sup>132</sup> and Tannhauser<sup>133</sup> have presented polaron models for the conductivity of  $\text{Fe}_3\text{O}_4$ . Haubenreisser attributed the maximum in conductivity to the magnitude of the electron-phonon interaction. With the assumption that sublattice magnetization is independent of temperature, he found that a maximum should appear in the polaron hopping probability at about 600°K, which differs from the observed value by a factor of 2. Tannhauser suggested a thermally activated hopping model to account for the conductivity of  $\text{Fe}_3\text{O}_4$  below 119°K.

#### 10. $\text{Mo}_9\text{O}_{26}$

$\text{Mo}_9\text{O}_{26}$  has two crystalline forms,<sup>134</sup> a triclinic phase with four molecules per unit cell, stable between 800° and 1000°K, and having low conductivity ( $\sigma \sim 4 \times 10^{-3} \Omega^{-1} \cdot \text{cm}^{-1}$ ), and a monoclinic phase with two molecules per unit cell, stable from 1000° to 1100°K, and having a conductivity a factor of  $10^2$  larger. This does not represent a real transition, however, since one phase does not transform into the other under normal conditions. The triclinic form decomposes into  $\text{MoO}_3$  and monoclinic  $\text{Mo}_4\text{O}_{11}$  above 1000°K, whereas the monoclinic form breaks up into  $\text{MoO}_3$  and orthorhombic  $\text{Mo}_4\text{O}_{11}$  above 1100°K. Nevertheless, it is interesting in connection with a discussion of nonmetal-metal transitions that the lower-symmetry, low-conductivity phase can be considered a distortion of the higher-symmetry, high-conductivity phase. This is consistent with the idea behind the crystalline-distortion model.

#### 11. NiS

NiS crystallizes in two forms, a rhombohedral phase (millerite),<sup>135</sup> and a hexagonal phase, with the NiAs structure.<sup>136</sup> The NiAs structure contains two molecules per unit cell, and has a variable  $c/a$  ratio which easily allows for the formation of nonstoichiometric materials,

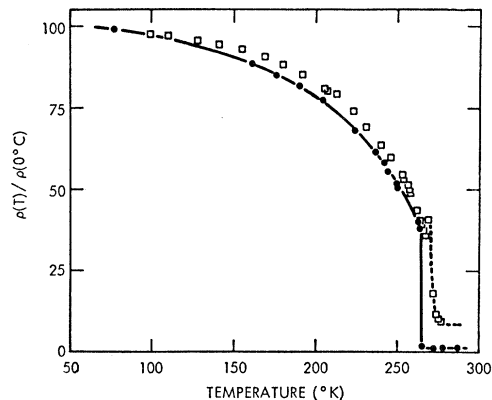


FIG. 10. Relative resistivity versus temperature for a single crystal of NiS (Sparks and Komoto<sup>139</sup>).

particularly with excess sulfur. Sparks and Komoto<sup>137</sup> determined that a first-order phase transformation occurs at 264°K; the  $c$  axis undergoes a 1% contraction while the  $a$  axis contracts 0.3%.

Tsubokawa<sup>138</sup> measured magnetic susceptibility, and found evidence for antiferromagnetism. The presence of antiferromagnetism was confirmed by a neutron-diffraction study of Sparks and Komoto,<sup>137,139</sup> who determined that successive ferromagnetic hexagonal basal planes were mutually antiparallel. The sublattice magnetization was  $1.66 \mu_B$  per cation at 4°K, and dropped very slowly to  $1.50 \mu_B$  at 264°K, at which point it vanished sharply.

Electrical properties have been measured by Sparks and Komoto,<sup>140</sup> who observed a semiconductor-metal transition at the Néel temperature. Below 264°K, conductivity was low and increased exponentially with temperature, with an activation energy of less than 0.01 eV from 77° to 170°K, then slowly increasing to a constant value of 0.12 eV from 242° to 264°K. At 264°K, conductivity abruptly jumped by a factor of 60, and at higher temperatures, resistivity increased linearly with temperature. There was a slight hysteresis between heating and cooling. Resistivity as a function of temperature is shown in Fig. 10.

NiS appears to be the first clearcut example of a nonmetal-metal transition entirely due to an antiferromagnetic transition. There is no crystalline distortion, and the transition is quite sharp rather than gradual. The antiferromagnetism model presented in Sec. III predicts a first-order transition as long as there is some degree of bandwidth. From the activation energy between 242° and 264°K, the exchange-induced gap appears to be 0.24 eV. The very low-temperature activation energy of 0.01 eV is almost definitely a

<sup>131</sup> N. F. Mott, *Advan. Phys.* **16**, 49 (1967).

<sup>132</sup> W. Haubenreisser, *Phys. Status Solidi* **1**, 619 (1961).

<sup>133</sup> D. S. Tannhauser, *Phys. Kondens. Materie* **3**, 146 (1964).

<sup>134</sup> L. Kihlborg, *Acta Chem. Scand.* **13**, 954 (1959).

<sup>135</sup> N. H. Kolkmeijer and A. L. Th. Moesveld, *Z. Krist.* **80**, 91 (1931).

<sup>136</sup> M. Laffitte, *Bull. Soc. Chim. France* **1959**, 1211 (1959).

<sup>137</sup> J. T. Sparks and T. Komoto, *J. Appl. Phys.* **34**, 1191 (1963).

<sup>138</sup> I. Tsubokawa, *J. Phys. Soc. Japan* **13**, 1432 (1958).

<sup>139</sup> J. T. Sparks and T. Komoto (to be published).

<sup>140</sup> J. T. Sparks and T. Komoto, *Phys. Letters* **25A**, 398 (1967).

donor or acceptor level. The transition temperature is somewhat lower than is predicted by the model. However, the model was worked out for constant volume, whereas in NiS there is a 1.7% volume contraction at  $T_N$ . As shown by Bean and Rodbell,<sup>141</sup> a dependence of exchange energy on interatomic spacing leads to a volume contraction and a decrease in transition temperature. This added effect would also account for the fact that the sublattice magnetization was 90% of its saturated value just below  $T_N$ , somewhat larger than the 80% predicted by the antiferromagnetism model alone.

## 12. CrS

At high temperatures CrS has the ordinary NiAs structure, but at low temperatures a monoclinic distortion, which can be looked at as a pairing of cations in the hexagonal basal plane, occurs.<sup>142,143</sup> This monoclinic structure resembles that of  $V_2O_3$ . Electrical properties were measured by Kamigaichi *et al.*,<sup>144</sup> who found that stoichiometric CrS was an extrinsic  $n$ -type semiconductor ( $\sigma \sim 1 \Omega^{-1} \cdot \text{cm}^{-1}$ ) below 200°K. From 200° to 600°K, conductivity increased with temperature with an activation energy increasing to approximately 0.15 eV. Semiconduction became  $p$  type in this region. At approximately 600°K, conductivity sharply increased by a factor of  $10^2$  to a metallic value ( $\sigma \sim 10^3 \Omega^{-1} \cdot \text{cm}^{-1}$ ). For up to 13% excess sulfur, the behavior remained much the same, with just an increase in conductivity in the extrinsic region. For 14%–20% excess sulfur, the material was metallic at all temperatures. However, an x-ray analysis showed that for compositions in this range, the structure was just the NiAs high-symmetry phase at all temperatures.

The conclusion for CrS appears clear. Once again, the low-symmetry form is semiconducting, the high-symmetry form is metallic. We should therefore expect the crystalline-distortion model to be applicable.

## 13. FeS

FeS, like CrS and NiS, crystallizes in two forms. The more common variety has the hexagonal NiAs structure.<sup>145</sup> Recently, a study of the bottom of the Mystic River in Boston has led to the discovery of a tetragonal phase, in which the  $\text{Fe}^{2+}$  ions have a tetrahedral environment.<sup>146</sup> Above 430°K, the tetragonal phase transforms into the hexagonal form with a 13% volume contraction.<sup>147</sup>

<sup>141</sup> C. P. Bean and D. S. Rodbell, *Phys. Rev.* **126**, 104 (1962).

<sup>142</sup> F. Jellinek, *Acta Cryst.* **10**, 620 (1957).

<sup>143</sup> M. Yuzuri, T. Hirone, H. Watanabe, S. Nagasaki, and S. Maeda, *J. Phys. Soc. Japan* **12**, 385 (1957).

<sup>144</sup> T. Kamigaichi, K. Masumoto, and T. Hihara, *J. Phys. Soc. Japan* **15**, 1355 (1960).

<sup>145</sup> E.-F. Bertaut, *Bull. Soc. Franc. Mineral. Crist.* **79**, 276 (1956).

<sup>146</sup> R. Berner, *Science* **137**, 669 (1962).

<sup>147</sup> E. R. Bertaut, P. Bulet, and J. Chappert, *Solid State Commun.* **3**, 335 (1965).

Magnetic properties of the hexagonal phase have been studied often.<sup>148–152</sup> It has been found that the material is antiferromagnetic below 600°K. However, there are two different spin alignments. Below 411°K, the spins are directed along the hexagonal  $c$  axis, but between 411°K and 600°K, they are perpendicular to the  $c$  axis.<sup>151</sup> In both regions, successive ferromagnetic basal planes are aligned mutually antiparallel.<sup>148,152</sup> Tetragonal FeS does not exhibit any long-range magnetic ordering.<sup>147</sup>

Electrical conductivity of single crystals of hexagonal FeS has been measured by Murakami,<sup>153</sup> see Fig. 11. Conductivity perpendicular to the  $c$  axis was metallic at all temperatures ( $\sigma \sim 3 \times 10^3 \Omega^{-1} \cdot \text{cm}^{-1}$ ), as was conductivity parallel to the  $c$  axis above 411°K. On the other hand, conductivity parallel to the  $c$  axis at low temperatures was significantly lower ( $\sigma \sim 4 \Omega^{-1} \cdot \text{cm}^{-1}$ ). Up to 300°K, the behavior was that of an extrinsic  $p$  type<sup>154</sup> semiconductor. From 300° to 411°K, the apparent activation energy sharply increased, and in the vicinity of 411°K,  $c$ -axis conduction jumped by a factor of over  $10^2$ .

The tetragonal phase of FeS is semiconducting at all temperatures below 430°K.<sup>147</sup> Conductivity increases slowly with temperatures from  $0.08 \Omega^{-1} \cdot \text{cm}^{-1}$  at 80°K to  $0.5 \Omega^{-1} \cdot \text{cm}^{-1}$  at 300°K, indicating a very small activation energy. At 430°K, there is a jump in conductivity of more than a factor of  $10^3$  as the tetragonal phase transforms to the hexagonal form.

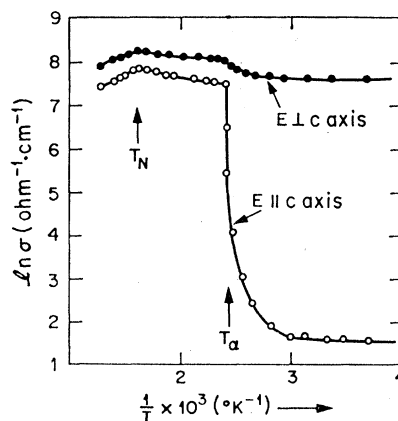


FIG. 11. Conductivity versus temperature for a single crystal of FeS (Murakami<sup>153</sup>).

<sup>148</sup> T. Hihara, M. Murakami, and E. Hirahara, *J. Phys. Soc. Japan* **12**, 743 (1957).

<sup>149</sup> E. Hirahara and M. Murakami, *J. Phys. Chem. Solids* **7**, 281 (1958).

<sup>150</sup> S. S. Sidhu, L. Heaton, and M. H. Mueller, *J. Appl. Phys.* **30**, 1323 (1959).

<sup>151</sup> H. Horita and E. Hirahara, *J. Phys. Soc. Japan* **21**, 1447 (1966).

<sup>152</sup> A. F. Andresen, *Acta Chem. Scand.* **14**, 919 (1960).

<sup>153</sup> M. Murakami, *J. Phys. Soc. Japan* **16**, 187 (1961).

<sup>154</sup> S. Fujime, M. Murakami, and E. Hirahara, *J. Phys. Soc. Japan* **16**, 183 (1961).

The electrical properties of hexagonal FeS are extremely interesting. The high-temperature phase is certainly metallic, even in its antiferromagnetic region. As the temperature is lowered, the crystal can lower its ground-state energy in either of two ways, by a distortion to tetragonal symmetry or by a change of axis of magnetization. The crystalline distortion leads to a completely semiconducting state, but the magnetic realignment produces a highly anisotropic phase with poor conductivity only parallel to the antiferromagnetic axis. It is possible that the large conductivity in the basal planes at low temperatures is not intrinsic, but due to interstitial  $\text{Fe}^{2+}$  ions.<sup>155</sup>

#### 14. VS

VS, like most of the monosulfides, crystallizes with the hexagonal NiAs structure.<sup>156</sup> As opposed to NiS, CrS, and FeS, no other form of VS has yet been found. The material appears to be antiferromagnetic, with a high Néel temperature, of the order of 1000°K.<sup>157</sup> There is a specific heat anomaly in the vicinity of 900°K,<sup>157</sup> and a resistivity anomaly near 1000°K.<sup>158</sup> No complete investigation of the electrical properties has been reported, but in view of the findings in the other monosulfides, the possibility of a semiconductor-metal transition exists.

### V. CONCLUSIONS

We have investigated the nonmetal-metal transitions which occur in a large number of transition-metal oxides and sulfides. For many of these, the experimental data are far from complete, but we try to group them into classes depending on what appears to be the most likely mechanism for the transition, *at the present time*.

(1) The band-overlap model now seems to be the most probable cause of the transition in only one material,  $\text{Ti}_2\text{O}_3$ .

(2) The crystalline distortion model is the most likely one for  $\text{VO}_2$ ,  $\text{NbO}_2$ ,  $\text{Mo}_9\text{O}_{26}$ , CrS, and tetragonal FeS. If the nonmetal-metal transitions are real, it may, in addition, be the explanation for  $\text{Ti}_3\text{O}_5$ ,  $\text{V}_3\text{O}_5$ , and  $\text{V}_4\text{O}_7$ .

(3) The antiferromagnetism model appears to definitely apply to NiS. A modification may be appropriate for hexagonal FeS. If transitions are found in  $\text{Ti}_5\text{O}_9$  or VS, this model is the most probable. If  $\text{Ti}_2\text{O}_3$  is eventually found to be antiferromagnetic, then the band-overlap interpretation will have to be replaced or modified.

(4) A combination of the crystalline-distortion and antiferromagnetism models is the most likely explanation of the very sharp transitions found in  $\text{V}_2\text{O}_3$  and VO. This is also a possibility for  $\text{V}_6\text{O}_{13}$ , because of the striking resemblance of its electrical properties to the other two in this group.

(5) A Mott transition appears to be the most probable mechanism for only one material,  $\text{Fe}_3\text{O}_4$ .

These conclusions are in accord with the remarks made when the various models were presented. Band-overlap and Mott transitions as functions of temperature should be quite rare, and indeed it was necessary to resort to them for only one material each. However, if neither crystalline distortions nor antiferromagnetism is found in some of the other materials, the number of band-overlap transitions and Mott transitions will grow.

Also, as we expected, the crystalline-distortion model appears to be applicable to a large number of the oxides and sulfides. In those cases where sufficient data have been obtained, quantitative agreement is found. This is gratifying because the distortion mechanism provides an explanation for the frequent occurrence of nonmetal-metal transitions in narrow-band materials. The model shows that a narrow-band, metallic crystal can lower its ground-state energy by distorting, and that a distortion which favors an insulating ground state will result in the lowest energy at  $T=0$ . As the temperature is then raised, the energy gaps introduced by the lowering of symmetry will decrease, and a metallic transition will occur at a critical  $T_0$ , at which point the distortion spontaneously disappears and metallic conductivity occurs.

We can conclude from this that nonmetal-metal transitions should be common phenomena not only in the oxides and sulfides, but in other narrow-band materials, such as the transition-metal selenides, fluorides, chlorides, bromides, and iodides. Electrical properties of these materials have not as yet been studied, but, for example, magnetic-susceptibility and x-ray data on  $\text{TiCl}_3$ <sup>159</sup> are quite analogous to a number of the materials discussed above.

To conclude, all this suggests a simple classification of all the transition-metal oxides and sulfides. Let us consider the materials which should be metallic according to an ordinary band calculation. Since the  $d$  band is so highly degenerate, this probably includes most of the compounds. We can then group the materials by bandwidth. Those with relatively wide  $d$  bands are good metals. Those with extremely narrow  $d$  bands become Mott insulators, and have very low conductivities. Finally, materials with intermediate bandwidths reduce their ground-state energies by undergoing a crystalline-distortion or antiferromagnetic ordering at low tem-

<sup>155</sup> J. B. Goodenough, *J. Appl. Phys.* **33**, 1197 (1962).

<sup>156</sup> W. Biltz and A. Koehler, *Z. Anorg. Allgem. Chem.* **241**, 324 (1939).

<sup>157</sup> I. Tsubokawa, *J. Phys. Soc. Japan* **14**, 196 (1959).

<sup>158</sup> T. Suzuoka (unpublished), quoted in Ref. 157.

<sup>159</sup> S. Ogawa, *J. Phys. Soc. Japan* **15**, 1901 (1960).

peratures, thus producing semiconducting behavior. As the temperature is raised, the energy gap must vanish at a given  $T_0$ , resulting in a semiconductor-metal transition. Put in these terms, it is not too surprising that the populations of all three classes are roughly the same.

#### ACKNOWLEDGMENTS

I have benefited from many conversations with Julius Feinleib. I should also like to thank William W. Warren, Joseph T. Sparks, Kay Kanazawa, Lawrence Ladd, and William Paul for sending me their data prior to publication.

#### Discussion of Adler's Paper

D. S. LIEBERMAN (University of Illinois): Two comments and one question. The first concerns the order of the transitions. In those cases which involve *discontinuous* changes in crystalline symmetry and/or crystalline distortions there is a relatively clear case of a discontinuity in at least one derivative of the free energy and hence a *first-order* phase transformation. In some of these cases, as in  $\text{BaTiO}_3$ , the volume change may be  $\sim 0$ , but the transformation is first order nonetheless.<sup>1</sup> However, there may be other extensive parameters which must be included in the total expression of the Gibbs free energy, such as  $\mathbf{M}$ , the magnetization  $\mathbf{P}$ , the electrical polarization, etc. It is possible that although all of the lattice constants (and hence the volume) are continuous going through the transformation, some other parameter may exhibit a discontinuity and hence the transformation will, in reality, be *first order*. Hence, unless *all* of the parameters are measured during the transformation, it may be interpreted and reported as second order. Further, application of specific intensive quantities, (fields) may alter the nature and order of the transformation, as in superconductivity. There is a phenomenological crystallographic theory of first-order phase transformations which relates the two crystal lattices, describes the habit plane separating the two phases during transformation, and explains the macroscopic shape deformation accompanying such transitions. This Wechsler-Lieberman-Read (W-L-R) theory<sup>2,3</sup>—or the equivalent Bowles-Mackenzie (B-M) formulation<sup>4</sup>—has been applied with remarkable accuracy to transformations in such systems as iron base alloys,<sup>2,5,6</sup>  $\text{AuCd}$ ,<sup>3,7</sup>  $\text{InTl}$ ,<sup>8</sup> and semiconducting KTN and  $\text{BaTiO}_3$ .<sup>9</sup> During this type of transformation, there is usually a decrease of crystalline symmetry on cooling, hysteresis is often exhibited, atoms move less than an interatomic distance and the degree of order possessed by the parent phase generally persists in the product; frequently there is the onset of (or change in) some important physical, mechanical, electrical, etc., property such as ferromagnetism in iron base alloys, ferroelectricity in the titanates, ferroelasticity in  $\text{AuCd}$ , etc. Surprisingly, it has been successfully applied to the order-disorder transformation in  $\text{AuCu}$ <sup>10</sup> and the formation of tantalum oxide.<sup>11</sup> The W-L-R theory has also been shown to be useful in providing information and insight into the nature and most probable mechanism in specific situations even when complete experimental data are not available. Thus the quite different twin plane exhibited by NiMn when it transforms from the CsCl parent to the twinned antiferromagnetic fct phase, in the one case on slow cooling<sup>12</sup> and in the other when rapidly quenched,<sup>13</sup> can apparently be explained by this theory<sup>14</sup>; why insulating KTN and  $\text{BaTiO}_3$  show different habit planes than when they are semiconducting is also understandable.<sup>15</sup> It is therefore suggested that this theory may be useful in understanding the semiconductor-metal transition, particularly those

involving a crystalline symmetry change. Incidentally, the MnNi case mentioned above where the transformation can be quite different depending on the thermal history and, in other cases too numerous to mention here, where the transformation behavior varies dramatically with purity, composition, departures from stoichiometry, handling, thermal treatment, etc., emphasizes the care that must be taken in specimen preparation and in comparing the results of different experiments which are ostensibly on samples of the same nominal composition—unless one is merely content to describe and characterize a specific specimen with a given unique history and treatment, and not a material. My question concerns cause and effect. Hyland<sup>16</sup> in the abstract of his paper “On the Electronic Phase Transitions in the Lower Oxides of Vanadium” says that “the population of the  $d$ -band increases catastrophically leading to a first-order phase transition into the metallic state” while Hanamura<sup>17</sup> in the abstract of his paper of the “Phonon Instability and Metal-Semiconductor Transition of Vanadium Dioxide and Vanadium Sesquioxide” says, in apparently referring to the same experimental work, “the lattice distortion induces the change of electronic states in  $\text{VO}_2$  and  $\text{V}_2\text{O}_3$ ,” thus inverting Hyland’s implied cause and effect. Again, in iron base alloys, the distorted product martensite is ferromagnetic and in  $\text{BaTiO}_3$ , the tetragonal product is ferroelectric. Can one determine the dominant driving force or cause of the transformation?

D. ADLER: Such questions can be chicken-or-egg problems.

D. S. LIEBERMAN: What I’m suggesting is that there may be something happening in another parameter equivalent to the softening of a vibrational mode corresponding to  $(\epsilon_{11}-\epsilon_{12})$  in bcc metals. This quantity becomes abnormally low indicating an incipient tendency toward instability well above the transformation temperature as first pointed out by Zener<sup>18</sup> and most recently by several groups<sup>19-22</sup> in  $\text{V}_3\text{Si}$  in which this mode goes very soft beginning well above the cubic to tetragonal transformation which just precedes the onset of superconductivity. Is there a “softening” or “modification” in any other extensive parameter which anticipates the transformation which is first order in (at least) that parameter on cooling? Incidentally, this type of behavior as well as the fact that the phases exhibit *decreasing* symmetry with *decreasing* temperature (such as cubic to tetragonal to orthorhombic in the titanates and in uranium alloys, for example) suggests that it may be more fruitful to first focus attention on transformations on cooling rather than on heating, as physicists frequently do.

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D. ADLER: It's clearly true in the case of a pairing type of distortion that gaps in the phonon spectrum are opening up along the new faces of the reduced first Brillouin zone. Since I'm attributing the cause of the transition to electronic effects, I don't believe there will be a softening of a phonon mode in these materials. The paper by Hanamura deals with the introduction of the electron-phonon interaction into the Adler-Brooks model. In answer to your first question, these are first-order transitions because there is a discontinuity in the temperature derivative of the Helmholtz free energy at  $T_0$ . This comes about because the free energies of the metallic and semiconducting states as functions of the temperature cross at  $T_0$ . It's not necessary to have a volume change at the transition.

W. KOHN (University of California, San Diego): I would like to just make a small remark about this chicken-or-egg question. There *are* cases where one can tell the difference between the chicken and the egg. For example, there are situations possible, although whether or not they have been clearly experimentally demonstrated is open to question, where if you would hold down with many pairs of tweezers all the nuclei, the electronic structure would nevertheless distort itself. And then if you let the nuclei go of course, then they will also be distorted. In that case, it is the electronic structure that's the cause. There are other cases where the electronic structure distorts itself only when you also allow the nuclei to move. Then I think you cannot tell the difference. In the first case you can incidentally also tell it experimentally because in the first case you do not have a phonon going soft and so you can just check the behavior of the phonon frequencies and you will not find a phonon going to zero frequency.

D. ADLER: The chicken-or-egg question I was referring to was whether the crystalline distortion was a magnetostriction due to the magnetic order, or whether the antiferromagnetism was a result of the ionic pairing. In these transition-metal oxides, I believe that the distortions and the antiferromagnetism are both caused by electronic effects, and that the material would go antiferromagnetic if the ion cores were held down by tweezers or would distort even if the spins were held in a random orientation by tweezers.

N. F. MOTT (Cambridge University): I agree with everything that Dr. Adler said in his excellent review except for the following three points. The first is about  $\text{Fe}_3\text{O}_4$ ; I think the electrical behavior of this material is best described as a kind of Wigner crystallization, because there are twice as many sites as electrons and at low temperatures the electrons crystallize among these sites. The second point is that I think the bandwidths in the absence of polaron formation are perhaps wider than he says, of the order of 0.3 eV; in many materials such as NiO or  $\text{V}_2\text{O}_5$  the bandwidth may be greatly narrowed by interaction with optical phonons (polaron formation). Thirdly, and most important, I think one has to look very carefully at the nature of what Dr. Adler calls the "metallic phase" in the intermediate materials. I am of course quite convinced that some transition metal oxides are really metallic, for example TiO. Here the

bandwidth is so great that they are on the metallic side of the Mott transition. But Adler and his colleagues in their *Physical Review* publications assume very large effective masses (50m) and a corresponding narrow bandwidth in, at any rate, some of the vanadium oxides, and they have to do this to obtain enough entropy to cause the transition and structure change. I think that under these conditions the metallic phase really consists of a nondegenerate gas of small polarons, not necessarily hopping, but moving by the band mechanism of Holstein. Barker and others [*Phys. Rev. Letters* **17**, 1286 (1966)] find evidence that in  $\text{VO}_2$  the number of carriers is only about 10% of the number of atoms and Hill working at the Electrical Research Association in London on the magnetic properties comes tentatively to a similar conclusion. I think that the polaron hypothesis accounts also for the rather low mobility and the big effect of crystal boundaries.

D. ADLER: With regard to the first point, for the purposes of this review I have been considering a Wigner crystallization as a type of Mott transition, that is a low density insulating state brought about by electronic correlation. As for the bandwidth of NiO, I certainly agree that the value of 0.3 eV is possible. As long as the intra-atomic Coulomb integral  $U$  is larger than this for NiO, the material will be a Mott insulator. The vanadium oxides can be metallic with even the same bandwidth, provided  $U$  is considerably smaller. Finally, in answer to your question on the nature of the high temperature phase, this can be answered only by experiment. In support of a metallic state, the resistivity increases linearly with temperature, and the Hall mobility and thermoelectric power of  $\text{VO}_2$  are consistent with one carrier per vanadium ion. When both of these occur, I would call the phase metallic, despite the low mobility. The mobilities measured both below and above the transition have been increasing as purer materials have been prepared. Yaha and Frederikse measured Hall mobilities in  $\text{Ti}_2\text{O}_3$  as of the order of  $1 \text{ cm}^2/\text{V}\cdot\text{sec}$  in 1961, but in a later paper today Honig will report mobilities for the same material of the order of  $10^3 \text{ cm}^2/\text{V}\cdot\text{sec}$ . I believe that within a few years the measured mobilities of all of the transition-metal oxides will approach those found by Honig on  $\text{Ti}_2\text{O}_3$ . If so, this will remove the doubt that the high temperature phases of the vanadium oxides are metallic.

R. M. MOON (Oak Ridge National Lab.): I'd like to comment on the issue of antiferromagnetism in  $\text{Ti}_2\text{O}_3$ . If you recall the work of Sidney Abrahams and Kendrick, Arrott, and Werner both saw the same set of neutron diffraction peaks. Abrahams thought these peaks arose from magnetic scattering; the other group argued that this was not magnetic scattering but a double reflection process involving two nuclear scattering processes similar to the Renninger effect, or Umwegangregung. So the issue here is whether these peaks were due to nuclear scattering or magnetic scattering. We have recently been exploring the possibilities in neutron diffraction techniques in which the beam is initially polarized. We then analyze the spin states of the scattered beam. We can measure the distribution of spins in the scattered beam. It turns out that if you set up the experiment properly, nuclear scattering will be nonspin-flip scattering; magnetic scattering will be spin-flip scattering. So this seemed like a very nice application. We got the same crystal that Abrahams used, or part of the same crystal, and we see absolutely no evidence for any coherent magnetic scattering. The conclusion is that, as far as neutron diffraction is concerned, up to now there is no evidence for antiferromagnetism in  $\text{Ti}_2\text{O}_3$ .

G. J. HYLAND (University of Liverpool): Dr. Adler's suggestion that the semiconductor→metal phase transition in  $\text{VO}_2$  occurs as a result of a band splitting is very neat. However, the wave functions he uses in the construction of the (unsplit) metallic band are highly anisotropic, and, unless one incorporates the oxygen ions it will be difficult to explain the approximate isotropy found in the magnetic susceptibility and electrical conductivity



of  $\text{VO}_2$  single crystals. Further, his metallic band (considering now only the V ions) is orbitally nondegenerate and, therefore, cannot support a Kubo temperature-independent paramagnetism; an experimental investigation of the NMR frequency shift as a function of the observed magnetic susceptibility would, no doubt, be of interest in this connection [E. D. Jones, *Phys. Rev.* **137**, A978 (1965)].

D. ADLER: A band anisotropy is not necessarily reflected by a conductivity anisotropy. In fact, quite the reverse often occurs. The conductivity is determined by the scattering process which dominates the mobility. In these materials, it is a reasonable assumption that impurity or defect scattering is predominant, and these types of scattering have a relatively weak dependence on the effective masses. It's likely that the effective masses of the valence and conduction bands in semiconducting  $\text{VO}_2$  are somewhat anisotropic, but this is extremely difficult to estimate without a detailed band calculation. But remember, even in cubic crystals nonspherical bands can lead to extremely anisotropic effective mass tensors, but the conductivity averages over this anisotropy, since it must be isotropic. In the metallic phase of  $\text{VO}_2$ , of course, this model predicts little or no anisotropy. The main point is that this is a band model. It's the localized models which will have great difficulties in accounting for the isotropy. In the metallic region at least two of the six  $t_{2g}$  bands are partially filled, and Kubo paramagnetism can indeed exist.

J. FEINLEIB (M.I.T. Lincoln Lab.): I think we have to consider that the  $d$  bands we are talking about are not caused by direct  $d$ - $d$  interaction of  $d$  cations. We have  $d$  electrons surrounded by oxygen anions and this is a very hybridized state. The  $d$  electrons can move around through the oxygen subband and we cannot really say anything about the anisotropy if we use this picture of highly hybridized  $d$  electrons in the oxygen sublattice. In fact, we should recognize this fact when we are

talking about Mott transitions for example. In these oxides, we are not dealing with a hydrogenlike set of atomic states where we can vary the interatomic distance. This is not an important parameter in these oxides. That's why nickel oxide, for example, has about the same interatomic distance as say a vanadium oxide but nickel oxide is an insulator and vanadium oxide is not. These properties certainly must have a lot to do with the effect of the oxygen on the  $d$  electrons.

W. PAUL (Harvard University): Along the same lines one may note that  $\text{V}_2\text{O}_3$  and all of these materials have their insulating state at low temperatures, where the separation of the atoms is smaller than it is in the high temperature metallic state.

J. B. GOODENOUGH (M.I.T.): I will restrict myself to two short comments which are related to the present discussion. First on the  $\text{VO}_2$  problem, there are really two bands that you have to worry about. One is formed from the orbitals which are directed along the  $c$  axis and the other from orbitals that  $\pi$  bond with the oxygen. In the high-temperature phase these bands appear to overlap so that you get metallic conductivity via the orbitals that  $\pi$  bond with the oxygen as well as via those that overlap directly. I have discussed this elsewhere [Bull. Soc. Chim. France **4**, 1200 (1965)]. I would also like to make a comment on iron sulfide,  $\text{FeS}$ . Six years ago this was discussed by K. Adachi [*J. Phys. Soc. Japan* **16**, 2187 (1961)] and by myself [*J. Appl. Phys. Suppl.* **33**, 1197 (1962)]. In iron sulfide there is a crystallographic transition from close packing to triangular clusters within the basal planes. Therefore you can treat this transition in the same way as you have discussed for  $\text{VO}_2$ . [See my papers in *Colloques Internationaux du C.N.R.S. No. 157*, "Colloque International sur des Derives Semimetalliques," Univ. of Paris 1965 (Editions du C.N.R.S. 1967) and *Czech. J. Phys.* **317**, 304 (1967).]