J. M. Honig

Localized and Itinerant Electrons in Oxides*

Abstract: Recent work concerning the electrical properties of ReO$_3$, PrO$_x$, ($1.5 \leq x \leq 2.0$), TiO$_2$, SrTiO$_3$, perovskites, CrO$_2$, NiO, Li$_x$Zn$_{1-x}$V$_2$O$_4$, V$_2$O$_3$, and Ti$_2$O$_3$ has been selectively reviewed in attempts to elucidate the conduction properties of the charge carriers. A number of controversial issues are pointed out: Frequently it is not known whether mobilities are activated or not, nor whether a given material should be classified as a polaronic or mixed-carrier material; neither is there agreement on the nature of electrical transitions. Discrepancies in electrical properties can generally be traced to insufficient control over preparation and characterization of samples.

1. Introduction

This very selective, cursory survey pertaining to localized and itinerant electrons in oxides is intended to highlight recent developments and to spotlight current controversies. With such a limited goal much relevant material had to be omitted; the large body of excluded research is no less meritorious than the work described in this summary. As is typical for a rapidly expanding field, many experimental results have a rather short lifetime; both the theoretical interpretation and the evaluations are thus continually in need of updating.

The rather arbitrary classification scheme offered below was constructed primarily as a convenience to the author, several attempts to provide a nonintersecting set of categories having proved fruitless.

2. Metallic oxides: ReO$_3$

Because of its simple structure, derived from the perovskite lattice, ReO$_3$ serves as an excellent prototype compound illustrating the properties of oxides with metallic characteristics. One of its striking features, which has repeatedly been noted,[33,35,54] is the rather low resistivity ρ, which increases with temperature. A comparison of ρ for several ReO$_3$ specimens with that of Cu is shown in Fig. 1. The material is further characterized by a very small negative Seebeck coefficient,[35] by an optical reflectance spectrum that can be interpreted in terms of a plasma edge and interband transitions,[33] by de Haas-van Alphen oscillatory phenomena,[61] and by magnetothermal oscillations.[47]

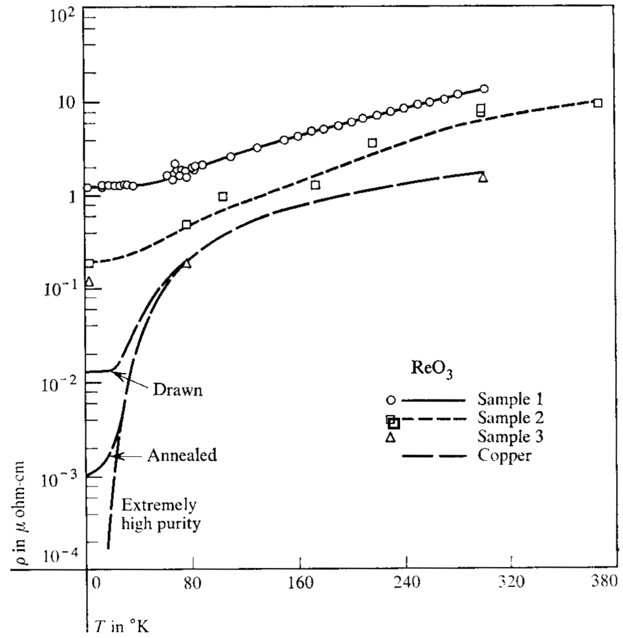

Figure 1 Resistivity vs temperature for several ReO$_{3\pm\delta}$ single crystal samples (data by J. M. Honig and A. J. Strauss, Ref. 54). Heavy solid lines represent corresponding curves for copper metal.

Goodenough[43] explained the metallic characteristics qualitatively by proposing a one-electron band structure scheme based on overlap of the various Re 5d, 6s and 6p orbitals with the various O 2s and 2p orbitals as dictated by the crystal symmetry. The scheme is depicted in Fig. 2, which shows on the left and on the right the atomic levels of Re and of O. Intercombinations permitted by group theory would normally lead to levels characteristic of ReO$_6$ clusters, but because of the large orbital overlap extending throughout the entire crystal, one obtains instead the band scheme depicted in the center of the

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The author is located at the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907.

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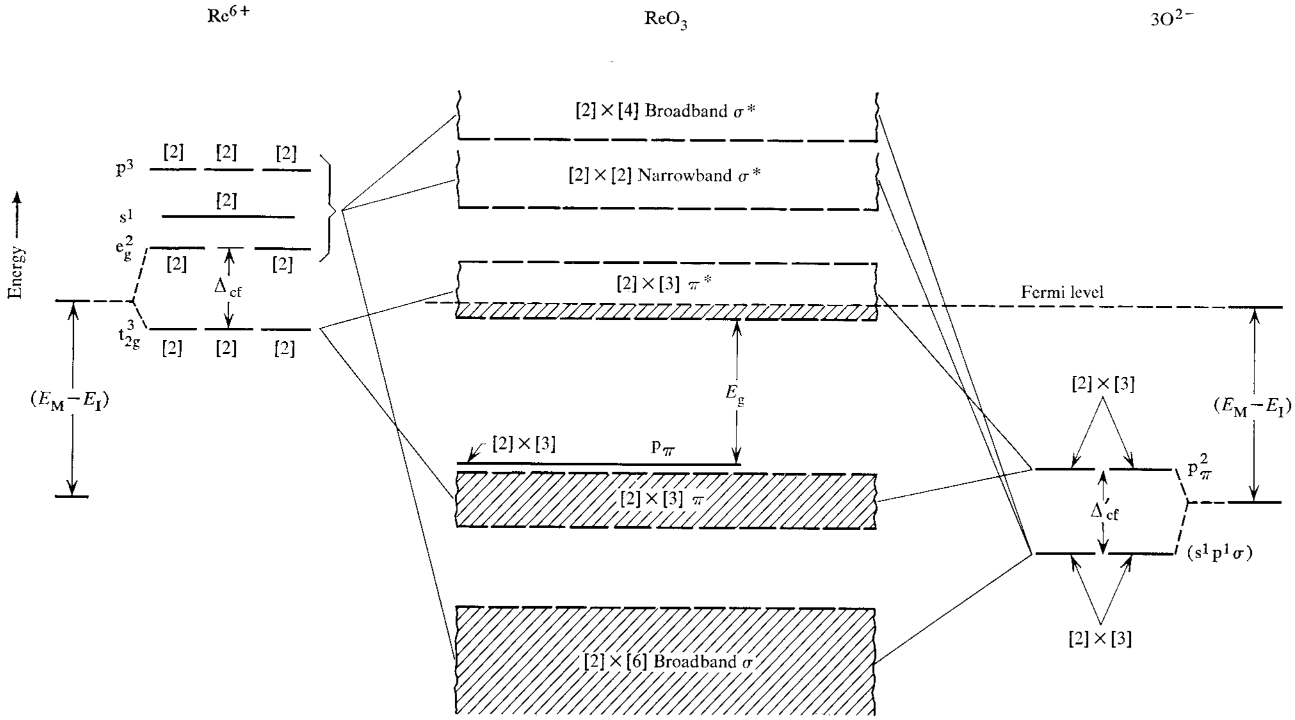


Figure 2 Elementary band structure scheme for ReO$_3$ (after J. B. Goodenough, Ref. 43).

diagram. In this extension of the molecular cluster approach, Goodenough was led to postulate the existence of wide σ-type "bonding" and "antibonding" bands, separated by a very large gap, within which is located a set of narrow π-type "bonding" and "antibonding" bands, separated by a small gap, which in turn contains a set of nonbonding O levels. When the 25 valence electrons per ReO$_3$ formula unit are accommodated, all bands and levels are filled up to the π* antibonding band, which is one-sixth full. The presence of the Fermi level within a band immediately rationalizes the observed metallic characteristics.

The above scheme has received support from an analytical study by Honig, Dimmock and Kleiner[52] based on the tight-binding approximation scheme. In the lowest order approximation, which involves a number of severe though not unphysical assumptions, the Goodenough band scheme is found to hold throughout the entire Brillouin zone. However, in a less restrictive approximation the neat separation of bands into σ, π and nonbonding types cannot be maintained; the interactions become scrambled and, in particular, the nonbonding levels broaden into a band. Extensive numerical calculations showing this effect have recently been completed by Mattheiss;[63] he combined the APW method with the tight-binding interpolation procedure of Slater and Koster,[84] and readjusted several parameters by fitting the calculations to selected experimental results. His band scheme corresponding to 5d-and 2p-type atomic wave functions is depicted in Fig. 3. It is seen that the Fermi surface intersects the $\Gamma_{25'}$ band, which is approximately 4 eV in total width and which is just barely overlapped by the much wider Γ_{12} band. Spin-orbit splitting, characterized by a coupling constant $\xi = 0.30$ eV, acts further to lift the degeneracy of the d-like bands. The intersection of the Fermi sufrace with these split bands produces three sheets: two closed electron-like sets of surfaces, and one which is open along the $\langle 100 \rangle$ directions in reciprocal space. The electron cyclotron masses in these sheets span the range $0.5 \leq m^*/m \leq 1$ and are anisotropic. The various oscillatory effects[47,61] are reproduced very well by Mattheiss's analysis.

In summary, because of considerable overlap between cationic and anionic wave functions, ReO$_3$ has the electrical characteristics of an ordinary metal. Among other oxides with metallic characteristics may be listed TiO, NbO and RuO$_2$. An APW calculation by Ern and Switendick[29] for TiO also exhibits a complex band structure, with the Fermi level intersecting several d-like bands of total width 7.5 eV. VO is a rather interesting case: Contrary to widespread assertions based on earlier measurements,[66,11] it now appears that VO$_x$ ($0.75 \leq x \leq 1.32$) does not suffer a semiconductor-metal transition,[10,59,87] but that it exhibits metallic characteristics over at least a part of this composition range.[15,56] Undoubtedly the bands in VO are quite narrow; extended

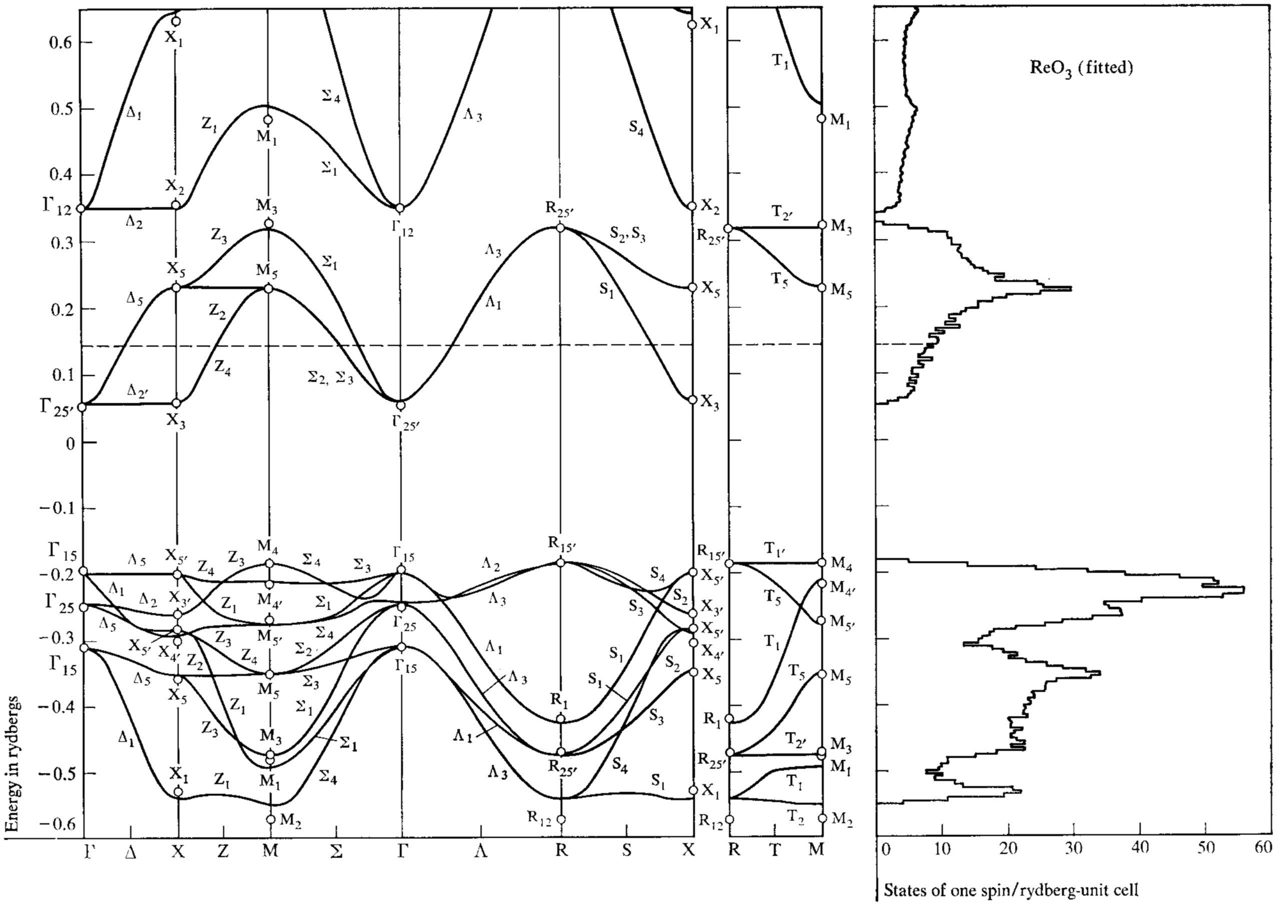


Figure 3 APW calculation for band structure and density-of-states curves of ReO_3. To get agreement with experiment the bandgap must be reduced to about 0.5 Ry (after L. F. Mattheiss, Ref. 63).

studies may later show up incipient electron correlation and/or polaron effects in this material. In RuO_2 the resistivity[62] is 2×10^{-9} ohm-cm at 1.1°K, but this oxide has a very large positive temperature coefficient of resistivity, so that at 300°K ρ has reached a value of 4×10^{-5} ohm-cm.

3. Oxides characterized by thermally activated mobilities: PrO_x

On the other end of the resistivity scale are oxides whose charge carriers are propelled via an activated hopping process. This occurs wherever overlap between wave functions on different atoms is so small that band formation is suppressed. In contrast to polaron materials, to be discussed later, there is no temperature range in which band-like properties of the charge carriers are observed; mobilities fall in the 10^{-4} to 10^{-8} cm^2/V-sec range. PrO_x $(1.5 \leq x \leq 2.0)$ with incomplete 4f shells is a prototype member of this class. In very naive terms, conduction in nonstoichiometric praseodymia occurs because trivalent Pr^{III} and quadrivalent Pr^{IV} are both present, thus permitting electron exchange through an activated transfer.

The electrical properties of PrO_x as a function of stoichiometry[51] are depicted in Fig. 4. These agree with predictions based on a diffusion model for electrical conductivity (σ) and Seebeck coefficient (α). According to very rudimentary theories[50] these transport coefficients are given by

$$\sigma = (C_0 e^2 \nu_0 / akT) c(c - 1) e^{-\Delta G/kT}$$

and

$$\alpha = -(k/e)\{\ln [(1 - c)/c] + S_t/k\},$$

where C_0 is a numerical factor, ν_0 an attempt frequency for electron transfer, a the lattice parameter, c the fraction of cations associated with an extra electron, ΔG the free energy of activation for electron transfer and S_t the thermal entropy associated with the hopping motion of electron transfer; the remaining symbols have their conventional significance. According to the above, at fixed temperature the maximum conductivity should occur for $c = 1/2$, i.e., in the middle of the stoichiometry range ($x = 1.75$), as is roughly confirmed experimentally. Also, α should vary as $\ln [(1 - c)/c]$ + const.; reference to Fig. 4 shows

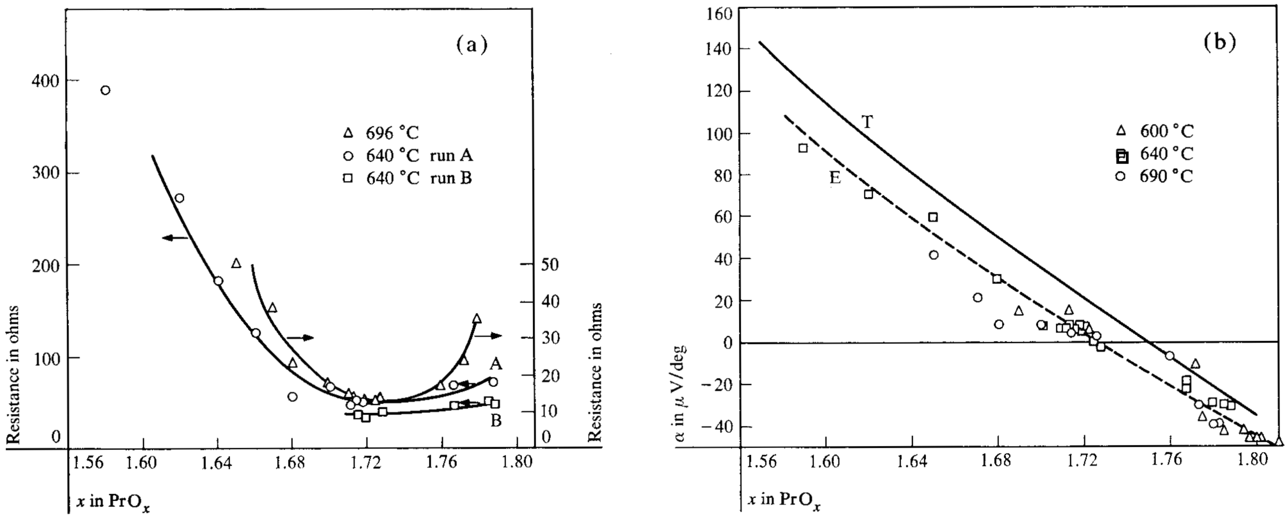


Figure 4(a) Resistance vs composition for a PrO$_x$ sintered pellet (after Ref. 51). (b) Seebeck coefficient of PrO$_x$ vs stoichiometry. Solid line represents theory based on a diffusion model of conductivity, which should agree with experimental curve (dashed) to within a constant (after Ref. 51).

that this is the observed variation. Further, σ is found to vary exponentially with temperature, whereas α is nearly independent of T. These findings are all consistent with the classification of PrO$_x$ as a 'hopper'.

4. Polaron materials: TiO$_2$(?), SrTiO$_3$

There exists a third class of materials with drift mobilities intermediate between those discussed in the two preceding sections. Here the carrier may be a polaron, i.e., an electron surrounded by a lattice polarization which tends to be carried along with the charge carrier. This type of coupling can greatly increase the effective mass of the carrier. Fundamental theoretical studies have shown[49] that when polarization is limited to the immediate surroundings of the electron, the polaron moves in band-like states for $T < \theta_D/2$ and via a hopping mechanism for $T > \theta_D/2$, where θ_D is the Debye temperature of the crystal. The bandwidth of polaron states at 0°K is much less than that of free electron states.

It is not a simple matter to document whether a given oxide with intermediate Hall mobilities, $0.01 \leq \mu_H \leq 100$ cm^2/V-sec, is to be classified as a polaron material. Thus TiO$_2$, VO$_2$, BaTiO$_3$, LaCO$_3$, CoO and NiO have variously been suggested as candidates for inclusion in this class, but in each instance the evidence is not unambiguous. A good case in point is TiO$_2$: Becker and Hosler[16] have measured resistivity and Hall coefficients between 2 and 600°K on a variety of nonstoichiometric samples. Except for compensated specimens, where ρ decreases sharply with rising temperature, the resistivity passes through a minimum between 40 and 100°K. These investigators interpret their findings in terms of mixed-carrier conduction, citing the marked changes of anisotropy in Hall coefficients with temperature as the principal evidence in support of their model. Comparable results had been cited earlier by Frederikse.[37] Since in mixed-carrier conduction under conditions explained in Sec. 9, Hall and drift mobilities may differ by orders of magnitude, the charge carriers in TiO$_2$ could well have substantial drift mobilities.

The case for including TiO$_2$ in the class of polaron materials has, on the other hand, been eloquently argued by Bogomolov, Kudinov and Firsov[18] as well as by Austin and Mott.[12] The former group, following the lead of Bogomolov et al.,[19] have analyzed all electrical and optical properties of TiO$_2$ on the assumption that ionization of impurity centers is complete above 100°K. For supporting evidence they cite optical absorption curves that are reasonably insensitive to doping and which are attributed to the interaction of radiation with charge carriers rather than with lattice defects as had previously been supposed. Until such an interpretation is confirmed it is not established that the variation of conductivity with temperature above 100°K reflects only a change in carrier mobility.

A further difficulty arises in conjuction with the Hall coefficients, R. These change by nearly three orders of magnitude in lightly doped or reduced samples,[2,16,37] precisely in the temperature range where the carrier density has been postulated to be constant.[18,19] As is well known, the theoretical interpretation of Hall constants in polaron-type materials remains uncertain because of conflicting theoretical results (see the review by Bogomolov, Kudinov and Firsov[18]); however, sample calculations[39] show that the ratio of Hall to drift mobility, $\mu_H/\mu_D = Ren$, can increase with T by over two orders of magnitude in the temperature range under study. Thus, for polaron materials R can indeed be altered enormously without necessarily requiring any change in n, but it remains to be established whether this situation applies to TiO_2.

The Seebeck coefficients determined by Thurber and Mante[89] exhibit a pronounced maximum in $-\alpha$ between 10 and 20°K; this is ascribed by them to the phonon drag effect. In agreement with Sakata[80] and Frederikse[37] they find that the Seebeck coefficient is numerically large ($-1 \leq \alpha \leq +0.5$ mV/deg) and independent of T above 100°K. These two particular features argue quite plausibly in favor of the small polaron model.

Resistivity data again lead to conflicting results. Whereas the workers at Leningrad report a maximum in the resistivity of reduced TiO_2 near 300°K, the work at the National Bureau of Standards shows a minimum in the 30 to 80°K range. Clearly, a changeover from the polaron band to the polaron hopping regime at constant charge carrier density can be argued only if the findings of Bogomolov et al.[18,19] are substantiated. We face here, as in subsequent sections, the question of whether small Hall mobilities ($\approx$10 cm^2/V-sec at 80°K, $\approx 10^{-2}$ cm^2/V-sec at 600°K) indicate polaron conduction in a single narrow band or mixed-carrier conduction in several bands. Obviously, nothing can be settled until concordant data are obtained. One should note finally that most measurements have been carried out on samples reduced under various conditions, without specification of the composition and related chemical characteristics of the resulting specimens. This leaves open the question whether most of the work relates to TiO_2 at all, since it is well known (see, e.g., Andersson[8]) that reduced titania forms a series of homologous compounds of composition Ti_NO_{2N-1}. Different reduction treatments lead to different homologs, and these in turn will have properties different from those of doped TiO_2. All these factors may account for the discrepancies noted above.

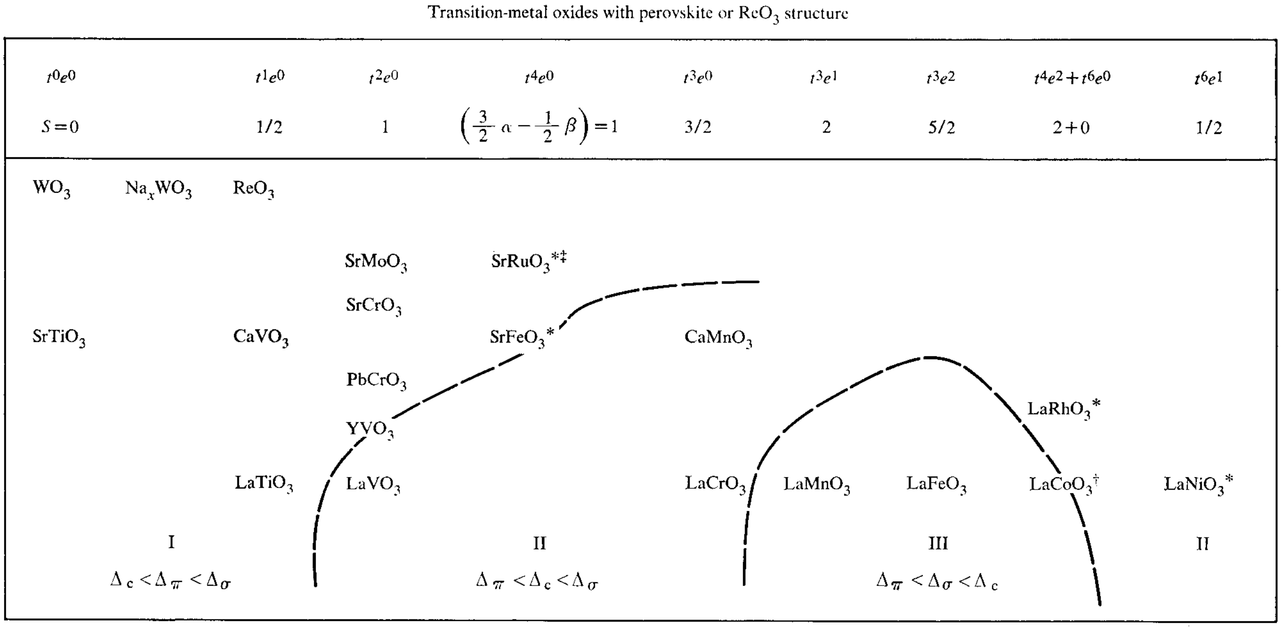
It appears that the high temperature phenomena are dominated by lattice defects. Thus Blumenthal et al.,[17] whose data agree well with those of Cronemeyer,[24] interpret their resistivity measurements in terms of electrons in equilibrium with triply and quadruply ionized interstitial titanium obtained on partial reduction of the sample at high temperatures.

We turn briefly to one other material: Nb- or La-doped $SrTiO_3$ is an extrinsic semiconductor[38] in which the electron drift mobility changes from 1.3×10^4 cm^2/V-sec at 4.2°K to 0.5 cm^2/V-sec at 1000°K. Due to its large dielectric constant, the donor exhaustion range has been reached at 4.2°K; thus the Hall coefficient remains independent of T over the entire temperature range under study. Above 200°K, Frederikse and Hosler[38] interpret their data in terms of polarons resulting from an intermediate coupling interaction between electrons and longitudinal optical phonons. Wemple et al.[96] have obtained similar results, but from hydrostatic pressure experiments involving resistivity and static dielectric constant measurements, they conclude that electrons in wide bands interact strongly with the soft, high amplitude, low frequency, transverse optical modes via lattice polarization fluctuations. Despite differences in detail, both groups have invoked electron-phonon interaction to account for the change in drift mobility from 20 to 0.5 cm^2/V-sec in the range 200 to 1000°K. Conductivity and thermoelectric studies on $SrTiO_3$ in equilibrium in the H_2O-H_2 ambients have been extended into the 1200 to 1600°K range by Walters and Grace.[94] They interpret their results in terms of a hopping model, with increasing oxygen vacancy defect and free electron concentrations resulting from the reaction of oxygen on lattice sites with H_2 in the gas phase.

5. Localized and itinerant electrons in perovskites

The class of perovskites of composition ABO_3 (including ReO_3 and WO_3) is well suited for a study of the effect of electron spin on the band formation arising from cation-anion interactions. For, in zero-order approximation,[43,52] the cationic species of type A (missing in ReO_3 or WO_3) does not appreciably alter the band structures close to the Fermi level; competition of A and B for bonding with O tends to narrow the π^* bands somewhat. Further, the smallest B-B or O-O separations are still so large that the corresponding orbital overlaps in the energy range of interest are small compared to the B-O orbital overlaps. Thus, the enormous changes in electrical properties among members in this isostructural series may be ascribed primarily to significant alterations in the B-O interactions arising from changes in the net spin S of species B.

In Fig. 5 is shown a listing[45,46] of various perovskites, arranged in rows according to the formal charge and principal quantum number of the outermost d electron shell for species B, and arranged in columns according to the electronic configuration $t_{2g}^m e_g^n$ or net spin S of species B. In light of the above comments, the band structure of all compounds should be qualitatively similar to that of ReO_3. Thus, if as a rough guide one accepts the zero-order subdivision and the ordering of bands schematized in Fig. 2, then all compounds listed in Fig. 5 have sufficient electrons to fill the σ, π, and p_π states and to partially populate the higher π^* and/or e_g^* states. Since the latter bands are intrinsically rather narrow, it is not surprising that the radial contraction of the electron orbitals, accompanying any increase in S, will eventually result in localization of the π^* (t_{2g}) and e_g^* states. Moreover, occupancy of such states by more than one electron will then lead to the usual crystal-field and exchange-



* Low-spin B cation.

† Low-spin Co^{3+} at 0 °K, both high- and low-spin states at finite T.

‡ Ferromagnetic $\mu_0 = 0.8\ \mu_B$ or $S = 0.4$.

Figure 5 Survey of properties of perovskites (after J. B. Goodenough, Refs. 45 and 46).

splitting effects associated with localized electrons. Accordingly, Goodenough[45,46] distinguishes among three possible regimes: Region I of Fig. 5 encompasses the 'low spin' cases $S = 0, 1/2$ and 1, where cation-anion overlap remains sufficiently extensive so that all electrons in d-like bands are itinerant; the band-structure scheme of Fig. 2 is qualitatively applicable. Region II envelops compounds for which $S = 3/2$ and 2, and where exchange effects are sufficiently strong to result in a splitting of d states into α- and β-spin substates. The radial extension of the orbitals is now such that π-type band formation can no longer be maintained, whereas e_g^* band formation is not yet suppressed. Accordingly, localized t_{2g}-α electrons coexist with itinerant e_g-α electrons, if any. Region III encompasses materials where $S = 2$ and $5/2$; the contraction of orbitals is now sufficient to localize all d electrons.

These elementary notions require considerable refinement before a quantitative analysis is feasible. However, a basic framework is available for rationalizing why, for example, ReO_3 is a metal while $LaFeO_3$ is an insulator. In this connection, the tungsten bronzes Na_xWO_3 ($0 < x < 1$) provide an excellent system for methodically exploring the lower edge of the π^*-like band in Figs. 2 or 3, by adjustment of x. These bronzes remain highly conducting only for $x > 0.25$[81]: There is a marked rise in ρ that coincides with the change in lattice symmetry from cubic at $x \gtrsim 0.5$ to tetragonal ($0.25 \lesssim x \lesssim 0.5$); this is followed by a change from metallic to semiconducting properties that coincides with a further transition to lower symmetry. The effect of these crystal transitions on electrical properties needs to be more thoroughly investigated, and probably is competitive in importance with the mechanism for the transition advocated by Mott.[72]

With the large values of S commonly encountered here, a prevalence of long-range magnetic ordering can be anticipated. The series YVO_3, $LaVO_3$, $PbCrO_3$, $CaCrO_3$ and $SrCrO_3$, in which the B ion remains in the $t_{2g}^2e_g^0$ configuration, is particularly instructive in this respect. In Goodenough's scheme $LaVO_3$ falls in Region II; indeed, a magnetostrictive distortion to tetragonal symmetry is observed at the Néel point, characteristic of localized electron orbitals ordering cooperatively via spin-orbit coupling below the magnetic ordering temperature. By contrast, $SrCrO_3$ is metallic and exhibits Pauli paramagnetism, as would be expected for electrons partially occupying normal band states. $CaCrO_3$ and $PbCrO_3$ exhibit antiferromagnetism but no distortions below the Néel point. This appears to be a manifestation of spontaneous band antiferromagnetism originating with itinerant electrons in relatively narrow bands. As re-emphasized recently by Goodenough,[46] as long as electrons remain localized, the increasing admixture of anionic with cationic wave functions raises the Néel point of the material in question. At a critical value of the overlap the system switches suddenly to a narrow-band regime, and the Néel point then drops quite rapidly with in-

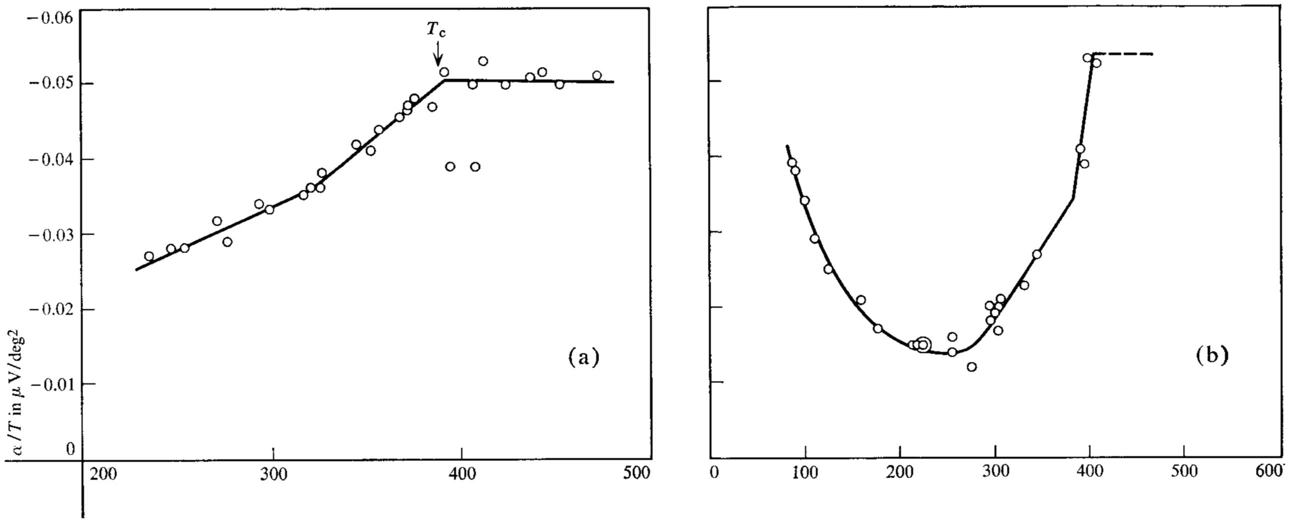


Figure 6 Plot of α/T vs T in the (a) high temperature range and (b) low temperature range for CrO_2 (after Ref. 22).

creasing bandwidth; this is the range of spontaneous band magnetism. Eventually the bands become so wide that Pauli paramagnetism prevails, except where a transition to the superconducting state occurs.

Other cases of magnetic ordering and the conditions required to stabilize ferromagnetism, antiferromagnetism or spiral spin arrangements are discussed by Goodenough[46] in further detail.

6. Ferromagnetic metallic oxides: CrO_2

Since the properties of the ferromagnetic insulator EuO are well covered elsewhere in this conference, we consider here only the case of the ferromagnetic metal CrO_2.

The electrical properties of CrO_2 and their interpretations are still at variance. Druilhe and Suchet[28] have summarized the evidence and presented further measurements indicating that the material is a semiconductor. Other investigators[21,22,77,78] have interpreted their results as showing that CrO_2 is metallic. Inasmuch as the work of Rodbell et al.[78] was done on single crystal films, their findings should be given special weight. Chrenko and Rodbell[23] carried out optical measurements in the infrared region of the spectrum and find that these support the claim that CrO_2 is a metal; they criticized similar work by Druilhe and Bonnerot,[27] who reached the opposite conclusion. However, it is at least definitely agreed by every worker that the material, first prepared by Wöhler in 1859, is ferromagnetic[48]; it has a Curie point of 392°K, and the magnetization follows the Brillouin function.[83] On the basis of Mössbauer studies, Shinjo et al.[82] report an internal field of approximately 530 kG at 0°K. Figure 6 shows the variation of α/T with T, where α is the Seebeck coefficient; this dramatically illustrates the change in conduction mechanism at the Curie temperature T_c. According to the elementary, particle-in-the-box approach to highly degenerate metals, $\alpha = (\pi^2/3)(k/e)(kT/\epsilon_F)$, where ϵ_F is the Fermi energy relative to the appropriate band edge. Thus, α/T is expected to be a constant, as is observed for $T > T_c$. The variation of α/T for $T < T_c$ may be ascribed to the increasing spin disorder with rising temperature. A similar effect is encountered in the resistivity, which increases much more markedly when $T < T_c$ than when $T > T_c$, again showing up the spin disorder effects.[78]

These electrical properties have been interpreted by Chapin et al.,[22] who employed a qualitative band structure scheme proposed by Goodenough.[43] In an extension of the molecular cluster approach to the rutile structure, Goodenough proposed that there should be a set of widely separated σ-type "bonding" and "antibonding" bands, a similar set of π-type bands nested within the gap separating the σ bands, and a set of nonbonding Cr levels that are split by intra-atomic exchange (Hund's rule splitting). Sixteen of the eighteen electrons per CrO_2 formula unit can be accommodated in the lowest lying σ and π bands, one of the two remaining electrons is placed in the lower Cr level (which has a capacity for one per Cr atom) and the second is placed with parallel spin in the next higher-lying π band. In this simple view, all the nearly localized electrons (one per Cr) are ferromagnetically coupled by an equal number of itinerant carriers of parallel spin. This at once preserves Hund's rule in Cr, thereby accounting for the observed magnetic moment of two Bohr magnetons, and for the metallic properties of CrO_2. Preliminary studies[30] have indicated that this approach to the band structure is greatly oversimplified, but until more sophisticated theories are developed pertaining to spontaneous magnetism in narrow bands (see Sec. 5), the above scheme remains useful in the interpretation of the characteristics of CrO_2.

7. Materials with nearly localized and nearly free electrons: NiO

Since the early investigations by de Boer and Verwey,[25] a voluminous literature of well over 60 articles has developed on NiO—with no sign of abatement in the publication rate. Nevertheless, the properties of this material are not understood, and many contradictory claims persist with regard both to the experimental data and to the theoretical interpretations.

At the outset it must be emphasized that most of the studies do not pertain to NiO per se but to Li-doped material. This doping procedure has generally been adopted in an attempt to "drown out" the effects of nonstoichiometry and of impurities accidentally incorporated in the specimen preparations. There is a real paucity of systematic data concerning highly purified, slightly nonstoichiometric NiO; as amplified later, most of the claims concerning NiO should be regarded with great caution.

The experimental findings on Li-doped NiO have been succinctly summarized by Adler[5] and by Feinleib and Adler.[32] Until 1963 it was taken for granted that charge transfer in doped NiO involved activated mobilities. Since then the weight of evidence has shifted in the other direction; the work of Bosman and Crevecoeur,[20] for example, argues in favor of a band regime.

Again, the interpretation of the electrical properties is fraught with complications. First, as Goodenough[46] has emphasized (see Sec. 5), the very high Néel temperature of this material argues for considerable superexchange, i.e., overlap between atomic orbitals, so that it should not be too surprising if narrow bands formed in this material. On the other hand, there have been repeated suggestions[13,36,88] that mixed-carrier conduction may occur. This could explain the sign reversal in the Hall coefficient at high temperature without a corresponding change in the Seebeck coefficient. On the other hand, the sign change has also been ascribed to the onset of long-range magnetic order below the Néel point.[90] Unfortunately, the effects of internal magnetic fields on the Hall coefficient are not well understood; also, the sign reversal is not encountered in CoO. Finally, impurity effects,[13,85] which are an ever present source of trouble in this material, obscure the interpretation of these phenomena.

Feinleib and Adler[32] have emphasized that optical, photoemission and transport measurements indicate the presence of both localized and itinerant electrons in NiO. They therefore suggest a model in which the d electrons are nearly localized in many-particle states; by contrast, the itinerant manifestations in NiO are linked to mobile holes in the 2p band of primarily anionic character. The model reconciles many data that are seemingly in conflict, and is consistent with the proposals for mixed-carrier conduction. However, this view has been criticized by Austin and Mott,[12] who ascribe the sharp lines in optical spectra to the interaction of radiation with excitons. They as well as Appel[9] interpret the properties of NiO in terms of a polaron model.

Again, it would appear that many of the problems that arise are due to the effects of impurities. This is dramatically illustrated in recent studies by Vest and Osburn.[93] Their resistivity studies are shown in Fig. 7 as a function of $1/T$ for a single crystal of NiO with a total impurity concentration less than 20 ppm by weight, as determined by mass spectrometer analysis. The marked kink in the graph is due to lack of equilibration with the ambience at lower temperatures. Slight contamination, picked up during the runs, alters the curves appreciably. Severe contamination introduces new kinks and bends, generally

Material: high purity NiO single crystal (66910)
Technique: 4-terminal dc

	$P_{O_2}=1$ atm		$P_{O_2}=10^{-2}$ atm		$P_{O_2}=10^{-4}$ atm	
	Symbol	ΔH(kcal)	Symbol	ΔH(kcal)	Symbol	ΔH(kcal)
Initial measurements	△	19.2 ± 1.5	○	19.9 ± 1.3	□	20.3 ± 1.9
Measurements after more than 50 hours above 1000 °C	▲	20.7 ± 0.5	●	19.6 ± 0.8	■	25.7 ± 1.0

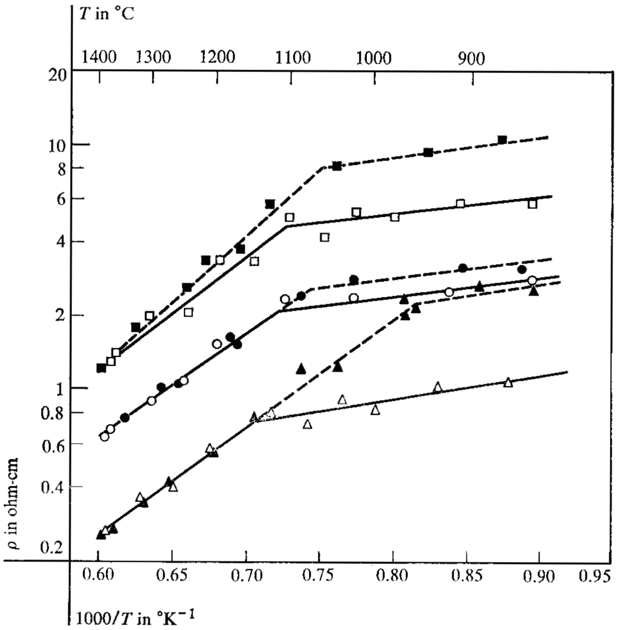


Figure 7 Resistivity as a function of $1/T$ for $NiO_{1+\delta}$ for various δ. Solid lines, original single crystals of high purity; dashed lines, slightly contaminated samples (courtesy of R. Vest and C. Osborn, Ref. 93).

in such a direction that observed resistivities are higher by several orders of magnitude than those shown in Fig. 7. Until thorough studies of this type concerning highly purified NiO and effects of small amounts of impurities become more generally available, the nature of the conduction process in this material remains in doubt.

8. The small-polaron-to-band transition: the LiV_2O_4–ZnV_2O_4 system

In a brief publication Reuter and Müller[76] reported on the infrared spectra and electrical properties of the mixed crystals $Li^{I}_{x}Zn^{II}_{1-x}(V^{III}_{2-x}V^{IV}_{x})O_4$ ($0 \leq x \leq 1$; I to IV represent the formal positive charges on the respective cations). These materials form spinels in which the octahedral sites are occupied exclusively by V; as x increases from 0 to 1, the V-V nearest neighbor distance diminishes linearly from 2.973 to 2.913 Å.

Marked changes occur in the electrical properties of the sintered pellets at $x = 0.55$: The Seebeck coefficient, which has a value of 180 μV/deg at $x = 0.05$, very nearly vanishes and does not change further for $x \geq 0.55$. The activation energy for electrical conductivity, which is approximately 0.2 eV for $x \leq 0.40$, decreases to 0.1 eV for higher values of x. Two strong infrared absorption peaks at 450 and 650 cm^{-1}, which are prominent for low x, decrease in strength with increasing intensity without changing their positions, and disappear entirely for $x > 0.55$. Single crystals of LiV_2O_4 are metallic.[79]

While absolute values of activation energies for sintered probes are usually too high, the trend toward lower values at larger values of x should be significant. Further, the values of the Seebeck coefficients and the optical studies should not be greatly affected by the state of subdivision of the sample. Thus, the weight of evidence points to a transition in electrical characteristics of this material, as the unit cell parameter diminishes. It is of interest that Reuter and Müller locate the critical intercationic distance at 2.94 Å, which is in excellent agreement with the value of 2.95 Å predicted much earlier by Goodenough.[41,42]

The above results suggest that this system may represent an example of a small-polaron-to-band transition in which the decrease in unit cell parameter, controlled by the ratio of Zn to Li in the material, results in a changeover from semiconducting to metallic characteristics. This transition is to be distinguished from that proposed by Mott,[67–71] since the number of electrons per V ion is variable and not integral. However, much more work is required, particularly with respect to the role of Li and Zn in conduction processes, to put this very tentative hypothesis on a firm footing.

9. Oxides exhibiting electrical transitions: V_2O_3

V_2O_3 is an example of an oxide that undergoes a first-order change in resistivity at a fixed temperature T_0. The transition is sharp and marked by hysteresis; T_0 is sensitive to stoichiometry, and the size of the discontinuity seems to depend on sample purity and stress.

Basically, the transition must be linked to the crystallographic phase change[73,95] from monoclinic ($T < T_0$) to rhombohedral symmetry ($T > T_0$). As Goodenough[44] has emphasized, a reduction in crystal symmetry is particularly likely to occur in narrow-band materials; for, there is a concomitant splitting of bands that opens up a gap at the Fermi level, thereby reducing the energy of virtually all occupied band states and increasing the energy of all unoccupied band states. The transition is thus qualitatively accounted for.

Unfortunately, in a more quantitative approach to the transition several problems arise which indicate that this simple interpretation requires refinements. In the first place, the Hall mobility of the so-called metallic phase falls in the range 0.2 to 0.6 cm^2/V-sec, which corresponds to a mean free path[34,97] of approximately 2 Å. Clearly one is not dealing with a simple metal here, and any explanation involving metallic conduction in a single, very narrow band[7,34] is likely to be inadequate. Actually, there are several ways of circumventing this difficulty. For example, one may assume with Mott[71] that conduction involves a nondegenerate gas of small polarons; some mechanism must then be found to have these "condense" at the transition temperature. Alternatively, one may appeal to a standard mixed-carrier conduction model. In the limit of low magnetic fields the total conductivity (σ) and Hall coefficient (R) for a two-band model are connected to the one-band contributions through the relations

$$\sigma = \sigma_n + \sigma_p \text{ and } R = (R_n\sigma_n^2 + R_p\sigma_p^2)/(\sigma_n + \sigma_p)^2.$$

On setting $\sigma_j = n_j e \mu_j$ and $R_j \approx \pm (n_j e)^{-1}$ the Hall mobility may be written as

$$\begin{aligned}\mu_H &= R\sigma \\ &= -\mu_n[1 - (n_p/n_n)(\mu_p/\mu_n)^2]/[1 + (n_p/n_n)(\mu_p/\mu_n)].\end{aligned}$$

This shows that μ_H and μ_n may differ by orders of magnitude when the numerator approaches zero, as in a mirror-image band model. This possibly important role of mixed-carrier conduction in V_2O_3 has also been stressed by Mott.[72] Clearly, it is not necessary to assume band overlap; as Mott points out, in materials with sufficiently small positive gaps and high dielectric constants the energy of formation of free charge carriers may well be less than that of the formation of two polarons.

Considerable evidence favoring a multiband conduction mechanism has recently come to light. Mixed-carrier conduction is indicated by the small value of the Seebeck coefficient, which remains positive and almost independent of temperature.[14] The Hall coefficient, measured with an ac technique, is similarly constant,[97] and on a one-band model would correspond to only 0.6 holes per V ion. McWhan and Rice[64] have recently shown that the transition to the monoclinic phase can be entirely suppressed by applying hydrostatic pressure in excess of 26 kbars. In this manner they were able to study the resistivity of compressed V_2O_3 in the range 0 to 300°K, observing that ρ (= 25 μohm-cm at 0°K) rises approximately as T^2 up to 50°K and then levels off to a linear rise with T at higher temperatures. The observed temperature dependence of resistivity is consistent with strong electron-hole (or electron-electron) scattering and suggests a degeneracy temperature near 100°K. On this basis McWhan and Rice proposed a multiband model with small overlap to explain the metallic properties; the overlap is lifted in the transition to the insulating phase, the transition being driven by the strong Coulombic attraction between holes and electrons. Their conclusion is that V_2O_3 is an example of an excitonic insulator displaying a crystalline distortion. That is, with diminishing pressure or temperature the overlap ultimately becomes so small that exciton formation ties up the free carriers. On the other hand, the most recent measurements by Rice and McWhan,[76a] reported in this conference, concerning the behavior of Ti- and Cr-doped V_2O_3 under stress, have led these investigators to regard the change of electrical properties in V_2O_3 as a manifestation of the Mott transition.

The transition has also been linked by Morin[66] to the onset of antiferromagnetic ordering. Hyland[57,58] has interpreted the transition in terms of a set of split-off, quasilocalized states, separated by a gap from a set of continuum states; in contrast with the Adler-Brooks or Mott models, no rearrangement of lattice atoms is required to effect the transition. This approach has been subjected to criticism[58] and its utility therefore remains in doubt.

Another alternative by Falicov and Kimball[31] stresses the importance of electron-hole interactions, which are responsible for an anomalous temperature dependence of charge carrier densities and which, when they exceed a certain critical value, can bring about electrical transitions. However, this model involves rather stringent assumptions concerning the electronic structure of the solid, and it is not clear for what materials these are satisfied.

The conduction mechanism in the monoclinic phase is also unsettled, primarily because of lack of information on the variation of carrier mobility with temperature. If one interprets the optical data of Feinleib and Paul[34] as indicating a bandgap $E_g \approx 0.1$ eV, then the observed activation energy for conductivity in the monoclinic phase, $E_a \approx 0.15$ eV, requires in the low-temperature range an activation energy of mobility of $E_a - E_g/2$. On the other hand, one may assume with Adler, Feinleib et al.[7] and with Austin and Turner[14] that the bandgap is close to 0.3 eV, in which event the conduction process in monoclinic V_2O_3 is nonactivated. The low value of the Seebeck coefficient in this range[14] cannot be taken as compelling evidence in favor of the band model because of possible interference by impurity conduction effects which become increasingly prominent at lower temperatures.

A theoretical investigation concerning the magnitude of the anticipated bandgap has been carried through by Adler et al.[7] This is based on the Adler-Brooks theory[6] of the semiconductor-metal transition, which occurs when a distorted lattice relaxes to a completely uniform atomic spacing. Adler and Brooks showed that as electrons are promoted with rising temperature across the gap of a band split by the asymmetric arrangement of atoms in the crystal, the gap is narrowed and the distortion reduced. This facilitates further promotion of electrons and, ultimately, results in a catastrophic collapse of the gap and the sudden elimination of the distortion. This theory is relevant to the transition in V_2O_3; however, its immediate quantitative application is inhibited by the need to generalize from one to three dimensions. From the estimated distortion, a bandgap of 0.1 eV is predicted at the transition temperature; this would correspond to a drop in carrier density by a factor of 10^{-2}. Since the discontinuity in resistivity spans seven orders of magnitude, the carrier mobility would have to drop by five orders of magnitude, indicating activated conduction in the monoclinic phase.

On the other hand, Adler et al. point out that a simultaneous onset of antiferromagnetism of the Cr_2O_3 type at the transition could, on the model of Adler and Brooks and of des Cloizeaux,[26] widen the bandgap considerably. An increase in E_g to 0.3 eV by this mechanism would then explain the observed resistivity change solely in terms of a drop in carrier density and would render the low-temperature conduction mechanism nonactivated. Until recently the situation was very much in doubt, since various magnetic susceptibility, heat capacity, Mössbauer and NMR studies had provided contradictory evidence. Antiferromagnetic order of the Fe_2O_3 type had been ruled out in two concordant neutron diffraction experiments.[74,60] In careful work just released by Moon,[64a] polarized neutrons have been employed to establish that V_2O_3 does indeed exhibit magnetic ordering in which ferromagnetically aligned atoms in (010) planes of the monoclinic phases are coupled in antiparallel alignment.

In this connection, Goodenough's earlier work[40,41] is relevant; he noted that in the low-temperature phase the conduction electrons might be trapped in homopolar pairwise bonding of the cations. This would tend to reduce or eliminate any magnetic moments, as has also been recently reiterated by Mott.[72] The new experimental information indicates, however, that this scheme, though undoubtedly appropriate for VO_2, does not hold for V_2O_3.

Finally, it should be noted that no less than six dif-

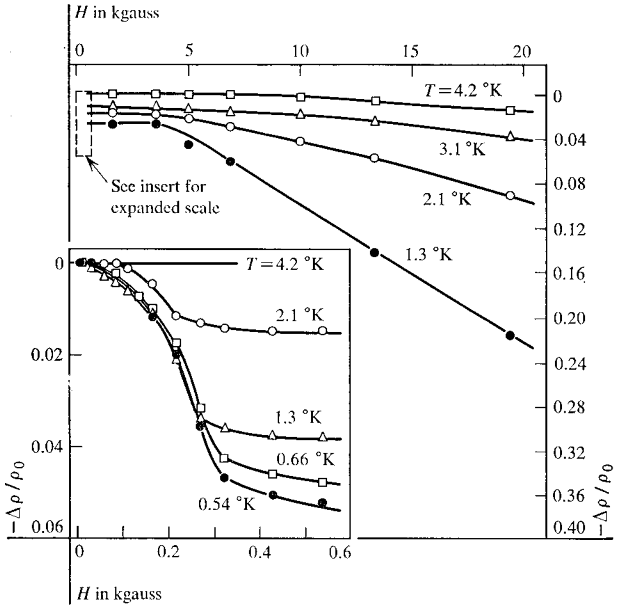


Figure 8 Negative magnetoresistance anomaly in Ti_2O_3 at low temperatures and low magnetic field strengths (after Ref. 92).

ferent mechanisms have so far been proposed to account for the transition in V_2O_3. The need for a more comprehensive perspective on first-order electrical transitions is clearly evident.

10. Transition anomaly in Ti_2O_3

We conclude with a brief description of selected properties of Ti_2O_3. Contrary to earlier findings,[1] recent neutron diffraction experiments[60,65] have shown rather conclusively that Ti_2O_3 is not antiferromagnetic at low temperatures. Hence, earlier interpretations[3] invoking magnetic ordering effects to account for the observed electrical transition stand in need of correction. Since no change in crystal symmetry occurs[86,75] in the temperature interval of the transition, Van Zandt et al.[91] and Honig and Reed[53] have invoked a gradual shifting and/or broadening with rising temperature of two close-lying bands. The intervening bandgap is assumed to narrow progressively and, ultimately, to give way to band overlap. This model is buttressed by repeated observations[86,75] that, coincident with the electrical transition, there is a distension of the unit cell. Highly purified Ti_2O_3 exhibits both a high resistivity and a large magnetoresistance increasing as H^2 at 4.2°K, as is consistent with the hypothesis that pure Ti_2O_3 is an intrinsic semiconductor in the liquid helium temperature range.[53]

When doped with 1 to 4 at.% V, Ti_2O_3 becomes a degenerate metal at 4.2°K. The positive magnetoresistance is now so small that a sizable latent negative effect comes into prominence;[55] there is no saturation effect even in fields as high as 220 kG. This phenomenon has been interpreted[55] as arising from the inelastic scattering of charge carriers by magnetic impurity centers; this mechanism runs in parallel with the usual elastic scattering processes. With rising magnetic field the increasing separation of the Zeeman levels of the magnetic impurities gradually closes off the inelastic scattering process, thereby reducing the resistance.

For $T < 4.2$°K and in low magnetic fields a transition in the magnetoresistance is encountered,[92] as shown in Fig. 8. The resistivity of the sample drops sharply with rising H in the range from 100 to 200 gauss, then levels off before merging into the normal negative magnetoresistance effect described above. This effect is tentatively interpreted by Van Zandt et al.[92] as another manifestation of the Kondo anomaly normally encountered in dilute alloys containing localized magnetic moments. In essence, the increasing magnetic field progressively perturbs the attractive interaction between the impurity and the oppositely directed electron spins, ultimately forcing both to align parallel with each other and against the impressed external field. The resulting repulsion between the electrons and the impurities alters the density-of-states functions and reduces the resistivity.

It is as yet too early to ascertain whether this interpretation will be sustained or whether some other effect such as superparamagnetism is involved. A possible objection, that the critical field of about 100 gauss is out of proportion with the temperature range of about 1°K at which the effect occurs, may be answered with the remark that the Kondo phenomenon has a parallel in superconductivity. There the critical field and temperature are also disparate, owing to the intervention of the lattice vibrations, with the associated Debye frequency $\hbar\omega_D$. In the present case a preliminary analysis indicates that the bandwidth Δ plays an important role, and that one should expect an equivalence of the form $kT_c(kT_c/\Delta) \approx g\mu_m H$. However, until a complete theory is constructed, this interpretation of the transition in magnetoresistance in Ti_2O_3 remains uncertain.

11. Conclusions

This survey reinforces the melancholy fact that, despite considerable research effort over many years, the electrical properties of a large number of oxides are not understood. Special efforts are needed to ensure a more careful characterization of materials under study, and a less rigid approach to the theoretical interpretation is required to resolve the many outstanding problems in this field.

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