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Metal-insulator Transition in Transition Metal Oxides

Abstract: The metal-insulator transition in the V_2O_3 system is discussed. A recent series of experiments on V_2O_3 and $(V_{1-x}Cr_x)_2O_3$ is reviewed. The phase diagram for the system is described. The Cr-doped mixed oxides are insulating at room temperature for $x \geq 0.009$ and transform to a metal with the application of pressure. This phase transition is identified as a Mott transition. A comparison is made between the experimental results and theoretical predictions of the Mott transition.

1. Introduction

The transition metal oxides form a very interesting class of materials. Their electrical properties range from very good metals to very good insulators with many compounds which lie on the borderline between metallic and insulating behavior. Among the insulating materials are compounds which on the basis of band theory should be metallic. While it is possible on the basis of Bloch–Wilson band theory to account for metallic behavior in systems with an even number of electrons per unit cell through band overlap it is not possible to explain insulating behavior when the number of electrons per unit cell is odd. This dilemma and its solution were pointed out by Mott[1] twenty years ago. Mott in particular observed that NiO is insulating both above and below the Néel temperature when on the basis of Bloch–Wilson band theory it should be metallic. He proposed that because of strong Coulomb repulsion between electrons the ground state wave function of NiO had a localized, or Heitler–London form, leading to insulating behavior in contrast to the band, or Bloch–Wilson, form which would be metallic. He proposed further that under the application of high pressure an abrupt transition would be made from a localized insulator to a band metal. This transition is now known as the Mott transition. We note that this is an electronic transition which may occur without any change in lattice symmetry.

On the other hand many of the metallic oxides are good metals and show no signs of abnormally strong interactions among electrons. In recent years it has become possible to use the techniques of metal physics, combining de Haas–van Alphen measurements and band structure calculations to obtain a detailed knowledge of the Fermi surface and band structure of some oxides, e.g. ReO_3 and RuO_2.[2–4]

The oxides with intermediate conductivities appear to lie on the borderline between those with very strong interactions such as NiO, Cr_2O_3, etc. and those with weak interactions such as ReO_3, RuO_2, etc. A number of the oxides with intermediate values of conductivity exhibit metal-to-insulator transitions with decreasing temperature.[5,6] For some materials, e.g. V_2O_3 and VO_2, this transition occurs as a sharp first order transition involving changes in conductivity of several orders of magnitude. For others, e.g. Ti_2O_3, the transition occurs as a region of anomalous behavior over which the conductivity varies rapidly but continuously. Since the crystal structure of Ti_2O_3 remains the same (α-corundum) above and below the metal insulator transition and there is no magnetic ordering[7] in the insulating region, this metal-insulator transition is not a phase transition in the thermodynamic sense. In the vanadium oxides VO_2 and V_2O_3 there are changes in long range order associated with the first order metal-insulator transitions. Under such circumstances, it is difficult to decide if the transition is primarily a Mott (localized to delocalized) transition or whether it is primarily associated with the additional band gaps due to the change in periodicity. These questions were extensively discussed at the San Francisco conference on metal-nonmetal transitions in 1968.[8]

Since that time there has been a lot of work on the V_2O_3 system.[9–13] This work has clarified the experimental situation in V_2O_3 and from a study of mixed oxides has led to the observation of a Mott transition. In this paper we review this recent work starting with an account of the properties of pure V_2O_3 in section 2. In section 3 we discuss the effects of doping with Cr and of pressure on the mixed oxide system. In section 4 we compare the observed phase diagram of the Mott transition and the theoretical results

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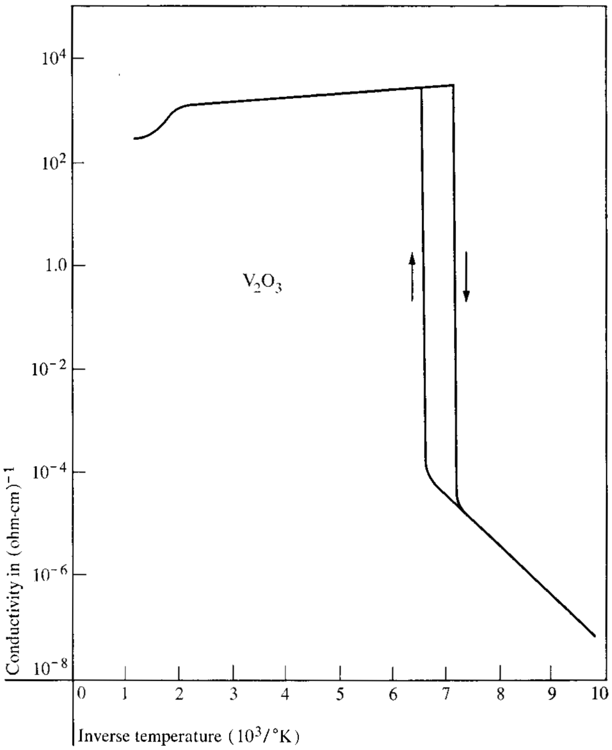

Figure 1 The conductivity of pure V_2O_3 at 1 atm as a function of temperature (from Ref. 15).

which have been obtained using the Hubbard model.[14] Finally in section 5 we state the conclusions.

2. Pure V_2O_3

The metal-insulator transition in V_2O_3 was discovered by Foex[5] in 1946. He found a sharp first order resistivity change of approximately 5 orders of magnitude at a temperature of 173°K. Below this temperature the resistivity was $\approx 10^4$ ohm-cm and showed an activation energy of 0.1 eV. Above 173°K the resistivity was $\approx 10^{-2}$ ohm-cm and rose linearly with increasing temperature. These facts were subsequently confirmed by Morin.[6] In addition to the primary metal-to-insulator transition there is an anomalous change in conductivity in the temperature region 400°K to 600°K. As the temperature is raised through this region the resistivity has a broad S-shaped anomaly. In Fig. 1 we show the conductivity of V_2O_3 as measured by Feinlieb and Paul,[15] which shows clearly both the high temperature anomaly and the metal-insulator transition.

Associated with the metal-insulator transition is a change in crystal symmetry. The high temperature metallic phase has the α-corundum structure. In the low temperature phase there is a distortion from rhombohedral to monoclinic symmetry.[16] However, the volume of this unit cell is not doubled and there is no superlattice set up by the lattice distortion.[10] Adler, Brooks, Feinlieb and Paul[17] have applied the Alder–Brooks lattice distortion model[18] to the transition in V_2O_3. The Adler–Brooks model is a generalization of the Jahn–Teller effect to a situation in which the metallic phase has a very narrow half-filled conduction band. At low temperatures there is a first order metal-insulator transition accompanied by a lattice distortion in which a superlattice is set up which doubles the unit cell volume and introduces new band gaps, producing an insulating state. The available experimental x-ray data[16,10] do not support this picture of the distortion in V_2O_3 and it now appears that the rhombohedral-to-monoclinic distortion at the metal-insulator transition is primarily magnetostrictive in origin and not of any fundamental importance.

The low temperature phase of V_2O_3 has now been definitely established to be antiferromagnetic. The disappearance of the NMR signal at the metal to insulator transition observed by Jones[19] and the splitting of the Mossbauer spectrum of Fe-doped V_2O_3 observed by Kosuge[20] below 170°K suggested antiferromagnetic ordering. However, attempts to observe magnetic structures similar to those found in other transition metal sesquioxides (Cr_2O_3, Fe_2O_3) were negative. The early neutron powder patterns of Paoletti and Pickart,[21] however, show a line which was not seen by x-rays. Very recently Moon,[22] using the technique of spin-flip neutron scattering, has confirmed that V_2O_3 is antiferromagnetic below 170°K. The structure, however, is unique among the sesquioxides. The moments line up ferromagnetically in a plane perpendicular to the monoclinic b axis (which is collinear with one of the a axes of the corundum structure) and the planes are stacked antiferromagnetically along the b axis. Preliminary measurements[22] show a value for the magnetic moment of only $\approx 1.2\mu_B$. This is substantially lower than the value expected ($2\mu_B$) for a localized V^{3+} ion. In the other insulating antiferromagnetic sesquioxides (e.g. Cr_2O_3 and Fe_2O_3) the full moment of the localized ion is found.

The application of pressure has the effect of reducing the transition or Néel temperature drastically. Austin[23] and Feinlieb and Paul[15] found an initial slope of ≈ -4°K/kbar. Subsequently the application of higher pressures showed that it is possible to completely suppress the transition for pressures in excess of 25 kbar.[8] As $T_N(P) \rightarrow 0$ the slope $dT_N/dP \rightarrow -\infty$ and from the magnitude of the discontinuous resistivity change it appears that the transition remains first order.

At pressures greater than 25 kbar the system remains metallic down to 2.2°K, the lowest temperature studied. The resistivity ρ is large ($\approx 10^2$ μohm-cm) and has an unusual temperature dependence.[9] At lower temperatures ($T \lesssim 100$°K) the resistivity accurately obeys the law $\rho(T) = \rho_0 + BT^2$, with a value for $B \approx 0.042$ μohm-cm-°K^{-2} which is 10^3 times that for a typical transition metal.

Further, at higher temperatures $\rho(T)$ bends over and varies linearly with T. In a typical transition metal a T^2 term is seen at low temperatures but as the temperature is raised the phonon scattering processes dominate and a faster variation is found. In V_2O_3, however, the T^2 term saturates at a temperature of $\approx$100°K. This suggests that at low temperature the dominant mechanism in the resistance is electron-hole or electron-electron scattering and that there is an effective degeneracy temperature for the electrons or holes of $\approx$100°K. Thus resistivity studies demonstrate the existence of a very low characteristic energy ($\approx$0.01 eV) in the conduction electrons of metallic V_2O_3.

The magnetic susceptibility in the metallic phase at 1 atm is large and temperature dependent.[19] However, the resistivity shows no sharp anomalies as a function of temperature above 25 kbar which would indicate a magnetic phase transition. This evidence is not conclusive since it could be argued that pressure inhomogeneities, etc., could easily smear such a transition. Very recently however, the paramagnetic nature of metallic V_2O_3 has been confirmed by Gossard, McWhan and Remeika.[12] They have observed the nuclear magnetic resonance lines in (pure) V_2O_3 at 4.2°K and pressures $P > 26$ kbar. At lower pressures the NMR line disappears, indicating an antiferromagnetic phase.

Gossard, McWhan and Remeika[12] find that the d-spin Knight shift k_d is strongly pressure dependent. They obtain a value $d \ln k_d \ln V = 8 \pm 5$ which may be compared with that for V metal: $d \ln k_d \ln V = 0.8$. The pressure dependence of the Knight shift is thus an order of magnitude larger than in a typical transition metal. Similar very large pressure derivatives are found in other properties too. The resistivity derivative has a value of $d \ln \rho / d \ln V = 42$ at $T = 298$°K, which again is an order of magnitude more than that of a typical transition metal. The coefficient B of the T^2 term in the resistance decreased by a factor of two between $P = 26$ kbar and $P = 52$ kbar. To sum up, the properties of the metallic state of V_2O_3 are highly anomalous, and they change rapidly with pressure in the direction of making it more metallic. All of this suggests that pure V_2O_3 is near a critical region and that the application of negative pressure would induce a transition. We shall see in the next section that doping with Cr has an empirical correspondence with applying negative pressure and indeed induces a metal-to-insulator transition.

3. Cr-doped V_2O_3

The addition of small amounts of Cr to V_2O_3 produces some dramatic effects. Newnham and de Haan[24] studied the crystal structure at room temperature across the $(V_{1-x}Cr_x)_2O_3$ mixed oxide series. All the mixed oxides, at this temperature, have the α-corundum structure. When one plots the c/a ratio of the corundum structure versus composition one finds a smooth variation from $x = 1$ down to $x = 0.02$ (the lowest value studied). However, the point for pure V_2O_3 deviates significantly from this curve. Recently it has been established that a discontinuity occurs at $x = 0.01$.[25] MacMillan[26] measured the electrical resistivity and the magnetic susceptibility of powdered compacts for this oxide series. He found that oxides with $x > 0.04$ showed insulating characteristics at room temperature. The resistivity was several orders of magnitude larger than that of the pure material and had a negative temperature coefficient. The magnetic susceptibility at room temperature also increased.

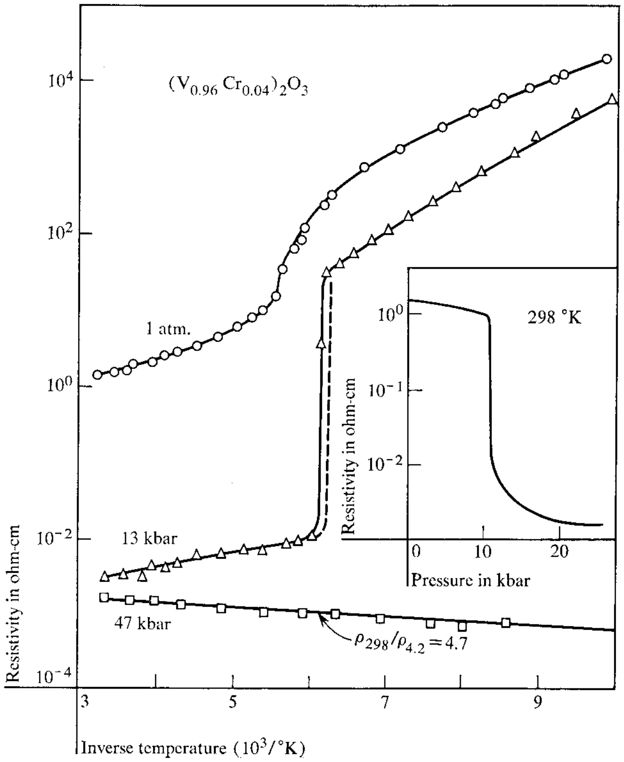

Figure 2 Resistivity vs reciprocal temperature at different pressures for $(V_{0.96}Cr_{0.04})_2O_3$. Inset shows I-M transition at room temperature as a function of pressure. Below 10 kbar the AF $\rightarrow$ I transition occurs on warming. Above 10 kbar the AF $\rightarrow$ M transition occurs. Above 40 kbar the sample is metallic from 4.2°K to 298°K.

Recently it has become possible, by using a new technique, to grow single crystals of these mixed oxides. In particular crystals with $x = 0.04$ have been studied extensively. Dernier[11] has refined the crystal structure of this oxide very accurately. The oxide has the α-corundum structure at room temperature. The volume of this mixed oxide is $\approx$1% larger than that of V_2O_3. All nearest neighbor V-V distances expand in the alloy. However the V-O nearest neighbor distances remain unchanged.

The resistivity of this oxide as a function of temperature is shown in Fig. 2.[19] For $T > 180$°K, $\rho \approx 1$ ohm-cm

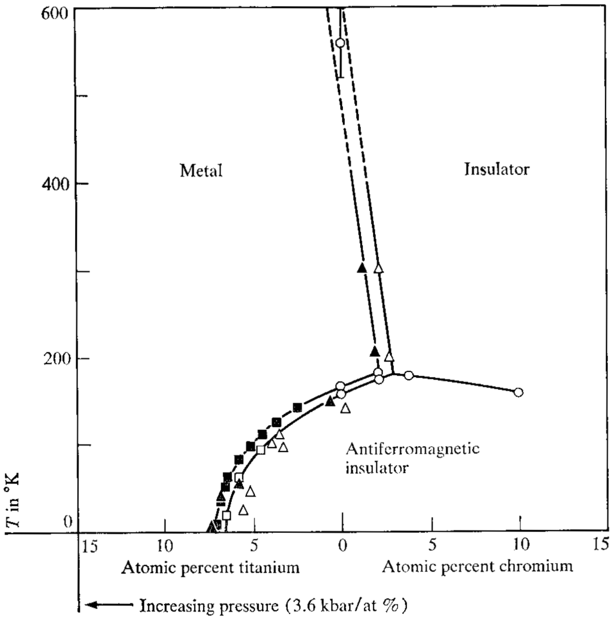

Figure 3 Generalized phase diagram of transition temperature vs. both pressure and atomic percent Cr and Ti in V_2O_3. Points (○) from mixed oxides at 1 atm, (■□) (V_2O_3 on increasing and decreasing pressure, respectively, (▲△) $(V_{0.96}Cr_{0.04})_2O_3$ on increasing and decreasing pressure, respectively. There are large experimental uncertainties (±2 kbar) in the pressure calibration below 10 kbar and therefore in the M-I phase boundary.

and shows thermal activation. At $T = 180°K$ a transition is observed to a more insulating state. This transition is accompanied by a lattice distortion to a monoclinic phase identical to that observed in antiferromagnetic V_2O_3. Clearly then, this mixed oxide has a transition between an insulating (I) phase and the antiferromagnetic (AF) phase at 180°K, in contrast to pure V_2O_3 which has a transition between a metallic (M) phase and the AF phase at 150 to 160°K. At an intermediate composition near the discontinuity, for example $x = 0.01$, both resistivity and x-ray measurements show a sequence of transitions on cooling of $I \rightarrow M \rightarrow AF$.

The M phase of the V_2O_3 system has a smaller volume than the I phase. This suggests that an I- to M- transition should be possible under pressure. The inset in Fig. 2 shows the pressure dependence of the resistivity at room temperature. A clear I-M transition involving a drop in resistivity by a factor of ≈ 150 is seen at ≈ 10 kbar. For $P \geq 10$ kbar the system shows a large first order change in the resistivity on cooling, corresponding to a M-AF transition. At high pressure, $P \geq 40$ kbar, the AF phase is found to be completely suppressed and the M phase is stable down to 4.2°K. A resistance ratio of ≈ 5 is found for the metallic phase. Thus this alloy for pressures around 15 kbar behaves in a similar way to pure V_2O_3 at one atm.

From the *P-T* phase diagrams for V_2O_3 and $(V_{0.96}Cr_{0.04})_2O_3$ and the *T*-composition phase diagram, a three-dimensional phase diagram can be constructed which separates the regions of stability of the M, I and AF phases. However, the similarity between $(V_{0.96}Cr_{0.04})_2O_3$ at 15 kbar and V_2O_3 at one atm suggests that we can scale the effects of pressure to those of changing Cr concentration. In this way the generalized phase diagram shown in Fig. 3 was obtained. Temperature is plotted vertically and the pressure and concentration are plotted horizontally. The scaling factor of 3.6 kbar per atm. percent was obtained by making the critical pressures for the suppression of the AF phase coincide. It is clear from Fig. 3 that alloying and pressure points coincide very well. The M-I phase boundary, when extrapolated to pure V_2O_3, occurs at a temperature of $\approx 500°K$. This is just the region of the high temperature anomaly discussed in section 2. At room temperature the M-I phase transition involves no change in the long range order. It may therefore terminate in a solid-solid critical point similar to that observed in Ce metal.[27] Very recently Jayaraman[13] has followed the M-I phase boundary in an $x = 0.04$ alloy to temperatures above room temperature. He finds that the magnitude of the change in resistivity at the first order transition drops continuously as the temperature is raised and goes to zero around 400°K. Thus the thermodynamic phase transition terminates in a solid-solid critical point. Jayaraman finds that for $x = 0.04$ this solid-solid critical point occurs at $T = 390 \pm 5°K$ and $P = 12 \pm 0.5$ kbar. Above this temperature an anomaly is seen in the resistivity but there is no longer a phase transition in the thermodynamic sense. The situation is similar to that observed in Ce.

The nature of the M-I phase transition is a delocalized-to-localized transition. This is clear from entropy considerations. From the slope of the M-I phase boundary one finds that the I phase has a higher entropy than the M phase. This clearly contradicts a simple band uncrossing for the M-I transition. Such a band uncrossing could also occur without a change in lattice symmetry. The AF phase could then be viewed as an "excitonic" phase. This suggestion, which was made earlier by the present authors,[9] can therefore be immediately ruled out by the slope of the M-I phase boundary. There is a large entropy change (2.6 cal/°K-mole) at the I-AF transition which is comparable to the disorder entropy of V^{3+} ions with $S = 1$ (4.4 cal/°K-mole). It is clear therefore that the I phase has local moments. The larger susceptibility and the insulating character of the phase all confirm this proposition. This M-I phase transition is one in which the conduction electrons of the metal localize to form an insulator. This is just the transition proposed by Mott in 1949,[1] now known as the Mott transition. The difference between this transition and Ce metal is that in the V_2O_3 system all the conduction electrons become localized whereas in Ce just one of the conduction electrons in the α-phase is promoted to the 4f state in the γ-phase.

The rest of the phase diagram can also be understood qualitatively. In the I phase the local moments order to give the AF phase. There is an additional free-energy reduction due to the ordering and this makes possible the sequence of phases I to M to AF as the temperature is lowered for certain pressures and compositions. It is interesting to note that the effect of the Mott transition on the ionic configuration is to move the metal ions farther apart in the I phase while preserving the metal-oxygen distances.[11] This, of course, is just what one would expect on a very simple model of the Mott transition. However, one knows that the band structure is strongly influenced by the hybridization of the d-wave functions with the oxygen 2p levels, so it is surprising that it is just the V-V distances which change. In the next section we shall review the theory of the Mott transition and make some comparisons with the experiments.

4. Theory of the Mott transition

Although it is now some twenty years since Mott's original proposal there is, as yet, no satisfactory microscopic theory of the Mott transition. In his original article[1] on the subject Mott argued that the transition would occur discontinuously as a function of the lattice spacing. His arguments were based on the screening effect of free carriers. As carriers are excited in the insulating phase they will in turn tend to more effectively screen out the long-range Coulomb repulsion. This, he argued, leads to a cascading process and a first-order transition at $T = 0°K$ between an insulating phase with no free carriers and a metallic phase with a finite density of free carriers.

Most of the theoretical analysis has started with a model Hamiltonian introduced by Hubbard.[14] In the Hubbard model a localized or Wannier representation is taken for the electronic wave functions and the Hamiltonian H consists of two terms. One represents the Coulomb repulsion energy U when two electrons are on the same site and the other term the tunneling of electrons from one site to its neighbors

$$H = \sum_{ij,\sigma} t_{ij} c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} \tag{1}$$

where $c^{\dagger}_{i\sigma}$ is the creation operator for an electron of spin σ in the atomic state at the ith lattice site, t_{ij} is the matrix element of the electron transfer between the states at the ith and jth sites and $n_{i\sigma} = c^{\dagger}_{i\sigma} c_{i\sigma}$.

In the atomic, or large U/t, limit for a single half-filled band there will be an electron localized on each site and the system will be in the Mott-Hubbard insulating phase. In this limit there is an antiferromagnetic coupling energy ($\approx t^2/U$) between the local moments due to Anderson kinetic exchange. Thus at low temperatures the system is antiferromagnetic with a Néel temperature defined by $kT_N \approx t^2/U$. However, the system is insulating both above and below T_N. There is an energy gap between the ground state and current carrying excited states known as the Mott-Hubbard correlation gap E_{MH}. In the atomic limit $E_{\mathrm{MH}} = U - ct$ where $t = t_{ij}$ for nearest neighbors and c is a numerical constant which depends on the choice of lattice. As t/U is increased the Hamiltonian (1) becomes very difficult to solve and there are no exact results. Hubbard[14] has used a Greens function decoupling scheme and neglected magnetic ordering. Within his approximation a continuous insulator to metal transition occurs as t/U increases to a critical value of $t/U = 1.15$. This result does not necessarily contradict Mott's original argument since Mott's reasoning was based on the long-range Coulomb interaction which is neglected in the Hubbard Hamiltonian (1). Nonetheless, as Hubbard has emphasized, it is not clear that this is the correct result for the Hubbard Hamiltonian.

A different suggestion has been made by Kohn.[28] He has suggested that the metal-insulator transition at 0°K progresses through an infinite nested sequence of second order transitions which terminate at a critical point. Starting from the metallic (small U) limit the Fermi surface is gradually truncated by a series of band gaps associated with the extra periodicities introduced at the phase transitions. He has considered only spinless Fermions, where the extra periodicities arise from charge density waves. More generally they could arise from spin density waves. In Kohn's model the number of carriers goes to zero continuously (but of course non-analytically) at the critical point corresponding to the termination of the infinite nested sequence. The detailed nature of the sequence of phases will depend on the band structure of the metal involved. Thus, for example, if we take the Hubbard Hamiltonian Eq. (1) for the bcc lattice we find that the ground state is antiferromagnetic and insulating even for U infinitesimally small because of the perfect "nesting" property of the tight-binding S-band surface for the bcc lattice. In general a finite value of U is required to obtain antiferromagnetism.

In comparing theory and experiment the main questions are, first, whether there is overall agreement on the shape of the phase diagram in the P-T plane and, second, whether there is agreement on the order of the three separate phase transitions M-AF, I-AF and I-M observed experimentally. It is clear that none of the theoretical models discussed above predicts completely the observed phase diagram.

There are, however, several complications in comparing the theoretical results outlined above and the experimental data. First, the experiments are performed by varying pressure whereas, in the theory, the parameters which are varied are smooth functions of volume. Thus it is possible that a transition which is first order as a function of pressure could be second order as a function of lattice parameter. In the second place, the AF phase observed in V_2O_3 is accompanied by a lattice distortion. Again it is possible that the AF-I or AF-M transitions would be second order if the lattice were held fixed but are converted to first order by the coupling to the lattice distortion. It is thus difficult, without further knowledge, to conclude that the observation of first order transitions at the I-M and AF-M transitions in the V_2O_3 system conclusively demonstrates the first order nature of the Mott transition. While one cannot rule out the Kohn picture of the Mott transition, it is nonetheless clear that the experimental situation in V_2O_3 at present does not support it either. At 0°K the transition observed is from an antiferromagnetic insulator to a paramagnetic metal and no intermediate phases, either metallic or insulating, with different periodicities have been observed.

A first order AF-I transition has been proposed theoretically, if the I phase has a small intrinsic energy gap, by Bulaevskii and Khomskii.[29] They proposed a semi-phenomenological form for the energy gap

$$\Delta = U - b(1 - s^2)^{1/2}, \qquad (2)$$

where U is defined as in Eq. (1), s is the sublattice magnetication normalized so that $s = 1$ at $T = 0°\mathrm{K}$ and b is a parameter related to t and possibly U defined in (1). At low temperatures $\Delta \approx U \approx 1$ to 2 eV while, at temperatures above T_N, $\Delta \approx U - b \ll 1$ eV. As the temperature is raised below T_N, the additional entropy from the destruction of the moments through the excitation of carriers favors the paramagnetic phase and converts the AF-I transition to first order. In the experiments on $(V_{0.96}Cr_{0.04})_2O_3$ there clearly is not a change of an order of magnitude in the activation energy between $T \ll T_N$ and $T > T_N$. However, because of possible impurity effects this may not be definitive. Bulaevskii and Khomskii[29] discuss only a thermally activated transition and their theory does not describe the M-AF transition at 0°K.

One interesting feature of the phase diagram in Fig. 3 is that the M-to-I transition occurs with increasing temperature. This is in contrast to the AF-to-M transition. Of course, in the AF phase the spins are ordered and the entropy of the metallic phase is higher. However when the spins are disordered as in the I phase they have an entropy of disorder of $R \ln (2S+1)$, corresponding to the $(2S+1)^N$ degenerate levels of spin direction. On the other hand the entropy of the metallic state, which is higher at very high temperatures, goes to zero as γT, where γ is proportional to the density-of-states, in the limit $T \rightarrow 0$. Thus it is clear that at sufficiently low temperatures the entropy of the paramagnetic insulating phase is higher than that of the metallic phase and that the observed transition from a metal to an insulator is consistent with this picture. This M-I transition is different from the kind of Mott transition proposed by Frohlich[30] and Hyland.[31] In their model there is a transition between a disordered insulator and a metal as the temperature is raised, due to the higher entropy of the metal. Such a transition, if it occurs in V_2O_3, will be at very high temperatures and will be to a metallic state which is much different from the M phase of V_2O_3. In fact above the temperature of the solid-solid critical point (≈400°K) there is no longer any real distinction between the M and I phases of the V_2O_3 system.

Another interesting feature to emerge from the experiments is the existence of a low characteristic temperature in the metallic phase. This is shown clearly by the resistivity results, which show a very large T^2 term at low temperatures that saturates at around 100°K.[9] It is also clear from entropy considerations. The large entropy change at the AF-M transition in pure V_2O_3 at one atm and small entropy change at the I-M transition indicate that the M-phase has a large entropy for $T \approx 180$ °K. On the other hand the specific heat of pure V_2O_3 at one atm shows only a very small change in specific heat at the AF-M transition.[32] Since the M phase is paramagnetic at 4.2°K, these results imply a large low-temperature peak in the specific heat to account for the entropy. It would clearly be desirable for the specific heat of the M-phase to be measurable directly down to low temperature. Such a low-temperature peak in the specific heat would be consistent with the conclusion that there is a low characteristic temperature in the M phase.

In Hubbard's picture[14] of the metal-insulator transition, the metallic state is characterized by the overlap of two pseudo-particle bands. This overlap shrinks to zero at the metal-insulator transition. The overlap energy is a possible choice for the low characteristic temperature. However, in his picture the Fermi level sits in a minimum of the density-of-states versus energy curve and the value of the density-of-states at the Fermi level goes continuously to zero as $U/t \rightarrow 1.15$. This would lead to an electronic specific heat γT, where γ was very small at low temperatures and would rise and saturate very slowly on the scale of U/k. This is clearly very different from the behavior which we have inferred from entropy considerations.

The anomalous behavior of the metallic phase can be understood, at least qualitatively, if we use the concept of spin fluctuations. Starting from the band picture of the metal as the Mott transition is approached there are strong spin fluctuations as the electrons become more and more localized. Many authors have discussed spin fluctuations, or paramagnons,[33–36] in systems which are near ferromagnetism. The theory of paramagnons predicts an enhanced specific heat at low temperatures and a large T^2 term in the resistivity.[36] Both of these phenomena occur below a characteristic temperature, referred to as T_{sf}, the spin fluctuation temperature, which is the Fermi temperature divided by the enhancement factor. As the ferromagnetic transition at $T = 0°K$ is approached, $T_{sf} \rightarrow 0$. Similar results are expected in antiferromagnetic systems. One expects that as the electrons become localized such paramagnon effects will be pronounced. In this case the susceptibility will be essentially independent of wave vector, which will reduce the range effects to a minimum. This is borne out by the observation that although V_2O_3 orders antiferromagnetically, the uniform susceptibility of the metallic phase is large and temperature dependent.[19]

Discussion of the M-I transition in the framework of the Hubbard Hamiltonian neglects completely the fact that V_2O_3 is a polar crystal and that electron-phonon interactions, among other things if they were large enough, might greatly modify the nature of the transition. Mott[37] has suggested an alternative model based on polaron effects to explain the high entropy and large susceptibility of the metallic phase. He has suggested that the metallic phase is really a degenerate gas of n- and p-type small polarons. If the lattice were held fixed there would be a finite Mott–Hubbard correlation gap E_{MH} and the system would be insulating. However, because of the binding of the small polarons E_p, it becomes energetically favorable to create pairs of n- and p-type small polarons when $E_p > \frac{1}{2}E_{MH}$, leading to a degenerate gas of small polarons. In this model the M-I transition would occur when $\frac{1}{2}E_{MH} = E_p$. The AF phase arises from the ordering of the local moments. However, in this model there are local moments in the metallic phase and one might expect magnetic ordering in the metallic phase under pressure at low temperatures. Mott,[37] however, has pointed out that the absence of such magnetic ordering can be accounted for by the formation of magnetic polarization clouds around the polarons, which disrupt the long-range order.

5. Conclusions

In this paper we have reviewed a recent series of experiments on the V_2O_3 system. These results show that the transition is basically a Mott transition in which the conduction electrons localize to form an insulating phase. The antiferromagnetic phase arises because of the ordering of the localized spins. We have compared the experimental results with the microscopic theory of the Mott transition. It is apparent that the current microscopic theories of the Mott transition are inadequate.

Finally we remark that there are important qualitative differences between the V_2O_3 transition and that which occurs in a number of other oxides. Both VO_2 or Ti_2O_3 remain paramagnetic[20,7] and thus in contrast to V_2O_3, are describable both above and below the metal-insulator transition by band theory. However, in view of the importance of the Coulomb interaction between the electrons in V_2O_3, we should expect important many-body effects also in the other oxides.

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