

Metal-insulator transition in pure and Cr-doped V_2O_3

C. Castellani,* C. R. Natoli,† and J. Ranninger

Groupe des Transitions de Phases, Centre National de la Recherche Scientifique, Boîte Postale 166, 38042 Grenoble Cedex, France

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On the basis of our theoretical examination of the insulating state of V_2O_3 reported in the preceding two papers and the experimental results of NMR and susceptibility measurements of the metallic phase, we conjecture the highly correlated electron-gas character in this latter phase of V_2O_3 . We present arguments for the first-order metal-insulator transition which we consider to be entropy driven passing from the insulating state to a paramagnetic metallic one of nearly equal inner energy but considerably different entropy due to the breakdown of the magnetic and orbital long-range order present in the insulating phase. We believe that the origin of the highly correlated electron gas in the paramagnetic metallic phase lies in the stability of the electronic molecular state of the V pairs along the c axis which persist through the metallic phase, a picture which estimates extremely well the observed entropy in this phase. The lattice distortion observed in the insulating phase is believed to be purely magnetostrictive and of no direct importance to the transition mechanism.

I. INTRODUCTION

In this, the third paper of a series, we shall analyze and put together the results obtained in the preceding two papers (I and II) on the insulating phase of V_2O_3 with what we can derive about the metallic phase on the basis of a phenomenological analysis, and thus hope to present a conclusive interpretation of the metal-insulator transition in V_2O_3 .

Since any discussion about this topic will inevitably involve the use of Mott's original argument,¹ it is not out of place to restate it here in order to emphasize the points which will be useful in the following.

As is well known, Mott has put forward the hypothesis that a crystalline array of hydrogen-like atoms or, more generally, atoms with incomplete shell, may not necessarily show metallic conduction, by which is meant a conductivity which does not vanish at absolute-zero temperature. The hypothesis states, moreover, that as the lattice parameter of the crystalline array is decreased, there will be at $T=0$ a *sharp* transition from a nonmetallic state (which is not conducting at absolute zero and in which there is a finite activation energy for conduction) to a metallic state with a finite or infinite conductivity at $T=0$. The reason resides in the long-range part of the Coulomb force which prevents an excited electron from being available for conduction due to the formation of a bound state with the hole left behind. It is only when there is a sufficient concentration of excited electrons per unit volume (such that the screening length of the screened Coulomb potential between particles and holes is of the order of the Bohr radius of the lowest bound state) that the mechanism hindering

conductivity breaks down and the excited electrons can become available for conduction.

In a subsequent paper,² Mott added more details to his picture especially as concerns the characterization of the nonconducting wave function in the insulating ground state of an array of monovalent atoms. The Heitler-London type of nonconductivity wave functions of the previous papers was explicitly constructed in the form of a Slater determinant of N functions (N is the number of atoms) $w_n(\vec{r})\chi_\alpha(\sigma)$, where $w_n(\vec{r})$ are Wannier functions, one for each site n , constructed out of all the Bloch wave functions in the band and $\chi_\alpha(\sigma)$ are spin-wave functions having a definite phase relation from site to site (for instance, antiferromagnetic, ferromagnetic, or describing some other spin order in more general cases). This wave function being real, hence describes a nonconducting state and clearly gives the lowest-ground-state energy for large interatomic distances. Mott further argued that the existence of metals leads one to believe that the Bloch-Wilson (band) state gives the lower energy for small interatomic distances. Moreover, he went on to sketch the behavior of the ground-state (GS) energy of a degenerate electron gas in the field of an array of ions and the GS energy of an array of overlapping hydrogenlike atoms with an antiferromagnetic spin arrangement. Plotted as a function of the lattice parameter b , this behavior is summarized in curve (a) of Fig. 5 of Sec. III where the portion ABC describes the metallic state and the portion DE describes the nonmetallic state. At $T=0$, only one of the two states is possible (one minimum slightly lower than the other), although for the case where the insulating state is more stable, a transition to the metallic state can be induced by application of an external

pressure which shifts and inverts the position of the two minima [curve (b)]. Notice that there might be a region of volume between points P and Q which is physically inaccessible.

Although not explicitly stated, it is clear from the context that the ground-state energy one is considering in this type of argument is the total energy of the *correlated* electron gas *interacting* with the ions of the lattice plus the interionic repulsion. As a consequence, because of the interplay between the outer potentially conducting electrons and the ions of the lattice, a possible distortion of the lattice (due to the different interaction of localized versus conducting electrons with the ions) is always to be expected when considering the phenomenon of metal-insulator transition in crystalline materials. This is despite the fact that at first appearance Mott's argument seems to suggest that the transition might occur without a change in long-range order in the lattice. Obviously the actual occurrence and the nature of the distortion vary from case to case, depending on the number of electrons in the incomplete shell, the number of relevant bands, their degeneracy and so on. It pertains to a correct analysis of the actual situation, case to case, to decide whether the observed transition is primarily a Mott (localized to delocalized) transition or whether it is primarily associated with a contingent opening of a band gap due to the change in periodicity. This is what we shall try to do in the case of V_2O_3 .

In this kind of investigation, it is important to understand the correlation among electrons in the insulating phase. Mott's 1961 paper² suggests a possible realization of an insulating ground state due to the interelectronic Coulomb repulsion, although that is not the only possible one (see the discussion on Ti_2O_3 ground state in Sec. V of II). Further elaboration of this theoretical model, through the work of Hubbard and many other investigations, has led to the description and definition of an insulating state of the Mott-Hubbard-Slater type, in which the electrons localize in the way suggested by Mott due to the Hubbard short-range repulsion U , the magnetic order being such as to maximize the number of jumps from one site to the other in order to minimize the kinetic energy. A Slater's type of gap is henceforth obtained which does moreover not necessarily disappear at the Néel temperature T_N , being due, as it is, to interelectronic short-range correlations. The insulating phase of V_2O_3 is a realization of this type of ground state.

Now it is well known that in a pure Hubbard model, where one neglects electron-phonon interaction, the transition from a Mott-Hubbard-

Slater insulating ground state to a conducting one with decreasing lattice parameter (that is to say with increasing hopping integrals in the model Hamiltonian) is of second-order. This is not surprising, one might argue, since the Hubbard model completely neglects the long-range part of Coulomb potential, which according to Mott's argument would be solely responsible for the sharpness of the transition. However, to our knowledge, it is not known as yet whether a pure Hubbard model with electron phonon interaction included would not lead to a first-order phase transition, even in absence of a Mott mechanism. On the other hand, this is a question that cannot be answered experimentally, but must be considered on a theoretical level, since in practice the two types of interactions are always present in the physical realization of the model. Hence, when we speak of a sample undergoing a Mott transition, we should do it with this proviso in mind.

Finally, we want to emphasize, as explicitly noted by Mott, "that the sharp transition described above is only expected in an *infinite* lattice. For a finite number of atoms, there will be a *gradual* decrease in the weight of the ionized states in the wave function as the interatomic distance is increased or, in other words, a gradual transition from the LCAO model to the Heitler-London model." This suggests that the observation of a sharp transition of the Mott type is more likely to be observed in those systems where the overall symmetry of the insulating state wave function is different from that of the conducting state the conducting state having simply the periodicity of the lattice. In such cases, the symmetry change of the wave function guarantees that the transition involves an infinite ($\approx 10^{23}$) number of atoms. However, there might be special situations where a broad metal-to-insulator transition occurs even though a Mott mechanism is at work. This happens where there are no symmetry changes of the wave function in the two phases, but only a gradual change of its features at a local level. We contend that this is what happens in Ti_2O_3 .

In the following sections, we will discuss the phenomenology of the metal-to insulator transition in Ti_2O_3 and V_2O_3 in the light of these considerations.

II. METALLIC PHASE IN V_2O_3

As discussed at length in the preceding paper (II),³ an unrestricted Hartree-Fock (HF) calculation provides a reliable description of interelectronic correlations in the ordered phase of V_2O_3 .

However, its restricted version proves to be completely insufficient to account for correlation between electrons in the paramagnetic metallic phase. Only for completeness, we listed the PO-PS state in Tables II and IV of II³ in order to indicate the closeness of its energy to that of the ordered state AO-RS. Actually, a correct description of the correlated metallic phase would give a much lower value for the GS energy of the paramagnetic metallic phase and much nearer to the ordered state. Unfortunately, a reliable technique for a satisfactory calculation of the interelectronic correlation in a Hubbard model with $U \simeq W$ is not available at present and the problem must await further theoretical investigation. However, a phenomenological study of the metallic phase of V_2O_3 can provide us with those physical quantities needed for a discussion on the nature of the metal-insulator transition, as for instance the ground-state energy, the total entropy, and the electronic specific heat as a function of temperature.

Let us first look at the metallic phase of V_2O_3 at atmospheric pressure and temperatures between 160 and 320 °K, that is to say along the dashed curve CD in Fig. 1, which represents the well-known phase diagram⁴ in the temperature-pressure (P - T) plane for V_2O_3 or, equivalently, in the temperature-composition plane when doping V_2O_3 with Cr or Ti. Along this path, the suscep-

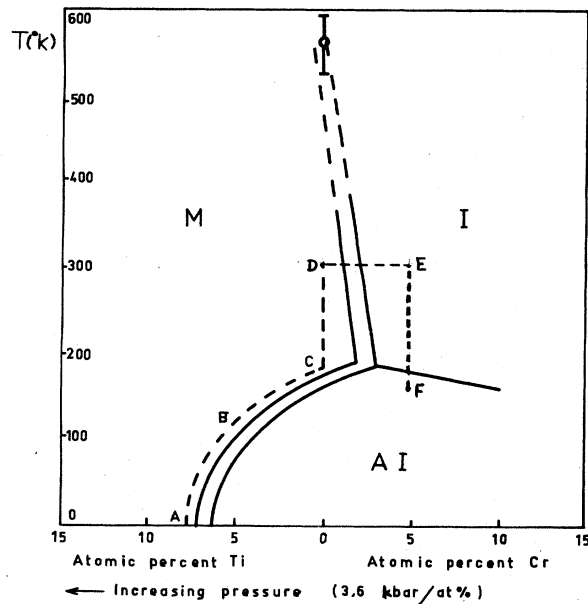


FIG. 1. Phase diagram for V_2O_3 as function of temperature, pressure, and doping (after McWhan *et al.* Ref. 4) (M-metallic, AI-antiferromagnetic insulator, I paramagnetic insulator).

tibility was measured⁵ in the temperature range 160–320 °K and interpreted on the basis of a Curie-Weiss law plus a Van Vleck contribution

$$\chi(T) = \chi_{VV} + \chi_a(T) \\ = 0.4 \times 10^{-3} + 1.3/(T + 600) \frac{\text{emu}}{\text{mole } V_2O_3}. \quad (2.1)$$

However, a more extensive set of measurements⁶ in the range 160–1000 °K has led to a somewhat lower value for the temperature-independent Van Vleck term with a fitting

$$\chi(T) = 0.21 \times 10^{-3} + 1.40/(T + 600), \\ 160 \text{ °K} < T < 350 \text{ °K}, \quad (2.2)$$

$$\chi(T) = 0.21 \times 10^{-3} + 1.78/(T + 600), \\ 580 \text{ °K} < T < 1000 \text{ °K},$$

with a cross-over region between the two regimes. Only for $\chi_{VV} = 0.21 \times 10^{-3}$ emu/(mole V_2O_3) was a Curie-Weiss behavior obtained for $\chi_a(T)$ in the high-temperature region. However, if there is enough evidence that the high-temperature phase (580 °K < T < 1000 °K) of V_2O_3 contains localized moments, as discussed more at length below, we feel that the magnetic susceptibility should be described in terms of a narrow-band temperature-dependent Stoner-enhanced Pauli paramagnetism, rather than a Curie-Weiss local moment approach in the lower-temperature region (160 °K < T < 350 °K). This point of view, suggested in Ref. 6 was also confirmed by the high-pressure low-temperature (4.2 °K) NMR results on V_2O_3 ,⁷ which showed that there are no localized magnetic moments in the metallic phase of V_2O_3 .

We want to show here that this interpretation is consistent with what we know about V_2O_3 in this temperature region, namely electronic specific heat, nuclear-spin relaxation rate and Stoner enhancement factor. For an m -fold degenerate band at the Fermi level (in our case $m = 2$, since the a_{1g} band has negligible contribution to the total density of states at the Fermi energy ϵ_F , as seen from Fig. 6 in II) we can write for the Stoner enhanced Pauli spin susceptibility

$$\chi_a(T) = N\mu_B^2 [\chi^0(T)/1 - \alpha(T)] \text{ (emu/mole } V_2O_3), \quad (2.3)$$

where

$$\chi^0(T) = \rho_b(\epsilon_F) \left\{ 1 + \frac{1}{6} \pi^2 (k_B T)^2 \right. \\ \left. \times \left[\frac{\rho_b''(\epsilon_F)}{\rho_b(\epsilon_F)} - \left(\frac{\rho_b'(\epsilon_F)}{\rho_b(\epsilon_F)} \right)^2 \right] \right\}, \quad (2.4)$$

$\rho_b(\epsilon_F)$ being the band density of states per eV and per molecule of V_2O_3 for both spin states and m bands. $\rho'_b(\epsilon_F)$ and $\rho''_b(\epsilon_F)$ represent the first and second derivative of the density of states $\rho_b(\epsilon)$ at the Fermi level. Thus, $\alpha(T)$ is given by

$$\alpha(T) = [U + (m-1)J]\chi^0(T)/4m, \quad (2.5)$$

since what appears in the Stoner enhancement factor is the density of states at the Fermi level per spin, per site, and per band. With a calculated value of $\rho'_b(\epsilon_F) = 20$ states/(molecule- V_2O_3 eV²) and $\rho''_b(\epsilon_F) = 0$, we see that the temperature correction at $T \approx 150$ K, just above the transition is negligible. Hence from a value of 1.8×10^{-3} emu/(mole V_2O_3), we find

$$\frac{\rho_b(\epsilon_F)}{1-\alpha} = 57.4 \frac{\text{states}}{\text{molecule } V_2O_3 \text{ eV}}. \quad (2.6)$$

Since we have calculated in Π^3 a value for $\rho_b(\epsilon_F) = 4$ states/(molecule- V_2O_3 eV), we find that α is very near to 1 (the precise value is not meaningful due to the uncertainty of the calculated $\rho_b(\epsilon_F)$ which in the permissible range of the hopping integrals in the kinetic-energy part of the Hubbard Hamiltonian varies between 4 and 5).

From

$$\alpha \sim 1 = \frac{4}{8}(U+J) = \frac{1}{2}(U+J), \quad (2.7)$$

we find that $U+J \approx 2$ eV which is what is barely necessary in order to obtain a gap in the calculated density of states in the ordered phase. Obviously, there might be a slight variation of U and J in going from the ordered phase to the metallic phase, but the consistency of the scheme is very satisfactory.

Notice that with a variation of $\chi^0(T)$ as a function of temperature of the type

$$\chi^0(T) = \chi^0(0)(1 - \beta T^2), \quad (2.8)$$

with $\beta T^2 \ll 1$ in the allowed range of temperatures, we derive

$$\chi^{-1}(T) \sim [1 - \alpha(0) + \beta T^2]/N\mu_B^2\chi^0(0); \quad (2.9)$$

that is to say, a quadratic variation of the inverse susceptibility with temperature. We cannot assess the validity of this conclusion since the only fit made for $160 \text{ K} < T < 350 \text{ K}$ for $1/\chi(T)$ is in terms of a linear law $aT + b$, and errors on measurements are not reported in the literature. It would probably be difficult to decide between aT and aT^2 behavior since the temperature interval of validity of (2.9) is very small. Another confirmation of the correctness of our description of V_2O_3 comes from the observation of the spin-lattice relaxation rate in NMR measurements for ^{51}V in V_2O_3 between 160 and 800 K.⁸ In the interval $160 \text{ K} < T < 350 \text{ K}$ a Korringa-type behavior

was observed for $1/T_1$ as a function of temperature ($1/T_1 T \approx \text{constant}$) which is characteristic for metallic behavior. Actually, if correctly interpreted, the measured values for $1/T_1 T$ in the above temperature range provide an independent confirmation that α is very near to 1 and varies approximately as $\alpha(T) = \alpha_0(1 - \beta T^2)$. Indeed, for a highly Stoner-enhanced electron gas, one can write

$$\frac{1}{T_1 T} = \frac{4\pi k_B}{\hbar} \left(\frac{\gamma_d}{\gamma_e} \right)^2 K_{cp}^2 \left[sK(\alpha) + r \left(\frac{H_{orb}^{hf}}{H_{spin}^{hf}} \right)^2 (1 - \alpha)^2 + t \left(\frac{H_{orb}^{hf}}{H_{spin}^{hf}} \right)^2 K(\alpha) \right], \quad (2.10)$$

where H_{orb}^{hf} is the hyperfine field due to the orbital magnetic moment and H_{spin}^{hf} is the hyperfine field due to the spin polarization of inner-core electrons by the magnetic moments of the outer d electrons. From an analysis of the Knight shift and susceptibility in metallic V_2O_3 , these fields were estimated by Jones⁵ to be 395 kOe/ μ_B and 140 kOe/ μ_B , respectively. (Actually, $H_{orb}^{hf} = 395$ kOe/ μ_B was estimated⁵ from the free-ion value $H_{orb}^{hf} = 2\beta\langle r^{-3} \rangle$ with $\langle r^{-3} \rangle = 3.2$ au for a V^{3+} ion. This led to a calculated Van Vleck susceptibility $\chi_{VV} = 0.4$ emu/(mole V_2O_3) which is twice what has been derived⁶ by fitting the high-temperature susceptibility measurements. If we trust this last value, H_{orb}^{hf} should be increased. (See discussion.) Moreover, $K_{cp} = (H_{orb}^{hf}/2N\beta)\chi_d(T)$ is the Knight shift due to the inner-core polarization [notice the factor $\frac{1}{2}$ since we are using susceptibility emu/(mole V_2O_3) unites, whereas Jones in Ref. 5 used susceptibility emu/mole V]. The quantities s , r , and t are the so-called core polarization, orbital, and dipolar reduction factors arising from the symmetry of the Fermi-surface $3d$ electrons.⁹ For instance, we have

$$q = f^2(a_{1g}) + \frac{1}{2}f^2(e_g) + \frac{1}{2}f^2(E_g), \quad (2.11)$$

where

$$f(\Gamma) = \sum_m \sum_{\alpha\sigma} \sum_{\lambda \vec{k}} |v_{\alpha m \sigma}^\lambda(\vec{k})|^2 \delta[\omega_\lambda(\vec{k}) - \omega_F] \rho(\omega_F)^{-1}, \quad (2.12)$$

the symbol $|v_{\alpha m \sigma}^\lambda(\vec{k})|^2$ indicating the Fermi-level fractional-admixture coefficients which have the same value for all m belonging to a given representation $\Gamma(m)$. The quantities $v_{\alpha m \sigma}^\lambda(\vec{k})$ have been defined in Eq. (3.37) of Π^3 and m denotes the symmetry character inside a given irreducible representation. From (2.12), it is obvious that

$$\sum_{\Gamma} f(\Gamma) = f(a_{1g}) + f(e_g) + f(E_g) = 1. \quad (2.13)$$

Reference 9 also gives expressions to calculate

r and t . Finally, the quantity $K(\alpha) = \langle |(1-\alpha)/[1-\alpha F(\vec{q})]|^2 \rangle$ represents the average of the quantity $|(1-\alpha)/[1-\alpha F(\vec{q})]|^2$ taken over the Fermi surface, i.e., over the values of \vec{q} satisfying $\epsilon_{\vec{k}+\vec{q}} = \epsilon_F$.¹⁰ The function $F(\vec{q})$ is defined by

$$\lim_{\omega \rightarrow 0} \chi'_0(\vec{q}, \omega) = \chi_0(\vec{q} = 0, 0) F(\vec{q}), \quad (2.14)$$

where $\chi_0(\vec{q}, \omega)$ is the noninteracting \vec{q} and ω -dependent susceptibility and $\chi'_0(\vec{q}, \omega)$ is its real part.

There are a number of ways in which our formula (2.10) for the relaxation-rate data differs from the one given in Ref. 8, namely

$$\frac{1}{T_1 T} = \frac{4\pi k_B}{\hbar} \left(\frac{\gamma_n}{\gamma_e} \right)^2 K_{cp}^2 \left[s + r \left(\frac{H_{orb}^{hf}}{H_{spin}^{hf}} \right)^2 \right] K(\alpha). \quad (2.15)$$

First of all, the quantity $K(\alpha)$ should not multiply the orbital part of the relaxation rate, since this latter is proportional to the density-density correlation function¹⁰ which is not enhanced. Hence only a factor $(1-\alpha)^2$ should appear in front of the orbital relaxation part, since we have pulled out K_{cp}^2 which is proportional to the square of the static uniform susceptibility, hence enhanced by the factor $(1-\alpha)^{-2}$. Secondly, we have retained the dipolar contribution to the relaxation rate which was neglected in Ref. 8 and indeed can usually be neglected. However, keeping in mind that the dipolar contribution is proportional to a spin-spin correlation function, in highly Stoner-enhanced systems the susceptibility enhancement factor can make up for this intrinsic smallness of the dipolar contribution. Finally the reduction factors s , r , and t are to be calculated remembering that in the metallic phase of V_2O_3 the partial density of states of a_{1g} character at the Fermi level is negligible as one can see from Fig. 6 of II. The same is true for the density of E_g character. Hence from (2.13) and (2.11) we derive $q = \frac{1}{2}$; this is to be compared with the value $q = \frac{1}{3}$ calculated in Ref. 8 by assuming an equal presence of fractional admixture coefficients for all the symmetry types belonging to the T_{2g} representation. In such a case $f(a_{1g}) = \frac{1}{3}$, $f(e_g) = \frac{2}{3}$, and $q = f^2(a_{1g}) + \frac{1}{2}f^2(e_g) = \frac{1}{3}$ as derived in Ref. 8. Under the same assumption, we calculate⁹ using the e_g subspace $r = \frac{2}{3}$ which happens to coincide with the value used in Ref. 8. Moreover, we estimate⁹ $t = \frac{1}{5} \frac{2}{3}$. By inserting the appropriate numerical values in Eq. (2.10) we obtain

$$\frac{1}{T_1 T} = (2.62 \times 10^5) K_{cp}^2 [0.85K(\alpha) + 1.77(1-\alpha)^2], \quad (2.16)$$

having used $|H_{orb}^{hf}/H_{spin}^{hf}| = 395/140$.⁵ The function

$K(\alpha)$ has been calculated by Narath⁹ for a spherical Fermi surface and is shown in Fig. 2 [curve indicated by $K^d(\alpha)$]. However, the d band of e_g character which we are concerned with in the case of metallic V_2O_3 is a very narrow band (≈ 0.5 eV) so that we expect in such a case a function $K^d(\alpha)$ of the form also shown in Fig. 2, since $F(\vec{q})$ in (2.14) is very near to 1. [In any case $K(\alpha)$ should go to zero at $\alpha = 1$ since the integral $\int d^3 q \delta(\epsilon_{\vec{k}+\vec{q}} - \epsilon_F) |1 - \alpha F(\vec{q})|^{-2}$ is convergent for $\alpha = 1$] (see Narath in Ref. 9). Table I shows the measured values⁸ of the quantity $1/TT_1$ in the temperature range $160^\circ K < T < 320^\circ K$ together with the values of $K_{cp} = \alpha_d \chi_d$ taken from Ref. 5 ($\alpha_d = -25[\text{emu}/(\text{mole } VO_{1.5})]^{-1}$ and $\chi_d(T) = 0.657/(T + 600)$ emu/(mole $VO_{1.5}$)) and the ratio $1/TT_1 K_{cp}$ (2.62×10^5). It appears that α is of the order of 0.8 and decreasing approximately as $(1 - \beta T^2)$. The actual value found for α should not be taken too seriously since it depends critically on the assumed value for H_{orb}^{hf} ⁵; however, it constitutes sufficient indication and extra evidence that the electron gas in the metallic phase of V_2O_3 is strongly Stoner enhanced, consistent with what we assumed at the beginning. To assess the kind of criticality present in the derivation of α , notice that the frequency shift $\Delta\nu/\nu = K_{tot}$ is given by

$$K_{tot} = K_{cp} + K_{orb} = (H_{spin}^{hf}/N\mu_B)\chi_d(T) + (H_{orb}^{hf}/N\mu_B)\chi_{VV}, \quad (2.17)$$

where $\alpha_d = H_{spin}^{hf}/N\mu_B$ is estimated⁵ to be $-25[\text{emu}/(\text{mole } VO_{1.5})]^{-1}$ from the slope of the plot K_{tot} vs $\chi_d(T)$ and $H_{orb}^{hf}/N\mu_B = 2/N\langle r^{-3} \rangle$ has been calculated assuming $\langle r^{-3} \rangle = 3.2$ au for the V^{3+} ion. Combined with the measurements of the total susceptibility,

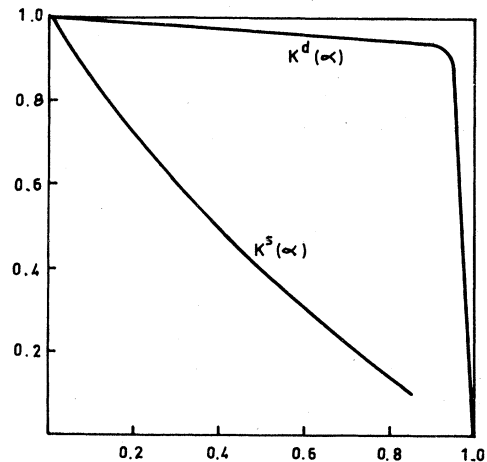


FIG. 2. Plot of the function $K(\alpha)$ of Eq. (2.10) for s and d electrons (after Narath, Ref. 9).

TABLE I. NMR relaxation time T_1 , susceptibility χ_d and the Knight shift in the temperature regime 160–320 °K.

$T(^{\circ}\text{K})$	160	200	240	280	320
$1/T_1 T \text{ sec}^{-1} \text{ } ^{\circ}\text{K}^{-1}$ ^a	113.2	102.8	92.6	86.4	82.9
$10^4 \chi_d \text{ emu/mole V}$ ^b	8.65	8.21	7.82	7.46	7.14
K_{cp} ^c	0.0216	0.0205	0.0195	0.0186	0.0178
$(\gamma_n/\gamma_e)^2 (4\pi k_B/\hbar) K_{cp}^2$ ^d	122.23	110.10	99.62	90.64	83.0
$[T_1 T (\gamma_n/\gamma_e)^2 (4\pi k_B/\hbar) K_{cp}^2]^{-1}$	0.93	0.93	0.93	0.95	1.00

^a From Ref. 8.

^b From Ref. 5 $\chi_d = 0.657/(T+600)$ [emu/(mole V)].

^c From Ref. 5 $K_{cp} = \alpha_d \chi_d$ with $\alpha_d = -25$ [emu/(mole V)].

^d $(\gamma_n/\gamma_e)^2 4\pi k_B/\hbar = 10^5 \times 2.62 \text{ sec } ^{\circ}\text{K}^{-1}$.

this value has provided⁵ the estimation $\chi_{VV} = 2.1 \times 10^{-4}$ emu/(mole $\text{VO}_{1.5}$), a value twice that found for χ_{VV} in the temperature region⁶ 580 °K $< T < 1000$ °K. We do not know the solution to this problem since one would be inclined to assume that χ_{VV} is constant in the region 160 °K $< T < 1000$ °K. If we believe the value found in Ref. 6, $\chi_{VV} = 0.1 \times 10^{-4}$ emu/(mole $\text{VO}_{1.5}$), we should double the value for H_{orb}^{hf} to be consistent with (2.17). Going back to (2.10), this would lead to a value of $\alpha \approx 1$. However, twice the value for $H_{orb}^{hf} = 2\mu_B \langle r^{-3} \rangle$ would imply for $\langle r^{-3} \rangle$ in V_2O_3 twice the value for V^{3+} free ion, an increase hardly justifiable.

Summarizing, we believe that the magnetic properties of metallic V_2O_3 in the temperature range 160 °K $< T < 350$ °K are satisfactorily described by a $3d$ (e_g symmetry) band model with highly Stoner-enhanced susceptibility. This is also true for the electronic properties of the system, as for instance the electronic specific heat, optical and soft-x-rays absorption spectra, resistivity, and Hall coefficient. We will not go into details but merely touch upon these points.

Concerning the electronic specific heat just above the transition, we calculate, using $\rho_b(\epsilon_F) = 4-5$ states/(eV molecule- V_2O_3), a value of $\gamma T_t = \frac{1}{3} \pi^2 N k_B^2 \rho_b(\epsilon_F) T_t \approx 0.4$ cal/(mole- V_2O_3 °K) for $T = T_t = 150$ °K. This is in keeping with what one can infer from total specific-heat measurements in V_2O_3 which shows practically no variation $[0 \pm 0.5 \text{ cal}/(\text{mole-}\text{V}_2\text{O}_3 \text{ } ^{\circ}\text{K})]$ ¹¹ of the observed total specific heat as measured just below and above the transition temperature T_t . If one assumes that the lattice specific heat does not vary at the transition, any discontinuity in the extrapolated specific-heat curve from below T_t would be a measure of the electronic contribution to it in the metallic phase. We shall actually see

that one also expects a slight increase in lattice specific heat by increasing temperature since the metallic phase is "softer" than the insulating phase. Hence any observed jump in the total specific heat presents an upper limit to the amount of electronic specific heat.

Regarding the other points (as for instance optical and soft-x-rays absorption spectra) there is reasonable agreements between calculated band structure and experimental results.¹² Also a p -type Hall coefficient is reasonably expected on the basis of the electron and hole Fermi surfaces in a two-band model,¹² whereas the resistivity behaves as that of a normal metal.¹³ However, an interesting feature emerges from resistivity measurements at low temperatures ($< T_t$) and high pressure.¹² The data clearly show a very large T^2 term at low temperatures in the resistivity that saturates at around 100 °K, where a normal metallic behavior takes over. This fact points to a low characteristic-correlation energy of the electron system on the order of 0.01 eV. Consequently, one also expects some kind of electronic specific-heat enhancement at low temperatures and high pressures. Indeed measurements under these conditions¹⁴ yield an effective density of state at the Fermi level on the order of ≈ 26 states/(eV molecule- V_2O_3) if one uses the relation $\gamma_{obs} = \frac{1}{3} \pi^2 N k_B^2 \rho_{eff}(\epsilon_F)$. This is one order of magnitude more than what is usually encountered in transition metals and indicates a strong mass enhancement of the electrons at the Fermi level. Moreover, it is natural to expect a decrease of the γ_{obs} value of the specific heat with temperature, with a marked drop around $T = 100$ °K corresponding to the turnover in the resistivity behavior. Putting together all these pieces of information, one expects that along the path ABC of Fig. 1, the behavior of $\gamma_{obs}(T)$ looks as sketched

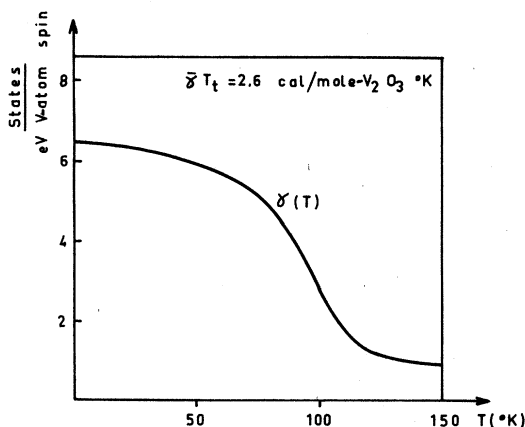


FIG. 3. Temperature dependence of the γ value for the specific heat.

in Fig. 3. Since the integral

$$\int_{ABC} \frac{C_v(T)}{T} dT = \int_{ABC} \gamma_{\text{obs}}(T) dT \quad (2.18)$$

represents the entropy of the electron system, the area underneath the $\gamma(T)$ curve in Fig. 3 provides an estimation of the electronic entropy content of the metallic phase at $T = T_t$ and atmospheric pressure. One finds that it roughly represents half the total entropy change observed at the antiferromagnetic insulator-metal transition at $T = T_t$, which is the area under the horizontal straight line at $\bar{\gamma}$, defined in such a way that $\bar{\gamma}T_t = \Delta S = 2.6$ cal/(mole- V_2O_3 °K). The rest of the entropy must then be provided by the lattice, as will be discussed later on. That the electron system in the metallic phase at atmospheric pressure is one of high-entropy content, is a speculation that has already been put forward by some authors¹⁵ from entropy considerations related to the phase diagram shown in Fig. 1. The same authors also have suggested that the anomalous behavior of the metallic phase of V_2O_3 at low temperatures under pressures can be at least qualitatively understood by using the concept of spin fluctuations. According to their argument, starting from the band picture of the metal as the metal-insulator transition is approached there are strong spin fluctuations (or paramagnons) as electrons become more and more localized. The theory of paramagnons¹⁶ predicts an enhanced specific heat at low temperature and a large T^2 term in the resistivity. 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. This behavior occurs near a ferromagnetic instability, although similar

results are expected in antiferromagnetic systems. Although apparently in qualitative agreement with experimental observations (quantitatively, the calculated T_{sf} turns out to be ≈ 500 °K for instance), the spin-fluctuation approach is unlikely to represent the true state of affairs in V_2O_3 . The reason is that spin correlations in this latter are typically short-ranged, confined mainly to within vertical pairs although interaction and correlation with neighboring pairs is not negligible. We shall try to sketch our point of view, although in a qualitative way, since calculation are difficult to carry out in the regime $U \approx W$ and have not yet been attempted.

Based on the experience gained in II, this new way of looking at V_2O_3 starts from the observation that the hopping integrals for e_g electrons are slightly stronger (by a factor approximately 1.5) for hopping inside the vertical pairs than for hopping to neighboring pairs (the a_{1g} electrons can be neglected in this argument since they already form covalent bonding pairs along the vertical direction and lie below the molecular level of the e_g electrons, so that they practically have no influence in determining the energetics of the system). Probably even the energy U to be paid to put the two electrons of the vertical pairs on the same site is slightly lower than the energy to put one of them on a site of the neighboring pairs, although this difference has been neglected in the model Hamiltonian of I¹⁷ and II.

All these facts lead us to consider to a very first approximation V_2O_3 as an assembly of diatomic molecules "weakly" interacting, with the *proviso* that at the end of the argument this intermolecular interaction should be substantially increased. The molecular-wave functions, together with the corresponding energies and degeneration are given in Table II where the labeling of the states has been made following the conventions used in Sec. III of I, and we remember that $\epsilon(x) = \frac{1}{2}[x - (x^2 + 16\mu^2)^{1/2}]$, μ being the transfer integral $t_{11} = t_{22}$ along the vertical direction. As one can see, there are three states which have energies ϵ_1 , ϵ_2 , and ϵ_3 very near the ground-state energy ϵ_G , the difference being on the order J/U whereas all other states have energies different from ϵ_G on the order of U . For N such weakly interacting molecules one would expect an energy spectrum of the type

$$E_G = N\epsilon_G, \quad E_{\text{ex}} = N\epsilon_G + \epsilon_i - \epsilon_G, \quad (2.19)$$

that is to say, with a finite gap between the ground state and the low-lying excited states, such that $(E_{\text{ex}} - E_G)/E_G \propto (\epsilon_i - \epsilon_G)/N$. It is assumed that this excitation-spectrum structure will hold with increasing strength of intermolecular interaction,

TABLE II. Molecular wave functions together with their corresponding degeneracies and energies.

State	Degeneracy	Energy	State	Degeneracy	Energy
0 $ \psi_s\rangle \phi_t\rangle$	3	$\epsilon(U' - J)$	4 $ \psi_s\rangle \phi_s\rangle$	1	0
1 $ \psi_t\rangle \phi_s\rangle$	1	$\epsilon(U' + J)$	5 $ \psi_t\rangle \phi_t\rangle$	3	0
2 $ \chi^-\rangle \phi_s\rangle$	1	$\epsilon(U - J)$	6 $ \chi^-\rangle \phi_t\rangle$	3	0
3 $ \chi^+\rangle \phi_s\rangle$	1	$\epsilon(U + J)$	7 $ \chi^+\rangle \phi_t\rangle$	3	0
$\epsilon(x) = \frac{1}{2}[x - (x^2 + 16\mu^2)^{1/2}]_{(\mu/x) \rightarrow 0} - 4\mu^2/x$					

provided it remains below a certain critical value, above which a Fermi-like type of excitation spectrum is obtained. As is well known in this latter case

$$E_G \simeq N\epsilon_F, \quad E_{\text{ex}} \simeq N\epsilon_F + (1/N)\epsilon_F, \quad (2.20)$$

so that

$$(E_{\text{ex}} - E_G)/E_c \propto \epsilon_F/N^2.$$

It is realized that the difference between the two excitation spectra is much like the one between an antiferromagnetic system and a Kondo system. A crossover between the two regimes can be obtained either by varying the intermolecular interaction strength or by increasing temperature such that

$$kT_c \simeq \epsilon_i - \epsilon_G \simeq O(J/U) \simeq 0.1 \text{ eV} \simeq 10^3 \text{ }^\circ\text{K}.$$

However, one expects that the intermolecular interaction, although below its critical strength, can widen $\epsilon_i - \epsilon_G$ into a band while always retaining a finite gap. In such a case T_c would be considerably lower.

It is to be noticed however, that this picture is complicated by the fact that the ground state ϵ_G in Eq. (2.19) is $3N$ -times spin degenerated. We think that a nondegenerate ground state is restored by formation of clusters of molecules with total spin equal to zero (in average, these clusters might be constituted by a molecule with six first neighbors). The intermolecular correlation might be such as to make the intramolecular excitations (from state 0 to state 1, 2, and 3 in Table II) lower in energy than those leading to the breaking of clusters. This is in keeping with the fact already noticed in Sec. IV of II that the PO-RS state is always much closer to the ground state AO-RS than all the others, including those having a different spin order, the excitation AO-RS \rightarrow PO-RS indicating an intramolecular orbital excitation. In such a case, the molecular states we started from should be considered as resonance states, which however are sufficiently

well defined to give a substantial entropy contribution for $T > T_c$.

Under this assumption for the excitation spectrum, it is natural to expect an enhancement of the low-temperature specific heat and a T^2 term in the resistivity due to the intramolecular excitations described above (they take the form of an electron-hole resonance scattering when itinerancy is included). They both are expected to fade out at $T > T_c$. Moreover at $T > T_c$, it is expected that the states of the fully interacting system arising from the molecular states labeled 1, 2, and 3 in Table II, being fully excited, contribute to the entropy of the system a quantity of the order of $Nk_B \ln 3 = 2.2 \text{ cal}/(\text{mole-V}_2\text{O}_3 \text{ }^\circ\text{K})$ perhaps substantially reduced due to itinerancy and partially effective Pauli principle (remember that we considered the $3N$ -fold spin degeneracy of the ground state to remain frozen above T_c). In any case, the entropy content of the metallic phase of V_2O_3 at $T > T_c$ should be substantially higher than for a noncorrelated Fermi gas at the same temperature typically of the order of $10^{-2} \text{ cal}/(\text{mole-V}_2\text{O}_3 \text{ }^\circ\text{K})$. At still higher temperatures, one expects that the clusters will break and the intramolecular correlation substantially reduced. The system will then be describable as Stoner-enhanced Fermi liquid, corresponding to V_2O_3 under normal pressure in the temperature range $150 \text{ }^\circ\text{K} < T < 300 \text{ }^\circ\text{K}$. If the above picture is correct, one would expect a maximum of the susceptibility along the $ABCD$ curve in Fig. 1 for $T_c \simeq 100 \text{ }^\circ\text{K} < T < 150 \text{ }^\circ\text{K}$, rather than a nearly constant value slowly decreasing with temperature.

III. THERMODYNAMIC AND MICROSCOPIC CONSIDERATIONS OF THE ANTIFERROMAGNETIC-INSULATOR-METAL TRANSITIONS

From a thermodynamic point of view, it is easily understandable that there are crystalline materials that undergo a phase transition either at relatively low temperatures ($500 \text{ }^\circ\text{K}$ or less) or

at pressures easily attainable under laboratory conditions. The reason is that more or less by chance there happens to be two electronic states of the system with markedly different conduction properties which are very close in total internal ground-state energies (on the order of some hundreds of an eV). This is the case, for instance, for V_2O_3 , VO_2 , and NiS. Transition-metal compounds are the best candidates for this to happen, since the interaction with the ligand raises the s band in such a way that its screening effects on the interaction among the d electrons are removed. Hence a greater variety of possible ground states becomes available to the system, the d electrons constituting highly correlated electron gas. By increasing their hopping possibilities as one varies the type of metal cation or ligand, one can shift from an insulating situation to a conducting one in a fairly smooth way. That the total internal energies of the antiferromagnetic-insulator state and the metallic state in V_2O_3 are very close to each other can be inferred from an analysis of the phase diagram in Fig. 1. For the first-order phase transition in pure V_2O_3 at $T = T_t = 150^\circ\text{K}$ and atmospheric pressure, we obtain, by equalizing the Gibbs potential in the two phases

$$\Delta G = 0 = \Delta U - T\Delta S + P\Delta V, \quad (3.1)$$

where $\Delta U = U_2 - U_1$, 2 indicates the metallic phase, 1 the antiferromagnetic-insulator phase. From the measured values at the transition, $\Delta S = 2.6$ cal/(mole- V_2O_3 °K) and $\Delta V = -0.41$ cm³/ (mole V_2O_3),⁴ we derive

$$U_2 - U_1 = 1.5 \times 10^{-2} \text{ eV}/(\text{molecule-}V_2O_3), \quad (3.2)$$

a very small value. The difference in Table V of II between the PO-PS state and the AO-RS(e_g)PS(a_g) state, relative to $U = 1.8$ eV, $U' = 1.44$ eV, and $J = 0.18$ eV is five times larger, showing our inability to properly handle the correlation in the metallic state. For the (very likely) first-order phases transition under the pressure of 26 kbar and $T = 0$, we obtain, by using the same argument,

$$U_2 - U_1 = -P\Delta V = 1.0 \times 10^{-2} \text{ eV}/(\text{molecule-}V_2O_3), \quad (3.3)$$

where we have assumed for ΔV the value observed at $T = T_t = 150^\circ\text{K}$. This implies that

$$U_2(P = 1 \text{ bar}, T = 150^\circ\text{K}) - U_2(P = 26 \text{ kbar}, T = 0) = 5 \times 10^{-3} \text{ eV}/(\text{molecule-}V_2O_3), \quad (3.4)$$

assuming that

$$U_1(P = 1 \text{ bar}, T = 150^\circ\text{K}) \approx U_1(P = 26 \text{ kbar}, T = 0).$$

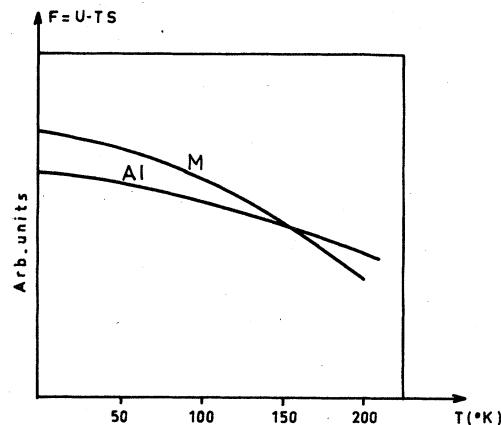


FIG. 4. Free energy as a function of temperature for the antiferromagnetic insulating (AI) and metallic paramagnetic (M) phase.

In such a case, the difference in (3.4) might reflect the difference in electronic correlation energies between the two metallic states of V_2O_3 , if the variation of the electron-lattice energy between them is neglected. Obviously, all this is highly speculative and much more refined calculations, including electron-phonon interaction would be needed before definitively accepting these conclusions.

In the light of the considerations in Sec. II, it is not surprising that the transition at $T = T_t$ is a first-order transition. Indeed, the entropy content of the metallic state is very high, even at moderately low temperatures (Fig. 3) and increases with temperatures much more rapidly than for the antiferromagnetic-insulator state. Hence the free-energy curves of the two states as a function of temperature are expected to cross with different slopes, as sketched in Fig. 4 [At atmospheric pressure the difference $P(V_2 - V_1)$ is negligible compared with the entropy term at all temperatures of interest, so that the term PV is constant in the two phases and can be dropped from the Gibbs potential.] Referring to Fig. 1, it is noticed that increasing pressure decreases the transition temperature which appears to remain first order as far as $T = 0$.¹⁵ Using the Clapeyron equation

$$\frac{dP_t}{dT_t} = \frac{\Delta S}{\Delta V}, \quad (3.5)$$

we can relate the derivation of the critical pressure P_t with respect to the transition temperature T_t and the ratio of the change of entropy at the transition over the change of volume. By assuming ΔV constant along the line separating the two phases and neglecting the entropy of the AI phase,

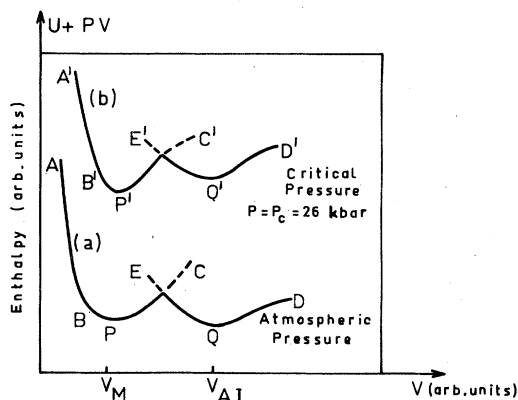


FIG. 5. Schematic drawing of the ground-state energies of an array of overlapping hydrogenlike atoms along with antiferromagnetic spin arrangement as a function of the lattice parameter.

the variation of $P_t(T_t)$ as a function of T_t should give an idea of the entropy of the metallic phase of V_2O_3 . Again, there is qualitative agreement with the area under the curve in Fig. 3, although the lack of numerical data for $P_t(T_t)$ did not allow a quantitative exploitation of Eq. (3.5).

Concerning in particular the transition under pressure at $T=0$, one might speculate about an internal total energy curve as a function of volume of the form shown in Fig. 5, with two minima corresponding to the two equilibrium positions of the lattice, respectively, in the antiferromagnetic-insulator phase and the metallic phase. At atmospheric pressure, the minimum corresponding to the insulating phase is lower than that corresponding to the metallic phase, whereas the contrary is true just above the critical pressure. However, the reason why the transition is first order should be sought at a microscopic level.

Indeed we feel that the metal insulator transitions along the curve $P_t(T_t)$ in Fig. 1 are driven by one and the same microscopic mechanism; only the way to excite the system varies, notably the thermal bath at a given temperature, pressure, or both together.

Let us start from the transition at $T=0$ under pressure. We think that the discussion on the insulating antiferromagnetic state in II^3 supports the conjecture that we are confronted in this case with an example of Mott transition (to be taken anyway with the proviso stated in the introduction). In fact the antiferromagnetic-insulator phase is an example of a Mott-Hubbard-Slater type of insulator, since the gap opens mainly because of a reduction of symmetry in the ground-state wave function brought about by interelectronic corre-

lations. In passing from the metallic state to the antiferromagnetic-insulator state the trigonal symmetry is lost because correlation between electrons in a doubly degenerate band energetically favors the kind of magnetic order discussed at length in I and II. In this type of ordering, one pair of V atoms in the basal plane wants to order ferromagnetically in contrast with the other two pairs for which an antiferromagnetic coupling is preferred [Fig. 5(a) of I]. Also the resulting distortion has been shown [Sec. VI of II] to be magnetostrictive in origin and, in any case, does not double the trigonal unit cell in the sense that the crystal's primitive cell has the same volume in the trigonal metallic phase as in the monoclinic phase.⁴ As a consequence, the Adler-Brooks mechanism¹⁸ for opening a gap is ruled out. It is however possible that the distortion cooperates with the interelectronic correlation mechanism to increase the width of the gap that would anyway have occurred, even in its absence. This is born out by a calculation in which we have reduced the hopping integrals along the directions where the distortion occurs (remember that there is an increase in distance along the vertical pair and one of the basal plane pairs in passing from the trigonal to the monoclinic phase).

It is tempting to consider the overall distortion as a result of a cooperative Jahn-Teller distortion taking place in molecular clusters like the one shown in Fig. 5(a) of I. This cluster is sufficient to reproduce the whole structure. It is evident that with one electron in a twofold degenerate level per site, one can have a molecular ground state which is orbitally degenerate, this degeneracy being lifted by the distortion of the cluster according to the instability already discussed. As a consequence, one expects the system to be sensitive to axial pressure in the basal plane and much less to axial pressure along the c axis. This is because in the basal plane the ferromagnetic coupling, to which the distortion is connected, is weaker [excitation energy of the order of $(t^2/U)(J/U)$] than for the other two antiferromagnetic couplings (excitation energy of the order of t^2/U) and applying pressure is equivalent to increasing the transfer integral and consequently the itinerancy of the electrons in such a way as to destroy the ferromagnetic spin polarization responsible for the distortion. Consequently, the trigonal symmetry is restored at a molecular level, favoring a local metallic state which serves as a nucleation center for other neighboring molecular clusters, until all the electronic solid "melts." The picture for the transition is similar at atmospheric pressure and $T = T_t = 150^\circ K$. There are two states of the system, the metallic

state and the antiferromagnetic-insulator state which have nearly equal internal energies, the metallic state having a big entropy content, the ordered antiferromagnetic insulator state having a low one. The metallic state is spin and orbit correlated at least at short range and this correlation becomes stronger as one approaches the AI phase from above ($T > T_t$). The transfer integrals are big enough not to support a long-range-ordered state. At $T = T_t$, some clusters begin to be magnetically polarized and distorted since locally the system gains energy by localizing the electrons and taking advantage of intra-site exchange energy. The arbitrary choice of a distortion axis of a molecule influences the next one in a sort of a cooperative Jahn-Teller effect, all three possible distortion axes being possible (the crystal is in fact twinned in the antiferromagnetic insulator state). On the other hand, increasing temperature in the AI phase creates spin deviations which at $T = T_t$ are sufficient enough to perturb some distorted molecules (the distortion being a consequence of the spin ordering!) which serve as nucleation centers for the electronic solid to "melt."

In both cases, whether the transition is brought about by increasing temperature or by pressure, the mechanism that seems to drive the transition is the disruption of the magnetic order which in turn restores the trigonal symmetry which favors the metallic state. The excitation of spin waves is a means to achieve a change of the relative weight of the polar states versus the nonpolar states, since, for instance, having an electron with the wrong sign on a site manifests the jumping possibilities of the neighboring electrons on that site. Accordingly the transition can be driven by one or by other means, provided they both lead to the ultimately essential feature, that is to say the modification of the relative weight of the polar versus the nonpolar states.

The precedent description of the low-temperature transition in V_2O_3 also points to a substantial contribution of the lattice degrees of freedom to the entropy of the metallic phase. Apart from the general consideration that the lattice in the metallic phase is softer than in the AI phase and therefore there are more phonons excited, the cooperative Jahn-Teller mechanism specifies the source of the lattice entropy. Indeed in the antiferromagnetic insulator phase the lattice is "ordered" since it has chosen in a cooperative way the distortion axis of the various molecular clusters. In the metallic phase however, the temperature is high enough to make the distortion axis uncorrelated with each other and even within the same probability so that the trigonal symmetry

is restored. It is the "excitation" of these degrees of freedom of the system that contribute to the extra lattice entropy at the transition.

Finally, we want to point out that in our interpretation of the low-temperature transition in V_2O_3 , the variation in the relative population of the a_{1g} band in the two phases plays little role, contrary to what has been suggested by some authors.¹⁹ Actually in both phases the a_{1g} electrons are engaged in a sort of covalent bond spread into a band; only a small number of states around the Fermi level is localized and promoted to the e_g band by the intra-atomic exchange mechanism in the AI phase as discussed in II and is affected by the transition to the metallic phase, more as a consequence of it rather than as a cause to it. The fact that the a_{1g} electrons are nearly all engaged in a diamagnetic bonding band throughout the V_2O_3 phase diagram in Fig. 1 should be kept in mind when calculating the spin entropy for the insulating phase. There is only one magnetic electron per site so that one expects a spin-disorder entropy in the insulating phase of the order $k_B \ln(2S+1)^{2N}$ where N is the number of molecules of V_2O_3 and $S = \frac{1}{2}$. This gives $S = 2.8$ cal/(mole- V_2O_3 °K) the value observed at the antiferromagnetic insulator-paramagnetic insulator transition for the Cr-doped samples.

IV. Cr-DOPED SAMPLES AND THE SECOND TRANSITION IN PURE V_2O_3

The phenomenology of the Cr-doped V_2O_3 samples can be read in the phase diagram of Fig. 1 and is thoroughly dealt with in the series of papers by McWhat *et al.* quoted in Ref. 1 of I. For our purpose, it suffices to recall that the metallic phase of V_2O_3 is completely suppressed by alloying with 2% or more of Cr so that along the path FE in Fig. 1 one passes from an antiferromagnetic insulator (AI) monoclinic phase to an insulating paramagnetic (I) trigonal phase. The interesting finding⁴ was that along the path ED at constant temperature of ≈ 300 °K by applying a pressure of ≈ 10 kbars, there is a reduction in resistivity of two orders of magnitude leading from a semiconducting to a metallic type of behavior. In passing from the I to the metallic M phase a strong reduction in volume [$\Delta V = -0.39$ cm³/(mole- V_2O_3)] takes place comparable to the one observed in the AI- M transition in pure V_2O_3 , but unlikely to the latter case, there is no change in symmetry at the transition. This was the feature which led the authors in Ref. 4 to conclude that they were confronted with a realization of a Mott transition. However if one takes a closer look at the system $(V_{1-x}Cr_x)_2O_3$, one realizes that

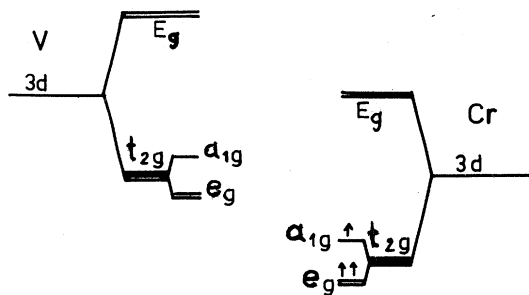


FIG. 6. The relative crystal-field-split energy levels of V and Cr for $(V_{1-x}Cr_x)_2O_3$.

the mechanism of the transition is not the one traditionally described by Mott,² although ultimately it is of course connected with a delocalization of the potentially conducting $3d$ electrons. In this respect, the transition in pure V_2O_3 at $T = 0$ pressure is much nearer to the original Mott description.

The mechanism of localization for the two $3d$ antibonding electrons in pure V_2O_3 when alloying with Cr_2O_3 is easily understood by looking at Fig. 6. Each Cr atom carries three $3d$ electrons occupying the t_{2g} subband coupled to spin $\frac{3}{2}$ according to intraatomic Hund's rule. To put another electron on a site occupied by a Cr atom would require in a weak-field scheme the occupancy of one of the upper E_g levels, with the same polarization as the other electrons. Taking into account the fact that the reference $3d$ level is lower for Cr atoms than for V atoms and that there is intra-atomic exchange energy gain if another electron with the right spin polarization occupies one of the E_g levels, the process might easily cost some fractions of an eV. In this way, it is as if each Cr-occupied site (Cr substitutionally replaces V atoms in the corundum lattice) has to be counted as a site onto which the V- $3d$ electrons cannot jump, due to the presence of an effective repulsive-potential barrier. Hence, increasing the Cr percentage effectively means increase of the nonpolar state weight versus the polar states, leading to a final situation of nonconductivity. In other words, we are confronted with a type of percolation problem and in this respect it is interesting that the same suppression of the metallic phase occurs by alloying with Al_2O_3 . Similarly in this latter case, one can argue that the next available state on an Al-occupied site is a $3s$ antibonding state, since the three electrons outside the Ne closed shell in the configuration $3s^23p^1$ in Al atoms have gone to

fill the ligand-field bonding states. However, since the $3s$ states are quite spread out, they mix quite strongly with the $2p$ oxygen states, so that the bonding-antibonding gap is quite large. Consequently, the same situation as for the Cr-doped samples is met.

Concerning the interpretation of the mechanism driving the transition, we are not aware as yet of a theoretical treatment of the model we have been describing including electron-phonon interaction. So it is difficult to disentangle the role of randomness in bringing about the electron localization from other specific factors causing localization. Nor is it possible to assess the order of the transition with and without a Mott mechanism at work. As in the case of the zero-temperature transition under pressure for pure V_2O_3 , it might as well be that a Hubbard model with electron-phonon interaction and a percentage of random sites occupied by Cr atoms having atomic levels as shown in Fig. 6 might lead to a first-order transition under pressure assuming that the main effect of pressure is to bring down the E_g levels at Cr-occupied sites besides increasing the intrasite hopping integrals.

In both cases, it would be very useful to assess the role of the phonon entropy in driving the $M-I$ or $M-AI$ transitions. Neutron measurements of the phonon spectrum below and above the transition would be very valuable in this respect.

Finally, we want to comment briefly on the nature of the second transition in pure V_2O_3 at atmospheric pressure around $T = 500$ °K. The transition manifests itself in an anomalous increase in the susceptibility spread in a temperature range of 200 °K (400 °K $< T < 600$ °K) with a connected increase in resistivity. The kind of microscopic state that the system assumes in this temperature region has already been described at the end of Sec. II. What remains to be illustrated is the reason why the transition is so broad. We feel that this reason resides in the fact that the wave function of the system is modified only at a local level, more explicitly at a molecular level. The situation should be similar to what happens in Ti_2O_3 where at the transition (as broad as the second one in V_2O_3) it is mainly the intramolecular correlations of the vertical pairs that are modified. The only difference in the two cases is the direction of change; in Ti_2O_3 the change is towards a weakening of the Hubbard U due to increasing screening with the result of increasing the strength of the polar states (more bandlike) whereas the contrary is true for V_2O_3 .

- *Present address: Istituto di Fisica, G. Marconi, Piazzale delle Scienze, 00100 Rome and Gruppo Nazionale di Struttura della Materia, L'Aquila, Italy.
- †Present address: Laboratori Nazionali Frascati, Istituto Nazionale di Fisica Nucleare, 00044 Frascati, Italy.
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