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Thermodynamic Theory of the Phase Diagram of Mixed Transition-Metal Oxides

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The model of Falicov and Kimball for metal-insulator transitions has been extended to include two types of localized states and the effect of spin-spin interactions. This allows for the description of the phase diagrams of mixed transition-metal oxides of the type $(V_{1-x}Cr_x)_2O_3$.

I. INTRODUCTION

Of the many systems that exhibit a metal-insulator transition the most extensively studied are V_2O_3 and systems with the generic composition $(V_xM_{1-x})_2O_3$ (where M may be Cr, Al, or Ti), particularly $(V_xCr_{1-x})_2O$. Crystalline and magnetic structures[1,2] as well as transport and magnetic properties[3,4] and optical absorption[5] have been experimentally determined by different methods.

This enabled McWhan, Rice, and Remeika[6] to propose a phase diagram for V_2O_3 doped with Cr and Ti presenting three phases: insulator (I), metal (M), and antiferromagnetic semiconductor (AF). Figure 1 shows this phase diagram for the case of 4 at.% Cr. For pressures up to about 6 kbar the low-temperature AF phase shows a transition to a paramagnetic state at 180 K accompanied by a structural change from monoclinic to

trigonal α-corundum. In the range 6–13 kbar the AF phase makes a sharp first-order transition to a metallic state at about 170 K with a similar structural change. Upon further heating in this pressure range, there is a second first-order transition to a paramagnetic insulating phase. The line in the p-T diagram along which this second transition occurs terminates at a critical point similar in every respect to the classical liquid-gas critical point. Above 13 kbar and up to 40 kbar the temperature for the AF-M transition decreases gradually to zero.

Addition of Cr or Ti has the general effect of displacing the phase boundaries to the right or to the left, respectively, at the rate of 3.6 kbar/at.% of impurity.

Susceptibility measurements[4] in the I phase give a Curie-Weiss law with an effective magneton number close to the spin-only value of the $3d^2$ configuration for V^{3+}.

Measurements of magnetic properties[4] in the metallic phase show strong paramagnetism but do not admit a straightforward interpretation. The metallic phase is peculiar in other respects as well. The resistivity shows a T^2 term which could be due to Baber electron-hole scattering, paramagnon scattering,[7] or other many-body effects derived from hybridization of the d states.

Several models have been proposed to explain metal-insulator transitions.[8] However, none of these can explain in a simple manner the existence of a critical point and the occurrence of two transitions for certain pressures. Neither does any of them rely on a mechanism which is shared by a whole family of substances (containing ions with unfilled d or f shells) which show this type of transitions.

A model that can be used to describe the phase diagram of all the substances in question has been proposed by Falicov and Kimball (FK).[9] It is based on the existence of localized or almost localized states (derived from the unfilled d or f states) and itinerant-electron states. The transition is brought about by the change in occupation of these states, the driving force being the Coulomb repulsion between both types of states.

There do not appear to be reliable band-structure calculations for V_2O_3 available at present. This precludes making a definite assignation of the localized and Bloch states as originating from different atomic orbitals. On the basis of the simplest considerations related to the nature of the states it would seem logical to identify the $3d$ and $4s$ bands with localized and extended states, respectively. In this picture the metal-insulator transition would result from the crossover of the $3d$ and $4s$ bands. However, the possibility of both types of states ensuing from the d band as a result of the combined influence of the crystal field and intra-atomic Coulomb repulsion among other effects should not be disregarded. In fact, Goodenough[10] has pointed out that the anisotropy of the $3d$ wave functions may permit the simultaneous existence of localized and collective $3d$ states.

In the following sections we shall discuss an extension of the FK model which enables us to include a magnetically ordered phase at low temperatures as well as the effect of impurities. The main results have been previously reported in a short publication.[11] The inclusion of a low-temperature antiferromagnetic phase has also been discussed by Falicov, Gonçalves da Silva, and Huberman.[12]

The similarity between the M-I transition in $(V_{1-x}Cr_x)_2O_3$ and the α-γ transition in Ce has been pointed out by Rice and McWhan.[13] This is implicit in the equivalence between the FK model and the model used for the α-γ transition by Ramirez and Falicov.[14] Our discussion of the effect of Cr impurities on V_2O_3 will follow the lines already laid out in Ref. 15 concerning the effect of rare-earth addition on the phase diagram of Ce.

In Sec. II we discuss the generalization of the FK model to allow for the inclusion of two types of localized states, corresponding to the addition of transition-metal impurities. In Sec. III we discuss the special case of Cr as an impurity and show how the equivalence between increasing Cr concentration and decreasing pressure arises as a natural consequence of the model. The inclusion of an exchange energy to describe a low-temperature antiferromagnetic phase and its influence on the thermodynamics of the system are discussed in Sec. IV. Section V is devoted to a discussion of the

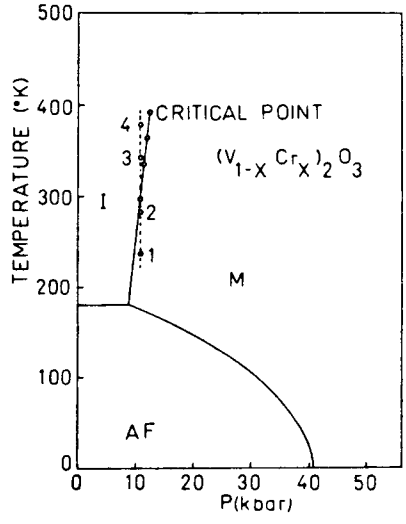

FIG. 1. Phase diagram for $(V_{1-x}Cr_x)_2O_3$ [as determined by Jarayaman, McWhan, Remeika, and Dernier (Ref. 17)].

limitations of the model and to general conclusions.

II MODEL HAMILTONIAN FOR MIXED OXIDES

In order to generalize the FK Hamiltonian to the case where two types of localized states are considered, we assume that reasonably small impurity concentrations do not affect either the position of the localized states in the host nor its band states. Thus we write

$$H=\sum_k \epsilon_k C_k^\dagger C_k+\Delta\sum_i b_i^\dagger b_i+\Delta'\sum_{i'} b_{i'}^\dagger b_{i'} + G\sum_i C_i^\dagger C_i b_i^\dagger b_i+G'\sum_{i'} C_{i'}^\dagger C_{i'} b_{i'}^\dagger b_{i'} \quad . \quad (2.1)$$

Here $C_k^\dagger$ creates an electron in a band state of energy ϵ_k; $b_i^\dagger$ creates an electron in a localized state at a V site (with energy Δ measured from the bottom of the conduction band); $b_{i'}^\dagger$ creates an electron in a localized state at an impurity site; G is the Coulomb interaction between an electron in the band and an electron in a localized state in V; G' is the Coulomb interaction between an electron in the band and an electron localized in an impurity site; and $C_i^\dagger$ creates an electron in the Wannier state at site i associated with the band. The localized states are assumed to be highly correlated atomiclike orbitals, with a given angular momentum.

Assuming now a rigid band and within the mean-field approximation we have for the energy

$$\mathcal{E}=\int_0^\infty d\epsilon\, D(\epsilon)n(\epsilon)+v\Delta N_0 n+x\Delta' N_0 n' + vGN_c n+xG' N_c n' \quad , \quad (2.2)$$

where $D(\epsilon)$ is the density of states in the band, $n(\epsilon)$ is the one-electron distribution function, N_0 is the number of transition-metal ions, v is the vanadium concentration, and $x=1-v$ the impurity concentration. N_c is the total number of conduction electrons

$$N_c=\int_0^\infty d\epsilon\, D(\epsilon)n(\epsilon) \quad . \quad (2.3)$$

Within the same approximation we have for the entropy:

$$\mathcal{S}=-\int_0^\infty d\epsilon\, D(\epsilon)\{n(\epsilon)\ln n(\epsilon)+[1-n(\epsilon)]\ln[1-n(\epsilon)]\} -N_0 v\,[n\ln n+(1-n)\ln(1-n)-n\ln g_I - (1-n)\ln g_M\,]-N_0 x\,[n'\ln n' +(1-n')\ln(1-n')-n'\ln g_I' -(1-n')\ln g_M'\,] \quad , \quad (2.4)$$

where the first term represents the entropy of the band electrons, while the second and third terms correspond to the V and impurity ions, respectively, the g's being the spin multiplicities of the localized states.

The next step is to minimize $\mathcal{F}=\mathcal{E}-T\mathcal{S}$ with respect to $n(\epsilon)$, n, and n' subject to the constraint

$$N_c+vN_0 n+xN_0 n'=vN_0+xN_0 \quad . \quad (2.5)$$

Variation with respect to $n(\epsilon)$ leads to

$$n(\epsilon)=\frac{1}{\exp[(\epsilon+Gvn+G'xn'-\lambda)/T]+1} \quad , \quad (2.6)$$

where λ is the Lagrange multiplier that accounts for the condition (2.5). In what follows, we shall replace the Fermi distribution (2.6) by a step function

$$n(\epsilon)=\Theta(\lambda-\epsilon-Gvn-G'xn') \quad . \quad (2.7)$$

We note that

$$\tilde{\epsilon}=\epsilon+Gvn+G'xn' \quad (2.8)$$

is the energy of the quasiparticles which includes the Coulomb repulsion with the localized electrons.

Explicit evaluation of N_c leads to

$$N_c=\alpha N_0(\lambda-Gvn-G'xn') \quad , \quad (2.9)$$

where the density of states has been taken as $D(\epsilon)=\alpha N_0$.

Combining (2.9) with (2.5) we have for the Fermi energy

$$\epsilon_F=\lambda=\frac{1-(vn+xn')}{\alpha}+Gvn+G'xn' \quad . \quad (2.10)$$

Using the step function for $n(\epsilon)$ implies neglecting the entropy of the conduction band. It is known[16] that the error one introduces thereby is of order αT per atom. We assume this to be negligible for the temperatures of interest here.

Using the above expression for the Fermi energy we can evaluate the energy of the band electrons $\mathcal{E}_b$. We obtain

$$\mathcal{E}_b=\int_0^\infty d\epsilon\, D(\epsilon)\epsilon n(\epsilon)=\tfrac{1}{2}\alpha N_0(\epsilon_F-Gvn-Gxn')^2 \quad . \quad (2.11)$$

Variation of $\mathcal{F}$ with respect to n and n' leads to the following expressions:

$$n=\frac{1}{(1/q')\exp[(\Delta+Gn_c-G_F)/T]+1} \quad , \quad (2.12)$$

$$n'=\frac{1}{(1/q')\exp[(\Delta'+Gn_c-G_F)/T]+1} \quad , \quad (2.13)$$

where $n_c=N_c/N_0$, $q=g_I/g_M$, $q'=g_I'/g_M'$.

It should again be noted that the energies of the localized states have been shifted by Gn_c. The factors $1/q$ in (2.12) and (2.13) appear as a consequence of the spin multiplicity of the localized states.

Inserting (2.11) into (2.2) and using (2.10) we can write the free energy as a function of n and n'.

III. EFFECT OF ALLOYING WITH Cr

On applying the model to the phase transitions in $(V_{1-x}Cr_x)_2O_3$ we feel justified in assuming that due to the similarity in electronic structure, the as-

sumptions made at the beginning of Sec. II are valid. The large distances[17] (~ 2.8 Å) between transition-metal ions as compared to their ionic radii (0.7 Å) give them further support.

From the fact that Cr_2O_3, having the same crystal structure, is an insulator, we infer that the Cr ion in V_2O_3 remains in the Cr^{3+} state for all temperatures and pressures of interest. This implies that Δ' is large and negative and therefore $n' = 1$.

Retaining only the terms which depend on n, the free energy per V atom is then

$$F = En - Bn^2 + T[n\ln n + (1-n)\ln(1-n) - n\ln q] \ , \tag{3.1}$$

where

$$E = E_0 - E_1 x \ , \tag{3.2a}$$

$$B = B_0(1-x) \ , \tag{3.2b}$$

with

$$E_0 = \Delta + G - 1/\alpha \ , \tag{3.2c}$$

$$E_1 = (G + G' - 1/\alpha) \ , \tag{3.2d}$$

$$E_0 = (G - 1/2\alpha) \ . \tag{3.2e}$$

For fixed values of E, B, and q the general shape of F at a temperature T_1 follows that of curve 1 in Fig. 2(a). Since the absolute minimum of F corresponds to n close to zero, we are in the metallic phase (such as point 1 in Fig. 1). As the temperature is increased F changes its shape as indicated by curves 2–4 of Fig. 2(a). For $T > T_2$ the absolute minimum of F has jumped to a value of n near to one, thus giving the M-I transition. This corresponds to moving through points 2–4 in the phase diagram (Fig. 1). The assumption that the V ions trap an electron on going from the M to the I phase is in agreement with the sudden increase in volume at the transition.

One may expect only small changes in the parameters Δ, G, and α with increasing pressure. However, since E and B are defined as differences between comparable quantities they will be sensitive to variations in pressure.[14]

If the changes are such that $E - B$ increases, a situation may be reached as in Fig. 2(b). For temperatures below the transition F has the shape of curve 1. Increasing T gives curves 2–4. Comparing with Fig. 2(a) we see a change from the previous abrupt jump in the value of n corresponding to the minimum of F to a gradual shift. This corresponds to a change in the order of the transition at T_c. Curve 3 corresponds to T_c and has a very flat minimum.

Figure 2(c) shows the variation of $F(n)$ at different temperatures for still higher pressures, corresponding to a supercritical transformation.

The extremal condition on F, Eq. (2.12), becomes

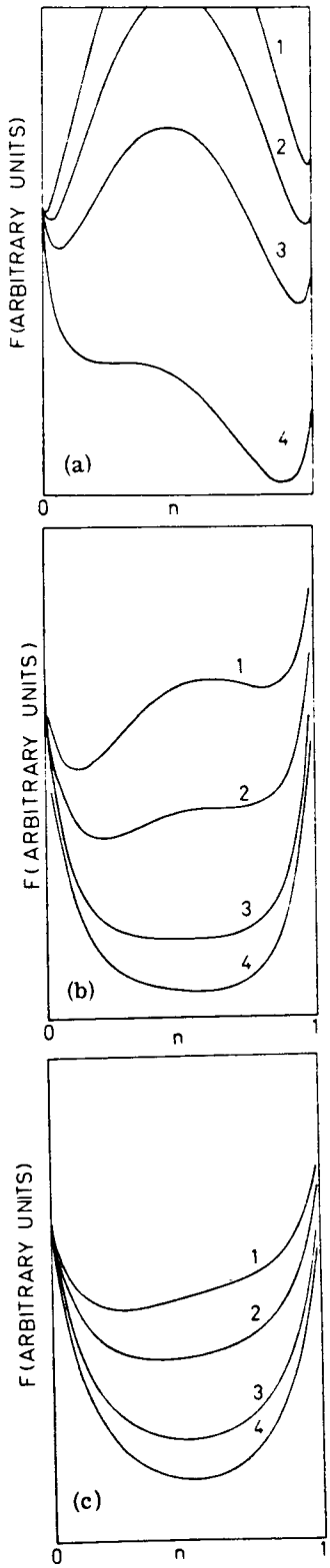

FIG. 2. Free energy as a function of n. Curves 1, 2, 3, and 4 are in order of increasing temperatures. (a) Curve 2 corresponds to a temperature at which a first-order transition occurs. (b) Curve 3 corresponds to a critical transition. (c) The situation for a supercritical transformation.

$$n = \frac{1}{(1/q)e^{E-2Bn/T}+1} = f(n) \quad . \tag{3.3}$$

This equation may in general have one, two, or three solutions. Figure 3 shows a graphical construction indicating a case where there are three solutions. In general, point B corresponds to the maximum in F, while A and C will correspond to the minima. It is necessary to calculate the values of F at these points to know which is the absolute minimum.

The transition temperatures are those at which the point corresponding to the maximum is located at $n = \frac{1}{2}$ (see Fig. 2). From (3.3) we have then

$$T_T = \frac{E-B}{\ln q} \quad . \tag{3.4}$$

The transition will be critical if dn/dT calculated at the transition temperature (T_c) is infinite. In this case, the three solutions in Fig. 2(c) have coalesced at $n = \frac{1}{2}$. Using (3.3) we have

$$\frac{dn}{dt} = \frac{\partial f}{\partial T} + \frac{\partial f}{\partial n}\frac{dn}{dT} \tag{3.5}$$

or

$$\frac{dn}{dT} = \frac{\partial f}{\partial T}\Big/\left(1 - \frac{\partial f}{\partial n}\right) \quad . \tag{3.6}$$

We see from (3.6) that the condition for a critical transition is $\partial f/\partial n = 1$ or

$$n^2 - n + T/2B = 0 \quad . \tag{3.7}$$

The condition for this equation to have a single solution at $n = \frac{1}{2}$ (corresponding to the coalescence of the three solutions in Fig. 3) implies

$$B_c = 2T_c \quad , \tag{3.8}$$

and from Eq. (3.4)

$$E_c = T_c(2 + \ln q) \quad , \tag{3.9}$$

where the subscript c indicates the values of the parameters that make the transition critical.

Following our previous argument we now take

$$E = E_0 - E_1 x + \gamma p \tag{3.10}$$

and

$$B = B_0(1-x) - \beta p \quad . \tag{3.11}$$

From Ref. 17 the critical pressures and temperatures with $x = 0.0375$, 0.0187, and 0.0135 are 12.5 kbar, 390 °K; 5.5 kbar, 433 °K; and 3.5 kbar, 443 °K, respectively. From Eqs. (3.8) and (3.11) we find

$$\frac{2T_c}{1-x} = B_0 - \beta\frac{p_c}{1-x} \quad . \tag{3.12}$$

The above given experimental values do in fact fall on the straight line given by Eq. (3.12). Graphical adjustment furnishes $B_0 = 936$ K and $\beta = 10$ K/kbar.

Existing experimental data[4] do not give clear indication regarding the degeneracy in the metallic phase. A number of effects could account for deviations from the spin-only value $g = 2$. These include hybridization of the localized state with the band, incomplete conversion to V^{4+}, crystal-field corrections and dynamic Jahn-Teller effect.[18] Many of these could lead to a temperature-dependent effective degeneracy $g_M(T)$.

In order to avoid as far as possible relying on the explicit form of $g_M(T)$ in the determination of the remaining parameters, we shall in Sec. IV discuss the second phase transition to the antiferromagnetic insulating phase and fix the parameters so as to reproduce the zero-temperature properties which are independent of entropy.

IV. ANTIFERROMAGNET-TO-METAL TRANSITION

In order to include the possibility of an antiferromagnetic phase, it is necessary to take into account the exchange energy between magnetic ions. The fact that increasing Cr concentration lowers the Néel temperature of $(V_{1-x}Cr_x)_2O_3$[4] suggests that one might neglect the exchange interaction of Cr ions. Gossard *et al.*[4] have found no evidence of ordering in the metallic phase down to 4.2 °K. For this reason we do not consider exchange interactions in this phase.

Within the molecular-field approximation we have for the exchange energy per V atom:

$$E_{ex} = -(1-x)T_N^0 n^2 \frac{3S}{2(S+1)} m^2 \quad , \tag{4.1}$$

where $T_N^0 = 185$ K is the Néel temperature of pure V_2O_3 extrapolated[19] from that of $(V_{1-x}Cr_x)_2O_3$, m is the reduced sublattice magnetization, and $S = 1$ is the total spin of the magnetic ion.

Accordingly, the term $n\ln g_I$ in (3.1) has to be replaced by the magnetic entropy

$$S_M = n\ln g_I - n\int_0^m B_S^{-1}(m')\,dm' \quad , \tag{4.2}$$

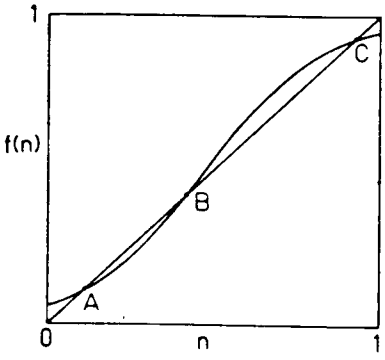

FIG. 3. Graphical determination of the solutions of Eq. (3.3).

where t is the reduced temperature T/T_N [$T_N = (1 - x)T_N^0$] and $B_S^{-1}(x)$ is the inverse Brillouin function.

Variation of the free energy with respect to n and m leads to the following equations to determine the values that minimize it:

$$m = B_S\left(\frac{3S}{S+1}\, n\, \frac{m}{t}\right) , \tag{4.3}$$

$$n = \left(\frac{1}{q'}\, e^{E-2B'n/T} + 1\right)^{-1} . \tag{4.4}$$

In (4.4)

$$B' = B + \frac{3S}{2(S+1)}\, T_N m^2 ,$$

$$q' = q \exp\left[-\int_0^m B_S^{-1}(m')\, dm'\right] . \tag{4.5}$$

The presence of n (equal to or smaller than 1) in the argument of $B_s(x)$ in (4.3) comes from the reduction in molecular field brought about by the decrease in the number of magnetic ions. Comparison of (4.4) with (3.3) shows a decrease of q due to magnetic ordering and an increase in B due to exchange energy. This stabilizes the insulating phase at low temperatures. For $T \ll T_N$ it follows from Eq. (4.4) that the number of electrons in the conduction band will be proportional to $\exp(-E_A/T)$ with an activation energy $E_A = 2B' - E$. For $T = 0$, the free energy reduces to the internal energy

$$U = En - Bn^2 - \tfrac{3}{4} T_N n^2 m^2 , \tag{4.6}$$

so that for the ground state we must have, for E and B' both positive,

$$m = 1 ,$$

$$n = \begin{cases} 0 & \text{for } E - B' > 0 \\ 1 & \text{for } E - B' < 0 \end{cases} ,$$

and the transition will take place at $E = B'$ or explicitly using (3.10), (3.11), and (4.5), at

$$E_0 - E_1 x + \gamma p = (1 - x)(B_0 + \tfrac{3}{4} T_N) - \beta p . \tag{4.7}$$

The pressure dependence of T_N has been neglected. Equation (4.7) gives the pressure for which the transition occurs at zero temperature for each concentration. Using the equivalence ratio between pressure and Cr concentration[13] (3.6 kbar/at.% Cr) we obtain from (4.7)

$$360\,(\gamma + \beta) = E_1 - B_0 - \tfrac{3}{4} T_N^0 . \tag{4.8}$$

For pure V_2O_3, (4.7) gives

$$E_0 + 25(\gamma + \beta) = B_0 + \tfrac{3}{4} T_N^0 . \tag{4.9}$$

Thus, the zero-temperature properties provide two more equations for the three unknowns E_0, E_1, and γ.

Combining (4.8) and (4.9) with (3.9) and (3.10) and using the above given values for T_c and p_c we get $E_0 = 1000$ °K, $E_1 = 2148$ °K, $\gamma = 7$ °K/kbar, and $q = 1.14$ at T_c, which corresponds to a $g_M(T_c) = 2.63$.

From these values we find for the activation energy of pure V_2O_3, $E_A = 1150$ K, $= 0.099$ eV, slightly smaller than the estimated experimental value[5] of 0.1 eV.

Taking g_M constant and equal to 2.63 and the above given values for the parameters, solution of Eqs. (4.3) and (4.4) gives the phase diagram shown in Fig. 4 (dotted line).

The assumption that the delocalization of the electrons from the V atoms could leave these in either of two states separated by an energy δ with degeneracies g_1 and g_2 leads to an effective $g_M(T)$ given by

$$g_M(T) = g_1 + g_2 e^{-\delta/T} .$$

The full line in Fig. 4 shows the phase diagram obtained by choosing $g_1 = 1$, $g_2 = 2$, $\delta = 85.5$ K.

V. CONCLUSIONS

We have presented here a model based on the FK theory for metal-insulator transitions[9] which, by allowing for two kinds of localized states and a magnetically ordered phase, can account for the main features in the behavior of $(V_{1-x}Cr_x)_2O_3$.

Although the model is successful in explaining the existence of two transitions and a critical point in one of them, several points deserve comment.

We believe that the thermodynamic behavior of the insulating phases is well described by including the magnetic free energy, the spin multiplicity, and the Coulomb repulsion between local-

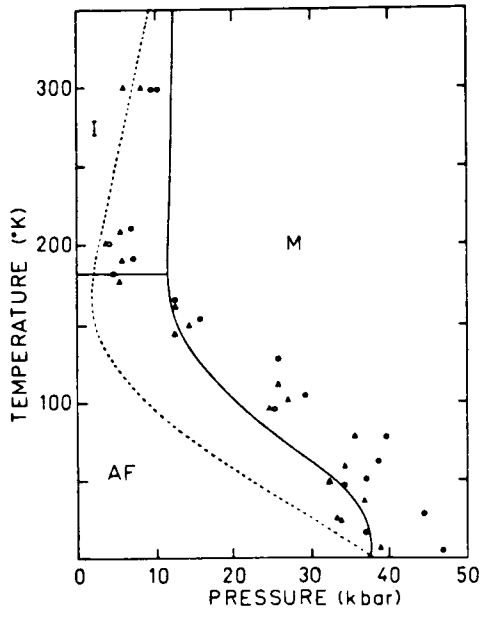

FIG. 4. Phase diagram for $(V_{1-x}Cr_x)_2O_3$ ($x = 0.0375$). Experimental points are taken from Ref. 6(b), Fig. 12. Dotted line: calculated for $g_M = 2.63$. Full line: calculated with $g_M(T) = 1 + 2\exp(0.49 T_N/T)$.

ized and band states that is essential to the FK model.

The situation in the metallic phase is far less clear and most likely one should include many-body effects to improve the agreement. The lack of a completely satisfactory theory of these effects and the intrinsic complication of any existing scheme make it preferable to first describe its thermodynamic properties in the semiphenomenological way we have followed here. We have taken the view that the high paramagnetic susceptibility and the T^2 dependence of the low-temperature conductivity in this phase are indicative of spin disorder. The entropy associated with this spin disorder makes the main contribution to the entropy of the metallic phase. As for the character of the conduction band it is an open question.

As pointed out by Falicov *et al.*[11] magnetoelastic terms which might be responsible for the structural changes in going into the AF phase are not included in the calculation. These terms may also influence the AF-to-I transition and make it take place at a temperature lower than needed for spin disorder. Indeed, Moon,[2] from the temperature variation of the sublattice magnetization, extrapolates a higher temperature than the one we use here.

Except for T_N, the parameters involved in the model are adjusted using only the critical behavior and the low-temperature properties. With these data we are able to draw phase diagrams (for different concentrations of Cr) that reproduce well the experimentally determined phase diagrams.

Furthermore, assuming that for Ti as an impurity one has Δ' large and positive and therefore $n' = 0$ in (2.2) and (2.4), we deduce that the M-I transition takes place along the line

$$T = \frac{E_0 - B_0 f - (\gamma - \beta) p}{\ln q} \quad ,$$

where f is the Ti concentration. With the parameters as we have obtained above this gives an equivalence ratio of -3.12 kbar at.% Ti.

If the reasonable assumption is made that the Coulomb repulsions between band states and localized states associated with Cr and V are equal ($G = G'$), one obtains equivalence ratios which are equal in magnitude and opposite in sign for Ti and Cr. Another encouraging fact is the reasonable agreement between calculated and experimental values for the activation energy in the AF phase.

It should be pointed out that taking the parameters as linear functions of the pressure is a convenient phenomenological way to relate the model to the p-T phase diagram. In actual fact the parameters depend on a number of physical quantities (interatomic distances, covalency, V-V overlap integrals) which change as pressure is applied. Using this description one could relate the sudden change in volume with the change in occupation numbers of the localized states, thus obtaining the excluded volume in a p-V diagram, as in Ref. 14.

In conclusion, we have shown that this model has all the pertinent features of the phase diagram of the V_2O_3 system accounted for, thus providing a basis for the understanding of the behavior of these substances and others of similar characteristics.

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