PHYSICAL REVIEW B VOLUME 19, NUMBER 7 1 APRIL 1979

Heuristic model for magnetic-nonmagnetic transitions in intermediate-valence systems

C. E. T. Gonçalves da Silva*
Institut de Physique Théorique, Université de Lausanne, CH-1015 Switzerland

(Received 16 October 1978)

We present a simple conceptual discussion of the competition between hybridization and exchange in the problem of magnetic-nonmagnetic transitions in intermediate-valence systems. Two atomic-like calculations are presented: a singlet-doublet and a doublet-doublet level systems. A phenomenological ferromagnetic coupling is introduced. In the singlet-doublet case, three distinct phases are possible: paramagnetic, induced ferromagnetic, and ferromagnetic, depending on the values of the parameters. Results for the enhanced susceptibility are also presented. In the doublet-doublet case, two phases occur, para- and ferromagnetic. The valence change upon ordering is discussed. We argue that not only the "magnetic" character of the configuration, but also the relative strength of the local-moment quenching component of the hybridization potential and of the exchange interaction, are important in determining the existence of a spontaneously polarized phase.

I. INTRODUCTION

Intermediate-valence compounds have been extensively studied experimentally in the past few years.[1] Unfortunately, the theoretical problems posed by the experimental results are still not solved. We possess a qualitative understanding of the properties of the ground state and (less so) of the elementary excitations, but no quantitative theory based on this understanding has as yet evolved. This is not surprising, given the intrinsic difficulty of the subject: highly correlated, atomic-like electrons interacting and mixing strongly with less correlated, Bloch-like electrons. But, until a quantitative theory is put forward which allows us to calculate specific heats, magnetic susceptibilities, spectroscopic properties, and other physical parameters for these systems, intermediate-valence compounds will remain quite puzzling. Some wide open problems which are beginning to attract the attention of theorists concern the question of magnetic ordering (why does TmSe order, but not SmS?), coherence lengths (is intermediate valence a purely local phenomenon or is there a coherence length associated with it?), crystal fields, stoichiometry, and defects, thermodynamical properties (cohesive energies, for instance), and others. In all these questions there is still room for heuristic and conceptual developments, as much as for quantitative theories.

The purpose of this paper is to discuss a simple model, which may shed some light on the magnetic properties of intermediate-valence compounds. We show that the competition between hybridization and exchange interaction is an important parameter in determining the presence or absence of magnetic order in a given intermediate-valence compound.[2] The magnetic character of the "fluctuating" configurations also plays a role, but this is not as important as it may seem. The problem is somewhat reminiscent of the competition between crystalline electric fields and exchange. Hybridization may favor a singlet state or a reduced local moment, but exchange opposes this effect. In our view, the spatial coexistence of magnetic order and intermediate valence indicates an effect of the hybridization on the local moment comparable to that of exchange interactions and hence a mixing width of the order of typical exchange constants ($\lesssim 10$ K). Experimental evidence supporting this view comes from measurements of the width of the quasielastic peak in neutron scattering. For $CePd_3$, a paramagnet, this width is 19 meV and temperature independent at low temperatures,[3] whereas for TmSe it is considerably smaller, 5 meV and decreases with temperature below T_N.[4] It would be interesting to determine the width of this peak in the collapsed phase of SmS. If our view is correct it should have a temperature dependence and a value more like $CePd_3$ than TmSe.

In order to investigate the competition between hybridization and exchange we study in this paper a purely "atomic" problem. Because of its "atomic" character we cannot expect that the model will reproduce excited states that bear any resemblance to those of an intermediate-valence system. Its value is mainly heuristic and conceptual in pointing out some interesting possibilities resulting from the balance of two opposing physical mechanisms. In Sec. II we present the singlet-doublet version of the model. This may be considered an extension of the work of de Châtel *et al.*[5] on the susceptibility of an isolated system. In Sec. III we discuss the doublet-doublet case. Finally, in Sec. IV we present our conclusions.

II. SINGLET-DOUBLET MODEL

In this model we place, at each site of a lattice, three atomic-like states: one singlet and one doublet. The singlet has no magnetic moment and is unaffected by an external magnetic field. These states are separated by an energy 3δ and hybridized (mixed) with a mixing element V, connecting only each member of the doublet to the singlet. In addition, the members of the doublet situated in the different sites are exchange coupled. This coupling J is taken as "ferromagnetic" and of nearest-neighbor only type. Although this model bears some resemblance to models of singlet ground-state magnetic systems,[6] it is important to note that in the present case, the mixing opposes magnetism. Moreover, we want to place an altogether different physical interpretation on the model.

The Hamiltonian is given by

$$H=\sum_i\left[\sum_{\nu=1}^{3}E_\nu|i\nu\rangle\langle i\nu|+V\sum_{\nu=2}^{3}(|i1\rangle\langle i\nu|+|i\nu\rangle\langle i1|)\right]-\frac{J}{z}\sum_{(i,j)}\sum_{\substack{\nu,\nu'\\ \mu,\mu'}}|i\nu\rangle\langle i\nu'|\,\vec{\sigma}_{\nu'\nu}\cdot\vec{\sigma}_{\mu'\mu}|j\mu'\rangle\langle j\mu| \ . \tag{2.1}$$

In Eq. (2.1) we have $E_1=0$ and $E_2=3\delta$, z is the coordination number of the lattice, $\vec{\sigma}$ is the Pauli spin-matrix vector; the summation over (ij) is restricted to nearest-neighbor pairs and that over μ, μ', ν, ν' to values 2 and 3 of these variables. The model has some of the features of intermediate-valence systems like SmS and Ce compounds for which one of the configurations is nonmagnetic. A complete identification is, clearly, not possible because the dynamics of the conduction electrons is ignored and the real level structure of the magnetic configuration is usually more complex than a doublet. In the case of SmS based compounds, the state $|1\rangle$ corresponds to the ground state of the ionic configuration $4f^6$ and the states $|2\rangle$ and $|3\rangle$ to that of the ionic configuration $4f^5 5d^1$. The basic assumption made throughout this work is that the magnetic moment is determined by the $4f$ electrons and that the d electrons are magnetically "dead". The d-electron spin is "killed" by pairing up with another d-electron spin when they form a band. The resulting Pauli susceptibility is not taken into account in the present model. Strictly speaking the states $|2\rangle$ and $|3\rangle$ cannot be taken as members of a spin-$\frac{1}{2}$ doublet. But, since they are polarizable in the presence of a magnetic field, whereas the state $|1\rangle$ is not, we continue to employ the terminology of magnetism, which is quite convenient.

In the mean-field approximation we reduce H to a sum of Hamiltonians of the form

$$H=\sum_{\nu=1}^{3}\tilde{E}_\nu|\nu\rangle\langle\nu|+V\sum_{\nu=2}^{3}(|1\rangle\langle\nu|+|\nu\rangle\langle 1|) \ , \tag{2.2}$$

where

$$\tilde{E}_1=0 \ , \quad \tilde{E}_2=3\delta-Jm \ , \quad \text{and } \tilde{E}_3=3\delta+Jm \ . \tag{2.3}$$

The "magnetization" is defined by

$$m=\langle\sigma_z\rangle \ , \tag{2.4}$$

where the angular brackets denote thermal averaging and must be calculated self-consistently.

The eigenvectors and eigenvalues of Eq. (2.2) may be computed exactly. The latter, in particular, are given by the roots of a third degree polynomial.[5]

We now analyze the self-consistency equation (2.4) at $T=0$. We can show, after some algebra, that it has always the trivial solution $m=0$ and that nontrivial solutions obey

$$[(\epsilon_1-3\delta)^2-m^2]^2+2V^2[(\epsilon_1-3\delta)^2+m^2+2(\epsilon_1-3\delta)]=0 \ , \tag{2.5}$$

where we have set $J=1$, and ϵ_1 is the ground-state energy of Eq. (2.2). For a given value of V, there exists a value δ_c, above which this equation has no solution. For $V=0$, δ_c reaches its maximum value of $\frac{1}{3}$. For small values of V, $\delta_c>0$ and in the interval $0<\delta<\delta_c$, we have a situation of induced "ferromagnetism", because the doublet lies higher than the singlet in the absence of exchange coupling. The transition from paramagnetism to induced ferromagnetism at $T=0$, as a function of δ, is abrupt for $V=0$, but smooth for $V\neq 0$. These results are shown in Fig. 1(a) and (b), which present $\delta_c(V)$ and $m(\delta, V)$, respectively. Note that, as V increases, for a given δ or δ decreases towards zero for a given V, even if the doublet lies below the singlet (in the absence of mixing), the ground state becomes paramagnetic. This is a "strong" mixing situation and it can be understood if we consider the eigenvectors of Eq. (2.2) in the case $J=0$ (or $m=0$). The expectation value of σ_z is strictly zero for any one of these eigenvectors, and in particular for the ground state. This arises from the fact that both "spin-up" and "spin-down" components of the doublet are present with the same weight in these states. In the strong mixing limit the exchange coupling cannot sustain eigenvectors with unequal weights for the two members of the doublet, i.e., it cannot "free" the doublet from the singlet and the system remains paramagnetic. But, as the levels move further apart, with the doublet below the singlet, we reach a situation in which the exchange coupling takes over and the system becomes magnetic, even though one of the "configurations" is nonmagnetic. It is our view that this is the correct manner of visualizing the lack of magnetism in many intermediate-valence compounds.

For $T \neq 0$ the self-consistency equation becomes

$$\frac{1}{Z}\sum_{j=1}^{3} m_j e^{-\beta\epsilon_j(m)} = m \ , \tag{2.6}$$

where Z is the partition function, $\epsilon_j(m)$ the jth eigenvector of Eq. (2.2), and

$$m_j = 4V^2 m(3\delta - \epsilon_j)Q_j(m) \ , \tag{2.7}$$

with

$$Q_j^{-1}(m) = [(\epsilon_j - 3\delta)^2 - m^2]^2 + 2V^2[(\epsilon_j - 3\delta)^2 + m^2] \ . \tag{2.8}$$

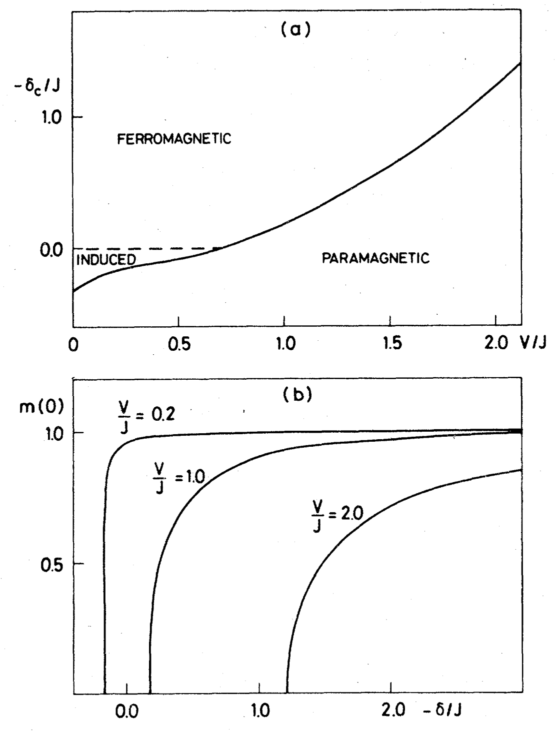

FIG. 1. (a) Phase diagram in the δ/J-V/J plane. The solid line determines the critical value of δ for which there is a magnetic-nonmagnetic transition. The dashed line separates the region of induced ($\delta > 0$) and normal ($\delta < 0$) ferromagnetism. (b) The reduced moment $m(0)$ at $T = 0$ for different values of V/J. Note that in both (a) and (b) δ/J decreases along the conventional positive axes.

Clearly $m = 0$ remains a solution together with a second possible nontrivial solution. The critical temperature below which this second solution exists is determined by taking the limit $m \to 0$ of Eq. (2.6), after eliminating the trivial solution. Alternatively we may compute the exchange enhanced susceptibility and determine the temperature at which it diverges. The (initial) nonenhanced susceptibility is given by

$$\chi_0 = \frac{1}{Z_0}\left[\frac{3\delta}{V^2} + \frac{4V^2}{(9\delta^2 + 8V^2)^{1/2}} \times \left(\frac{e^{-\beta\epsilon_-}}{(\epsilon_- - 3\delta)^2} - \frac{e^{-\beta\epsilon_+}}{(\epsilon_+ - 3\delta)^2}\right)\right] \tag{2.9}$$

where Z_0 is the zero-field partition function and $\epsilon_0 = 3\delta$,

$$\epsilon_\pm = \tfrac{1}{2}[3\delta \pm (9\delta^2 + 8V^2)]^{1/2} \ . \tag{2.10}$$

The exchange enhanced susceptibility is then shown to be

$$\chi = \chi_0(1 - J\chi_0)^{-1} \ . \tag{2.11}$$

The critical temperature is determined by the equation

$$1 - J\chi_0(T_c) = 0 \ . \tag{2.12}$$

The solution of this equation yields the following results for T_c: It approaches the limit $T_c = 1$ as we move into the weak mixing limit with the doublet below the singlet, i.e., $\delta < 0$ and $|\delta| > V$. As we move into the strong mixing limit $T_c \to 0$. For a given V, we have $T_c = 0$ at $\delta = \delta_c$, as expected. In Fig. 2(a) we present these results graphically. They are entirely in accord with those shown in Fig. 1 in that the highest critical temperatures correspond to the highest saturation magnetization. In Fig. 2(b) we present some results for $m(T)$. They are characteristic of mean-field theories and we do not discuss them further, except to point out that $m(T)/m(0)$ is not a function of T/T_c. We also show the average occupancy of the singlet state for $\delta = 0.05J$ and $V = 0.5J$, both for $m = 0$ and $m \neq 0$ in the ordered phase. The curve for $m = 0$ below T_c has no physical significance. It just illustrates the decrease in occupancy of the singlet which occurs as a result of the ordering, which partly "quenches" the valence fluctuations.

The enhanced susceptibility (2.11), in the paramagnetic region of the phase diagram shown in Fig. 1 behaves qualitatively in the same way as that presented by de Châtel *et al.*[5] In Fig. 3, we show χ for $\delta = 0.1$ and $V = 0.50$, i.e., a strong mixing case, but in the neighborhood of a phase transition. The strong enhancement at low temperature is clearly seen. Such an enhancement of the susceptibility at low T is observed in α-Ce,[7] where it has been established that it is not an impurity effect. This phase is believed to be formed by predominantly tetravalent Ce ions, i.e., the singlet state being occupied more than the magnetic one. Although our model cannot reproduce the susceptibility minimum which is observed in α-Ce, it must be kept in mind that the position of the levels (or their occupancy) is strongly affected by electron-electron[8] and electron-phonon[9] interactions. This introduces an additional temperature dependence which is not included in our model. This susceptibility minimum in α-Ce may result from a faster than Boltzmann factor occupancy rate of the magnetic configuration with increasing temperature.

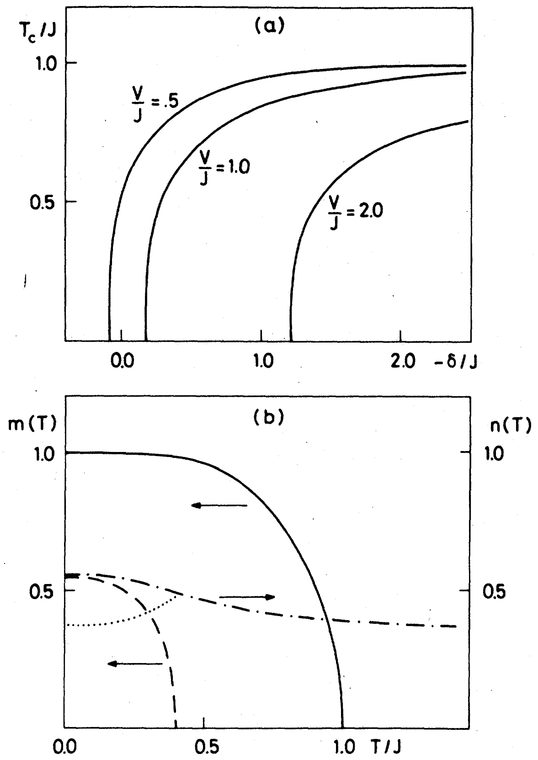

FIG. 2. (a) Critical temperature vs δ/J for different values of V/J. (b) Spontaneous magnetization $m(T)$ as a function of temperature for different values of the parameters. Full line: $\delta = -4J$, $V = 0.5J$; dashed line: $\delta = +0.05J$, $V = 0.5J$. The occupation of the singlet state is also indicated for $m = 0$ (dotted-dashed line) and $m \neq 0$ (dotted line) in the ordered phase, for the second set of values of δ and V.

To summarize, the model presented above has the following interesting features: (i) It gives paramagnetic solutions for all temperatures, or it has a paramagnetic-ferromagnetic second-order transition at a critical temperature depending on the values of the parameters δ and V. The magnetism may be of the induced or the normal type. (ii) The paramagnetic solution arises when the doublet configuration (magnetic), lies below or nearby the singlet configuration (nonmagnetic), in the strong mixing limit. There is also a "normal" paramagnetism when the singlet lies below the doublet. (iii) In the weak mixing limit, ferromagnetism may occur, but with a saturation moment that is determined by the amount of mixing and is a function of applied field. (iv) In the nearly ferromagnetic case, the susceptibility is strongly exchange enhanced at low temperatures.

III. DOUBLET-DOUBLET MODEL

The simplest possible model of two realistic fluctuating magnetic configurations is that of a doublet and a triplet ($J = 1$) or quartet ($J = 0$ and $J = 1$). However, since the qualitative results remain unaltered, we discuss here the simplified case of two doublets. The important point is that the two confi-

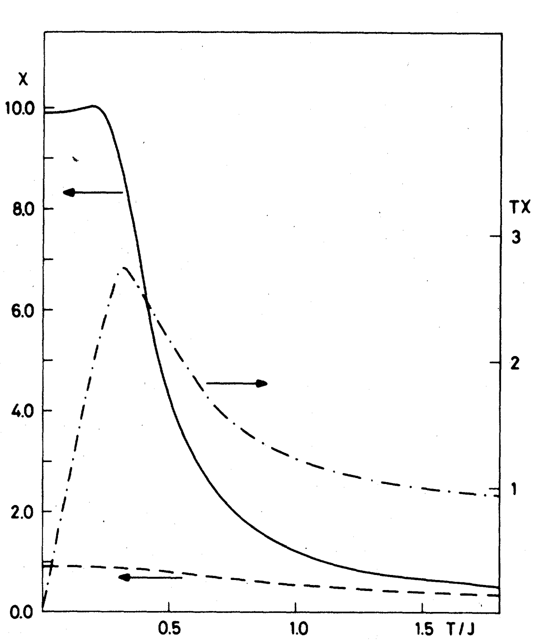

FIG. 3. Full line: enhanced susceptibility (arbitrary units). Dashed line: isolated impurity susceptibility (arbitrary units). Dotted-dashed line: square of the effective moment ($T\chi$). Note that in the limit $T \rightarrow \infty$, for the present model, $T\chi \rightarrow \frac{2}{3}$. The values of $\delta = 0.10J$ and $V = 0.50J$.

gurations are now magnetic, in the sense that they are both split by a magnetic field. The reservations stated in Sec. II concerning the limitations of such a model are still valid. Two important modifications are introduced in the Hamiltonian of this model compared with the singlet-doublet one. First, there is now the possibility of a different coupling of each magnetic configuration with the external field. We assume that they have the same gyromagnetic ratio, i.e., a "symmetric" case. Obviously, this assumption is not critical. Second, there are now many more hybridization parameters. In the spirit of the "symmetric" approximation above we reduce these to only two. The mean-field matrix Hamiltonian may finally be written

$$H_{\mathrm{mf}}=\begin{vmatrix} -Jm & 0 & V_1 & V_2 \\ 0 & Jm & V_2 & V_1 \\ V_1 & V_2 & \delta-Jm & 0 \\ V_2 & V_1 & 0 & \delta+Jm \end{vmatrix} , \tag{3.1}$$

Observe that states $|1\rangle$ and $|3\rangle$ have their energies lowered and states $|2\rangle$ and $|4\rangle$ have their energies increased in the presence of the exchange field ($J>0$). The "magnetization" is defined by

$$m=\langle P_1-P_2+P_3-P_4\rangle \ , \tag{3.2}$$

where the angular brackets denote thermal averaging and P_j is a projection operator onto the jth state. A self-consistent solution of Eq. (3.2) with $m\neq 0$ corresponds to a magnetically polarized state. Although V_1 and V_2 both induce configuration mixing, they affect the magnetic behavior of the system in different ways. Since V_1 mixes states which behave in the same way in the presence of the exchange field, the magnetization is only weakly dependent on it. However, V_2 mixes states which behave differently in the presence of the field, and hence V_2 tends to "quench" spontaneous polarization. In the degenerate case ($\delta=0$) at $T=0$, we obtain the following nontrivial solution for m:

$$m=\begin{cases}[1-(V_2/J)^2]^{1/2} & \text{if } V_2\leq J \ , \\ 0 & \text{otherwise} \ . \end{cases} \tag{3.3}$$

Hence a spontaneously polarized ground state is possible only if the exchange exceeds a certain critical value, even though both configurations are polarizable. A phase diagram for the case $V_1=V_2=V$ is shown in Fig. 4. Also shown in Fig. 4 is the behavior of m at $T=0$ for increasing values of δ, as a function of V. As expected, increasing δ reduces the overall mixing and increases m.

Another point of interest is the behavior of the "valence", i.e., fractional occupation of the configurations. This is illustrated in Figs. 5 and 6 for different values of the parameters. In Fig. 5 we plot as a function of T for $\delta=1.0J$, $V_1=0.5J$ and $V_2=1.0J$, (i) the total magnetization, (ii) the partial magnetization of the upper configuration, (iii) the lower configuration occupation probability in the nonpolarized phase, and (iv) in the polarized phase. The important point is that the occupation probability of the lower configuration is increased in the ordered phase with respect to its value in the nonordered phase (assumed metastable at the same temperature). Also, the possibility that magnetic ordering results in a "quenching" of valence fluctuations is displayed in Fig. 5. In Fig. 6 the same quantities are displayed for different values of the parameters ($V_1=1.0J$, $V_2=0.5J$). Decreasing V_2 results in a more stable polarized phase, but the increase in V_1 leads to a reduced occupancy of the lower configuration at $T=0$. Note also that the upper configuration polarization is increased.

IV. CONCLUSIONS

The two models presented in this paper, although highly simplified, point out the importance of the competition between hybridization and exchange interaction in determining the existence of magnetic

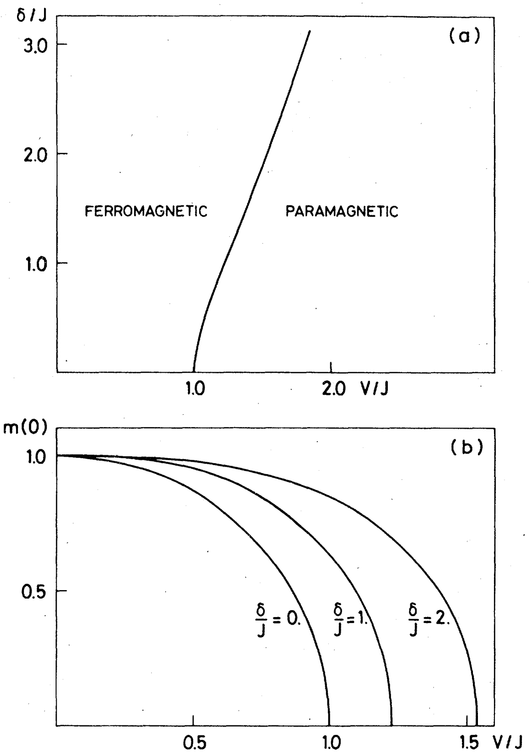

FIG. 4. (a) Phase diagram for magnetic-nonmagnetic transitions. (b) The $T=0$ saturation moment for different values of δ/J.

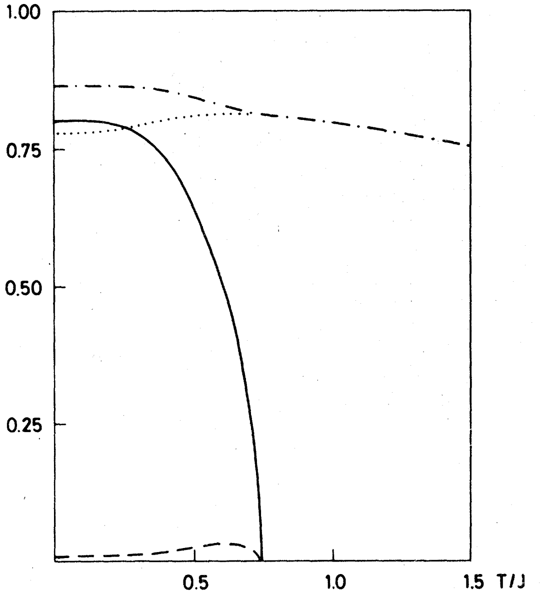

FIG. 5. Full line: total magnetization. Dashed line: upper configuration magnetization. Dotted-dashed line: lower configuration occupation probability for the equilibrium value of the magnetization. Dotted line: lower configuration occupation probability for $m=0$. The values of $\delta=J$, $V_1=0.5J$ and $V_2=J$.

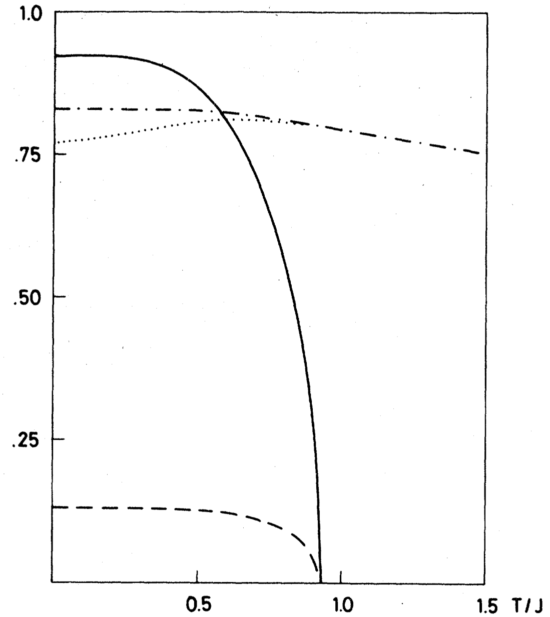

FIG. 6. Full line: total magnetization. Dashed line: upper configuration magnetization. Dotted-dashed line: lower configuration occupation probability for the equilibrium value of the magnetization. Dotted line: lower configuration occupation probability for $m=0$. The values of $\delta=J$, $V_1=J$ and $V_2=0.5J$.

ordering in the intermediate-valence compounds. For an intermediate-valence compound to order magnetically the exchange interaction must dominate over the local moment quenching effects of mixing. In the case of Ce $4f^1$-$4f^0$,[3,10] and Yb $4f^{13}$-$4f^{14}$,[11] intermediate-valence compounds the mixing has a very strong effect on the local moment because one of the configurations is nonmagnetic. Although, in principle, magnetic ordering is not excluded in these compounds, it seems that the material parameters of systems investigated thus far are such that the exchange coupling is not sufficiently large to oppose the effects of mixing. Enhancement of the susceptibility at low temperatures, not associated with impurities, is seen clearly in α-Ce. In SmS $4f^5$-$4f^6$, on the other hand, a strong spin orbit splitting of the $4f^6$ configuration produces a nonmagnetic ground state and we have a situation similar to that of Ce or Yb compounds. In TmSe $4f^{12}$-$4f^{13}$,[12,13] the crystal-field effects on the non-Kramers configuration are much smaller, so that both configurations may have a local moment. The constraints on the exchange interaction are then much less than in SmS and magnetic ordering is produced.

Since our aim was to discuss the problem of magnetism and intermediate valence in a general way, we have not considered the extremely important question of the origin of the exchange interaction. For systems which are near a valence instability we proposed a theory for the exchange interaction several years ago.[14] Recently, Varma[15] has studied the double-exchange mechanism which is important in the intermediate-valence phase. At the moment, however, we cannot say that the question is closed. The problems touched upon in this work still offer a wide scope for further investigations.

ACKNOWLEDGMENT

This work was supported in part by Grant No. 2.478-0.77 of the Swiss National Science Foundation.

[*] Guggenheim Fellow, 1978. On leave of absence from Instituto de Fisica, UNICAMP, Campinas, Brasil.

[1] For a review, see *Valence Instabilities and Related Narrow Band Phenomena,* edited by R. D. Parks (Plenum, New York, 1977).

[2] See, N. F. Mott, *Metal-Insulator Transitions,* (Taylor and Francis, London, 1974) p. 165.

[3] E. Holland-Moritz, M. Loewenhaupt, W. Schmatz, and D. K. Wohlleben, Phys. Rev. Lett. 38, 983 (1977).

[4] M. Loewenhaupt and E. Holland-Moritz, J. Magn. Magn. Mater., (to be published) (1978).

[5] P. F. de Châtel, J. Aarts, and J. C. P. Klaasse, Commun. on Phys. 2, 151 (1977).

[6] G. T. Trammel, Phys. Rev. 131, 932 (1963); B. Bleaney, Proc. Roy. Soc. London A 236, 19 (1963); R. J. Birgeneau AIP Conf. Proc. 10, 1664 (1973).

[7] K. A. Gschneidner, Jr., see Ref. 1, p. 89.

[8] L. M. Falicov and J. C. Kimball, Phys. Rev. Lett. 22, 997 (1969).

[9] M. Avignon, S. K. Ghatak, K. H. Bennemann, and F. Brouers, J. Phys. (Paris), (to be published).

[10] S. M. Shapiro, J. D. Axe, R. J. Birgeneau, J. M. Lawrence, and R. D. Parks, Phys. Rev. B 16, 2225 (1977).

[11] W. C. M. Mattens, R. A. Elenbaas, and F. R. de Boer, Commun. on Phys. 2, 147 (1977).

[12] R. P. Guertin, S. Forner, and F. P. Missell, Phys. Rev. Lett. 37, 529 (1976).

[13] H. Bjerrum-Møller, S. M. Shapiro, and R. J. Birgeneau, Phys. Rev. Lett. 39, 1021 (1977).

[4] C. E. T. Gonçalves da Silva and L. M. Falicov, J. Phys. C 5, 63 (1972).

[15] C. Varma, J. Phys. (Paris), (to be published).