

Phase Transitions and Band Structure in Metallic Perovskites (Carbides and Nitrides)

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Properties of Mn_3XN and Mn_3XC types of compounds are analyzed on the basis of a model for the electronic band structure, which consists of a large conduction band overlapping a narrow band that results from the strong hybridization between the p orbitals of the metalloid and some of the d orbitals of the manganese. The crystal field at the sites of manganese is assumed to be strong. The structure of the narrow band is calculated in the tight-binding model. The Fermi energy lies very close to a sharp singularity in the density of states. In the cubic and Pauli paramagnetic phase, such a singularity has a sixfold degeneracy. The magnetic and structural instabilities, which appear when the temperature is decreased, are explained by the removal of that degeneracy by a shear strain and the formation of small magnetic moments. The phase transitions can be studied in detail by expanding the variation of the free energy with respect to the shear strains and the magnetic moments. The coefficients of the expansion are calculated as functions of the temperature. The variation of the volume is explained by the existence of coupling terms to the shear strain and to the magnetic moments.

Introduction

The Mn_3XN and Mn_3XC types of compounds, with the perovskite structure, form a rather extended family because of the large number of substitutions which can be made on the third element X . All of them are magnetic conductors, and they are of great interest because of the existence, in the temperature range lying roughly between 200 and 500°K, of magnetic and structural phase transitions, which have been extensively investigated during the last ten years by several experimental techniques, such as X-ray and neutron diffraction and magnetic and thermal measurements (1-21).

In the high-temperature limit all these compounds are in a cubic and Pauli para-

magnetic phase, as is shown by the diffraction data and by the behavior of the paramagnetic susceptibility which becomes nearly temperature independent for large values of the temperature. When the temperature decreases, one observes a general tendency of these compounds to undergo a first-order structural phase transition which consists of a small tetragonal shear strain of the cubic unit cell, with a c/a ratio which can be a little larger or a little smaller than unity. Also, a second-order magnetic phase transition is observed, which consists of the formation of small magnetic moments on the manganese atoms, with several possible structures of the resulting ordered magnetic phase. According to the individual case, the structural and the magnetic phase transitions take place or not at the same critical

value of the temperature. Phase transitions with a discontinuity in the variation of the volume *alone* have never been observed. But a variation of the volume can be induced by the coupling to a shear strain or to the formation of small magnetic moments.

A systematic study of the effect of the substitutions on the precise features of the previous properties, such as, for instance, the numerical values of the critical temperatures, of the shear strains, of the magnetic moments, and so on, shows the great influence of the number of electrons which occupy the energy bands.

In this article, we show how the previous properties can be analyzed in detail on the basis of a model we have proposed before for the electronic structure of these compounds. In Section I, we recall the salient features of our model. In Section II, we calculate the effect of a shear strain and of the formation of small magnetic moments on the electronic structure. In Section III, we discuss the stability of the cubic and Pauli paramagnetic phase at absolute zero. In Section IV, we calculate the effect of the temperature, and we discuss the features of the different possible phase transitions in our model.

I. Model for the Band Structure

In this section we recall the salient features of the model we have introduced in previous publications (22–26), and we go more deeply into the discussion of some of the parameters of this model.

I.1. Physical Hypothesis

Our model is based on the following physical hypothesis:

(1) The Fermi energy E_F lies inside a narrow d - p band partly overlapping a much larger conduction band.

(2) The crystal field acting on the manganese atoms located at the centers of the faces of the cubic unit cell (Fig. 1) is as-

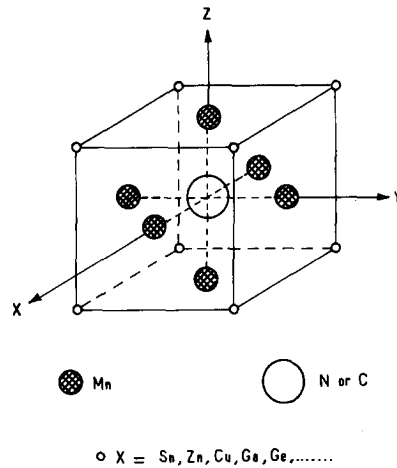


FIG. 1. The perovskite structure.

sumed to be strong enough to split the d band into well-separated subbands, the symmetries of which are, respectively, a_{1g} , e_g , b_{1g} , and b_{2g} in the direction of decreasing energies (Fig. 2).

(3) The d band as a whole being roughly half-occupied, the Fermi energy E_F is assumed to lie inside the e_g subband.

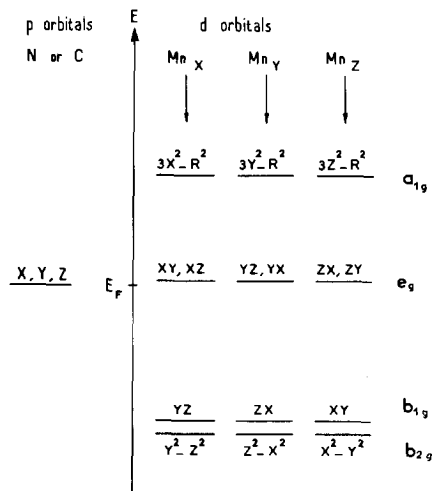


FIG. 2. The atomic levels of the p orbitals of the metalloid (N or C) and of the d orbitals of the three manganese atoms Mn_α (where Mn_α is the manganese atom on the α axis of Fig. 1, with $\alpha = X, Y, \text{ or } Z$). The crystal field at the sites Mn_α has the symmetry D_{4h} , and is assumed to be strong. E_F is the Fermi energy.

(4) The energy levels of the p states of the metalloid (N or C), which is located at the center of the cubic unit cell (Fig. 1), are assumed to be very close to the Fermi energy E_F , and thus to the energy levels of the d subband with the symmetry e_g (Fig. 2); this hypothesis is supported by several experiments (3, 17, 18) concerning the atomic form factor of the metalloid in these compounds, which show that the p orbitals are only partly occupied; thus, when calculating the band structure in the neighborhood of the Fermi energy, one must take into account both the p states of the metalloid and the d states of symmetry e_g of the manganese; as a result, the Fermi energy E_F lies inside a narrow $p-d_{e_g}$ subband well separated from the other d subbands.

(5) The structure of this narrow $p-d_{e_g}$ subband has been calculated (25) in the tight-binding approximation, by taking into account, as a first approximation, the transfer integrals between nearest neighbors only, that is, between the p orbitals of the metalloid at the center of the cubic unit cell and the d orbitals with symmetry e_g of the manganese atoms at the centers of the faces of the same unit cell; the transfer integrals between next-nearest neighbors, and thus between different manganese atoms, were neglected; the mixing of the narrow $p-d_{e_g}$ subband with the orbitals of the metallic atoms located at the corners of the cubic unit cell was also neglected, these last orbitals probably contributing to the large conduction band.

1.2. Structure of the Narrow $p-d_{e_g}$ Subband

In the nearest-neighbor approximation, the narrow $p-d_{e_g}$ subband is made of three degenerate subbands, S_X , S_Y , and S_Z , each being built with three orbitals per unit cell, namely,

S_X with the orbitals p_X , $d_{YX}(\text{Mn}_Y)$, $d_{ZX}(\text{Mn}_Z)$,

S_Y with the orbitals p_Y , $d_{ZY}(\text{Mn}_Z)$, $d_{XY}(\text{Mn}_X)$,
 S_Z with the orbitals p_Z , $d_{XZ}(\text{Mn}_X)$, $d_{YZ}(\text{Mn}_Y)$,

where the three orbitals p_α , with $\alpha = X, Y$, or Z , belong to the metalloid at the center O of the unit cell (Fig. 1), and where $d_{\gamma\alpha}(\text{Mn}_\gamma)$, with $\gamma, \alpha = X, Y$, or Z , are the d orbitals with symmetry e_g belonging to the manganese atoms Mn_γ located at the centers of the faces of the unit cell, respectively, in the directions of the three axes $\gamma = X, Y$, and Z from the center O of the unit cell (Fig. 1).

Thus in the cubic paramagnetic phase there are both a threefold degeneracy due to the fact that the three subbands S_X , S_Y , and S_Z are identical and a twofold degeneracy due to the spin.

Detailed calculations show that each of the three subbands S_α involves a bonding subband and an antibonding subband, well separated from each other, and a residual unhybridized d subband, the width of which vanishes in the nearest-neighbor approximation. When calculating the density of states $n(E)$ one obtains finite discontinuities at the edges of the bonding and antibonding subbands and logarithmic singularities roughly in their middles. We must add to these singularities the infinite one, described by a Dirac delta function, which results from the unhybridized d subband with vanishing width (Fig. 3).

1.3. The Fermi Level Position

Experimental data for the electronic specific heat (21) indicate a large numerical value of the electronic density of states $n(E_F)$ at the Fermi level. It can be explained in our model by assuming that the Fermi energy E_F is very close to one of the infinite singularities of the density of states $n(E)$. By going more deeply into the discussion of the filling of the bands, one can show that, at least in some of the compounds we are interested in, the Fermi energy E_F should

be very close to the energy E_s of the logarithmic singularity in the antibonding subband (Fig. 3). We have thus retained this hypothesis for our present calculations; but we may notice that we would probably have obtained similar physical results if E_F had been assumed to be very close to one of the two other infinite singularities of $n(E)$.

I.4. Analytical Expression of the Density of States

In the neighborhood of the energy E_s of the logarithmic singularity in the antibonding subband, we can use for the total electronic density of states, in the cubic paramagnetic phase and for each of the two spin directions, the approximate expression

$$\frac{1}{2}n(E) = 3\bar{n}(E - E_s) + R(E), \quad (1)$$

where the factor 3 in front of the first term, which contains the singularity, comes from the threefold degeneracy between the three subbands S_X , S_Y , and S_Z , identical in the cubic phase, and where the second term $R(E)$, which is entirely regular, is mainly due to the large conduction band; the analytical expression of the singularity is

$$\bar{n}(E - E_s) = C \text{Log} \frac{\nu}{|E - E_s|}, \quad (2)$$

with

$$E_s = \frac{1}{2}(E_p + E_d) + \frac{1}{2}\sqrt{\Delta^2 + 16\beta^2}, \quad (3)$$

$$\nu = \frac{16\beta^2}{\sqrt{\Delta^2 + 16\beta^2}}, \quad \text{and} \quad C = \frac{8}{\pi^2\nu} \quad (4)$$

where E_p and E_d are the intraatomic energies of an electron occupying, respectively, a p orbital on the metalloid and a d_{e_g} orbital on the manganese, $\Delta = E_p - E_d$, and β is the transfer integral between a p_α orbital on the metalloid and a $d_{\gamma\alpha}(\text{Mn}_\gamma)$ orbital of symmetry e_g on the nearest-neighbor manganese Mn_γ , with $\alpha, \gamma = X, Y, \text{ or } Z$ and $\alpha \neq \gamma$.

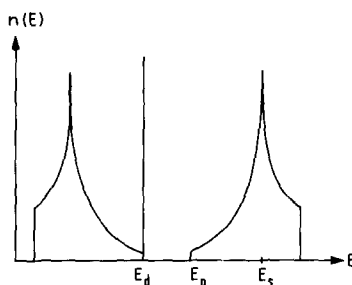


FIG. 3. Electronic density of states of the p - d_{e_g} subband as calculated in our model.

I.5. Physical Origin of the Parameters E_p and E_d

As is usually the case in narrow bands (25), we may assume that, inside the p - d_{e_g} subband in our model, the interaction between two electrons occupying the same atomic site is much larger than the interaction between two electrons occupying two different atomic sites. This is equivalent to assuming that the main part of the interaction between the electrons in that subband is contained in the intraatomic energies $E_\sigma(p_\alpha)$ and $E_\sigma[d_{\gamma\alpha}(\text{Mn}_\gamma)]$ of an electron with the spin σ occupying, respectively, the orbital p_α ($\alpha = X, Y, \text{ or } Z$) on a metalloidic site or the orbital $d_{\gamma\alpha}(\text{Mn}_\gamma)$ ($\alpha, \gamma = X, Y, \text{ or } Z$; $\alpha \neq \gamma$) on the site Mn_γ .

In the Hartree-Fock approximation, these intraatomic energies can be written as

$$E_\sigma(p_\alpha) = T(p_\alpha) + U_p^0 \langle n_{-\sigma}(p_\alpha) \rangle + U_p^1 \sum_{\alpha' \neq \alpha} \langle n_{-\sigma}(p_{\alpha'}) \rangle + (U_p^1 - J_p) \sum_{\alpha' \neq \alpha} \langle n_\sigma(p_{\alpha'}) \rangle, \quad (5)$$

$$E_\sigma[d_{\gamma\alpha}(\text{Mn}_\gamma)] = T[d_{\gamma\alpha}(\text{Mn}_\gamma)] + U_d^0 \langle n_{-\sigma}[d_{\gamma\alpha}(\text{Mn}_\gamma)] \rangle + U_d^1 \langle n_{-\sigma}[d_{\gamma\alpha}(\text{Mn}_\gamma)] \rangle + (U_d^1 - J_d) \langle n_\sigma[d_{\gamma\alpha}(\text{Mn}_\gamma)] \rangle, \quad (6)$$

where $T(p_\alpha)$ and $T[d_{\gamma\alpha}(\text{Mn}_\gamma)]$ include the kinetic energy of the electron occupying the

orbital p_α or $d_{\gamma\alpha}(\text{Mn}_\gamma)$ and its interaction with the hard cores of the nucleus in the crystal, i.e., with the hard core of the nucleus at the site occupied by the electron and with the part of the crystal field which is produced by the hard cores of the nucleus at the other sites; U_p^i and U_d^i ($i = 0$ or 1) are the direct Coulomb interactions between two electrons on the same site, occupying the same (p or d) orbital for $i = 0$, and two different (p or d) orbitals for $i = 1$; J_p and J_d are the corresponding intra-atomic exchange interactions; $\langle n_\sigma(p_\alpha) \rangle$ and $\langle n_\sigma[d_{\gamma\alpha}(\text{Mn}_\gamma)] \rangle$ are the averaged values, in the Hartree-Fock approximation, of the numbers of electrons with the spin σ on the orbitals p_α and $d_{\gamma\alpha}(\text{Mn}_\gamma)$, respectively; finally we must take $\gamma' \neq \gamma$ in Eq. (6).

The numerical estimation of the parameters appearing in Eqs. (5) and (6) is difficult. But we shall not reduce much the generality of our results by assuming that:

(1) $U_p^0 = U_p^1 (= U_p)$ and $U_d^0 = U_d^1 (= U_d)$;

(2) $T(p_\alpha)$ and $T[d_{\gamma\alpha}(\text{Mn}_\gamma)]$ do not much depend on α ($\neq \gamma$), and they will be simply written, respectively, $T(p)$ and $T[d(\text{Mn}_\gamma)]$ for any α ;

(3) all the p or d_{eg} orbitals belonging to the same site are roughly equally occupied by electrons with a given spin σ , i.e.,

$$\langle n_\sigma(p_\alpha) \rangle \approx \frac{1}{3} \langle n_-(\text{N}) \rangle$$

and

$$\langle n_\sigma[d_{\gamma\alpha}(\text{Mn}_\gamma)] \rangle \approx \frac{1}{2} \langle n_\sigma(\text{Mn}_\gamma) \rangle,$$

where $\langle n_\sigma(\text{N}) \rangle$ and $\langle n_\sigma(\text{Mn}_\gamma) \rangle$ are, respectively, the averaged total numbers of p electrons on a metalloidic site (N or C) and of d_{eg} electrons on a Mn_γ site, both of them with the spin σ . With these further approximations, the energies $E_\sigma(p_\alpha)$ and $E_\sigma[d_{\gamma\alpha}(\text{Mn}_\gamma)]$ no longer depend on α ; they will be written, respectively, $E_\sigma(p)$ and $E_\sigma[d(\text{Mn}_\gamma)]$; and Eqs. (5) and (6) take

the simpler forms

$$E_\sigma(p) = T(p) + \frac{5U_p - 2J_p}{6} n(\text{N}) - \sigma \frac{U_p + 2J_p}{6} m(\text{N}), \quad (7)$$

$$E_\sigma[d(\text{Mn}_\gamma)] = T[d(\text{Mn}_\gamma)] + \frac{3U_d - J_d}{4} n(\text{Mn}_\gamma) - \sigma \frac{U_d + J_d}{4} m(\text{Mn}_\gamma), \quad (8)$$

where the spin σ may have the two values \pm , and where we have introduced the total averaged numbers of electrons

$$n(\text{N}) = \langle n_+(\text{N}) \rangle + \langle n_-(\text{N}) \rangle,$$

$$n(\text{Mn}_\gamma) = \langle n_+(\text{Mn}_\gamma) \rangle + \langle n_-(\text{Mn}_\gamma) \rangle$$

and the magnetic moments (in Bohr magneton units)

$$m(\text{N}) = \langle n_+(\text{N}) \rangle - \langle n_-(\text{N}) \rangle,$$

$$m(\text{Mn}_\gamma) = \langle n_+(\text{Mn}_\gamma) \rangle - \langle n_-(\text{Mn}_\gamma) \rangle,$$

respectively, on a metalloidic site (N or C) and on a site Mn_γ .

Equations (7) and (8) are valid in the general case where small lattice distortions and magnetic moments are present. But in the special case of the cubic paramagnetic phase, the magnetic moments $m(\text{N})$ and $m(\text{Mn}_\gamma)$ vanish, and the parameters $T[d(\text{Mn}_\gamma)]$ no longer depend on γ and can be simply written $T(d)$; we obtain the expressions of the two parameters we had introduced in Section I.4 for the cubic paramagnetic phase:

$$E_p = T(p) + \frac{5U_p - 2J_p}{6} n(\text{N}), \quad (9)$$

$$E_d = T(d) + \frac{3U_d - J_d}{4} n(\text{Mn}). \quad (10)$$

II. Perturbation of the Band Structure by Small Distortions and Magnetic Moments

Equation (1) gives the density of states $n(E)$ in the neighborhood of the logarithmic singularity E_s in the cubic paramagnetic phase. As we can see from Eqs. (2), (3), and (4), $n(E)$ depends on the three parameters β , E_p , and E_d , and it can be shown that a small lattice distortion and the appearance of small magnetic moments perturb the density of states in the neighborhood of the singularity essentially by their effects on these three parameters. In particular, the perturbation of the regular part $R(E)$ of the density of states $n(E)$ given by Eq. (1) is assumed to be very small and will be neglected.

By a small lattice distortion which produces distinct variations of the lattice parameter a along the three orthogonal edges of the cubic unit cell, the transfer integral β between next-nearest neighbors gets different values,

$$\beta_\alpha = \beta \exp(-\frac{1}{2}aqe_{\alpha\alpha}), \quad (11)$$

along the three directions $\alpha = X, Y, Z$, where $e_{\alpha\alpha}$ are the diagonal components of the strain tensor and q is a coefficient which governs the exponential variation of the overlap between p and d_{eg} orbitals belonging to next-nearest neighbors when the interatomic distance varies.

The effect of a small lattice distortion which lowers the symmetry can be a splitting of the value of the first term $T[d(\text{Mn}_\gamma)]$ in Eq. (8) into three different values depending on γ . But it is clear that the electronic population $n(\text{Mn}_\gamma)$ increases (respectively decreases) when the energy level $T[d(\text{Mn}_\gamma)]$ is decreased (respectively increased) by the distortion. And, as $3U_d - J_d$ is large and positive, we shall assume that the opposite effects of the lattice distortion on the first two terms of Eq. (8) roughly cancel each other.

Thus we are led to assume that E_p and E_d

are not very sensitive to a small lattice distortion but are split by the appearance of small magnetic moments $m(\text{N})$ and $m(\text{Mn}_\gamma)$ into new values which depend on the spin σ , and which, according to Eqs. (7), (8), (9), and (10), are given by

$$E_\sigma(p) = E_p - \frac{\sigma}{2} I_p m(\text{N}), \quad (12)$$

$$E_\sigma[d(\text{Mn}_\gamma)] = E_d - \frac{\sigma}{2} I_d m(\text{Mn}_\gamma), \quad (13)$$

where $\sigma = \pm$, and where we have introduced the effective parameters

$$I_p = \frac{U_p + 2J_p}{3} \quad \text{and} \quad I_d = \frac{U_d + J_d}{2}.$$

We have shown in Section I.2 that in the cubic and Pauli paramagnetic phase the narrow p - d_{eg} subband is itself made of six identical $S_{\alpha\sigma}$ subbands, where $\alpha = X, Y$, or Z and where $\sigma = \pm$ are the up and down spin directions; in particular, all these six subbands have the same logarithmic singularity of their density of states at exactly the same energy E_s . The effect of a small lattice distortion, by which the lengths of the three orthogonal edges of the cubic unit cell no longer remain identical, and of the appearance of small magnetic moments $m(\text{N})$ and $m(\text{Mn}_\gamma)$ will be to remove, at least partly, this sixfold degeneracy, and in particular to split the logarithmic singularity into several new distinct logarithmic singularities, the respective energies of which, a little shifted from E_s , can be calculated from Eqs. (3), (11), (12), and (13).

More precisely, the structure of each subband S_α is determined by the two transfer integrals β_γ and $\beta_{\gamma'}$ between nearest neighbors, from the orbital p_α to the orbitals $d_{\gamma\alpha}(\text{Mn}_\gamma)$ and $d_{\gamma'\alpha}(\text{Mn}_{\gamma'})$, respectively, where the sequence of the indices α, γ , and γ' is a permutation of X, Y , and Z . Equation (11) shows that, under the action of a lattice distortion with components $e_{\gamma\gamma} \neq e_{\gamma'\gamma'}$ of the strain tensor, the transfer integrals β_γ and

β_γ , which were equal in the cubic phase, get into values which are different from each other; it follows from Eq. (3) that, for each spin direction, the singularity of the subband S_α , which is located at the energy E_s in the cubic phase, is split into two new distinct singularities located at the energies $E_{s\gamma}$ and $E_{s\gamma'}$ which are the new values obtained in place of E_s when substituting, respectively, β_γ and $\beta_{\gamma'}$ for β in Eq. (3). Thus the singularity of the subband S_α is split by the lattice distortion into two new ones when $e_{\gamma\gamma} \neq e_{\gamma'\gamma'}$, and is not split, but simply a little shifted from E_s , when $e_{\gamma\gamma} = e_{\gamma'\gamma'}$.

Furthermore, for nonvanishing magnetic moments $m(N)$ and $m(Mn_\gamma)$, the parameters E_p and E_d , which occur in Eq. (3) and in $\Delta = E_p - E_d$, must be replaced, respectively, by $E_\sigma(p)$ and $E_\sigma[d(Mn_\gamma)]$, the expressions of which are given by Eqs. (12) and (13). Thus we see that, besides the splittings induced by the lattice distortion, the appearance of small magnetic moments $m(N)$ and $m(Mn_\gamma)$ gives rise to small shifts of the energy E_s of the singularity, which have opposite values for the two opposite spin directions $\sigma = \pm$; it follows that there is an additional splitting of the singularities. In the calculation, the small variations of the parameter Δ in Eq. (3) are taken into account by expanding the square root to the first order in the small magnetic moments. Moreover, it seems reasonable to assume that the intraatomic Coulomb repulsion between two electrons is much smaller inside the metalloid than inside the manganese, and thus to neglect the parameter I_p in Eq. (12) with respect to the parameter I_d in Eq. (13).

Thus, as a result of both a small lattice distortion and the appearance of small magnetic moments, the singularity of each subband S_α , which is located at the energy E_s in the cubic and Pauli paramagnetic phase, can be split into four distinct new singularities located at the energies

$$E_{\gamma,\sigma} = E_s + \lambda e_{\gamma\gamma} - \frac{\sigma}{2} I_c m_\gamma, \quad (14)$$

where $m_\gamma = m(Mn_\gamma)$ is a simplified notation for the magnetic moment at the site Mn, $\sigma = \pm$ are the up and down spin directions, the index γ has two possible values which are the two symbols of the sequence X, Y, and Z which differ from α (i.e., $\gamma = Y$ or Z when $\alpha = X$, and so on by permutation of X, Y, and Z), and we have introduced the two new effective parameters

$$\lambda = \frac{-4\beta^2 a q}{\sqrt{\Delta^2 + 16\beta^2}} \quad \text{and} \quad I_c = \frac{1}{2} I_d \left(1 - \frac{\Delta}{\sqrt{\Delta^2 + 16\beta^2}} \right).$$

We see from Eq. (14) that the splitting of the singularity is complete when all the diagonal components $e_{\gamma\gamma}$ of the strain tensor and all the magnetic moments m_γ at the different Mn $_\gamma$ sites are different, but it is not complete when some of the diagonal components $e_{\gamma\gamma}$ and some of the magnetic moments m_γ are equal. We also see that in any case two singularities of the distorted and magnetic phase are located at the same energy $E_{\gamma,\sigma}$, each one in one of the two distinct subbands S_α and $S_{\alpha'}$, such that the sequence of indices γ , α , and α' is a permutation of X, Y, and Z. Thus, even in the extreme case of a complete splitting, the singularity is split only into six new distinct singularities, which are associated with $\gamma = X, Y$, or Z and $\sigma = \pm$; and this result is in agreement with the existence of a sixfold degeneracy in the cubic and Pauli paramagnetic phase.

The small lattice distortion and the appearance of small magnetic moments give rise to small variations of the parameters C and ν which occur in Eq. (2) and are given by Eqs. (4). But the effect of these small variations on the density of states is very small when compared to the effect of the splitting of the singularity. Therefore we shall consider C and ν as constant parameters. As a consequence of this approximation, the new density of states $n_{S_{\alpha,\sigma}}(E)$ of

the subband $S_{\alpha,\sigma}$, in the neighborhood of the split singularity, in the distorted and magnetic phase, simply results from the splitting of the density of states $\bar{n}(E - E_s)$ into two identical new ones, with equal weights, but centered at the two distinct energies $E_{\gamma,\sigma}$ and $E_{\gamma',\sigma}$, i.e.,

$$n_{S_{\alpha\sigma}}(E) = \frac{1}{2}\bar{n}(E - E_{\gamma,\sigma}) + \frac{1}{2}\bar{n}(E - E_{\gamma',\sigma}), \quad (15)$$

where the analytical expression of \bar{n} is given by Eq. (2), and the sequence of indices α , γ , and γ' is a permutation of X , Y , and Z .

Finally, the approximate expression $n^*(E)$ of the total density of states in the neighborhood of the split singularity, in the distorted and magnetic phase, is given by

$$n^*(E) = \sum_{\substack{\alpha=X,Y,Z \\ \sigma=\pm}} n_{S_{\alpha,\sigma}}(E). \quad (16)$$

By using expression (15) for $n_{S_{\alpha,\sigma}}(E)$, and as each one of the energies $E_{\gamma,\sigma}$ appears twice in Eq. (16), we obtain as a final result

$$n^*(E) = \sum_{\substack{\gamma=X,Y,Z \\ \sigma=\pm}} \bar{n}(E - E_{\gamma,\sigma}) + 2R(E), \quad (17)$$

where, as indicated at the beginning of this section, the regular contribution $R(E)$, due to the large conduction band, is assumed to be nearly unaffected by the small lattice distortion and the appearance of small magnetic moments.

III. Discussion of the Stability of the Undistorted Cubic and Pauli Paramagnetic Phase at Absolute Zero

As usual, to discuss the stabilities of the different possible phases of the crystal we must compare their free energies; and thus, to discuss the stability of the undistorted cubic and Pauli paramagnetic phase, we must calculate the variation δF of the free energy of the crystal when going from that

phase to any of the distorted magnetic phases, an instability being expected in the cases where δF is negative. But it is clear that, when the Fermi energy E_F is close to a sharp singularity of the density of states, which can be split into several new singularities both by small lattice distortions and by the appearance of small magnetic moments, a large contribution δF_e to δF arises from the relatively large number of electrons which are transferred, inside the $p-d_{e_g}$ subband in our model, from the new singularities with higher energies to the new ones with lower energies (Fig. 4). Since the energies of the transferred electrons are lowered, the contribution δF_e is negative and thus can produce an instability of the undistorted cubic and Pauli paramagnetic phase. Furthermore, this electronic transfer being largest at low temperature, where the Fermi Dirac function well separates occupied from unoccupied states, the magnitude of the absolute value of the term δF_e and thus the tendency to the instability are largest at low temperature.

The previous contribution δF_e , which is specific of conducting materials with narrow degenerate subbands at the Fermi energy, can be explicitly calculated in our model. But to obtain the entire expression

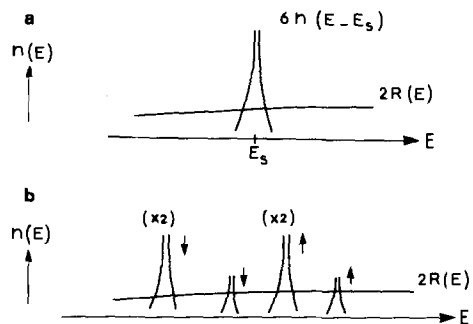


FIG. 4. Splitting of the degenerate singularity in the electronic density of states by a tetragonal shear strain and the formation of small magnetic moments on the manganese atoms. The density of states is pictured (a) in the cubic and Pauli paramagnetic phase and (b) in the distorted and magnetic phase.

of δF , we must add to δF_e a term δF_0 which takes into account all the other contributions, which are not specific of that kind of materials, and, for instance, exist in any normal metal. This last term δF_0 is difficult to calculate; but it is reasonable to assume that:

(1) δF_0 tends to stabilize the undistorted cubic and Pauli paramagnetic phase (which indeed is known to exist at high temperature), and thus δF_0 is positive;

(2) as usual in the normal metals, for instance, where the variation of the elastic constants with the temperature is known to be rather small, δF_0 does not depend much on the temperature, the opposite of δF_e ;

(3) δF_0 probably has the same order of magnitude as in the normal metals.

To sum up the previous discussion, the sign of δF , and thus the possible instability of the undistorted cubic and Pauli paramagnetic phase, depends on the competition between the term δF_0 , which is positive and nearly temperature independent, and the term δF_e , which can be negative and depends greatly on the temperature. Furthermore, the term δF_e can be calculated in our model as a function of the temperature, but the nearly constant term δF_0 cannot be calculated, but only roughly estimated, and it will be introduced in our calculations as an adjustable parameter independent of the temperature.

In this section we calculate δF_e , and thus discuss the stability of the undistorted cubic and Pauli paramagnetic phase, at absolute zero. The effect of the temperature will be calculated and discussed in Section IV.

As usual in the Hartree-Fock approximation, the total energy of the narrow subband can be obtained by summing the energies of all the electrons contained in that subband, and then subtracting from the result the averaged interaction energy between them, which has been counted twice when doing the summation of the electron energies. The averaged interaction energy between

all the electrons occupying the subband is difficult to calculate. But, according to the approximations we made in Sections I.5 and II, the largest contribution to the variation of this interaction energy comes from the appearance of small magnetic moments m_γ on the manganese sites γ . Thus, at absolute zero, the term δF_e , in the total variation δF of the free energy, is given by

$$\delta F_e = \int^{E_F^*} En^*(E) dE - \int^{E_F} En(E) dE + \frac{1}{4} I_d \sum_{\gamma=X,Y,Z} m_\gamma^2, \quad (18)$$

where E_F and E_F^* are the Fermi energies in the undistorted nonmagnetic and distorted magnetic phases, respectively, and where we do not need to specify the lower limits in the integrals, since the contributions from the energy levels far below the Fermi energy either cancel or are included in the term δF_0 of δF . The relation between E_F^* and E_F results from the conservation of the total number of electrons in the crystal, and thus is given by

$$\int^{E_F^*} n^*(E) dE = \int^{E_F} n(E) dE. \quad (19)$$

The densities of states $n(E)$ and $n^*(E)$ are given by Eqs. (1) and (17), respectively. By obvious changes in the variables of integration, equations (18) and (19) can be written, respectively,

$$\delta F_e = \sum_{\gamma,\sigma} \int^{E_F^* - E_{\gamma,\Delta} + E_s} (E + E_{\gamma,\sigma} - E_s) \bar{n}(E - E_s) dE - 6 \int^{E_F} E \bar{n}(E - E_s) dE + 2 \int_{E_F}^{E_F^*} ER(E) dE + \frac{1}{4} I_d \sum_{\gamma} m_\gamma^2 \quad (20)$$

and

$$\sum_{\gamma,\sigma} \int_{E_F}^{E_F^* - E_{\gamma,\sigma} + E_s} \bar{n}(E - E_s) dE + 2 \int_{E_F}^{E_F^*} R(E) dE = 0, \quad (21)$$

where the expression of $E_{\gamma,\sigma}$ as a function of the diagonal component $e_{\gamma\gamma}$ of the strain tensor and of the magnetic moment m_γ is given by Eq. (14).

As we show in the Appendix, expression (20) is equivalent to

$$\begin{aligned} \delta F_e = & \sum_{\gamma,\sigma} \int_{E_F}^{E_F^* - E_{\gamma,\sigma} + E_s} (E - E_s) \bar{n}(E - E_s) dE \\ & + \sum_{\gamma,\sigma} E_{\gamma,\sigma} \int_{E_F}^{E_F^* - E_{\gamma,\sigma} + E_s} \bar{n}(E - E_s) dE \\ & + 2\lambda\eta \int_{E_F}^{E_F^*} \bar{n}(E - E_s) dE \\ & + 2 \int_{E_F}^{E_F^*} ER(E) dE + \frac{1}{4} I_d \sum_{\gamma} m_\gamma^2, \quad (22) \end{aligned}$$

where $\eta = \sum_{\gamma} e_{\gamma\gamma}$ is the relative volume variation.

As the Fermi energy E_F has been assumed to be very close to the singularity E_s , and for distortions and magnetic moments small enough, the difference $E - E_s$ is very small for any value of E lying inside the narrow interval of integration in the first term of expression (22), and this term can be neglected as compared to the second term. Furthermore, on taking into account the relation (21), we have

$$\begin{aligned} 2 \int_{E_F}^{E_F^*} ER(E) dE & \approx 2E_s \int_{E_F}^{E_F^*} R(E) dE \\ & = -E_s \sum_{\gamma,\sigma} \int_{E_F}^{E_F^* - E_{\gamma,\sigma} + E_s} \bar{n}(E - E_s) dE. \quad (23) \end{aligned}$$

Combining Eqs. (22) and (23), we obtain

$$\begin{aligned} \delta F_e = & \sum_{\gamma,\sigma} (E_{\gamma,\sigma} - E_s) \\ & \int_{E_F}^{E_F^* - E_{\gamma,\sigma} + E_s} \bar{n}(E - E_s) dE \\ & + 2\lambda\eta \int_{E_F}^{E_F^*} \bar{n}(E - E_s) dE + \frac{1}{4} I_d \sum_{\gamma} m_\gamma^2, \quad (24) \end{aligned}$$

where the new value E_F^* of the Fermi energy must be determined by using Eq. (21).

The second term in expression (24) of

δF_e is linear in the relative volume variation η . Thus a stable state of the system can exist only if we assume that this term of δF_e is exactly cancelled by an opposite term in δF_0 , which comes from other contributions to the free energy. Moreover, δF_0 contains elastic terms $K_0 \eta^2$ and $M_0 \sum_{\gamma} (e_{\gamma\gamma} - \eta/3)^2$,

where K_0 and M_0 are the ordinary contributions to, respectively, the bulk modulus and the shear modulus involved in that kind of distortion. Thus, at absolute zero, the variation of the total free energy of the crystal can be written as

$$\begin{aligned} \delta F = & \sum_{\gamma,\sigma} (E_{\gamma,\sigma} - E) \\ & \int_{E_F}^{E_F^* - E_{\gamma,\sigma} + E_s} \bar{n}(E - E_s) dE + \frac{1}{4} I_d \sum_{\gamma} m_\gamma^2 \\ & + K_0 \eta^2 + M_0 \sum_{\gamma} (e_{\gamma\gamma} - \eta/3)^2. \quad (25) \end{aligned}$$

By expanding expression (25) of δF to the second order with respect to $e_{\gamma\gamma}$, m_γ , and $\eta = \sum_{\gamma} e_{\gamma\gamma}$ we obtain

$$\begin{aligned} \delta F = & \bar{n}(E_F - E_s) \\ & \left\{ (E_F^* - E_F) \sum_{\gamma,\sigma} u_{\gamma,\sigma} - \sum_{\gamma,\sigma} u_{\gamma,\sigma}^2 \right\} \\ & + \frac{1}{4} I_d \sum_{\gamma} m_\gamma^2 + K_0 \eta^2 + M_0 \sum_{\gamma} (e_{\gamma\gamma} - \eta/3)^2, \quad (26) \end{aligned}$$

where, according to Eq. (14), we have introduced the new quantities

$$u_{\gamma,\sigma} = E_{\gamma,\sigma} - E_s = \lambda e_{\gamma\gamma} - \frac{\sigma}{2} I_c m_\gamma \quad (27)$$

$$\sum_{\gamma,\sigma} u_{\gamma,\sigma} = 2\lambda \sum_{\gamma} e_{\gamma\gamma} = 2\lambda\eta, \quad (28)$$

which satisfy the relations

$$\sum_{\gamma,\sigma} u_{\gamma,\sigma}^2 = 2\lambda^2 \sum_{\gamma} e_{\gamma\gamma}^2 + \frac{1}{2} I_c^2 \sum_{\gamma} m_\gamma^2. \quad (29)$$

We can see from expression (26) that, to obtain the expansion of δF to the second order, we need to know the expansion of E_F^*

$-E_F$ only to the first order with respect to the same quantities. By expanding Eq. (21) to the first order, and using property (28), we obtain

$$6(E_F^* - E_F)\bar{n}(E_F - E_s) - 2\lambda\eta\bar{n}(E_F - E_s) + 2(E_F^* - E_s)R(E_s) = 0. \quad (30)$$

The result (30) shows that only a variation of the volume of the crystal can induce a linear variation of the Fermi energy.

Finally, by using Eqs. (26), (28), (29), and (30), we explicitly find the expansion to the second order of the variation δF of the total free energy of the crystal at absolute zero,

$$\delta F = K\eta^2 + M\sum_{\gamma} (e_{\gamma\gamma} - \eta/3)^2 + \frac{1}{2}I\sum_{\gamma} m_{\gamma\gamma}^2, \quad (31)$$

where the total bulk modulus K , the total shear modulus M , and the coefficient I have the expressions

$$K = K_0 - \frac{2}{3}\lambda^2 R(E_s), \quad (32)$$

$$M = M_0 - 2\lambda^2\bar{n}(E_F - E_s), \quad (33)$$

$$I = I_d - 2I_e^2\bar{n}(E_F - E_s). \quad (34)$$

In our model, the density of states $\bar{n}(E - E_s)$ is given by Eq. (2). It is the larger as the energy E is the closer to the energy E_s of the logarithmic singularity. Thus we see from Eqs. (31) and (33) that the cubic phase is unstable at absolute zero when the Fermi energy E_F is close enough to the singularity E_s to make $\bar{n}(E_F - E_s)$ larger than $M_0/2\lambda^2$, and thus to make the total shear modulus M negative. Similarly, we see from Eqs. (31) and (34) that the Pauli paramagnetic phase is unstable at absolute zero when E_F is close enough to E_s to make $\bar{n}(E_F - E_s)$ larger than $I_d/2I_e^2$, and thus to make the coefficient I negative. As $\bar{n}(E - E_s)$ is an even function of $E - E_s$, which monotonically decreases as $|E - E_s|$ increases, we shall introduce the critical values $E_{F_c}^{\pm} = E_s \pm X_{F_c}$ and $E_{F_m}^{\pm} = E_s \pm X_{F_m}$, where X_{F_c} and X_{F_m} are positive and

are defined by the conditions $M_0 = 2\lambda^2\bar{n}(X_{F_c})$ and $I_d = 2I_e^2\bar{n}(X_{F_m})$. When $|E_F - E_s|$ is larger than X_{F_c} and X_{F_m} , the cubic phase and the Pauli paramagnetic phase are both stable, or at least metastable,¹ at absolute zero. On the contrary, when $|E_F - E_s|$ is smaller than X_{F_c} and X_{F_m} , the cubic phase and the Pauli paramagnetic phase are both unstable at absolute zero. When the value of $|E_F - E_s|$ lies between X_{F_c} and X_{F_m} , either the cubic or the Pauli paramagnetic phase is unstable at absolute zero: when M_0/λ^2 is larger than I_d/I_e^2 , X_{F_c} is smaller than X_{F_m} , and when the Fermi energy E_F satisfies the condition $X_{F_c} < |E_F - E_s| < X_{F_m}$, the cubic phase is stable, or metastable, at absolute zero, but it has nonvanishing magnetic moments; on the contrary, when M_0/λ^2 is smaller than I_d/I_e^2 , X_{F_c} is larger than X_{F_m} , and when E_F satisfies the condition $X_{F_m} < |E_F - E_s| < X_{F_c}$, the Pauli paramagnetic phase is stable, or metastable, at absolute zero, but a nonvanishing lattice distortion takes place.

As a conclusion, our theoretical model predicts that small lattice distortions and small magnetic moments coexist or not at absolute zero, according to the exact value of the parameter $|E_F - E_s|$, where E_F is the Fermi energy and E_s the energy of the singularity in the electronic density of states. This parameter could depend on the exact chemical composition of a given compound, and could vary from one compound to another.

IV. Influence of the Temperature and Phase Transitions

For a nonvanishing value of the temperature T , the contribution δF_c to the variation

¹ They could only be metastable if higher-order terms in the expansion of δF would lead to the existence of more stable states with large distortions and magnetic moments.

of the free energy has the expression

$$\begin{aligned} \delta F_e = & \int_{-\infty}^{+\infty} n^*(E)\phi(E - E_F^*) dE \\ & - \int_{-\infty}^{+\infty} n(E)\phi(E - E_F) dE \\ & + (E_F^* - E_F) Q + \frac{1}{2} I_d \sum_{\gamma} m_{\gamma}^2, \end{aligned} \quad (35)$$

with

$$\begin{aligned} \phi(E - E_F) \\ = -k_B T \text{Log} \left(1 + \exp \frac{E_F - E}{k_B T} \right), \end{aligned} \quad (36)$$

where k_B is the Boltzmann constant. Q is the *total* number of electrons contained in all the bands; it keeps the same value in the different phases, and we have

$$\begin{aligned} Q = & \int_{-\infty}^{+\infty} n^*(E) f(E - E_F^*) dE \\ = & \int_{-\infty}^{+\infty} n(E) f(E - E_F) dE, \end{aligned} \quad (37)$$

where we have introduced the Fermi-Dirac function

$$f(E - E_F) = \left(1 + \exp \frac{E - E_F}{k_B T} \right)^{-1}. \quad (38)$$

Replacing the densities of states $n(E)$ and $n^*(E)$ by their expressions (1) and (17), respectively, changing the variable of integration from E to $E + u_{\gamma,\sigma}$, where $u_{\gamma,\sigma}$ has been defined by Eq. (27), expanding the integrals with respect to the small quantities $u_{\gamma,\sigma}$, assuming that $R(E)$ has a constant value $R(E_s)$ in the neighborhood of the singularity E_s , and adding the temperature-independent contribution δF_0 to δF_e , we obtain

$$\begin{aligned} \delta F = & \sum_{p=1}^{\infty} \frac{1}{p+1} A_{p+1} \sum_{\gamma,\sigma} \\ & (u_{\gamma,\sigma} + E_F - E_F^*)^{p+1} - (E_F - E_F^*)^2 R(E_s) \\ & + \frac{1}{2} I_d \sum_{\gamma} m_{\gamma}^2 + K_0 \eta^2 + M_0 \sum_{\gamma} \left(e_{\gamma\gamma} - \frac{\eta}{3} \right)^2, \end{aligned} \quad (39)$$

where p is an integer, and

$$A_p = \frac{1}{(p-1)!} \int_{-\infty}^{+\infty} \tilde{n}(E - E_s) f^{(p-1)}(E - E_F) dE \quad (40)$$

$$= \frac{1}{(p-1)!} \int_{-\infty}^{+\infty} \tilde{n}(E - E_s) \phi^{(p)}(E - E_F) dE \quad (41)$$

with the notation $f^{(p)}(X) = \frac{d^p}{dX^p} f(X)$.

The conservation of the total number of electrons is ensured by

$$\begin{aligned} \sum_{p=1}^{\infty} A_{p+1} \sum_{\gamma,\sigma} (u_{\gamma,\sigma} + E_F - E_F^*)^p \\ - 2(E_F - E_F^*) R(E_s) = 0, \end{aligned} \quad (42)$$

which is obtained from Eq. (37).

By eliminating $R(E_s)$ between Eqs. (39) and (42), Eq. (39) can be written in the simpler form

$$\begin{aligned} \delta F = & \sum_{p=1}^{\infty} \frac{1}{p+1} A_{p+1} \sum_{\gamma,\sigma} (u_{\gamma,\sigma} + E_F - E_F^*)^p \\ & \left\{ u_{\gamma,\sigma} + \frac{p-1}{2} (E_F^* - E_F) \right\}. \end{aligned} \quad (43)$$

In Eqs. (42) and (43), the effect of the temperature is contained in the coefficients $A_p = A_p(T)$, which can be calculated by Eqs. (40) and (38).

Replacing, in Eq. (43), $E_F^* - E_F$ by its expansion with respect to the small quantities $u_{\gamma,\sigma}$, which can be calculated from the implicit Eq. (42), we get the explicit expansion of δF with respect to the $u_{\gamma,\sigma}$. Then, the $u_{\gamma,\sigma}$ can be expressed as linear combinations of the relative volume variation η , the tetragonal shear strain ϵ , the orthorhombic shear strain ϵ' , and the three small magnetic moments m_{γ} , by using Eq. (27), with

$$\begin{aligned} e_{XX} = & \frac{\eta}{3} - \frac{\epsilon}{2} + \frac{\epsilon'}{2}, & e_{YY} = & \frac{\eta}{3} - \frac{\epsilon}{2} - \frac{\epsilon'}{2}, \\ e_{ZZ} = & \frac{\eta}{3} + \epsilon. \end{aligned} \quad (44)$$

By limiting, for instance, the expansion of δF to the terms of the fourth order in the

$u_{\gamma,\sigma}$, and retaining the linear terms only in the small quantity $R(E_s)$, we obtain

$$\delta F = \delta F^{(2)} + \delta F^{(3)} + \delta F^{(4)} \quad (45)$$

with

$$\delta F^{(2)} = K(T) \eta^2 + \frac{1}{2} M(T) (3\epsilon^2 + \epsilon'^2) + \frac{1}{4} I(T) (m_X^2 + m_Y^2 + m_Z^2), \quad (46)$$

where

$$K(T) = K_0 - \frac{3}{8} \lambda^2 R(E_s), \quad (47)$$

$$M(T) = M_0 + \lambda^2 A_2(T), \quad (48)$$

$$I(T) = I_d + I_e^2 A_2(T), \quad (49)$$

$$\begin{aligned} \delta F^{(3)} = & -\frac{R(E_s) A_3(T)}{9 A_2(T)} \\ & \lambda \eta \left\{ \lambda^2 (3\epsilon^2 + \epsilon'^2) + \frac{I_e^2}{2} (m_X^2 + m_Y^2 + m_Z^2) \right\} \\ & + \frac{A_3(T)}{4} \lambda I_e^2 \{ \epsilon (2m_Z^2 + m_X^2 + m_Y^2) \\ & + \epsilon' (m_X^2 - m_Y^2) \} \\ & + \frac{A_3(T)}{2} \lambda^3 \epsilon (\epsilon^2 - \epsilon'^2), \quad (50) \end{aligned}$$

$$\begin{aligned} \delta F^{(4)} = & -\frac{R(E_s) A_4(T)}{12 A_2(T)} \lambda^2 \eta \{ 2\lambda^2 \epsilon (\epsilon^2 - \epsilon'^2) \\ & + I_e^2 [\epsilon (2m_Z^2 - m_X^2 - m_Y^2) \\ & + \epsilon' (m_X^2 - m_Y^2)] \} + \frac{A_4(T)}{16} \lambda^4 \\ & \{ \epsilon^4 + \epsilon'^4 + 6\epsilon^2 \epsilon'^2 \} + \frac{3}{16} A_4(T) \lambda^2 I_e^2 \\ & \{ \epsilon^2 (m_X^2 + m_Y^2 + 4m_Z^2) + \epsilon'^2 (m_X^2 + m_Y^2) \\ & + 2\epsilon\epsilon' (m_Y^2 - m_X^2) \} + \frac{A_4(T)}{32} \\ & I_e^4 (m_X^4 + m_Y^4 + m_Z^4) - \frac{A_3^2(T)}{12 A_2(T)} \\ & \left[1 + \frac{R(E_s)}{3 A_2(T)} \right] \\ & I_e^4 (m_Y^2 m_Z^2 + m_Z^2 m_X^2 + m_X^2 m_Y^2). \quad (51) \end{aligned}$$

The next step is to calculate the coefficients $A_p(T)$ as functions of the temperature. As we have shown in Section III, it is only when the Fermi energy E_F is very close to the singularity E_s that an instability of the cubic and Pauli paramagnetic phase

can be expected. Moreover, in that kind of compound, phase transitions are observed for values of the temperature which are not small, as compared, for instance, to room temperature. Thus, in this temperature range, we can assume that $|E_F - E_s|$ is much smaller than $k_B T$, and expand the coefficients $A_p(T)$ with respect to $(E_F - E_s)/k_B T$. To do that, at first we expand the successive derivatives of the Fermi Dirac function (38) in the form

$$\begin{aligned} f^{(p)}(E - E_F) &= f^{(p)}(E - E_s + E_s - E_F) \\ &= \sum_{q=0}^{\infty} \frac{1}{q!} (E_s - E_F)^q f^{(p+q)}(E - E_s). \quad (52) \end{aligned}$$

Substituting the expansion (52) into expression (40), we obtain

$$A_{p+1}(T) = \frac{1}{p!} \sum_{q=0}^{\infty} \frac{1}{q!} (E_s - E_F)^q I_{p+q} \quad (53)$$

with

$$I_n = \int_{-\infty}^{+\infty} \bar{n}(E) f^{(n)}(E) dE. \quad (54)$$

By using the explicit expression (2) of $\bar{n}(E)$, we find

$$\begin{aligned} I_{2m} = 0, \quad I_{2m+1} = & -\frac{C}{(k_B T)^{2m}} \\ & \left\{ \delta_{m,0} \text{Log} \frac{\nu}{k_B T} + \Gamma_{2m+1} \right\}, \quad (55) \end{aligned}$$

where $\delta_{m,0}$ is equal to zero for $m \neq 0$, and to unity for $m = 0$, and

$$\Gamma_n = \int_{-\infty}^{+\infty} \text{Log} |\zeta| g^{(n)}(\zeta) d\zeta, \quad (56)$$

where

$$g(\zeta) = f(\zeta k_B T) = (1 + e^\zeta)^{-1}.$$

The quantities Γ_n are numbers, which are easily computed from Eq. (56); we find $\Gamma_1 = \text{Log} 1.14$, $\Gamma_3 = -0.43$, $\Gamma_5 = 0.49$, and so on. Finally, from Eqs. (53) and (55), we obtain

$$\begin{aligned} A_2(T) = C \left\{ \text{Log} \frac{k_B T}{1.14\nu} + \frac{0.43}{2} \right. \\ \left. \left(\frac{E_F - E_s}{k_B T} \right)^2 - \frac{0.49}{6} \left(\frac{E_F - E_s}{k_B T} \right)^4 \dots \right\}, \quad (57) \end{aligned}$$

$$A_3(T) = -\frac{C}{2} \frac{E_F - E_s}{(k_B T)^2} \left\{ 0.43 - \frac{0.49}{6} \left(\frac{E_F - E_s}{k_B T} \right)^2 \dots \right\}, \quad (58)$$

$$A_4(T) = \frac{1}{6} \frac{C}{(k_B T)^2} \left\{ 0.43 - \frac{0.49}{2} \left(\frac{E_F - E_s}{k_B T} \right)^2 \dots \right\}. \quad (59)$$

Furthermore, the Fermi energy E_F at the temperature T can be related to the value E_F^0 it would have at absolute zero (if the cubic and Pauli paramagnetic phase would remain stable in that limit) by writing the conservation of the total number of electrons. If we neglect $R(E_s)$, we find

$$E_F - E_s = (E_F^0 - E_s) \left(\text{Log} \frac{|E_F^0 - E_s|}{2.7\nu} \right) \left(\text{Log} \frac{k_B T}{1.14\nu} \right)^{-1}. \quad (60)$$

It results from Eq. (47) that the calculated bulk modulus $K = K(T)$ in fact does not depend on the temperature. Moreover, as $R(E_s)$ is very small, we have $K \approx K_0 > 0$. Thus, in our model, we do not expect an instability of the crystal which would involve a variation of the volume *alone*. However, we shall see later that, because of the existence of coupling terms in Eq. (50), a small variation of the volume can be induced by a shear strain or by the appearance of small magnetic moments.

Since $k_B T$ is always much smaller than the parameter ν , the expression of which is given by Eq. (4), it results from Eq. (57) that, for $|E_F - E_s|$ much smaller than $k_B T$, the coefficient $A_2(T)$ is negative, with an absolute value which increases as the temperature decreases. And thus, since the parameters M_0 and I_d are positive, Eqs. (48) and (49) show that the shear modulus $M(T)$ and the coefficient $I(T)$, which is proportional to the inverse of the Pauli paramagnetic susceptibility, decrease as the temperature decreases. Taking into account Eq. (60), we find that $M(T)$ and $I(T)$ go to zero

at critical values of the temperature T_0 and T_m respectively, the expression of which are easily calculated as

$$T_0 = T_0^{(0)} \{1 - \theta_0(|E_F^0 - E_s|)\}, \quad (61)$$

$$T_m = T_m^{(0)} \{1 - \theta_m(|E_F^0 - E_s|)\}, \quad (62)$$

with

$$k_B T_0^{(0)} = 1.14 \nu \exp \left(-\frac{M_0}{\lambda^2 C} \right), \quad (63)$$

$$k_B T_m^{(0)} = 1.14 \nu \exp \left(-\frac{I_d}{I_c^2 C} \right), \quad (64)$$

$$\theta_\alpha(|X|) = \frac{0.43}{2} \left(X \text{Log} \frac{|X|}{2.7\nu} \right)^2 \left(k_B T_\alpha^{(0)} \text{Log} \frac{k_B T_\alpha^{(0)}}{1.14\nu} \right)^{-2}, \quad (65)$$

where by α we mean one of the two symbols 0 or m.

It results from Eqs. (61), (62), and (65) that the critical temperatures T_0 and T_m have their largest values $T_0^{(0)}$ and $T_m^{(0)}$ when the Fermi energy E_F^0 exactly coincides with the energy E_s of the singularity of the density of states. And Eqs. (61) to (65) show that T_0 is larger (smaller) than T_m when M_0/ν^2 is smaller (respectively larger) than I_d/I_c^2 .

First, let us consider the case when M_0/λ^2 is smaller than I_d/I_c^2 , and thus T_0 is larger than T_m . We see from expression (46) of the second-order terms $\delta F^{(2)}$ in the expansion of the free energy that, when the decreasing temperature T reaches the critical value T_0 , the shear modulus $M(T)$ goes to zero alone, whereas the coefficient $I(T)$ has yet a positive value, the bulk modulus $K(T)$ being always positive as we have just established. Thus, when T lies in the neighborhood of T_0 , and remains larger than T_m , we expect as a precursive phenomenon an instability of the cubic phase with respect to a shear strain only, the other instabilities eventually appearing as secondary effects to be induced by the coupling terms between the shear strain and the other parameters in Eq. (50). Assuming, as a starting point, that a

nonvanishing tetragonal shear strain ϵ takes place alone, all the other parameters m_X , m_Y , m_Z , η , and ϵ' remaining equal to zero, we obtain from Eqs. (46), (50), and (51) the following reduced form of the expansion of the free energy variation:

$$\delta F[\epsilon] = \frac{3}{2} M(T) \epsilon^2 + \frac{1}{2} A_3(T) (\lambda \epsilon)^3 + \frac{1}{16} A_4(T) (\lambda \epsilon)^4. \quad (66)$$

Equation (59) shows that the coefficient $A_4(T)$ is positive (at least for not too small values of the temperature T). Thus we can be sure that expression (66) of $\delta F[\epsilon]$ has an absolute minimum. When calculating that minimum, we find there exists a critical value $T'_0 > T_0$ of the temperature T , defined by the relation

$$M(T'_0) = 2\lambda^2 A_3^2(T'_0)/3A_4(T'_0) \quad (67)$$

and such that $\delta F[\epsilon]$ reaches its minimum for a value of ϵ which is equal to zero when T is larger than T'_0 , and to

$$\epsilon_0(T) = \frac{1}{\lambda A_4(T)} \left\{ -3A_3(T) \pm \sqrt{9A_3^2(T) - 12A_4(T) \frac{M(T)}{\lambda^2}} \right\} \quad (68)$$

when T is smaller than T'_0 , with the sign minus (plus) when $A_3(T)$ is positive (respectively negative).

Thus a structural phase transition takes place at the temperature T'_0 , from the cubic phase, stable for $T > T'_0$ to a tetragonal phase, stable for $T < T'_0$. The amplitude $\epsilon_0(T)$ of the tetragonal distortion is given by Eq. (68). The parameter λ is negative. And according to Eqs. (58) and (60), the coefficient $A_3(T)$ has the same sign as $E_s - E_F^0$. Thus the distortion $\epsilon_0(T)$ is positive (negative) when E_F^0 is smaller (respectively larger) than E_s . The discontinuity $\epsilon_0(T'_0)$ of the distortion at the transition temperature T'_0 can be easily calculated by using Eqs. (67) and (68), and is found to be

$$\epsilon_0(T'_0) = -\frac{4}{\lambda} \frac{A_3(T'_0)}{A_4(T'_0)}. \quad (69)$$

It vanishes when $A_3(T'_0)$ does, and thus when $E_F^0 = E_s$, as follows from Eqs. (58) and (60). We conclude from that result that the structural phase transition is a first-order phase transition when $E_F^0 \neq E_s$, and a second-order one when $E_F^0 = E_s$.

The latent heat associated with the transition is equal to the variation ΔU of the internal energy when going, at the temperature T'_0 , from the state with $\epsilon = \epsilon_0(T'_0)$ to the state $\epsilon = 0$. By using the Gibbs-Helmoltz formula, the fact that when $\delta F[\epsilon]$ is minimum its first derivative with respect to ϵ is equal to zero, and keeping only the largest term in the result, we obtain

$$\Delta U = T'_0 \frac{3}{2} \epsilon_0^2(T'_0) \left[\frac{d}{dT} M(T) \right]_{T=T'_0}, \quad (70)$$

which, according to Eqs. (48) and (57), is equal to

$$\Delta U = T'_0 \frac{3}{2} \lambda^2 \epsilon_0^2(T'_0) \left[\frac{d}{dT} A_2(T) \right]_{T=T'_0} = \frac{3}{2} C \lambda^2 \epsilon_0^2(T'_0). \quad (71)$$

It vanishes when $E_F^0 = E_s$.

The stability of the tetragonal phase, at a temperature $T < T'_0$, with respect to a small orthorhombic distortion ϵ' , can be discussed by starting from the tetragonal state with its equilibrium distortion $\epsilon_0(T)$, and writing the expansion of the variation $\delta F[\epsilon_0(T), \epsilon']$ of the free energy which results from a small additive orthorhombic distortion ϵ' . By assuming $m_X = m_Y = m_Z = \eta = 0$, $\epsilon = \epsilon_0(T)$, and $\epsilon' \neq 0$, in Eqs. (45), (46), (50), and (51), one gets

$$\delta F[\epsilon_0(T), \epsilon'] = \delta F[\epsilon_0(T)] + \Gamma_2 \epsilon'^2 + \Gamma_4 \epsilon'^4, \quad (72)$$

where $\delta F[\epsilon_0(T)]$ is obtained by substituting $\epsilon_0(T)$ to ϵ into expression (66) and with

$$\Gamma_2 = \frac{3}{2} \lambda^4 A_4(T) \epsilon_0^2(T) - \frac{1}{2} \lambda^3 A_3(T) \epsilon_0(T) + \frac{1}{2} M(T), \quad (73)$$

$$\Gamma_4 = \frac{1}{16} \lambda^4 A_4(T). \quad (74)$$

Since the coefficient $A_4(T)$ is positive, it follows from Eq. (74) that the coefficient Γ_4 is positive too. By eliminating $M(T)$ between Eqs. (68) and (73), the coefficient Γ_2 can be written in the form

$$\Gamma_2 = \frac{1}{2}\lambda^4 A_4(T) \epsilon_0^2(T) - \frac{3}{4}\lambda^3 A_3(T) \epsilon_0(T). \quad (75)$$

As, according to Eq. (68), the product $\lambda A_3(T) \epsilon_0(T)$ is always negative, Eq. (75) shows that Γ_2 is always positive. Thus, as the two coefficients Γ_2 and Γ_4 in the expansion (72) are positive, the minimum of $\delta F[\epsilon_0(T), \epsilon']$ is obtained with $\epsilon' = 0$, and the tetragonal phase is stable with respect to an orthorhombic distortion.

Similarly, the stability of the tetragonal phase, at a temperature $T < T'_0$, with respect to a small relative variation η of the volume can be discussed by calculating the variation $\delta F[\epsilon_0(T), \eta]$ of the free energy it produces. By assuming $m_X = m_Y = m_Z = \epsilon' = 0$, $\epsilon = \epsilon_0(T)$, and $\eta \neq 0$, in Eqs. (45), (46), (50), and (51), one gets

$$\delta F[\epsilon_0(T), \eta] = \delta F[\epsilon_0(T)] - \frac{\lambda^3 R(E_s)}{3 A_2(T)} [A_3(T) + \frac{\lambda}{2} A_4(T) \epsilon_0(T)] \epsilon_0^2(T) \eta + K \eta^2. \quad (76)$$

We see from Eq. (76) that, because of the coupling term between $\epsilon_0(T)$ and η , the tetragonal distortion $\epsilon_0(T)$ induces a linear term in η in the variation of the free energy. Thus, although the bulk modulus K has been found large, positive, and temperature independent, as shown by Eq. (47), a small variation of the volume results from that linear term in η . Indeed, expression (76) is minimum when η has the value

$$\eta_0(T) = \frac{\lambda^3 R(E_s)}{6K A_2(T)} [A_3(T) + \frac{\lambda}{2} A_4(T) \epsilon_0(T)] \epsilon_0^2(T). \quad (77)$$

It results from Eqs. (69) and (77) that, at the

critical temperature T'_0 , the structural transition induces a discontinuity in the relative variation of the volume, which is equal to

$$\eta_0(T'_0) = \frac{\lambda^4 R(E_s) A_4(T'_0)}{24 K A_2(T'_0)} \epsilon_0^3(T'_0). \quad (78)$$

It vanishes when $E_F^0 = E_s$.

When the temperature T goes on to decrease below T'_0 , whereas we still assume M_0/λ^2 to be smaller than I_d/I_e^2 , the Pauli paramagnetic tetragonal phase can become unstable with respect to the appearance of small magnetic moments m_γ at some critical value of the temperature. To discuss that additive instability, we shall write the expansion of the variation $\delta F[\epsilon_0(T), \eta_0(T), m_X, m_Y, m_Z]$ of the free energy, obtained by putting $\epsilon = \epsilon_0(T)$, $\eta = \eta_0(T)$, $\epsilon' = 0$, and $m_\gamma \neq 0$, with $\gamma = X, Y$, or Z , into Eqs. (45), (46), (50), and (51). Keeping only the terms which actually are at the most of fourth order, and neglecting that one of the fourth-order terms, the coefficient of which is proportional to $A_3^2(T)/A_2(T)$, which is very small with respect to $A_4(T)$, as results from expansions (57), (58), and (59), one gets

$$\begin{aligned} \delta F[\epsilon_0(T), \eta_0(T), m_X, m_Y, m_Z] \\ = \delta F[\epsilon_0(T), \eta_0(T)] + \frac{I_1(T)}{4} (m_X^2 + m_Y^2) \\ + \frac{I_2(T)}{4} m_Z^2 + \frac{A_4(T)}{32} I_e^4 (m_X^4 + m_Y^4 + m_Z^4) \end{aligned} \quad (79)$$

with

$$I_1(T) = I(T) + \frac{\lambda}{4} I_e^2 \epsilon_0(T) [3\lambda A_4(T) \epsilon_0(T) - 4 A_3(T)] \quad (80)$$

and

$$I_2(T) = I(T) + \lambda I_e^2 \epsilon_0(T) [3\lambda A_4(T) \epsilon_0(T) + 2 A_3(T)]. \quad (81)$$

The coefficients $I_1(T)$ and $I_2(T)$, respectively, vanish for critical values T_1 and T_2 of

the temperature T , which only differ from the temperature T_m at which $I(T)$ vanishes by small corrections which are easily calculated. We find

$$T_1 = T_m \left\{ 1 - \frac{\lambda \epsilon_0(T_m)}{4C} \right. \\ \left. [3\lambda A_4(T_m) \epsilon_0(T_m) - 4 A_3(T_m)] \right\}, \quad (82)$$

$$T_2 = T_m \left\{ 1 - \frac{\lambda \epsilon_0(T_m)}{C} \right. \\ \left. [3\lambda A_4(T_m) \epsilon_0(T_m) + 2 A_3(T_m)] \right\}. \quad (83)$$

It follows from Eqs. (82) and (83) that $T_2 < T_1 < T_m$. By calculating, at a given value of the temperature T , the values of the magnetic moments for which expression (79) is minimum, we obtain

$$m_X(T) = m_Y(T) = \begin{cases} 0 & \text{for } T > T_1, \\ m_1(T) & \text{for } T < T_1, \end{cases} \quad (84)$$

and

$$m_Z(T) = \begin{cases} 0 & \text{for } T > T_2, \\ m_2(T) & \text{for } T < T_2, \end{cases} \quad (85)$$

with

$$m_i(T) = \frac{2}{I_c} \sqrt{-\frac{I_i(T)}{A_4(T)}} \\ \text{(where } i = 1 \text{ or } 2). \quad (86)$$

Thus, as could have been expected, the magnetic moments in the tetragonal phase have the same value $m_1(T)$ at the sites X and Y , but a different value $m_2(T)$ at the sites Z . Furthermore, there are no discontinuities at the critical temperatures T_1 and T_2 in the variations of $m_1(T)$ and $m_2(T)$ with respect to the temperature. Thus the phase transitions which take place at these temperatures T_1 and T_2 , with appearance of small magnetic moments, are second-order phase transitions.

A similar analysis can be made when M_0/λ^2 is larger than I_d/I_c^2 . Then it follows from Eqs. (61) to (64) that T_m is larger than T_0 .

And, as the temperature T decreases, the first phase transition to take place is the second-order phase transition with the appearance of small magnetic moments at the critical temperature T_m . For $T_0 < T < T_m$, these magnetic moments have the same value $m_0(T)$ at the three sites X , Y , and Z , with

$$m_0(T) = \frac{2}{I_c} \sqrt{-\frac{I(T)}{A_4(T)}} \\ = 7.47 \frac{k_B T_m}{I_c} \sqrt{1 - \frac{T}{T_m}}. \quad (87)$$

Furthermore, as the coupling term between η and $m_X = m_Y = m_Z = m_0(T)$ in Eq. (50) is linear in η , the appearance of magnetic moments induces a small relative variation of the volume equal to

$$\eta_m(T) = \frac{\lambda}{12} \frac{R(E_s) A_3(T)}{K A_2(T)} I_c^2 m_0^2(T). \quad (88)$$

It vanishes when $A_3(T)$ does, and thus when $E_F^0 = E_s$.

When the temperature T goes on to decrease below T_m , the stability of the cubic phase can be discussed by using the expansion of the variation $\delta F[m_0(T), \eta_m(T), \epsilon, \epsilon']$ of the free energy, which is obtained by assuming $m_X = m_Y = m_Z = m_0(T)$ in Eqs. (45), (46), (50), and (51). We get

$$\delta F[m_0(T), \eta_m(T), \epsilon, \epsilon'] \\ = \delta F[m_0(T), \eta_m(T)] + \delta F[\epsilon, \epsilon'] \\ + \frac{3}{8} A_4(T) \lambda^2 I_c^2 m_0^2(T) (3\epsilon^2 + \epsilon'^2). \quad (89)$$

The expansion (89) leads to physical results that are entirely similar to those derived from Eqs. (66) to (78), providing that we replace the shear modulus $M(T)$ by its corrected expression

$$M_m(T) = M(T) + \frac{3}{8} A_4(T) \lambda^2 I_c^2 m_0^2(T). \quad (90)$$

Conclusion

The instabilities of the cubic and Pauli paramagnetic phase, which are observed in

the manganese perovskite type of compounds when the temperature decreases, can be explained by the existence of a sharp and degenerate singularity in the electronic density of states in the neighborhood of the Fermi energy. The salient features of the structural phase transition are found in good agreement with the experimental data: the low-temperature phase is tetragonal, but generally is not orthorhombic; the c/a ratio can be larger or smaller than unity, according as the Fermi energy E_F is, respectively, smaller or larger than the energy E_s of the singularity; the structural transformation generally is a first-order phase transition, but the discontinuity of the c/a ratio at the transition, and the corresponding latent heat, are the larger as $|E_F - E_s|$ is the larger, a second-order phase transition being obtained in the special case when $E_F = E_s$. The strong influence of the parameter $E_F - E_s$ on all the previous properties explains that one of the number of electrons occupying the bands. The appearance of small magnetic moments on the manganese atoms, as the temperature decreases, is also explained. The critical values T'_0 and T_m of the temperature, at which the structural and the magnetic phase transitions, respectively, take place, simply depend on the parameters of the model: the two cases with $T_m < T'_0$ and $T_m > T'_0$ are found as being possible, and the special case with $T_m \simeq T'_0$ cannot be excluded. The observed variations of the volume are easily explained by the existence of coupling terms between the volume and the shear strain or the magnetic moments in the expansion of the free energy. These terms are proportional to the electronic transfer between the large and the narrow band, and thus they are linear in the volume variation.

Of course, besides the previous success, a lot of phenomena have been observed in these compounds that remain to be explained, such as the different types of magnetic ordering in the low-temperature

phases, the contributions to the magnetic susceptibility other than the Pauli paramagnetic one, the effect of the substitutions between N and C on the metalloidic site, and so on. But our model could be a reasonable starting point for further theoretical developments, for instance, by taking into account the interactions between next-nearest neighbors, the effect of the spin fluctuations, the Van Vleck paramagnetism, and also by calculating the stability of periodic arrangements of the magnetic moments which could lead to a nesting of the Fermi surface. The effect of the substitutions between N and C on the electronic density of states should be calculated by using the coherent potential approximation.

Appendix

By an obvious manipulation of the limits of the integrals, the first term of Eq. (20) can be transformed to

$$\sum_{\gamma,\sigma} \int^{E_F} (E + E_{\gamma,\sigma} - E_s) \bar{n}(E - E_s) dE + \sum_{\gamma,\sigma} \int_{E_F}^{E_F - E_{\gamma,\sigma} + E_s} (E + E_{\gamma,\sigma} - E_s) \bar{n}(E - E_s) dE, \quad (\text{A.1})$$

which is equal to

$$\sum_{\gamma,\sigma} (E_{\gamma,\sigma} - E_s) \int^{E_F} \bar{n}(E - E_s) dE + 6 \int^{E_F} E \bar{n}(E - E_s) dE + \sum_{\gamma,\sigma} E_{\gamma,\sigma} \int_{E_F}^{E_F - E_{\gamma,\sigma} + E_s} \bar{n}(E - E_s) dE + \sum_{\gamma,\sigma} \int_{E_F}^{E_F - E_{\gamma,\sigma} + E_s} (E - E_s) \bar{n}(E - E_s) dE. \quad (\text{A.2})$$

But the summation of Eq. (14) on the indices $\gamma = X, Y, Z$ and $\sigma = +, -$ leads to

$$\sum_{\gamma,\sigma} (E_{\gamma,\sigma} - E_s) = 2 \lambda \eta. \quad (\text{A.3})$$

By replacing the first term of Eq. (20) by its

expression (A.2), and taking into account the relation (A.3), we obtain Eq. (22).

References

1. J-P. BOUCHAUD, Thèse, Paris (1967), No. 1592, CNRS.
2. R. MADAR, Thèse, Paris (1970), No. 690, CNRS.
3. M. BARBERON, Thèse, Paris (1973), No. 702, CNRS.
4. D. FRUCHART, Thèse, Grenoble (1976), No. A.0 11922, CNRS.
5. D. FRUCHART, E. F. BERTAUT, R. MADAR, AND R. FRUCHART, *J. Phys. B* **32**, 876 (1971).
6. D. FRUCHART, E. F. BERTAUT, R. MADAR, G. LORTHIOIR, AND R. FRUCHART, *Solid State Commun.* **9**, 1793 (1971).
7. E. F. BERTAUT AND D. FRUCHART, *Int. J. Magn.* **2**, 259 (1972).
8. D. FRUCHART, R. MADAR, E. FRUCHART, AND M. BARBERON, *Int. Kern Kerntechn A* **8**, 1326 (1973).
9. D. FRUCHART, E. F. BERTAUT, J-P. SENATEUR, AND R. FRUCHART, *J. Phys. Lett.* **38**, 21 (1977).
10. D. FRUCHART AND E. F. BERTAUT, *J. Phys. Soc. Japan* **44**, 781 (1978).
11. R. FRUCHART, J-P. BOUCHAUD, E. FRUCHART, G. LORTHIOIR, R. MADAR, AND A. ROVAULT, *Mater. Res. Bull.* **2**, 1009 (1967).
12. E. F. BERTAUT, D. FRUCHART, J-P. BOUCHAUD, AND R. FRUCHART, *Solid State Commun.* **6**, 251 (1968).
13. M. BARBERON, E. FRUCHART, R. FRUCHART, G. LORTHIOIR, R. MADAR, AND M. NARDIN, *Mater. Res. Bull.* **7**, 109 (1972).
14. M. BARBERON, R. MADAR, E. FRUCHART, G. LORTHIOIR, AND R. FRUCHART, *Mater. Res. Bull.* **5**, 1 (1970).
15. M. BARBERON, R. MADAR, E. FRUCHART, G. LORTHIOIR, AND R. FRUCHART, *Mater. Res. Bull.* **5**, 903 (1970).
16. P. L'HERITIER, Thèse, Grenoble (1980).
17. S. NAGAKURA AND K. TANEHOSKI, *J. Phys. Soc. Japan* **25**, 840 (1968).
18. S. NAGAKURA AND N. OTSUKA, "Proc. Int. Conf. Crist. Melbourne (1974)."
19. J. GARCIA, R. NAVARRO, J. BARTOLOME, R. BURIÉL, D. GONZALES, AND D. FRUCHART, "Int. Conf. Magnetism, Munish (1979)."
20. R. FRUCHART, R. MADAR, M. BARBERON, E. FRUCHART, AND G. LORTHIOIR, *J. Phys. Colloq.* **32**, C1 982 (1971).
21. J. GARCIA, Thèse, Zaragoza (1981).
22. J-P. JARDIN AND J. LABBE, *J. Phys.* **36**, 1317 (1975).
23. J-P. JARDIN AND J. LABBE, "Vème Int. Conf. Solid Compounds of Transition Elements, Uppsala, Juin 1976."
24. J-P. JARDIN AND J. LABBE, Meeting on "Lattice Instabilities of Electronic Origin," Bad Honeff, April 1978.
25. J-P. JARDIN, Thèse, Paris (1980).
26. J-P. JARDIN AND J. LABBE, Meeting on "Magnetism and Magnetic Materials" (1980); *J. Appl. Phys.* **52**(3), March 1981.