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Excitations in Magnetic Systems with a Singlet Ground State*

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We have studied the magnetic properties of a system with a crystal-field-only singlet ground state and a triplet first excited state in the presence of exchange interactions by using a pseudospin formalism, in the molecular-field and the random-phase approximations. By using the molecular-field results as a first approximation, we obtain the low-lying collective excitation spectra at zero temperature. The spontaneous magnetization and the correlation functions at finite temperatures can then be deduced. As a practical application of the model, we extend the calculations to a face-centered-cubic antiferromagnet and calculate the excitation spectra of the rare-earth compound TbSb. An estimate of the validity of this application is given and further studies and possible improvements of the present calculations are also suggested.

I. INTRODUCTION

The importance of crystal field effects in magnetic materials has long been recognized. For certain rare-earth compounds, such as those of NaCl structure with group-V anions, it is possible for the crystal field to be comparable to or even dominant over the exchange interaction between the rare-earth ions. Thus, the crystal field is expected to play a very important role in the nature of the macroscopic magnetic properties in such materials.[1-11] The most striking situation occurs when the crystal-field-only ground state of the rare-earth ion is a singlet, which can happen when its total angular momentum is an integer. It was found[2,12,13] that in such systems, there would be a threshold value for the ratio of exchange to crystal field interaction necessary for nonvanishing magnetic ordering even at zero temperature. As the exchange interaction increases, magnetic ordering at low temperature occurs not through the usual process of alignment of permanent ionic moments, but rather through a polarization (or induced-moment) process corresponding to the Van Vleck susceptibility in a paramagnet with the exchange field taking the place of an applied external magnetic field. Trammell[2,3] first pointed out the possibility of such ordering. The case where the first excited state is also a singlet state (the singlet-singlet problem) was first studied by Bleaney[12] in the molecular-field approximation (MFA). The singlet-triplet system, i.e., where the first excited state is a triplet, has been studied by Blume,[14] and Kitano and Trammell,[15] again in the MFA. Recently, Cooper[13] calculated this critical value in the constant-coupling approximation and found that this value was significantly increased over that in the MFA.

The energy spectrum of the low-lying collective excitations for such systems is rather important, not only in itself but also because its behavior provides a criterion for the threshold value of the exchange interaction necessary for magnetic ordering. One also hopes to observe the excitation spectrum directly from an inelastic neutron-scattering experiment. This in turn should allow us to determine the exchange interaction, as has been done in terbium[16] and erbium[17] metals. These excitations have been investigated using the techniques of Bogoliubov[18] by a number of people, e.g., Bozorth and Van Vleck[19] in their investigation of the paramagnetic regime of metallic europium, Trammell[2] in his treatment of the rare-earth nitrides, and Grover[20] for both ferro- and antiferromagnetic materials. It is found[13] that the critical value in this approximation is exactly the same as obtained in the MFA for the singlet-singlet system. Quite recently, an improved calculation has been done by Wang and Cooper[21,22] on this problem by using a pseudospin formalism. This approach has the advantage over the Bogoliubov formalism in that it can, in principle, take into account the fluctuations of the ground state as well as the interactions of the excitations. The same problem has also been approached by Pink,[23] using a similar technique. Pink has studied the simple singlet-triplet problem, in which the magnetization is due both to an induced moment and to nonzero eigenvalues of the spin operator associated with crystal field eigenstates.

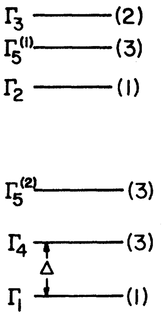

FIG. 1. Level scheme for Tm^{3+} or Tb^{3+} ($J=6$) in octahedral crystal field with degeneracies of levels indicated.

Figure 1 shows the level scheme for Tm^{3+} or Tb^{3+} in an octahedral crystal field with level of degeneracies indicated. Within the physical range of interest for rare-earth group-V compounds, the ground state is a Γ_1 singlet and the first excited state is a Γ_4 triplet. These two lowest states are separated by an energy splitting Δ, which is about 100 °K for TmN,[13] 30–40 °K for the heavier compounds,[13] and 11.9 °K for[24] TbSb in zero magnetic field. We assume that at low temperatures, only these two low-lying levels are important in the thermodynamics, the justification of which will be discussed in Sec. V. In Sec. II, we use a spin-Hamiltonian formalism, replacing the original Hamiltonian of the ion with all its states by another one which can accurately describe the two low-lying states. The advantage of this pseudospin formalism is that we reduce the original complicated problem to a simpler one in a pseudospin space so that the well-developed algebra of angular momentum can be used. Such a Hamiltonian is constructed by using two spin-$\frac{1}{2}$ operators to describe the singlet-triplet system, instead of a single spin-$\frac{3}{2}$ operator. The model we develop can hence be used as an interpolation scheme for real compounds. By taking appropriate limits of the model, it can be seen that this Hamiltonian corresponds to several different specific problems in magnetism. The Hamiltonian is then first studied in the MFA in Sec. III, where we reproduce the phase diagram of three regions of magnetic ordering as obtained by Kitano and Trammell,[15] study the nature of phase transition and Curie temperature of magnetic ordering according to the theory of Landau,[25] and the temperature dependence of magnetization and various thermodynamic correlation functions. The calculations are also extended to the case of a fcc antiferromagnet. In Sec. IV, we apply the double-time Green's-function method to study the pseudospin Hamiltonian in the random phase approximation, both for ferro- and antiferromagnetic exchange interactions. By using the molecular-field results as a first approximation, we obtain the excitation spectrum at zero temperature and thermodynamic functions at finite temperatures. The transitions to which the excitations are attributed can be identified in the molecular-field picture. Application is also made to the excitation spectrum at zero temperature. An estimate of the validity of this application is discussed in Sec. V, where we also compare the results obtained from these two approximations. Possible improvements on the techniques used in this paper and suggestions for further studies are also provided.

II. HAMILTONIAN

In the absence of an external magnetic field, the Hamiltonian for rare-earth group-V compounds assumes the form

$$\mathcal{H}=\sum_{i} V_{ci}-\sum_{i,j} \mathcal{J}(i-j)\,\vec{J}_i\cdot\vec{J}_j\ . \tag{2.1}$$

Here V_{ci} is the single-ion crystal field potential which gives a singlet ground state and a triplet excited state separated by an energy gap Δ for the present problem under consideration. $\vec{J}_i$ is the total angular-momentum operator of the rare-earth ion at the ith site and $\mathcal{J}(i-j)$ is the effective exchange interaction between ions at i and j. We have considered only the simplest form of isotropic exchange. More complicated mechanisms, e.g., orbital effects on exchange,[26] biquadratic exchange,[27] anisotropy, etc., can be included without difficulty.

Our work next is then to find the equivalent pseudospin operators corresponding to these operators in real space to operate in their own fictitious spin space. It is natural to think that we can use a fictitious spin $S'=\frac{3}{2}$ to describe the present level scheme. Since, in the representation of spin-$\frac{3}{2}$ space, there are 16 linearly independent operators,[28] any 4×4 matrix can be written as a linear combination of these operators. The tranformed Hamiltonian would in this case be even more complicated than the original, however. A simpler approach is then to consider two spin-$\frac{1}{2}$ operators S and T. Pink[23] has already used the expression $\Delta\vec{S}\cdot\vec{T}$ to explain the singlet-triplet level of scheme of the crystal field term. To find the representation of the angular-momentum operator in this fictitious spin space, we note that the system under consideration is of induced-moment nature. From the requirement that the thermal average of the total angular momentum along a certain direction J_z is proportional to the magnetization, we try the following linear combination of S and T with real coefficients a and b, respectively:

$$J_z \rightarrow aS_z + bT_z\ . \tag{2.2}$$

Its matrix elements in the representation of $F=S+T$ space are

$$\begin{array}{c|cccc} & |0,0\rangle & |1,1\rangle & |1,0\rangle & |1,-1\rangle \\ \hline \langle 0,0| & 0 & 0 & \frac{1}{2}(a-b) & 0 \\ \langle 1,1| & 0 & \frac{1}{2}(a+b) & 0 & 0 \\ \langle 1,0| & \frac{1}{2}(a-b) & 0 & 0 & 0 \\ \langle 1,-1| & 0 & 0 & 0 & -\frac{1}{2}(a+b) \end{array} , \qquad (2.3)$$

where

$$|0,0\rangle = \sqrt{\tfrac{1}{2}}(|\tfrac{1}{2},-\tfrac{1}{2}\rangle - |-\tfrac{1}{2},\tfrac{1}{2}\rangle) ,$$

$$|1,1\rangle = |\tfrac{1}{2},\tfrac{1}{2}\rangle ,$$

$$|1,0\rangle = \sqrt{\tfrac{1}{2}}(|\tfrac{1}{2},-\tfrac{1}{2}\rangle + |-\tfrac{1}{2},\tfrac{1}{2}\rangle) ,$$

$$|1,-1\rangle = |-\tfrac{1}{2},-\tfrac{1}{2}\rangle .$$

The ket vector on the left-hand side of these equations refers to $|F, M_F\rangle$ and that on the right-hand side refers to $|M_S, M_T\rangle$.

As an example we consider the levels of Tb^{3+} or Tm^{3+} in an octahedral crystalline field. According to Lea, Leask, and Wolf,[29] the Γ_1 and Γ_4 states have the following representations in the manifold of constant angular momentum ($J=6$):

$$\begin{aligned} |\Gamma_1\rangle &= -\tfrac{1}{4}\sqrt{7}\,|4\rangle + \tfrac{1}{4}\sqrt{2}\,|0\rangle - \tfrac{1}{4}\sqrt{7}\,|-4\rangle , \\ |\Gamma_4^+\rangle &= \tfrac{1}{8}\sqrt{30}\,|-3\rangle - \tfrac{1}{4}\sqrt{3}\,|1\rangle + \tfrac{1}{8}\sqrt{22}\,|5\rangle , \\ |\Gamma_4^0\rangle &= -\tfrac{1}{2}\sqrt{2}\,|4\rangle + \tfrac{1}{2}\sqrt{2}\,|-4\rangle , \\ |\Gamma_4^-\rangle &= \tfrac{1}{8}\sqrt{30}\,|3\rangle - \tfrac{1}{4}\sqrt{3}\,|-1\rangle + \tfrac{1}{8}\sqrt{22}\,|-5\rangle . \end{aligned} \qquad (2.4)$$

The matrix elements of J_z in this space are

$$\begin{array}{c|cccc} & |\Gamma_1\rangle & |\Gamma_4^+\rangle & |\Gamma_4^0\rangle & |\Gamma_4^-\rangle \\ \hline \langle\Gamma_1| & 0 & 0 & \sqrt{14} & 0 \\ \langle\Gamma_4^+| & 0 & \frac{1}{2} & 0 & 0 \\ \langle\Gamma_4^0| & \sqrt{14} & 0 & 0 & 0 \\ \langle\Gamma_4^-| & 0 & 0 & 0 & -\frac{1}{2} \end{array} . \qquad (2.5)$$

A comparison of Eqs. (2.3) and (2.5) shows that a and b are determined by

$$a-b=2\sqrt{14} , \qquad a+b=1 ,$$

or (2.6)

$$a=\tfrac{1}{2}(1+2\sqrt{14}) , \quad b=\tfrac{1}{2}(1-2\sqrt{14}) .$$

The representation of the angular-momentum operator $\vec{J}$ has hence been found to be

$$\vec{J}=a\vec{S}+b\vec{T} . \qquad (2.7)$$

The Hamiltonian (2.1) is then transformed into this fictitious spin space and assumes the form

$$\mathcal{H}=\Delta\sum_i \vec{S}_i\cdot\vec{T}_i - \sum_{i,j}\mathcal{J}(i-j)\,(a\vec{S}_i+b\vec{T}_i)\cdot(a\vec{S}_j+b\vec{T}_j) , \qquad (2.8)$$

where we neglect the constant term $\frac{3}{4}N\Delta$. By taking different values of a, b, and Δ in Eq. (2.8), our model corresponds to some specific problems in magnetism. For example, if we take $a=b=1$ or $a=-b=1$, it reduces to the singlet-triplet problem considered by Pink,[23] and if we take $a=1$, $b=0$, Δ to be the hyperfine interaction between the electronic spin $\vec{S}$ and nuclear spin $\vec{T}$, it reduces to the problem of simultaneous excitation on nuclear and electronic spin waves discussed by de Gennes *et al.*[30] and Ninio and Keffer.[31] The details of these limiting examples will be studied in Sec. IV. We note also that since we have assigned two spin-$\frac{1}{2}$ operators with different weights on each site, Eq. (2.8) corresponds to a particular model of ferrimagnetism.

III. MOLECULAR-FIELD APPROXIMATION

We first work out the ferromagnetic case by assuming all $\mathcal{J}$'s > 0 and begin from the Bogoliubov variational principle[32] to obtain the molecular-field equations. Since we have assigned two spins $\vec{S}$ and $\vec{T}$ on each site, we are obliged to introduce two effective fields H_S and H_T. Hence we take the trial Hamiltonian

$$\mathcal{H}_0=\Delta\textstyle\sum_i \vec{S}_i\cdot\vec{T}_i+2\sum_i(H_SS_i^z+H_TT_i^z) . \qquad (3.1)$$

$\mathcal{H}_0$ can be diagonalized in the direct product space of the single-ion Hamiltonian, which has the following complete set of eigenfunctions and eigenvalues:

$$\begin{aligned} &|1\rangle=|1,1\rangle , && E_1=\Delta+(H_S+H_T) , \\ &|2\rangle=|1,-1\rangle , && E_2=\Delta-(H_S+H_T) , \\ &|3\rangle=\alpha_3|0,0\rangle+\beta_3|1,0\rangle , && \\ &\qquad E_3=\tfrac{1}{2}\{\Delta+[\Delta^2+4(H_S-H_T)^2]^{1/2}\} , && \\ &|4\rangle=\alpha_4|0,0\rangle+\beta_4|1,0\rangle , && \\ &\qquad E_4=\tfrac{1}{2}\{\Delta-[\Delta^2+4(H_S-H_T)^2]^{1/2}\} , && \end{aligned} \qquad (3.2)$$

where

$$\alpha_i=\frac{H_S-H_T}{[E_i^2+(H_S-H_T)^2]^{1/2}} ,$$
$$\beta_i=\frac{E_i}{[E_i^2+(H_S-H_T)^2]^{1/2}} , \quad i=3,4 . \qquad (3.3)$$

Bogoliubov's inequality then states

$$(1/N)F\le-(k_BT)\ln Z_0-J(0)\,(a\langle S_z\rangle+b\langle T_z\rangle)^2 - 2(H_S\langle S_z\rangle+H_T\langle T_z\rangle) .$$

Here F is the free energy, Z_0 is the partition function, and $J(0)=\sum_i\mathcal{J}(i-j)$. Subject to the variational principle, this free energy is to be minimized with respect to the two molecular-field parameters H_S and H_T,

$$\frac{\partial F}{\partial H_S}=0\ ,\quad \frac{\partial F}{\partial H_T}=0\ .$$

The combination of these two results gives the two molecular-field equations

$$H_S=-aJ(0)M\ ,\quad H_T=-bJ(0)M\ . \tag{3.4}$$

Here M is the magnetization and is to be determined self-consistently by the equation

$$\begin{aligned} M&=a\langle S_z\rangle+b\langle T_z\rangle\\ &=\frac{1}{Z_0}\biggl(\tfrac{1}{2}(a+b)\,(e^{-\beta E_1}-e^{-\beta E_2})\\ &\qquad-\frac{J(0)\,(a-b)^2M}{[\Delta^2+4(a-b)^2J^2(0)M^2]^{1/2}}\,(e^{-\beta E_3}-e^{-\beta E_4})\biggr) \end{aligned} \tag{3.5}$$

and

$$Z_0=\sum_{i=1}^{4}e^{-\beta E_i}\ ,\quad \beta=1/k_BT\ .$$

The single-ion energy levels are then given by

$$\begin{aligned} E_1&=\Delta-(a+b)J(0)M\ ,\\ E_2&=\Delta+(a+b)J(0)M\ ,\\ E_3&=\tfrac{1}{2}\{\Delta+[\Delta^2+4(a-b)^2J^2(0)M^2]^{1/2}\}\ ,\\ E_4&=\tfrac{1}{2}\{\Delta-[\Delta^2+4(a-b)^2J^2(0)M^2]^{1/2}\}\ . \end{aligned} \tag{3.6}$$

The idea of heat magnetization in such a singlet-triplet system has already been discussed by Kitano and Trammell.[15] We will not repeat their analysis here, instead we just state the main results which will be needed in later discussions. In terms of our parameters a, b, and Δ, three regions of magnetic ordering can be classified as follows:

(i) The molecular-field ground state is ferromagnetic and the magnetization is fully saturated, i.e., $M=\frac{1}{2}(a+b)$, if

$$J(0)\,(a-b)^2>\Delta \text{ and } J(0)\,(a+b)^2>4\Delta\ . \tag{3.7}$$

(ii) The molecular-field ground state is ferromagnetic but magnetization is not fully saturated, but given by

$$M=\frac{[J^2(0)\,(a-b)^4-\Delta^2]^{1/2}}{2J(0)\,(a-b)} \tag{3.8}$$

if

$$J(0)\,(a-b)^2>\Delta\ . \tag{3.9}$$

(iii) The molecular-field ground state is nonmagnetic, i.e., $M=0$ at 0 °K, if

$$J(0)\,(a-b)^2<\Delta \text{ and } J(0)\,(a+b)^2<4\Delta\ . \tag{3.10}$$

To show the above picture, we have done some numerical calculations and plot the temperature dependences of magnetization in Fig. 2. The low-temperature behavior of curve (c) is known as heat magnetization, which is due to the fact that the unmagnetized singlet is lower than the triplet in energy and the exchange field is not large enough to overcome the crystal field splitting. As the temperature is raised, the triplet will be populated and hence the exchange field gets larger. This in turn will lower the triplet. All these processes will work self-consistently in the molecular-field picture. The unsaturated curve (b) at 0 °K is due to the fact that the exchange field is compatible with the crystal field splitting so that both the triplet and the singlet are populated at zero temperature. The magnetization at low temperatures is indeed affected by the crystalline field, as has already been predicted by Trammell's work.[2,3]

The correlation functions which are of interest and turn out to be useful later on are those between the S and T spins on the same site, e.g., $\langle S^xT^x\rangle$, $\langle S^yT^y\rangle$, and $\langle S^zT^z\rangle$. We give their expressions both in the ferromagnetic and paramagnetic phases. In ferromagnetic phase, we have

$$\begin{aligned} \langle S^xT^x\rangle&=\langle S^yT^y\rangle=\tfrac{1}{2}\langle S^+T^-\rangle=\tfrac{1}{2}\langle S^-T^+\rangle\\ &=\frac{\Delta}{4Z_0[\Delta^2+4(a-b)^2J^2(0)M^2]^{1/2}}\,(e^{-\beta E_3}-e^{-\beta E_4})\ , \end{aligned} \tag{3.11}$$

$$\langle S^zT^z\rangle=\frac{1}{4Z_0}\,(e^{-\beta E_1}+e^{-\beta E_2}-e^{-\beta E_3}-e^{-\beta E_4})\ . \tag{3.12}$$

The E_i's are given by Eq. (3.6).

Values of these correlations at 0 °K are rather important for later use; we write them out explicitly in accordance with the three different classes of molecular-field ground states:

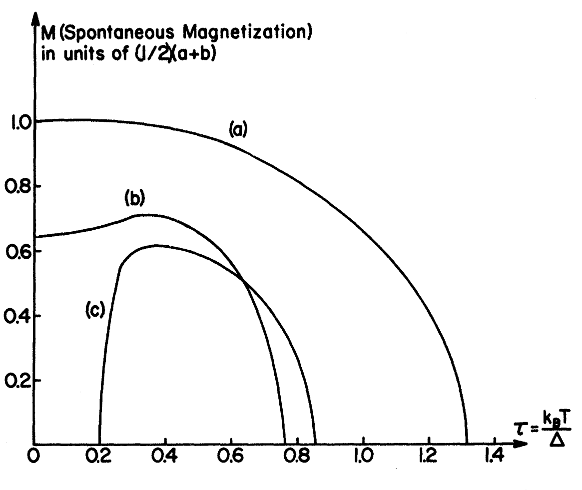

FIG. 2. Spontaneous magnetization M in units of $\frac{1}{2}(a+b)$ as function of temperature for different values of parameters: (a) $J(0)\,(a-b)^2=0.5\Delta$, $J(0)\,(a+b)^2=6\Delta$; (b) $J(0)\,(a-b)^2=1.5\Delta$, $J(0)\,(a+b)^2=2\Delta$; (c) $J(0)\,(a-b)^2=0.9\Delta$, $J(0)\,(a+b)^2=3.6\Delta$.

$$\langle S^{+}T^{-}\rangle=\begin{cases} 0 & \text{when } M|_{0\,^\circ\mathrm{K}}=\frac{1}{2}(a+b) \\ -\dfrac{\Delta}{2J(0)(a-b)^2} & \text{when } M|_{0\,^\circ\mathrm{K}}=\dfrac{[J^2(0)\,(a-b)^4-\Delta^2]^{1/2}}{2J(0)\,(a-b)} \\ -\frac{1}{2} & \text{when } M|_{0\,^\circ\mathrm{K}}=0 \end{cases}\quad, \tag{3.13}$$

$$\langle S^{z}T^{z}\rangle=\begin{cases} \frac{1}{4} & \text{when } M|_{0\,^\circ\mathrm{K}}=\frac{1}{2}(a+b) \\ -\frac{1}{4} & \text{when } M|_{0\,^\circ\mathrm{K}}=0 \text{ or } \dfrac{[J^2(a-b)^4-\Delta^2]^{1/2}}{2J(0)\,(a-b)} \end{cases}\quad. \tag{3.14}$$

In paramagnetic phase, we have

$$\langle S^{x}T^{x}\rangle=\langle S^{y}T^{y}\rangle=\langle S^{z}T^{z}\rangle=-\frac{1-e^{-\beta\Delta}}{4(1+3e^{-\beta\Delta})}\ . \tag{3.15}$$

Figures 3–5 show the temperature dependences of these functions with the same parameters chosen as in Fig. 2, and the values of M are also borrowed from that figure. Manifestations of the unsaturated and heat-magnetized ground state are hence reflected in these functions.

The nature of phase transitions and Curie temperature has been studied by using Landau's theory of second-order phase transition.[25] The Curie temperature T_C is determined by the equation

$$1+3e^{-\Delta/k_BT_C}=\frac{1}{\Delta}\,(a-b)^2J(0)\,(1-e^{-\Delta/k_BT_C})+\frac{J(0)}{k_BT_C}\,(a+b)^2\,e^{-\Delta/k_BT_C}\ . \tag{3.16}$$

It reduces to Blume's result[14] on the UO_2 model if we put $a=b=1$, while for $\Delta=0$ and $a=1$, $b=0$ (or $a=0$, $b=1$), it reduces to the usual expression for a Heisenberg ferromagnet ($S=\frac{1}{2}$) in MFA.

Eventually, we will apply our model to the rare-earth compound TbSb, which is a two-sublattice antiferromagnet with fcc structure. By limiting our calculations to this case, we find all the conclusions obtained in the ferromagnetic case are valid with the replacement of $J(0)$ by $-6J_2$, where J_2 is the exchange interaction between next nearest neighbors. The Néel temperature T_N is now determined by

$$1+3e^{-\Delta/k_BT_N}=-\frac{6J_2(a-b)^2}{\Delta}\,(1-e^{-\Delta/k_BT_N})-\frac{6(a+b)^2J_2}{k_BT_N}\,e^{-\Delta/k_BT_N}\ . \tag{3.17}$$

IV. DOUBLE-TIME GREEN'S-FUNCTION METHOD: RANDOM-PHASE APPROXIMATION

A. Transverse Modes and Decoupling Scheme

To study the transverse mode, we look at the Green's function

$$G_{g,l}(t-t')\equiv\langle\langle S_g^{+}(t)|\,S_l^{-}(t')\rangle\rangle=-i\theta(t-t')\,\langle[S_g^{+}(t),\,S_l^{-}(t')]_{-}\rangle$$

as defined by Zubarev.[33] Its equation of motion is

$$i\frac{d}{dt}\,G_{g,l}(t-t')=2\delta(t-t')\delta_{g,l}\,\langle S_g^{z}\rangle+\Delta\langle\langle S_g^{z}(t)T_g^{+}(t)-S_g^{+}(t)T_g^{z}(t)|\,S_l^{-}(t')\rangle\rangle$$
$$-2a\textstyle\sum_i \mathcal{J}(i-g)[a\langle\langle S_i^{+}(t)S_g^{z}(t)-S_g^{+}(t)S_i^{z}(t)|\,S_l^{-}(t')\rangle\rangle+b\langle\langle S_g^{z}(t)T_i^{+}(t)-S_g^{+}(t)T_i^{z}(t)|\,S_l^{-}(t')\rangle\rangle]\ . \tag{4.1}$$

Here we put $\hbar=1$. The right-hand side now involves Green's functions of higher order. Since we are now interested in the case where the crystal field splitting Δ is comparable with respect to the exchange interaction, we regard the operators on the same site (the crystal field term) as independent Green's functions. For Green's functions which involve operators on different sites, we use the simplest random-phase decoupling, namely,

$$\langle\langle S_i^{+}(t)S_g^{z}(t)|\,S_l^{-}(t')\rangle\rangle\rightarrow\langle S_g^{z}\rangle\,\langle\langle S_i^{+}(t)|\,S_l^{-}(t')\rangle\rangle\ .$$

Equation (4.1) now becomes

$$i\frac{d}{dt}\,G_{g,l}(t-t')=2\delta(t-t')\delta_{g,l}\,\langle S^{z}\rangle+\Delta\langle\langle S_g^{z}(t)T_g^{+}(t)-S_g^{+}(t)T_g^{z}(t)|\,S_l^{-}(t')\rangle\rangle$$
$$-2\textstyle\sum_i \mathcal{J}(i-g)\{a^2\langle S^{z}\rangle\,\langle\langle S_i^{+}(t)-S_g^{+}(t)|\,S_l^{-}(t')\rangle\rangle+ab[\langle S^{z}\rangle\langle\langle T_i^{+}(t)|\,S_l^{-}(t')\rangle\rangle-\langle T^{z}\rangle\langle\langle S_g^{+}(t)|\,S_l^{-}(t')\rangle\rangle]\}\ . \tag{4.2}$$

The above expression shows that we need to consider three other independent Green's functions $\langle\langle T_g^+(t) | S_l^-(t')\rangle\rangle$, $\langle\langle S_g^z(t) T_g^+(t) | S_l^-(t')\rangle\rangle$, and $\langle\langle S_g^+(t) T_g^z(t) | S_l^-(t')\rangle\rangle$. By using the same approximation, the equations of motion of these three Green's functions are

$$i\frac{d}{dt}\langle\langle T_g^+(t) | S_l^-(t')\rangle\rangle = -\Delta\langle\langle S_g^z(t)T_g^+(t) - S_g^+(t)T_g^z(t) | S_l^-(t')\rangle\rangle$$
$$-2\textstyle\sum_i \mathcal{J}(i-g)[b^2\langle\langle T_i^+(t)T_g^z(t) - T_g^+(t)T_i^z(t) | S_l^-(t')\rangle\rangle + ab\,\langle\langle S_i^+(t)T_g^z(t) - S_i^z(t)T_g^+(t) | S_l^-(t')\rangle\rangle] , \quad (4.3)$$

$$i\frac{d}{dt}\langle\langle S_g^z(t)T_g^+(t) | S_l^-(t')\rangle\rangle$$
$$= -\delta(t-t')\delta_{g,l}\langle S^-T^+\rangle + \tfrac{1}{4}\Delta\langle\langle S_g^+(t) - T_g^+(t) | S_l^-(t')\rangle\rangle - \textstyle\sum_i \mathcal{J}(i-g)\{2b^2\langle\langle S_g^z(t)[T_i^+(t)T_g^z(t) - T_i^z(t)T_g^+(t)] | S_l^-(t')\rangle\rangle$$
$$+a^2\langle\langle T_g^+(t)[S_g^+(t)S_i^-(t) - S_i^+(t)S_g^-(t)] | S_l^-(t')\rangle\rangle + ab\langle\langle [S_g^+(t)T_i^-(t) - S_g^-(t)T_i^+(t)]T_g^+(t) | S_l^-(t')\rangle\rangle$$
$$+2ab\langle\langle S_g^z(t)(S_i^+(t)T_g^z(t) - S_i^z(t)T_g^+(t)) | S_l^-(t')\rangle\rangle\} , \quad (4.4)$$

$$i\frac{d}{dt}\langle\langle S_g^+(t)\,T_g^z(t) | S_l^-(t')\rangle\rangle$$
$$= 2\delta(t-t')\,\delta_{g,l}\langle S_g^z T_g^z\rangle - \tfrac{1}{4}\Delta\langle\langle S_g^+(t) - T_g^+(t) | S_l^-(t')\rangle\rangle - \textstyle\sum_i \mathcal{J}(i-g)\{2a^2\langle\langle T_g^z(t)[S_i^+(t)S_g^z(t) - S_i^z(t)S_g^+(t)] | S_l^-(t')\rangle\rangle$$
$$+b^2\langle\langle S_g^+(t)[T_g^+(t)T_i^-(t) - T_i^+(t)T_g^-(t)] | S_l^-(t')\rangle\rangle + ab\langle\langle [S_i^-(t)T_g^+(t) - S_i^+(t)T_g^-(t)]S_g^+(t) | S_l^-(t')\rangle\rangle$$
$$+2ab\langle\langle T_g^z(t)[S_g^z(t)T_i^+(t) - S_g^+(t)T_i^z(t)] | S_l^-(t')\rangle\rangle\} . \quad (4.5)$$

Furthermore, the other higher-order Green's functions on the right-hand side of Eqs. (4.4) and (4.5) can also be decoupled in this approximation with the consideration on the symmetry properties of the original Hamiltonian. We then have

$$\begin{aligned}
&\langle\langle S_g^+(t)\,T_g^+(t)\,S_i^-(t) | S_l^-(t')\rangle\rangle \to 0 , && \langle\langle S_g^+(t)\,T_g^+(t)\,T_i^-(t) | S_l^-(t')\rangle\rangle \to 0 ,\\
&\langle\langle S_g^-(t)\,T_g^+(t)\,S_i^+(t) | S_l^-(t')\rangle\rangle \to \langle S^-T^+\rangle\langle\langle S_i^+(t) | S_l^-(t')\rangle\rangle , && \langle\langle S_g^-(t)\,T_g^+(t)\,T_i^+(t) | S_l^-(t')\rangle\rangle \to \langle S^-T^+\rangle\langle\langle T_i^+(t) | S_l^-(t')\rangle\rangle ,\\
&\langle\langle S_g^z(t)\,T_g^z(t)\,S_i^+(t) | S_l^-(t')\rangle\rangle \to \langle S^zT^z\rangle\langle\langle S_i^+(t) | S_l^-(t')\rangle\rangle , && \langle\langle S_g^z(t)\,T_g^z(t)\,T_i^+(t) | S_l^-(t')\rangle\rangle \to \langle S^zT^z\rangle\langle\langle T_i^+(t) | S_l^-(t')\rangle\rangle ,\\
&\langle\langle S_g^z(t)\,T_g^+(t)\,S_i^z(t) | S_l^-(t')\rangle\rangle \to \langle S^z\rangle\langle\langle S_g^z(t)\,T_g^+(t) | S_l^-(t')\rangle\rangle , && \langle\langle S_g^z(t)\,T_g^+(t)\,T_i^z(t) | S_l^-(t')\rangle\rangle \to \langle T^z\rangle\langle\langle S_g^z(t)\,T_g^+(t) | S_l^-(t')\rangle\rangle .
\end{aligned} \quad (4.6)$$

By introducing the parameters $M = a\langle S_z\rangle + b\langle T_z\rangle$ and $J(0) = \sum_i \mathcal{J}(i-g)$, and using Eq. (4.6), Eqs. (4.2)–(4.5) can be written

$$i\frac{d}{dt}\langle\langle S_g^+(t) | S_l^-(t')\rangle\rangle = 2\delta(t-t')\,\delta_{g,l}\langle S^z\rangle$$
$$+\Delta\langle\langle S_g^z(t)\,T_g^+(t) - S_g^+(t)\,T_g^z(t) | S_l^-(t')\rangle\rangle - 2a\langle S_z\rangle\textstyle\sum_i \mathcal{J}(i-g)\langle\langle aS_i^+(t) + bT_i^+(t) | S_l^-(t')\rangle\rangle + 2aM\,J(0)\langle\langle S_g^+(t) | S_l^-(t')\rangle\rangle ,$$
$$(4.7)$$

$$i\frac{d}{dt}\langle\langle T_g^+(t) | S_l^-(t')\rangle\rangle = -\Delta\langle\langle S_g^z(t)\,T_g^+(t)$$
$$-S_g^+(t)\,T_g^z(t) | S_l^-(t')\rangle\rangle - 2b\langle T_z\rangle\textstyle\sum_i \mathcal{J}(i-g)\langle\langle aS_i^+(t) + bT_i^+(t) | S_l^-(t')\rangle\rangle + 2b\,J(0)\,M\langle\langle T_g^+(t) | S_l^-(t')\rangle\rangle , \quad (4.8)$$

$$i\frac{d}{dt}\langle\langle S_g^z(t)\,T_g^+(t) | S_l^-(t')\rangle\rangle = -\delta(t-t')\,\delta_{g,l}\langle S^-T^+\rangle + \tfrac{1}{4}\Delta\langle\langle S_g^+(t) - T_g^+(t) | S_l^-(t')\rangle\rangle$$
$$+(a\langle S^-T^+\rangle - 2b\langle S^zT^z\rangle)\textstyle\sum_i \mathcal{J}(i-g)\langle\langle aS_i^+(t) + bT_i^+(t) | S_l^-(t')\rangle\rangle + 2bM\,J(0)\langle\langle S_g^z(t)\,T_g^+(t) | S_l^-(t')\rangle\rangle , \quad (4.9)$$

$$i\frac{d}{dt}\langle\langle S_g^+(t)\,T_g^z(t) | S_l^-(t')\rangle\rangle = 2\delta(t-t')\,\delta_{g,l}\langle S^zT^z\rangle - \tfrac{1}{4}\Delta\langle\langle S_g^+(t) - T_g^+(t) | S_l^-(t')\rangle\rangle$$
$$+(b\langle S^+T^-\rangle - 2a\langle S^zT^z\rangle)\textstyle\sum_i \mathcal{J}(i-g)\langle\langle aS_i^+(t) + bT_i^+(t) | S_l^-(t')\rangle\rangle + 2aM\,J(0)\langle\langle S_g^+(t)\,T_g^z(t) | S_l^-(t')\rangle\rangle . \quad (4.10)$$

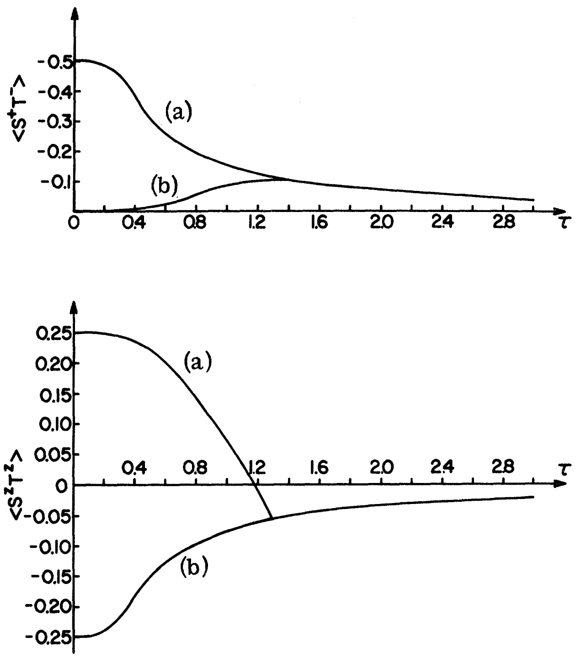

FIG. 3. $\tau = k_BT/\Delta$. Temperature dependence of the correlation functions $\langle S^+T^-\rangle$ and $\langle S^zT^z\rangle$ corresponding to case (a) in Fig. 2. (a) denotes the ferromagnetic state and (b) denotes the paramagnetic state.

Again, because of translational invariance, we can Fourier transform our Green's functions with respect to the reciprocal lattice, e.g.,

$$\langle\langle S_g^+ | S_l^- \rangle\rangle_E = (1/N)\textstyle\sum_k G_k(E)\, e^{ik(g-l)} ,$$
$$G_k(E) = (1/N)\sum_{g,l} \langle\langle S_g^+ | S_l^- \rangle\rangle_E\, e^{-ik(g-l)} , \tag{4.11}$$

where the summation over k is to be summed over all wave vectors within the first Brillouin zone and N is the total number of spins in the lattice. For convenience, we label the Fourier transform of the above four Green's functions as follows:

$G_k^{(1)}(E)$ is the Fourier transform of $\langle\langle S_g^+ | S_l^- \rangle\rangle_E$,

$G_k^{(2)}(E)$ is the Fourier transform of $\langle\langle T_g^+ | S_l^- \rangle\rangle_E$,
(4.12)
$G_k^{(3)}(E)$ is the Fourier transform of $\langle\langle S_g^z T_g^+ | S_l^- \rangle\rangle_E$,

$G_k^{(4)}(E)$ is the Fourier transform of $\langle\langle S_g^+ T_g^z | S_l^- \rangle\rangle_E$.

After doubly Fourier transforming Eqs. (4.7)–(4.10), we finally come to the following set of equations:

$$\{E - 2a[MJ(0) - a\langle S_z\rangle J(k)]\}\, G_k^{(1)}(E) + 2abJ(k)\langle S_z\rangle G_k^{(2)}(E) - \Delta G_k^{(3)}(E) + \Delta G_k^{(4)}(E) = \frac{1}{\pi}\langle S_z\rangle ,$$
$$2ab\langle T_z\rangle J(k)\, G_k^{(1)}(E) + \{E - 2b[MJ(0) - b\langle T_z\rangle J(k)]\}\, G_k^{(2)}(E) + \Delta G_k^{(3)}(E) - \Delta G_k^{(4)}(E) = 0 ,$$
$$-[\tfrac14\Delta + aJ(k)(a\langle S^-T^+\rangle - 2b\langle S^zT^z\rangle)]\, G_k^{(1)}(E) + [\tfrac14\Delta - bJ(k)(a\langle S^-T^+\rangle - 2b\langle S^zT^z\rangle)]\, G_k^{(2)}(E) - [E - 2bMJ(0)]\, G_k^{(3)}(E) = -(1/2\pi)\langle S^-T^+\rangle , \tag{4.13}$$
$$[\tfrac14\Delta - aJ(k)(b\langle S^+T^-\rangle - 2a\langle S^zT^z\rangle)]\, G_k^{(1)}(E) - [\tfrac14\Delta + bJ(k)(b\langle S^+T^-\rangle - 2a\langle S^zT^z\rangle)]\, G_k^{(2)}(E) + [E - 2aMJ(0)]\, G_k^{(4)}(E) = (1/\pi)\langle S^zT^z\rangle ,$$

where

$$J(k) = \textstyle\sum_l \mathcal{J}(g-l)\, e^{ik(g-l)} . \tag{4.14}$$

The Green's functions considered above will give the following correlation functions:

$$\langle\langle S_g^+ | S_l^- \rangle\rangle|_{g=l} \to \langle S^-S^+\rangle = \tfrac12 - \langle S^z\rangle ,$$
$$\langle\langle T_g^+ | S_l^- \rangle\rangle|_{g=l} \to \langle S^-T^+\rangle ,$$
$$\langle\langle S_g^z T_g^+ | S_l^- \rangle\rangle|_{g=l} \to \langle S^-S^zT^+\rangle = \tfrac12\langle S^-T^+\rangle , \tag{4.15}$$
$$\langle\langle S_g^+ T_g^- | S_l^- \rangle\rangle|_{g=l} \to \langle S^-S^+T^-\rangle = \tfrac12\langle T_z\rangle - \langle S^zT^z\rangle .$$

Note that the third line of the above equations differs from the second only by a factor of $\frac12$. This originates from the fact that we have used spin-$\frac12$ operators so that the identity $S^-S^z = \frac12 S^-$ holds.

The above set of Green's functions do not provide the correlation $\langle S^+T^-\rangle$ which does show up in the fourth equation of Eq. (4.13). In order to complete this information, we consider another set of Green's functions. They are labeled as

$H_k^{(1)}(E)$ is the Fourier transform of $\langle\langle T_g^+ | T_l^- \rangle\rangle_E$,

$H_k^{(2)}(E)$ is the Fourier transform of $\langle\langle S_g^+ | T_l^- \rangle\rangle_E$,
(4.16)
$H_k^{(3)}(E)$ is the Fourier transform of $\langle\langle S_g^z T_g^+ | T_l^- \rangle\rangle_E$,

$H_k^{(4)}(E)$ is the Fourier transform of $\langle\langle S_g^+ T_g^- | T_l^- \rangle\rangle$,

and their corresponding equations of motion after using the same decoupling scheme as above and doubly Fourier transforming are

$$
\begin{aligned}
&\{E-2b[MJ(0)-b\langle T_z\rangle J(k)]\}H_k^{(1)}(E)+2ab\langle T_z\rangle J(k)H_k^{(2)}(E)+\Delta H_k^{(3)}(E)-\Delta H_k^{(4)}(E)=\frac{1}{\pi}\langle T_z\rangle\ ,\\
&2ab\langle S_z\rangle J(k)H_k^{(1)}(E)+\{E-2a[MJ(0)-a\langle S_z\rangle J(k)]\}H_k^{(2)}(E)-\Delta H_k^{(3)}+\Delta H_k^{(4)}(E)=0\ ,\\
&[\tfrac{1}{4}\Delta-bJ(k)(a\langle S^-T^+\rangle-2b\langle S^zT^z\rangle)]H_k^{(1)}(E)-[\tfrac{1}{4}\Delta+aJ(k)(a\langle S^-T^+\rangle-2b\langle S^zT^z\rangle)]H_k^{(2)}(E)+[E-2bJ(0)M]H_k^{(3)}(E)\\
&\qquad\qquad=(1/\pi)\langle S^zT^z\rangle\ ,\\
&-[\tfrac{1}{4}\Delta+bJ(k)(b\langle S^+T^-\rangle-2a\langle S^zT^z\rangle)]H_k^{(1)}(E)+[\tfrac{1}{4}\Delta-aJ(k)(b\langle S^+T^-\rangle-2a\langle S^zT^z\rangle)]H_k^{(2)}(E)+[E-2aJ(0)M]H_k^{(4)}(E)\\
&\qquad\qquad=-(1/2\pi)\langle S^+T^-\rangle\ .
\end{aligned}
\tag{4.17}
$$

Hence the Green's functions introduced in Eq. (4.16) will give the following thermodynamic correlation functions:

$$\langle\langle T_g^+|T_l^-\rangle\rangle|_{g=l}\rightarrow\langle T^-T^+\rangle=\tfrac{1}{2}-\langle T_z\rangle\ ,$$

$$\langle\langle S_g^+|T_l^-\rangle\rangle|_{g=l}\rightarrow\langle T^-S^+\rangle\ ,$$

$$\langle\langle T_g^+S_g^z|T_l^-\rangle\rangle|_{g=l}\rightarrow\langle T^-T^+S^z\rangle=\tfrac{1}{2}\langle S^z\rangle-\langle S^zT^z\rangle\ ,$$

$$\langle\langle S_g^+T_g^z|T_l^-\rangle\rangle|_{g=l}\rightarrow\langle T^-S^+T^z\rangle=\tfrac{1}{2}\langle S^+T^-\rangle\ . \tag{4.18}$$

Each individual Green's function is then obtained by solving these two sets of linear equations (4.13) and (4.17). The transverse excitation spectrum is then determined by the vanishing of the determinants of the coefficients in these two sets of equations. One can easily show that both determinants are equal to

$$
\begin{aligned}
\Delta'=&\begin{vmatrix}
E-2a[MJ(0)-a\langle S_z\rangle J(k)] & 2ab\langle S_z\rangle J(k) & -\Delta & \Delta\\
2ab\langle T_z\rangle J(k) & E-2b[MJ(0)-b\langle T_z\rangle J(k)] & \Delta & -\Delta\\
-\tfrac{1}{4}\Delta-aJ(k)(a\langle S^-T^+\rangle-2b\langle S^zT^z\rangle) & \tfrac{1}{4}\Delta-bJ(k)(a\langle S^-T^+\rangle-2b\langle S^zT^z\rangle) & E-2bMJ(0) & 0\\
\tfrac{1}{4}\Delta-aJ(k)(b\langle S^+T^-\rangle-2a\langle S^zT^z\rangle) & -\tfrac{1}{4}\Delta-bJ(k)(b\langle S^+T^-\rangle-2a\langle S^zT^z\rangle) & 0 & E-2aMJ(0)
\end{vmatrix}\\
&=E^4-2E^3[2(a+b)MJ(0)-(a^2\langle S_z\rangle+b^2\langle T_z\rangle)J(k)]+E^2(4J(0)M\{(a^2+4ab+b^2)J(0)M\\
&\quad-[abM+(a+b)(a^2\langle S_z\rangle+b^2\langle T_z\rangle)]J(k)\}+\Delta\{-\Delta+(a-b)J(k)[b\langle S^+T^-\rangle-a\langle S^-T^+\rangle-2(a-b)\langle S^zT^z\rangle]\})\\
&\quad-E\{8abJ^2(0)M^2[2(a+b)MJ(0)-(a+b)MJ(k)-(a^2\langle S_z\rangle+b^2\langle T_z\rangle)J(k)]-\Delta[2\Delta(a+b)MJ(0)-\Delta M(a+b)J(k)\\
&\quad+2(a-b)J(0)J(k)M(a^2\langle S^-T^+\rangle-b^2\langle S^+T^-\rangle)]\}+J(0)M^2[J(0)-J(k)][16a^2b^2J^2(0)M^2-\Delta^2(a+b)^2]\ .
\end{aligned}
\tag{4.19}
$$

This equation is symmetric with respect to $a \leftrightarrow b$ and $S \leftrightarrow T$, as it should be since the original Hamiltonian does have this property.

B. Two Limiting Examples

To illustrate the generality of our model, we reproduce the results of two examples which have been considered previously.

1. *System of Pure Singlet-Triplet Crystal Field States*

The properties of this system have already been investigated by Pink.[23] By just putting $a=b=1$ in our model, we are then considering the same problem as Pink. Equation (4.19), which determines the excitation spectrum, for example, becomes

$$
\begin{aligned}
&E^4-2ME^3[4J(0)-J(k)]+E^2\{4J(0)M^2[6J(0)-3J(k)]-\Delta^2\}-2ME\{4J^2(0)M^2[4J(0)-3J(k)]-\Delta^2[2J(0)-J(k)]\}\\
&\qquad+4J(0)M^2[J(0)-J(k)][4J^2(0)M^2-\Delta^2]=0\ .
\end{aligned}
$$

It has the following four real roots:

$$2M[J(0)-J(k)]\ ,\quad 2MJ(0)\ ,\quad \Delta+2J(0)M\ ,\quad -\Delta+2J(0)M\ .$$

They are exactly the same as obtained by Pink.

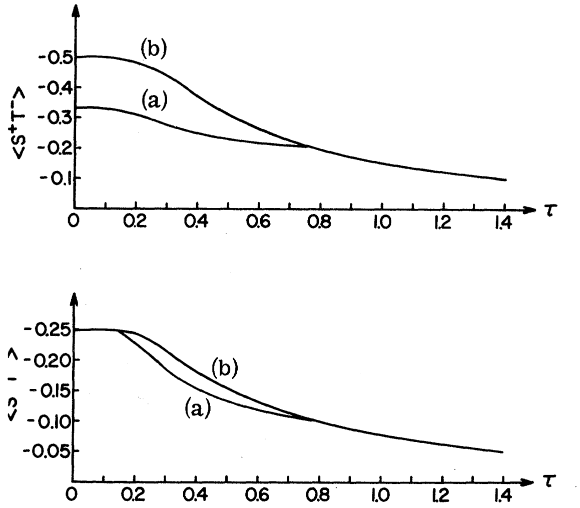

FIG. 4. Temperature dependence of the correlation functions $\langle S^+T^-\rangle$ and $\langle S^zT^z\rangle$ corresponding to case (b) in Fig. 2. (a) and (b) denote the ferromagnetic and paramagnetic states, respectively.

This is to be expected since we have used the same decoupling scheme. Other physical properties can hence be reproduced according to the Green's-function formalism. However, one can see that this system is not of induced-moment nature from Eq. (2. 3) in the molecular-field picture since it contains no contribution from the off-diagonal matrix elements.

2. *Simultaneous Excitation of Nuclear and Electronic Spin Waves*

It has been shown by de Gennes *et al.*[30] that because of hyperfine interaction, a ferromagnet in which the magnetic ions also carry a nuclear moment has two spin-wave branches at sufficiently low temperatures. The upper branch relates essentially to the electronic system and deviates slightly from the usual electronic spin-wave spectrum while the lower branch refers essentially to the nuclear system but deviates to a relatively greater extent from the usual NMR frequency. This effect can easily be demonstrated in our model by putting either $a=1$, $b=0$ or $a=0$, $b=1$. We take the first case, so that the Hamiltonian now takes the form

$$\mathcal{H}=\Delta\sum_i \vec{S}_i\cdot\vec{T}_i-\sum_{i,j}\mathcal{J}(i-j)\vec{S}_i\cdot\vec{S}_j ,$$

where Δ now represents the electron-nucleus hyperfine coupling, S refers to the electronic spin, and T the nuclear spin. If an external magnetic field H is applied in the z-direction, we have to add the corresponding electronic and nuclear Zeeman energies, namely,

$$\mathcal{H}=\Delta\sum_i \vec{S}_i\cdot\vec{T}_i-\sum_{i,j}\mathcal{J}(i-j)\vec{S}_i\cdot\vec{S}_j$$
$$-\gamma_e\hbar H\sum_i S_i^z-\gamma_n\hbar H\sum_i T_i^z .$$

Here γ_e and γ_n are the electronic and nuclear magnetogyric ratios, respectively.

If we now put $a=1$ and $b=0$ in Eq. (4. 19), the equation that determines the excitation spectra becomes

$$E^4-2\langle S_z\rangle E^3[2J(0)-J(k)]+E^2\{4J(0)\langle S_z\rangle^2[J(0)-J(k)]-\Delta[\Delta+J(k)(\langle S^-T^+\rangle+2\langle S^zT^z\rangle)]\}$$
$$+\Delta\langle S_z\rangle E[2\Delta J(0)-\Delta J(k)+2J(0)J(k)\langle S^-T^+\rangle]-\Delta^2J(0)\langle S_z\rangle[J(0)-J(k)]=0.$$

This equation corresponds neither to the results of de Gennes *et al.*[30] nor of Ninio and Keffer[31] in that we have here four branches of excitation spectra and the spectra contain the correlation functions between the electronic and nuclear spins, e.g., $\langle S^-T^+\rangle$ and $\langle S^zT^z\rangle$. It should be the correct expression to determine the excitation spectrum if Δ is comparable with respect to the exchange interaction J's. However, their results can be reproduced by using a different decoupling scheme, if we do not stress the coupling between S and T spins. For this purpose, we consider the following Green's functions:

$$\langle\langle S_g^+(t)|S_l^-(t')\rangle\rangle,\quad \langle\langle T_g^+(t)|S_l^-(t')\rangle\rangle ,$$

since

$$[S_g^+,\mathcal{H}]=\Delta(S_g^zT_g^+-S_g^+T_g^z)$$
$$-2\textstyle\sum_i\mathcal{J}(i-g)(S_i^+S_g^z-S_g^+S_i^z)+\gamma_eHS_g^+ .$$

As Δ, the hyperfine interaction, is usually much smaller than the exchange interaction J, we decouple the operators $S_g^zT_g^+$ and $S_g^+T_g^z$ in the following way:

$$S_g^zT_g^+\to\langle S_z\rangle T_g^+ ,\qquad S_g^+T_g^z\to\langle T_z\rangle S_g^+ ,$$

while the random-phase approximation is still used on the S spins on different sites. After doubly Fourier transforming the equations of motion, we have

$$EG_k^{(a)}(E)=1/\pi\langle S_z\rangle+\Delta\langle S_z\rangle G_k^{(b)}(E)-\Delta\langle T_z\rangle G_k^{(a)}(E)$$

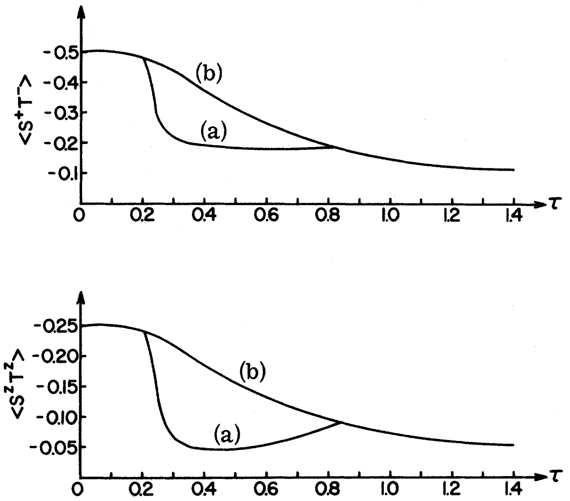

FIG. 5. Temperature dependence of the correlation functions $\langle S^+T^-\rangle$ and $\langle S^zT^z\rangle$ corresponding to case (c) in Fig. 2. (a) and (b) denote the ferromagnetic and paramagnetic states, respectively.

$$+\,2\langle S_z\rangle[J(0)-J(k)]G_k^{(a)}+\gamma_e H G_k^{(a)}(E)$$

or

$$\{E-\gamma_e H-2\langle S_z\rangle[J(0)-J(k)]+\Delta\langle T_z\rangle\}G_k^{(a)}(E)$$
$$-\,\Delta\langle S_z\rangle G_k^{(b)}(E)=1/\pi\langle S_z\rangle\ ,$$

where $G_k^{(a)}(E)$ is the energy-momentum Fourier transform of the Green's function $\langle\langle S_g^+(t)\,|S_1^-(t')\rangle\rangle$. $G_k^{(b)}(E)$ is the energy-momentum Fourier transform of the Green's function $\langle\langle T_g^+(t)\,|S_1^-(t')\rangle\rangle$. Similar calculations on $\langle\langle T_g^+(t)\,|S_1^-(t')\rangle\rangle$ give the equation

$$-\,\Delta\langle T_z\rangle G_k^{(a)}(E)+[E-\gamma_n H+\Delta\langle S_z\rangle]G_k^{(b)}(E)=0.$$

The equation which determines the excitation spectra of the system is then given by

$$\{E-\gamma_e H-2\langle S_z\rangle[J(0)-J(k)]+\Delta\langle T_z\rangle\}$$
$$\times(E-\gamma_n H+\Delta\langle S_z\rangle)-\Delta^2\langle S_z\rangle\langle T_z\rangle=0.$$

The roots are

$$\omega_{0e}\simeq\omega_e+\Delta^2\langle S_z\rangle\langle T_z\rangle/(\omega_e-\omega_n)\ ,$$
$$\omega_{0n}\simeq\omega_n-\Delta^2\langle S_z\rangle\langle T_z\rangle/(\omega_e-\omega_n)\ ,$$

with

$$\omega_e=\gamma_e H+2\langle S_z\rangle[J(0)-J(k)]-\Delta\langle T_z\rangle\ ,$$
$$\omega_n=\gamma_n H-\Delta\langle S_z\rangle\ .$$

These are just the results obtained by de Gennes *et al.*[30]

C. Zero-Temperature Excitation Spectra in MFA

The Green's-function formalism tells us how to obtain the collective excitation dispersion relations of those appropriate modes as well as the interesting thermodynamic correlation functions. A glance at Eq. (4.19) shows that, even in this simplest decoupling scheme, the equation itself involves the correlations $\langle S^+T^-\rangle$, $\langle S^-T^+\rangle$, $\langle S^zT^z\rangle$, ..., etc. Yet these correlations cannot be calculated unless the excitation spectra were determined in the first place, according to the formalism. Hence, as a first approximation, we use the results for these correlations from molecular-field calculations to determine the excitation spectra and from which to obtain the correlations according to the formalism.

As discussed in Sec. IV B, the ground state of the present model in the molecular-field approximation will be determined by the appropriate relations between the parameters a, b, $J(0)$, and Δ. We work out three different cases as classified in Sec. III.

1. Ferromagnetic and Fully Magnetized Ground State

At $T=0$ °K, the correlations have the values

$$\langle S_z\rangle=\langle T_z\rangle=\tfrac{1}{2},\quad\langle S^+T^-\rangle=\langle S^-T^+\rangle=0,\quad\langle S^zT^z\rangle=\tfrac{1}{4}\ .\tag{4.20}$$

The right-hand side of Eq. (4.19) now assumes the following form:

$$E^4-2E^3[(a+b)^2J(0)-\tfrac{1}{2}(a^2+b^2)J(k)]+E^2[(a+b)^2(a^2+4ab+b^2)J^2(0)-(a+b)^2(a^2+ab+b^2)J(0)J(k)-\Delta^2$$
$$-\tfrac{1}{2}\Delta(a-b)^2J(k)]\ -E\,\{2ab(a+b)^2J^2(0)\,[(a+b)^2J(0)-(a^2+ab+b^2)J(k)]-\Delta^2\,(a+b)^2[J(0)-\tfrac{1}{2}J(k)]\}$$
$$+\,J(0)\,[J(0)-J(k)]\,(a+b)^4\,[a^2b^2J^2(0)-\tfrac{1}{4}\Delta^2]\ .$$

For more convenience in computation, we introduce the parameters α, β, and $\gamma(k)$:

$$(a+b)^2J(0)=\alpha\Delta\ ,$$
$$(a-b)^2J(0)=\beta\Delta\ ,\tag{4.21}$$
$$J(k)/J(0)=\gamma(k)\ .$$

The above secular equation can be solved exactly and has the following four roots:

$$R_1(k)=\tfrac{1}{2}\{J(0)\,(a+b)^2-\Delta-(a^2+b^2)J(k)$$
$$+\,[\Delta^2+J^2(0)\,(a^2-b^2)^2-4ab\,\Delta J(k)$$
$$-\,2J(0)J(k)\,(a^2-b^2)^2+(a^2+b^2)^2J^2(k)]^{1/2}\}\ ,$$

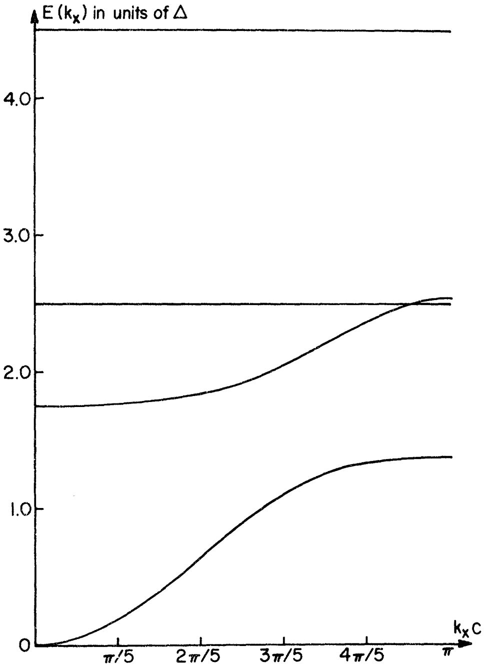

FIG. 6. Excitation spectra at 0 °K in RPA for case (a) in Fig. 2.

$$R_2(k)=\tfrac{1}{2}\{\Delta+J(0)\,(a+b)^2-[\Delta^2+J^2(0)\,(a^2-b^2)^2]^{1/2}\}\ ,$$

$$R_3(k)=\tfrac{1}{2}\{\Delta+J(0)\,(a+b)^2+[\Delta^2+J^2(0)\,(a^2-b^2)^2]^{1/2}\}\ ,\tag{4.22}$$

$$\begin{aligned}R_4(k)=\tfrac{1}{2}\{&J(0)\,(a+b)^2-\Delta-(a^2+b^2)J(k)\\&-[\Delta^2+J^2(0)\,(a^2-b^2)^2-4ab\,\Delta J(k)\\&\quad-2J(0)J(k)\,(a^2-b^2)^2+(a^2+b^2)^2J^2(k)]^{1/2}\}\ .\end{aligned}$$

Figure 6 shows their k dependence along the x axis for a simple-cubic nearest-neighbor interaction and $\alpha=6$, $\beta=0.5$.

It should be noted that two of the excitation spectra are independent of the wave vector. One would like to understand the reason behind as well as to which transitions these excitations can be attributed. This can be achieved by looking back at the molecular-field picture. By assuming full magnetization $M=\frac{1}{2}(a+b)$ at $T=0$ °K, the energy levels Eq. (3.6) now assume the following values:

$$\epsilon_1=\tfrac{1}{2}\{\Delta-[\Delta^2+(a^2-b^2)^2J^2(0)]^{1/2}\}\ ,$$

$$\epsilon_2=\tfrac{1}{2}\{\Delta+[\Delta^2+(a^2-b^2)^2J^2(0)]^{1/2}\}\ ,$$

$$\epsilon_3=\Delta-\tfrac{1}{2}(a+b)^2J(0)\ ,$$

$$\epsilon_4=\Delta+\tfrac{1}{2}(a+b)^2J(0)\ .$$

We can easily see that

$$\epsilon_4-\epsilon_1=R_3\ ,\qquad \epsilon_4-\epsilon_2=R_2\ .$$

Hence, the transitions can then be identified as denoted by arrows shown in Fig. 7. For $R_1(k)$ and $R_4(k)$, we remember that for crystals of cubic symmetry the following relation always holds: namely, near $k=0$,

$$J(k)=J(0)\,(1-\eta\,k^2c^2\cdots)\ .$$

η depends on the geometry of the crystal. Substituting this expansion into the expressions of $R_1(k)$ and $R_4(k)$, up to orders of k^2, we have

$$R_1(k)_{k\to 0}\sim\tfrac{1}{2}(a+b)^2\eta\,k^2c^2\ ,$$

$$R_4(k)_{k\to 0}\sim 2ab\,J(0)-\Delta+\tfrac{1}{2}(a-b)^2\eta\,J(0)\,k^2c^2\ .$$

We would then identify $R_1(k)$ as the spin-wave excitation and $R_4(k)$ as spin excitons.[21,34]

The reason that there are two spectra which should be independent of k is the following. Since we have used the molecular-field results, it is easy to see that the original four equations are redundant, e.g., the third equation of (4.13) now assumes the same form as the second and the fourth is the same form as the first. Hence, we have only two independent Green's functions.

We have justified the following conclusion: If the system under consideration has a fully magnetized ground state, we then have four branches of excitation spectra; two [$R_1(k)$ and R_2] are due to the spin-flip origin and the other two [R_3 and $R_4(k)$] are of excitonic origin. Yet only $R_1(k)$ and $R_4(k)$ do have a propagating nature. The other two branches provide only the molecular-field background and do not contribute to the physical properties (such as magnetization and correlation functions) as is shown in Secs. IV D and IV E.

2. *Ferromagnetic but not Fully Magnetized Ground State*

The correlation functions for this case in the molecular-field picture are

$$\langle S_z\rangle=-\langle T_z\rangle=\frac{M}{(a-b)}=\frac{[J^2(0)\,(a-b)^4-\Delta^2]^{1/2}}{2J(0)\,(a-b)^2}\ ,$$

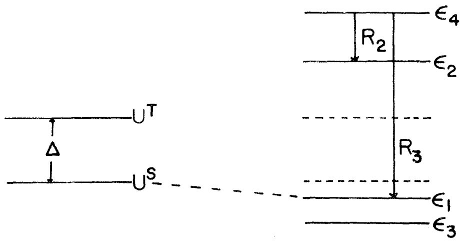

FIG. 7. Energy levels which show the corresponding transition for a fully magnetized molecular-field ground state.

$$\langle S^+T^-\rangle = \langle S^-T^+\rangle = -\Delta/2J(0)\,(a-b)^2\,,$$
$$\langle S^zT^z\rangle = -\tfrac{1}{4}\,. \qquad (4.23)$$

The right-hand side of the quartic equation (4.19) now becomes

$$E^4 - 2(a+b)M[2J(0)-J(k)]E^3 + E^2\{4J^2(0)M^2(a^2+4ab+b^2) - 4M^2J(0)J(k)\,(a^2+3ab+b^2)$$
$$-\Delta^2 + [\Delta^2/2J(0)]J(k) + \tfrac{1}{2}\Delta(a-b)^2J(k)\} - E\{16ab\,(a+b)J^2(0)M^3[J(0)-J(k)] - 2\Delta^2(a+b)M[J(0)-J(k)]\}$$
$$+J(0)M^2[J(0)-J(k)][16a^2b^2J^2(0)M^2 - \Delta^2(a+b)^2]\,,$$

with M given by $[J^2(0)\,(a-b)^4 - \Delta^2]^{1/2}/2J(0)\,(a-b)$. Again, it can be solved exactly:

$$R_1(k) = \frac{1}{2}\left((a+b)\left(J^2(0)\,(a-b)^2 - \frac{\Delta^2}{(a-b)^2}\right)^{1/2}\left(1-\frac{J(k)}{J(0)}\right)\right.$$
$$\left. + \left(1-\frac{J(k)}{J(0)}\right)^{1/2}\left\{[\Delta+J(0)\,(a-b)^2]^2 - \frac{J(k)}{J(0)}\left[J^2(0)\,(a^2-b^2)^2 - \left(\frac{a+b}{a-b}\right)^2\Delta^2\right]\right\}^{1/2}\right)$$

$$R_2(k) = \frac{1}{2}\left[(a+b)\left(J^2(0)\,(a-b)^2 - \frac{\Delta^2}{(a-b)^2}\right)^{1/2} - J(0)(a-b)^2 + \Delta\right]\,,$$

$$R_3(k) = \frac{1}{2}\left[(a+b)\left(J^2(0)\,(a-b)^2 - \frac{\Delta^2}{(a-b)^2}\right)^{1/2} + J(0)\,(a-b)^2 - \Delta\right]\,, \qquad (4.24)$$

$$R_4(k) = \frac{1}{2}\left((a+b)\left(J^2(0)\,(a-b)^2 - \frac{\Delta^2}{(a-b)^2}\right)^{1/2}\left(1-\frac{J(k)}{J(0)}\right)\right.$$
$$\left. - \left(1-\frac{J(k)}{J(0)}\right)^{1/2}\left\{[\Delta+J(0)\,(a-b)^2]^2 - \frac{J(k)}{J(0)}\left[J^2(0)\,(a^2-b^2)^2 - \left(\frac{a+b}{a-b}\right)^2\Delta^2\right]\right\}^{1/2}\right).$$

Their k dependences are shown in Fig. 8, again for a simple cubic with nearest-neighbor interaction and $\alpha = 2$, $\beta = 1.5$.

To see what transitions these excitations correspond to, we again examine the energy levels in the molecular-field picture. They are now given by

$$\epsilon_1 = \tfrac{1}{2}[\Delta - J(0)\,(a-b)^2]\,,$$
$$\epsilon_2 = \tfrac{1}{2}[\Delta + J(0)\,(a-b)^2]\,,$$
$$\epsilon_3 = \Delta - \tfrac{1}{2}(a+b)\,[J^2(0)\,(a-b)^2 - \Delta^2/(a-b)^2]^{1/2}\,,$$
$$\epsilon_4 = \Delta + \tfrac{1}{2}(a+b)\,[J^2(0)\,(a-b)^2 - \Delta^2/(a-b)^2]^{1/2}\,.$$

One can easily see that

$$\epsilon_2 - \epsilon_3 = R_3\,, \quad \epsilon_4 - \epsilon_2 = R_2\,.$$

The corresponding transitions are again denoted by arrows in Fig. 9. Hence, both R_2 and R_3 are of spin-flip origin and there is no excitonic transition in this category. Furthermore, one can show that both $R_1(k)$ and $R_4(k)$ are linearly proportional to k in the long-wavelength limit. This can be seen by expanding $R_1(k)$ and $R_4(k)$ near $k \sim 0$. We have

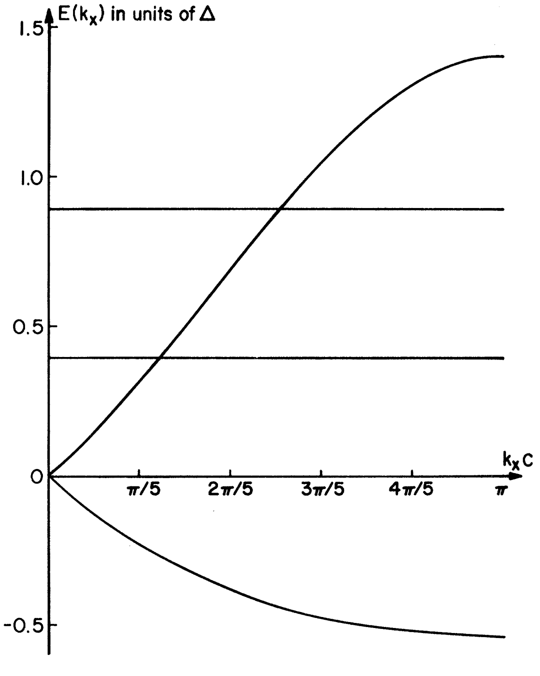

FIG. 8. Excitation spectra at 0 °K in RPA for case (b) in Fig. 2.

$$\left.\begin{matrix} R_1(k) \\ R_4(k) \end{matrix}\right\}_{k\to 0} \sim \frac{1}{2}\left[\frac{a+b}{a-b}[J^2(0)(a-b)^4-\Delta^2]^{1/2}\eta k^2c^2 \pm \sqrt{\eta}\,|k|\left(2\frac{a^2+b^2}{(a-b)^2}\Delta^2+2\Delta J(0)(a-b)^2-4ab(a-b)^2J^2(0)\right)^{1/2}\right.$$

$$\left. +\eta k^2c^2\left(\frac{a+b}{a-b}\right)^2[J^2(0)(a-b)^4-\Delta^2]\left(\frac{2(a^2+b^2)}{(a-b)^2}\Delta^2+2\Delta J(0)(a-b)^2-4ab(a-b)^2\,J^2(0)\right)^{1/2} + O(k^4c^4)\right].$$

One finds that in the long-wavelength limit, the linear dependence in k will be dominant for these two branches of excitations. They look more or less like antiferromagnetic magnons, a result which is rather peculiar in itself but certainly consistent with the molecular-field picture since the S and T spins are now antiparallel on each site.

3. Nonmagnetic Ground State

The last case to be discussed is that when there is no magnetic ordering even at zero temperature. The molecular-field values of the correlation functions are

$$\langle S_z\rangle = \langle T_z\rangle = M = 0\,,$$

$$\langle S^+T^-\rangle = \langle S^-T^+\rangle = \tfrac{1}{2}, \quad \langle S^zT^z\rangle = -\tfrac{1}{4}\,,$$

and the quartic equation now becomes

$$E^2\{E^2-[\Delta^2-(a-b)^2\Delta J(k)]\}=0\,.$$

The roots are 0, 0, $\pm[\Delta^2-\Delta(a-b)^2J(k)]^{1/2}$, which are exactly the same as obtained by Wang and Cooper.[21] They show that, however, instead of having spin deviations, excitations from the crystal field ground state to the excited state are passing from one site to another. The spectra have been plotted in Fig. 10. We notice that the energy spectrum shows a gap, and this gap decreases as β increases toward 1 and becomes imaginary for $\beta > 1$, indicating that the paramagnetic ground state is not stable for $\beta = 1$. The critical ratio is the same as predicted in the molecular-field approximation.

D. Spontaneous Magnetization at $T \neq 0\,^\circ$K

The Green's-function formalism allows us to determine the spontaneous magnetization at any temperature. As pointed out in Sec. IV C, this will always involve a self-consistent calculation because of the fact that the excitation spectra depend on the correlation functions, which is a consequence of the random-phase decoupling. In this subsection, we give some computations on physical magnetization as a function of temperature by using the molecular-field values as a first approximation. We also limit the regions of temperature of interest to low temperature and temperatures just below the Curie temperatures, since it is in these two regions that we can make series expansions.

We first look at the case where the molecular-field ground state is fully magnetized. From Eqs. (4.15) and (4.18), we know that their sum determines the magnetization. Again, by using the molecular-field values as a first approximation, we have

$$aG_k^{(1)}(E)+bH_k^{(1)}(E)=\frac{a+b}{2\pi}\left(\frac{B_1}{E-R_1(k)}+\frac{B_4}{E-R_4(k)}\right)\,,$$

where

$$B_1=\frac{1}{R_1(k)-R_4(k)}[R_1(k)+\tfrac{1}{2}(1-\alpha+\beta)+\tfrac{1}{4}(\alpha-\beta)\gamma(k)]\,,$$

$$B_4=\frac{-1}{R_1(k)-R_4(k)}[R_4(k)+\tfrac{1}{2}(1-\alpha+\beta)+\tfrac{1}{4}(\alpha-\beta)\gamma(k)]\,.$$

Hence

$$\tfrac{1}{2}(a+b)-(a\langle S_z\rangle+b\langle T_z\rangle)$$

$$=\frac{a+b}{N}\sum_k\left(\frac{B_1}{e^{R_1(k)/k_BT}-1}+\frac{B_4}{e^{R_4(k)/k_BT}-1}\right)\,.$$

Substituting the expressions of $R_1(k)$ and $R_4(k)$ into the above equation and rearranging it, we have, in the limit of large N,

$$\langle J_z\rangle = a\langle S_z\rangle + b\langle T_z\rangle$$

$$=\tfrac{1}{2}(a+b)-\frac{(a+b)}{2(2\pi)^3}\int_{-\pi}^{\pi}dk_x\int_{-\pi}^{\pi}dk_y\int_{-\pi}^{\pi}dk_z\left[\left(\frac{1}{e^{R_1(k)/k_BT}-1}+\frac{1}{e^{R_4(k)/k_BT}-1}\right)\right.$$

$$\left.+\beta[1-\gamma(k)][1+\alpha\beta-\gamma(k)(\alpha-\beta+2\alpha\beta)+\tfrac{1}{4}(\alpha+\beta)^2\gamma^2(k)]^{-1/2}\left(\frac{1}{e^{R_1(k)/k_BT}-1}-\frac{1}{e^{R_4(k)/k_BT}-1}\right)\right]. \qquad (4.25)$$

The first term in the integrand comes from the spin-wave and excitonic excitations. The second term comes from the interference or interaction of these two excitations since it is proportional to $(a-b)^2$, which is the off-diagonal matrix element representing the interference between the S and T

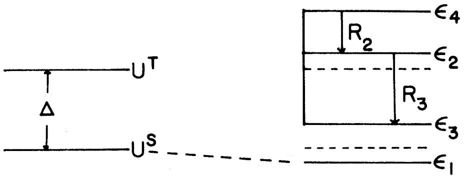

FIG. 9. Energy levels which show the corresponding transition for a nonsaturated molecular-field ground state.

spins in the molecular-field picture. We see immediately that this interacting term will contribute rather significantly to the magnetization both at low temperatures and high temperatures.

The results computed for a simple-cubic nearest-neighbor interaction are shown in Fig. 11. A comparison with the molecular-field calculations shows that at low temperatures it is of $T^{3/2}$ dependence, i.e., typical spin-wave nature. At high temperatures, e.g., near the Curie temperature, it shows a linear dependence on temperature, very different from that of a pure Heisenberg ferromagnet. We can see these two features by making appropriate series expansions.

At first, we write Eq. (4.25) in the following form:

$$\langle J_z\rangle / \tfrac{1}{2}(a+b) = 1 - (\Phi_1 + \Phi_2 + \Phi_3 - \Phi_4),$$

where

$$\Phi_1 = \frac{1}{N}\sum_k \frac{1}{e^{R_1(k)/k_BT}-1},$$

$$\Phi_2 = \frac{1}{N}\sum_k \frac{1}{e^{R_4(k)/k_BT}-1},$$

$$\Phi_3 = \frac{1}{N}\sum_k \beta[1-\gamma(k)][1+\alpha\beta-(\alpha-\beta+2\alpha\beta)\gamma(k)$$

$$+\tfrac{1}{4}(\alpha+\beta)^2\gamma^2(k)]^{-1/2}\frac{1}{e^{R_1(k)/k_BT}-1},$$

$$\Phi_4 = \frac{1}{N}\sum_k \beta[1-\gamma(k)][1+\alpha\beta-(\alpha-\beta+2\alpha\beta)\gamma(k)$$

$$+\tfrac{1}{4}(\alpha+\beta)^2\gamma^2(k)]^{-1/2}\frac{1}{e^{R_4(k)/k_BT}-1}.$$

The summation over k is limited to the first Brillouin zone, but at low temperatures we may replace it by an integral over the whole k space. For example, we can replace Φ_1 in the following form:

$$\Phi_1 = \frac{c^3}{(2\pi)^3}\int_0^{2\pi} d\psi \int_0^{\pi} \sin\theta\, d\theta \int_0^{\infty} k^2 dk \sum_{l=1}^{\infty} e^{-lR_1(k)/k_BT}.$$

Since only small values of k will appreciably contribute to Φ_1, we expand $R_1(k)$ in powers of k. Note also for a simple-cubic and nearest-neighbor interaction, $\gamma(k)$ is given by

$$\gamma(k) = \tfrac{1}{3}(\cos k_x c + \cos k_y c + \cos k_z c).$$

Hence, near $k \sim 0$, we have

$$R_1(k) \sim \tfrac{1}{2}\alpha[1-\gamma(k)]$$

$$\sim \tfrac{1}{2}\alpha\left(\tfrac{1}{6}k^2c^2 - \frac{c^4}{3\times 4!}(k_x^4+k_y^4+k_z^4)+\cdots\right),$$

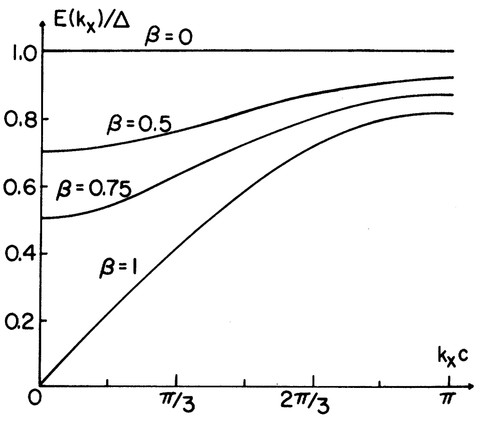

FIG. 10. Excitation spectra at 0 °K in RPA for a nonmagnetic ground state.

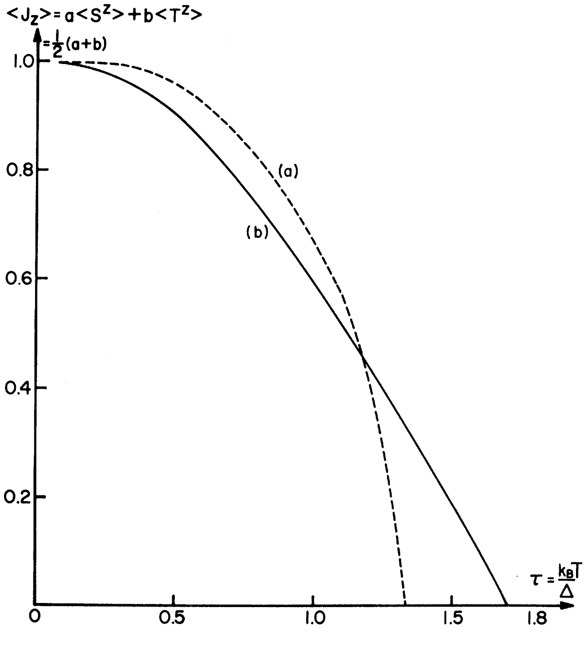

FIG. 11. Temperature dependence of spontaneous magnetization in units of $\frac{1}{2}(a+b)$ for a simple-cubic nearest-neighbor interaction and parameters corresponding to case (a) in Fig. 2. (a) and (b) are results from MFA and RPA, respectively.

$$\Phi_1 = a_0\left(\frac{3k_BT}{\pi\alpha\Delta}\right)^{3/2} + a_1\left(\frac{3k_BT}{\pi\alpha\Delta}\right)^{5/2} + a_2\left(\frac{3k_BT}{\pi\alpha\Delta}\right)^{7/2} + \cdots ,$$

where

$$a_0 = \zeta(\tfrac{3}{2}), \qquad a_1 = \tfrac{3}{4}\pi\zeta(\tfrac{5}{2}), \qquad a_2 = \tfrac{33}{32}\pi^2\zeta(\tfrac{7}{2}),$$

and $\zeta(n)$ is the Riemann ζ function.

Similarly,

$$R_4(k) \sim \tfrac{1}{2}(\alpha - \beta - 2) + \tfrac{1}{2}\beta[1 - \gamma(k)]$$

$$= \tfrac{1}{2}(\alpha - \beta - 2) + \tfrac{1}{2}\beta\left(\tfrac{1}{6}k^2c^2 - \frac{c^4}{3\times 4!}(k_x^4 + k_y^4 + k_z^4) + \cdots\right),$$

$$\Phi_2 = e^{-[(\alpha-\beta-2)/2k_BT]\Delta}\left[a_0\left(\frac{3k_BT}{\pi\beta\Delta}\right)^{3/2} + a_1\left(\frac{3k_BT}{\pi\beta\Delta}\right)^{5/2} + a_2\left(\frac{3k_BT}{\pi\beta\Delta}\right)^{7/2} + \cdots\right].$$

For Φ_3 and Φ_4, we note that near $k \sim 0$

$$[1 - \gamma(k)][1 + \alpha\beta - (\alpha - \beta + 2\alpha\beta)\gamma(k) + \tfrac{1}{4}(\alpha + \beta)^2\gamma^2(k)]^{-1/2} \sim \frac{2[1 - \gamma(k)]}{2 - \alpha + \beta} - \frac{2(\alpha - \beta)[1 - \gamma(k)]^2}{(2 - \alpha + \beta)^2} + \cdots ,$$

so

$$\Phi_3 = \frac{\beta c^3}{(2\pi)^3}\int_0^{2\pi} d\psi \int_0^{\pi} \sin\theta\, d\theta \int_0^{\infty} k^2 dk \left(\frac{2[1 - \gamma(k)]}{2 - \alpha + \beta} - \frac{2(\alpha - \beta)[1 - \gamma(k)]^2}{(2 - \alpha + \beta)^2} + \cdots\right)\sum_{l=1}^{\infty} e^{-lR_1(k)/k_BT}$$

$$= \frac{\beta\sqrt{\pi}\,\zeta(\frac{5}{2})}{4\times 4\pi^2(2 - \alpha + \beta)}\left(\frac{12k_BT}{\alpha\Delta}\right)^{5/2} - \frac{5\sqrt{\pi}\,\beta(2 + \alpha - \beta)}{384\,\pi^2(2 - \alpha + \beta)^2}\left(\frac{12k_BT}{\alpha\Delta}\right)^{7/2}\zeta(\tfrac{7}{2}) + \cdots .$$

Similarly,

$$\Phi_4 = \frac{\beta c^3}{(2\pi)^3}\int_0^{2\pi} d\psi \int_0^{\pi} \sin\theta\, d\theta \int_0^{\infty} k^2 dk \left(\frac{2[1 - \gamma(k)]}{2 - \alpha + \beta} - \frac{2(\alpha - \beta)[1 - \gamma(k)]^2}{(2 - \alpha + \beta)^2} + \cdots\right)\sum_{l=1}^{\infty} e^{-lR_4(k)/k_BT}$$

$$= e^{-[(\alpha-\beta-2)/2k_BT]\Delta}\left[\frac{\beta\sqrt{\pi}\,\zeta(\frac{5}{2})}{4\times 4\,\pi^2(2 - \alpha + \beta)}\left(\frac{12k_BT}{\beta\Delta}\right)^{5/2} - \frac{5\sqrt{\pi}\,\beta(2 + \alpha - \beta)}{384\pi^2(2 - \alpha + \beta)^2}\left(\frac{12k_BT}{\beta\Delta}\right)^{7/2}\zeta(\tfrac{7}{2}) + \cdots\right].$$

One can easily see that at low temperatures, as long as $\alpha > \beta + 2$, Φ_1 is the dominating term, i.e., a spin-wave $T^{3/2}$ contribution. The physical reason behind this criterion can be traced back again to the molecular-field picture. Namely, if we look at the level scheme, we find that the magnitude of ϵ_3 and ϵ_1 determines the nature of the ground state, a ferromagnetic, nonmagnetic, or degenerate magnetic according to $\epsilon_1 > \epsilon_3$, $\epsilon_1 < \epsilon_3$, or $\epsilon_1 = \epsilon_3$, respectively. In terms of the parameters α and β, it is just the condition $\alpha > \beta + 2$, $\alpha < \beta + 2$, and $\alpha = \beta + 2$. Hence, we expect the whole argument will break down if we start from a nonmagnetic or degenerate ground state.

In total, the temperature dependence of spontaneous magnetization at low temperatures can be written

$$\frac{\langle J_z\rangle}{\frac{1}{2}(a + b)} = 1 - [(A_0 + A_1 e^{-[(\alpha-\beta-2)/2k_BT]\Delta})T^{3/2} + (B_0 + B_1 e^{-[(\alpha-\beta+2)/2k_BT]\Delta})T^{5/2} + \cdots],$$

where A_0, A_1, B_0, B_1 are only numerical constants. The dependence of $T^{3/2}$, $T^{5/2}$, $T^{7/2}$, ... are typical contributions from spin waves and are due to the discrete nature of the crystal, not of spin-wave interactions. The exponential terms are due, in the molecular-field picture, to the excitonic transitions.

We next come to the region of temperatures just below the Curie temperature, where we can make high-temperature expansions. Φ_1 can be written in the form

$$1 + 2\Phi_1 = (1/N)\textstyle\sum_k \coth[R_1(k)/2k_BT].$$

The following expression is also used:

$$\coth Z = \frac{1}{Z} + \frac{Z}{3} + \frac{Z^3}{45} + \frac{2Z^5}{945} - \cdots , \quad |Z| < \pi .$$

Hence,

$$1 + 2\Phi_1 = \frac{1}{N}\sum_k\left(\frac{2k_BT}{R_1(k)} + \frac{R_1(k)}{6k_BT} - \frac{R_1^3(k)}{360(k_BT)^3} + \cdots\right).$$

Similarly,

$$1 + 2\Phi_2 = \frac{1}{N}\sum_k\left(\frac{2k_BT}{R_4(k)} + \frac{R_4(k)}{6k_BT} - \frac{R_4^3(k)}{360(k_BT)^3} + \cdots\right),$$

so that

$$2 + 2(\Phi_1 + \Phi_2) = \frac{1}{N}\sum_k\left[2k_BT\left(\frac{1}{R_1} + \frac{1}{R_4}\right) + \frac{(R_1 + R_4)}{6k_BT}\right.$$

$$-\frac{1}{360(k_BT)^3}\,(R_1^3+R_4^3)+\cdots\Big] .$$

To calculate the above sum, we note that the following results for simple-cubic crystals have been calculated[35]:

$$F(-1)=1.5638, \quad F(1)=1, \quad F(2)=\tfrac{7}{6},$$

$$F(3)=1.5, \text{ etc.},$$

with $F(n)$ defined by

$$F(n)=(1/N)\textstyle\sum_k(1-J(k)/J(0))^n .$$

Substituting the explicit expressions of R_1 and R_4 and using the above numerical results, we find

$$2+2(\Phi_1+\Phi_2)=\frac{4}{\Delta}(k_BT)\left(\frac{F(-1)}{\alpha}+\frac{\alpha+\beta}{\alpha(\alpha-\beta-2)}\right)+\frac{(\alpha-1)k_BT}{6\Delta}$$

$$-\frac{(k_BT)^3}{16\times 360\times\Delta^3}\,(5\alpha^3+16\alpha^2\beta-14\alpha\beta+3\alpha\beta^2-2\beta^2-12\alpha^2+24\alpha-16)+\cdots .$$

The high-temperature expansions of Φ_3 and Φ_4 can be found similarly:

$$\Phi_3-\Phi_4=\frac{\beta}{N}\sum_k\left(-\frac{2(k_BT)}{\alpha(\alpha-\beta-2)\Delta}+\frac{1}{240k_BT}[1-\gamma(k)]\right.$$

$$\left.-\frac{1}{1440(k_BT)^3}\{\tfrac{1}{4}(\alpha-\beta-2)^2[1-\gamma(k)]+\tfrac{1}{4}(\alpha+2\beta)(\alpha-2-\beta)[1-\gamma(k)]^2+\tfrac{1}{4}(\alpha+\beta)^2[1-\gamma(k)]^3\}+\cdots\right)$$

$$=\frac{\beta}{2}\left(-\frac{4(k_BT)}{\alpha(\alpha-\beta-2)}+\frac{\Delta}{12k_BT}-\frac{\Delta^3}{720(k_BT)^3}[\tfrac{1}{4}(\alpha-\beta-2)^2+\tfrac{1}{4}(\alpha+2\beta)(\alpha-2-\beta)\tfrac{7}{6}+\tfrac{3}{8}(\alpha+\beta)^2]+\cdots\right) .$$

Hence, one has

$$\frac{\langle J_z\rangle}{\frac{1}{2}(a+b)}=2-\frac{2k_BT}{\Delta}\left(\frac{F(-1)}{\alpha}+\frac{1}{\alpha-\beta-2}\right)-\frac{\Delta}{12k_BT}(\alpha-\beta-2)$$

$$-\frac{\Delta^3}{720\times 48(k_BT)^3}[15\alpha^3+70\alpha^2\beta-80\alpha\beta+22\alpha\beta^2-10\beta^2-36\alpha^2+72\alpha+24\beta+\beta^3-48]+\cdots .$$

Since the coefficient of the last term in the above equation is rather small, we can neglect the terms from this on, and to determine the Curie temperature we just set $\langle J_z\rangle=0$,

$$2=2\tau_C\left(\frac{F(-1)}{\alpha}+\frac{1}{\alpha-\beta-2}\right)+\frac{1}{12\tau_C}(\alpha-2-\beta),$$

where $\tau_C=k_BT_C/\Delta$. As a check, we calculate the transition temperature for the case $\alpha=6$, $\beta=0.5$. Now it becomes

$$0.536\,\tau_C^2-\tau_C+3.5/24=0 .$$

One solution is $\tau_C=1.705$, which is in excellent agreement with that which has been obtained in Fig. 11.

To find the temperature dependence of the spontaneous magnetization near the Curie point, we set

$$\Delta\tau=\tau_C-\tau \quad\text{or}\quad \tau=\tau_C-\Delta\tau .$$

Then

$$\frac{\langle J_z\rangle}{\frac{1}{2}(a+b)}=2-2\left(\frac{F(-1)}{\alpha}+\frac{1}{\alpha-\beta-2}\right)(\tau_C-\Delta\tau)$$

$$-\frac{\alpha-2\beta}{12}\,\frac{1}{\tau_C-\Delta\tau}+\frac{\delta}{(\tau_C-\Delta\tau)^3}+\cdots ,$$

where δ is very small. We also use the expansion

$$\frac{1}{\tau_C-\Delta\tau}=\frac{1}{\tau_C}\left(1-\frac{\Delta\tau}{\tau_C}\right)^{-1}$$

$$\simeq\frac{1}{\tau_C}\left[1+\frac{\Delta\tau}{\tau_C}+\left(\frac{\Delta\tau}{\tau_C}\right)^2+\cdots\right] .$$

Hence

$$\frac{\langle J_z\rangle}{\frac{1}{2}(a+b)}=\left(\frac{2F(-1)}{\alpha}+\frac{2}{\alpha-\beta-2}-\frac{\alpha-\beta-2}{12\tau_C^2}\right)\Delta\tau+\cdots .$$

The above expression shows that at temperatures near the Curie point, the magnetization has a linear dependence on temperature rather than the usual $(\tau_C-\tau)^{1/2}$ dependence for a pure Heisenberg ferromagnet.[36] One can attribute the reason for this to the fact that we have used the molecular-field values in determining the excitation spectra, which no longer depends on the magnetization, so that we have not iterated the results back to correct the excitation spectra. In fact, the deficiency that M, $\langle S^+T^-\rangle$, and $\langle S^zT^z\rangle$ show in Figs. 11, 13, and 14 at high temperatures has the same cause.

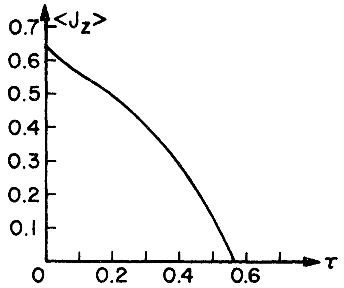

FIG. 12. Temperature dependence of spontaneous magnetization in units of $\frac{1}{2}(a+b)$ in RPA for a simple-cubic nearest-neighbor interaction and parameters corresponding to case (b) in Fig. 2.

We next consider the case where the ground state is not fully magnetized. Again we find

$$aG_k^{(1)}(E)+bH_k^{(1)}(E)=\frac{M}{\pi}\,\frac{E-\lambda(k)}{(E-R_1)(E-R_4)}\ ,$$

where M is given by Eq. (3.8) and

$$\lambda(k)=\frac{a+b}{M}\left(\frac{2ab}{a-b}\,M^2J(k)-\frac{\Delta^2}{4J(0)(a-b)^2}-\frac{\Delta}{4}\right).$$

Writing in partial fractions, we then have

$$aG_k^{(1)}(E)+bH_k^{(1)}(E)=\frac{M}{\pi(R_1-R_4)}\left(\frac{R_1-\lambda}{E-R_1}+\frac{\lambda-R_4}{E-R_4}\right)\ ,$$

so that

$$\tfrac{1}{2}(a+b)-(a\langle S_z\rangle+b\langle T_z\rangle)$$

$$=\frac{2M}{N}\sum_k\frac{1}{R_1-R_4}\left(\frac{R_1-\lambda}{e^{R_1/k_BT}-1}+\frac{\lambda-R_4}{e^{R_4/k_BT}-1}\right),$$

$$\langle J_z\rangle=\tfrac{1}{2}(a+b)\left[1-\frac{4M}{(a+b)N}\right.$$

$$\left.\times\sum_k\frac{1}{R_1-R_4}\left(\frac{R_1-\lambda}{e^{R_1/k_BT}-1}+\frac{\lambda-R_4}{e^{R4/k_BT}-1}\right)\right].$$

The results after numerical integration for a simple-cubic nearest-neighbor interaction and $\alpha=2$, $\beta=1.5$ are shown in Fig. 12. Similar analysis can be carried out without difficulty.

The last case where we have a nonmagnetic ground state has been discussed elsewhere[21]; we will not repeat their results here.

E. Various Thermodynamic Correlation Functions

We again use the molecular-field values as a first approximation to calculate the correlation functions according to the Green's functions formalism. The first case to be worked out is the one where we have a ferromagnetic fully magnetized ground state in the MFA.

(a). $\langle S^+T^-\rangle$ and $\langle S^-T^+\rangle$. Since $\langle S^-T^+\rangle$ and $\langle S^+T^-\rangle$ are determined by $G_k^{(2)}(E)$ and $H_k^{(2)}(E)$, respectively, we solve these two Green's functions from Eqs. (4.13) and (4.17). They are given by

$$G_k^{(2)}(E)=(1/\Delta')\big((1/\pi)\langle S_z\rangle\{2ab\,\langle T_z\rangle J(k)[E-2a\,J(0)M][E-2bJ(0)M]$$

$$+\Delta[E-2bJ(0)M][\tfrac{1}{4}\Delta-aJ(k)(b\langle S^+T^-\rangle-2a\langle S^zT^z\rangle)]+\Delta[E-2aJ(0)M][\tfrac{1}{4}\Delta+aJ(k)(a\langle S^-T^+\rangle-2b\langle S^zT^z\rangle)]\}$$

$$-(\Delta/\pi)\{E-2aM[J(0)-J(k)]\}\{\langle S^zT^z\rangle[E-2bJ(0)M]+\tfrac{1}{2}\langle S^-T^+\rangle[E-2aJ(0)M]\}\big)\ ,$$

$$H_k^{(2)}(E)=(1/\Delta')\big((1/\pi)\langle T_z\rangle\{2ab\langle S_z\rangle\,J(k)[E-2aJ(0)M][E-2bJ(0)M]$$

$$+\Delta[E-2aJ(0)M][\tfrac{1}{4}\Delta-bJ(k)(a\langle S^-T^+\rangle-2b\langle S^zT^z\rangle)]+\Delta[E-2bJ(0)M][\tfrac{1}{4}\Delta+bJ(k)(b\langle S^+T^-\rangle-2a\langle S^zT^z\rangle)]\}$$

$$-(\Delta/\pi)\{E-2bM[J(0)-J(k)]\}\{\langle S^zT^z\rangle[E-2aJ(0)M]+\tfrac{1}{2}\langle S^+T^-\rangle[E-2bJ(0)M]\}\big)\ ,$$

where Δ' is the quartic equation given by (4.19). One finds that $G_k^{(2)}(E)$ is not equal to $H_k^{(2)}(E)$ and hence $\langle S^-T^+\rangle\neq\langle S^+T^-\rangle$. This is reasonable since S and T do not have the same weight in the original Hamiltonian. After substituting the corresponding molecular-field values into the above expressions, we find

$$G_k^{(2)}(E)=H_k^{(2)}(E)$$

$$=\frac{\Delta}{4\pi}\,\frac{1-\frac{1}{2}(\alpha-\beta)\gamma(k)}{[E-R_1(k)][E-R_4(k)]}$$

$$=\frac{\Delta}{4\pi}\,\frac{1-\frac{1}{2}(\alpha-\beta)\gamma(k)}{R_1(k)-R_4(k)}\left(\frac{1}{E-R_1(k)}-\frac{1}{E-R_4(k)}\right).$$

The above equation shows that $\langle S^-T^+\rangle=\langle S^+T^-\rangle$, a result consistent with the molecular-field picture. The correlations are then given by

$$\langle S^-T^+\rangle=\langle S^+T^-\rangle=\frac{\Delta}{2N}\sum_k\frac{1-\frac{1}{2}(\alpha-\beta)\gamma(k)}{R_1(k)-R_4(k)}$$

$$\times\left(\frac{1}{e^{R_1(k)/k_BT}-1}-\frac{1}{e^{R_4(k)/k_BT}-1}\right).$$

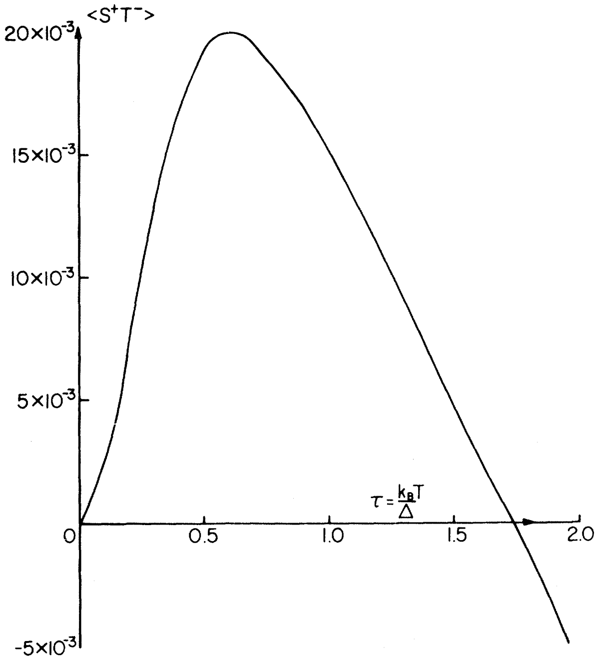

FIG. 13. Temperature dependence of correlation $\langle S^+T^-\rangle$ in RPA, using parameters of case (a) in Fig. 2.

In the limit of large N, the summation over k can be replaced by the integral

$$\langle S^-T^+\rangle = \langle S^+T^-\rangle$$

$$= \frac{\Delta}{2(2\pi)^3}\int_{-\pi}^{\pi} dk_x \int_{-\pi}^{\pi} dk_y \int_{-\pi}^{\pi} dk_z \, \frac{1-\frac{1}{2}(\alpha-\beta)\gamma(k)}{R_1(k)-R_4(k)} \times\left(\frac{1}{e^{R_1(k)/k_BT}-1} - \frac{1}{e^{R_4(k)/k_BT}-1}\right). \qquad (4.26)$$

An example for a simple cubic with nearest-neighbor interaction and $\alpha = 6$, $\beta = 0.5$ has been computed by using computers and the result is shown in Fig. 13. A comparison with the molecular-field result (Fig. 3) shows that their behaviors as functions of temperatures are quite different. The random-phase picture shows that correlation between S and T spins first increases as temperatures go up from zero, reaches a maximum, then indefinitely decreases linearly at high temperatures after vanishing at the Curie point without concaving back to horizontal axis as in the molecular-field picture. This behavior can be explained by looking at Eq. (4.26) which shows that this correlation comes essentially from the difference between the contributions of the spin-wave and excitonic excitations. Hence the compatibility between these two excitations gives this manifestation. While the linear dependence on temperature near the Curie point can still be seen in the following way.

At high temperatures, the integrand can be written

$$\frac{1-\frac{1}{2}(\alpha-\beta)\gamma(k)}{R_1(k)-R_4(k)}\left(\frac{k_BT}{R_1(k)} - \frac{k_BT}{R_4(k)}\right)$$

$$= -\frac{k_BT}{R_1(k)R_4(k)}\left[1-\tfrac{1}{2}(\alpha-\beta)\gamma(k)\right]$$

$$= -\frac{k_BT}{\Delta^2}\,\frac{4\left[1-\frac{1}{2}(\alpha-\beta)\gamma(k)\right]}{\alpha(\alpha-\beta-2)[1-\gamma(k)]},$$

and hence

$$\langle S^-T^+\rangle = \langle S^+T^-\rangle$$

$$\simeq -\frac{k_BT}{\alpha(\alpha-\beta-2)\Delta}\,\frac{1}{N}\sum_k \frac{2-(\alpha-\beta)\gamma(k)}{1-\gamma(k)}$$

$$= -\frac{k_BT}{\alpha\Delta}\left(-F(-1)+\frac{\alpha-\beta}{\alpha-\beta-2}\right).$$

We note also that the magnitude of this correlation is of the order of 1% This gives a good justification to the approximation which we used in the original decoupling scheme.

(b) $\langle S^zT^z\rangle$. Equations (4.15) and (4.18) tell us that this correlation cannot be calculated unless $\langle S_z\rangle$ and $\langle T_z\rangle$ are known. Hence we solve $G_k^{(1)}(E)$ and $H_k^{(1)}(E)$ first:

$$G_k^{(1)}(E) = (1/\Delta')\big((1/\pi)\,\langle S_z\rangle\{[E-2aJ(0)M][E-2bJ(0)M][E-2bJ(0)+2b^2J(k)\langle T_z\rangle]$$
$$+\Delta[E-2aMJ(0)][-\tfrac{1}{4}\Delta+bJ(k)(a\langle S^+T^-\rangle-2b\langle S^zT^z\rangle)]-\Delta[E-2bMJ(0)][\tfrac{1}{4}\Delta+bJ(k)(b\langle S^-T^+\rangle-2a\langle S^zT^z\rangle)]\}$$
$$-(\Delta/\pi)\{E-2bMJ(0)[1-\gamma(k)]\}\{\tfrac{1}{2}\langle S^-T^+\rangle[E-2aJ(0)M]+\langle S^zT^z\rangle[E-2bJ(0)M]\}\big),$$

$$H_k^{(1)}(E) = (1/\Delta')\big((1/\pi)\langle T_z\rangle\{[E-2aJ(0)M][E-2bJ(0)M][E-2aJ(0)M+2a^2J(k)\langle S_z\rangle]$$
$$+\Delta[E-2bJ(0)M][-\tfrac{1}{4}\Delta+aJ(k)(b\langle S^+T^-\rangle-2a\langle S^zT^z\rangle)]-\Delta[E-2aJ(0)M][\tfrac{1}{4}\Delta+aJ(k)(a\langle S^-T^+\rangle-2b\langle S^zT^z\rangle)]\}$$
$$-(\Delta/\pi)\{E-2aMJ(0)[1-\gamma(k)]\}\{\tfrac{1}{2}\langle S^+T^-\rangle[E-2bJ(0)M]+\langle S^zT^z\rangle[E-2aJ(0)M]\}\big).$$

After substituting the corresponding molecular-field values into the above expressions, they become

$$G_k^{(1)}(E) = (1/2\pi\Delta')\{[E-2aJ(0)M][E-2bJ(0)M][E-2bJ(0)M+b^2J(k)] - \tfrac{1}{2}\Delta[E-2bJ(0)M]^2$$

$$-\Delta[\tfrac{1}{2}\Delta+b^2J(k)][E-(a+b)J(0)M]\},$$

$$H_k^{(1)}(E)=(1/2\pi\Delta')\{[E-2aJ(0)M][E-2bJ(0)M][E-2aJ(0)M+a^2J(k)]-\tfrac{1}{2}\Delta[E-2aJ(0)M]^2$$
$$-\Delta[\tfrac{1}{2}\Delta+a^2J(k)][E-(a+b)J(0)M]\}.$$

They are not equal, and hence $\langle S_z\rangle\neq\langle T_z\rangle$. But

$$G_k^{(1)}(E)+H_k^{(1)}(E)=\frac{1}{2\pi}\left(\frac{1}{E-R_1(k)}+\frac{1}{E-R_4(k)}\right),$$

so that

$$1-(\langle S_z\rangle+\langle T_z\rangle)=\frac{1}{N}\sum_k\left(\frac{1}{e^{R_1(k)/k_BT}-1}+\frac{1}{e^{R_4(k)/k_BT}-1}\right),$$

or (4.27)

$$\langle S_z\rangle+\langle T_z\rangle=1-\frac{1}{N}\sum_k\left(\frac{1}{e^{R_1(k)/k_BT}-1}+\frac{1}{e^{R_4(k)/k_BT}-1}\right).$$

Similarly, we have

$$G_k^{(4)}(E)+H_k^{(3)}(E)=\frac{1}{4\pi}\left(\frac{1}{E-R_1(k)}+\frac{1}{E-R_4(k)}\right),$$

which leads to the following result:

$$\tfrac{1}{2}(\langle S_z\rangle+\langle T_z\rangle)-2\langle S^zT^z\rangle=\frac{1}{2N}\sum_k\left(\frac{1}{e^{R_1(k)/k_BT}-1}+\frac{1}{e^{R_4(k)/k_BT}-1}\right).$$

Combining with (4.27), we get

$$\langle S^zT^z\rangle=\frac{1}{4}-\frac{1}{2N}\sum_k\left(\frac{1}{e^{R_1(k)/k_BT}-1}+\frac{1}{e^{R_4(k)/k_BT}-1}\right),$$

and in the limit of large N, it becomes

$$\langle S^zT^z\rangle=\frac{1}{4}-\frac{1}{2(2\pi)^3}\int_{-\pi}^{\pi}dk_x\int_{-\pi}^{\pi}dk_y\int_{-\pi}^{\pi}dk_z\times\left(\frac{1}{e^{R_1(k)/k_BT}-1}+\frac{1}{e^{R_4(k)/k_BT}-1}\right). \tag{4.28}$$

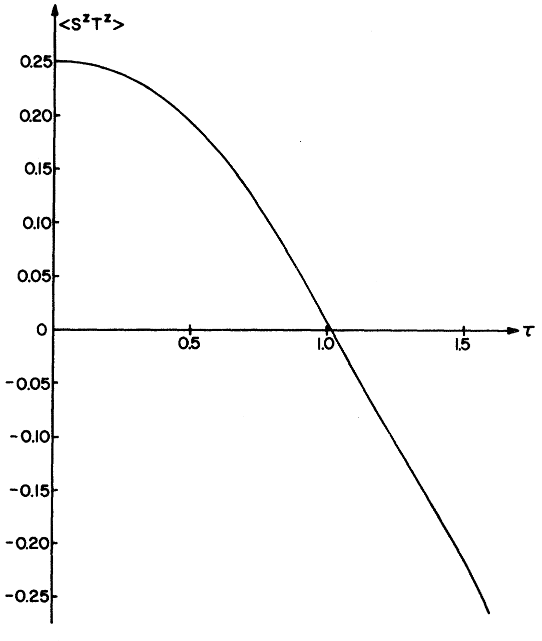

FIG. 14. Temperature dependence of correlation $\langle S^zT^z\rangle$ in RPA, using parameters of case (a) in Fig. 2.

A similar example as $\langle S^-T^+\rangle$ has been done by computers and plotted in Fig. 14. A comparison of this figure and Fig. 3 can also be made. One sees that these two curves look similar at low temperature, though the molecular-field approach has an exponential dependence at low temperatures while the random-phase one has a $T^{3/2}$ dependence due to spin-wave excitation in addition to the exponential one which is due to the excitonic excitation. This can be seen from the above equation by taking the low-temperature limit. By taking the high-temperature limit, the linear dependence will again be seen.

We next consider the case where the ground state is not fully magnetized.

(a) $\langle S^+T^-\rangle$ and $\langle S^-T^+\rangle$. With the corresponding molecular-field values at 0 °K, we have

$$G_k^{(2)}(E)=\left[\left(\Delta+\frac{\Delta^2}{J(0)(a-b)^2}-\frac{8abJ(k)}{(a-b)^2}M^2\right)\Big/4\pi[R_1(k)-R_4(k)]\right]\left(\frac{1}{E-R_1(k)}-\frac{1}{E-R_4(k)}\right).$$

The correlation is then given by

$$\langle S^-T^+\rangle=\langle S^+T^-\rangle=\frac{1}{2N}\sum_k\frac{(1+1/\beta)[1-\frac{1}{2}(\alpha-\beta)(1-1/\beta)\gamma(k)]}{(1/\Delta)[R_1(k)-R_4(k)]}\times\left(\frac{1}{e^{R_1(k)/k_BT}-1}-\frac{1}{e^{R_4(k)/k_BT}-1}\right),$$

and in the limit of large N, we have

$$\langle S^-T^+\rangle=\langle S^+T^-\rangle=\frac{1}{2(2\pi)^3}\int_{-\pi}^{\pi}dk_x\int_{-\pi}^{\pi}dk_y\int_{-\pi}^{\pi}dk_z\times\frac{(1+1/\beta)[1-\frac{1}{2}(\alpha-\beta)(1-1/\beta)\gamma(k)]}{(1/\Delta)[R_1(k)-R_4(k)]}\times\left(\frac{1}{e^{R_1(k)/k_BT}-1}-\frac{1}{e^{R_4(k)/k_BT}-1}\right). \tag{4.29}$$

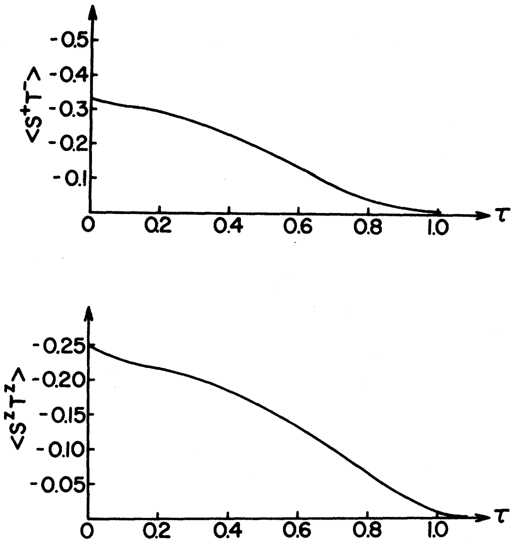

FIG. 15. Temperature dependence of $\langle S^+T^-\rangle$ and $\langle S^zT^z\rangle$ in RPA, using parameters of case (b) in Fig. 2.

The numerical integration has again been computed by using computers and the result is shown in Fig. 15.

(b) $\langle S^zT^z\rangle$. By using the molecular-field values, we have

$$G_k^{(1)}(E)+H_k^{(1)}(E)=\frac{(1+\beta)-\frac{1}{2}(\alpha+\beta)(1-1/\beta^2)\gamma(k)}{(2\pi/\Delta)[R_1(k)-R_4(k)]}\times\left(\frac{1}{E-R_1(k)}-\frac{1}{E-R_4(k)}\right).$$

Hence,

$$\langle S_z\rangle+\langle T_z\rangle=1-\frac{1}{N}\sum_k\frac{(1+\beta)-\frac{1}{2}(\alpha+\beta)(1-1/\beta^2)\gamma(k)}{(1/\Delta)[R_1(k)-R_4(k)]}\times\left(\frac{1}{e^{R_1(k)/k_BT}-1}-\frac{1}{e^{R_4(k)/k_BT}-1}\right). \quad (4.30)$$

Note also that

$$G_k^{(4)}(E)+H_k^{(3)}(E)=-\frac{1}{4\pi}\left(\frac{1}{E-R_1(k)}+\frac{1}{E-R_4(k)}\right)$$

or

$$\tfrac{1}{2}(\langle S_z\rangle+\langle T_z\rangle)-2\langle S_zT_z\rangle=-\frac{1}{2N}\sum_k\left(\frac{1}{e^{R_1(k)/k_BT}-1}+\frac{1}{e^{R_4(k)/k_BT}-1}\right).$$

By combining with Eq. (4.30), we then have

$$\langle S^zT^z\rangle=\frac{1}{4}\left[1-\frac{1}{N}\sum_k\frac{(1+\beta)-\frac{1}{2}(\alpha+\beta)(1-1/\beta^2)\gamma(k)}{(1/\Delta)[R_1(k)-R_4(k)]}\times\left(\frac{1}{e^{R_1(k)/k_BT}-1}-\frac{1}{e^{R_4(k)/k_BT}-1}\right)+\frac{1}{N}\sum_k\left(\frac{1}{e^{R_1(k)/k_BT}-1}+\frac{1}{e^{R_4(k)/k_BT}-1}\right)\right], \quad (4.31)$$

and in the limit of large N, the summation is replaced by integral over k,

$$\langle S^zT^z\rangle=\frac{1}{4}\left[1-\frac{1}{(2\pi)^3}\int_{-\pi}^{\pi}dk_x\int_{-\pi}^{\pi}dk_y\int_{-\pi}^{\pi}dk_z\,\frac{(1+\beta)-\frac{1}{2}(\alpha+\beta)(1-1/\beta^2)\gamma(k)}{(1/\Delta)[R_1(k)-R_4(k)]}\left(\frac{1}{e^{R_1(k)/k_BT}-1}-\frac{1}{e^{R_4(k)/k_BT}-1}\right)+\frac{1}{(2\pi)^3}\int_{-\pi}^{\pi}dk_x\int_{-\pi}^{\pi}dk_y\int_{-\pi}^{\pi}dk_z\left(\frac{1}{e^{R_1(k)/k_BT}-1}+\frac{1}{e^{R_4(k)/k_BT}-1}\right)\right].$$

Numerical integrations have been done by computers and the results are also shown in Fig. 15.

F. Temperature Dependence of Excitation Spectra

We have seen from Eq. (4.19) that even in this simple random-phase approximation, the equation which determines the excitation spectra depends on magnetization as well as on those correlation functions. These quantities are all temperature dependent. They can be determined self-consistently through the Green's function method. We have used the molecular-field values as a first approximation to obtain these quantities according to the formalism. Their values can again be substituted into the equations as a second iteration. This iteration process can be carried out to the accuracy as desired. An example has been done on the excitation spectra for a second iteration. The results are shown in Fig. 16 for the parameters used in Fig. 6 and at a finite temperature of $k_BT=0.3\,\Delta$. One can easily see that all four branches are now depending on wave vector.

G. Antiferromagnetic Case

As most of the rare-earth compounds are either antiferromagnetic or ferrimagnetic at low temperatures, we now extend our previous calculations to the antiferromagnetic case. We shall follow rather closely the notations used by Lines.[37] Early experiments[1] revealed that with the exception of

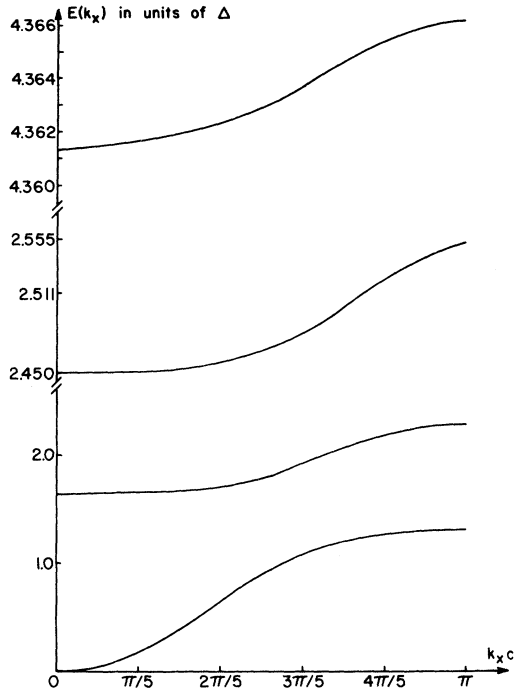

FIG. 16. Excitation spectra for a simple-cubic nearest-neighbor interaction along (100) direction in RPA at finite temperature after first iteration ($k_BT/\Delta = 0.3$).

HoP and all nitrides, all rare-earth compounds become antiferromagnetic at low temperatures. The magnetic structures are identical for all these compounds and correspond to MnO type, i.e., there are ferromagnetic sheets perpendicular to the cubic diagonal and the moment orientation in adjacent sheets is antiparallel. Hence the spin structure can be separated into two translationally invariant ferromagnetic sublattices. In the absence of external magnetic field, our model still assumes the following Hamiltonian with simple exchange of Heisenberg type:

$$\mathcal{H} = \Delta\sum_i \vec{S}_i\cdot\vec{T}_i - \sum_{\langle i,j\rangle} \mathcal{J}(i-j)\,(a\vec{S}_i+b\vec{T}_i)\,(a\vec{S}_j+b\vec{T}_j) \;.$$

Here the summation $\sum_{\langle i,j\rangle}$ runs over all pairs of spins in the lattice and $\mathcal{J}(i,j)$ is the exchange integral between spins at $\mathbf{r}_i$ and $\mathbf{r}_j$.

Due to the presence of two sublattices, we have considered the following eight Green's functions and used the same decoupling schemes as in the ferromagnetic case. Because of translational invariance within one sublattice and time invariance, the Fourier transforms of these Green's functions can also be defined.

Let $G_k^{(1)}(E)$ be the double Fourier transform of the Green's function $\langle\langle S_g^+(t)\,|\,S_l^-(t')\rangle\rangle$, when g and l are in the same sublattice. For abbreviation, we denote the above definition by

$$G_k^{(1)}(E), \qquad \langle\langle S_g^+(t)\,|\,S_l^-(t')\rangle\rangle, \qquad \text{same.}$$

Similarly, we have

$$G_k^{(2)}(E), \qquad \langle\langle S_g^+(t)\,|\,S_l^-(t')\rangle\rangle, \qquad \text{opposite}$$
$$G_k^{(3)}(E), \qquad \langle\langle T_g^+(t)\,|\,S_l^-(t')\rangle\rangle, \qquad \text{same}$$
$$G_k^{(4)}(E), \qquad \langle\langle T_g^+(E)\,|\,S_l^-(t')\rangle\rangle, \qquad \text{opposite}$$
$$G_k^{(5)}(E), \qquad \langle\langle S_g^z(t)T_g^+(t)\,|\,S_l^-(t')\rangle\rangle, \qquad \text{same}$$
$$G_k^{(6)}(E), \qquad \langle\langle S_g^z(t)T_g^+(t)\,|\,S_l^-(t')\rangle\rangle, \qquad \text{opposite}$$
$$G_k^{(7)}(E), \qquad \langle\langle S_g^+(t)T_g^z(t)\,|\,S_l^-(t')\rangle\rangle, \qquad \text{same}$$
$$G_k^{(8)}(E), \qquad \langle\langle S_g^+(t)T_g^z(t)\,|\,S_l^-(t')\rangle\rangle, \qquad \text{opposite .}$$

After doubly Fourier transforming these equations of motion, we have

$$(E+2aA_{(1)})G_k^{(1)}(E)+2a[A_{(2)}G_k^{(2)}(E)+A_{(3)}G_k^{(3)}(E)+A_{(4)}G_k^{(4)}(E)]-\Delta G_k^{(5)}(E)+\Delta G_k^{(7)}(E)=\frac{1}{\pi}\overline{S}\;,$$

$$-2aA_{(2)}G_k^{(1)}(E)+(E-2aA_{(1)})G_k^{(2)}(E)-2a[A_{(4)}G_k^{(3)}(E)+A_{(3)}G_k^{(4)}(E)]-\Delta G_k^{(6)}(E)+\Delta G_k^{(8)}(E)=0\,,$$

$$2\frac{\overline{T}}{\overline{S}}[aA_{(3)}G_k^{(1)}(E)+bA_{(2)}G_k^{(2)}(E)]+(E+2bB_{(3)})G_k^{(3)}(E)+26\frac{\overline{T}}{\overline{S}}A_{(4)}G_k^{(4)}(E)+\Delta G_k^{(5)}(E)-\Delta G_k^{(7)}(E)=0\,,$$

$$-2\frac{\overline{T}}{\overline{S}}[bA_{(2)}G_k^{(1)}(E)+aA_{(3)}G_k^{(2)}(E)+bA_{(4)}G_k^{(3)}(E)]+(E-2bB_{(3)})G_k^{(4)}(E)+\Delta G_k^{(6)}(E)-\Delta G_k^{(8)}(E)=0\,,$$

$$-\left(\frac{\Delta}{4}+\frac{aD^+}{b\overline{S}}A_{(3)}\right)G_k^{(1)}(E)-\frac{aD^+}{b\overline{S}}A_{(4)}G_k^{(2)}(E)-\frac{D^+}{\overline{S}}A_{(4)}G_k^{(4)}(E)+\left(\frac{\Delta}{4}-\frac{D^+}{\overline{S}}A_{(3)}\right)G_k^{(3)}(E)$$
$$+\Big\{E-2b(a\overline{S}+b\overline{T})\Big[\sum_j^{s}\mathcal{J}(j-g)-\sum_j^{d}\mathcal{J}(j-g)\Big]\Big\}G_k^{(5)}(E)=-\frac{1}{2\pi}\langle S_g^- T_g^+\rangle,$$

$$-\frac{aD^-}{b\overline{S}}A_{(4)}G_k^{(1)}(E)-\left(\frac{\Delta}{4}+\frac{aD^-}{b\overline{S}}A_{(3)}\right)G_k^{(2)}(E)-\frac{D^-}{\overline{S}}A_{(4)}G_k^{(3)}(E)+\left(\frac{\Delta}{4}-\frac{\overline{D}}{\overline{S}}A_{(3)}\right)G_k^{(4)}(E)$$

$$+\{E-2b(a\bar{S}+b\bar{T})[\sum_j^d \mathcal{J}(j-g)-\sum_j^S \mathcal{J}(j-g)]\}G_k^{(6)}(E)=0\,,$$

$$\left(\frac{\Delta}{4}-\frac{aE^+}{b\bar{S}}A_{(3)}\right)G_k^{(1)}(E)-\frac{aE^+}{b\bar{S}}A_{(4)}G_k^{(2)}(E)-\left(\frac{\Delta}{4}+\frac{E^+}{\bar{S}}A_{(3)}\right)G_k^{(3)}(E)-\frac{E^+}{\bar{S}}A_{(4)}G_k^{(4)}(E)$$

$$+\{E-2a(a\bar{S}+b\bar{T})[\sum_j^d \mathcal{J}(j-g)-\sum_j^S \mathcal{J}(j-g)]\}G_k^{(7)}(E)=\frac{1}{\pi}\langle S_g^z T_g^z\rangle\,,$$

$$-\frac{aE^-}{b\bar{S}}A_{(4)}G_k^{(1)}(E)+\left(\frac{\Delta}{4}-\frac{aE^-}{b\bar{S}}A_{(3)}\right)G_k^{(2)}(E)-\frac{\bar{E}}{\bar{S}}A_{(4)}G_k^{(3)}(E)-\left(\frac{\Delta}{4}+\frac{\bar{E}}{\bar{S}}A_{(3)}\right)G_k^{(4)}(E)$$

$$+\{E-2a(a\bar{S}+b\bar{T})[\sum_j^d \mathcal{J}(j-g)-\sum_j^S \mathcal{J}(j-g)]\}G_k^{(8)}(E)=0\,,\qquad(4.32)$$

where

$$A_{(1)}=a\bar{S}\,[\sum_j^s \mathcal{J}(j-g)(e^{ik(j-g)}-1)+\sum_j^d \mathcal{J}(j-g)]+b\bar{T}\,(\sum_j^d-\sum_j^s)\mathcal{J}(j-g)\,,$$

$$A_{(2)}=a\bar{S}\sum_j^d \mathcal{J}(j-g)\,e^{ik(j-g)}\,,\qquad A_{(3)}=b\bar{S}\sum_j^s \mathcal{J}(j-g)\,e^{ik(j-g)}\,,\qquad A_{(4)}=b\bar{S}\sum_j^d \mathcal{J}(j-g)\,e^{ik(j-g)}\,,$$

$$B_{(3)}=b\bar{T}[\sum_j^s \mathcal{J}(j-g)(e^{ik(j-g)}-1)+\sum_j^d \mathcal{J}(j-g)]+a\bar{S}(\sum_j^d-\sum_j^s)\mathcal{J}(j-g)\,,\qquad(4.33)$$

$$D^+=(a\langle S^-T^+\rangle-2b\langle S^zT^z\rangle)_u\,,\qquad D^-=(a\langle S^-T^+\rangle-2b\langle S^zT^z\rangle)_D\,,$$

$$E^+=(b\langle S^+T^-\rangle-2a\langle S^zT^z\rangle]_u,\qquad E^-=(b\langle S^+T^-\rangle-2a\langle S^zT^z\rangle)_D\,.$$

The summations $\sum^s$ and $\sum^d$ sum over lattice points in the same and different sublattices, respectively. Note also that we have assumed average values of $\bar{S}$ and $\bar{T}$ in the "up" sublattice and $-\bar{S}$ and $-\bar{T}$ in the "down" sublattice.

We now restrict our discussions to a fcc crystal and the exchange interactions to nearest and next nearest neighbors J_1 and J_2, respectively. We then have

$$\sum_j^d \mathcal{J}(j-g)=6(J_1+J_2)\,,\qquad \sum_j^s \mathcal{J}(j-g)=6J_1\,,$$

$$\begin{aligned}\lambda&=\sum_j^d \mathcal{J}(j-g)\,e^{ik(j-g)}\\&=2J_1[\cos\tfrac{1}{2}f(k_x+k_y)\\&\quad+\cos\tfrac{1}{2}f(k_y+k_z)+\cos\tfrac{1}{2}f(k_x+k_z)]\\&\quad+2J_2[\cos k_xf+\cos k_yf+\cos k_zf]\,,\end{aligned}\qquad(4.34)$$

$$\begin{aligned}\mu&=\sum_j^s \mathcal{J}(j-g)\,e^{ik(j-g)}\\&=2J_1[\cos\tfrac{1}{2}f(k_x+k_y)+\cos\tfrac{1}{2}f(k_y+k_z)\\&\quad+\cos\tfrac{1}{2}f(k_x+k_z)]\,,\end{aligned}$$

where f is the distance between next-nearest neighbors. The A's and B's in Eq. (4.33) are then simplified as

$$A_{(1)}=a\bar{S}\mu+6J_2(a\bar{S}+b\bar{T})\,,$$

$$A_{(2)}=a\bar{S}\lambda,\quad A_{(3)}=b\bar{S}\mu,\quad A_{(4)}=b\bar{S}\lambda,$$

$$B_{(3)}=b\bar{T}\mu+6J_2(a\bar{S}+b\bar{T}).$$

Again we see that all these Green's functions are connected with various thermodynamic correlation functions in this simple random-phase approximation. As a first approximation, we use the molecular-field values for these correlations to determine the excitation spectra. In the case where spins in each sublattice are fully magnetized at zero temperature, we have the following molecular-field values:

$$\bar{S}=\bar{T}=\tfrac{1}{2},\quad\langle S^zT^z\rangle=\tfrac{1}{4},\quad\langle S^+T^-\rangle=\langle S^-T^+\rangle=0\,,$$

so that

$$\begin{aligned}&A_{(1)}=\tfrac{1}{2}a\mu+3(a+b)J_2\,,\\&A_{(2)}=\tfrac{1}{2}a\mu,\qquad A_{(3)}=\tfrac{1}{2}b\mu,\qquad A_{(4)}=\tfrac{1}{2}b\lambda,\\&B_{(3)}=\tfrac{1}{2}b\mu+3(a+b)J_2,\\&D^+=D^-=-\tfrac{1}{2}b,\qquad E^+=E^-=-\tfrac{1}{2}a.\end{aligned}\qquad(4.35)$$

Within this approximation, the above set of eight equations becomes

$$[E+a^2\mu+6a(a+b)J_2]G_k^{(1)}(E)+a^2\lambda G_k^{(2)}(E)+ab\mu G_k^{(3)}(E)+ab\lambda G_k^{(4)}(E)-\Delta G_k^{(5)}(E)+\Delta G_k^{(7)}(E)=1/2\pi,$$

$$-a^2\lambda G_k^{(1)}(E)+[E-a^2\mu-6a(a+b)J_2]G_k^{(2)}(E)-ab\lambda G_k^{(3)}(E)-ab\mu G_k^{(4)}(E)-\Delta G_k^{(6)}(E)+\Delta G_k^{(8)}(E)=0,$$

$$ab\mu G_k^{(1)}(E)+ab\lambda G_k^{(2)}(E)+[E+b^2\mu+6b(a+b)J_2]G_k^{(3)}(E)+b^2\lambda G_k^{(4)}(E)+\Delta G_k^{(5)}(E)-\Delta G_k^{(7)}(E)=0,$$

$$-ab\lambda G_k^{(1)}(E)-ab\mu G_k^{(2)}(E)-b^2\lambda G_k^{(3)}(E)+[E-b^2\mu-6b(a+b)J_2]G_k^{(4)}(E)+\Delta G_k^{(6)}(E)-\Delta G_k^{(8)}(E)=0,$$

$$-(\tfrac{1}{4}\Delta-\tfrac{1}{2}ab\mu)G_k^{(1)}(E)+\tfrac{1}{2}ab\lambda G_k^{(2)}(E)+(\tfrac{1}{4}\Delta+\tfrac{1}{2}b^2\lambda)G_k^{(3)}(E)+\tfrac{1}{2}b^2\lambda G_k^{(4)}(E)+[E+6b(a+b)J_2]G_k^{(5)}(E)=0,$$

$$\tfrac{1}{2}ab\lambda G_k^{(1)}(E)-(\tfrac{1}{4}\Delta-\tfrac{1}{2}ab\mu)G_k^{(2)}(E)+\tfrac{1}{2}b^2\lambda G_k^{(3)}(E)+(\tfrac{1}{4}\Delta+\tfrac{1}{2}b^2\mu)G_k^{(4)}(E)+[E-6b(a+b)J_2]G_k^{(6)}(E)=0,$$

$$(\tfrac{1}{4}\Delta+\tfrac{1}{2}a^2\mu)G_k^{(1)}(E)+\tfrac{1}{2}a^2\lambda G_k^{(2)}(E)-(\tfrac{1}{4}\Delta-\tfrac{1}{2}ab\mu)G_k^{(3)}(E)+\tfrac{1}{2}ab\lambda G_k^{(4)}(E)+[E+6a(a+b)J_2]G_k^{(7)}(E)=1/4\pi,$$

$$\tfrac{1}{2}a^2\lambda G_k^{(1)}(E)+(\tfrac{1}{4}\Delta+\tfrac{1}{2}a^2\mu)G_k^{(2)}(E)+\tfrac{1}{2}ab\lambda G_k^{(3)}(E)-(\tfrac{1}{4}\Delta-\tfrac{1}{2}ab\mu)G_k^{(4)}(E)+[E-6a(a+b)J_2]G_k^{(8)}(E)=0.$$

The excitation spectra at 0 °K are then determined by the vanishing of the determinant of the coefficients of the above eight linear equations. Once the excitation spectra are found, the other thermodynamic correlations can then be determined. We shall not go further than this step, but turn our attention to the case where the molecular-field ground state is not fully magnetized. This is indeed the case for TbSb experimentally.[1] It can also be seen from our model. If we assume that the ordered magnetic moment of this material comes mainly from the crystal field singlet and triplet state (the justification of this assumption will be discussed in Sec. V) we have the values of a and b given by Eq. (2.6). The values of J_1 and J_2 are taken from the experimental data of Busch[8] to be 0.1 and − 0.34 °K, respectively. The singlet-triplet crystal splitting Δ is taken from the work of Cooper and Vogt[24] to be 11.9 °K. We immediately find $J(0)\,(a-b)^2/\Delta = 6\times 0.34\times 56/11.9 > 1$, for which, according to Eq. (3.9), the magnetization is not saturated. To take a step further, we would like to predict the excitation spectra of TbSb at 0 °K. For this purpose, we list the molecular-field values for these correlation functions needed in the random-phase calculation:

$$\bar{S}=M/(a-b)=-\bar{T},\quad \langle S^zT^z\rangle=-\tfrac{1}{4},$$

$$\langle S^+T^-\rangle=\langle S^-T^+\rangle=-\Delta/12J_2(a-b)^2,$$

$$M=[36J_2^2(a-b)^4-\Delta^2]^{1/2}/12(a-b)J_2.$$

The quantities which are involved in the coefficients of the set of Green's functions now assume the following values:

$$\begin{aligned}
A_{(1)}&=[a/(a-b)]M\mu+6J_2M,\\
A_{(2)}&=[a/(a-b)]M\lambda,\\
A_{(3)}&=[b/(a-b)]M\mu,\\
A_{(4)}&=[b/(a-b)]M\lambda,\\
B_{(3)}&=-[b/(a-b)]M\mu+6J_2M,\\
D^+&=D^-=-a\Delta/12(a-b)J_2+\tfrac{1}{2}b,\\
E^+&=E^-=-b\Delta/12(a-b)J_2+\tfrac{1}{2}a.
\end{aligned}\qquad(4.36)$$

Hence the above set of eight Green's functions can be simplified:

$$(E+2aA_{(1)})G_k^{(1)}(E)+2aA_{(2)}G_k^{(2)}(E)+2aA_{(3)}G_k^{(3)}(E)+2aA_{(4)}G_k^{(4)}(E)-\Delta G_k^{(5)}(E)+\Delta G_k^{(7)}(E)=(1/\pi)\bar{S},$$

$$-2aA_{(2)}G_k^{(1)}(E)+(E-2aA_{(1)})G_k^{(2)}(E)-2aA_{(4)}G_k^{(3)}(E)-2aA_{(3)}G_k^{(4)}(E)-\Delta G_k^{(6)}(E)+\Delta G_k^{(8)}(E)=0,$$

$$-2aA_{(3)}G_k^{(1)}(E)-2bA_{(2)}G_k^{(2)}(E)+(E+2bB_{(3)})G_k^{(3)}(E)-2bA_{(4)}G_k^{(4)}(E)+\Delta G_k^{(5)}(E)-\Delta G_k^{(7)}(E)=0,$$

$$2bA_{(2)}G_k^{(1)}(E)+2aA_{(3)}G_k^{(2)}(E)+2bA_{(4)}G_k^{(3)}(E)+(E-2bB_{(3)})G_k^{(4)}(E)+\Delta G_k^{(6)}(E)-\Delta G_k^{(8)}(E)=0,$$

$$-(\tfrac{1}{4}\Delta+aD^+\mu)G_k^{(1)}(E)-aD^+\lambda G_k^{(2)}(E)+(\tfrac{1}{4}\Delta-bD^+\mu)G_k^{(3)}(E)-bD^+\lambda G_k^{(4)}(E)+(E+12bJ_2M)G_k^{(5)}(E)=-(1/2\pi)\langle S^-T^+\rangle,$$

$$-aD^+\lambda G_k^{(1)}(E)-(\tfrac{1}{4}\Delta+aD^+\mu)G_k^{(2)}(E)-bD^+\lambda G_k^{(3)}(E)+(\tfrac{1}{4}\Delta-bD^+\mu)G_k^{(4)}(E)+(E-12bJ_2M)G_k^{(6)}(E)=0,$$

$$(\tfrac{1}{4}\Delta - aE^+\mu)\, G_k^{(1)}(E) - aE^+\lambda\, G_k^{(2)}(E) - (\tfrac{1}{4}\Delta + bE^+\mu)\, G_k^{(3)}(E) - bE^+\lambda\, G_k^{(4)}(E) + (E + 12aJ_2M)\, G_k^{(7)}(E) = (1/\pi)\langle S^zT^z\rangle\,,$$

$$-aE^+\lambda\, G_k^{(1)}(E) + (\tfrac{1}{4}\Delta - aE^+\mu)\, G_k^{(2)}(E) - bE^+\lambda\, G_k^{(3)}(E) - (\tfrac{1}{4}\Delta + bE^+\mu)\, G_k^{(4)}(E) + (E - 12aJ_2M)\, G_k^{(8)}(E) = 0\,.$$

The excitation spectra are then determined by the vanishing of the determinant of the coefficients of this set of equations:

$$\begin{vmatrix} E+2aA_{(1)} & 2aA_{(2)} & 2aA_{(3)} & 2aA_{(4)} & -\Delta & 0 & \Delta & 0 \\ -2aA_{(2)} & E-2aA_{(1)} & -2aA_{(4)} & -2aA_{(3)} & 0 & -\Delta & 0 & \Delta \\ -2aA_{(3)} & -2bA_{(2)} & E+2bB_{(3)} & -2bA_{(4)} & \Delta & 0 & -\Delta & 0 \\ 2bA_{(2)} & 2aA_{(3)} & 2bA_{(4)} & E-2bB_{(3)} & 0 & \Delta & 0 & -\Delta \\ -(\tfrac{1}{4}\Delta + aD^+\mu) & -aD^+\lambda & \tfrac{1}{4}\Delta - bD^+\mu & -bD^+\lambda & E+12bMJ_2 & 0 & 0 & 0 \\ -aD^+\lambda & -(\tfrac{1}{4}\Delta + aD^+\mu) & -bD^+\lambda & \tfrac{1}{4}\Delta - bD^+\mu & 0 & E-12bMJ_2 & 0 & 0 \\ \tfrac{1}{4}\Delta - aE^+\mu & -aE^+\lambda & -(\tfrac{1}{4}\Delta + bE^+\mu) & -bE^+\lambda & 0 & 0 & E+12aMJ_2 & 0 \\ -\lambda aE^+ & \tfrac{1}{4}\Delta - aE^+\mu & -bE^+\lambda & -(\tfrac{1}{4}\Delta + bE^+\mu) & 0 & 0 & 0 & E-12aMJ_2 \end{vmatrix} = 0\,.$$

One easily finds that the above determinant is invariant under the change of $E \leftrightarrow -E$, so that it can be expanded into the following form:

$$E^8 + C(1)\,E^6 + C(2)\,E^4 + C(3)\,E^2 + C(4) = 0\,, \qquad (4.37)$$

which certainly means that we have four branches of excitations, and each is doubly degenerated. Substituting the above-mentioned numerical values for a, b, Δ, J_1, and J_2, we have

$$\begin{aligned} C(1) &= 0.3911\,(\lambda^2 - \mu^2) + 27.7557\,\mu - 94.7877\,, \\ C(2) &= -185.8674(\lambda^2 - \mu^2) \\ &\qquad - 1790.9083\,\mu + 3247.3592\,, \\ C(3) &= 6811.5844(\lambda^2 - \mu^2) \\ &\qquad + 37\,134.5941\,\mu - 47\,600.0155\,, \\ C(4) &= -60\,215.4035(\lambda^2 - \mu^2) \\ &\qquad - 245\,678.8463\,\mu + 250\,592.4232\,, \end{aligned} \qquad (4.38)$$

where λ and μ are defined in (4.34). To look at the dispersion relations along a particular direction, say the x axis, λ and μ now assume the values

$$\lambda = 2J_1(1 + 2\cos\tfrac{1}{2}k_xf) + 2J_2(2 + \cos k_xf)\,,$$

$$\mu = 2J_1(1 + 2\cos\tfrac{1}{2}k_xf)\,.$$

The quartic equation (4.37) has been solved by computers as a function of k_xf and plotted in Fig. 17. To determine what transitions these excitations correspond to, we look at the values of each excitation in the long-wavelength limit, i.e., $k = 0$, which would be the molecular-field values. In units of °K, each of the four levels now assumes the following values:

$$\epsilon_1 = -51.1699, \quad \epsilon_2 = 63.0699,$$

$$\epsilon_3 = 4.3086, \quad \epsilon_2 = 19.4914,$$

so that

$$\epsilon_2 - \epsilon_3 = 58.7613 = E_1, \qquad \epsilon_2 - \epsilon_4 = 43.5785 = E_2\,,$$

$$\epsilon_4 - \epsilon_1 = 70.6613 = E_3\,.$$

The corresponding transitions have been identified

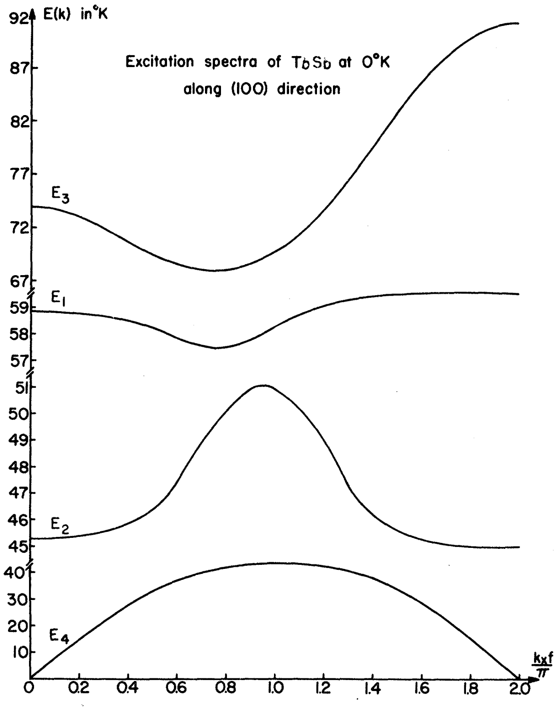

FIG. 17. Excitation spectra predicted for TbSb at 0 °K along (100) direction in RPA.

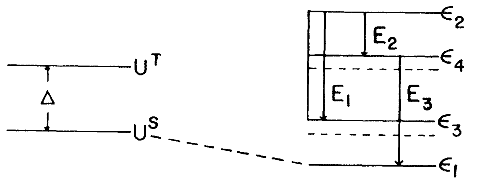

FIG. 18. Crystal field energy levels for TbSb, which show the corresponding transitions in molecular-field picture.

and labeled in Fig. 18. One recognizes that the above numerical values of E_1, E_2, and E_3 do not coincide exactly with the values marked along the $k_xf=0$ axis in Fig. 17. This can be attributed to the fact that we have taken the correlations between opposite sublattices into consideration. But one can easily recognize that the E_4 branch in Fig. 17 is of the antiferromagnetic magnons excitation since it shows a linear dependence of wave vector at the long-wavelength limit.

V. DISCUSSIONS AND CONCLUSIONS

We have studied the magnetic properties of systems with crystal-field-only singlet ground state and triplet excited state in the pseudospin formalism. The crystal field level scheme and the exchange interactions are explained by using proper combinations of two fictitious spin-$\frac{1}{2}$ operators instead of a single spin-$\frac{3}{2}$ operator. Calculations have been done both in the MFA and the random-phase approximation (RPA) of the double-time Green's-function method. Owing to the complexity of the latter approach, we have substituted the molecular-field results at 0 °K to the random-phase approximation as a first iteration; the finite-temperature behaviors of those thermodynamic quantities are hence deduced from the formalism. Comparisons on the results of these two approaches have also been made in Sec. IV. We see that the molecular-field effects reflect in most of the RPA results. An example is to look at the criteria for no magnetic long-range ordering at zero temperature. By requiring that the excitation spectra be real at $k=0$, Sec. IV C tells us no more than that obtained from the MFA.

The molecular-field ground state is not the true ground state of the system with the Hamiltonian (2.8) as can easily be seen from the fact that $[\mathcal{H},\ aS_z+bT_z]\neq 0$. Hence the nonzero population of the excited molecular-field state at zero temperature needs to be estimated. We have done this numerically and find that the deviations of $\langle S_z\rangle$ and $\langle T_z\rangle$ from their assumed values of fully magnetized values (4.20) are of a few percent and of the not fully magnetized values (4.23) are of orders of 15%. The calculations are again estimated for a simple-cubic crystal with nearest-neighbor interactions. One can hence say that the molecular-field results are good approximations for the RPA to start within the former case, and for the latter case we need more iterations. The fact that one of the exctiation spectrum (see Fig. 8) is always less than zero, which implies that this excitation is not stable, has again some connection with this nonzero popularity of the excited state at zero temperature.

In Sec. IV G, we have applied our present model to the case of TbSb. The excitation spectra at zero temperature have hence been predicted. But how good the experimental data of this compound is compared with our model remains unanswered. By using the experimental value of the Néel temperature of TbSb to be 15.1 °K,[24] we find that our Eq. (3.17), which determines the transition temperature in the molecular-field picture, is satisfied to within a 10% difference on both sides. The magnetic moment predicted by our model in the molecular-field approximation, Eq. (3.8), is $5.7\mu_B$. This comparison is rather poor. The reason behind it is the following. We have considered only the singlet ground state and the first triplet excited state contributing to the exchange mechanism at low temperatures. Contributions from other higher excited states to the magnetic moment at zero temperature certainly need to be included. One can estimate this contribution by putting an effective magnetic field in our Hamiltonian. This work is still under detailed investigation. For this application, we conclude by saying that at low temperatures, it is necessary to consider the contributions from other higher excited states than the first one to the exchange mechanism.

As far as the decoupling scheme is concerned, we have used the simplest one, the RPA; hence correlation effects of excitations on different sites are not included. The RPA used here is certainly not a satisfactory one. Improved decoupling schemes such as used by Callen[38] should be tried. This is particularly needed in the case when we have a nonsaturated molecular-field ground state.

Another point to be mentioned is that we have assumed that there is no crystal field or symmetry change which would affect the crystal field structure as exchange interactions are increased. For a more involved situation, a change of symmetry due to crystal distortion will certainly introduce a further complication.

It is certainly desirable to extend our present calculations to the case of ferrimagnetic materials since many rare-earth compounds belong to this category. For the time being, we have only the experimental data for TbSb on the crystal-field-splitting quantity Δ in Fig. 1. Determinations on these splittings beyond the first excited state as well as on other compounds are therefore encouraged.

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PHYSICAL REVIEW B VOLUME 6, NUMBER 7 1 OCTOBER 1972

Induced-Moment Systems: Paramagnetic Region of La_3Tl-Pr_3Tl

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Superconducting and magnetic properties in the La_3Tl-Pr_3Tl system are discussed. Superconductivity persists up to very high Pr concentrations, Pr^{3+} being in a crystal-field-singlet ground state. The Van Vleck susceptibility per Pr^{3+} ion at $T=0$ increases with increasing Pr concentration, indicating ferromagnetic exchange coupling between the Pr ions. At concentrations higher than 93-at.% Pr the system becomes ferromagnetic. No current theoretical model accounts for the observed magnetic behavior.

I. INTRODUCTION

It is well known that many rare-earth compounds with an even number of 4*f* electrons exhibit a crystal-field-singlet ground state. It has been shown by various authors using different models[1–4] that such materials exhibit Van Vleck paramagnetism if the exchange forces do not exceed a certain strength. On the other hand, if the exchange interaction exceeds a certain limit, we expect a