

## Excitations in Magnetic Systems with a Singlet Ground State. II\*

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The pseudospin formalism developed in a previous work to study the magnetic properties of the singlet-triplet system has been extended to the present case where the crystal-field-only levels are two singlets and one doublet, again in the presence of exchange interactions. The lowest-four crystal-field levels of the Pr<sup>+</sup> in Pr<sub>3</sub>Tl and the hexagonal sites of double hcp Pr are believed to have such a level structure. Using a simplified hybrid molecular-field and random-phase approximation, we obtain the excitation spectrum both in the ferromagnetic and paramagnetic regions. Of particular interest is that the present calculation does not show full soft-mode behavior at critical point, similar to the singlet-triplet case. The present model has been used to look at the experimental work on the excitation modes propagating along the hexagonal sites of double hcp Pr single crystals using Bleaney and Rainford's level schemes. Discussions and suggestions are provided.

### I. MODEL AND MOLECULAR-FIELD APPROXIMATION

In a previous work<sup>1</sup> (referred to as I), we studied the magnetic properties of the singlet-triplet systems in the presence of exchange interactions by using a pseudospin formalism both in the molecular-field (MF) and the random-phase (RP) approximations. Although the singlet-singlet systems have been studied quite extensively both in the ferro- and paramagnetic regions by Wang and Cooper,<sup>2</sup> the necessity of including the other higher excited states seems to be the unavoidable conclusion when real materials are encountered.<sup>1,3,4</sup> Moreover, the modified level scheme proposed recently by Rainford<sup>5</sup> for the hexagonal sites in double hexagonal-close-packed (dhcp) Pr single crystals reverses the order of the first (another singlet) and the second (a doublet) excited crystal-field levels proposed by Bleaney<sup>6</sup> to account for the correct anisotropy of the susceptibility measurement.<sup>7</sup> We shall therefore work out a scheme which can encompass all these four levels.

Taking account of the nonideal  $c/a$  ratio, the crystal-field potential for the hexagonal site in dhcp Pr on a point-charge model can be written<sup>8</sup>

$$V = b_2 O_2^0 + \frac{1}{80} b_4 O_4^0 + \frac{1}{1280} b_6 (O_6^0 + \frac{77}{8} O_6^8), \quad (1)$$

where the  $b$ 's are the crystal-field parameters and the  $O$ 's are the equivalent operators. The eigenvalues and eigenfunctions of  $V$  in the manifold of  $J=4$  are then given by

$$\begin{aligned} E_1' &= -20b_2 + 18b_4 - 20b_6, & |\psi_1\rangle &= |0\rangle, \\ E_2' &= -17b_2 + 9b_4 + b_6, & |\psi_2^\pm\rangle &= |\pm 1\rangle, \\ E_3' &= 7b_2 - 21b_4 + \frac{9}{4}b_6, & |\psi_3\rangle &= (1/\sqrt{2})(|3\rangle + |-3\rangle), \\ E_4' &= 7b_2 - 21b_4 - \frac{143}{4}b_6, & |\psi_4\rangle &= (1/\sqrt{2})(|3\rangle - |-3\rangle), \\ E_{5,6}' &= \frac{1}{2}\{e + f \pm [(e - f)^2 + 4d^2]^{1/2}\}, & |\psi_{5,6}^\pm\rangle &= C_{5,6} |\pm 4\rangle + C_{5,6}' |\mp 2\rangle, \end{aligned} \quad (2)$$

where

$$\begin{aligned} C_{5,6}' &= \frac{E_{5,6}' - f}{[(E_{5,6}' - f)^2 + d^2]^{1/2}}, & C_{5,6} &= \frac{d}{[(E_{5,6}' - f)^2 + d^2]^{1/2}}, \\ e &= 28b_2 + 14b_4 + 4b_6, \\ f &= -8b_2 - 11b_4 + 22b_6, \\ d &= \frac{1}{2} \sqrt{7} b_6. \end{aligned}$$

$|\psi_4\rangle, |\psi_3\rangle, |\psi_6^\pm\rangle$  and  $|\psi_1\rangle, |\psi_2^\pm\rangle, |\psi_4\rangle$  are the lowest four levels according to Bleaney<sup>6</sup> and Rainford,<sup>5</sup> respectively. Working in the same spirit as in I, the pseudospin Hamiltonian which can account for the aforementioned level schemes in the presence of bilinear exchange interactions can be written

$$\begin{aligned} \mathcal{H} &= \sum_i [\frac{1}{2} \Delta_1 (S_i^+ T_i^- + S_i^- T_i^+) + \Delta_1 S_i^z T_i^z] \\ &\quad - \sum_{i,j} J(i-j) [(a' S_i^+ + b' T_i^+) (a' S_j^- + b' T_j^-) \\ &\quad\quad + (a S_i^z + b T_i^z) (a S_j^z + b T_j^z)], \quad (3) \end{aligned}$$

where  $\Delta_1$  is the crystal-field splitting between the singlets  $|G_1\rangle$  and  $|G_2\rangle$ ,  $\Delta_1' = 2\Delta' - \Delta_1$ , where  $\Delta'$  is the splitting between the doublet  $|D^*\rangle$  and the ground singlet  $|G_1\rangle$ .  $S_i$  and  $T_i$  are spin- $\frac{1}{2}$  operators assigned to the  $i$ th ion.  $J(i-j)$  is the exchange interaction between ions  $i$  and  $j$ .  $a', b', a$ , and  $b$  are determined by the relations

$$\begin{aligned} \langle D^* | J^+ | G_2 \rangle &= -\langle G_2 | J^+ | D^* \rangle = (1/\sqrt{2})(a' + b'), \\ \langle G_1 | J^+ | D^* \rangle &= -\langle D^* | J^+ | G_1 \rangle = (1/\sqrt{2})(a' - b'), \\ \langle D^* | J_z | D^* \rangle &= -\langle D^* | J_z | D^* \rangle = \frac{1}{2}(a + b), \\ \langle G_1 | J_z | G_2 \rangle &= \frac{1}{2}(a - b). \end{aligned} \quad (4)$$

Anisotropic exchange is therefore introduced as a result of the present level scheme.

Molecular-field calculations show that in the presence of exchange fields, the crystal-field levels become

$$\begin{aligned}
E_1 &= \Delta' - (a+b)J(0)M, \\
E_2 &= \Delta' + (a+b)J(0)M, \\
E_3 &= \frac{1}{2} \{ \Delta_1 + [\Delta_1^2 + 4(a-b)^2 J^2(0)M^2]^{1/2} \}, \\
E_4 &= \frac{1}{2} \{ \Delta_1 - [\Delta_1^2 + 4(a-b)^2 J^2(0)M^2]^{1/2} \},
\end{aligned} \tag{5}$$

where  $M = a\langle S_\mu \rangle + b\langle T_\mu \rangle$  and  $J(0) = \sum_i J(i-j)$ . In terms of these parameters, we again find three regions of magnetic ordering near  $T=0$ : (i) The MF ground state is fully saturated, i. e.,  $M = \frac{1}{2}(a+b)$ , if

$$J(0)(a+b)^2 > 4\Delta'$$

and

$$[\Delta_1^2 + J^2(0)(a^2 - b^2)^2]^{1/2} < \Delta_1 - 2\Delta' + J(0)(a+b)^2.$$

(ii) The MF ground state is of induced moment and  $M$  is given by

$$M = \frac{[J^2(0)(a-b)^4 - \Delta_1^2]^{1/2}}{2J(0)(a-b)}$$

if

$$J(0)(a-b)^2 > \Delta_1$$

and

$$\left( J^2(0)(a^2 - b^2)^2 - \frac{\Delta_1^2}{(a-b)^2} \right)^{1/2} < 2\Delta' - \Delta_1 + J(0)(a-b)^2.$$

(iii) The MF ground state is nonmagnetic, i. e.,  $M=0$ , if

$$J(0)(a-b)^2 < \Delta_1 \text{ and } J(0)(a+b)^2 < 4\Delta'.$$

At finite temperatures,  $M$  has to be determined self-consistently,

$$\begin{aligned}
M &= \frac{1}{Z_0} \left( \frac{1}{2}(a+b)(e^{-\beta E_1} - e^{-\beta E_2}) \right. \\
&\quad \left. + \frac{(a-b)^2 J(0)M}{[\Delta_1^2 + 4(a-b)^2 J^2(0)M^2]^{1/2}} (e^{-\beta E_4} - e^{-\beta E_3}) \right),
\end{aligned}$$

where

$$Z_0 = \sum_{m=1}^4 e^{-\beta E_m}, \quad \beta = 1/k_B T,$$

and the  $E$ 's are given by Eq. (5).

Correlations on the same site between the  $S$  and  $T$  spins are then given by

$$\begin{aligned}
\langle S^+ T^- \rangle &= \langle S^- T^+ \rangle = \frac{\Delta_1 (e^{-\beta E_3} - e^{-\beta E_4})}{2Z_0 [\Delta_1^2 + 4(a-b)^2 J^2(0)M^2]^{1/2}}, \\
\langle S^x T^x \rangle &= \frac{e^{-\beta E_1} + e^{-\beta E_2} - e^{-\beta E_3} - e^{-\beta E_4}}{4Z_0}.
\end{aligned}$$

The Curie temperature  $T_C$  is determined by

$$1 + e^{-\beta C \Delta_1} + 2e^{-\beta C \Delta'} = [J(0)/\Delta_1](a-b)^2(1 - e^{-\beta C \Delta_1}) + [J(0)/k_B T_C](a+b)^2 e^{-\beta C \Delta'} \tag{6}$$

and above  $T_C$ ,  $\langle S^+ T^- \rangle$  and  $\langle S^x T^x \rangle$  become

$$\begin{aligned}
\langle S^+ T^- \rangle &= -\frac{1 - e^{-\beta \Delta_1}}{2(1 + e^{-\beta \Delta_1} + 2e^{-\beta \Delta'})}, \\
\langle S^x T^x \rangle &= -\frac{1 + e^{-\beta \Delta_1} - 2e^{-\beta \Delta'}}{4(1 + e^{-\beta \Delta_1} + 2e^{-\beta \Delta'})}.
\end{aligned} \tag{7}$$

Heat magnetization is also to be expected to show up in the present level scheme. The criterion is

$$\frac{A \Delta'}{k_B T'} > 2 + A + \frac{1+B}{C} e^{(\Delta' - \Delta_1)/k_B T'},$$

with  $T'$  determined by

$$A = (1-B)e^{\Delta'/k_B T'} + (1+B)(1-1/C)e^{(\Delta' - \Delta_1)/k_B T'}$$

and

$$A = \frac{J(0)(a+b)^2}{\Delta'}, \quad B = \frac{J(0)(a-b)^2}{\Delta_1}, \quad C = \frac{\Delta'}{\Delta_1}. \tag{8}$$

To show the roles which the present level scheme can play, we present some numerical results in Fig. 1 which are comparable to the previous work.<sup>1</sup>

## II. EXCITATIONS IN THE RANDOM-PHASE APPROXIMATION (RPA)

### A. Transverse Mode

By considering the same Green functions and decoupling scheme as in I and after Fourier transforming them, we have

$$\begin{aligned}
&[E - 2aMJ(0) + 2a'^2 \langle S_\mu \rangle J(k)]G_k^{(1)}(E) + 2a'b' \langle S_\mu \rangle J(k)G_k^{(2)}(E) - \Delta_1 G_k^{(3)}(E) + \Delta_1' G_k^{(4)}(E) = \langle S_\mu \rangle / \pi, \\
&2a'b' \langle T_\mu \rangle J(k)G_k^{(1)}(E) + [E - 2bMJ(0) + 2b'^2 \langle T_\mu \rangle J(k)]G_k^{(2)}(E) + \Delta_1' G_k^{(3)}(E) - \Delta_1 G_k^{(4)}(E) = 0, \\
&- [\frac{1}{4} \Delta_1 + a'J(k)S_{a'b'}]G_k^{(1)}(E) + [\frac{1}{4} \Delta_1' - b'J(k)S_{a'b'}]G_k^{(2)}(E) + [E - 2bMJ(0)]G_k^{(3)}(E) = -\langle S^+ T^- \rangle / 2\pi, \\
&[\frac{1}{4} \Delta_1' - a'J(k)S_{b'a'}]G_k^{(1)}(E) - [\frac{1}{4} \Delta_1 + b'J(k)S_{b'a'}]G_k^{(2)}(E) + [E - 2aMJ(0)]G_k^{(4)}(E) = \langle S^x T^x \rangle / \pi,
\end{aligned}$$

where

$$\begin{aligned}
J(k) &= \sum_g J(g-n) e^{ik(g-n)}, \\
S_{a'b'} &= a' \langle S^+ T^- \rangle - 2b' \langle S^x T^x \rangle, \\
S_{b'a'} &= b' \langle S^+ T^- \rangle - 2a' \langle S^x T^x \rangle,
\end{aligned} \tag{9}$$

and the Fourier transforms (FT) follow:

$$\begin{aligned}
G_k^{(1)}(E) &\equiv \text{FT of } \langle \langle S_\mu^+(t) | S_\mu^-(t') \rangle \rangle, \\
G_k^{(2)}(E) &\equiv \text{FT of } \langle \langle T_\mu^+(t) | S_\mu^-(t') \rangle \rangle, \\
G_k^{(3)}(E) &\equiv \text{FT of } \langle \langle S_\mu^+(t) T_\mu^+(t) | S_\mu^-(t') \rangle \rangle,
\end{aligned}$$

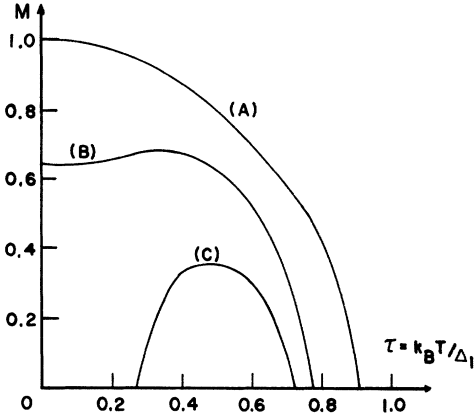


FIG. 1. Temperature dependence of the spontaneous magnetization  $M$  in units of  $\frac{1}{2}(a+b)$  for various crystal-field and exchange parameters defined in Eq. (8). (A)  $A=4.5$ ,  $B=0.9$ ,  $C=0.8$ . (B)  $A=1.82$ ,  $B=1.5$ ,  $C=1.1$ . (C)  $A=3.0$ ,  $B=0.9$ ,  $C=1.2$ .

$$G_k^{(4)}(E) \equiv \text{FT of } \langle\langle S_r^z(t) T_r^z(t) | S_n^z(t') \rangle\rangle.$$

#### B. Longitudinal Mode

Similarly, we have the following set of equations:

$$EH_k^{(1)}(E) - \frac{1}{2} \Delta_1 H_k^{(3)}(E) + \frac{1}{2} \Delta_1 H_k^{(4)}(E) = 0,$$

$$\begin{aligned} &EH_k^{(2)}(E) + \frac{1}{2} \Delta_1 H_k^{(3)}(E) - \frac{1}{2} \Delta_1 H_k^{(4)}(E) = 0, \\ &- [\frac{1}{2} \Delta_1 + 2a(a-b) \langle S^+ T^- \rangle J(k)] H_k^{(1)}(E) \\ &\quad + [\frac{1}{2} \Delta_1 - 2b(a-b) \langle S^+ T^- \rangle J(k)] H_k^{(2)}(E) \\ &\quad + [E - 2(a-b)MJ(0)] H_k^{(3)}(E) = - \langle S^+ T^- \rangle / 2\pi, \\ &[\frac{1}{2} \Delta_1 + 2a(a-b) \langle S^+ T^- \rangle J(k)] H_k^{(1)}(E) \\ &\quad - [\frac{1}{2} \Delta_1 - 2b(a-b) \langle S^+ T^- \rangle J(k)] H_k^{(2)}(E) \\ &\quad + [E + 2(a-b)MJ(0)] H_k^{(4)}(E) = \langle S^+ T^- \rangle / 2\pi, \end{aligned}$$

where

$$\begin{aligned} H_k^{(1)}(E) &\equiv \text{FT of } \langle\langle S_r^z(t) | S_n^z(t') \rangle\rangle, \\ H_k^{(2)}(E) &\equiv \text{FT of } \langle\langle T_r^z(t) | S_n^z(t') \rangle\rangle, \\ H_k^{(3)}(E) &\equiv \text{FT of } \langle\langle S_r^z(t) T_r^z(t) | S_n^z(t') \rangle\rangle, \\ H_k^{(4)}(E) &\equiv \text{FT of } \langle\langle S_r^z(t) T_r^z(t) | S_n^z(t') \rangle\rangle. \end{aligned}$$

The excitation modes are then determined by the vanishing of the determinants of the respective coefficients in the above two sets of equations. We shall classify them according to the MF ground states listed in Sec. I.

*a. MF ground state fully magnetized.* The transverse modes have the following four branches of excitations at  $T=0$ :

$$\begin{aligned} R_1 &= \frac{1}{2} \{ \Delta_1' + (a+b)^2 J(0) - [\Delta_1^2 + J^2(0)(a^2 - b^2)^2]^{1/2} \}, \\ R_2 &= \frac{1}{2} \{ \Delta_1' + (a+b)^2 J(0) + [\Delta_1^2 + J^2(0)(a^2 - b^2)^2]^{1/2} \}, \\ R_3 &= \frac{1}{2} \{ (a+b)^2 J(0) - \Delta_1' - (a'^2 + b'^2) J(k) + \{ [\Delta_1 - 2a'b'J(k)]^2 + [(a^2 - b^2)J(0) - (a'^2 - b'^2)J(k)]^2 \}^{1/2} \}, \\ R_4 &= \frac{1}{2} \{ (a+b)^2 J(0) - \Delta_1' - (a'^2 + b'^2) J(k) - \{ [\Delta_1 - 2a'b'J(k)]^2 + [(a^2 - b^2)J(0) - (a'^2 - b'^2)J(k)]^2 \}^{1/2} \}. \end{aligned} \quad (10)$$

$R_1$  and  $R_2$  are independent of  $k$  and can be identified in the MF picture to be  $E_2 - E_3$  and  $E_2 - E_4$ , respectively.  $R_3$  and  $R_4$  do have a propagating nature. However, owing to the anisotropy introduced in the exchange interaction, they do not vanish at  $k=0$ .

*b. MF ground state of induced-moment nature.* We again find that there are four branches of excitations at  $T=0$ .

$$\begin{aligned} R_1' &= \frac{1}{2} [2(a+b)J(0)M + \Delta_1' - (a-b)^2 J(0)], \\ R_2' &= \frac{1}{2} [2(a+b)J(0)M - \Delta_1' + (a-b)^2 J(0)], \\ R_3' &= M[(a+b)J(0) - (a'^2 - b'^2)J(k)/(a-b)] + \frac{1}{2} R, \\ R_4' &= M[(a+b)J(0) - (a'^2 - b'^2)J(k)/(a-b)] - \frac{1}{2} R, \end{aligned} \quad (11)$$

with

$$M = \frac{[J^2(0)(a-b)^4 - \Delta_1^2]^{1/2}}{2J(0)(a-b)},$$

$$R^2 = \left[ \Delta_1' + J(0)(a-b)^2 - (a' - b')^2 J(k) \left( 1 + \frac{\Delta_1}{J(0)(a-b)^2} \right) \right]$$

$$\begin{aligned} &\times \left[ \Delta_1' + J(0)(a-b)^2 - (a' + b')^2 J(k) \right. \\ &\quad \left. \times \left( 1 - \frac{\Delta_1}{J(0)(a-b)^2} \right) \right]. \end{aligned}$$

$R_1'$  and  $R_2'$  can similarly be identified in the MF picture to be  $E_3 - E_1$  and  $E_2 - E_3$ , respectively. The same situation occurs at  $k=0$  for  $R_3'$  and  $R_4'$ .

*c. MF ground state nonmagnetic.* Excitation energies are then given by  $\Delta' - \Delta_1$  and  $\Delta'^2 - \Delta' \times (a' - b')^2 J(k)$ . They are single-ion crystal-field transitions which propagate through the lattice via the exchange interaction. However, they are transitions from the doublet to the singlets, not between the singlets as in the singlet-singlet case.<sup>2</sup>

For the longitudinal mode, we have

$$E^2 = \Delta_1^2 + 2(a-b)^2 [\Delta_1 \langle S^+ T^- \rangle J(k) + 2M^2 J^2(0)], \quad (12)$$

which reduces to  $\Delta_1^2 + (a^2 - b^2)^2 J^2(0)$ ,  $(a-b)^2 J^2(0) - \Delta_1^2 J(k)/J(0)$ , and  $\Delta_1^2 - \Delta_1(a-b)^2 J(k)$  for saturated, induced-moment, and nonmagnetic MF ground states, respectively. They are quite different

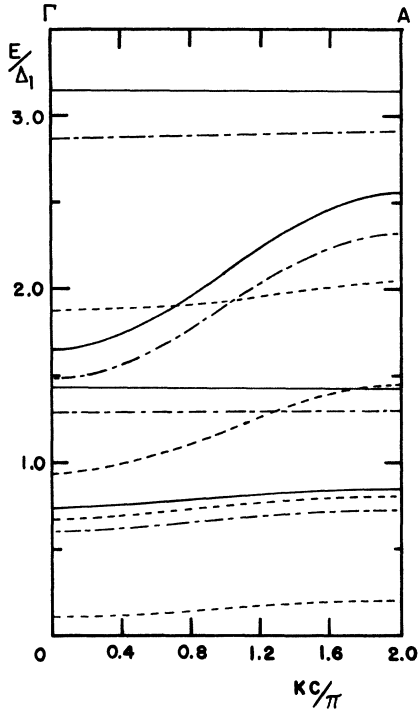


FIG. 2. Temperature dependence of the excitation spectrum for a fully saturated MF ground state, corresponding to case (A) in Fig. 1. Solid line is for  $\tau=0.1$ ; dot-dashed line is for  $\tau=0.37$ ; dashed line is for  $\tau=0.73$ .

from the transverse modes and are all magnetic excitons.

Temperature dependences of the excitation spectra are also of great interest. MF values of those correlation functions can be substituted to find them. Examples for a sample of hexagonal structure and nearest-neighbor interactions with saturated and induced-moment ground states are shown in Figs. 2 and 3 using the parameters from Fig. 1. All four branches are now  $k$  dependent when  $T \neq 0$ . Excitation energies decrease in general as the temperature is raised. In the paramagnetic region where the temperature is above the Curie point, the transverse modes have the energies

$$E_1^2 = \frac{1}{2} \left( \frac{1}{2} (\Delta_1^2 + \Delta_1'^2) + X - Y + \{ [\Delta_1 \Delta_1' + (X - Y)]^2 + 2(\Delta_1' - \Delta_1)(\Delta_1' X + \Delta_1 Y) \}^{1/2} \right), \quad (13)$$

$$E_2^2 = \frac{1}{2} \left( \frac{1}{2} (\Delta_1^2 + \Delta_1'^2) + X - Y - \{ [\Delta_1 \Delta_1' + (X - Y)]^2 + 2(\Delta_1' - \Delta_1)(\Delta_1' X + \Delta_1 Y) \}^{1/2} \right),$$

with

$$X = \Delta_1 J(k) [(a'^2 + b'^2) \langle S^* T^* \rangle - 4a'b' \langle S^* T^* \rangle], \quad (14)$$

$$Y = 2\Delta_1' J(k) [a'b' \langle S^* T^* \rangle - (a'^2 + b'^2) \langle S^* T^* \rangle],$$

and the longitudinal mode becomes  $\Delta_1^2 + 2\Delta_1(a-b)^2$

$\times \langle S^* T^* \rangle J(k)$ . If we again use the temperature-dependent correlations in the MF picture, i. e., Eq. (7), together with Eq. (6) for these energies, we see that all three modes do not become zero for  $k=0$  at the Curie temperature; hence they do not show full soft-mode behavior. A similar picture has already been found in the singlet-triplet case.<sup>9,10</sup> Figures 4 and 5 show the temperature dependence of the paramagnetic excitons for which  $\Delta_1$  is smaller or larger than  $2\Delta_1'$ , respectively.

### III. APPLICATION TO dhcp PRASEODYMIUM SINGLE CRYSTALS

Praseodymium has the double hexagonal-close-packed structure in which the stacking sequence along the  $c$  axis is  $ABAC$ . Atoms in the  $A$  layers have a local environment of approximately cubic symmetry, while in the  $B$  and  $C$  layers, the atoms have a hcp symmetry. The lowest crystal-field levels at the cubic sites ( $A$  layers) are a singlet and a triplet, while for those at the hexagonal sites ( $B$  or  $C$  layers), they are two singlets and one doublet.<sup>5,6</sup> Since at present there is no information available which allows us to characterize the wave functions of the eigenstates for the cubic sites,<sup>5</sup> we shall concentrate on the excitations

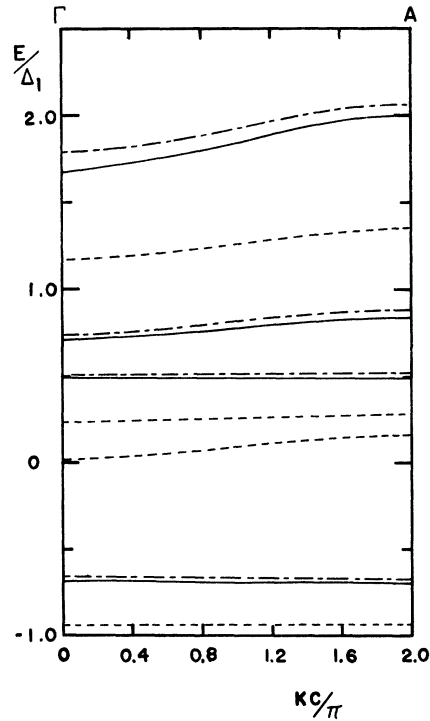


FIG. 3. Temperature dependence of the excitation spectrum for a partially saturated MF ground state, corresponding to case (B) in Fig. 1. Solid line is for  $\tau=0.1$ ; dot-dashed line is for  $\tau=0.37$ ; dashed line is for  $\tau=0.73$ .

which propagate on the hexagonal sites.

The pseudospin Hamiltonian which accounts for

the crystal-field and exchange interactions between the Pr atoms in the *B* and *C* layers is

$$\mathcal{H} = \sum_i \left[ \frac{1}{2} \Delta_1 (S_i^+ T_i^+ + S_i^- T_i^-) + \Delta_1' S_i^z T_i^z \right] + \sum_j \left[ \frac{1}{2} \Delta_1 (S_j^+ T_j^+ + S_j^- T_j^-) + \Delta_1' S_j^z T_j^z \right] \\ - \sum_{i>i'} \mathcal{J}(i-i') \vec{J}_i \cdot \vec{J}_{i'} - \sum_{j>j'} \mathcal{J}(j-j') \vec{J}_j \cdot \vec{J}_{j'} - \sum_{i>j} \mathcal{J}'(i-j) \vec{J}_i \cdot \vec{J}_j,$$

where

$$J_i^\pm = a' S_i^\pm + b' T_i^\pm \quad \text{and} \quad J_i^z = a S_i^z + b T_i^z.$$

The notations have been explained in Sec. I. The indices *i*, *i'* and *j*, *j'* refer to atoms in the *B* and *C* layers, respectively.

To study the transverse modes, we look at the following eight Green's functions and use the same RP decoupling scheme. For abbreviation, we introduce the following notations:

$$G_k^{(1)}(E) \equiv \text{FT of } {}_B \langle \langle S_k^+(t) | S_n^-(t') \rangle \rangle_B,$$

$$G_k^{(2)}(E) \equiv \text{FT of } {}_B \langle \langle T_k^+(t) | S_n^-(t') \rangle \rangle_B,$$

$$G_k^{(3)}(E) \equiv \text{FT of } {}_B \langle \langle S_k^+(t) T_k^+(t) | S_n^-(t') \rangle \rangle_B,$$

$$G_k^{(4)}(E) \equiv \text{FT of } {}_B \langle \langle S_k^+(t) T_k^-(t) | S_n^-(t') \rangle \rangle_B,$$

$$G_k^{(5)}(E) \equiv \text{FT of } {}_C \langle \langle S_k^+(t) | S_n^-(t') \rangle \rangle_B,$$

$$G_k^{(6)}(E) \equiv \text{FT of } {}_C \langle \langle T_k^+(t) | S_n^-(t') \rangle \rangle_B,$$

$$G_k^{(7)}(E) \equiv \text{FT of } {}_C \langle \langle S_k^+(t) T_k^+(t) | S_n^-(t') \rangle \rangle_B,$$

$$G_k^{(8)}(E) \equiv \text{FT of } {}_C \langle \langle S_k^+(t) T_k^-(t) | S_n^-(t') \rangle \rangle_B.$$

The scripts *B* and *C* refer to the respective layers. After Fourier transforming the equations of motion of the above Green functions and substituting the molecular-field values for these correlation functions, we have the following set of equations, in the paramagnetic region:

$$EG_k^{(1)}(E) - \Delta_1 G_k^{(3)}(E) + \Delta_1' G_k^{(4)}(E) = 0, \quad EG_k^{(2)}(E) + \Delta_1' G_k^{(3)}(E) - \Delta_1 G_k^{(4)}(E) = 0, \\ - \left[ \frac{1}{4} \Delta_1 + a' \mathcal{J}(k) S_{a'b'} \right] G_k^{(1)}(E) + \left[ \frac{1}{4} \Delta_1' - b' \mathcal{J}(k) S_{a'b'} \right] G_k^{(2)}(E) + EG_k^{(3)}(E) - [a' G_k^{(5)}(E) + b' G_k^{(6)}(E)] S_{a'b'} \mathcal{J}'(k) = - \langle S^+ T^+ \rangle / 2\pi, \\ \left[ \frac{1}{4} \Delta_1 - a' \mathcal{J}(k) S_{b'a'} \right] G_k^{(1)}(E) - \left[ \frac{1}{4} \Delta_1 + b' \mathcal{J}(k) S_{b'a'} \right] G_k^{(2)}(E) + EG_k^{(4)}(E) - [a' G_k^{(5)}(E) + b' G_k^{(6)}(E)] S_{b'a'} \mathcal{J}'(k) = \langle S^+ T^+ \rangle / \pi, \\ EG_k^{(5)}(E) - \Delta_1 G_k^{(7)}(E) + \Delta_1' G_k^{(8)}(E) = 0, \quad EG_k^{(6)}(E) + \Delta_1' G_k^{(7)}(E) - \Delta_1 G_k^{(8)}(E) = 0, \\ - [a' G_k^{(1)}(E) + b' G_k^{(2)}(E)] S_{a'b'} \mathcal{J}'(k) - \left[ \frac{1}{4} \Delta_1 + a' S_{a'b'} \mathcal{J}(k) \right] G_k^{(5)}(E) + \left[ \frac{1}{4} \Delta_1' - b' S_{a'b'} \mathcal{J}(k) \right] G_k^{(6)}(E) + EG_k^{(7)}(E) = 0, \\ - [a' G_k^{(1)}(E) + b' G_k^{(2)}(E)] S_{b'a'} \mathcal{J}'(k) + \left[ \frac{1}{4} \Delta_1' - a' S_{b'a'} \mathcal{J}(k) \right] G_k^{(5)}(E) - \left[ \frac{1}{4} \Delta_1 + b' S_{b'a'} \mathcal{J}(k) \right] G_k^{(6)}(E) + EG_k^{(8)}(E) = 0,$$

where  $\mathcal{J}(k)$  and  $\mathcal{J}'(k)$  are the Fourier transforms of the exchange interactions  $\mathcal{J}(i-i')$  and  $\mathcal{J}'(i-j)$ , respectively.  $S_{a'b'}$  and  $S_{b'a'}$  are defined in Eq. (9).

Correlations  $\langle S^+ T^+ \rangle$  and  $\langle S^+ T^- \rangle$  are given by Eq. (7).

We then find that there are four branches of excitations, all doubly degenerate:

$$E_1^2 = X_1 + Y_1, \quad E_2^2 = X_1 - Y_1, \\ E_3^2 = X_2 + Y_2, \quad E_4^2 = X_2 - Y_2, \quad (15)$$

where

$$X_1 = \frac{1}{4} (\Delta_1^2 + \Delta_1'^2) + \frac{1}{2} (X - Y) [\mathcal{J}(k) + \mathcal{J}'(k)], \\ X_2 = \frac{1}{4} (\Delta_1^2 + \Delta_1'^2) + \frac{1}{2} (X - Y) [\mathcal{J}(k) - \mathcal{J}'(k)], \\ Y_1^2 = \frac{1}{4} \{ \Delta_1^2 \Delta_1'^2 + 2(X \Delta_1'^2 - Y \Delta_1^2) [\mathcal{J}(k) + \mathcal{J}'(k)] \\ + (X - Y)^2 [\mathcal{J}(k) + \mathcal{J}'(k)]^2 \}, \\ Y_2^2 = \frac{1}{4} \{ \Delta_1^2 \Delta_1'^2 + 2(X \Delta_1'^2 - Y \Delta_1^2) [\mathcal{J}(k) - \mathcal{J}'(k)] \\ + (X - Y)^2 [\mathcal{J}(k) - \mathcal{J}'(k)]^2 \},$$

$$X = \Delta_1 [(a'^2 + b'^2) \langle S^+ T^- \rangle - 4a'b' \langle S^+ T^+ \rangle],$$

$$Y = 2\Delta_1' [a'b' \langle S^+ T^- \rangle - (a'^2 + b'^2) \langle S^+ T^+ \rangle].$$

We note that at  $T=0$ ,  $E_2 = E_4 = \Delta'$  and

$$E_1^2 = \Delta'^2 - \Delta'(a' - b')^2 [\mathcal{J}(k) + \mathcal{J}'(k)],$$

$$E_3^2 = \Delta'^2 - \Delta'(a' - b')^2 [\mathcal{J}(k) - \mathcal{J}'(k)].$$

The latter are exactly the same as obtained by Rainford and Houmann,<sup>11</sup> while for  $a' + b' = 0$ , Eq. (15) reduces to  $E_2 = E_4 = \Delta'$ ,

$$E_1^2 = \Delta'^2 + 2\Delta'(a' - b') S_{a'b'} [\mathcal{J}(k) + \mathcal{J}'(k)]$$

and

$$E_3^2 = \Delta'^2 + 2\Delta'(a' - b') S_{a'b'} [\mathcal{J}(k) - \mathcal{J}'(k)].$$

Hence there are only two *k*-dependent branches since in this case the matrix element of  $\mathcal{J}^*$  between the doublet and the excited singlet is zero.

The above results have been used to fit the ex-

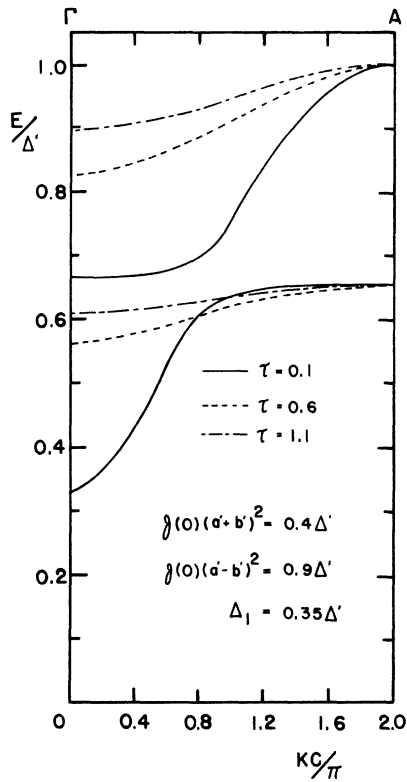


FIG. 4. Temperature dependence of the paramagnetic excitation spectrum for a system where  $\Delta_1 < 2\Delta'$ .

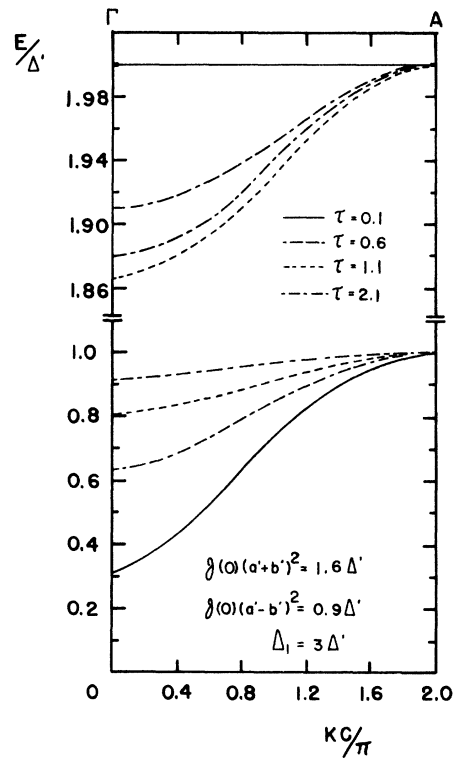


FIG. 5. Temperature dependence of the paramagnetic excitation spectrum for a system where  $\Delta_1 > 2\Delta'$ .

perimental data<sup>11</sup> at points  $\Gamma$ ,  $A$ ,  $\Gamma'$ ,  $K$ , and  $M$  using Rainford's<sup>5</sup> (where  $a' + b' = 0$ ) and Bleaney's<sup>6</sup> level schemes at 4.2 °K. The exchange integrals are found to have the values  $J(\text{nns}) = 1.39$  °K,  $J(\text{nnns}) = -0.76$  °K,  $J(\text{nnnns}) = -0.51$  °K,  $J'(\text{nnd}) = -0.11$  °K, and  $J'(\text{nnnd}) = -0.146$  °K for Rainford's scheme and the corresponding values for the

Bleaney's are  $-0.25$ ,  $1.12$ ,  $1.47$ ,  $-0.154$ , and  $-0.206$  °K. The abbreviations nns and nnd stand for nearest neighbors on the same and different sublattices, respectively, nnn for next nearest neighbors, and so forth. These parameters show several interesting features. They suggest that the exchange in Pr is long ranged and resulted

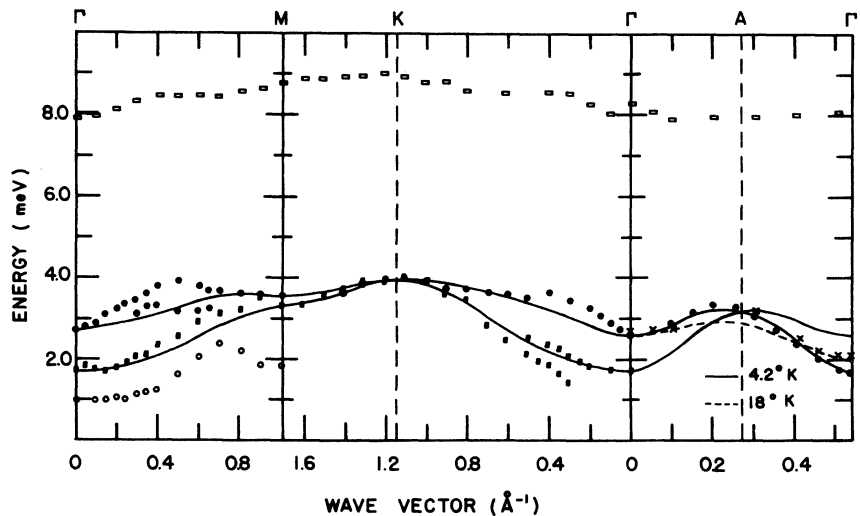


FIG. 6. Dispersion curves (solid and dashed lines) fitted and plotted in various directions using Rainford's level scheme. The points are the experimental results of Rainford and Houmann.

from a large conduction-electron contribution. The sign of  $\mathcal{J}'$  indicates that the hcp sites in Pr have a tendency to order antiferromagnetically along the  $c$  axis. With these values, we plot the whole spectra in various directions at 4.2 °K and one (four) for the Rainford's (Bleaney's) scheme at 18 °K. Results are shown in Figs. 6 and 7.

#### IV. DISCUSSIONS AND CONCLUSIONS

The collective excitations in magnetic systems with one doublet and two singlets crystal-field-only level scheme and their temperature dependence in the ferro- and paramagnetic phases have been studied in a simplified hybrid MF-RP approximation again using pseudospin formalism. Anisotropic exchange is introduced because of its symmetry-broken level structure. To have stable transverse modes, one needs criteria among the exchange and crystal-field parameters even at  $T=0$  in addition to that provided by the MFA [e. g., see Eqs. (10) and (11)]. Nevertheless, the present calculations show that the critical values for the exchange interaction to have the nonmagnetic ground state to be unstable are different for the transverse mode [ $\mathcal{J}(0)(a' - b')^2 = \Delta'$ ] and the longitudinal one [ $\mathcal{J}(0)(a - b)^2 = \Delta_1$ ]. This originates from the present level structure which naturally provides such transitions among them. It would be very interesting to see this experimentally.

The temperature dependence on the excitation modes in ferromagnetic state in general reflects the results from MFA. Hence as shown in Fig. 3, energy gaps between the levels can at first increase as the temperature is raised from zero. When the temperature is further increased, spontaneous magnetization begins to decrease. As a result, excitation energies between the levels will be narrowed as well.

Using a hybrid MF-RP approximation, the present model again shows no soft-mode behavior at the critical temperature. However, the calculation is so simplified that probably one should draw no conclusion about the phase transition from it. In particular, whether RPA is applicable at critical point is still an open question. To have a reliable picture, as mentioned in I, one needs at least to do the RPA self-consistently. For a further study on this problem, it should be helpful to use the high-temperature series-expansion method. These possibilities are at present under detailed investigation.

It is of particular interest to notice that the present model offers two branches of transverse excitations, both are  $k$  dependent even at  $T=0$  when the system is in the paramagnetic phase and  $\Delta_1 < 2\Delta'$ . An example is shown in Fig. 4, where the two branches show quite different dispersions since the matrix elements of  $\mathcal{J}'$  is different between the doublet and the two singlets. However, when  $\Delta_1 > 2\Delta'$  as shown in Fig. 5, there is only one  $k$ -dependent branch at  $T=0$ , while the other one does not show any dispersion at all. As the temperature is raised, it first decreases in energy and shows little dispersion. As the temperature is further increased, it begins to increase and finally at high temperature, to the original crystal-field level difference. One can trace this peculiar behavior back to our pseudospin treatment, Eq. (3), where we see as  $\Delta_1 > 2\Delta'$ , so that  $\Delta'_1 < 0$ , the paramagnetic ground state, where the  $S$  and  $T$  spins on each site are antiparallel to each other, is no longer stable since the ferromagnetic (parallel arrangement of  $S$  and  $T$  spins) state will have an energy which is less than the paramagnetic one.

The present model has been used to look at the experimental data<sup>11</sup> on the modes propagating along

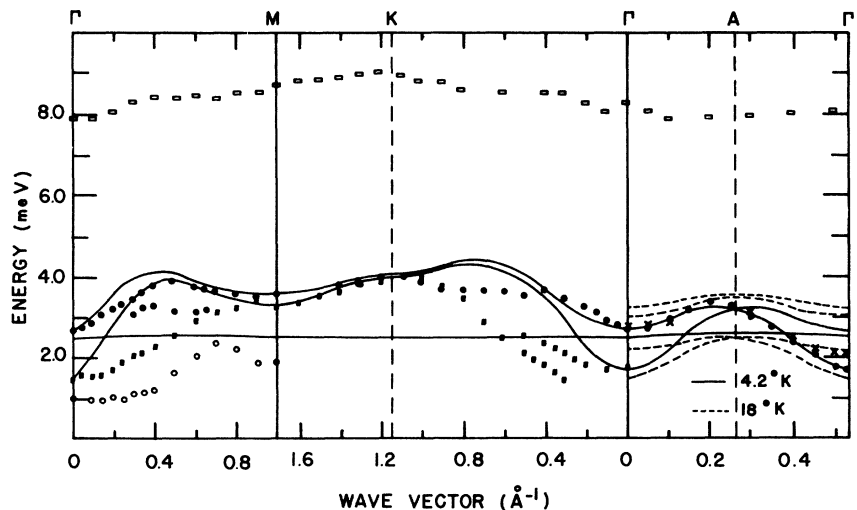


FIG. 7. Dispersion curves (solid and dashed lines) fitted and plotted in various directions using Bleaney's level scheme.

the hexagonal sites of dhcp Pr single crystals, using Rainford's<sup>5</sup> and Bleaney's<sup>6</sup> level schemes. We see that the comparison between our calculations and the data is in general good except at small wave vectors. This lack of agreement is due to the reason that we have neglected the interactions between atoms in the *B* or *C* layer and that in the *A* layer, which we have already shown<sup>10,12</sup> to be rather important and connected with that branch of excitation propagating along the cubic sites. Unfortunately, there is no detailed information available on this branch at the present time. Experimental studies (e. g. , measurements on the dispersion of the exciton mode of this branch in the presence of high magnetic field, temperature dependences of the induced magnetization, and the susceptibilities) are therefore strongly recommended.

It should be pointed out that if we regard the lowest four crystal-field levels to be responsible

for the transitions, Rainford's scheme can only give two branches of transverse mode since the matrix element of  $J^z$  between the doublet and the excited singlet is zero in his scheme. In case where this matrix element is nonzero, as in the Bleaney's scheme, our model gives four branches of excitations, a third possibility other than those proposed elsewhere.<sup>11,5</sup> Yet the use of Bleaney's level scheme to see this possibility is not successful. We see that in Fig. 7 the other two branches are almost indistinguishable from each other and show very little dispersion at 4.2 °K. They are clearly separated from each other at 18 °K. Although susceptibility measurement favors the Rainford's level scheme, there are discrepancies which should not be overlooked.<sup>5</sup> A thorough understanding on the magnetic properties of dhcp Pr is possible only when enough experimental information is in hand.

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