measured near $T_c$. However, the $\kappa$ values do not vary strongly with temperature and, therefore, the above numerical work is approximately correct below $T_c$. Corrections for the temperature dependence of $\kappa$ can be obtained from Maki's calculations.[15] Unfortunately, the relation there[15] between $\kappa$ and $H_{c1}$ applies only for $\kappa \gg 1$. It appears that, in principle at least, experimental results obtained at temperatures far below $T_c$ can be compared with the above calculations by calculating the appropriate $\kappa$ near $T_c$ from Ref. 15.

*Note added in proof.* When applying Maki's results[15] caution should be exercised with regard to his $\kappa_2$ values. Experiments by G. Bon Mardion, B. B. Goodman, and A. Lacaze [J. Phys. Chem. Solids **26**, 1143 (1965)] disagree with the calculated values.[15] For an extension of our work to the critical state of the surface sheath see H. J. Fink and L. J. Barnes [Phys. Rev. Letters **15**, 792 (1965)].

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[15] K. Maki, Physics **1**, 21, 127, 201 (1964).

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# Dynamical Properties of Induced-Moment Systems*

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The low-temperature excitation spectrum for ferro- and antiferromagnets with large crystalline-field splittings is derived using the Bogoliubov transformation. Specific application is made to those systems where the single-ion ground state is a singlet and the magnetization of the coupled ions arises from the Van Vleck temperature-independent susceptibility. $Pr^{3+}$ and $Eu^{3+}$ in cubic and hexagonal environments are used as examples. The specific heat, magnetization, and nuclear-nuclear coupling are computed for both the ordered and paramagnetic regimes. The results in the paramagnetic limit display a characteristic energy gap $\Delta[1\text{-}\alpha(K/\Delta)]^{1/2}$, where $\Delta$ is the crystalline field splitting (or, in $Eu^{3+}$, the spin-orbit splitting) between the ground singlet and first excited state, $K$ is the exchange integral, and $\alpha$ is a constant proportional to the Van Vleck temperature-independent susceptibility. In the magnetically ordered state, the same behavior is found for longitudinal excitations in $Pr^{3+}$ and $Eu^{3+}$ salts with a gap equal to $(\alpha^2K^2\text{-}\Delta^2)^{1/2}$, while transverse excitations are found to exhibit a linear dispersion law without an apparent gap in the limit of complete isotropy. The phase transition between the paramagnetic and ordered regimes is shown to be of second order. However, the entropy of ordering is shown to be reduced from the usual value $NK\ln(2S+1)$.

## I. INTRODUCTION

It has been demonstrated by Trammell[1] and Bleaney[2] that exchange interactions between ions which possess a magnetic singlet ground level could lead to a ferromagnetic state by virtue of the Van Vleck temperature-independent susceptibility. Their results were confined to the molecular-field approximation. In this paper we wish to examine the low-lying excitations of these ordered materials in the Bogoliubov[3] approximation. Our approach will be similar to that of Bozorth and Van Vleck[4] who used this technique to investigate the paramagnetic regime, and of Trammell[5] in his treatment of the rare-earth nitrides. Once the excitation spectrum is known it is a simple matter to compute the thermodynamic properties of these systems. This is done in Secs. II–IV for some representative examples of paramagnetic ions which can exhibit this type of collective behavior under appropriate circumstances. Section V of this paper is a brief description of the properties at the phase transition. The entropy of ordering is derived and shown to be reduced from the "free" spin value $Nk\ln(2S+1)$.

To establish notation we shall first repeat some of Bleaney's results.[2] For an ion whose low-lying energy levels are characterized by $\mathbf{J}=\mathbf{L}+\mathbf{S}$, the isotropic exchange interaction may be written as $V_{\text{ex}}=-2\times\sum_{i>j}K_{ij}\mathbf{J}_i\cdot\mathbf{J}_j$ where $K_{ij}=K_{ij}'(\Lambda-1)^2$, $K'$ being the exchange integral characterizing the interactions between the total spins $\mathbf{S}$ of the ions $i$ and $j$, and $\Lambda$ the

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[1] G. T. Trammell, Phys. Rev. **131**, 932 (1963).

[2] B. Bleaney, Proc. Roy. Soc. (London) **276A**, 19 (1963).

[3] N. N. Bogliubov and S. V. Tiablikov, Izv. Akad. Nauk SSSR Ser. Fiz. **21**, 849 (1957).

[4] R. M. Bozorth and J. H. Van Vleck, Phys. Rev. **118**, 1493 (1960).

[5] G. T. Trammell, J. Appl. Phys. **31**, 362S (1960).

Lande factor defined by $\mathbf{L}+2\mathbf{S}=\Lambda\mathbf{J}$. The exchange interaction when restricted to nearest neighbors can be described in the molecular-field approximation by $\sum_i V_i^{\mathrm{ex}}=\sum_i \Lambda\beta\lambda\mathbf{M}\cdot\mathbf{J}_i$ where the molecular field $\lambda\mathbf{M}=-2Kz\langle\mathbf{J}\rangle/\beta\Lambda$, $z$ being the number of nearest neighbors, $\beta$ the Bohr magneton, and $K$ the near-neighbor exchange integral. Bleaney took as a model a system where the two lowest lying single-ion states $|A\rangle$ and $|B\rangle$ were magnetic singlets, separated by a splitting $\Delta$. The exchange field was assumed to connect the two states by virtue of the Van Vleck "off-diagonal" magnetization. This was described by a constant $c\equiv\langle A|J_i^z|B\rangle$. In terms of this constant the secular equation was solved to yield the magnetic states

$$\begin{aligned}|g\rangle&=\cos\theta|A\rangle+\sin\theta|B\rangle,\\|e\rangle&=\sin\theta|A\rangle-\cos\theta|B\rangle,\end{aligned}\tag{1}$$

where $|g\rangle$ and $|e\rangle$ represent the coupled ground and excited states, respectively, with energies

$$\begin{aligned}&E_g=\tfrac{1}{2}(\Delta-W),\quad E_e=\tfrac{1}{2}(\Delta+W),\\&W=[\Delta^2+(2c\Lambda\beta\lambda M)^2]^{1/2},\end{aligned}\tag{2}$$

and angle $2\theta=\tan^{-1}(-2c\Lambda\beta\lambda M/\Delta)$. The total magnetization is found from

$$M=\{(NW_0/2\lambda)[(p_g-p_e)^2-x^2]\}^{1/2},\tag{3}$$

where $W_0=4c^2Kz$ is the zero-temperature value for $W$; $p_g$ and $p_e$ are the probabilities of occupation of the states (1), and $x\equiv\Delta/W_0$. Bleaney derived the temperature variation of $W$ and the transition temperature to the paramagnetic state from the molecular-field equations

$$(W_0-W)/W_0=2p_e,\quad \tanh(\Delta/2kT_c)=x.\tag{4}$$

Equation (4) shows that the interacting paramagnetic system will spontaneously order at a finite temperature when $W_0=4c^2Kz>\Delta$. The system will remain paramagnetic down to $T=0$ for exchange interactions weaker than the value $\Delta/4c^2z$.

Before considering in detail some specific systems, we shall sketch the way in which the Bogoliubov transformation will be used. In a second-quantized representation $\psi(r_i)=\sum_m\langle m|C_{i,m}$ annihilates an electron at the lattice site $\mathbf{r}_i$, where $\langle m|$ represents the $m$th crystal field level of the $i$th paramagnetic ion. The $C_{i,m}$ are fermion operators. At low temperatures $n_{i,g}=C_{i,g}{}^\dagger C_{i,g}$, the occupation of the ground state, is nearly unity. This enables the commutator of the product operators $a_{i,m}{}^\dagger=C_{i,m}{}^\dagger C_{i,g}$, $a_{i,m}=C_{i,g}{}^\dagger C_{i,m}$, for $m\neq g$,

$$\begin{aligned}&[a_{i,m},a_{j,m}]=0,\\&[a_{i,m},a_{j,n}{}^\dagger]=\delta_{i,j}\delta_{m,n}n_{i,g}-\delta_{i,j}C_{i,m}{}^\dagger C_{j,n},\end{aligned}\tag{5}$$

to be approximated by the Bose result

$$[a_{i,m},a_{j,n}{}^\dagger]=\delta_{i,j}\delta_{m,n}.\tag{6}$$

The neglect of the second term on the right in (5) compared to the first term is clearly a low-temperature approximation and severely limits the validity of the use of Bose statistics at higher temperatures.

The Hamiltonian can be written in a quadratic form using the boson operators $a_{i,m}$ and may be diagonalized by a canonical transformation to normal-mode coordinates. The operator $a_{i,m}{}^\dagger$ can be interpreted as raising the $i$th atom from the ground to the $m$th excited eigenstate. The normal modes correspond to an excitation wave in the same sense that a spin deviation is passed on from atom to atom in the usual Holstein-Primakoff theory of spin waves.[6]

In Sec. II the paramagnetic, ferromagnetic, and antiferromagnetic excitation spectra of $\mathrm{Pr}^{3+}$ ions in a hexagonal crystal field are found, and the associated thermodynamic properties are compured. In Sec. III the ferromagnetic spectrum of $\mathrm{Pr}^{3+}$ in a cubic crystalline field is analyzed. In Sec. IV Bozorth and Van Vleck's treatment of paramagnetic $\mathrm{Eu}^{3+}$ in the presence of an $S_i^zS_j^z$ exchange interaction is extended to both the ferromagnetic and paramagnetic limits for an isotropic exchange interaction $\mathbf{S}_i\cdot\mathbf{S}_j$. The longitudinal excitation spectrum is found to contain an energy gap for all cases considered, while the transverse spectrum for ferromagnetic $\mathrm{Pr}^{3+}$ and $\mathrm{Eu}^{3+}$ exhibits a linear dispersion law. The existence of an energy gap in conjunction with the virtual emission and absorption of the excitation modes gives rise to an indirect nuclear spin-spin coupling similar in form to the Suhl-Nakamura interaction,[7,8] and an associated contribution to the specific heat.

## II. Pr³⁺ IN A HEXAGONAL CRYSTAL FIELD

### A. Paramagnetic Region

In the limit that exchange interactions are not of sufficient strength to induce magnetic ordering between $\mathrm{Pr}^{3+}$ ions in the presence of a hexagonal field, the basis functions are given by the low-lying crystal-field states

$$\begin{aligned}|B\rangle&=(1/\sqrt{2})(|+3\rangle+|-3\rangle),\\|A\rangle&=(1/\sqrt{2})(|+3\rangle-|-3\rangle),\end{aligned}\tag{7}$$

with energies

$$E_B{}^c=\Delta,\quad E_A{}^c=0.$$

The coupling to higher lying states is neglected because (6) is valid only in the low-temperature limit $kT\ll\Delta$. The Hamiltonian is given by

$$H=\sum_i V_i{}^c-2K\sum_{i,\delta}(\mathbf{J}_i\cdot\mathbf{J}_{i+\delta}),\tag{8}$$

where $\delta$ runs over the $z$ nearest neighbors, and $V_i{}^c$ represents the crystalline-field Hamiltonian. The only nonvanishing matrix element of $\mathbf{J}_i$ between $|A\rangle$ and $|B\rangle$ is $J_i{}^z=c(a_i{}^\dagger+a_i)$, where $c=\langle A|J_i{}^z|B\rangle$, and $a_i{}^\dagger=C_{i,B}{}^\dagger C_{i,A}$.

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[6] T. Holstein and H. Primakoff, Phys. Rev. **58**, 1098 (1940).

[7] H. Suhl, J. Phys. Radium **20**, 333 (1959).

[8] T. Nakamura, Progr. Theoret. Phys. (Kyoto) **20**, 542 (1958).

### *1. Excitation Spectrum*

The Hamiltonian (8) is rewritten using the Fourier transform of the Bogoliubov operators (6), with basis functions $\langle m|$ given by (7). Defining $a_i^\dagger=(N)^{-1/2}\times\sum_k \exp(i\mathbf{k}\cdot\mathbf{r}_i)a_k^\dagger$, the Hamiltonian (8) becomes

$$H=\sum_k[W_1 a_k^\dagger a_k-(W_2/2)(a_k^\dagger a_{-k}^\dagger+a_k a_{-k})], \qquad (9)$$

where

$$W_1=\Delta-2c^2Kz\Upsilon_k,\ \ W_2=2c^2Kz\Upsilon_k,\ \ \Upsilon_k=(z)^{-1}\sum_\delta \cos(k\cdot\delta).$$

$H$ is diagonalized by the canonical transformation

$$\alpha_k^\dagger=u_k a_k^\dagger-v_k a_{-k}, \qquad (10)$$

where

$$u_k=\cosh\theta_k,\quad v_k=\sinh\theta_k,\quad \tanh 2\theta_k=W_2/W_1.$$

Substituting (10) into (9), the Hamiltonian can be brought into harmonic-oscillator form

$$E=\sum_k \hbar\omega_k(n_k+\tfrac{1}{2})-\tfrac{1}{2}\sum_k W_1, \qquad (11)$$

with excitation energies

$$\hbar\omega_k=\Delta^{1/2}(\Delta-4c^2Kz\gamma_k)^{1/2}.$$

The lowest lying excitations for a simple cubic lattice of lattice constant $a$ are given by the long-wavelength limit of (11):

$$\hbar\omega_k=\Omega(1+A^2a^2k^2)^{1/2}, \qquad (12)$$

where

$$\Omega=\Delta(1-\eta)^{1/2},\quad A^2=\eta/z(1-\eta),\quad \eta=4c^2Kz/\Delta.$$

The result (12) is formally identical to the case of paramagnetic $\mathrm{Eu}^{3+}$ discussed by Bozorth and Van Vleck.[4]

### *2. Electronic Specific Heat*

The electronic contribution to the low-temperature specific heat is obtained by expressing (11) in the form

$$E=\frac{Na^3}{(2\pi)^3}\sum_{n=1}^{\infty}\int d\mathbf{k}\,\Omega\cosh(u)\exp(-n\beta\Omega\cosh u). \qquad (13)$$

The spectrum (12) is used in (13), and is written as $\hbar\omega_k=\Omega\cosh u$, where $\sinh^2 u=A^2a^2k^2$. We find a result identical with that of Bozorth and Van Vleck[4]:

$$C_v=\frac{Nk}{2\pi^2A^3}(\Omega/kT)\sum_{n=1}^{\infty}\left[\frac{3}{Z}K_1(Z)+\left(1+\frac{12}{Z^2}\right)K_2(Z)\right], \qquad (14)$$

where $Z=n\beta\Omega$, $\beta=1/kT$, and $K_\nu(Z)$ is a Bessel function of the second kind of imaginary argument given by[9]

$$K_\nu(Z)=\frac{\Gamma(\frac{1}{2})(\frac{1}{2}Z)^\nu}{\Gamma(\nu+\frac{1}{2})}\int_0^\infty du\,\sinh^{2\nu}(u)\exp(-Z\cosh u). \qquad (15)$$

For temperatures $kT\ll\Omega$, (14) reduces to the form

$$C_v=\frac{Nk}{(2\pi)^{3/2}A^3}\left(\frac{\Omega}{kT}\right)^{1/2}\exp\left(-\frac{\Omega}{kT}\right). \qquad (16)$$

As pointed out by Bozorth and Van Vleck, the specific heat (16) derived from the excitation spectrum (12) is enhanced over that given by the use of Boltzmann probabilities appropriate to the uncoupled ions.

### *3. Nuclear Coupling*

An indirect nuclear spin-spin coupling, similar in form to the Suhl-Nakamura interaction,[7,8] can in fact exist in the paramagnetic region. This indirect term arises through the virtual emission and absorption of an excitation wave defined by (10). The second-order perturbation energy of the hyperfine interaction $V=A\sum_i(\mathbf{I}_i\cdot\mathbf{J}_i)$ equals

$$E^{(2)}=-\sum_k|\langle 0|V|1_k\rangle|^2/\hbar\omega_k. \qquad (17)$$

The sum goes over all possible excitation wave states, $|0\rangle$ is the ground state, and $|1_k\rangle$ is the state of one excitation wave of wave vector **k**. To evaluate (17) we transform $\mathbf{J}_i$ to the excitation wave representation

$$J_i^z=cN^{-1/2}\sum_k[(u_k\alpha_k^\dagger+v_k\alpha_{-k})\exp(i\mathbf{k}\cdot\mathbf{r}_i)+\text{c.c.}], \qquad (18)$$

where the inverse of (10) has been used. In the long-wavelength limit, (17) reduces to

$$E^{(2)}=-A^2c^2\sum_{i,j}(I_i^zI_j^z)1/N\sum_k(E_a+E_{\text{ex}}a^2k^2)^{-1}\times\exp(i\mathbf{k}\cdot\mathbf{r}_{ij}), \qquad (19)$$

where

$$E_a=\Delta-4c^2Kz,\quad E_{\text{ex}}=4c^2K.$$

If $|\mathbf{r}_{ij}|=|\mathbf{r}_i-\mathbf{r}_j|\gg a$, we may replace the sum over **k** by an integral and extend the integration to infinity. The result of the usual contour integration gives

$$E^{(2)}=\frac{-A^2c^2}{4\pi E_{\text{ex}}}\sum_{i,j}(I_i^zI_j^z)R(r_{ij}), \qquad (20)$$

where

$$R(r_{ij})=(a/r_{ij})\exp[-(E_a/E_{\text{ex}})^{1/2}r_{ij}/a].$$

The coupling between nuclear spins is anisotropic, reflecting the hexagonal symmetry of the crystalline field.

The coupling (20) will give a broadening of the resonance line which may be obtained from Van Vleck's formula for the second moment,[10]

$$\langle h^2\Delta\nu^2\rangle_{\text{av}}=[I(I+1)/3]\textstyle\sum_i B_{ij}^2.$$

We find

$$\langle h^2\Delta\nu^2\rangle_{\text{av}}=(1/6\pi)I(I+1)\frac{A^4c^4}{E_{\text{ex}}^2}(E_{\text{ex}}/E_a)^{1/2}. \qquad (21)$$

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[9] G. N. Watson, *A Treatise on the Theory of Bessel Functions* (Cambridge University Press, New York, 1952), 2nd ed., p. 172.

[10] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

The nuclear-nuclear coupling term (20) will give rise to a contribution to the specific heat additional to (16). Neglecting the $i=j$ terms in (19), which give rise to a pseudoquadrupole effect, we find

$$C_vT^2/R=\frac{A^4c^4I^2(I+1)^2}{36\pi k^2E_{\text{ex}}^2}(E_{\text{ex}}/E_a)^{1/2}. \tag{22}$$

### B. Ferromagnetic Region

When exchange interactions are of sufficient strength so that $4c^2Kz>\Delta$, a spontaneous magnetization can be obtained as discussed in Sec. I.

With the states (1) as basis functions $H$ may be transformed using the Bogoliubov transformation. Retaining again terms up to second order in the boson operators, the Hamiltonian becomes

$$H=E_0+\sum_k[W_1a_k^\dagger a_k-W_2/2(a_k^\dagger a_{-k}^\dagger+a_ka_{-k})], \tag{23}$$

where

$$W_1=W_0-\frac{\Delta^2}{2W_0}\Upsilon_k,\quad W_2=\frac{\Delta^2}{2W_0}\Upsilon_k,$$

$$E_0=-\tfrac{1}{2}\lambda M_0^2+\tfrac{1}{2}N\Delta\left(1-\frac{\Delta}{W_0}\right),$$

with

$$W_0=4c^2Kz,\quad M_0^2=(N\Lambda\beta c)^2\ (\eta^2-1)/\eta^2.$$

$H$ is diagonalized by the transformation defined in (10) with $W_1$, $W_2$ given by (23). The ferromagnetic excitation spectrum[11] becomes

$$E=E_0+\sum_k\hbar\omega_k(n_k+\tfrac{1}{2})-\tfrac{1}{2}\sum_k W_1, \tag{24}$$

with

$$\hbar\omega_k=(W_0^2-\Delta^2\gamma_k)^{1/2}.$$

The long-wavelength limit of (24) is

$$\hbar\omega_k=\Omega(1+A^2a^2k^2)^{1/2}, \tag{25}$$

where

$$\Omega=\Delta(\eta^2-1)^{1/2},\quad A^2=1/z(\eta^2-1),\quad \eta=W_0/\Delta.$$

The low-temperature specific heat of this ferromagnetic system is given by (14) with the replacement of $\Omega$, $A^2$, $\eta$ by the quantities defined in (25). The nuclear spin-spin coupling and anomalous specific heat in the ferromagnetic limit are also given by (20) and (22) except that now $E_a=W_0(\eta^2-1)$. With this replacement the second moment is (21).

The temperature dependence of the induced magnetization for ferromagnetic $\mathrm{Pr}^{3+}$ in a hexagonal field may be obtained at low temperatures by expressing (3) in the form

$$\Delta M/M_0=[\eta^2/(\eta^2-1)]^2\langle p_e\rangle, \tag{26}$$

where $\Delta M=M_0-M(T)$. The thermal average of $p_e$ is given by

$$\langle p_e\rangle=(1/N)\sum_k[(u_k^2+v_k^2)\langle n_k\rangle+v_k^2], \tag{27}$$

where $u_k$, $v_k$ are defined in (10) with $W_1$, $W_2$ given by (23). After dropping the small zero-point term in (27) we find

$$\Delta M/M_0=\frac{z^{3/2}}{2\pi^2}\eta\sum_{n=1}\left[(2\eta^2-1)\frac{K_1(Z)}{Z}+(\eta^2-1)\frac{3K_2(Z)}{Z^2}\right], \tag{28}$$

where $Z=n\beta\Delta(\eta^2-1)^{1/2}$. When $kT\ll\Omega$, Eq. (28) reduces to the limiting form

$$\Delta M/M_0=(z/2\pi)^{3/2}\eta(2\eta^2-1)(kT/\Omega)^{3/2}\times\exp(-\Omega/kT). \tag{29}$$

By comparison, the molecular-field approximation yields

$$\Delta M/M_0=[2\eta^2/(\eta^2-1)]\exp(-\Delta\eta/kT). \tag{30}$$

### C. Antiferromagnetic Region

When exchange interactions favor antiferromagnetic ordering and the condition $W_0>\Delta$ is met, an induced antiferromagnetic state can be obtained for $\mathrm{Pr}^{3+}$ in a hexagonal field. The Curie point, sublattice magnetization and magnetic eigenvalues are found to be identical to those derived by Bleaney for the ferromagnetic system described in Sec. I. Assuming two sublattices $A$ and $B$, the basis functions for the antiferromagnetic regime are found from (1), where $\tan 2\theta$ for the two sublattices is given by

$$\tan 2\theta_A=-\tan 2\theta_B=2c\Lambda\beta\lambda M_A/\Delta. \tag{31}$$

This condition insures that $\langle n|J^z|n\rangle_A=-\langle n|J^z|n\rangle_B$, as required for antiferromagnetic ordering.

The system Hamiltonian is given by

$$H=\sum_i V_i^c+2K\sum_{i,\delta}(\mathbf{J}_i\cdot\mathbf{J}_{i+\delta}), \tag{32}$$

where $\delta$ runs over the $z$ nearest neighbors on the opposite sublattice. Because the two sublattices are distinguishable, the boson operators used in the Bogoliubov representation are defined by $a_i^\dagger=C_{i,e}^\dagger C_{i,g}$ for lattice $A$, and $b_i^\dagger=C_{i,e}^\dagger C_{i,u}$ for lattice $B$. To second order in these operators, the Fourier transform of (32) becomes

$$H=E_0+\sum_k[W_0(a_k^\dagger a_k+b_k^\dagger b_k)+W_1(a_k^\dagger b_{-k}^\dagger+a_kb_{-k}+a_k^\dagger b_k+a_kb_k^\dagger)], \tag{33}$$

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[11] General excitation spectra which reduce to Eqs. (24) and (44) have been derived by Y. Kitano, F. Specht, and G. T. Trammel, in *Proceedings of the International Conference on Magnetism, Nottingham* (Institute of Physics and the Physical Society, London, 1965), page 480.

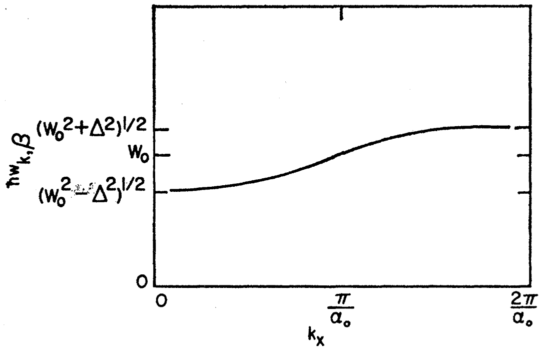

FIG. 1. The antiferromagnetic excitation spectrum of $Pr^{3+}$ in a hexagonal field. The $Pr^{3+}$ ions are taken to form a body-centered cube of side $a_0$.

where

$$a_i^\dagger = N^{-1/2}\sum_k \exp(i\mathbf{k}\cdot\mathbf{r}_i)a_k^\dagger ,$$

$$b_i^\dagger = N^{-1/2}\sum_k \exp(i\mathbf{k}\cdot\mathbf{r}_i)b_k^\dagger ,$$

$$W_0 = 4c^2Kz ,$$

$$W_1 = (\Delta^2/2W_0)\gamma_k ,$$

$$E_0 = -\lambda M_0^2 + N\Delta(1-\Delta/W_0) .$$

$H$ is diagonalized by the usual canonical transformation

$$\begin{aligned}\alpha_k^\dagger &= u_k(a_k^\dagger+b_k^\dagger)/\sqrt{2}+v_k(a_{-k}+b_{-k})/\sqrt{2} ,\\ \beta_k^\dagger &= w_k(a_k^\dagger-b_k^\dagger)/\sqrt{2}-x_k(a_{-k}-b_{-k})/\sqrt{2} ,\end{aligned} \tag{34}$$

where

$$u_k=\cosh\theta_k ,\quad v_k=\sinh\theta_k ,\quad \tanh 2\theta_k = W_1/(W_0+W_1) ,$$

$$w_k=\cosh\phi_k ,\quad x_k=\sinh\phi_k ,\quad \tanh 2\phi_k = W_1/(W_0-W_1) .$$

In the reduced zone, $0\leq k_x\leq \pi/a$, the low temperature excitation energy is found to be

$$E=E_0+\sum_k[\hbar\omega_{k,\alpha}(n_{k,\alpha}+\tfrac{1}{2}) + \hbar\omega_{k,\beta}(n_{k,\beta}+\tfrac{1}{2})]-\sum_k W_0 , \tag{35}$$

where

$$\hbar\omega_{k,\alpha}=(W_0^2+\Delta^2\gamma_k)^{1/2} ,\quad \hbar\omega_{k,\beta}=(W_0^2-\Delta^2\gamma_k)^{1/2} .$$

Working in an extended-zone scheme, $0\leq k_x\leq 2\pi/a$, we have

$$E=E_0+\sum_k \hbar\omega_{k,\beta}(n_{k,\beta}+\tfrac{1}{2})-\tfrac{1}{2}\sum_k W_0 . \tag{36}$$

The dispersion law for the longitudinal antiferromagnetic excitations is sketched on Fig. 1, and is identical to that found for the ferromagnetic spectrum (24).

Using the low-energy form of $\hbar\omega_{k,\beta}$, as given by (25), we find the specific heat and sublattice magnetization for antiferromagnetic $Pr^{3+}$ in a hexagonal field are identical to that found in part B for ferromagnetic $Pr^{3+}$.

A nuclear spin-spin coupling also exists for antiferromagnetic $Pr^{3+}$ and is of the same form as the ferromagnetic result

$$E^{(2)}=\frac{-A^2c^2}{4\pi E_{\text{ex}}}\sum_{i,j}(\pm)I_i^zI_j^zR(r_{ij}) , \tag{37}$$

where (+) if $i$ and $j$ are on same sublattice, (−) if on different.

The anomalous nuclear specific heat and the broadening of the nuclear resonance linewidth for antiferromagnetic $Pr^{3+}$ are found to be identical to the ferromagnetic result.

## III. FERROMAGNETIC $Pr^{3+}$ IN A CUBIC FIELD

The low-lying states of $Pr^{3+}$ in a crystal field of cubic symmetry are given by[2]

triplet at $E^c=\Delta$

$$\begin{aligned}|B\rangle &= (2/9)^{1/2}|+4\rangle-(7/18)^{1/2}(|+1\rangle+|-2\rangle) ,\\ |C\rangle &= (2/9)^{1/2}|-4\rangle+(7/18)^{1/2}(|-1\rangle-|+2\rangle) ,\\ |A\rangle &= (1/2)^{1/2}(|+3\rangle+|-3\rangle) ,\end{aligned} \tag{38}$$

singlet ground state

$$|G\rangle=(10/27)^{1/2}(|+3\rangle-|-3\rangle)-(7/27)^{1/2}|0\rangle .$$

For this manifold the total angular momentum operator $J=4$, and the Landé factor $\Lambda=\frac{4}{5}$. With the Hamiltonian (8), the condition for ferromagnetic ordering is again that $W_0>\Delta$, where $c=\langle A|J_1^z|G\rangle$. Solving the secular equation for the crystal-field states joined by the exchange field, we find the basis functions for the collective state to be

$$\begin{aligned}&|B\rangle ,\ |C\rangle ,\ |e\rangle=\sin\theta|G\rangle-\cos\theta|A\rangle ,\\ &|g\rangle=\cos\theta|G\rangle+\sin\theta|A\rangle ,\end{aligned} \tag{39}$$

with

$$E_B=\Delta+\tfrac{1}{2}\Lambda\beta\lambda M ,\quad E_c=\Delta-\tfrac{1}{2}\Lambda\beta\lambda M ,$$

$$E_e=(\Delta+W)/2 ,\quad E_g=(\Delta-W)/2 ,$$

and

$$\tan 2\theta=-2c\Lambda\beta\lambda M/\Delta .$$

The self-consistent expression for the magnetization in the low-temperature region is

$$\begin{aligned}M_0^2-M^2&=(N\Lambda\beta c)^2(4p_e+2p_B+2p_C) ,\\ M_0^2&=(N\Lambda\beta c)^2(\eta^2-1)/\eta^2 .\end{aligned} \tag{40}$$

In deriving (40), the contribution to $M^2$ made by the states $|B\rangle$ and $|C\rangle$ is neglected compared to that from $|e\rangle$ and $|g\rangle$, since the inequality $(p_g-p_e)^2\gg(p_B-p_C)^2$ is assumed to hold.

### 1. Excitation Spectrum

The Hamiltonian (8) is rewritten using the Fourier transform of the Bogoliubov operators $a_i^\dagger=C_{i,e}^\dagger C_{i,g}$,

$b_i^\dagger = C_{i,B}^\dagger C_{i,g}$, $c_i^\dagger = C_{i,C}^\dagger C_{i,g}$, with basis functions given by (39). We find, using

$$
\begin{aligned}
J_i^z &= c\sin 2\theta(1-2a_i^\dagger a_i - b_i^\dagger b_i - c_i^\dagger c_i) + \tfrac{1}{2}(b_i^\dagger b_i - c_i^\dagger c_i) \\
&\qquad - c\cos 2\theta(a_i^\dagger + a_i)\,, \\
J_i^\dagger &= (c\sqrt{2}\cos\theta - \tfrac{1}{2}\sqrt{2}\sin\theta) b_i^\dagger \\
&\qquad - (c\sqrt{2}\cos\theta + \tfrac{1}{2}\sqrt{2}\sin\theta) c_i\,, \qquad (41) \\
J_i^- &= (c\sqrt{2}\cos\theta - \tfrac{1}{2}\sqrt{2}\sin\theta) b_i - (c\sqrt{2}\cos\theta + \tfrac{1}{2}\sqrt{2}\sin\theta) c_i^\dagger\,,
\end{aligned}
$$

where $J_i^\pm = J_i^x \pm i J_i^y$, that

$$
\begin{aligned}
H = E_0 + \sum_k \big[ &W_1 a_k^\dagger a_k - (W_2/2)(a_k^\dagger a_{-k}^\dagger + a_k a_{-k}) \\
&+ W_3 b_k^\dagger b_k + W_4 c_k^\dagger c_k + W_5 (b_k^\dagger c_k^\dagger + c_k b_k) \big]\,, \qquad (42)
\end{aligned}
$$

and

$$
\begin{aligned}
E_0 &= -\tfrac{1}{2}\lambda M_0^2 + (N\Delta/2)(1-\Delta/W_0)\,, \\
W_1 &= W_0 - (\Delta^2/2W_0)\gamma_k\,, \\
W_2 &= (\Delta^2/2W_0)\gamma_k\,, \\
W_3 &= \tfrac{1}{2}(\Delta+W_0) - Kcz\sin 2\theta(1-\gamma_k) - Kxz\gamma_k\,, \\
&\qquad x = \tfrac{1}{12}(83+77\cos 2\theta)\,, \\
W_4 &= \tfrac{1}{2}(\Delta+W_0) + Kcz\sin 2\theta(1-\gamma_k) - Kxz\gamma_k\,, \\
&\qquad y = \tfrac{1}{12}(77+83\cos 2\theta)\,, \\
W_5 &= Kyz\gamma_k\,.
\end{aligned}
$$

$H$ is diagonalized by the canonical transformation,

$$
\begin{aligned}
\alpha_k^\dagger &= u_k a_k^\dagger - v_k a_{-k}\,, \\
\beta_k^\dagger &= w_k b_k^\dagger + x_k c_k\,, \qquad (43) \\
\gamma_k^\dagger &= w_k c_k^\dagger + x_k b_k\,,
\end{aligned}
$$

where

$$
\begin{aligned}
&u_k = \cosh\theta_k\,, \quad v_k = \sinh\theta_k\,, \quad \tanh 2\theta_k = W_2/W_1\,, \\
&w_k = \cosh\phi_k\,, \quad x_k = \sinh\phi_k\,, \quad \tanh 2\phi_k = 2W_5/(W_3+W_4)\,.
\end{aligned}
$$

The excitation spectrum becomes

$$
E = E_0 + \sum_{k,r} \hbar\omega_{k,r}(n_{k,r}+\tfrac{1}{2}) - \tfrac{1}{2}\sum_k (W_1+W_3+W_4)\,, \qquad (44)
$$

where $r$ denotes the normal modes $(\alpha,\beta,\gamma)$, with

$$
\begin{aligned}
\hbar\omega_{k,\alpha} &= (W_0^2 - \Delta^2\gamma_k)^{1/2}\,, \\
\hbar\omega_{k,\beta} &= +\left[\frac{W_0^2-\Delta^2}{16c^2}\right]^{1/2}(1-\gamma_k) + \left(\frac{\Delta+W_0}{2}\right)^{1/2} \\
&\quad \times \left[\frac{\Delta+W_0}{2} - \frac{(83W_0+77\Delta)\gamma_k}{24c^2} + \frac{(W_0-\Delta)}{8c^2}\gamma_k^2\right]^{1/2}\,, \\
\hbar\omega_{k,\gamma} &= \hbar\omega_{k,\beta} - 2\left[\frac{W_0^2-\Delta^2}{16c^2}\right]^{1/2}(1-\gamma_k)\,.
\end{aligned}
$$

The dispersion law for the three modes is sketched in Fig. 2. The longitudinal excitation $(r=\alpha)$ is identical in form to the excitation wave found for $\mathrm{Pr}^{3+}$ in a hexagonal field, and contains an energy gap. The transverse modes $(r=\beta,\gamma)$, which are present in the cubic representation, have a vanishing energy gap.

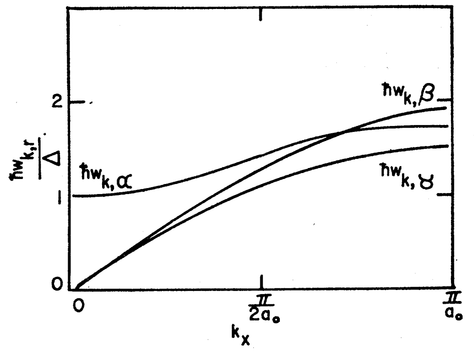

FIG. 2. The ferromagnetic excitation spectrum of $\mathrm{Pr}^{3+}$ in a cubic field. The parameter $\eta = W_0/\Delta$ is chosen to equal $\sqrt{2}$, and the $\mathrm{Pr}^{3+}$ ions from a simple cube of side $a_0$.

In the limit of long wavelengths we find

$$
\hbar\omega_{k,\alpha} = \Omega(1+A^2a^2k^2)^{1/2}\,, \quad \hbar\omega_{k,\beta} = \hbar\omega_{k,\gamma} = Dak\,, \qquad (45)
$$

where

$$
\begin{aligned}
&\Omega = (W_0^2-\Delta^2)^{1/2}\,, \quad A^2 = 1/z(\eta^2-1)\,, \\
&D = \left[\frac{\Delta+W_0}{2z}\right]^{1/2}\left[\frac{77W_0+83\Delta}{24c^2}\right]^{1/2}.
\end{aligned}
$$

### 2. Thermodynamic Properties

The temperature dependence of the magnetization for $\mathrm{Pr}^{3+}$ in a cubic field is obtained by replacing (40) by the approximate low-temperature form

$$
\Delta M/M_0 = [\eta^2/(\eta^2-1)](2\langle p_e\rangle + \langle p_B\rangle + \langle p_C\rangle)\,, \qquad (46)
$$

where $\Delta M = M_0 - M(T)$. The thermal average of the excited-state probabilities is given by

$$
\begin{aligned}
\langle p_e\rangle &= \frac{1}{N}\sum_k [(u_k^2+v_k^2)\langle n_{k,\alpha}\rangle + v_k^2]\,, \\
&\qquad\qquad\qquad\qquad (47) \\
\langle p_B\rangle + \langle p_C\rangle &= \frac{1}{N}\sum_k [(w_k^2+x_k^2)(\langle n_{k,\beta}\rangle + \langle n_{k,\gamma}\rangle) + 2x_k^2]\,.
\end{aligned}
$$

Neglecting zero-point terms, we find, in the limit $kT \ll D, \Omega$:

$$
\begin{aligned}
\frac{\Delta M}{M_0} = \frac{\eta^2}{\eta^2-1}\,&\frac{(77W_0+83\Delta)}{1920D}\left(\frac{kT}{D}\right)^2 + \left(\frac{z}{2\pi}\right)^{3/2} \\
&\times \eta(2\eta^2-1)\left(\frac{kT}{\Omega}\right)^{3/2}\exp\left(\frac{-\Omega}{kT}\right). \qquad (48)
\end{aligned}
$$

The low-temperature dependence of the specific heat is obtained from the spectrum (45). We find that the contribution to $C_v$ made by the three excitation waves

$\boldsymbol{r}=(\alpha,\beta,\gamma)$ in the limit $kT\ll D$, $\Omega$ is given by

$$C_v/N_k=4\pi^2/15(kT/D)^3+(z/2\pi)^{3/2}(\eta^2-1)^{3/2} \times(\Omega/kT)^{1/2}\exp(-\Omega/kT). \quad (49)$$

Only the lowest order terms in the expansion of the contribution by each normal mode have been kept in (48) and (49). The lack of an energy gap for transverse excitations results in a large contribution to $C_v$ and $\Delta M/M_0$ at low temperatures.

The nuclear-nuclear coupling, and the associated specific heat of ferromagnetic Pr$^{3+}$ in a cubic field, is of the form already found for Pr$^{3+}$ in a hexagonal field, i.e., given by (20) and (22), respectively. Again, $E_{\text{ex}}=4c^2K$ and $E_a{}^z=W_0(\eta^2-1)$. Because of the lack of an energy gap for transverse excitations, however, the effective transverse anisotropy field $E_a{}^x$ is zero. We have, of course, neglected any true anisotropy in the electronic system. The introduction of an anisotropy field, coming from, for example, second-order dipolar interactions, will result in a finite $E_a{}^x$, and remove the divergence in the nuclear specific heat associated with the transverse excitations.

## IV. Eu$^{3+}$ IN A CUBIC FIELD

### A. Paramagnetic Region

When exchange effects are not of sufficient strength to support magnetic ordering, the low-lying levels of paramagnetic Eu$^{3+}$ in a cubic crystalline field are given by the spin-orbit split states: $J=1$ triplet at $E=\Delta$

$$|B\rangle=|1,1\rangle, \quad |A\rangle+|1,0\rangle, \quad |C\rangle=|1,-1\rangle, \quad (50)$$

$J=0$ ground state

$$|G\rangle=|0,0\rangle.$$

The Hamiltonian (8) is rewritten in terms of the spin operators $\mathbf{S}_i$ using the Bogoliubov operators $a_i{}^\dagger=C_{i,A}{}^\dagger \times C_{i,G}$, $b_i{}^\dagger=C_{i,B}{}^\dagger C_{i,G}$, $c_i{}^\dagger=C_{i,C}{}^\dagger C_{i,G}$, with basis functions given by (50). The excitation spectrum at low temperatures becomes, after transforming to normal mode corrdinates: $\alpha_k{}^\dagger=u_ka_k{}^\dagger-v_ka_{-k}$, $\beta_k{}^\dagger=u_kc_k{}^\dagger+v_kb_k$, $\gamma_k{}^\dagger=u_kb_k{}^\dagger+v_kc_k$, with $u_k$, $v_k$ as defined in (10).

$$E=\sum_k \hbar\omega_k(n_{k,\alpha}+n_{k,\beta}+n_{k,\gamma}+\tfrac{3}{2})-\tfrac{3}{2}\sum_k W_1,$$
$$\hbar\omega_k=\Delta^{1/2}(\Delta-4c^2Kz\gamma_k)^{1/2}, \quad (51)$$
$$W_1=\Delta-2Kc^2z\gamma_k, \quad c=\langle A|S^z|G\rangle.$$

The $n_{k,\alpha}$ term of (51) was found by Bozorth and Van Vleck[4] using an $S_i{}^zS_j{}^z$ exchange. The indirect nuclear spin-spin coupling for this paramagnetic region will be, due to the cubic symmetry of the problem, an isotropic term of the form

$$E^{(2)}=\frac{-A^2c^2}{4\pi E_{\text{ex}}}\sum_{i,j}(\mathbf{I}_i\cdot\mathbf{I}_j)R(r_{ij}), \quad (52)$$

where $E_{\text{ex}}$ and $R(r_{ij})$ are given by (19) and (20).

### B. Ferromagnetic Region

Starting from the states (50), the low-temperature excitation energy of ferromagnetic Eu$^{3+}$ in a cubic crystalline field is found, in a manner formally identical to that of Sec. III, to be

$$E=E_0+\sum_{k,r}\hbar\omega_{k,r}(n_{k,r}+\tfrac{1}{2})-\tfrac{1}{2}\sum_k(W_1+W_3+W_4), \quad (53)$$

where

$$\hbar\omega_{k,\alpha}=(W_0{}^2-\Delta^2\gamma_k)^{1/2},$$
$$\hbar\omega_{k,\beta}=+E_1+E_2,$$
$$\hbar\omega_{k,\gamma}=-E_1+E_2,$$

with

$$E_1=(W_0{}^2-\Delta^2)^{1/2}(1-\gamma_k)/8,$$
$$E_2=(W_0+\Delta)^{1/2}[16(W_0+\Delta)-(17W_0+15\Delta)\gamma_k +(W_0-\Delta)\gamma_k{}^2]^{1/2}/8.$$

In the limit of long wavelengths (53) becomes

$$\hbar\omega_{k,\alpha}=\Omega(1+A^2a^2k^2)^{1/2}, \quad \hbar\omega_{k,\beta}=\hbar\omega_{k,\gamma}=Dak, \quad (54)$$

where

$$\Omega=\Delta(\eta^2-1)^{1/2}, \quad A^2=1/z(\eta^2-1), \quad \eta=W_0/\Delta,$$
$$D=(W_0+\Delta)^{1/2}(15W_0+17\Delta)^{1/2}8z^{1/2}.$$

We find that the thermodynamic properties of Eu$^{3+}$ are identical to those for Pr$^{3+}$ in a cubic field, apart from numerical factors resulting from the different value of the constant $c$ in the two cases. The low-temperature magnetization in the limit $kT\ll D$, $\Omega$ is given by

$$\Delta M/M_0=\frac{\eta^2}{\eta^2-1}\frac{(15W_0+17\Delta)}{384D}(kT/D)^2+(z/2\pi)^{3/2} \times\eta(2\eta^2-1)(kT/\Omega)^{3/2}\exp(-\Omega/kT), \quad (55)$$

and the specific heat by (49) with $D$, $\Omega$ as defined in (54). The nuclear coupling is also formally identical to that found in Sec. III.

## V. PHASE TRANSITION

One identication that the magnetization is due to an induced moment, and not conventional ferromagnetic alignment, is that the entropy of ordering at the Curie point is less than the $Nk\ln(2S+1)$ value of a spin-$S$ ferromagnet. To prove this, we consider the two-singlet-state system discussed by Bleaney, ferromagnetic Pr$^{3+}$ in a hexagonal field, and calculate its thermodynamic behavior in the vicinity of the Curie point. We express the excited- and ground-state probabilities in terms of the magnetization by rewriting (3) as

$$p_e=\tfrac{1}{2}[1-(x^2+(1-x^2)\sigma^2)^{1/2}],$$
$$p_g=\tfrac{1}{2}[1+(x^2+(1-x^2)\sigma^2)^{1/2}], \quad (56)$$

where $\sigma = M(T)/M_0$ and $x = \Delta/W_0$. The entropy of ordering may be obtained from the usual Boltzmann expression $S = -Nk(p_e \ln p_e + p_g \ln p_g)$. Expanding $S$ to fourth order in $\sigma$ find

$$S/Nk = \tfrac{1}{2}(1-x)\ln(2/1-x) + \tfrac{1}{2}(1+x)\ln(2/1+x) - \frac{(1-x^2)}{2x}\tanh^{-1}x\sigma^2 - \frac{(1-x^2)}{8x^2} \times \left[1 - \frac{(1-x^2)}{x}\tanh^{-1}x\right]\sigma^4. \quad (57)$$

In the vicinity of the Curie point the entropy is given by the first two terms in (57). When this portion of $S$ is plotted versus $x$ we obtain Fig. 3. For any value of $x$ between zero and one, the system will have an entropy of ordering which is lower than the $Nk \ln 2$ value of a conventional spin-$\frac{1}{2}$ ferromagnet at the Curie point. To determine the nature of this transition we form the free energy $F = U - TS$, where

$$U = -\tfrac{1}{2}\lambda M_0^2\sigma^2 = -(NW_0/4)(1-x^2)\sigma^2.$$

Minimizing $F$ with respect to $\sigma$, and solving for $\sigma$ near $T_c$,

$$\sigma^2 = G(x)(T_c - T)/T, \quad (58)$$

where

$$G(x) = 2x^2(\tanh^{-1}x)/[x - (1-x^2)\tanh^{-1}x] > 0,$$
$$\tanh^{-1}x = \Delta/2kT_c.$$

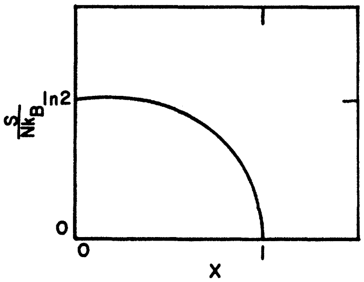

FIG. 3. Entropy of ordering at the ferromagnetic Curie point for a two-singlet-state system versus the parameter $x = \Delta/W_0$.

The free energy is then

$$F(T<T_c) = F(T>T_c) - \tfrac{1}{4}NW_0(1-x^2)G(x) \times [(T_c - T)^2/TT_c]. \quad (59)$$

There is no discontinuity in $S = -(\partial F/\partial T)$ at $T_c$ and hence no latent heat associated with the transition. There is, however, a discontinuity in the specific heat classifying the transition as one of the second kind. We find

$$\Delta C_v(T_c) = NkG(x)(1-x^2)\tanh^{-1}x/x. \quad (60)$$

This should be compared with the usual discontinuity of $3Nk/2$ for a conventional ferromagnet of spin $\frac{1}{2}$.

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