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Theory of collective magnetic excitations in strong crystal fields. II. Application to $S = 1$ singlet ground-state ferromagnet

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The theory of collective magnetic excitations based upon the set of Green's functions of angular momentum spherical tensor operators is applied to the exchange-coupled ($S = 1$) magnet with a singlet crystal-field ground state. The spin Hamiltonian is brought to an approximately diagonal form via a unitary transformation by a spin operator functional, the best single-site approximation being located variationally. This enables the set of equations of motion for the Green's tensor to be linearized by conventional techniques. The essential features of induced-moment systems are clarified and displayed in the theory and numerical calculations, respectively. In particular, soft-mode behaviors at the second-order phase transition to ferromagnetism, mode-mode interactions, and a lack of temperature dependence for the excitation energies except at small wave vectors are evident. The nature of the phase transition is examined in detail and a relationship between the divergence of the static susceptibility and the soft-mode behavior is derived from the unitary transformation to pseudospace.

I. INTRODUCTION

When the ground state of the crystalline-electric-field (CEF) Hamiltonian is singlet, magnetic long-range order cannot be established unless the exchange constant is greater than a certain critical value which is related to the CEF parameters. The phenomenon of singlet-ground-state magnetism, which is the most extreme example of induced-moment magnetism, has recently been the subject of several theoretical and experimental studies.[1] As was noted in the previous paper[2] (to be referred to hereafter as I), there are two conventional approaches to the study of the dynamics of spin systems in a strong CEF. These are the spin-wave and the molecular-field exciton theories, respectively. The majority of existing theories of collective excitations in singlet-ground-state systems adopt the molecular-field exciton approach,[3-8] while attempts have been made to construct more sophisticated theories via the psuedospin method.[9-12] The molecular-field exciton theories have been generally successful in explaining several conspicuous properties of spin excitations in singlet-ground-state systems. The early effective boson theories have schematized the collective excitation spectra, which were later observed experimentally.[13,14] Holden and Buyers extended the effective-boson theory to include thermal effects,[15] and were able to explain the remarkable lack of temperature dependence of the excitation energies of Pr_3Tl in terms of mode-mode interactions between the excitations.[16,17] The molecular-field exciton theory thus far developed, however, is deficient in that the population of the levels is computed in the molecular-field approximation (MFA). Therefore the excitation energy is renormalized correctly only at high temperatures where dispersion in the excitation energy is not significant. This implies that, since the effect of the rapid growth of population of any softening mode is not properly reflected in the temperature renormalization, the molecular-field exciton theory may not adequately describe the soft-mode problem at the transition temperature. In order to approach the soft-mode problem a self-consistent theory must be formulated in which the population of each state is computed from the excitation energies. In our view it should be possible to proceed further with the Holden-Buyers theory to make it self-consistent. However, the simplicity of the theory would be lost, and it is not possible to foresee the results without an involved numerical calculation. The pseudospin theory,[9-12] on the other hand, is a self-consistent theory. But since only low-lying states are considered, CEF symmetry is not reflected in the pseudospin Hamiltonian. Thus it may also provide an inadequate description of the soft-mode problem.

The spin-tensor-operator Green's-function technique, developed in the preceding paper (I), is a self-consistent theory for the complete level scheme. In principle, it correctly describes dynamical and kinematical interactions among the excitations, since spin dynamics is described by physical spin operators rather than effective fermion and boson operators. The central issue here, however, is the decoupling (or linearization) procedure. In order to achieve optimum decoupling of the Green's functions within the framework of familar decoupling techniques, we have introduced a unitary transformation of the Hamiltonian by a spin operator functional that produces, essentially, a generalized pseudospin formalism.[18]

The organization of this paper is as follows. In Sec. II the theory of the unitary transformation is outlined and applied, as an example, to the $S=1$ ferromagnet with a singlet CEF ground state. The criterion to determine the transformation parameter and its physical meaning are discussed, followed by the calculation of the static susceptibility in the present formalism. Complete spin dynamics of the system are developed in Sec. III, via the spin-tensor-operator Green's functions. In Sec. IV some numerical results are presented and the occurrence of the mode softening at the transition temperature is discussed in some detail. The conclusion is given in Sec. V.

II. UNITARY TRANSFORMATION

A. General remarks

In I we have studied the $S=1$ ferromagnet with twofold crystal field, for the case where B_2^0 is negative so that the easy direction is along the symmetry axis and the crystal-field ground state is a doublet. When B_2^0 is positive, an easy plane develops perpendicular to the symmetry axis and the ground state is a singlet. If the z axis is rotated by 90° it becomes directed parallel to the magnetization (as in I we take $S^z=-1$ to be the saturated state, then $-1 \leq \langle \tilde{O}_1^0 \rangle \leq 0$) which lies in the easy plane. The Hamiltonian (4.1) of I may be written in a representation with S_z ($\tilde{O}_1^0$) diagonal:

$$\mathcal{H} = -\sum_{\vec{n}_1\vec{n}_2} J(\vec{n}_1-\vec{n}_2)[\tilde{O}_1^0(\vec{n}_1)\tilde{O}_1^0(\vec{n}_2) - 2\tilde{O}_1^1(\vec{n}_1)\tilde{O}_1^{-1}(\vec{n}_2)] + B_2^0 \sum_{\vec{n}_1}[-\tfrac{1}{2}\tilde{O}_2^0(\vec{n}_1) + \tfrac{1}{2}\sqrt{6}\,\overline{O}_2^2(\vec{n}_1)] , \qquad (2.1)$$

where the Zeeman term was neglected and

$$\overline{O}_l^m = \tfrac{1}{2}(\tilde{O}_l^m + \tilde{O}_l^{-m}) . \qquad (2.2)$$

When B_2^0 is small compared with $J(0)$, the conventional spin-wave approximation appears to be valid, provided that the theory is extended to take the nonzero off-diagonal correlation function $\langle \overline{O}_2^2 \rangle$ into account.[19,20] If B_2^0 is large, however, the concept of decoupling, e.g., Eq. (3.4) of I, is in doubt; the spin precession is highly elliptical, and S^z does not approximate to a constant of the motion.

The difficulty will be avoided if one introduces a transformation that diagonalizes (2.1) by eliminating $\overline{O}_2^2$. In general, the class of Hamiltonians of interest have the form

$$\mathcal{H} = \mathcal{H}_{\text{ex}} + \sum_{\vec{n}} [B_l^0 \tilde{O}_l^0(\vec{n}) + B_l^l \overline{O}_l^l(\vec{n})] , \qquad (2.3)$$

where $\mathcal{H}_{\text{ex}}$ is the exchange Hamiltonian. The true ground state of (2.3) is a many-body state, and rigorous diagonalization is obviously intractable. Instead, we propose a unitary transformation that leads to the best single-site representation of (2.3). Such a transformation is

$$\tilde{\mathcal{H}}(\beta) = e^{-R_l^l}\mathcal{H}e^{R_l^l} , \qquad (2.4)$$

where

$$R_l^l = i\beta \sum_{\vec{n}} \hat{O}_l^l(\vec{n}) \qquad (2.5)$$

and

$$\hat{O}_l^m = -\tfrac{1}{2}i(\tilde{O}_l^m - \tilde{O}_l^{-m}) . \qquad (2.6)$$

The transformation (2.4) may be evaluated by means of expansion

$$e^{-R_l^l}\mathcal{H}e^{R_l^l} = \mathcal{H} + [\mathcal{H}, R_l^l] + (1/2!)[[\mathcal{H}, R_l^l], R_l^l] + \cdots \qquad (2.7)$$

and the commutation formula (2.2) of I. Generally it is possible to find a way to sum the infinite series (2.7) and to obtain a compact expression. The transformations of each of the tensor operators by R_2^2, for the case $S=1$, are tabulated in Table I. If (2.5) is applied to a crystal-field Hamiltonian, the transformed Hamiltonian contains the spin-tensor operators with $m=0, l, 2l$. If $2S+1$ is less than $2l$, the term with $m=2l$ has no matrix element, then the diagonalization is completed by adjusting β such that the term with $m=l$ vanishes.

B. Application to $S=1$ magnet

To illustrate this procedure, we reduce (2.1), in the molecular-field approximation, to

$$\mathcal{H}^{\text{MFA}} = \sum_{\vec{n}} [2\sigma J(0)\tilde{O}_1^0(\vec{n}) - \tfrac{1}{2}B_2^0\tilde{O}_2^0(\vec{n}) + \tfrac{1}{2}\sqrt{6}B_2^0\overline{O}_2^2(\vec{n})] , \qquad (2.8)$$

where $\sigma = -\langle O_1^0 \rangle$. After the transformation, (2.8) becomes

$$\tilde{\mathcal{H}}^{\text{MFA}}(\theta) = \sum_{\vec{n}} \{[2\sigma J(0)\cos\theta + \tfrac{3}{4}B_2^0\sin\theta]\tilde{O}_1^0(\vec{n}) - \tfrac{1}{2}B_2^0\tilde{O}_2^0(\vec{n}) + \tfrac{1}{2}\sqrt{6}\,[B_2^0\cos\theta - \tfrac{8}{3}\sigma J(0)\sin\theta]\overline{O}_2^2(\vec{n})\} , \qquad (2.9)$$

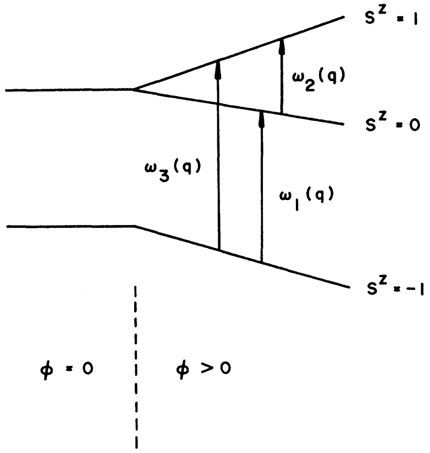

FIG. 1. Schematic diagram of the molecular-field states as functions of the molecular field ϕ and the excitation energies for the transition among the states.

where

$$\theta = -\sqrt{\tfrac{3}{2}}\,\beta \ . \tag{2.10}$$

(2.9) is diagonal if θ satisfies the condition

$$\tan\theta = \frac{3}{8}\,\frac{B_2^0}{\sigma J(0)} = \frac{D}{4\sigma J(0)}\,, \tag{2.11}$$

where $D = \frac{3}{2} B_2^0$ is the crystal-field splitting between the singlet and doublet when σ is zero. Since $\tilde{O}_1^0$ is transformed as

$$e^{-R}\tilde{O}_1^0 e^{R} = \cos\theta\,\tilde{O}_1^0 - \tfrac{2}{3}\sqrt{6}\,\sin\theta\,\overline{O}_2^2 \ . \tag{2.12}$$

TABLE I. Table of transformed operators by Eq. (2.4) with $l=2$. θ is equal to $-\sqrt{\frac{3}{2}}\,\beta$.

$\tilde{O}_l^m$	$e^{-R_2^2}\tilde{O}_l^m O^{R_2^2}$
$\tilde{O}_1^0$	$\cos\theta\,\tilde{O}_1^0 - \frac{2}{3}\sqrt{6}\,\sin\theta\,\overline{O}_2^2$
$\tilde{O}_1^{\pm1}$	$\cos\frac{\theta}{2}\,\tilde{O}_1^{\pm1} - \frac{2}{3}\sqrt{3}\,\sin\frac{1}{2}\theta\,\tilde{O}_2^{\mp1}$
$\tilde{O}_2^0$	$\tilde{O}_2^0$
$\tilde{O}_2^{\pm1}$	$\cos\frac{\theta}{2}\,\tilde{O}_2^{\pm1} + \frac{1}{2}\sqrt{3}\,\sin\frac{1}{2}\theta\,\tilde{O}_1^{\mp1}$
$\overline{O}_2^2$	$\cos\theta\,\overline{O}_2^2 + \frac{1}{4}\sqrt{6}\,\sin\theta\,\tilde{O}_1^0$
$\hat{O}_2^2$	$\hat{O}_2^2$

σ is related to the relative magnetization of the transformed system, m, by

$$\sigma = m\cos\theta \ . \tag{2.13}$$

Therefore the condition (2.11) becomes

$$\sin\theta = D/4m\,J(0) \ . \tag{2.14}$$

Note that θ is renormalized by temperature through the temperature dependence of m. A diagram of the molecular-field energy levels, as a function of molecular field, is shown in Fig. 1.

Under the transformation (2.4) the full Hamiltonian (2.1) takes the form

$$\tilde{\mathcal{H}}(\theta) = \tilde{\mathcal{H}}_d(\theta) + \tilde{\mathcal{H}}_t(\theta) + \tilde{\mathcal{H}}_n(\theta)\,, \tag{2.15}$$

where $\tilde{\mathcal{H}}_d$ is the diagonal part of the Hamiltonian

$$\tilde{\mathcal{H}}_d(\theta) = \sum_{\vec{n}_1,\vec{n}_2} J(\vec{n}_1 - \vec{n}_2)\cos^2\theta\,\tilde{O}_1^0(\vec{n}_1)\tilde{O}_1^0(\vec{n}_2) - \tfrac{1}{2}B_2^0\sum_{\vec{n}_1}[\tilde{O}_2^0(\vec{n}_1) - \tfrac{3}{2}\sin\theta\,\tilde{O}_1^0(\vec{n}_1)] \ . \tag{2.16}$$

$\tilde{\mathcal{H}}_t$ is the transverse exchange Hamiltonian

$$\tilde{\mathcal{H}}_t(\theta) = \sum_{\vec{n}_1,\vec{n}_2} J(\vec{n}_1 - \vec{n}_2)(2\cos^2\tfrac{1}{2}\theta\,\tilde{O}_1^1(\vec{n}_1)\,\tilde{O}_1^{-1}(\vec{n}_2) + \tfrac{8}{3}\sin^2\tfrac{1}{2}\theta\,\tilde{O}_2^1(\vec{n}_1)\tilde{O}_2^{-1}(\vec{n}_2))\,, \tag{2.17}$$

and $\tilde{\mathcal{H}}_n$ is the nondiagonal part

$$\begin{aligned}\tilde{\mathcal{H}}_n(\theta) = {} & \tfrac{1}{2}\sqrt{6}\cos\theta\sum_{\vec{n}_1}\overline{O}_2^2(\vec{n}_1)\left(B_2^0 + \frac{8}{3}\sum_{\vec{n}_2} J(\vec{n}_1 - \vec{n}_2)\sin\theta\,\tilde{O}_1^0(\vec{n}_2)\right) - \frac{8}{3}\sum_{\vec{n}_1,\vec{n}_2} J(\vec{n}_1 - \vec{n}_2)\sin^2\theta\,\overline{O}_2^2(\vec{n}_1)\,\overline{O}_2^2(\vec{n}_2) \\ & + \frac{2\sqrt{3}}{3}\sum_{\vec{n}_1,\vec{n}_2} J(\vec{n}_1 - \vec{n}_2)\sin\theta[\tilde{O}_1^1(\vec{n}_1)\tilde{O}_2^1(\vec{n}_2) + \tilde{O}_1^{-1}(\vec{n}_1)\tilde{O}_2^{-1}(\vec{n}_2)] \ . \end{aligned} \tag{2.18}$$

Thus the transformation will not completely diagonalize the Hamiltonian by completely removing $\tilde{\mathcal{H}}_n(\theta)$. It is possible, however, to minimize the effect of $\tilde{\mathcal{H}}_n(\theta)$ and to obtain the best single-site representation.

C. Variational determination of the transformation angle θ

The criterion upon which the optimum value of θ rests, is derived from the minimum principle for the free energy.[21] The functional

$$F=\mathrm{Tr}\rho\mathcal{H}+(1/\beta)\,\mathrm{Tr}\rho\ln\rho, \tag{2.19}$$

with an arbitrary ρ is an absolute upper bound to the free energy of the system and takes its minimum value when ρ is the true density matrix. In the spirit of the Green's-function equations-of-motion (Sec. III), we utilize an approximate density matrix ρ_d, that is diagonal in the representation in which $\tilde{O}_n^0$, of the transformed system (2.4), is diagonal. No further specification of ρ_d is necessary for present purposes. The functional (2.19) is minimized with respect to θ, hence

$$\frac{\partial F}{\partial\theta}=\frac{\partial}{\partial\theta}\mathrm{Tr}\rho_d\tilde{\mathcal{H}}=\frac{\partial}{\partial\theta}\langle\tilde{\mathcal{H}}\rangle_d=0, \tag{2.20}$$

where $\langle\ \rangle_d$ denotes the thermodynamic average over the diagonal density matrix ρ_d. An interpretation of (2.20) is that the abstract torque in the θ plane is zero. Alternatively (2.20) implies that

$$\langle[\mathcal{H},\ \hat{O}_2^2]\rangle_d=0 \tag{2.21}$$

in that $\tilde{\mathcal{H}}$ should include no term containing $\overline{O}_2^2$.

If (2.20) is applied to (2.16) and the difference between $\langle\tilde{O}_1^1(\vec{n}_1)\tilde{O}_1^{-1}(\vec{n}_2)\rangle$ and $\frac{4}{3}\langle\tilde{O}_2^1(\vec{n}_1)\tilde{O}_2^{-1}(\vec{n}_2)\rangle$ is neglected—this is a good approximation according to (4.5) of I—(2.14) is recovered. We note that θ could have been chosen from the condition

$$\langle\overline{O}_l^l\rangle=0. \tag{2.22}$$

However (2.22) is strongly dependent upon the decoupling approximation. When the equation of motion was decoupled in the random-phase approximation (RPA), (2.22) was not fulfilled; but with θ chosen from (2.20), (2.22) must follow in principle.

D. Static susceptibility

The static susceptibility may be studied by adding to the Hamiltonian (2.1) the Zeeman term

$$\mathcal{H}'=-\gamma H\sum_n\tilde{O}_1^0(n), \tag{2.23}$$

where $\gamma=\mu_B g$, g is the Landé g factor. The condition determining θ (2.20) becomes

$$\frac{\partial}{\partial\theta}\langle\tilde{\mathcal{H}}(\theta)\rangle_d+\gamma H\sin\theta\langle\tilde{O}_1^0\rangle=0. \tag{2.24}$$

If we assume

$$\frac{\partial}{\partial\theta}\langle\tilde{\mathcal{H}}(\theta)\rangle_d\Big|_{\theta=\theta_0}=0 \tag{2.25}$$

where $|_{\theta=\theta_0}$ denotes the value of the derivative at $\theta=\theta_0$, then for $\delta\theta=\theta-\theta_0\ll1$,

$$\frac{\partial}{\partial\theta}\langle\tilde{\mathcal{H}}(\theta)\rangle_d=\frac{\partial^2}{\partial\theta^2}\langle\tilde{\mathcal{H}}(\theta)\rangle_d\Big|_{\theta=\theta_0}\delta\theta+\cdots+\tilde{U}(\theta_0)\delta\theta+\cdots, \tag{2.26}$$

where $\tilde{U}(\theta_0)$ is the contribution arising from the change in the density matrix during the athermal rotation through $\delta\theta$. If (2.24) and (2.26) are combined, one obtains

$$\frac{\partial\theta}{\partial H}=-\frac{\gamma\sin\theta\langle\tilde{O}_1^0\rangle}{(\partial^2/\partial\theta^2)\langle\tilde{\mathcal{H}}(\theta_0)\rangle_d|_{\theta=\theta_0}+\tilde{U}(\theta_0)}. \tag{2.27}$$

The static susceptibility is therefore

$$\begin{aligned}\chi(T)&=\frac{\partial\sigma(T)}{\partial H}=\sin\theta\frac{\partial\theta}{\partial H}\langle\tilde{O}_1^0\rangle-\cos\theta\frac{\partial\langle\tilde{O}_1^0\rangle}{\partial H}\\&=\frac{\gamma\sin^2\theta\langle\tilde{O}_1^0\rangle^2}{(\partial^2/\partial\theta^2)\langle\tilde{\mathcal{H}}(\theta)\rangle_d|_{\theta=\theta_0}+\tilde{U}(\theta_0)}-\cos\theta\frac{\partial\langle\tilde{O}_1^0\rangle}{\partial H}.\end{aligned} \tag{2.28}$$

The second term in (2.28) is similar in nature to the $\tilde{U}(\theta_0)$ contribution. Thus the static susceptibility is composed of both the perturbation terms arising from a change in the density matrix and the second derivative of $\langle\tilde{\mathcal{H}}(\theta)\rangle_d$. The latter contribution will be related to the excitation energy in in Sec. IV.

III. SPIN DYNAMICS OF THE $S=1$ MAGNET WITH A SINGLET CRYSTAL-FIELD GROUND STATE

The spin-tensor-operator Green's-function approach described in the previous paper (I) is now applied to the singlet-ground-state system characterized by the Hamiltonian (2.15). The equations of motion will be linearized by RPA for simplicity. For $O_1^{-1}(q)$ and $O_2^{-1}(q)$ these equations are of the form

$$\begin{aligned}[\tilde{O}_1^{-1}(q),\ \mathcal{H}]&=A_1(q)\tilde{O}_1^{-1}(q)+B(q)\tilde{O}_1^1(q)\\&\quad+(2/\sqrt{3})[C_1(q)\tilde{O}_2^{-1}(q)+D(q)\tilde{O}_2^1(q)],\\ [\tilde{O}_2^{-1}(q),\ \mathcal{H}]&=A_2(q)\tilde{O}_2^{-1}(q)+B(q)\tilde{O}_2^1(q)\\&\quad+\tfrac{1}{2}\sqrt{3}[C_2(q)\tilde{O}_1^{-1}(q)+D(q)\tilde{O}_1^1(q)],\end{aligned} \tag{3.1}$$

where

$$\begin{aligned}A_1(q)&=\tfrac{1}{2}D\sin\theta-2\langle\tilde{O}_1^0\rangle[J(0)\cos^2\theta-J(q)\cos^2\tfrac{1}{2}\theta],\\A_2(q)&=\tfrac{1}{2}D\sin\theta-2\langle\tilde{O}_1^0\rangle[J(0)\cos^2\theta-J(q)\sin^2\tfrac{1}{2}\theta],\\B(q)&=-2\langle\tilde{O}_2^0\rangle J(q)\sin\theta,\\C_1(q)&=-\tfrac{1}{2}D+4\langle\tilde{O}_2^0\rangle J(q)\sin^2\tfrac{1}{2}\theta,\\C_2(q)&=-\tfrac{1}{2}D+4\langle\tilde{O}_2^0\rangle J(q)\cos^2\tfrac{1}{2}\theta,\\D(q)&=-\langle\tilde{O}_1^0\rangle J(q)\sin\theta,\end{aligned} \tag{3.2}$$

and the equation of motion of $\tilde{O}_2^{-2}(q)$ is

$$[\tilde{O}_2^{-2}(q),\ \mathcal{H}]=A_3(q)\tilde{O}_2^{-2}(q)+B_3(q)\tilde{O}_2^2(q), \tag{3.3}$$

where

$$\begin{aligned}A_3(q)&=-2\langle\tilde{O}_1^0\rangle[2J(0)-J(q)\sin^2\theta],\\B_3(q)&=2\langle\tilde{O}_1^0\rangle J(q)\sin^2\theta.\end{aligned} \tag{3.4}$$

The Green's functions, the correlation functions, and the order parameters $\langle \tilde{O}_1^0 \rangle$ and $\langle \tilde{O}_2^0 \rangle$ are calculated from these equations in the manner described in I, using the equal weight decomposition, Eq. (4.6) of I. The magnetic excitation energies of the dipolar modes $\omega_1(q)$ and $\omega_2(q)$ are given by the positive roots of the equation

$$\omega^4 - 2\omega^2\{\tfrac{1}{2}[A_1(q)^2 + A_2(q)^2] + C_1(q)C_2(q) - B(q)^2 - D(q)^2\} + \{[A_1(q)+B(q)][A_2(q)+B(q)] - [C_1(q)+D(q)][C_2(q)+D(q)]\} \times\{[A_1(q)-B(q)][A_2(q)-B(q)] - [C_1(q)-D(q)][C_2(q)-D(q)]\} = 0. \tag{3.5}$$

This can be combined with (2.14) to show that

$$\omega_1(0)\omega_2(0) = 0, \tag{3.6}$$

satisfying the Goldstone theorem, or physically, indicating that no torque is required to rotate the spin in the easy plane of the Hamiltonian (2.1). This supports the belief that the condition (2.14) is sound. Because of the RPA decoupling, (2.22) was not fulfilled except for above $T_C(\theta = \frac{1}{2}\pi)$, although $\langle \tilde{O}_2^2 \rangle$ is very small when computed from the correct combination of the Green's functions. The excitation energy of the quadrupole mode is

$$\omega_3(q) = [A_3(q)^2 - B_3(q)^2]^{1/2}. \tag{3.7}$$

The reader is cautioned that the algebra and terminology at present refers to pseudospin space. The quadrupole pseudospin mode (3.7) therefore corresponds to the longitudinal mode in the real space.

In order to obtain qualitative understandings about the excitation energies, we now assume

$$\langle \tilde{O}_1^0 + 2\tilde{O}_2^0 \rangle = 0. \tag{3.8}$$

This assumption reduces the present theory to the unrenormalized effective boson theory. In return the expression for the excitation energies becomes much more simplified. Below the phase transition temperature, the excitation energies are

$$\begin{aligned}
\omega_1(q) &= \frac{W+D}{2}\left[[1-\lambda(q)]\left(1-\lambda(q)\frac{W-D}{W+D}\right)\right]^{1/2},\\
\omega_2(q) &= \frac{W-D}{2},\\
\omega_3(q) &= W\left(1-\frac{D^2}{W^2}\lambda(q)\right)^{1/2},
\end{aligned} \tag{3.9}$$

where we have used a notation similar to that by Rainford[22]:

$$\begin{aligned}
D &= \tfrac{3}{2}B_2^0 \quad \text{(CEF splitting)},\\
W &= (D^2 + 4h^2)^{1/2},\\
h &= 2J(0)\sigma(T) + \gamma H \quad \text{(total internal field)},\\
\lambda(q) &= J(q)/J(0).
\end{aligned} \tag{3.10}$$

An inspection of the spectroscopic densities of the Green's functions show that $\omega_1(q)$ and $\omega_2(q)$ correspond to excitation energies for the transition from $|-1\rangle$ to $|0\rangle$, and from $|0\rangle$ to $|1\rangle$, respectively. As D is reduced to zero, the $\omega_1(q)$ mode makes a continuous transition to the spin wave, and the $\omega_2(q)$ mode to the molecular-field excitation, in agreement with the result obtained in I. The dispersions of the two dipolar modes, $\omega_1(q)$ and $\omega_2(q)$, are schematically shown in Fig. 2; the two modes cross each other without interaction.

In general, however, (3.12) does not hold below T_C. As a consequence, the two modes interact strongly in the crossover region, acquiring a mixed character (Fig. 2). The mode interaction occurs even at $T=0$, as will be displayed in Sec. IV. The origin of the mode interaction at $T=0$ is the fact (2.15) is not completely diagonal. In particular, the last term in (2.18) represents the off-diagonal exchange interaction, which is mainly responsible for levitating the ground state of the system above the MFA ground state through the zero-point fluctuation, just as in the case of antiferromagnets.[23] Even at $T=0$, therefore, the excited states in MFA are slightly populated and the order parameters, $\langle -\tilde{O}_1^0 \rangle$ and $2\langle \tilde{O}_2^0 \rangle$, are not fully saturated. This forthright indicates that *the unrenormalized effective boson theory is inaccurate even at* $T=0$, *since it fails to describe some subtle features of the excitation spectrum such as the mode-mode interaction.*

Because of the mode mixing, we now label the

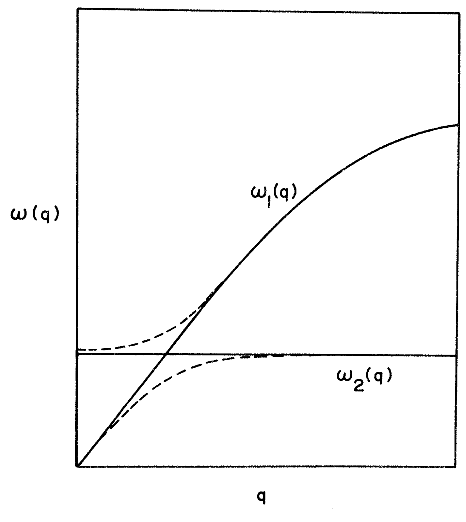

FIG. 2. Schematic dispersion relation for the cases when (3.12) is assumed (solid line), and when (3.12) is not assumed so that the two modes interact (dashed line).

upper branch $\omega_1(q)$ and the lower branch $\omega_2(q)$. The spin-wave character is now retained by $\omega_1(q)$ mode at high q, and by $\omega_2(q)$ mode at low q. Equation (3.20) is satisfied by $\omega_2(q=0)$ being constantly zero.

Finally we note, following the discussion of I, Sec. IV, that we have discussed the thermodynamics properties in terms of the dipolar modes for which RPA is appropriate. The quadrupolar mode is degenerate with the $\omega_1(q)$ mode in the paramagnetic regime. Therefore the detailed calculations of the softening behavior of $\omega_1(q)$ in Sec. IV apply equally to $\omega_3(q)$.

IV. NUMERICAL CALCULATIONS AND SOFT-MODE BEHAVIOR

It is possible to gain information about soft-mode behavior of the system from a further inspection of Eq. (3.5). Above the phase transition temperature T_C

$$\left.\begin{aligned}&\theta=\tfrac{1}{2}\pi,\\&\langle\tilde{O}_1^0+2\tilde{O}_2^0\rangle=0,\end{aligned}\right.\qquad (T\geqslant T_C)\qquad(4.1)$$

and $|0\rangle$, $|1\rangle$ are degenerate. The excitation energies are

$$\omega_1(q)=\omega_3(q)=D[1+(4\langle\tilde{O}_1^0\rangle/D)\,J(q)]^{1/2},\qquad(4.2)$$

$$\omega_2(q)=0.\qquad(4.3)$$

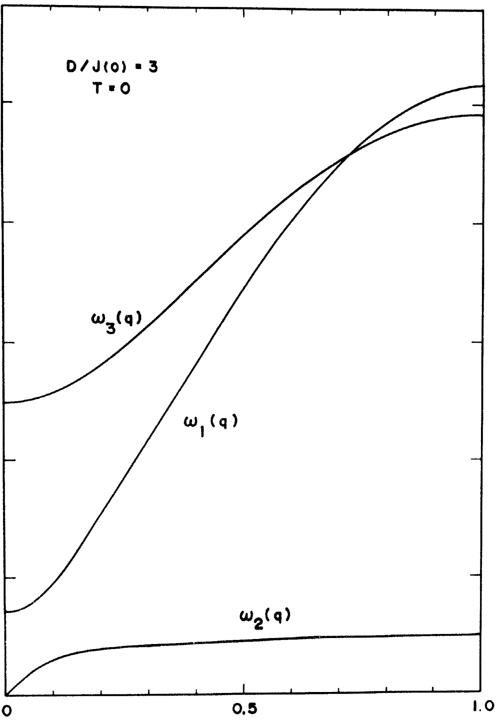

FIG. 3. Excitation energy dispersion relation at $T=0$, for $D/J(0)=3$.

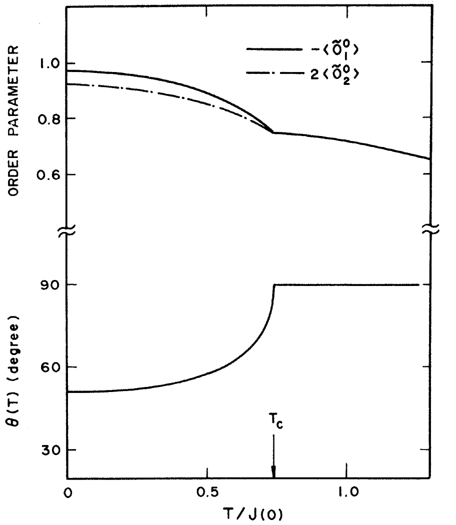

FIG. 4. Temperature dependence of the order parameters $\langle-\tilde{O}_1^0\rangle$, $2\langle\tilde{O}_2^0\rangle$, $\theta(T)$, for $D/J(0)=3$.

The $\omega_1(q)$ and $\omega_3(q)$ become soft at $q=0$, when

$$D=-4\langle\tilde{O}_1^0\rangle J(0).\qquad(4.4)$$

This soft-mode criterion is consistent with the ordering condition deduced from (2.14). It is particularly worthy to note that the phase transition temperature calculated from this soft-mode condition agrees, in the isotropic limit of $D\to 0$, with the result obtained in I for the isotropic ferromagnet,

$$\frac{kT_C}{J(0)}=\frac{4}{3}\,\frac{2}{1+F(-1)},\qquad(4.5)$$

where

$$F(-1)=\frac{1}{N}\sum_q\frac{J(0)}{J(0)-J(q)}.\qquad(4.6)$$

This result is obtained from any equivalent combinations of dipolar correlation functions to calculate the order parameter when $B_2>0$, but only from the equal-weight decomposition when $B_2<0$. Thus only the equal-weight decomposition gives the internally consistent results in the whole range of values for B_2.

Below T_C, the excitation energies of the zero-wave vector modes are

$$\begin{aligned}\omega_1(0)=2J(0)[\langle\tilde{O}_1^0\rangle^2(1+\sin^2\theta)\\+4\langle\tilde{O}_1^0\rangle\langle\tilde{O}_2^0\rangle\sin\theta]^{1/2},\end{aligned}\qquad(4.7)$$

$$\omega_2(0)=0,\qquad(4.8)$$

$$\begin{aligned}\omega_3(0)&=-4\langle\tilde{O}_1^0\rangle J(0)\cos\theta\\&=4\sigma(T)\,J(0).\end{aligned}\qquad(4.9)$$

Equation (4.1) may be combined with (2.13) and (4.4) to show that $\omega_1(0)$ and $\omega_3(0)$ also fall to zero at the Curie temperature. Thus it is evident that

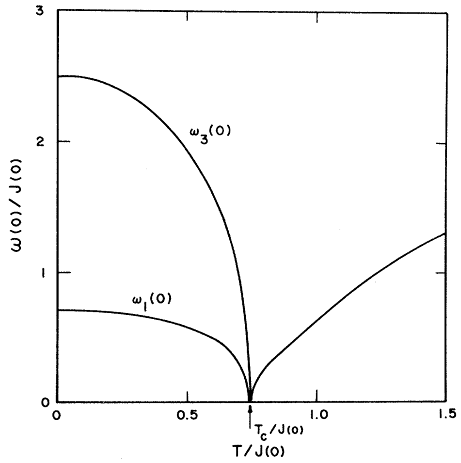

FIG. 5. Temperature dependence of $\omega_1(0)$ and $\omega_3(0)$. The two modes become soft at T_C and are degenerated above T_C.

$\omega_1(0)$ and $\omega_3(0)$ become soft at T_C.

Numerical calculations were undertaken to solve Eqs. (3.1)–(3.16) self-consistently subject to the approximations outlined in I. The excitation energy dispersion relations at $T=0$ and the temperature dependence of the order parameters are shown in Figs. 3 and 4, respectively, for $D/J(0)=3$. In Fig. 5 the temperature dependence of the zero wave vector dispersion relations is shown and the results confirm the above analysis, $\omega_1(q)$ and $\omega_3(q)$ becoming soft at T_C. The renormalization of the excitation energies at small and large wave vectors differs markedly, which is typical behavior for singlet-ground-state systems. Figure 6 shows the temperature dependence of the real magnetization in both RPA and MFA. Our results differ from the results of pseudoboson theory in that we find no abrupt change in the magnetization and that the phase transition is second order.

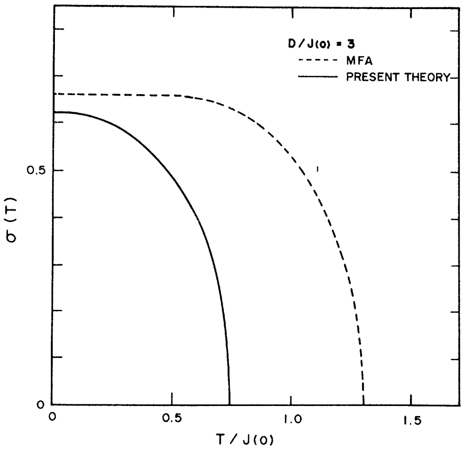

FIG. 6. Real magnetization $\sigma(T)$ as a function of temperature, calculated by the MFA and by the present theory.

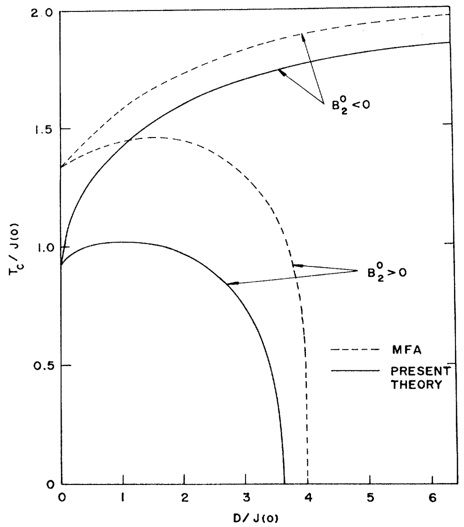

FIG. 7. Curie temperature $T_C/J(0)$ as a function of $D/J(0)$, calculated by the MFA and by the present theory, and compared to the case when $B_2^0<0$ (Paper I).

The phase transition temperature T_C was computed as a function of $D/J(0)$ (Fig. 7). The critical value of $D/J(0)$ is 3.62 and is 10% smaller than the value computed in MFA.

Finally, the renormalized dispersion relation $\omega_1(q)/J(0)$ and $\omega_3(q)/J(0)$ are shown in Fig. 8 for three ratios of $T/J(0)$ near $T=T_C$. The essential feature is that the temperature dependence of the

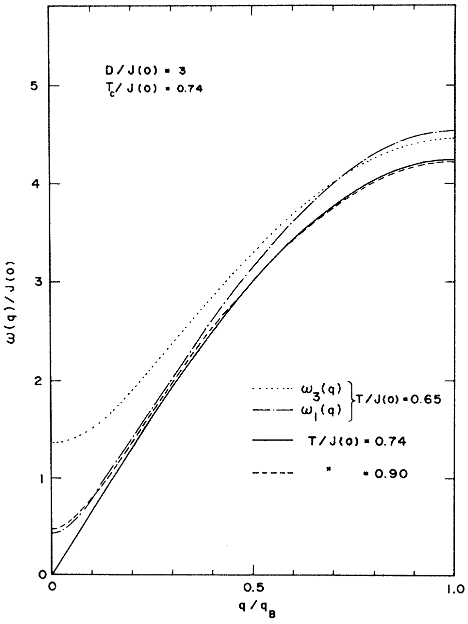

FIG. 8. Renormalized dispersion relation $\omega_1(q)/J(0)$ at, above, and below, the Curie temperature, for $D/J(0)=3$.

excitation energy is insignificant even in the neighborhood of T_C, except for the region of q space near the origin. This behavior contrasts with that of systems with a saturated moment in the CEF ground level and is a characteristic of induced-moment systems.[1,14,16] The small temperature dependence of the excitation energies, particularly of $\omega_1(q)$ mode, for all but small q values, makes the detection of mode softening by neutrons in elastic scattering experiments difficult.

The soft-mode problem may now be subject to more fundamental considerations. In Sec. II D the static susceptibility was related to the second derivative of $\langle\tilde{\mathcal{H}}(\theta)\rangle_d$. An inspection of (2.12) and (2.23) indicates that the Zeeman Hamiltonian has no diagonal matrix element when $\theta=\pi/2$, therefore the change in the density matrix due to the application of a small field at $T=T_C$ is of second order; critical spin fluctuations could not otherwise occur. The expansion

$$\langle\tilde{\mathcal{H}}(\theta+\delta\theta)\rangle_d=\langle\tilde{\mathcal{H}}(\theta)\rangle_d+\langle[\tilde{\mathcal{H}}(\theta),R]\rangle_d c\,\delta\theta +\langle[[\tilde{\mathcal{H}}(\theta),R],R]\rangle_d(c^2/2!)(\delta\theta)^2+\cdots, \tag{4.10}$$

where $c=\beta/\theta$ describes physically both static and dynamic processes. The first-order term in $\delta\theta$ represents the abstract torque that is set equal to zero by (2.20). The second-order term describes the curvature of the potential at equilibrium and is directly related to the static susceptibility by (2.28). The divergence of the longitudinal susceptibility at T_C implies

$$\langle[[\tilde{\mathcal{H}}(\theta),R],R]\rangle=0 \quad (T=T_C) \tag{4.11}$$

and, in general, when the Hamiltonian is diagonal

$$[\mathcal{H},\tilde{O}_2^2]=-\alpha\tilde{O}_2^2; \quad [\mathcal{H},\tilde{O}_2^{-2}]=\alpha\tilde{O}_2^{-2}, \tag{4.12}$$

therefore,

$$[\mathcal{H},\overline{O}_2^2]=-\alpha i\hat{O}_2^2; \quad [\mathcal{H},i\hat{O}_2^2]=\alpha\overline{O}_2^2, \tag{4.13}$$

where α is some coupling constant. Since $R=i\beta\hat{O}_2^2$, (4.11) implies that $\alpha=0$ if the Roth[24] prescription for decoupling many-body equations of motion is utilized. Therefore

$$[\tilde{\mathcal{H}},\overline{O}_2^2]=[\tilde{\mathcal{H}}\,\hat{O}_2^2]=0 \quad (T=T_C). \tag{4.14}$$

It follows that the zero wave vector $\overline{O}_2^2(q)$ and $\hat{O}_2^2(q)$ modes have zero frequency at the Curie temperature. We note from Eq. (2.12) that $\overline{O}_2^2(q)$ in pseudospace corresponds to $\tilde{O}_1^0(q)$ in real space when $\theta=\pi/2$. Consequently Eq. (4.14) implies a softening of the longitudinal mode, in real space, at the transition temperature.

V. CONCLUSION

The theory of the spin-tensor-operator Green's functions developed in I was applied to a system with a singlet CEF ground state. The optimum decoupling approximation is obtained via a unitary transformation which enables a change of representation within the framework of single-site theory. The parameter (θ) of the transformation was determined by a macroscopic thermodynamic criterion. Thus it was possible to extend the representation theory to finite temperatures. The theory was applied to the $S=1$ induced-moment magnet. The phase transition to the paramagnetic phase occurs when the ground state becomes a singlet with off-diagonal order. The transition was found to be second order and accompanied by soft-mode behavior.

Although the theory is thus far restricted to the magnet with spin 1, it is self-consistent and the essential characteristics of induced-moment systems are evident.

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