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Green's function theory of phase transitions in quadrupolar-coupled systems

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The method of two-time temperature-dependent Green's functions is applied to a quadrupolar-coupled quasi-Heisenberg system with the motivation to discuss the occurrence of two phase transitions in some rare-earth compounds. The hierarchy of equations of motion is terminated by means of some suitable decoupling approximations previously introduced by the author in connection with an isotropic biquadratic coupling system. Solution of the equation of motion yields the excitation spectrum of the system. The variation of the excitation spectrum for different values of the anisotropy parameter and the quadrupolar-coupling parameter is discussed. The possibilities of occurrence of different kinds of ordering are critically studied. It is seen that a pure dipolar ordering in which the system undergoes a second-order phase transition from a pure dipolar state to the paramagnetic state at a temperature T_d is not physically realizable. There may exist a pure quadrupolar ordering for which the system undergoes a second-order transition from a pure quadrupolar state to the paramagnetic state at a temperature T_Q. It was also found that there exists the possibility of occurrence of a mixed ordering which leads to two distinct phase transitions occurring at temperatures T_m and T_Q corresponding to magnetic and crystallographic transitions, respectively. The transition temperatures in these three cases are derived. It is seen that in the case of pure quadrupolar ordering the transition temperature is not much sensitive to quadrupolar coupling. Regarding the mixed ordering we find that the magnetic transition occurs at lower temperature. The theory is then applied to $DyVO_4$ and the agreement with the observed data is found to be satisfactory.

I. INTRODUCTION

Biquadratic coupling systems are now of current theoretical interest. They refer to the compounds which possess large unquenched orbital angular momentum so that they can be described by a Hamiltonian which consists of some high-degree interaction term in addition to the usual Heisenberg bilinear term.[1-6] According to the form of this high-degree interaction term, two general classifications can be made. One of these is the isotropic biquadratic coupling system which corresponds to the Hamiltonian[7-11]

$$H = -J_1 \sum_{\langle ij\rangle} (\vec{S}_i \cdot \vec{S}_j) - J_2 \sum_{\langle ij\rangle} (\vec{S}_i \cdot \vec{S}_j)^2 , \tag{1}$$

where J_1 is the Heisenberg bilinear exchange constant and J_2 is the so-called biquadratic exchange constant and the summation runs over all nearest-neighbor pairs i and j.

The other class refers to the anisotropic biquadratic coupling system.[12-14] This class includes all different forms of bilinear term and the biquadratic term. In this paper we consider the following typical combination:

$$\begin{aligned} H = -J \sum_{\langle ij\rangle} & [S_i^z S_j^z + \tfrac{1}{2}\eta (S_i^+ S_j^- + S_i^- S_j^+)] \\ & - \tfrac{3}{2}\alpha J \sum_{\langle ij\rangle} (Q_i Q_j) , \end{aligned} \tag{2}$$

where $Q_i = (S_j)^2 - \frac{1}{3}(S+1)S$, $\alpha = D/J$, D being a high-degree interaction parameter, J the bilinear exchange constant. The symbol η stands for the axial anisotropy. The second term in Eq. (2) is commonly called the quadrupolar coupling term in the literature.

The statistical-mechanical properties of the isotropic biaquadratic coupling system were studied in great detail by using a molecular-field approximation[8-11] and a Green's-function approximation.[15-24] From these studies two important facts were obtained. (i) This kind of system does not favor two second-order phase transitions. In particular, these sytems do not demonstrate a ferromagnetic-quadrupolar and quadrupolar-paramagnetic transition at two different temperatures provided these are both second-order transitions and also if the ground state is ferromagnetic. (ii) When the value of the parameter J_2/J_1 exceeds a certain critical value, the system demonstrates a first-order phase transition which provides a strong basis in understanding the first-order transition occurring in UO_2.[20]

There exists also quite a good number of discussions in the literature on different aspects of anisotropic biquadratic coupling systems. Sivardiere and Blume,[12] using the molecular-field approximation, studied a quadrupolar-coupled Ising system in order to have a satisfactory qualitative understand- of the magnetic and crystallographic transitions in $DyVO_4$. Sivardiere *et al.*[25] later discussed the general quadrupolar systems for all spins. Thorpe and Blume[26] and Liu and Joseph[27] treated a linear chain of isotropically coupled classical quadrupoles. Chen and Levy,[10] using the molecular-field approximation, treated the statistical mechanics of $S=1, \frac{5}{2}$ ferromagnets considering the uniaxial symmetry and special cases of cubic and axial symmetry. Sivardiere[13] made an intensive study on the appearance of elementary excitations in quadrupolar-coupled systems. Tanaka and Mannari[28] studied the statistical mechanics of the systems on the basis of the Husimi-Temperely model. The recent work of Iwashita and Urya[29] should also be mentioned. An elaborate discussion has been presented on the appearance of elementary excitations by Chiu-Tsao *et al.*[14]

Most of the methods presented by earlier authors to discuss the thermodynamic properties of biquadratic coupling systems of anisotropic type were largely based on the molecular-field approximation (MFA) which cannot be expected to provide any satisfactory qualitative understanding of the experimental situations since MFA does not take into account the spin correlations in proper manner. Barma[30] employed the Green's-function method using the quasiboson approximation and a proper decoupling approximation to obtain consistent excitation spectra for a typical anisotropic biquadratic coupling system. His decoupling deals with the situation where the dipolar ordering is absent even at $T=0$ K. Recently, attempts have been made to deal with such systems on the basis of the Green's-function diagrammatic technique, but these treatments are not at present capable of giving complete description of the statistical mechanics of the systems.

The purpose of the present paper is to develop a satisfactory Green's-function method with the chief motivation to discuss different aspects of phase transitions and the effect of quadrupole excitations on the spin-wave spectrum whose effective spins are coupled by the Hamiltonian (2). The use of the finite-temperature two-time Green's function in the present case leads, however, to the complicated problem of uncoupling the typical Green's function like $\langle\langle(S^z_g S^+_g + S^+_g S^z_g); S^-_m\rangle\rangle$. A method similar to that utilized by the author[17,20] in the case of isotropic biquadratic coupling system is used here with a new set of ground-state requirements appropriate for the problem. The three-spin bilinear Green's functions like $\langle\langle S^z_g S^+_f; S^-_m\rangle\rangle$ are decoupled by means of a new scheme introduced recently by the author[18] which reproduces the Padé-approximant results at the Curie temperature in a Heisenberg ferromagnet. The energy spectrum obtained from the linearized equation of motion is employed to derive the two transition temperatures T_m and T_Q corresponding to the magnetic and crystallographic transitions, respectively. The results are found to be satisfactory.

The paper is organized as follows. In Sec. II we present the formal aspects of the Green's function technique as applied to a quadrupolar-coupled system. The decoupling of higher-order Green's functions is done by procedure devised by the author. Section III gives us the excitation spectrum of the system. The excitation spectra for various combinations of η and α are critically studied. In Sec. IV a thorough discussion is presented regarding the appearance of several phases in the system. Section V is devoted to numerical estimates and the results of their application to $\mathrm{DyVO_4}$. Some critical remarks are made in Sec. VI.

II. GREEN'S-FUNCTION APPROXIMATION

The two-time thermodynamic Green's function is defined as

$$\begin{aligned} G(t-t') &= \langle\langle A(t); B(t')\rangle\rangle \\ &= -i\Theta(t-t')\langle[A(t), B(t')]\rangle , \end{aligned} \tag{3}$$

where $A(t)$ and $B(t')$ are two Heisenberg operators, the angular bracket $\langle X\rangle$ denotes the canonical ensemble average of the operator X, and the square bracket denotes the commutator. $\Theta(t-t')$ is the heaviside unit-step function having the property: $\Theta(t)=0$ for $t<0$, and 1 for $t>0$. The equation of motion for the Fourier-transformed Green's function is given by

$$E\langle\langle A; B\rangle\rangle_E = (1/2\pi)\langle[A,B]\rangle + \langle\langle[A,H]; B\rangle\rangle , \tag{4}$$

which when solved gives the energy spectrum of the system.

Before setting up the equation of motion and other mathematical formalities we derive the expression for the simple spin-wave energy using a boson transformation since it will be necessary for the construction of the ground-state requirements for the problem. One may utilize the transformation: $S^z_i = S - a^\dagger_i a$, $S^+_i = (2S)^{1/2} a_i$, $S^- = (2S)^{1/2} a^\dagger_i$, where $a^\dagger_i$ and a_i create and destroy bosons at the lattice site i, respectively. The transformed Hamiltonian becomes

$$H = 2J^r S \sum_{i,j,\Delta} \left(\delta_{ji} - \frac{\eta}{\epsilon}\ \delta_{j,i+\Delta}\right) a^\dagger_i a_j , \tag{5}$$

where $J^r = J\epsilon$, $\epsilon = 1 + \alpha S(2S-1)^2$, $\vec{\Delta}$ being the nearest-neighbor vector. It is to be noted that for the spin-$\frac{1}{2}$ case, $J^r = J$ and $\epsilon = 1$, and thus the system behaves like an anistropic bilinear ferromagnet, which may be compared with the situation occurring for a spin-1 isotropic biquadratic coupling ferromagnet. Equation (5) gives the simple spin-wave energy

$$E_k = 2J^r S z[1 - (\eta/\epsilon)\gamma_k] , \tag{6}$$

where $\gamma_k = (1/z)\sum_\Delta \exp(i\vec{k}\cdot\vec{\Delta})$, z being the number of nearest neighbors. The complete energy spectrum corresponding to the Hamiltonian (2) will be such that it reduces to Eq. (6).

The complete energy spectrum of the system will be obtained by solving the equation of motion for the two-spin Green's function $\langle\langle S_g^+; S_m^-\rangle\rangle$ which is

$$E\langle\langle S_g^+; S_m^-\rangle\rangle = \frac{\langle S_g^z\rangle}{\pi}\ \delta_{gm} + 2J\sum_f [\langle\langle (S_f^z S_g^+ + S_g^z S_f^+); S_m^-\rangle\rangle + \tfrac{3}{2}\alpha\langle\langle Q_f L_g^+; S_m^-\rangle\rangle_E] , \tag{7}$$

g and m being the lattice sites and

$$Q_f = (S_f^z)^2 - \tfrac{1}{2} C_0 ,$$

$$C_0 = \tfrac{2}{3}\ S(S+1) ,$$

$$L_g^+ = S_g^z S_g^+ + S_g^+ S_g^z .$$

Utilizing the author's procedure higher-order Green's functions are decoupled with the use of new set of ground-state requirements appropriate for the present problem. These requirements are (i) for a spin-$\frac{1}{2}$ lattice, one must have

$$1 + \lambda_1\langle S_g^- S_g\rangle + \lambda_2(\langle S_g^- S_g^+\rangle)^2 = 0;$$

(ii) for all spins, the energy spectrum must reduce to Eq. (6) as $T \rightarrow 0$ K. One thus obtains the solution of Eq. (7),

$$G_{gm}(E) = \frac{\langle S^2\rangle}{\pi}\ \frac{1}{N}\sum_k \frac{\exp[i\vec{k}\cdot(\vec{R}_g - \vec{R}_m)]}{E - E_k} , \tag{8}$$

where E_k stands for the temperature-dependent renormalized energy spectrum given by

$$E_k = 2zJmR(1 - t\gamma_k) , \tag{9}$$

with $m = \langle S^z\rangle$ and the symbols R and t are

$$R = 1 - a(1+\lambda)(C_0 - B - m - \eta f) + \tfrac{3}{2}\ \alpha B(1 + \lambda_1 + W + \lambda_2 W^2) ,$$

$$t = (1/R)[\eta + a(1+\lambda)(f - \eta W)] ,$$

$$W = C_0 - B - m ,$$

where $a = 1/2S^2$; λ, λ_1, λ_2 are the decoupling parameters; and f is Fourier transform of the spin correlation $\langle S_f^- S_g^+\rangle$.

It is now rather straightforward to obtain the expressions for the decoupling parameters λ_1 and λ_2. As $T \rightarrow 0$ K one should have $\lambda \rightarrow -1$. We utilize this value of λ so that the ground-state requirements when utilized in the energy spectrum yield the following expressions for λ_1 and λ_2

$$\lambda_1 = (2S+5)/(S+1) , \quad \lambda_2 = 6/(S+1) .$$

We, therefore, get $\lambda_1 = \frac{7}{2}$ and $\lambda_2 = 3$ for spin-1 case which may be compared with the values of λ_1 and λ_2 for the isotropic biquadratic coupling system: $\lambda_1 = \frac{13}{4}$ and $\lambda_2 = \frac{5}{2}$. Thus λ_1 is always greater than λ_2.

III. EXCITATION SPECTRUM

It is indeed possible to obtain some important information about any magnetic system from the study of the excitation spectra for various modes. This section presents a discussion on the possible influences of the axial anisotropy and the quadrupolar coupling on the qualitative and quantitative nature of the excitation spectra for a quadrupolar-coupled quasi-Heisenberg system. Barma[30] studied a biquadratic coupling system with a general Hamiltonian and developed the method of Green's functions which are constructed by quasiboson operators. His method introduces a decoupling which also involves two unknown parameters. He assumes one of these parameters to be zero due to the fact that the system does not favor dipolar ordering. In this manner the consistent excitation spectra were obtained. However, in more general cases, dipolar ordering does not vanish and in that situation it seems rather difficult to obtain proper values for the two decoupling parameters occurring Barma's treatment.

In recent years, attempts have been made to develop a suitable Green's function diagrammatic technique which has the spirit of reproducing accurate excitation spectra for any magnetic system. In a series of papers, Yang and Wang[31] developed such a technique which they applied to several problems of magnetism. Westwansky[32] and Westwansky and Skrobis[33] attempted to construct a proper diagrammatic technique on the basis of a Wick-like theorem.[34] But it must be admitted that it has not become possible at this state to obtain even satisfactory quantitative results from Green's-function diagrammatic technique.

On the other hand, the present Green's-function method is not only able to provide consistent excitation spectra, but also much qualitative and quantitative information regarding the phase transitions occurring in the system.

The excitation spectra for a spin-$\frac{3}{2}$ bcc lattice are shown in Figs. 1 and 2. The figures demonstrate some interesting results. First, it is quite readily seen that the effect of quadrupole coupling is simply to alter the size of the dispersion for a particular value of the anisotropy. It is relevant to mention that this result is also found to occur in the case of isotropic biquadratic coupling system; in that case, the dispersion curve shifts by the factor $1+2bS(S-1)$, where $b=J_2/J_1$ is called the biquadratic parameter. The magnitude of the shift in the case of quadrupolar-coupled system is not so simply related to the quadrupolar coupling parameter α. It is nevertheless evident that the magnitude of the shift decreases with the increase of α. A trivial fact to be noted is that for spin-$\frac{1}{2}$ case the quadrupolar coupling has no effect on the dispersion curves. Second, it is seen that there exists a limiting value of α for which the excitation spectrum shows singularities. As α approaches this value, the dispersion curve tends to graze along the Brillouin-zone boundary. For a spin-$\frac{3}{2}$ bcc lattice this limiting value has been found to be -1.3 if $\eta=1$. Beyond this value no spin-wave excitation is possible. Consequently, the system does not have any magnetic ground state. The limiting value of η is found to depend on the anisotropy η: as η decreases this value increases. Third, it is interesting to note that some negative α may create a probable situation for the existence of Goldstone modes even in the presence of axial ansiotropy. This is clearly demonstrated in Fig. 2. This result may have some qualitative correspondence to the experimental situations occurring in several Jahn-Teller systems which, although prossessing a large anisotropy, are found to have an accoustical branch of excitation and hence a Goldstone mode.[13] It may be noted that in such cases the role of the quadrupole coupling is simply to renormalize the bilinear exchange constant; that is, the system behaves like an isotropic Heisenberg ferromagnet with the exchange constant being properly renormalized by the quadrupolar coupling and the axial anisotropy. Last, we should mention that the study of the excitation spectra may also provide the quantitative measures of different physical parameters of the system. We shall come to this point again in Sec. V D in studying the excitation spectrum for DyV$_{04}$.

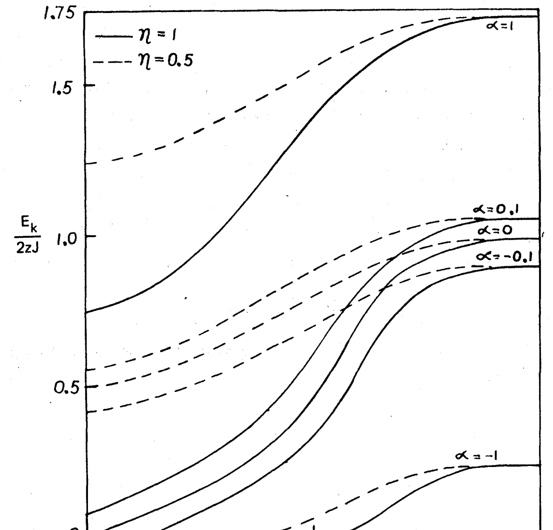

FIG. 1. Excitation spectra for a spin-$\frac{3}{2}$ body-centered-cubic lattice for various modes in the first Brillouin zone. The solid curves refer to $\eta=1$ and the dashed curves refer to $\eta=0.5$. The curves are drawn for five values of the biquadratic coupling parameter.

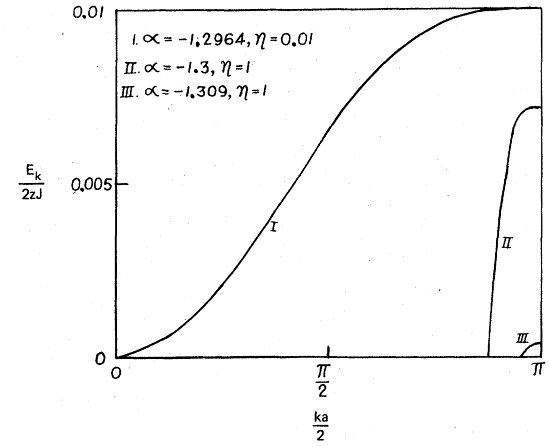

FIG. 2. Excitation spectra for a spin-$\frac{3}{2}$ body-centered cubic lattice. Curve *I* represents the excitation branch for a typical combination of α and η such that the system possesses a Goldstone mode. Curves II and III refer to the case $\eta=1$ showing the occurrence of a limiting value of α for which the excitation just grazes the Brillouin-zone boundary.

IV. PHASE TRANSITIONS

The occurrence of different possible phases in the present class of compounds becomes complicated in view of the appearance of two different ordering parameters m and B in the theory. We have already observed such complications while dealing with the similar aspects in the case of an isotropic biquadratic coupling system. In the present situation one finds likewise three different possibilities of occurrence of phases in the system. First one may consider a pure dipolar ordering which corresponds to the situation $m\neq 0$, $B=0$ so that no quadrupolar ordering occurs. [It may be recalled that B is the quadrupolar ordering parameter and stands for $B=(S^z)^2-\frac{1}{3}S(S+1)$; the existence of a quadrupolar ordering is specified by the condition $B\neq 0$]. In this situation it is possible to conceive only one transition—the system undergoes a transition from a pure dipolar state to the paramagnetic state a temperature T_d. Second, one may consider a pure quadrupolar ordering corresponding to the situation $m = 0$, $B \neq 0$ so that in this case no dipolar ordering appears in the system. The corresponding transition from a quadrupolar state to the paramagnetic state may either be second order or first order and the temperature at which this transition occurs may be identical with or different from the dipolar transition temperature T_d. Third, one may consider a case of mixed ordering which corresponds to the situation $m \neq 0$, $B \neq 0$. This type of ordering leads to two distinct phase transtions under certain circumstances. We discuss below the three kinds of orderings separately.

A. Pure dipolar ordering

Pure dipolar phase and its associated transition have already been discussed in connection with the biquadratic-exchange problem and the transition temperature in the present case can be derived in a similar manner. The result is

$$\tau_d = k_B T_d / zJ = C_0 R_d / F(t_d)\,, \tag{10}$$

where R_d, t_d are the expressions for R, t at $m = 0$ and T_d is the dipolar transition temperature (or Curie temperature). Ignoring certain smaller terms one can simplify the above equation to the following form

$$\tau_d = \frac{C_0}{F(\eta)} \left\{ (1-x) \Big/ \left[1 - \left(\frac{x}{1-x} \right) \frac{F(\eta)-1}{F(\eta)} \right] \right\}, \tag{11}$$

where $x = aC_0(1+\lambda)$.

It is necessary to make some critical remarks about the situation mentioned which leads to a pure dipolar ordering. Although a transition temperature has been derived above and in a previous paper while dealing with an isotropic biquadratic coupling system, one may argue that the situation which corresponds to the condition $m \neq 0$, $B = 0$ cannot be possible. Since at $T = 0$ K one gets $m = S$, the equality $B = 0$ cannot be possible. This is true even if α goes to zero. Therefore, a nonzero B must appear at some temperature. The renormalization-group calculations of Wegner[35] confirm that B is nonzero below the Curie temperature. This result also follows from molecular field calculations. Hence, one cannot have a phase in which $m \neq 0$, $B = 0$, and the calculation of the transition temperature presented above is only of theoretical interest.

B. Pure quadrupolar ordering

We now find the possibility of occurrence of a pure quadrupolar phase which corresponds to the situation $m = 0$, $B \neq 0$. This is, indeed, true that one finds it possible to arrive at this typical situation. But in this case the system undergoes a single transition. The transition occurs from a pure quadrupolar state to the paramagnetic state. The temperature at which this transition occurs may easily be found. One finds that the expression for B can be written

$$B = C_0 - \frac{m}{N} \sum_k \coth(\tfrac{1}{2}\beta E_k)\,. \tag{12}$$

We utilize the expression for the energy spectrum and substitute $m = 0$. In the resulting equation we take the limit $B \to 0$ which thus gives the following expression for the transition temperature at which the system undergoes the phase transition from a pure quadrupolar state to the paramagnetic state:

$$\tau_Q = k_B T_Q / zJ = C_0 R_Q / F(t_Q)\,, \tag{13}$$

where R_Q and t_Q are the expressions for R and t in the limit $B \to 0$.

Equation (13) is a complicated one. Ignoring certain smaller terms as done in the case of τ_d one can easily show that τ_Q is identical to τ_d. It is thus found that τ_d is not very sensitive to the quadrupolar coupling. It may be argued in this context that this result is caused by the decoupling approximations utilized inthe theory. In fact, the random-phase approximation decoupling for

$$\langle\langle Q_f (S^z_g S^+_g + S^+_g S^z_g)\,;S^-_m \rangle\rangle \to \langle Q_f \rangle \langle\langle (S^z_g S^+_g + S^+_g S^z_g); S^-_m \rangle\rangle$$

may be responsible for the occurrence of this result. It may be anticipated that a small dependence of τ_Q on α may be generated by taking into consideration the interspin correlations in this decoupling approximation. But it is undoubtedly an impossible task to make even a guess about this correlation term in view of the present status of our knowledge regarding the Green's-function decoupling. In spite of this one may be unambiguous in admitting the fact that this term, even if found accurately, cannot be very large compared to the dominant term involving $\langle Q_f \rangle$. It may, however, be felt in general, that the dependence of τ_Q on α may be generated from a second-order Green's-function calculation which involves further taking in the equations of motion of the Green's functions $\langle\langle S^z_g S^+_f ; S^-_m \rangle\rangle$, $\langle\langle S^z_f S^+_g ; S^-_m \rangle\rangle$, and $\langle\langle (S^z_g S^+_g + S^+_g S^z_g); S^-_m \rangle\rangle$. The calculations have been carried out in this fashion, but the result showed that τ_Q remains almost independent of α.

C. Mixed ordering

The most interesting and physically realizable situation is created when the system exhibits a mixed ordering in which the low-temperature states of the system are populated both by magnons and quadrons (quadrupole excitations) with equal significance so that neither the dipole ordering parameter nor the quadrupole ordering parameter goes to zero. Evidently, in such cases the ground state happens to be complicated and hence it becomes a difficult task to made a complete study of the thermodynamics of such ordering. To examine the simplest case we assume that the ground state is still ferromagnetic. To investigate the simultaneous thermal evolution of m and B from a ferromagnetic ground state one should note, in the first place, that a situation may, in general, arise where m and B do not go to zero at the same temperature, thus giving rise to an intermediate quadrupolar phase. One finds, therefore, the possibility of occurrence of three different phases: a mixed or true ferromagnetic phase F; a quadrupolar phase Q, and a paramagnetic phase P. The phase transitions can be considered in two different ways: (i) true ferromagnetic → pure quadrupolar → paramagnetic, (ii) true ferromagnetic → pure dipolar → paramagnetic. Evidently, the second possibility does not arise because it goes through a pure dipolar phase which is not physically realizable.

The problem is now reduced to one of calculating two transition temperatures T_m and T_Q, where FQ and QP transitions occur, respectively. The expression for T_Q has been derived earlier and that for T_m may be obtained in the manner T_d was obtained. The result is

$$\tau_m = \frac{k_B T_Q}{zJ} \simeq \frac{C_0}{F(\eta)} \left\{ f(B) \Big/ \left[1 - \frac{x}{f(B)} \left(\frac{F(\eta) - 1}{F(\eta)} \right) \right] \right\}, \tag{14}$$

where $f(B)$ is a polynomial in B given by

$$f(B) = \epsilon_0 + \epsilon_1 B - \epsilon_2 B^2 + \epsilon_3 B^3 ,$$

$\epsilon_0, \epsilon_1, \epsilon_2, \epsilon_3$ being given by the expressions

$$\epsilon_0 = 1 - x ,$$

$$\epsilon_1 = a(1+\lambda) + (\tfrac{3}{2})\alpha(1 + \lambda_1 C_0 + \lambda_2 C_0^2) ,$$

$$\epsilon_2 = \tfrac{3}{2}\alpha(1 + 2C_0\lambda_2), \quad \epsilon_3 = \tfrac{3}{2}\alpha\lambda_2 .$$

It may be noted that if one takes the limit $B \to 0$ further, Eq. (14) reduces simply to Eq. (13), thus representing the transition from a pure quadrupolar state to the paramagnetic state. One should, however, note that for physically realizable τ_m the necessary condition is $R > 0$ which also makes $T_Q - T_m$ positive, the latter condition being a necessary one for the QP transition to become an intermediate one. A little inspection will reveal the fact that under some circumstances R may be greater than zero. The consideration of a quadrupolar-coupling term to the usual dipolar term is thus found to lead to two separate but closely coupled phase transitions.

V. APPLICATION TO DYSPROSIUM VANADATE

We have seen in Sec. IV that under certain conditions a quadrupolar-coupled system may demonstrate two second-order phase transitions, one at T_m which may be identified as the magnetic transition and the other at T_Q which may be characterized as the crystallographic transition. This general qualitative result agrees with the experimentally observed transitions in certain rare-earth compounds such as $DyVO_4$, $TbVO_4$, $TbPO_4$, $TmAsO_4$, etc.[36-40] However, when one compares the results quantitatively one becomes embarrassed with the unpleasant feature that except for $DyVO_4$ the chosen Hamiltonian differs considerably. Furthermore, the requisite observed data for all such compounds (with the exception of $DyVO_4$) are not sufficient for the estimation of the important parameters of the theory such as J, α, B, etc. We therefore consider the application of our theorectical result to $DyVO_4$ of which sufficient data are available. We must, however, mention that $DyVO_4$ undergoes an antiferromagnetic transition at 3.07 K and therefore the model Hamiltonian cannot be applied as such. Fortunately it may be noted that all Green's-function calculations (using the same decoupling) for a ferromagnet[41] or an antiferromagnet[42] lead to identical expressions for the transition temperatures.

For the numerical estimates of the quantities which are our consideration it is first necessary to find out the experimental values of different physical parameters appearing in the theory. These are J, α, B, $f(B)$, and η and it is well known that no accurate theoretical methods exist to calculate these parameters. We make use of the experimental data for the evaluation of these parameters. To begin with, we take into consideration that for $DyVO_4$ the axial anisotropy is very large so that the anisotropy parameter is almost zero.

A. Ground-state energy

The ground-state energy of the spin system satisfying our spin-Hamiltonian can be readily shown to have the form

$$|E_0| = \tfrac{1}{2} z\, |J|\, (S^2 + \tfrac{3}{2}\, \alpha C_0^2) . \tag{15}$$

The absolute values are taken due to the fact that we are working with an antiferromagnetic lattice.

Cooke *et al.*[35] found that $|E_0|/k_B \simeq 2.518$ and therefore one obtains from Eq. (15),

$$|J/k_B|(1 + 4.16\alpha) = 0.56 . \tag{16}$$

Below, we shall find another equation involving α and J/k_B from the specific-heat data.

B. Specific heat near T_m

Specific heat of a spin system is obtained from the first temperature derivative of the internal energy and it is very difficult to calculate it over a large range of temperatures using the first-order Green's-function theory. However, one can readily find the specific heat near T_m. We calculate it from the following expression for internal energy

$$|E| = \tfrac{1}{4}zN|J|(1+2\eta)\langle S_i^+ S_j^-\rangle + \tfrac{3}{4}zN\alpha|J|B^2. \tag{17}$$

We consider the external magnetic field H_0 applied along the $+z$ direction so that the energy spectrum becomes

$$E_k = h + 2zJmR(1 - t\gamma_k), \tag{18}$$

where $h = g\mu_B H_0$ with usual meaning.

One, therefore, finds in the quadrupolar region

$$B = C_0 - \frac{2}{\beta N}\sum_k \frac{1}{1/\chi + 2zJR(1 - t\gamma_K)}, \tag{19}$$

$$\langle S_i^+ S_j^-\rangle = \frac{2}{\beta N}\sum_k \frac{\gamma_k}{1/\chi + 2zJR(1 - t\gamma_k)}, \tag{20}$$

where $\chi = m/h$ is the reduced susceptibility.

We therefore get, in the vicinity of T_m,

$$\frac{|E|}{Nk_B} = \frac{1}{4}\left(\frac{1+2}{\eta}\right)[F(\eta) - 1]T + \tfrac{3}{4}C_0\alpha z\frac{|J|}{k_B} - \tfrac{3}{2}\alpha C_0 T F(\eta) + \tfrac{3}{4}\alpha T^2 \frac{k_B}{|J|z}[F(\eta)]^2. \tag{21}$$

Considering the fact that for linear, square, and cubic lattices

$$\frac{1}{N}\sum_k \gamma_k^2 = \frac{1}{z}, \quad \frac{1}{N}\sum_k \gamma_k^4 = \frac{3(z-1)}{z^3}, \quad \text{etc.},$$

one finds for small η,

$$F(\eta) \simeq 1 + \eta^2/z + 3\eta^4(z-1)/z^3.$$

Since for $DyVO_4$, $\eta \simeq 0$, one has $F(\eta) \simeq 1$ and $[F(\eta) - 1]/\eta = 0$. Therefore, the specific heat near T_m is

$$|C_H|/Nk_B \simeq 1.147\alpha/|J/k_B| - 3.75\alpha. \tag{22}$$

Cooke *et al.* found

$$|C_H|Nk_B \simeq 0.24 + 0.072(T/T_m) \text{ (to order } T). \tag{23}$$

Near T_m this is equal to 0.312 and thus Eq. (22) yields the relation

$$|J|/k_B(1 + 12.02\alpha) = 3.67\alpha. \tag{24}$$

C. Numerical estimates

It is now straightforward to obtain the values of α and $|J|/k_B$. Solving Eqs. (16) and (24) one gets

$$\alpha \simeq -0.116, \quad |J|/k_B \simeq 1.08 \text{ K}.$$

Using these values of α and $|J|/k_B$ we shall now calculate the values of two other important parameters, B and $f(B)$. For this we utilize the equations for B and $f(B)$ whence we get

$$B \simeq 0.115, \quad f(B) \simeq 0.4.$$

We thus see that B is not zero at T_m which is the expected result. This result also shows that beyond T_m a pure quadrupolar phase can exist.

Utilizing the values of all the required parameters mentioned above we obtain the following estimates for the transition temperatures:

$$T_m \simeq 4.2 \text{ K}, \quad T_Q \simeq 11.2 \text{ K},$$

which agree satisfactorily with the experimental values of T_m and T_Q obtained by Cooke *et al.*: $T_m = 3.07$ K, $T_Q = 14$ K.

In addition to the numerical estimates of the parameters stated above one can calculate another physical quantity—the internal energy at T_m. The result is $E(T_m) \simeq -1.983$ K which may be compared with the observed value $E(T_m) \simeq -1.922$ K. The result is thus quite satisfactory.

D. Excitation spectrum for $DyVO_4$

We now examine the excitation spectrum for $DyVO_4$ in light of the discussions presented earlier for a general quadrupolar system. The compound has the effective spin $S = \frac{3}{2}$ and the interaction parameters $\alpha = -0.116$, $|J|/k_B = 1.08$ K as estimated above along with the fact that it possesses a square lattice. We have drawn several branches for a spin-$\frac{3}{2}$ square lattice for different values of the anisotropy parameter η. The general features which are evident from Fig. 3 are: (i) the excitation spectrum is very sensitive to the axial anisotropy and (ii) as η decreases from unity the excitation spectrum shifts upward. To find the particular branch which may correspond to $DyVO_4$, we choose that value of η which reproduces the ground-state energy. We find that the branch of excitation which corresponds to $\eta = 0.051$ reproduces approximately the ground-state energy as obtained by Cooke *et al.* Consequently, this branch may be regarded as that for $DyVO_4$. It is nevertheless important to note that this branch does not indicate the existence of a Goldstone mode. It is, in fact, true that a highly anisotropic crystal like $DyVO_4$ does not have Goldstone modes. However, Fig. 3 shows that in a quadrupolar-coupled quasi-Heisenberg system of the present type the

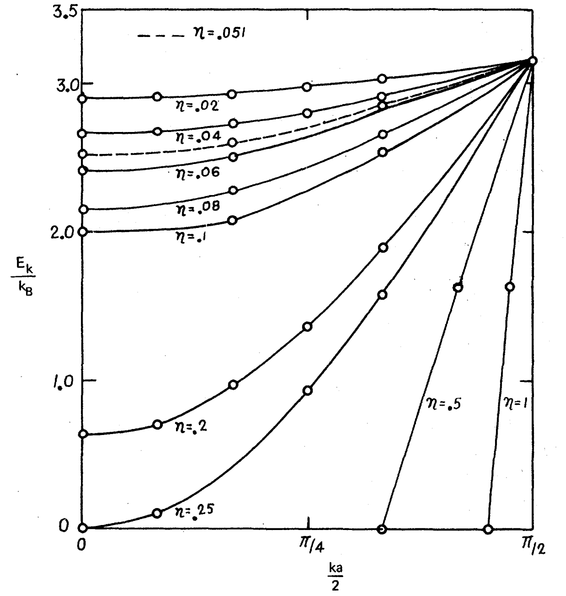

FIG. 3. Excitation spectra for a spin-$\frac{3}{2}$ square lattice considering $\alpha=-0.116$, $|J/k_B|=1.08$ K which correspond to $DyVo_4$ as obtained from the present approach. Various curves are drawn for different values of the anisotropy parameter η. The dashed curve refers to $\eta=0.051$ which may correspond to the excitation spectra for $DyVo_4$. It is seen that a Goldstone mode appears for $\eta=0.25$.

Goldstone modes may occur for some particular value of the anisotropy parameter. This value is found to be $\eta=0.25$.

It may be remarked that the value of η obtained above for $DyVO_4$ may change our numerical estimates for the transition temperatures and the physical parameters like B, $f(B)$, etc. But the calculations show that this change is not perceptible mainly due to the fact that the Watson sum $F(0.051)$ is not much different from unity, which was our approximation.

VI. CONCLUDING REMARKS

A simple Green's-function theory has been developed in the preceding sections to discuss the thermodynamic properties of rare-earth compounds which show two different phase transitions. The theory can be extended to more-complex systems showing multiple phase transitions for which more than two order parameters are to be employed, but this extension evidently involves many mathematical complications. It is, however, important to point out the fundamental necessity in framing up a satisfactory theory for the present class of compounds is the basic Hamiltonian which should have a form properly corresponding to the real crystallographic configuration. Consequently, one must feel it indispensable to utilize the well-known Pytte-Stenvens model[43] along with suitably extended form of Sivardiere[44] in order to develop an accurate spin Hamiltonina for any particular compound.

In addition to this, we mention the recent work of Tanaka and Mannari[28] who studied a quadrupolar-coupled Ising system on the basis of Husimi-Temperely model.[28] These two authors observed that a ferromagnetic transition is first order for $1>\alpha\geq 0.5$ and is second order for $\alpha\geq 1$. They also noted that if T_d is the transition temperature corresponding to a ferromagnetic-paramagnetic transition and T_Q be the transition temperature corresponding to a quadrupolar-paramagnetic transition, then the paramagnetic susceptibility above T_d for $\alpha>0.5$ and above T_Q for $\alpha<0.5$ obeys the Curie-Weiss form. The present Green's-function approach does not, however, reproduce the results. Investigations in this regard are necessary.

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