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Mean-field solution of a spherical model for Heisenberg spins with complicated coupling

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Mean-field solution of a spherical model for complicated magnetic systems is presented. The magnetic systems include those which favor dipolar, quadrupolar, and biaxial ordering. We employ a Lagrange multiplier method to calculate the partition functions of the systems and hence the expressions for the ordering parameters. The phase transitions of the model systems are studied and the results are compared with those obtained by earlier approximation methods.

I. INTRODUCTION

It is well known that a lattice of Heisenberg spins coupled with the usual bilinear interaction and various higher-degree interactions disposes a considerably complicated mathematical problem which is not easily solvable. However, many fruitful attempts were made in the last decade to employ different approximation methods for the study of the thermodynamic properties of the systems.[1-10] For example, we mention two main approaches, one due to the molecular-field approximation[2,3] (MFA) and other due to the Green-function approximation[4-9] (GFA). MFA overestimates the important aspect of spin correlations and in GFA one has to allow the arbitrariness of the decoupling schemes. In addition to these intrinsic faults, these methods lead to complicated expressions for the order parameters. Such limitations were also noticed in other methods. In the literature no attempt was made to deal with the above problems from the viewpoint of the spherical-model transcription.[11]

The purpose of the present paper is to study the statistical mechanical properties of a spherical model for Heisenberg spins coupled by various types of interactions.[2,3,12-15] The original spin system is replaced by a spherical model in which the spins are assumed to be distributed over the surface of a hypersphere in 3N-dimensional space, N being the total number of spins in the original system. The spherical constraint prescribed by such an approximation is complicated and it is very difficult to obtain an exact solution. A mean-field approximation is, therefore, employed along with a Lagrange multiplier method for the simplification of the partition function of the systems. The method was first employed by Vertogen and Van der Meyer[16] in connection with an analytical study of Meyer and Lubensky's model[17] for nematic and smectic liquid crystal phases. The method provides a very simple way of arriving at the desired expressions for different ordering parameters. The expressions are rather simple and easily computable.

The plan of the paper is as follows: Sec. II presents a brief description of the spherical model and the method of calculating the partition function. In Sec. III a uniaxial Heisenberg ferromagnet with dipolar and quadrupolar exchange is studied. The expressions for the ordering parameters and the specific heat are studied. Section IV deals with a uniaxial ferromagnet with dipolar, quadrupolar, and three-atom interactions. In Sec. V we study the phase transitions in rare earths which can be described by a Sivardiere Hamiltonian. The paper ends with some concluding remarks in Sec. VI.

II. SPHERICAL MODEL

The spherical model for an Ising system was first proposed and solved by Berlin and Kac.[11] In this model the original spin system is replaced by a configuration in which the spins are assumed to be arranged on the surface of a hypersphere in 2N-dimensional space, N being the total number of spins in the original spin pattern. In this model, the spins are coupled by the Ising interaction and the equation of the hypersphere is

$$S_1^2+S_2^2+\cdots+S_N^2=N\ , \tag{1}$$

where S_i represents the z component of the ith spin. Equation (1) is called the spherical constraint for the Ising model.

If the spins are coupled by a Heisenberg interaction we have to consider the three components S_{ix}, S_{iy}, and S_{iz} for each spin at the lattice site i. The spin components are connected by the usual relation

$$S_{ix}^2+S_{iy}^2+S_{iz}^2=a \ , \tag{2}$$

where $a=S(S+1)$, S being the spin quantum number.

Equation (2) describes a sphere of radius $a^{1/2}$ in three-dimensional Cartesian space. Since there are N spins in total, we can conceive a hypersphere in $3N$-dimensional space described by

$$\sum_{i=1}^{3N} S_i^2=Na \ . \tag{3}$$

The radius of the hypersphere is now $\sqrt{Na}$ which depends on the spin quantum number unlike the sphere described by Eq. (1). Equation (3) is the spherical constraint for the spherical spin configuration of the Heisenberg system.

Let H be the Hamiltonian for the Heisenberg spins coupled by various types of desirable interactions. The partition function may thus be calculated from the following expression:

$$Q_N(H)=\prod_{i=1}^{N}\left[\int_{-\infty}^{\infty} d^3S_i \exp(-\beta H)\right] . \tag{4}$$

Since the forms of H considered in the present paper are complicated it is very difficult to obtain the exact solution of the problem even within the spherical approximation.

Following Vertogen and Van der Meyer[16] we employ a mean-field approximation for the simplification of the Hamiltonian. Such an approximation involves the following decoupling of the operator product:

$$AB=A\langle B\rangle+B\langle A\rangle-\langle A\rangle\langle B\rangle \ , \tag{5}$$

where the fluctuations $A-\langle A\rangle$ and $B-\langle B\rangle$ are ignored. With the use of Eq. (5) the products like $S_{ix}S_{jx}$ and other higher-order terms appearing in H are decoupled. In this way the original Hamiltonian H is replaced by a mean-field Hamiltonian H_m.

With the use of the above mean-field Hamiltonian, H_m and the spherical constraint described by Eq. (3) one can simplify Eq. (4) by the Lagrange multiplier method. One gets

$$Q_N(H_m)=\prod_{i=1}^{N}\int_{-\infty}^{\infty} d^3S_i \exp\left[-\beta H_m-\beta\lambda\left[\sum_{i=1}^{3N} S_i^2-Na\right]\right] . \tag{6}$$

The above expression is utilized to get the free energy f of the system governed by any particular Hamiltonian. The parameter λ is determined or eliminated (as is desired) from the equations obtained from the equilibrium conditions

$$\frac{\partial f}{\partial\lambda}=0, \ \frac{\partial f}{\partial\theta}=0 \ , \tag{7}$$

where θ stands for the ordering parameters of the system.

III. UNIAXIAL FERROMAGNET WITH DIPOLAR AND BIQUADRATIC INTERACTIONS

We consider the Hamiltonian[1–8]

$$H=D\sum_i S_{iz}^2-J\sum_{\langle ij\rangle}(\vec{S}_i\cdot\vec{S}_j)-K\sum_{\langle ij\rangle}(\vec{S}_i\cdot\vec{S}_j)^2 \ , \tag{8}$$

where D is the single-ion anisotropy, and J and K are the nearest-neighbor bilinear and biquadratic exchange constants. The summation runs over nearest-neighbor pairs i and j.

With the use of Eq. (5) we get the following expression for the mean-field Hamiltonian H_m:

$$H_m=\sum_{i=1}^{N}\sum_g \{N(JM_g^2+KQ_g^2) -[2JM_gS_{ig}+(2KQ_g-D\delta_{gz})S_{ig}^2]\} \ , \tag{9}$$

where

$$g=x,y,z, \ \ M_g=\langle S_g\rangle, \ \ Q_g=\langle S_g^2\rangle \ .$$

Equation (4) therefore takes the following form:

$$Q_N(H_m)=\exp\left[\lambda\beta Na-N\beta\sum_g(JM_g^2+KQ_g^2)\right] \times\prod_{i=1}^{N}\int_{-\infty}^{\infty} d^3S_i \exp\left[-\sum_{i,g}[\beta(\lambda+D\delta_{gz}-2KQ_g)S_{ig}^2-2\beta JM_gS_{ig}]\right] . \tag{10}$$

The free energy of the configuration is thus

$$\begin{aligned}F&=-\frac{N}{\beta}\ln Q_N(H_m)\\&=-N\lambda a+N\sum_g(JM_g^2+KQ_g^2)\\&\quad-\frac{1}{\beta}\ln\left[\prod_{i=1}^{N}\int dS_{ix}dS_{iy}dS_{iz}\phi_x\phi_y\phi_z\right],\end{aligned}\tag{11}$$

where

$$\begin{aligned}\phi_g&=\exp[A_gS_{ig}-(B_g+D\delta_{gz})S_{ig}^2],\\A_g&=2\beta JM_g,\\B_g&=\beta(\lambda-2KQ_g).\end{aligned}$$

With the use of the integral

$$\int_{-\infty}^{\infty}dx\,\exp[-(Bx^2-Ax)]=(\pi/B)^{1/2}\exp(A^2/4B),\tag{12}$$

we get the following expression for free energy per spin:

$$\begin{aligned}f&=-\lambda a+\sum_i(JM_i^2+KQ_i^2)\\&\quad-\frac{1}{2\beta}\sum_i\ln\left[\frac{\pi}{\beta(\lambda-2KQ_i)}\right]\\&\quad-\sum_i\frac{J^2M_i^2}{\lambda-2KQ_i},\quad i=x,y,z.\end{aligned}\tag{13}$$

We shall study the following special cases.

A. Case I: $M_x=M_y=0,\ Q_x=Q_y=a/3$

The expression for free energy per spin becomes

$$\begin{aligned}f&=-\lambda a+JM_z^2+KQ_z^2-\frac{1}{\beta}\ln\left[\frac{\pi}{\beta(\lambda-\frac{2}{3}Ka)}\right]\\&\quad-\frac{1}{\beta}\ln\left[\frac{\pi}{\beta(\lambda+D-2KQ_z)}\right]-\frac{J^2M_z^2}{\lambda+D-2KQ_z}.\end{aligned}\tag{14}$$

The equilibrium conditions

$$\frac{\partial f}{\partial\lambda}=0,\quad\frac{\partial f}{\partial M_z}=0,\quad\frac{\partial f}{\partial Q_z}=0$$

yield the following equations:

$$\begin{aligned}a-\frac{1}{\beta(\lambda-\frac{2}{3}Ka)}&=\frac{1}{2\beta(\lambda+D-2KQ_z)}\\&\quad+\frac{J^2M_z^2}{(\lambda+D-2KQ_z)^2},\end{aligned}\tag{15}$$

$$2JM_z-\frac{2J^2M_z}{\lambda+D-2KQ_z}=0,\tag{16}$$

$$2KQ_z-\frac{K}{\beta(\lambda+D-2KQ_z)}-\frac{2KJ^2M_z^2}{(\lambda+D-2KQ_z)^2}=0.\tag{17}$$

We rewrite Eqs. (16) and (17) in the following forms:

$$2JM_z\left[1-\frac{J}{\lambda+D-2KQ_z}\right]=0,\tag{18}$$

$$2K\left[Q_z-\left[a-\frac{1}{\beta(\lambda-\frac{2}{3}Ka)}\right]\right]=0.\tag{19}$$

In writing Eq. (19) we have utilized Eq. (15).

Order parameters and phase transitions. The solution of Eqs. (18) and (19) is

$$M_z=0,\tag{20}$$

$$Q_z=a-\frac{1}{\beta(\lambda-\frac{2}{3}Ka)},\tag{21}$$

which may be regarded as the paramagnetic solution.

Now it may be noted that depending on the value of λ one may classify following different phases: (i) $M_z\neq0$, $Q_z\neq0$, (ii) $M_z=0$, $Q_z\neq0$, and (iii) $M_z=0$, $Q_z=0$. This classification of phases has to be modified in view of the fact that from Eq. (17) one gets

$$M_z^2=Q_z-\frac{1}{2\beta J},\tag{22}$$

which demands that M_z and Q_z cannot be zero simultaneously at any finite temperature.

It may also be noted that one cannot use

$$Q_z-\left[a-\frac{1}{\beta(\lambda-\frac{2}{3}Ka)}\right]\tag{23}$$

as the quadrupolar order parameter since this is always zero in the present case in view of Eq. (19). We choose the quadrupolar order parameter $q=Q_z-(a/3)$ which, as we shall see later, is consistent with Eq. (21) at T_c, the paramagnetic transition temperature.

With the use of Eqs. (17)–(19) we get after simplifications

$$t=(\tfrac{2}{3}a-9)\left[1-\frac{D}{J}+2\alpha q\right],\tag{24}$$

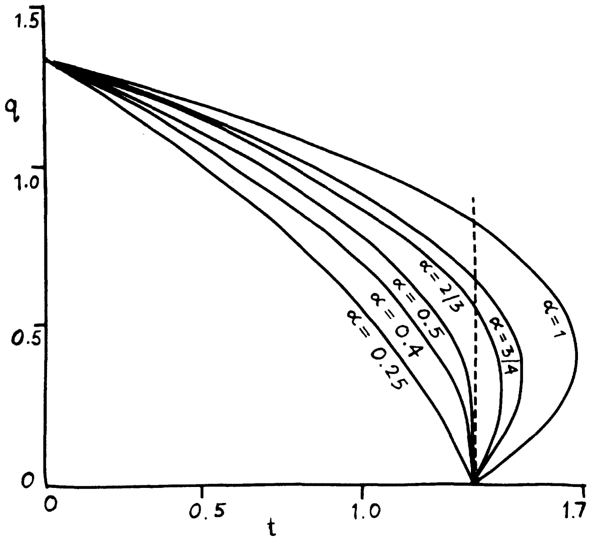

FIG. 1. Variation of quadrupolar ordering parameter q with temperature for $D/J=0$ and $\alpha=0.25$, 0.4, 0.5, $\frac{2}{3}$, $\frac{3}{4}$, and 1. Dotted vertical line represents the points of minimum free energy. Solutions beyond this temperature are unstable. Hence for $\alpha \geq 0.5$ the discontinuities are appreciable and lead to first-order QP transition. Magnitude of the jump at $\alpha=1$ is approximately equal to 0.83 which is, however, less than that obtained from rigorous Green-function theory (Ref. 7).

$$M_z = \left[q + \frac{a}{3} - \frac{t}{2} \right]^{1/2}, \tag{25}$$

where $\alpha=K/J$.

The above two equations completely describe the thermal evolution of the quadrupolar ordering parameters for a spin-1 Heisenberg system with dipolar and quadrupolar interactions. These equations are much simpler than those obtained by earlier authors using different approximation methods. These are even much simpler than those obtained by MFA.[2] At the same time we shall see below that the above equations are able to reproduce the essential physical features of the problem.

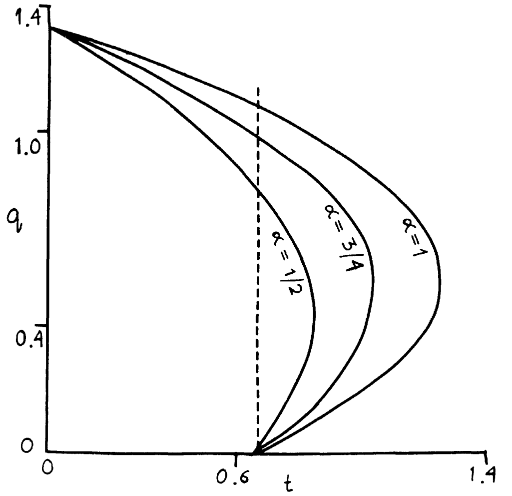

FIG. 2. Variation of q against t for $D/J=\frac{1}{2}$ and $\alpha=\frac{1}{2}$, $\frac{3}{4}$, and 1. Both discontinuous and continuous transitions occur at $t_c=\frac{2}{3}$ depending on the values of α.

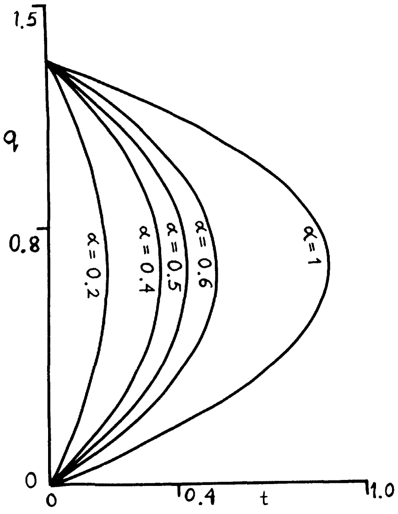

FIG. 3. Typical q-t curves showing the nonexistence of an ordered phase at any nonzero temperature.

For $D/J=0$ we get $t_c=\frac{2}{3}a$ for $q=0$ at which M_z also vanishes. Hence q may be treated as the quadrupolar ordering parameter and consequently we can classify the following phases: (i) ferromagnetic phase (F), $M_z=0$, $q\neq0$, (ii) quadrupolar phase (Q), $M_z=0$, $q\neq0$, and (iii) paramagnetic phase (P), $M_z=0$, $q=0$.

Also at $t_c=\frac{2}{3}a$ both the parameters M_z and q vanish. This implies that the quadrupolar phase does not appear as an intermediate phase. This result agrees with that obtained by Nauciel-Bloch *et al.*[2]

However, if $D/J\neq0$ we get FQ and QP transition temperatures, respectively, as

$$t_q=\frac{2}{3}a, \tag{26}$$

$$t_c=\frac{2}{3}a\left[1-\frac{D}{J}\right]. \tag{27}$$

For an intermediate quadrupolar phase one must have $t_c > t_q$ and this is possible if $D/J<0$.

One can investigate the detail nature of variation of M_z and q with t from Eqs. (24) and (25). The results are shown in Figs. 1–5 for various values of D/J and α. Depending on the values of D/J and α the system undergoes both first- and second-order

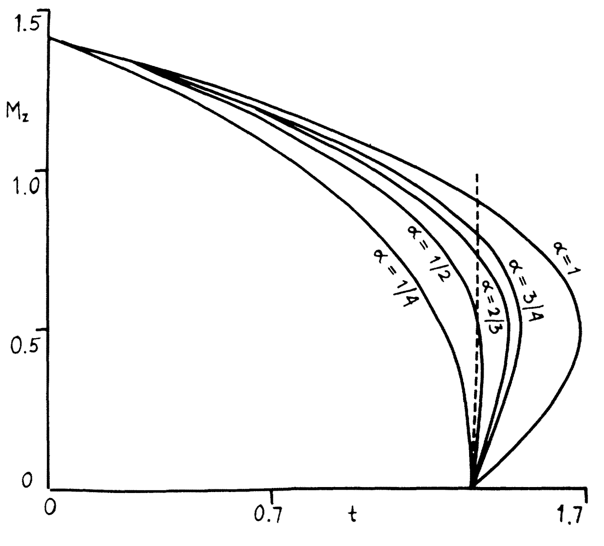

FIG. 4. Variation of M with temperature for $D/J=0$, $\alpha=0.25$, 0.5, $\frac{2}{3}$, $\frac{3}{4}$, and 1. Dotted line represents the points of minimum free energy. Both continuous and discontinuous transitions occur at $t_c=\frac{4}{3}$ depending on the value of α. Solutions beyond t_c are unstable.

transitions at t_c. It may be noted that in all these figures we have considered positive values of D/J. We find that as D/J increases t_c decreases and that for $D/J=1$, t_c vanishes. It implies that for this value of D/J the system does not exhibit any ordered phase.

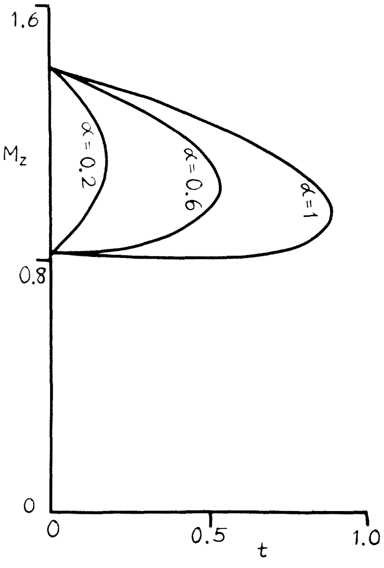

FIG. 5. Case for $D/J=1$ showing the absence of any dipolar phase at nonzero temperature.

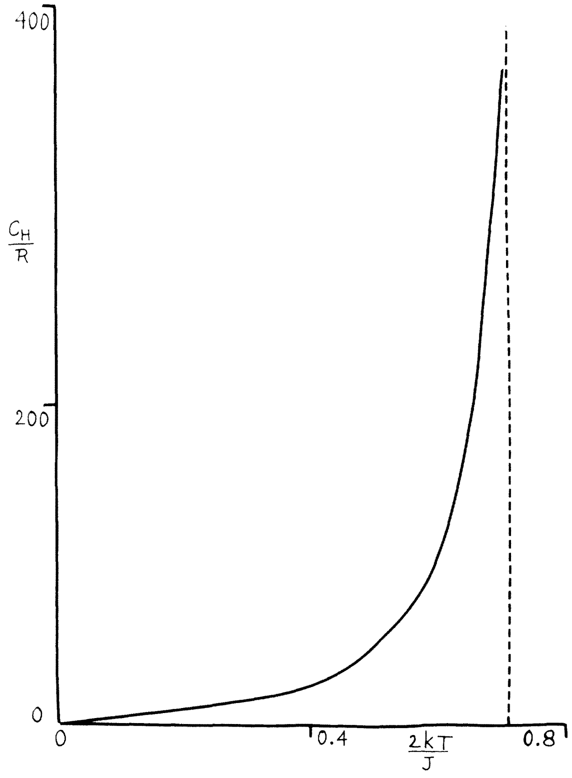

FIG. 6. Variation of specific heat with temperature for $D/J=1$, $S=1$ for the case $M_x=M_y=0$, $Q_x=Q_y=0$, $M_z\neq 0$, and $Q_z\neq 0$.

Specific heat. We shall study the temperature variation of the specific heat for the case $M_x=M_y=Q_x=Q_x=0$, $D=0$. The free energy can be written as

$$\frac{f}{k_BT}=-\tfrac{3}{2}\ln\pi+\tfrac{5}{2}\ln 2+\tfrac{3}{2}\ln\phi+\ln y+2\alpha\phi Q_z^2-4\alpha y\phi\ , \qquad (28)$$

where

$$\phi=J/2k_BT,\quad y=\lambda/2J\ .$$

The results for the specific heat are to be calculated from the expression

$$C_H=-k_B\phi^2\frac{\partial^2}{\partial\phi^2}(f/k_BT)\ . \qquad (29)$$

The variation of C_H with ϕ is shown in Fig. 6. The qualitative nature of variation of specific heat with temperature resembles the result of the MFA applied to the Heisenberg model of the original spin configuration.

B. Case II: $M_x=M_y=M_z=0$, $Q_z=0$, $Q_x\neq Q_y$

This is a simple case of biaxial ordering. The free energy in this case is given by

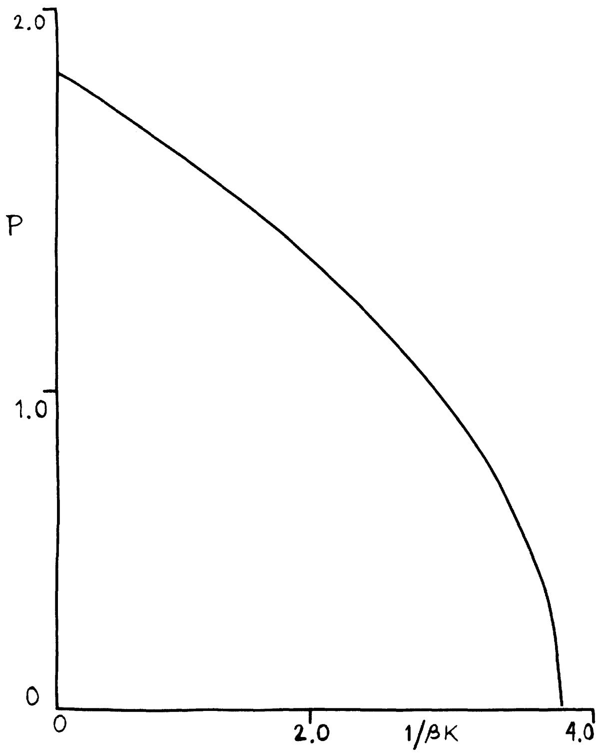

FIG. 7. Thermal variation of the biaxial ordering parameter P for $S=1$. Second-order transition occurs at $T_B=4(K/k_B)$.

$$f=-\lambda a-\frac{1}{2\beta}\sum_i \ln\left[\frac{\pi}{\beta(\lambda-2KQ_i)}\right],\qquad i=x,y,z\ . \tag{30}$$

The equilibrium conditions give us the following equations:

$$\sum_i [2\beta(\lambda-2KQ_i)]^{-1}=a \tag{31}$$

$$Q_i=[2\beta(\lambda-2KQ_i)]^{-1},\quad i=x,y\ . \tag{32}$$

Equations (32) give

$$1=K[\beta(\lambda-2KQ_x)(\lambda-2KQ_y)]^{-1}\ , \tag{33}$$

$$Q_x+Q_y=\lambda/2K\ , \tag{34}$$

$$Q_xQ_y=1/4\beta K\ , \tag{35}$$

which lead to the following expressions for Q_x and Q_y:

$$Q_x=\frac{\lambda}{4K}+\frac{1}{2}\left[\frac{\lambda^2}{4K^2}-\frac{1}{\beta K}\right]^{1/2}, \tag{36}$$

$$Q_y=\frac{\lambda}{4K}-\frac{1}{2}\left[\frac{\lambda^2}{4K^2}-\frac{1}{\beta K}\right]^{1/2}. \tag{37}$$

In combination of Eq. (31) above two equations result in the following simple expression for the biaxial ordering parameter, $P=Q_x-Q_y$,

$$P=\left[a^2-\frac{1}{\beta K}\right]^{1/2}. \tag{38}$$

The variation of P with temperature is shown in Fig. 7. A second-order phase transition occurs at a temperature T_B given by

$$T_B=(K/k_B)a^2\ . \tag{39}$$

For a spin-1 lattice, $T_B=4K/k_B$.

C. Case III: $Q_x\neq Q_y\neq Q_z\neq 0$, $M_x=M_y=M_z=0$

This is the case of both biaxial and quadrupolar ordering. The equilibrium conditions yield

$$\sum_i [2\beta(\lambda+D\delta_{iz}-2KQ_i)]^{-1}=a\ , \tag{40}$$

$$Q_i=[2\beta(\lambda+D\delta_{iz}-2KQ_i)]^{-1},\quad i=x,y,z \tag{41}$$

From Eq. (41) we get

$$Q_x+Q_y=\frac{\lambda}{2K}\ . \tag{42}$$

With the use of this in Eq. (41) we get, for a spin-1 case,

$$t=8(q+\tfrac{2}{3})\left[\tfrac{1}{3}-q+\frac{D}{4K}\right], \tag{43}$$

and the expression for P becomes

$$P=[(\tfrac{4}{3}-q)^2-t]^{1/2}\ , \tag{44}$$

where $q=Q_z-\frac{2}{3}$ is the quadrupolar order parameter for a spin-1 system. We can distinguish three different phases: the mixed phase ($P\neq 0$, $q\neq 0$), the biaxial phase ($P\neq 0$, $q=0$), and the paramagnetic phase ($P=0$, $q=0$). When a second-order transition from biaxial to paramagnetic phase occurs, the temperature for such a transition is simply given by $t_c=\frac{16}{9}$. For the second-order transition from the mixed phase to the biaxial phase the temperature is given by the following expression:

$$t_q=\tfrac{16}{9}\left[1+\frac{3D}{4K}\right]. \tag{45}$$

Thus for two such successive second-order phase transitions one should have $D/K<0$ because for such possibility t_c must always be greater than t_q.

The temperature variation of q and P with temperature is shown in Fig. 8 for various values of D/K. The figure shows some peculiar characteris-

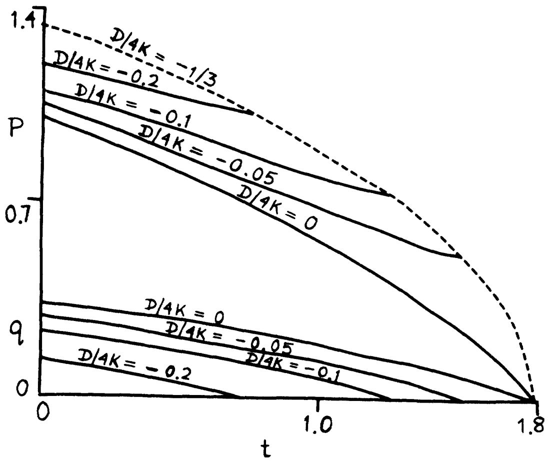

FIG. 8. Thermal variation of q and P for spin-1 system for various values of D/K.

tics of variation. We may now sum up the role played by the uniaxial anisotropy. We find that in its absence the system undergoes only one second-order phase transition, but its presence triggers two second-order phase transitions, with either the quadrupolar phase or the biaxial phase as the intermediate one, depending on specific situations.

IV. UNIAXIAL FERROMAGNET WITH DIPOLAR, BIQUADRATIC, AND THREE-ATOM INTERACTIONS

We consider a system of spins governed by the following Hamiltonian:

$$H = H_{ij} + H_{ijk} \,, \tag{46}$$

where H_{ij} is given by Eq. (8) and H_{ijk} is the three-atom interaction given by

$$H_{ijk} = -R \sum_{i,j,k} (\vec{S}_i \cdot \vec{S}_j)(\vec{S}_j \cdot \vec{S}_k) \,. \tag{47}$$

This term was first introduced by Uryu and Friedberg[18] to explain the properties of a complex acetate of chromium. This was subsequently studied by Kobayashi *et al.*,[19] Munro and Girardeau,[20] Akasmit and Westwansky,[12,13] and Iwashita and Uryu.[21]

The expression for the free energy per spin for the above Hamiltonian in the spherical model is obtained in the following form using the procedure adopted in the preceding pages:

$$f = -\lambda a + \sum_i (JM_i^2 + KQ_i^2 + RM_i^2 Q_i) - \frac{1}{2\beta} \sum_i \ln\{\pi/[\beta(\lambda + D\delta_{iz} - 2KQ_i - RM_i^2)]\} - \sum_i \frac{M_i^2 (J + RQ_i)^2}{\lambda + D\delta_{iz} - 2KQ_i - RM_i^2} \,. \tag{48}$$

We restrict ourselves to the special case $M_x = M_y = 0$, $Q_x = Q_y = 0$. The equilibrium conditions are

$$\frac{\partial f}{\partial \lambda} = 0 \,, \tag{49}$$

$$\frac{\partial f}{\partial M_z} = 0 \,, \tag{50}$$

$$\frac{\partial f}{\partial Q_z} = 0 \,, \tag{51}$$

and the stability conditions are

$$\frac{\partial^2 f}{\partial M_z^2} > 0 \,, \tag{52}$$

$$\left[\frac{\partial^2 f}{\partial M_z^2} \frac{\partial^2 f}{\partial Q_z^2} - \left[\frac{\partial^2 f}{\partial M_z \partial Q_z} \right]^2 \right] > 0 \,. \tag{53}$$

Equations (50) and (51) lead to

$$JM^z = \frac{M_z v^2}{\lambda + u} - RM_z \left[Q_z - \left[a - \frac{1}{\beta\lambda} \right] \right] , \tag{54}$$

$$\left[Q_z - \left[a - \frac{1}{\beta\lambda} \right] \right] + \tfrac{1}{2}(R/K) M_z^2 \left[1 - \frac{2v}{\lambda + u} \right] = 0 \,, \tag{55}$$

where

$$u = D - 2KQ_z - RM_z^2 , \quad v = J + RQ_z \,.$$

Equations (54) and (55) are satisfied by

$$M_z = 0 , \quad Q_z = a - \frac{1}{\beta\lambda} \,. \tag{56}$$

This may be regarded as the paramagnetic solution and under this situation,

$$(\lambda + u)^{-1} = Jv^{-1} = 2\beta Q_z \,, \tag{57}$$

which is obtained from Eqs. (49) and (54).

The quadrupolar solution as stated in Eq. (56) reduces to the paramagnetic solution when $\lambda=\lambda_c=3/(2a\beta_c)$ such that the quadrupolar order parameter $q=Q-(a/3)=0$, β_c being equal to $1/k_BT_c$ with T_c as the temperature at which $M_z=0$, $q=0$.

The quadrupolar ordering is stable when

$$[2J+2RQ_z-R\beta^{-1}(1+\lambda)^{-1}-2v^2(\lambda+u)^{-1}]>0\ , \tag{58}$$

$$[2K-2K^2\beta^{-1}(\lambda+u)^{-2}]>0\ , \tag{59}$$

which implies

$$t>t_1=(2Q_z/\alpha)(1+\gamma Q_z)^2\ , \tag{60}$$

$$t>t_2=4Q_z^2\ . \tag{61}$$

We can study the thermal variation of Q_z with the aid of Eq. (57); we get

$$Q_z^3-Q_z^2(a+b)+\tfrac{3}{4}Q_z(t+4ab)-(at/4)=0\ , \tag{62}$$

where $b=D/2K$, $t=k_BT/K$. It may be noted that this equation is independent of three-atom interaction. The ferromagnetic phase is, however, strongly influenced by the three-atom interaction. Unfortunately, it is very complicated to solve for M_z from the coupled equations. However, we may study the following interesting special cases.

A. Case I: $2v/(\lambda+u)=1$, $v^2/(\lambda u)=J$

We find that $M_z\neq 0$, $Q_z=a-(1/\beta\lambda)$ satisfy Eqs. (54) and (55). With the use of Eq. (49) we get, under this situation,

$$M_z^2=\frac{\alpha}{2}(t_Q-t)\ , \tag{63}$$

where t_Q is the second-order quadrupolar transition temperature given by

$$t_Q=\frac{8}{\alpha\gamma}\ , \tag{64}$$

provided $\alpha\neq 0$, $\gamma\neq 0$. At this temperature $Q_z=1/\gamma$.

B. Case II: $J\gg K$, $J\gg R$

We can approximate $v\simeq J$, $\lambda+u\simeq\lambda$ for $D=0$. Thus Eqs. (49), (54), and (55) give

$$1=\frac{J}{\lambda}-\gamma\left[Q_z-\left(a-\frac{1}{\beta\lambda}\right)\right]\ , \tag{65}$$

$$Q_z-\left(a-\frac{1}{\beta\lambda}\right)+\tfrac{1}{2}(\gamma/\alpha)M_z^2\left(1-\frac{2J}{\lambda}\right)=0\ , \tag{66}$$

$$a-\frac{1}{\beta\lambda}=\frac{1}{2\beta\lambda}+\frac{M_z^2J^2}{\lambda^2}\ . \tag{67}$$

The above equations yield, after simplifications,

$$2\alpha y^3-(2\alpha-3t\gamma^2)y^2-\left(2\alpha\gamma^2+\frac{3t}{2}\right)y+a\gamma^2=0\ , \tag{68}$$

$$Q_z=(1/\gamma)[(1-\gamma t)y-1+\gamma a]\ , \tag{69}$$

$$M_z^2=\frac{2\alpha(y-1)}{\gamma^2(2y-1)}\ , \tag{70}$$

where $t=(\beta J)^{-1}$, $\gamma=R/J$, $\alpha\neq 0$, $\gamma\neq 0$, and $y=J/\lambda$.

Equation (70) shows that M_z vanishes at t_Q given by

$$t_Q=\frac{a\gamma^2}{3(\gamma^2-\frac{1}{2})}\ . \tag{71}$$

It shows that γ^2 must be greater than $\frac{1}{2}$. A tricritical point appears at

$$t_0=\frac{2\alpha}{3(\gamma^2-1)}\ .$$

C. Case III

We have studied case I under the special circumstances for which $M_z\neq 0$, $Q_z=a-1/\beta\lambda$ satisfy the equilibrium conditions. In general, this should not be the case. It may be noted from Eq. (55) that if $M_z\neq 0$ one does not have $Q_z=a-1/\beta\lambda$. Thus different phases appearing in the system should be redefined as follows: ferromagnetic phase—$M_z\neq 0$, $Q_z\neq a-1/\beta\lambda$, quadrupolar phase—$M_z=0$, $Q_z\neq a-1/\beta\lambda$, and paramagnetic phase—$M_z=0$, $Q_z=a/3$. We have seen in case II that M_z vanishes at $y=1$. So we can write Eq. (55) as

$$Q_z=a-ty+(\gamma/2\alpha)M_z^2\ , \tag{72}$$

where $t=1/\beta J$. Using Eq. (54) we get

$$(\gamma^4/4\alpha^2)M_z^4+M_z^2[(\gamma^2/\alpha)+(\gamma^3/\alpha)(a-ty)-(\gamma^2/\alpha y)+\gamma^2(a-ty)]+\{[1+\gamma(a-ty)]^2-(1/y)+2\alpha(a-ty)\}=0\ , \tag{73}$$

With the use of Eq. (49) we again get (up to the M_z^4 term)

$$(\gamma^2/\alpha)(1+\gamma)M_z^4+[1+\gamma(a-ty)]^2M_z^2+t[(2/y)-4\alpha(a-ty)]-(a-ty)[(2/y)-4\alpha(a-ty)]^2=0 . \tag{74}$$

Taking the limit $M_z \rightarrow 0$ in Eqs. (73) and (74) we get the transition temperature

$$t_Q=a+\frac{2}{\gamma}+\frac{2\alpha}{\gamma^2} , \tag{75}$$

which shows that as γ increases t_Q decreases.

V. BLUME-CAPEL HAMILTONIAN

We shall consider a typical Blume-Capel (BC) Hamiltonian[14] to study the phase transitions from the standpoint of the present spherical model. It may be remarked that such a Hamiltonian was also studied by Sivardiere[15] using the MFA. The Hamiltonian is

$$H_{\rm BC}=-\Delta\sum_i S_{iz}^2-\sum_{i,j} L_{ij}P_iP_j , \tag{76}$$

where $P_i=S_{ix}^2-S_{iy}^2$.

The spherical model gives the following expression for free energy per spin

$$f=-\lambda a+LP^2 -(1/2\beta)\ln\left[\frac{\pi^3/\beta^3}{(\lambda^2-4L^2P^2)(\lambda-2\Delta LP)}\right] , \tag{77}$$

where $P=\langle S_{ix}^2-S_{iy}^2\rangle$ describes the orthorhombic distortion, and

$$L=L(0)=\sum_j L_{ij} , \tag{78}$$

with λ, a, and β having the same meaning as before.

The equilibrium conditions are

$$\frac{\partial f}{\partial\lambda}=-a+\frac{\lambda/\beta}{\lambda^2-4L^2P^2}+\frac{1/2\beta}{\lambda-2\Delta LP}=0 , \tag{79}$$

$$\frac{\partial f}{\partial P}=2LP-\frac{4LP/\beta}{\lambda^2-4L^2P^2}-\frac{\Delta L/\beta}{\lambda-2\Delta LP}=0 . \tag{80}$$

The above equations are not satisfied for $P=0$ unless $\Delta=0$. Hence there is no transition for $\Delta\neq 0$. On the other hand, we find that the MFA drives a phase transition even for $\Delta\neq 0$.

For $\Delta=0$, Eqs. (79) and (80) become

$$\frac{a-1}{2\beta\lambda}=\frac{\lambda/\beta}{\lambda^2-4L^2P^2} , \tag{81}$$

$$P=\frac{2LP/\beta}{\lambda^2-4L^2P^2} . \tag{82}$$

Eliminating λ we get, after simplifications,

$$P^4-P^2(a^2-3t)-t\left[a^2\frac{9t}{4}\right]=0 , \tag{83}$$

where $t=1/2\beta L$. If we take the limit $P\rightarrow 0$ in the above equation we get the following expression for a second-order transition temperature t_B:

$$t_B=\frac{4a^2}{9} . \tag{84}$$

For computation of Eq. (83) we write it in the form of a quadratic in t whose solution consistent with Eq. (84) is

$$t=\tfrac{2}{9}(a^2-3P^2)+\tfrac{2}{9}a(a^2+3P^2)^{1/2} . \tag{85}$$

Equation (85) has been computed and the results are shown in Fig. 9.

We see from the figure that a second-order transition from a biaxial phase to the paramagnetic phase occurs at a temperature t_B given by Eq. (84). The question of a first order phase transition does not arise.

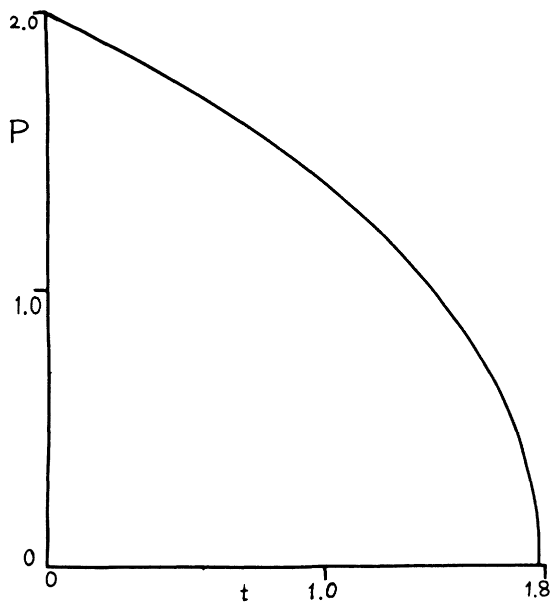

FIG. 9. Biaxial ordering in Blume-Capel model for $S=1$ and $\Delta=0$.

VI. SIVARDIERE HAMILTONIAN FOR RARE EARTHS

To develop the molecular-field theory of successive second-order phase transitions in several rare-earth vanadates, arsenates, and phosphates, Sivardiere[15] studied the effects of different kinds of interactions on the Blume-Capel model. We consider here the effects of inclusion of the dipolar interaction so that the Hamiltonian becomes

$$H=H_{\mathrm{BC}}-\sum_{i,j}(J_xS_{ix}S_{jx}+J_yS_{iy}S_{jy}+J_zS_{iz}S_{jz})\ , \tag{86}$$

where J_x, J_y, and J_z are the dipolar exchange constants corresponding to the interactions along the x, y, and z axes, respectively.

The free energy per spin in the spherical model becomes

$$f=-\lambda a+LP^2+\sum_i J_iM_i^2-(1/2\beta)\ln\left[\frac{\pi^3/\beta^3}{(\lambda^2-4L^2P^2)(\lambda-\Delta)}\right]-\sum_i\frac{J_i^2M_i^2}{\lambda-2\epsilon_iLP-\Delta\delta_{iz}}\ ,\quad i=x,y,z \tag{87}$$

where $\epsilon_i=+1$ for $i=x$, $\epsilon_i=-1$ for $i=y$, and $\epsilon_i=0$ for $i=z$.

Considering the appropriate equilibrium conditions we can study the following cases.

A. Case I: $J_x=J_y=0$

The equilibrium conditions yield

$$\lambda=J_z+\Delta\ , \tag{88}$$

$$a=\frac{(J_z+\Delta)/\beta}{(J_z+\Delta)^2-4L^2P^2}+\frac{1}{2\beta J_z}+M_z^2\ , \tag{89}$$

$$P=\frac{4LP/\beta}{(J_z+\Delta)^2-4L^2P^2}+\frac{\Delta}{4\beta J_zL}\ . \tag{90}$$

It is seen that the equations for $\partial f/\partial P=0$, $\partial f/\partial M_z=0$ are satisfied by $M_z=0$, $P=0$ if $\Delta=0$. This may be regarded as the paramagnetic solution. It may further be noted that Eq. (90) is independent of M_z. So, there may be a single phase transition: either from a pure biaxial ($M_z=0$, $P\neq0$) to the paramagnetic phase ($M_z=0$, $P=0$), from a pure dipolar phase ($M_z\neq0$, $P=0$) to the paramagnetic phase, or from a mixed phase ($M_z\neq0$, $P\neq0$) to the paramagnetic phase. Combining Eqs. (89) and (90) we get

$$P=-a+M_z^2+\frac{1}{2\beta J}\left[1+\frac{\Delta}{2L}\right]+\frac{1/\beta}{J+\Delta-2LP}\ . \tag{91}$$

For a pure dipolar phase we get

$$M_z=\left[a-t\left[1+\frac{\Delta}{2L}+\frac{2}{1+(\Delta/J)}\right]\right]^{1/2}\ , \tag{92}$$

where $t=1/2\beta J$. The transition temperature is

$$t_M=a\Bigg/\left[1+\frac{\Delta}{2L}+\frac{2}{1+(\Delta/J)}\right]\ . \tag{93}$$

Similarly for a pure biaxial phase we get

$$\alpha P^2+P\left[t+(\alpha/2)\left[\alpha+\frac{\Delta}{L}\right]-a\alpha\right]+\left[\tfrac{1}{2}a\alpha\left[\alpha+\frac{\Delta}{L}\right]-\alpha t-\tfrac{1}{2}t(1+\alpha)\left[\alpha+\frac{\Delta}{L}\right]\right]=0\ , \tag{94}$$

where now $\alpha=J/L$, $t=1/2L$. The transition temperature is given by the same expression of Eq. (93). It may be remarked that Eqs. (92)–(94) may also describe a mixed phase and a second-order transition may occur at t_M.

B. Case II: $J_y=0, J_z=0$

In this situation the equilibrium conditions yield the following relations:

$$\lambda=J+2LP\ , \tag{95}$$

$$a=\frac{\lambda/\beta}{\lambda^2-4L^2P^2}+\frac{1/2\beta}{\lambda-\Delta}+\frac{J_x^2M_x^2}{(\lambda-2LP)^2}\ , \tag{96}$$

$$P=\frac{2LP/\beta}{\lambda^2-4L^2P^2}+\frac{\Delta/4\beta L}{\lambda-\Delta}+\frac{J_x^2M_x^2}{(\lambda-2LP)^2}\ . \tag{97}$$

With the use of the notations $J_x'=J_x/2L$, $\Delta'=\Delta/2L$, we get, from Eqs. (95)–(97), by subtraction,

$$4P^3-2a_1P^2+a_2P+a_3=0\ , \tag{98}$$

where

$$a_1=2a-(3J_x'-\Delta')\ ,$$

$$a_2=2J_x'(J_x'-\Delta')+t(3-2\Delta')-2a(3J_x'-\Delta')\ ,$$

$$a_3=t(2J_x'-\Delta'-J_x'\Delta')-2aJ_x'(J_x'-\Delta')\ ,$$

with $t=1/2\beta L$. P vanishes at t_P given by

$$t_P=\frac{2aJ_x'[1-(\Delta/J_x)]}{1-\Delta'-(\Delta/J_x)}\ . \tag{99}$$

The above equation represents the temperature for the transition from a pure biaxial phase to the paramagnetic phase. For the mixed phase we get, by adding Eqs. (96) and (97),

$$M_x=\left[\frac{P}{2}+\frac{1}{2}\left[a-\frac{t}{J_x'}\right]-\frac{(1+\Delta')t}{4(P+J_x'-\Delta')}\right]^{1/2}\ . \tag{100}$$

A transition may now occur from a mixed phase to the paramagnetic phase. The transition temperature is given by

$$t_M=\frac{2aJ_x'[1-(\Delta/J_x)]}{3+\Delta'-2(\Delta/J_x)}\ . \tag{101}$$

For $T_P>T_M$ one should have

$$\frac{\Delta}{J_x}>1+\frac{\Delta}{2L}\ . \tag{102}$$

Under this situation we should say that an orthorhombic distortion is followed at a lower temperature by a magnetic ordering in M_x, giving rise to two successive second-order phase transitions. Let us apply these results to interpret the phase transitions in $TbPO_4$. From the experimental point of view two successive second-order phase transitions appear, one being the magnetic transition at 2.2 K and the other a crystallographic transition at 3.5 K. In the first place, if we then put $\Delta=0$ for $J_x=1.8$ K (as chosen by Sivardiere), then Eqs. (99) and (101) do not yield the correct transition temperatures. These are reproducible for $J_x=1.8$ K, $L=-1.7308$ K, and $\Delta=0.6522$ K. As compared to Sivardiere's result L is now negative and $\Delta\neq0$.

VII. CONCLUSION

In the previous sections attempts were made to discuss the essential physical features of phase transitions appearing in some complex magnetic systems utilizing a method which has exploited the constraint prescribed by the spherical model substituted for the original spin pattern. The method also involves the application of the mean-field approximation for simplification of the complex Hamiltonians. In addition to the relative simplicity of the mathematical formulation of the problem one finds that the most important results of well-known calculations of earlier authors are very simply reproducible. A lot of other complex magnetic systems with complicated Hamiltonians may be comfortably treated by the present method.

However, it is well known that the exact treatment of the spherical model for a certain spin configuration favors a lower Curie temperature than the actual one. It is at least true for an Ising system, but is believed to be true for complex magnetic systems also. It is interesting to note that the mean-field approximation for the spherical model of a spin-1 Heisenberg system yields a Curie temperature $k_BT_c/J=\frac{4}{3}$, which is exactly the MFA value. However, the result is found to be different when a higher-order interaction is included. The results will be quantitatively better if the fluctuations are considered. The mean-field approximation applied to a spherical model yields a higher critical temperature than the exact treatment of the spherical model but it yields the same critical temperature as that of the MFA in the bilinear limit (Heisenberg bilinear Hamiltonian). The differences are pronounced when the higher-order interactions are included.

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