Dipole and Quadrupole Phase Transitions in Spin-1 Models^{*}

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(Received 30 October 1972)

A spin-1 Hamiltonian with arbitrary bilinear and biquadratic pair interactions has been studied in the molecular-field approximation by using one- and two-sublattice models. Various types of orderings and transitions are found for the Hamiltonians with different symmetries. For a system described by a one-sublattice Hamiltonian with Ising, isotropic, or cubic symmetry, only one phase transition is found; either from the paramagnetic phase to a ferroquadrupolar.) For the one-sublattice Hamiltonian with axial symmetry, we find two separate phase transitions; first from the paramagnetic phase and then to a ferromagnetic phase. A two-sublattice system described by a lising or isotropic Hamiltonian can have a transition either from the paramagnetic phase to a ferromagnetic phase. Additional transitions are also found from the ferromagnetic phase and then back to the ferromagnetic phase. The system can have as many as three successive transitions. For a two-sublattice Hamiltonian with cubic symmetry, besides the transitions found in Ising systems, there are "reorientation" phase transitions; i.e., transitions from a quadrupole ordering along the cube edge to an ordering along the cube diagonal. This system can have more than three successive phase transitions.

I. INTRODUCTION

Pair interactions between magnetic ions which are described by higher-degree spin operators have been known to exist for some time.¹ Their origins are rather diverse and range from multipole expansions of the Coulomb and exchange interactions to virtual phonon exchange. Except for the few studies to be mentioned, higher-degree pair interactions have been assumed to be small when compared to bilinear ones. However, recent work on magnetic systems, especially rare-earth compounds, has provided examples where the higherdegree interactions are comparable to the bilinear ones.^{2,3}

Towards a better understanding of the effects of higher-degree pair interactions on the magnetothermal behavior of systems, we have studied the simplest system which admits these interactions, i.e., spin-1 systems with arbitrary amounts of bilinear and biguadratic pair interactions. Our work differs from that of previous authors in that we are primarily interested in determining the various dipolar and quadrupolar orderings that appear by using Hamiltonians with different symmetries. Therefore we have considered Hamiltonians with the following symmetries: Ising, axial, cubic, and isotropic. We find that for spin-1 systems which favor parallel ordering of quadrupoles (ferroquadrupolar ordering), two transitions occur for axial symmetry. When the biquadratic interactions favor ferriquadrupolar ordering, e.g., two sublattices with quadrupole moments of unequal magnitudes and possibly opposite signs, we find multiple transitions for all symmetries.

Whereas most treatments of the magnetic prop-

erties of solids have assumed that higher-degree pair interactions are small compared to bilinear exchange, some recent works have considered the consequences of large higher-degree interactions. Allan and Betts⁴ have used high-temperature-series expansions to determine the effects of biquadratic exchange on magnetothermal properties. Chen and Joseph⁵ have used a similar expansion to find the properties of the Schrödinger exchange interaction for arbitrary spin. In this model there is only one phase transition; all the multipoles order at the same temperature at which the dipoles order. Blume et al.⁶ and Oran⁷ have studied spin-1 Ising models. Allen⁸ has considered a special case of a spin-1 model which is relevant to UO_2 . Nauciel-Bloch et al.⁹ and Brown¹⁰ have considered an isotropic spin-1 model restricted to cases where the ground state of the system is ferromagnetic. Finally, Sivardière et al.¹¹ have considered the spin- $\frac{3}{2}$ Ising model as well as some other restricted symmetries for arbitrary spin.

The opposite limit of only higher-degree interactions and no bilinear coupling has also received some attention, e.g., the quadrupolar ordering of molecules in solid hydrogen, ¹² in liquid crystals, ¹³ and the cooperative Jahn-Teller (structural) phase transitions in magnetic crystals (most recently $DyVO_4$). ^{11,14} As we are interested in determining the conditions for spin-1 systems to have distinct dipole and quadrupole phase transitions we need not consider here the limit of zero bilinear coupling; pure quadrupolar coupling does not produce two transitions for a spin-1 model.

The exchange interactions for an effective spin-1 system can be completely described by the Hamiltonian

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$$\mathcal{W} = -\sum_{\langle ij \rangle} \left[\sum_{t=x,y,z} J_{ij}^{[t]} S_{ti} S_{tj} + \sum_{t=0,2,xy,yz,xz} K_{ij}^{[t]} Q_{ti} Q_{tj} \right],$$
(1)

where

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$$Q_0 \equiv 3S_x^2 - 2$$
, $Q_2 \equiv S_x^2 - S_y^2$, $Q_{xy} \equiv S_x S_y + S_y S_x$,

and the first summation is taken over all pairs of ions i and j. When there are relationships among the exchange constants, the Hamiltonian may have certain kinds of symmetry. As is well known there are phase transitions associated with the ordering of the dipole moments S_x , S_y , and S_z ; with the presence of quadrupole moments Q_2 , Q_0 , Q_{xy} , Q_{yz} and Q_{xz} , there may be additional phase transitions. In this paper we first consider this Hamiltonian with positive values of the exchange constants. In this case the dipole and the quadrupole moments of the ions tend to align themselves along the same direction, and the system can be treated as a onesublattice model in the molecular-field approximation. We then consider Hamiltonians with negative biquadratic exchange constants, and present solutions based on two-sublattice models appropriate for loose-packed lattices.

In Sec. II we briefly discuss the molecular-field approximation, and present some general properties of systems containing quadrupole moments. The Ising, isotropic, and cubic Hamiltonians are studied in Sec. III for values of the exchange constants commensurate with a one-sublattice model. We find that, aside from the direction of ordering, these three systems have exactly the same thermodynamic properties. They exhibit only a single phase transition, either the dipole and the quadrupole order simultaneously, or the dipole does not order at all. We next consider a Hamiltonian with axial symmetry. We find that this system shows two separate phase transitions. The quadrupoles order first, subsequently the dipoles order at a lower temperature.

In Sec. IV we consider cases where some of the interactions constants are negative. We present two-sublattice models with Ising, cubic, and spherical symmetry. For the Ising and isotropic Hamiltonians, we find transitions from the paramagnetic to a ferromagnetic phase, from ferromagnetic to a ferrimagnetic phase and from the ferrimagnetic back to a ferromagnetic phase. For the Hamiltonian with cubic symmetry we find an additional transition in which quadrupoles aligned parallel to a cube diagonal reorient themselves into an array of quadrupoles parallel to the cube edges. Specific heats for some of these systems as well as the effect of an external magnetic field on the order parameters are discussed in Sec. V. We summarize our results in Sec. VI.

II. SOME GENERAL PROPERTIES

For the Hamiltonian Eq. (1) the one-ion molecular-field Hamiltonian is given by

$$\Im C_{0} = -I \left[\sum_{t=x,y,z} \alpha_{t} \langle S_{t} \rangle S_{t} + \sum_{t=0,2,xy,yz,xz} \beta_{t} \langle Q_{t} \rangle Q_{t} \right],$$
(2)

where

$$I\alpha_t = \sum_j J_{ij}^{[t]}, \quad I\beta_t = \sum_j K_{ij}^{[t]}, \quad \beta_0 = \frac{1}{3}.$$

The thermal averages $\langle S_t \rangle$ and $\langle Q_t \rangle$ are the set of values which minimizes the Gibbs free energy¹⁵

$$G = -kT\ln(\operatorname{Tr} e^{-\mathcal{K}_0/kT}) - \frac{1}{2} \langle \mathcal{H}_0 \rangle , \qquad (3)$$

where $\operatorname{Tr} e^{-\mathfrak{X}_0/kT}$ is a partition function Z_0 and the Hamiltonian \mathfrak{K}_0 is given by Eq. (2). Note the term $-\frac{1}{2}\langle \mathfrak{K}_0 \rangle$ in Eq. (3). The correct internal energy Uof the system per ion is $\frac{1}{2}\langle \mathfrak{K}_0 \rangle$. Therefore the proper Hamiltonian in the molecular-field approximation is

$$\mathcal{H}_{M} = \mathcal{H}_{0} - \frac{1}{2} \langle \mathcal{H}_{0} \rangle . \tag{4}$$

The term $-\frac{1}{2}\langle \mathcal{H}_0 \rangle$ is a constant matrix, and may be neglected in Eq. (2) for simplicity. However, $-\frac{1}{2}\langle \mathcal{H}_0 \rangle$ is a function of the dipole and quadrupole moments, and must be included in the Gibbs free energy.

The thermal expectation values $\langle S_t \rangle$ and $\langle O_t \rangle$ can be determined from the set of self-consistent equations

$$\frac{\partial G}{\partial \langle S_t \rangle} = \frac{\partial G}{\partial \langle Q_t \rangle} = 0 .$$
 (5)

These equations yield the following relations:

$$\langle S_t \rangle = \frac{kT}{I\alpha_t} \frac{\partial \ln Z_0}{\partial \langle S_t \rangle} \tag{5'}$$

and

$$\langle Q_t \rangle = \frac{kT}{I\beta_t} \frac{\partial \ln Z_0}{\partial \langle Q_t \rangle}$$

These self-consistent equations may have many solutions; the one which has the lowest Gibbs free energy, Eq. (3), describes the equilibrium state of the system.

Before investigating in detail specific values of the interaction constants in Eq. (2), we state without proof in this section some simple and useful properties of systems having dipole and quadrupole moments.

(a) In the one-sublattice molecular-field approximation, and at T=0 °K, the system is in a pure state. A spin-1 particle can be described by the wave functions

$$\psi = (a+ib) | m_z = 1 \rangle + (c+id) | m_z = 0 \rangle + (c+if) | m_z = -1 \rangle.$$
 (6)

As we are free to choose the three coordinate axes,

the phase, and the normalization we are left only one variable, e.g., the magnetic moment m. Therefore if each ion in the system has a dipole moment $\langle S_x \rangle = m$ (the z axis is so chosen that $\langle S_x \rangle = \langle S_y \rangle = 0$), and if we choose the x axis such that $\langle Q_{xy} \rangle = 0$, then the other moments for each ion are $\langle Q_0 \rangle = 1$, $\langle Q_2 \rangle = (1 - m^2)^{1/2}$, and $\langle Q_{xz} \rangle = \langle Q_{yz} \rangle = 0$.

(b) Two relations among the expectation values of the various moments at T=0 °K which can be obtained from the wave function, Eq. (6), are

$$\sum_{t=x,y,z} \langle S_t \rangle^2 + \sum_{t=2, xy, yz, xz} \langle Q_t \rangle^2 + \frac{1}{3} \langle Q_0 \rangle^2 = \frac{4}{3}, \qquad (7a)$$

$$-\frac{4}{3} \leq \sum_{\substack{t=x,y,z\\t=2,xy,yz,xz}} \langle S_{ti} \rangle \langle S_{tj} \rangle + \sum_{\substack{t=2,xy,yz,xz}} \langle Q_{ti} \rangle \langle Q_{tj} \rangle + \frac{1}{3} \langle Q_{0i} \rangle \langle Q_{0j} \rangle \leq \frac{4}{3} .$$
(7b)

In Eq. (7b), *i* and *j* refer to ions in different sublattices. One important consequence of Eq. (7a) is that the system will have $\langle Q_0 \rangle = -2$ and other moments vanish at T=0 °K if the interaction constants α_i and β_i in Eq. (2) are less than unity, i.e., the system has zero magnetic moment even at zero temperature.

(c) At finite temperatures the system is no longer in a pure state, and the system is described by a density matrix (with eight variables). Then the relation among the thermal average of the various moments, Eq. (7a), becomes an inequality with the left-hand side less than $\frac{4}{3}$.

(d) Another inequality given by Fano¹⁸ states that if we choose the coordinates so that $\langle Q_{xy} \rangle = \langle Q_{yz} \rangle$ = $\langle Q_{xz} \rangle = 0$, then the tip of the vector $\langle \vec{S} \rangle$ is confined within an ellipsoid whose axes lie along the coordinates

$$\frac{\langle S_x \rangle^2}{\langle (1-S_y^2)(1-S_z^2) \rangle} + \frac{\langle S_y \rangle^2}{\langle (1-S_x^2)(1-S_z^2) \rangle} + \frac{\langle S_z \rangle^2}{\langle (1-S_x^2)(1-S_y^2) \rangle} \le 4.$$
(8)

The values $\langle Q_0 \rangle$, $\langle Q_2 \rangle$, i.e., $\langle S_x^2 \rangle$, $\langle S_y^2 \rangle$, and $\langle S_z^2 \rangle$, and the position of the vector $\langle \mathbf{S} \rangle$ in the ellipsoid depend on the details of the Hamiltonian. We have considered the Hamiltonian Eq. (2) for various symmetries, Ising, spherical, cubic, and cylindrical. We find that for these Hamiltonians the Gibbs free energy, Eq. (3), is minimized only when the dipole moment lies along one of the coordinate axes. For instance, if $\langle S_x^2 \rangle$ is greater than $\langle S_y^2 \rangle$ and $\langle S_z^2 \rangle$, then the dipole moments order along the x axis.

III. ONE-SUBLATTICE MODELS

A. Ising Hamiltonian

$$\mathcal{K}_0 = -I\left[\alpha m_z S_z + \frac{1}{3}q_0 Q_0\right]$$

$$Z_0 = \mathrm{Tr} e^{-\mathfrak{X}_0/kT} = e^{a_0 K/3} \left[e^{-a_0 K} + 2 \cosh K \alpha m_z \right],$$
(9)

and

$$G/I = -\frac{1}{K} \ln Z_0 + \frac{1}{2} \alpha m_z^2 + \frac{1}{6} q_0^2.$$

Here and in the following sections, the convenient notations K, m_x , m_z , q_0 , q_2 , and q_{xy} stand for the normalized inverse temperature I/kT and the expectation values $\langle S_x \rangle$, $\langle S_z \rangle$, $\langle Q_0 \rangle$, $\langle Q_2 \rangle$, and $\langle Q_{xy} \rangle$, respectively. From Eq. (5) we find the set of self-consistent equations

$$m_{z} = \frac{2 \sinh K \alpha m_{z}}{e^{-q_{0}K} + 2 \cosh K \alpha m_{z}},$$

$$q_{0} = 1 - \frac{3 e^{-q_{0}K}}{e^{-q_{0}K} + 2 \cosh K \alpha m_{z}}.$$
(10)

For zero external magnetic field the partition function, Eq. (9), is an even function of m_z , and the solutions with $\langle S_z \rangle = \pm |m_z|$ have exactly the same properties. So, we assume $m_z > 0$ in the following discussion. Equations (10) have three sets of solutions: (1) $m_z \neq 0$, $q_0 \neq 0$, (2) $m_z = 0$, $q_0 \neq 0$, and (3) $m_z = q_0 = 0$. By comparing the free energy of these solutions we find the following results.

(a) For $\alpha > 1$, the solution with $m_z > q_0 > 0$ has the lowest free energy. At very low temperatures m_z and q_0 are approximately given by

$$m_{a}=1-e^{-K(\alpha+1)}$$

and

$$a_{\alpha} = 1 - 3e^{-K(\alpha+1)}$$

For α large enough, the system behaves as the usual Ising model, the transition occurs at $kT_c/I = \frac{1}{3}\alpha S(S+1) = \frac{2}{3}\alpha$, and is of the second order. About the critical point $T \lesssim T_c$, the magnetization is small, $m_z \ll 1$, and we can use the expansion

$$\frac{k}{I}(T_c - T) = Am_z + Bm_z^2 + \cdots, \quad T \to T_c^-.$$
(12)

By eliminating q_0 from Eqs. (10) and by expanding the resulting expression in power of m_z we immediately find that A = 0 (as required by symmetry of m_z), and $B = \alpha(\alpha - 2)/4(\alpha - 1)$, i.e.,

$$m_{g} = \left[\frac{4(\alpha-1)}{\alpha(\alpha-2)} \frac{k}{I} (T_{c}-T)\right]^{1/2}, \quad T \to T_{c}^{-}.$$
(13)

By substituting Eq. (13) into Eqs. (10), we find

$$q_0 = \frac{3}{\alpha - 2} \frac{k}{I} (T_c - T), \quad T - T_c^-.$$
(14)

Equations (13) and (14) are valid only if $\alpha > 2$. For $\alpha < 2$, q_0 (or m_z) has a positive slope in a $q_0(m_z)$ vs T plot when $q_0(m_z) \ll 1$. This means that for $\alpha < 2$, the phase transition occurs at a temperature $kT/I > \frac{2}{3}\alpha$, and that the transition is first order. In the (α, T) phase diagram the point $\alpha = 2$, $kT/I = \frac{4}{3}$ is a tricritical point. This result agrees with

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(11)

Nauciel-Bloch *et al.*⁹ who used Landau's theory of second-order phase transitions¹⁷ to obtain the tricritical point.

(b) For $\alpha < 1$ the solution with no dipole ordering $m_z = 0$, and $q_0 < 0$ has the lowest free energy for $kT/I < 1/\ln 4 = 0.72$. For $kT/I > 1/\ln 4$ the solution with $m_z = q_0 = 0$ has the lowest free energy. We define a positive function Q(kT/I) which occurs frequently in the following discussions:

$$Q\left(\frac{kT}{I}\right) = -\frac{1}{2}\tilde{q}_{0} \quad \text{for } \frac{kT}{I} \le \frac{1}{\ln 4}$$
$$= 0 \qquad \text{for } \frac{kT}{I} > \frac{1}{\ln 4}, \tag{15}$$

where $\tilde{q}_0 < 0$ is the solution q_0 of Eq. (10) for $\alpha = 0$. At T = 0 °K, Q = 1; at $kT/I = 1/\ln 4$, $Q = \frac{1}{2}$. At very low temperatures $(T \rightarrow 0$ °K)

$$Q(kT/I) = 1 - 3e^{-2I/kT}$$
(16a)

and near the transition point, $kT_Q/I = 1/\ln 4$,

$$Q\left(\frac{kT}{I}\right) = \frac{1}{2} + \frac{(\ln 4)^2}{3 - 2\ln 4} \frac{k}{I} (T_Q - T), \quad T \to T_Q^-.$$
(16b)

Therefore, for $\alpha < 1$ the system has zero magnetic dipole moment and a transition from the paramagnetic phase to a ferroquadrupolar phase. The quadrupole moment $q_0 = -2Q(kT/I)$ appears at $kT_Q/I = 1/\ln 4$, with a discontinuity equal to 50% of its saturation value.¹⁸

(c) For $\alpha = 1$, the system has two degenerate solutions. One with $q_0 = m_z = Q(kT/I)$; another with $m_z = 0$, $q_0 = -2Q(kT/I)$. These two sets of solutions have the same Gibbs potential and coexist at all temperatures $T < T_Q$.

For a given temperature T, and α , the equilibrium values of the dipole moment m_z and quadrupole moment q_0 can also be directly obtained by calculating the Gibbs free energy, Eq. (9), at all points in the m_z - q_0 plane. The phase diagram for the Hamiltonian Eq. (9) is shown in Fig. 1 and thermal variations of m_z and q_0 for several values of α are plotted in Fig. 2.

B. Isotropic Hamiltonian

For a spin-1 system with isotropic exchange interactions between ions, the Hamiltonian is given by

$$\mathcal{H} = -\sum_{\langle ij \rangle} \left[J_{ij} \vec{\mathbf{S}}_i \cdot \vec{\mathbf{S}}_j + K_{ij} (\vec{\mathbf{S}}_i \cdot \vec{\mathbf{S}}_j)^2 \right].$$
(17)

When $K_{ij} = 0$, this reduces to the Heisenberg Hamiltonian. For $K_{ij} = J_{ij}$, the Hamiltonian reduces to the exchange interaction model for S = 1. In the molecular-field approximation the Hamiltonian for each spin is

$$\mathcal{H}_0 = -I\left[\alpha \vec{\mathbf{m}} \cdot \vec{\mathbf{S}} + q_2 Q_2 + \frac{1}{3} q_0 Q_0\right], \qquad (18)$$
 where



FIG. 1. Phase diagram for a spin-1 system described by an Ising Hamiltonian, Eq. (9), with I > 0. Region I represents a disordered state of the system; region II a ferroquadrupolar phase with $q_0 < 0$ and $m_z = 0$; region III a ferromagnetic state with ordering parameters $m_z > q_0$ > 0. Dashed lines indicate first-order transitions, solid lines, second-order transitions.

$$I=\frac{1}{2}\sum_{j}K_{ij}, \quad (\alpha+1)I=\sum_{j}J_{ij}.$$

In deriving Eq. (18) we have chosen coordinates (the Hamiltonian is spherically symmetric) such that $q_{xy} = q_{yz} = q_{xz} = 0$, and we have dropped a constant $-\frac{6}{3}I$.

As mentioned in Sec. II, if $q_{xy} = q_{yz} = q_{xz} = 0$, the dipole moment will order along one of the coordinate axes. Without loss of generality we assume that the dipole orders along the z axis. Then Eq. (18) is written as

$$\mathcal{K}_{0} = -I \left[\alpha m_{z} S_{z} + q_{2} Q_{2} + \frac{1}{3} q_{0} Q_{0} \right].$$

The partition function is given as

$$Z_0 = \mathrm{Tr} e^{-\mathfrak{K}_0 / kT}$$

$$= e^{q_0 K/3} \left[e^{-q_0 K} + 2 \cosh K (q_2^2 + \alpha^2 m_z^2)^{1/2} \right]$$
(19a)

and the Gibbs free energy is

$$\frac{G}{I} = -\frac{1}{K} \ln Z_0 + \frac{\alpha}{2} m_z^2 + \frac{1}{2} q_2^2 + \frac{1}{6} q_0^2.$$
(19b)

By using Eqs. (5) we find that a necessary condition for the Gibbs free energy to be a minimum is

$$(\alpha - 1) m_z q_2 = 0. (20)$$

For $\alpha \neq 1$, we have three solutions, $m_x \neq 0$, $q_2 = 0$; $m_z = 0$, $q_2 \neq 0$, or both m_z and q_2 vanish. When

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FIG. 2. Thermal variations of the dipole and quadrupole moments m_z , q_0 , and the specific heat for spin-1 systems described by the Ising Hamiltonian, Eq. (9), for (a) $\alpha < 1.0$, (b) $\alpha = 1.5$, and (c) $\alpha = 2.0$.

 $q_2 = 0$, Eqs. (19) reduce exactly to those for the Ising Hamiltonian, Eq. (9). So, we have only to investigate here the case $q_2 \neq 0$. For $q_2 \neq 0$, $m_z = 0$, and the self-consistent equations for q_2 and q_0 are

$$q_{2} = \frac{2 \sinh Kq_{2}}{e^{-\bar{q}_{0}K} + 2 \cosh Kq_{2}}$$

and
$$q_{0} = 1 - \frac{3 e^{-\bar{q}_{0}K}}{e^{-\bar{q}_{0}K} + 2 \cosh Kq_{2}}.$$
 (21)

This set of equations is similar to Eqs. (10) with $\alpha \rightarrow 1$ and $m_x \rightarrow q_2$. From the discussions in Sec. III A we know that Eqs. (21) have two degenerate solutions:

(i)
$$q_2 = q_0 = Q(kT/I)$$
, (ii) $q_2 = 0$, $q_0 = -2Q(kT/I)$.

A rotation which brings the y into the z axis transforms the solution $q_2 = q_0 = Q(kT/I)$ into the solution $q_2 = 0$, $q_0 = -2Q(kT/I)$; these two solutions are equivalent. Therefore, for $\alpha \neq 1$, we can always choose the coordinates such that m_x and q_0 are the only nonvanishing moments.

In other words, within the molecular-field theory, for $\alpha \neq 1$, the isotropic Hamiltonian has exactly the same thermodynamic properties as the Ising Hamiltonian. The dipoles and the quadrupoles order simultaneously for $\alpha > 1$; and the dipoles do not order for $\alpha < 1$. The only difference between the two Hamiltonians is that for the isotropic Hamiltonian the dipoles and the quadrupoles can order in any direction, while for the Ising Hamiltonian they order only along the z axis.

For $\alpha = 1$, m_z and q_2 cannot be determined uniquely, but are related by

$$(m_{g}^{2}+q_{2}^{2})^{1/2}=q_{0}=Q(kT/I)$$
.

This solution has exactly the same free energy as the solution

$$m_z = q_2 = 0, \qquad q_0 = -2Q(kT/I).$$

C. Cubic Hamiltonian

For a system with cubic symmetry, the molecular-field Hamiltonian can be written¹⁹

$$\mathcal{H}_{0} = -I\left(\alpha \vec{m} \cdot \vec{S} + \beta \mathcal{H}^{(1)} + \mathcal{H}^{(0)}\right), \qquad (22)$$

where

and K

$$\mathcal{H}^{(0)} = q_2 Q_2 + \frac{1}{3} q_0 Q_1$$

$$^{(1)} = q_{xy}Q_{xy} + q_{yz}Q_{yz} + q_{xz}Q_{xz}.$$

We first consider two special cases of the above Hamiltonian.

(a) For $\beta = 0$, Eq. (22) reduces to Eq. (18). From Sec. III B we know that both the dipole and the quadrupole moments of the system order along one of the cube edges when $\alpha > 1$, and that only the quadrupole moment q_0 occurs when $\alpha < 1$.

(b) For $\beta \gg 1$, Eq. (22) reduces to

$$\mathcal{H}_{0} = -I \left[\alpha \mathbf{m} \cdot \mathbf{S} + \beta \mathcal{H}^{(1)} \right].$$
⁽²³⁾

By using the procedures described in Sec. II, we find that the stable states of the above Hamiltonian are as follows:

(i) For $\alpha < \beta$ the lowest-free-energy solution of Eq. (23) is

$$m=q_2=q_0=0$$

and

$$q_{xy} = q_{yz} = q_{xz} = -\frac{2}{3} Q(kT/I\beta)$$
.

This system is in what we call a ferroquadrupolar phase with the symmetry axis of the quadrupoles parallel to the [111] direction.

(ii) For $\alpha > \beta$ the lowest-free-energy solution of the Hamiltonian describes a ferromagnetic state with the dipole and quadrupole moments pointing

q

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along the [111] direction, i.e.,

$$q_2 = q_0 = 0$$
,

$$m_x = m_y = m_z = m/\sqrt{3},$$

and

$$q_{xy} = q_{yz} = q_{xz} = \frac{1}{3}q$$
.

Here q and m are given by

$$m = \frac{2\sinh K\alpha m}{e^{-\alpha\beta K} + 2\cosh K\alpha m}$$
(24)

and

$$q = 1 - \frac{3e^{-qBK}}{e^{-qBK} + 2\cosh K\alpha m}$$

. ...

With proper normalization $[K\beta \rightarrow K', \alpha/\beta \rightarrow \alpha']$, the above equations reduce exactly to Eqs. (10). This means that the Hamiltonian described by Eq. (23) has exactly the same properties as an Ising Hamiltonian with bilinear and biquadratic interaction constants $I\alpha$ and $I\beta/3$, respectively. The only difference is that Eq. (23) prefers an ordering along the [111] direction, while the Ising system only orders along the z axis.

For general values of β , we rewrite Eq. (22) as

$$\mathscr{K}_{0} = -I\left[\mathscr{K}^{(1)} + \mathscr{K}^{(0)}\right] - I\left[\alpha \vec{\mathbf{m}} \cdot \vec{\mathbf{S}} + (\beta - 1)\mathscr{K}^{(1)}\right].$$
(25)

The first term in the above Hamiltonian is spherically symmetry, and does not prefer any direction of ordering. If $\beta > 1$, all the constants *I*, α , and $(\beta - 1)$ are positive, the direction of ordering of the cubic Hamiltonian will be determined only by the second term in Eq. (25). From the preceding discussions we know that the second term prefers an ordering along the [111] direction; so does the cubic Hamiltonian. When the system orders along the [111] direction, $q_2 = q_0 = 0$ and $\mathfrak{R}^{(0)}$ vanish; therefore for $\beta > 1$, the cubic Hamiltonian, Eq. (22), reduces exactly to Eq. (23).

When $\beta < 1$, the exchange constant $I(\beta - 1)$ is negative, and the above argument is not applicable. We rewrite the cubic Hamiltonian as

$$\mathcal{H}_{0} = -I\beta \left[\mathcal{H}^{(1)} + \mathcal{H}^{(0)}\right] - I \left[\alpha \vec{\mathbf{m}} \cdot \vec{\mathbf{S}} + (1-\beta) \mathcal{H}^{(0)}\right].$$
(26)

In the above equation the interaction constants $I\beta$, $I\alpha$, and $I(1 - \beta)$ are positive, and the first term is spherically symmetric. The direction of ordering is only determined by the second term, which forms an ordering along the [100] direction. This shows that for $\beta < 1$, $q_{xy} = q_{yz} = q_{xz} = 0$, and the cubic Hamiltonian reduces to Eq. (18).

We see that a cubic Hamiltonian can order either along the [111] direction, or along the [100] direction, and the system may have either the dipoles and the quadrupoles order simultaneously or only quadrupolar ordering occurs. In Fig. 3 we show the types of ordering of the system for different values of α and β . The thermal variations of the dipole and the quadrupole moments for the cubic Hamiltonian are the same as for the Ising model; it exhibits only one phase transitior.

D. Axially Symmetric Hamiltonian

In this section we study systems which are invariant under rotations about the z axis.²⁰ The Hamiltonian has the form

$$\mathcal{K}_{0} = -I \left[\alpha \vec{\mathbf{m}} \cdot \vec{\mathbf{S}} + \beta (q_{2} Q_{2} + q_{xy} Q_{xy}) + \frac{1}{3} q_{0} Q_{0} \right].$$
(27)

Here we assume that the interaction constants for Q_{yz} and for Q_{xz} are much smaller than $I\beta$ and I, therefore, they are neglected. The form of Eq. (27) is unchanged under rotation about the z axis. We can choose the x axis such that $q_{xy} = 0$; throughout this section we will assume that $q_{xy} = 0$.

Before investigating the finite-temperature behavior, we consider the zero-temperature spin configurations of the system described by Eq. (27). The procedure is as follows. Assume at T = 0 °K that the system has a magnetic dipole moment mpointing along an axis z'. Along $\bar{z'}$ axis, $q'_0 = 1$, and we can choose the x' axis such that q'_2 $=(1-m^2)^{1/2}$, and all other moments zero. We then reexpress the moments m'_z , q'_0 , q'_2 , referred to the x'y'z' axes in terms of moments referred to the coordinates xyz. The axes are related to one another by the Euler angles $\{\theta_1, \theta_2, \theta_3\}$. The free energy of the system at T = 0 °K, which is equal to the internal energy $U = \frac{1}{2} \langle \mathcal{H}_0 \rangle$, is expressed as a function of m, θ_1 , θ_2 , and θ_3 . For each set of values of the interaction constants α and β , we can minimize the free energy to find m and $\{\theta_i\}$. In fact, if we allowed q_{xy} to be nonzero, due to the symmetry of the Hamiltonian, θ_3 can be any value.

By using this method we have found the zerotemperature spin configurations shown in Fig. 4(a). Spin configurations obtained by rotating the spin arrangement about the z axis are equivalent. In Fig. 4(a) region I represents a quadrupole state with $q_0 = -2$; the dipole moment and other quadrupole moments are zero. Region II also represents a zero-dipole-moment state with $q_0 = q_2 = 1$. In region III the system has a magnetic moment pointing in the z direction with $m_z = q_0 = 1$. Region IV represents a state with the dipole ordering along the x axis and

$$m_{x} = \frac{2[2(\alpha - 1)(2\alpha - \beta - 1)]^{1/2}}{4\alpha - \beta - 3},$$

$$q_{0} = \frac{2(\beta - \alpha)}{4\alpha - \beta - 3},$$

$$q_{2} = \frac{2(\alpha - 1)}{4\alpha - \beta - 3}.$$
(28)

At finite temperatures the system described by Eq. (27) may have no dipolar ordering; it may have the dipoles pointing along the z axis or along the x



FIG. 3. Various types of ordering for a one-sublattice Hamiltonian with cubic symmetry, Eq. (22). In regions I and IV only quadrupolar ordering exists. In regions II and III both the dipoles and quadrupoles order. The moments order along the [100] axis in regions I and II, and along the [111] direction in regions III and IV. The phase transition is second order in the shaded area, and first order, elsewhere.

axis. Dipoles pointing along the y axis are equivalent to those pointing along the x axis, with $q_2 - q_2$. We will consider these cases separately.

(i) When the system is in a ferroquadrupolar

phase, $\vec{m} = 0$, and the equations for q_2 and q_0 are

$$q_2 = \frac{2\sinh K\beta q_2}{e^{-q_0K} + 2\cosh K\beta q_2}$$



FIG. 4. Various types of ordering for an axially symmetric Hamiltonian with positive interaction constants, Eq. (27). (a) The nonvanishing moments in each region are (I) $q_0 < 0$, (II) $q_2 > q_0 > 0$, (III) $m_x > q_0 > 0$, and (IV) m_x , $q_2 > q_0$. A single first-order transition occurs in region I and the unshaded area of regions II and III. A single second-order transition occurs for $\beta > 2$ in region II and for $\alpha > 2$ in region III. (b) The details of region IV are shown in Fig. 4(b). Region (a) has a single dipole and quadrupole transition of second order; region (b) has a single transition of first order. In regions (c), (d), (e), and (f) two separate dipole and quadrupole transitions are found. The dipole transition is first order in regions (c) and (d), and first order in regions (d) and (f). The quadrupole transition is second order in regions (c) and (d), and first order in (e) and (f).

(29)

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$$q_0 = 1 - \frac{3e^{-a_0K}}{e^{-a_0K} + 2\cosh K\beta q_2} \ .$$

These equations are similar to Eqs. (10), with $\alpha \rightarrow \beta$ and $m_x \rightarrow q_2$. Equations (29) have one solution with $q_2 = 0$, $q_0 = -2Q(kT/I)$. This is the lowest-free-energy solution for Eq. (27) when α and β are less than one, i.e., in region I. Another solution of Eq. (29) has $q_2 > q_0 > 0$. This solution is the low-est-free-energy solution of Eq. (27) at all temperatures below T_Q in region II and also at some temperatures for $\beta > \alpha$ in part of region IV.

(ii) When the dipoles order along the z axis, the possible nonzero moments are m_z , q_2 , and q_0 . By using Eqs. (5) we find that

$$(\alpha - \beta) m_z q_2 = 0. \tag{30}$$

Since $m_z \neq 0$, when $\alpha \neq \beta$, q_2 vanishes, and the Hamiltonian (27) reduces to the Ising-Hamiltonian, Eq. (9). The magnetization m_z and quadrupole moment q_0 are given by Eq. (10). This set of solutions has the lowest free energy for an axially symmetric Hamiltonian when $\alpha > 1$ and $\beta < 1$ (region III).

(iii) In region IV the dipoles order along the x axis. The Hamiltonian (27) is

$$\mathcal{H}_{0} = -I\left[\alpha m_{x} S_{x} + \beta q_{2} Q_{2} + \frac{1}{3} q_{0} Q_{0}\right]$$
(31)

and the partition function is given as

$$Z_0 = e^{a_0 K/3} \left\{ e^{-\alpha 2^{\beta K}} + 2e^{K(\alpha_2 \beta - \alpha_0)/2} \cosh K \left[\frac{1}{4} (\beta q_2 + q_0)^2 + \alpha^2 m_x^2 \right]^{1/2} \right\} \,.$$

By using Eqs. (5) we find that the self-consistent equations are

$$q_0 = \frac{\beta - \alpha}{\alpha - 1} q_2 , \qquad (32a)$$

$$q_2 = \frac{2(\alpha - 1)}{4\alpha - \beta - 3} \left(1 - \frac{3}{\Delta} e^{-q_2 \beta K} \right), \qquad (32b)$$

$$Y = \frac{2\alpha}{\Delta} e^{-\alpha_2 bK} \sinh KY, \qquad (32c)$$

where

 $\Delta = e^{-q_2\beta K} + 2e^{-q_2bK} \cosh KY,$

$$Y = \left[a^2 q_2^2 + \alpha^2 m_r^2\right]^{1/2}$$

and

$$a=rac{lpha(eta-1)}{2(lpha-1)}$$
, $b=rac{lphaeta-2eta+lpha}{2(lpha-1)}$.

The Gibbs free energy G is given as

$$\frac{G}{I} = -\frac{1}{K}\ln\Delta - \frac{q_0}{3} + \frac{\alpha m_x^2}{2} + \frac{\beta q_2^2}{2} + \frac{q_0^2}{6}.$$
 (33)

Equations (32) and (33) are valid only when $m_x \neq 0$. When $m_x = 0$ the equations for q_0 and q_2 reduce to Eqs. (29). The general behavior of the Hamiltonian (31) is as follows: Either q_2 , q_0 , and m_x order simultaneously at a single transition temperature T_{DQ} , or q_2 and q_0 order at a higher temperature T_Q than m_x , which orders at $T = T_D$.

At very low temperatures, $K \rightarrow \infty$, Eq. (32c) is approximately

$$Y = \alpha \left[1 - e^{-pK} - 2e^{-2\alpha K} \right],$$
 (34a)

where

$$p = \frac{2(2\alpha^2 + \alpha\beta - \alpha - 2\beta)}{4\alpha - \beta - 3}$$

By placing this in Eqs. (32a) and (32b) we find

$$\frac{\alpha-1}{\beta-\alpha} q_0 = q_2 = \frac{2(\alpha-1)}{4\alpha-\beta-3} (1-3e^{-\beta K}).$$
(34b)

Phase transitions occurring at T_{DQ} , T_Q , or T_D may be first order or second order. We now examine these three cases separately.

(i) For a transition from the paramagnetic phase to the ferromagnetic m_x , q_2 , and q_0 order simultaneously and we find from Eqs. (32) that

$$q_2 = \frac{2(\alpha - 1)}{4\alpha - \beta - 3} \left(-2 + \frac{3}{\alpha} Y \coth KY \right) .$$
 (35)

If the transition is second order, q_2 , m_x are very small near T_{DQ} . Then q_0 and Y, which are related to q_2 and m_x by Eqs. (32), are also very small. We can eliminate Y from Eqs. (32) and (35) and express q_2 in powers of m_x :

$$q_{2} = A(\alpha, \beta, T) m_{x}^{2} + B(\alpha, \beta, T) m_{x}^{4} + \cdots, \quad T \to T_{DQ}^{-}.$$
(35')

To see whether the transition corresponds to a real second-order transition, we perform a Landau development of the free energy G, Eq. (33), by using Eq. (35'):

$$\frac{G}{I} = G_0 + G_2\left(\alpha, \beta, \frac{kT}{I}\right)m_x^2 + G_4\left(\alpha, \beta, \frac{kT}{I}\right)m_x^4 + \cdots,$$
(36)

where

$$G_0 = -(1/K) \ln 3$$

At the transition temperature $T_{\rm DQ}$,

$$G_2(\alpha, \beta, kT/I) = 0, \qquad (36')$$

and we find that the transition temperature is $kT_{\rm DQ}/I = \frac{2}{3}\alpha$. If the transition is second order, $G_4(\alpha, \beta, kT_{\rm DQ}/I)$ should be positive. We find that $G_4 > 0$ if

$$\alpha > \frac{1}{8} \left[7\beta + 5 + (49\beta^2 - 58\beta + 25)^{1/2} \right].$$
(37)

This is the condition for a second-order phase transition to be found in region IV at the transition temperature $kT_{DQ}/I = \frac{2}{3}\alpha$. This region is shown in Fig. 4(b) as region (a). Just below $T_{DQ}(=2\alpha I/3k)$ all the moments m_x , q_2 , q_0 appear, and are given by (38)

$$(k/I)(T_{\rm DQ}-T)=Am_x^2$$

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$$\frac{\alpha - 1}{3 - \alpha} q_0 = q_2 = \frac{2(\alpha - 1)}{4\alpha - \beta - 3} \left(\frac{3}{2} - \frac{3A}{\alpha}\right) m_x^2$$

where

$$A = \frac{\alpha(4\alpha^2 - 7\alpha\beta - 5\alpha + 8\beta)}{16(\alpha - \beta)(\alpha - 1)}$$

(ii) We now consider the case when q_2 and q_0 order first at T_Q and m_x order at a lower temperature T_D . Below T_Q and above T_D , q_2 and q_0 are given by Eqs. (29). From the discussion in Sec. III A we know that the transition at T_{ρ} is first order for $\beta < 2$, and is second order for $\beta > 2$. Just below the transition temperature T_D , m_x goes to zero while q_2 and q_0 remain large; the quadrupole moments q_0 and q_2 are given by Eqs. (29) and related by Eq. (32a). For given values of α and β , if the dipole transition is second order, the transition temperature T_D and the values of q_2 and q_0 at T_D can be found by solving Eqs. (29) and (32a). This can be done numerically. We find T_p exists only if $\frac{1}{2}(\beta+1) \le \alpha \le \beta$, and $0 \le kT_D/I \le \frac{2}{3}\beta$. In particular $kT_D/I = \frac{2}{3}\beta$ for $\alpha = \beta$, and $T_D = 0$ for $\alpha = \frac{1}{2}(\beta + 1)$.

To check whether the phase transitions at T_D are real second-order transitions we performed a Landau development of the Gibbs free energy near T_D . For a second-order phase transition m_x is small, and we expand q_2 in terms of m_x by using Eq. (35) where Y is given in Eq. (32c):

$$q_{2} = q + A\left(\alpha, \beta, \frac{kT}{I}\right) m_{x}^{2} + B\left(\alpha, \beta, \frac{kT}{I}\right) m_{x}^{4} + \cdots,$$
$$T - T_{D}^{2}. \quad (39)$$

This equation is valid for temperatures T near the transition T_D . Here q and T_D are solutions of q_2 and T for Eqs. (29) and (32a). With this expansion the free energy is written as

$$\frac{G}{I} = G_0 + G_2\left(\alpha, \beta, q_2, \frac{kT}{I}\right) + G_4\left(\alpha, \beta, q_2, \frac{kT}{I}\right) + \cdots$$
(40)

At T_D , $q_2 = q$, and $G_2(\alpha, \beta, q, kT_D/I) = 0$, and the transition is second order when $G_4(\alpha, \beta, q, kT_D/I) > 0$.

So far we have determined T_D only when the transition is second order. If the transition is first order, T_D can be obtained only by numerically solving the simultaneous equations (32) and by comparing the free energy with $m_x \neq 0$ to the free energy with $m_x = 0$, q_2 , $q_0 \neq 0$. We find that the region IV in Fig. 4(a) can be divided into six subregions as shown in Fig. 4(b). In region (a) a single secondorder phase transition occurs at $kT_{\rm DQ}/I = \frac{2}{3}\alpha$. In region (b) a single first-order phase transition occurs at $kT_{\rm DQ}/I > \frac{2}{3}\alpha$. Regions (c), (d), (e), and (f) are the regions where two *separate* phase transitions are found. In regions (c) and (d) quadrupole transitions are second order and occur at kT_Q/I $=\frac{2}{3}\beta$. In regions (e) and (f) the quadrupole phase transitions are first order and $kT_Q/I > \frac{2}{3}\beta$. The dipole transition at T_D is first order in regions (c) and (e) and is second order in regions (d) and (f).

In Fig. 5 we show phase diagrams for $\beta = 1.5$ and $\beta = 3.0$, respectively. Thermal variations of m_x , q_2 , and q_0 for $\beta = 3.0$ and $\alpha = 2.1$, 2.2, and 2.8 are plotted in Fig. 6.

IV. TWO-SUBLATTICE MODELS

When some of the interaction constants are negative, the spin and quadrupole moments may not be the same at each ion, and we need several sublattices to describe the system. If we confine our attention only to loose-packed lattices with nearestneighbor interactions, a two-sublattice model will be sufficient to describe the system in the molecular-field approximation. In a loose-packed lattice, if we change α to $-\alpha$, the thermodynamic properties of the system are unchanged except that the dipole moment (if any) in one of the two sublattices reverses its direction. Therefore, in this section we will assume that the dipole exchange interaction favors a parallel alignment of the dipole moments. We will not discuss the Hamiltonian with axial symmetry because the number of different solutions is indeed staggering.

A. Ising Hamiltonian

For a loose-packed lattice with Ising interactions between nearest-neighbor ions, the molecular-field Hamiltonians for sublattices A and B are

$$\mathcal{H}_{0}^{B} = -I\left[-\alpha m_{g}^{A}S_{g}^{B} + \frac{1}{3}q_{0}^{A}Q_{0}^{B}\right].$$

 $\mathcal{H}_0^A = -I\left[-\alpha m_g^B S_g^A + \frac{1}{3}q_0^B Q_0^A\right]$

If the interaction constant I is positive, the lowestfree-energy solution is the same as for the onesublattice case, $q_0^A = q_0^B$ and $|m_z^A| = |m_z^B|$. Therefore we will study in this section only systems with I < 0. With the methods described in Sec. II we find that

$$Z_{0}^{A} = e^{-q_{0}^{B}K/3} (e^{q_{0}^{B}K'} + 2\cosh K\alpha m_{z}^{B}),$$

$$Z_{0}^{B} = e^{-q_{0}^{A}K/3} (e^{q_{0}^{A}K} + 2\cosh K\alpha m_{z}^{A}).$$
(42)

The dipole and quadrupole moments are determined by the following set of self-consistent equations:

$$m_{z}^{A} = \frac{2 \sinh K\alpha m_{z}^{B}}{e^{q_{0}^{B}K} + 2 \cosh K\alpha m_{z}^{B}} ,$$

$$m_{z}^{B} = \frac{2 \sinh K\alpha m_{z}^{A}}{e^{q_{0}^{B}K} + 2 \cosh K\alpha m_{z}^{A}} ,$$

$$q_{0}^{A} = 1 - \frac{3 e^{q_{0}^{B}K}}{e^{q_{0}^{B}K} + 2 \cosh K\alpha m_{z}^{B}} ,$$

(41)



FIG. 5. Phase diagrams for the axially symmetric Hamiltonian Eq. (27) for (a) $\beta = 1.5$ and (b) $\beta = 3.0$. Dashed lines indicate first-order transitions, and solid lines second-order transitions. *P* means paramagnetic, *Q* ferroquadrupolar, and *M* ferromagnetic.

and

$$q_0^B = 1 - \frac{3e^{q_0^A K}}{e^{q_0^A K} + 2\cosh K\alpha m_z^A}$$
(43)

Here the normalized inverse temperature is K = |I|/kT. The average Gibbs free energy per ion is

$$\frac{G}{|I|} = -\frac{1}{2K} \ln(Z_0^A Z_0^B) + \frac{\alpha}{2} m_z^A m_z^B - \frac{1}{6} q_0^A q_0^B.$$
(44)

As in the one-sublattice case, the self-consistent equations may have several sets of solutions, and the one which has minimum Gibbs free energy describes the equilibrium state of the system. It is interesting to note that the solutions of Eqs. (43) do not correspond to the minima of the Gibbs free energy G, but are saddle points on the hypersurface of G.

Equations (43) have the following sets of solutions: (i) A trivial solution $m_x^4 = m_x^8 = q_0^0 = q_0^8 = 0$. This

solution describes a disordered state and is the lowest-free-energy solution at high temperatures. (ii) A zero-dipole-moment solution. With m_{π}^{A}

 $m_z^B = 0$, Eqs. (43) reduce to

$$q_0^A = 1 - \frac{3e^{q_0^{BK}}}{e^{q_0^{BK}} + 2}$$

and

$$q_0^B = 1 - \frac{3e^{a_0^A \kappa}}{e^{a_0^A \kappa} + 2} .$$
 (45)

Here q_0^A and q_0^B not only have unequal magnitudes but have opposite signs. This solution describes a ferriquadrupolar phase of the system. As $T \rightarrow 0$ °K,

$$q_0^A = 1 - \frac{3}{2} e^{-2K}, \qquad (45')$$
$$q_0^B = -2 + 6e^{-K}.$$

When the temperature T increases the magnitudes of q_0^A and q_0^B decrease, and approach zero at $kT_Q/|I| = \frac{2}{3}$. The transition is second order and as $T \rightarrow T_Q$

$$q_0^A = -q_0^B = \left[\frac{8k}{|I|} \left(T_Q - T\right)\right]^{1/2}.$$
 (45")

This solution is independent of α and has lowest free energy for $\alpha < 1$. The thermal variations of q_0^A and q_0^B are shown in Fig. 7(a).

(iii) A solution with $m_z^A = m_z^B = m_z$ and $q_0^A = q_0^B = q_0$. When the two sublattices have the same moments, the equations for m_z and q_0 reduce to

$$m_{g} = \frac{2\sinh K\alpha m_{g}}{e^{a_{0}K} + 2\cosh K\alpha m_{g}}$$

and

$$q_0 = 1 - \frac{3e^{a_0 n}}{e^{a_0 K} + 2\cosh K \alpha m_z} .$$
 (46)

This solution has the lowest free energy for all temperatures below T_c for $\alpha > 1.18$, and only for some temperatures below T_c for $1 < \alpha < 1.18$. At very low temperatures, m_z and q_0 are given approximately as

$$m_z = 1 - e^{-K(\alpha - 1)}$$

and (46')

 $q_0 = 1 - 3e^{-K(\alpha - 1)}$

As T increases, a second-order phase transition occurs at $kT/|I| = \frac{2}{3}\alpha$, and just below T_c :

 $m_{z} = \left[\frac{4(\alpha+1)}{\alpha(\alpha+2)} \frac{k}{|I|} (T_{c}-T)\right]^{1/2}, \quad T \to T_{c}^{-}$



FIG. 6. Thermal variations of the dipole and quadrupole moments m_x , q_0 , q_2 and the specific heat for the one-sublattice axially symmetric Hamiltonian, Eq. (27), for $\beta = 3.0$ and for (a) $\alpha = 2.1$, (b) $\alpha = 2.2$, and (c) $\alpha = 2.8$.

and

$$q_0 = \frac{3}{\alpha + 2} \frac{k}{|I|} (T_c - T), \quad T \to T_c^-.$$
 (46")

As can be seen in Fig. 7(b), these equations are approximately valid for temperatures as low as $\frac{1}{2}T_c$.

(iv) The most interesting solution of Eqs. (43) is the one with $m_z^A \neq m_z^B$ and $q_0^A \neq q_0^B$. The solution exists only for some values of α and for certain ranges of temperature. Before solving Eqs. (43) explicitly, we examine the conditions under which the solution $m_{g}^{A} \neq m_{g}^{B}$ may occur. By eliminating q_0^A and q_0^B in Eqs. (43), we find that

$$2m_s^A \cosh K\alpha m_s^B - 2\sinh K\alpha m_s^B$$

$$+ m_z^A \exp\left[-2K + 3Km_z^B \coth K\alpha m_z^A\right] = 0$$
(47)

and

 $2m_{s}^{B}\cosh K\alpha m_{s}^{A} - 2\sinh K\alpha m_{s}^{A}$

$$+m_g^B \exp\left[-2K+3Km_g^A \coth K\alpha m_g^B\right]=0$$
.

If the solution $m_z^A \neq m_z^B$ exists, there must be a temperature T_c at which $m_s^A = m_s^B = m_c$, and either above or below the critical temperature, $m_{z}^{A} = m_{c} + \delta^{A}$, and $m_{z}^{B} = m_{c} + \delta^{B}$, with δ^{A} , δ^{B} going to zero as $T \rightarrow T_c$. By expanding m_z^A and m_z^B in Eqs. (47) about m_c for the inverse temperature K near K_c , and by keeping the zero and first-order terms in δ^A and δ^B , we find that for a given α , K_c and m_c satisfy the following equations:

 $2m_c \cosh K_c \alpha m_c - 2 \sinh K_c \alpha m_c - m_c \exp(K_c q_c) = 0$ and

 $2\cosh K_c \alpha m_c + \exp(K_c q_c) - 3K_c^2 m_c^2 \alpha \exp(K_c q_c)$ $\times \operatorname{csch}^{2} K_{c} \alpha m_{c} = \pm \left[2 K_{c} \alpha m_{c} \operatorname{sinh} K_{c} \alpha m_{c} + 3 K_{c} m_{c} \right]$

 $\times \exp(K_c q_c) \operatorname{coth} K_c \alpha m_c$

 $-2K_c\alpha \cosh K_c\alpha m_c$], (47')

where

 $q_c = -2 + 3m_c \coth K_c \alpha m_c$

is the value of q_0^A and q_0^B at the critical temperature. In Eq. (47a) the plus sign corresponds to the solution with $\delta^{A} = -\delta^{B}$; this solution has the lowest Gibbs free energy. The minus sign is related to a solution with higher free energy, and will not be considered further.

By using the positive sign in Eq. (47a), K_c and m_c are solved numerically. Solutions exist only when $1\alpha < 1.18$. For each α we find two critical temperatures, T_{c1} and T_{c2} , shown in Fig. 8. T_{c1} is associated with the transition from a ferromagnetic phase $(m_z^A = m_z^B)$ to a ferrimagnetic phase $(m_z^A \neq m_z^B)$. T_{c2} is associated with the transition from the ferrimagnetic phase back to the ferromagnetic phase. The thermal variations of m_z^A , m_z^B , q_0^A , and q_0^B for $\alpha = 1.10$ are shown in Fig. 7(c).

For $\alpha = 1$, two sets of solutions have exactly the

(49)



FIG. 7. Thermal variation of dipole and quadrupole moments q_0^A , q_0^B , m_{π}^A , and m_{π}^B for the two-sublattice Ising Hamiltonian Eqs. (41) for (a) $\alpha \leq 1.0$, (b) $\alpha = 1.5$, and (c) $\alpha = 1.1$. The specific heats for $\alpha = 1.1$ and 1.5 are also shown.

same free energy. The solution with $m_x^A \neq m_z^B$ has the moments related as follows: $m_x^A = q_0^A$ and $-m_z^B$ $= q_0^B$. The values of q_0^A and q_0^B are equal to minus one-half of the q_0^B and q_0^A shown in Fig. 7(a). The other solution is given by Eqs. (45).

The phase diagram of the Ising Hamiltonian is shown in Fig. 8. All of the phase transitions in the figure are second order.

B. Isotropic Hamiltonian

For an isotropic system we can choose the axes such that q_{xy} , q_{yz} , and q_{xz} vanish in one of the sublattices. Within the molecular-field approximation the q'_{xy} , q'_{yz} , and q'_{xz} on the second sublattice are decoupled from the first because the terms to which these moments are coupled, the q_{xy} , q_{yz} , q_{xz} of the first sublattice, are zero. Similar to the one-sublattice case, when q_{xy} , q_{yz} , and $q_{xz} = 0$, the dipole moments order along one of the coordinate axes, e.g., the z axis. The Hamiltonian for sublattice A reduces to

$$\mathcal{H}_{0}^{A} = + \left| I \right| \left(- \alpha \, m_{z}^{B} S_{z}^{A} + q_{2}^{B} Q_{2}^{A} + \frac{1}{3} \, q_{0}^{B} Q_{0}^{A} \right) \tag{48}$$

Here we assume I is negative. The thermal averages of m_z^A , q_2^A , and q_0^A are given by

$$\begin{aligned} q_0^A &= 1 - (3/\Delta_B) e^{q_0^B K} ,\\ m_z^A &= (1/\Delta_B) 2 \sinh(KY_B) \alpha m_z^B / Y_E \end{aligned}$$

 $q_2^A = (1/\Delta_B) 2 \sinh(KY_B) q_2^B/Y_B$

where

and

$$\Delta_B = e^{q_0^B K} + 2\cosh K Y_B$$

and

or

$$Y_{B} = [(\alpha m_{z}^{B})^{2} + (q_{2}^{B})^{2}]^{1/2}$$

If either q_2^A or m_z^A is nonzero we find by using these equations

$$m_z^A q_2^B = \alpha m_z^B q_2^A$$
.

Similarly, from B sublattice we find

$$m_z^B q_2^A = \alpha m_z^A q_2^E$$

$$(\alpha^2 - 1)m_{_B}^A q_2^B = 0$$
.

For $\alpha \neq 1$ we have either $m_x^A = 0$ (this implies $m_z^B = 0$) or $q_2^B = 0$ (this implies $q_2^A = 0$). For $\alpha > 1$, we find that the solution with $m_z \neq 0$ has the lowest free energy, and the thermal variations of m_z^A , m_z^B , q_0^A , and q_0^B are exactly the same as for the Ising Hamiltonian (43).

For $\alpha < 1$, the stable states of the system have $m_x^A = m_z^B = 0$. Two solutions with the same lowest free energy are found. One solution has $q_2^A = q_2^B = 0$ and the values of q_0^A and q_0^B are exactly the same as for the Ising Hamiltonian, Fig. 7(a). Another solution has $q_2^A = q_0^A > 0$ and $q_2^B = q_0^B < 0$. These two solu-



FIG. 8. Phase diagram for a two-sublattice Ising Hamiltonian Eqs. (41). Region I represents a disordered phase of the system, region II a ferriquadrupolar phase with $-q_0^B$ $>q_0^A>0$, region III a ferromagnetic phase with $m_z^A = m_z^B$, $q_0^A = q_0^B$, and region IV represents a ferrimagnetic phase with $m_z^A \neq m_z^B$, $q_0^A \neq q_0^B$. All the transitions are second order. Details of the phase diagram for the ferrimagnetic phase are shown in the inset.

tions are equivalent and are transformable into one another by a rotation of the coordinate axes.

When $\alpha = 1$, q_2^A and m_z^A as well as q_2^B and m_z^B cannot be uniquely determined; however, the quantities $[(q_2^A)^2 + (m_z^A)^2]^{1/2}$ and $[(q_2^B)^2 + (m_z^B)^2]^{1/2}$ take the roles of m_z^A and m_z^B in Eqs. (43) for the Ising Hamiltonian.

We conclude that for $\alpha \neq 1$, besides the arbitrary direction of ordering, the isotropic Hamiltonian has exactly the same properties as the Ising Hamiltonian.

C. Cubic Hamiltonian

For a system with cubic symmetry, the Hamiltonian for one of the two sublattices is written as

$$\mathcal{K}_{0}^{(A)} = -I_{1}m^{B}S^{A} - I_{2}\left[q_{xy}^{B}Q_{xy}^{A} + q_{yz}^{B}Q_{yz}^{A} + q_{xz}^{B}Q_{xz}^{A}\right] - I\left[q_{2}^{B}Q_{2}^{A} + \frac{1}{3}q_{0}^{B}Q_{0}^{A}\right].$$
(50)

In Sec. III C we studied cases where the interaction constants I and I_2 are positive. In this section we will consider the other possibilities, i.e., (1) I > 0, $I_2 < 0$, (2) I < 0, $I_2 > 0$, and (3) I < 0, $I_2 < 0$. As mentioned before we assume that I_1 is positive. We define the parameters K = |I|/kT, $\alpha = I_1/|I|$, and $\beta = |I_2|/|I_1|$.

(i) When I > 0 and $I_2 < 0$, the $\alpha - \beta$ plane can be divided into three regions as shown in Fig. 9(a). In region I the system has a quadrupole moment q_0 = -2Q(kT/I) where the function Q is defined by Eq. (15), and other moments are zero. In region II the nonvanishing moments are q_0 and m_z ; they satisfy Eqs. (10). Therefore in region I and II a system has the same behavior as systems described by the Hamiltonian (18). Phase transitions are first order for $\alpha < 2$, and second order for $\alpha > 2$. In region III a system forms two sublattices A and B with $q_0^A = q_0^B = q_0$ and $q_{xy}^A = -q_{xy}^B = q_{xy}$; the dipole moments and other quadrupole moments are zero. The values q_0 and q_{xy} are given by

$$q_{xy} = \frac{2\sinh K\beta q_{xy}}{e^{-a_0K} + 2\cosh K\beta q_{xy}} ,$$

$$q_0 = 1 - \frac{3e^{-a_0K}}{e^{-a_0K} + 2\cosh K\beta q_{xy}} .$$
(51)

When we replace β by α and q_{xy} by m_z , the above equations exactly reduce to Eqs. (10). This means that systems in regions II and III have the same thermodynamic properties although their ordering parameters are different.

(ii) In the case I < 0 and $I_2 > 0$, the $\alpha - \beta$ plane is divided into five regions as shown in Fig. 9(b). Systems in region I have nonzero moments q_0^A and q_0^B . The thermal variations of q_0^A and q_0^B are exactly the same as those shown in Fig. 7(a). In region II the nonzero moments are $m_x = m_y = m_g$ and q_{xy} $=q_{yz}=q_{xz}$. The thermal variations of these moments are the same as those of a system with the same α and β in region III of Fig. 3. The phase transition is first order for $\alpha < 2\beta$ and is second order for $\alpha > 2\beta$. In region III the nonzero moments are $q_{xy} = q_{yz} = q_{xz} < 0$. A system in this region has exactly the same properties as a system with the same β in region IV of Fig. 3. A first-order transition with a 50% discontinuity occurs at kT/|I| $= \beta/\ln 4$. In regions IV and V systems exhibit two phase transitions. At $kT/|I| = \frac{2}{3}$ a system transforms from a disordered state to a ferriquadrupolar phase with $q_0^A > 0$ and $q_0^B < 0$ as in region I with all

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FIG. 9. Various types of ordering for two-sublattice systems with cubic symmetry [see Eq. (50)]. (a) I > 0, $I_2 < 0$, (b) I < 0, $I_2 > 0$, and (c) I < 0, $I_2 < 0$. $\alpha \equiv I_1 / |I|$ and $\beta \equiv |I_2| / |I|$. See text for discussion of ordering in the different regions.

dipole moments zero. At a lower temperature a system in region V *reorients* its quadrupole moments to a one-sublattice ordered state with $q_{xy} = q_{yz} = q_{xz} < 0$, as in region III. Also a system in region IV at lower temperatures transforms into a one-sublattice state with $m_x = m_y = m_z$ and $q_{xy} = q_{yz} = q_{xz}$, as in region II. The thermal variations of the various moments in region IV, e.g., $\alpha = 0.8$, $\beta = 0.4$ and in region V, e.g., $\alpha < \beta = 0.8$ are shown in Figs. 10(a) and 10(b), respectively.

(iii) When both I and I_2 are negative, the α - β plane is divided into five regions as shown in Fig.

9(c). The behavior of systems in region I is the same as for region I in Fig. 9(b). The ordered state of a system has the quadrupole moments q_0^A and q_0^B as shown in Fig. 7(a). In region II systems order along the [111] direction with $m_x^A = m_y^A = m_z^A$ $= m^{A}/\sqrt{3}, \ m_{x}^{B} = m_{y}^{B} = m_{z}^{B} = m^{B}/\sqrt{3}, \ q_{xy}^{A} = q_{yz}^{A} = q_{xz}^{A} = q^{A}/3,$ and $q_{xy}^{B} = q_{yz}^{B} = q_{xz}^{B} = q^{B}/3.$ Here $m^{A}, \ m^{B}, \ q^{A}$, and q^{B} are given by equations similar to Eqs. (43). If we make the substitutions $m_z^A \rightarrow m^A$, $m_z^B \rightarrow m^B$, $q_0^A \rightarrow q^A$, $q_0^B \rightarrow q^B$, $K \rightarrow K\beta$, and $\alpha \rightarrow \alpha/\beta$, then Eqs. (43) become the equations for m^A , m^B , q^A , and q^B . From the discussion in Sec. IV A we know that for α >1.18 β a single second-order phase transition occurs at $kT/|I| = \frac{2}{3}\alpha$. When $\alpha < 1.18\beta$, the shaded area of region II in Fig. 9(c), three separate second-order transitions are found. There are transitions from a disordered state to a ferromagnetic state, from a ferromagnetic to a ferrimagnetic and from ferrimagnetic back to the ferromagnetic state.

In region III the ordering is along the [100] di-



FIG. 10. Thermal variations of the dipole and quadrupole moments for a "reorientation" phase transition in a system described by a cubic Hamiltonian with I < 0 and $I_2 > 0$. (a) $\alpha = 0.8$ and $\beta = 0.4$. (b) $\alpha < \beta$ and $\beta = 0.8$. At low temperatures the system orders along the [111] direction as systems in regions II and III of Fig. 9(b). At higher temperatures the moments order along the [100] direction in an identical fashion to systems in region Iof Fig. 9(b).

rection with m_z^A , m_z^B , q_0^A , and q_0^B described by Eqs. (43). Again a single second-order transition occurs at $kT/|I| = \frac{2}{3}\alpha$ for $\alpha > 1.18$ and three separate second-order transitions are found in the shaded area of region III for $\alpha < 1.18$. In region IV the ordered state has the nonzero moments q_0^A , q_0^B , $q_{xy}^A > 0$, and $q_{xy}^B < 0$. If we replace m_z^A by q_{xy}^A , m_z^B by $-q_{xy}^B$, and α by β , then Eqs. (43) describe the various quadrupole moments for this region. A single second-order transition occurs at $kT/|I| = \frac{2}{3}\beta$ for $\beta > 1.18$, and three second-order transitions are found for $\beta < 1.18$. In region V at low temperatures a system has both the dipole and quadrupole moments order along the [111] direction as in region II. As the temperature increases the dipole moments vanish and the quadrupole moments reorient and point along the [100] direction with $q_0^A > 0$ and $q_0^B < 0$ as in region I. Finally for $\alpha < 1.18\beta$, the shaded area in region V, in addition to a quadrupole reorientation transition there are transitions from a disordered to ordered state, from the ferromagnetic to ferrimagnetic state, and from the ferrimagnetic back to ferromagnetic state. Therefore in this region more than three separate phase transitions are found.

V. MAGNETOTHERMAL PROPERTIES

A. Influence of a Magnetic Field

When an external field exists the thermal variations of the dipole and quadrupole moments are changed. In this section we consider a simple but most interesting case, the one-sublattice isotropic Hamiltonian of Sec. III B with an external magnetic field. The molecular-field Hamiltonian, Eq. (18) including the Zeeman energy $-g\mu_B HS_z = -IhS_z$, is

$$\mathcal{K}_{M} = -I[(\alpha m_{z} + h)S_{z} + q_{2}Q_{2} + \frac{1}{3}q_{0}Q_{0}] + I(\frac{1}{2}\alpha m_{z}^{2} + \frac{1}{2}q_{2}^{2} + \frac{1}{6}q_{0}^{2})$$
$$= \mathcal{K}_{0} + \frac{1}{2}I(\alpha m_{z}^{2} + q_{2}^{2} + \frac{1}{3}q_{0}^{2}), \qquad (52)$$

where the second term is the energy correction due to double counting of the exchange energy in the molecular-field approximation. The partition function is

$$Z_{0} = \operatorname{Tr} e^{-x_{0}/kT}$$

= $e^{a_{0}K/3} \{ e^{-a_{0}K} + 2 \cosh K [q_{2}^{2} + (\alpha m_{z} + h)^{2}]^{1/2} \}.$
(53)

By using Eq. (5) the self-consistent equations for m_x , q_2 , and q_0 are

$$m_{z} = \frac{2(\alpha m_{z} + h)}{\Delta Y} \sinh KY, \qquad (54)$$

$$q_2 = (2q_2 / \Delta Y) \sinh KY,$$

and

$$q_0 = 1 - (3/\Delta) e^{-q_0 K}$$
.

Here Δ is defined as

$$\Delta = e^{-q_0 K} + 2 \cosh K Y$$

and Y is given as

$$Y = [q_2^2 + (\alpha m_z + h)^2]^{1/2}.$$

When the quadrupole moment $q_2 = 0$, Eqs. (54) reduce to

$$m_{z} = \frac{2\sinh K(\alpha m_{z} + h)}{e^{-c_{0}K} + 2\cosh K(\alpha m_{z} + h)}$$

and

Ç

$$\gamma_0 = 1 - \frac{3 e^{-q_0 K}}{e^{-q_0 K} + 2 \cosh K(\alpha m_{\mu} + h)} .$$

Equations (55) are the same equations as for a system with an Ising Hamiltonian with external magnetic field. Both m_z and q_0 have a high-temperature tail.

If the quadrupole moment $q_2 \neq 0$, we immediately find from Eqs. (54) that

$$m_z = h/(1-\alpha)$$
 and $q_2 = [Y^2 - m_z^2]^{1/2}$.

This means that as long as $q_2 \neq 0$, the magnetic moment m_x is *independent of temperature*. The values of Y and q_0 are determined by the same equations as Eqs. (21) with q_2 replaced by Y. Therefore for $q_2 \neq 0$ we find that $Y = q_0 = Q(kT/I)$ for $kT/I < 1/\ln 4$. For $kT/I > 1/\ln 4$, Y and q_0 may not be zero. By comparing the free energy for the two sets solutions, q = 0 and $q \neq 0$, we find that if $\alpha > 1$ or $h > (1 - \alpha)$, the system is in a state with $q_2 = 0$. If $\alpha < 1$ and $h < (1 - \alpha)$, the system has a *constant* magnetic moment $m_x = h/(1 - \alpha)$ for temperatures below T_Q . Above T_Q , $q_2 = 0$ and m_x decreases. Typical plots showing the influence of magnetic field on the isotropic spin-1 systems are shown in Fig. 11.

For systems with lower symmetry the influence of the external field strongly depends on the relative direction between the external field and the symmetry axes of the system. For systems which are described by two or more sublattices, each sublattice responds differently to the external field. These cases are very complicated and will not be considered here.

B. Specific Heat

The constant-field specific heat of a magnetic system in the molecular-field approximation is

$$C = \frac{dU}{dT} = \frac{d\langle 3\mathcal{C}_M \rangle}{dT} \,. \tag{56}$$

The thermal average of the various moments m and q have zero slope at T=0 °K, so that C=0 at absolute zero. At each transition temperature, except for the quadrupole reorientation in Sec. IV C, either the slope -dm/dT or -dq/dT reaches its maximum, and the specific heat has a peak. Therefore, we observe two peaks in the specific-heat curve

(55)

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FIG. 11. Thermal variation of the dipole and quadrupole moments m_z , q_0 , q_2 and the specific heat for systems described by the one-sublattice isotropic Hamiltonian in an external magnetic field. (a) $\alpha = 1$, h = 0.1, (b) $\alpha = 0.5$, h = 0.1, (c) $\alpha = 0.5$, h = 0.4. The constants refer to Eq. (52).

when there are two separate transitions.

Above the highest transition temperature, i.e., in the disordered state, the specific heat is identically zero in the molecular-field approximation. For a second-order phase transition from the paramagnetic to an ordered state, the discontinuity in the specific heat $\Delta C/k$ can be found from Eq. (56) and from the asymptotic form of the ordering parameter near the transition. For example, by using Eqs. (13), (46"), and (56) we find for an Ising system that the discontinuity in the specific heat in going from the paramagnetic to the ferromagnetic state is $\Delta C/k = 2(\alpha - 1)/(\alpha - 2)$ for I > 0 and $\alpha > 2$, and $\Delta C/k = 2(\alpha + 1)/(\alpha + 2)$ for I < 0 and $\alpha > 1$. The dipole moments fully account for this discontinuity in the specific heats, there is no contribution from the quadrupole moments. For I < 0 and $\alpha < 1$, the discontinuity in specific heat associated with the transition from the disordered state to a ferriquadrupole phase is $\Delta C/k = \frac{4}{3}$. Finite discontinuities in the specific heat are also found for transitions between the ferrimagnetic phase and the ferromagnetic phase. The specific heat shown in Fig. 7(c) has a minimum in the ferromagnetic phase.

For finite external magnetic fields a system may not have a phase transition, e.g., when $\alpha > 1$ or $h > (1 - \alpha)$ in Eq. (52). However, the specific curve has a maximum. As shown in Fig. 11(c), the specific heat has a peak associated with the ordering of the quadrupole moment q_2 and has a maximum at a higher temperature where no transitions occur.

As a final point we mention that when the magnetization is independent of temperature, see Fig. 11, the specific heat can be written

$$\frac{C}{k} = K^2 \frac{d}{dK} \left(\frac{1}{2} \alpha \, m_z^2 + \frac{1}{2} q_2^2 + \frac{1}{6} \, q_0^2 + h m_z \right)$$
$$= \frac{2}{3} K^2 \frac{d}{dK} \left(q_0^2 \right).$$
(57)

To derive this result we used $dm_z/dT = 0$ and $q_2 = (q_0^2 - m_z^2)^{1/2}$. Therefore as long as $q_2 \neq 0$ the specific-heat curve depends neither on the external field h, nor on the dipole exchange constant α .

VI. DISCUSSION OF RESULTS AND SUMMARY

In this paper we have studied the thermodynamic properties of a spin-1 Hamiltonian containing bilinear and biquadratic interactions. We have considered several symmetries within the molecularfield approximation. We find that for the one-sublattice model where all the interaction constants are positive, the Ising, isotropic, and cubic Hamiltonians have exactly the same thermodynamic properties. They show only one phase transition, either the dipoles and quadrupoles order simultaneously or only the quadrupoles order. The reason for the identical thermodynamic behavior is that the dipoles and quadrupoles are aligned parallel²¹ to one another in these three systems. The one difference in these systems is that the dipole and the quadrupole moments of an isotropic Hamiltonian can order in any direction, for a cubic Hamiltonian the moments can order either along the [111] direction or the [100] direction, and for the Ising Hamiltonian ordering occurs along the z axis. To have separate dipole and quadrupole phase transitions the system must have axial or lower symmetry. With axial symmetry and in the two phase transition region the dipoles order perpendicular to the symmetry axis of the system and the quadrupoles are aligned so that q_0 or q_{xy} are nonzero.

For the two sublattice models where some of the quadrupole interaction constants are negative the isotropic and Ising Hamiltonian have the same thermodynamic properties. They differ only in their directions of ordering. When the quadrupole interaction is negative and $\alpha < 1$ the ordered state of the system has zero dipole moment; and the quadrupole moments are in a ferriquadrupolar phase, i.e., the quadrupole moments in the two sublattices have different magnitudes and opposite signs. When the quadrupole interaction is small, $\alpha > 1.18$, the system has a single phase transition from the paramagnetic state to a ferromagnetic state. For comparable dipole and quadrupole interactions, $1.0 < \alpha < 1.18$, the system undergoes two additional transitions, i.e., from a ferromagnetic to ferrimagnetic state and from ferrimagnetic back to ferromagnetic state.

For the two-sublattice model of the cubic Hamiltonian, additional transitions are found. They are the transition from the disordered state to one with perpendicular quadrupole alignment, i.e., $q_{xy}^A = -q_{xy}^B$. There are also transitions associated with the reorientation of the quadrupole moments.

When comparing our results to others we find our work on the Ising model agrees with that of Oran.⁷ Our Hamiltonian (27) reduces to the one studied by Allen,^{8,20} and our results agree with those he found except for a small discrepancy in the phase diagram. We find that when α and $\beta \rightarrow \infty$. two separate phase transitions will be found in the range 0.5 < α/β < 0.88 while Allen's result is 0.5 $< \alpha/\beta < 1.0$ [in our notation Eq. (27)]. Nauciel-Bloch et al.⁹ find that the sufficient condition for a ferromagnetic ground state is $-J_{ij}/2 < K_{ij} < J_{ij}$ and $J_{ij} > 0$ [in the notation of our Eq. (17) and for S=1]. In the molecular-field approximation we find that the necessary and sufficient condition for a ferromagnetic ground state at T = 0 °K is $K_{ij} < J_{ij}$ and $J_{ii} > 0$. The condition for an ordered state to be the ferromagnetic state at finite temperatures is $-2J_{ij}/(1.18-1) < K_{ij} < J_{ij}$ and $J_{ij} > 0$.

From a comparison of Figs. 2 and 7, we see that in the *ferromagnetic* state for I>0, biquadratic exchange interactions tend to enhance the magnetization. For sufficiently large biquadratic exchange $I > \frac{1}{2}I\alpha$ the transition becomes first order and the transition temperature increases. When I < 0, the biquadratic exchange interactions tend to decrease the magnetization but the transition temperature remains the same.

On comparing the result for the spin-1 Ising Hamiltonian to those for spin $S = \frac{3}{2}^{11}$ we find most of the properties of these systems are the same. The major differences are the following. (i) The quadrupole phase transition is always first order in spin-1 system when I > 0, while the corresponding transition is second order in the $S = \frac{3}{2}$ system. (ii) For I < 0, in the nonmagnetic phase, the quadrupole moments in the two sublattices have equal magnitudes and opposite signs for the $S = \frac{3}{2}$ system. For S=1, the quadrupole moments in the two sublattices have unequal magnitudes and opposite signs. The above differences can be explained by the fact that the Hamiltonian for a spin- $\frac{3}{2}$ system with pure biguadratic interaction has the same thermodynamic behavior as a spin- $\frac{1}{2}$ system with pure bilinear interactions. (iii) For the spin-1 Hamiltonian the ferrimagnetic state is not a proper ground state at T = 0 °K, except for $\alpha = 1$. It is for this reason that the systems we have studied undergo transitions from a ferrimagnetic state to the ferromagnetic state as $T \rightarrow 0$ °K. However, the ferrimagnetic state is a ground state for the $S = \frac{3}{2}$ Hamiltonian at T = 0 °K; therefore the above-mentioned transition is not found in $S = \frac{3}{2}$ systems.

Finally, our molecular-field results can also be compared to those found for a spin-1 isotropic Hamiltonian in the constant-coupling approximation.¹⁰ We find in the region where the constantcoupling model was evaluated that the molecularfield approximation always predicts higher transition temperatures. This is to be expected because the Curie temperatures for bilinear exchange interactions display the same behavior.

ACKNOWLEDGMENTS

We should like to thank Dr. M. Blume, Dr. E. S. Oran, Dr. W. A. Smith, and Dr. M. F. Thorpe for some very helpful discussions. We also want to thank Dr. J. Sivardière for very useful discussions and for sending us preprints of his work.

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^{*}Work supported in part by the U.S. Air Force Office of Scientific Research under Grant No. AFOSR-70-1909 and the National Science Foundation under Grant No. GH 32422.

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(B){[1 + (1/2) $\langle Q_0 \rangle - (3/2) \langle Q_2 \rangle$] $\langle S_x \rangle^2$

 $+ [1 + (1/2) \langle Q_0 \rangle + (3/2) \langle Q_2 \rangle] \langle S_y \rangle^2$ $+ (1 - \langle Q_0 \rangle) \langle S_y \rangle^2 \le (1 - \langle Q_0 \rangle) \{ [(1/3) \langle Q_0 \rangle + 2/3]^2$

 $-\langle Q_2 \rangle^2$. Equation (B) is the same as our Eq. (8).

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⁸S. Strässler and C. Kittel, Phys. Rev. 139, A758 (1965). ¹⁹We take this opportunity to point out an error in our letter, Ref. 15. We neglected the possibility of ordering along the [111] direction and reached the erroneous conclusion in Ref. 15 that a one-sublattice system with cubic symmetric Hamiltonian will have two phase transitions. As shown in Sec. III C we find that a system with cubic symmetry orders along the [111] direction and has one phase transition for that range of interaction constants in which we originally thought two transitions occured. If we let $I_x = I_y = I_z = I \alpha$, $I_{xy} = I_{22} = I \beta$, and $I_{yz} = I_{xz} = 0$, then Fig. 1(c) in Ref. 15 is in fact the phase diagram for an axially symmetric Hamiltonian, Eq. (27), for $\alpha,\beta \gg 1.$

²⁰For $\alpha,\beta >>1$ and for dipolar ordering along the [110] direction instead of along the x axis, our Hamiltonian, Eq. (27) reduces to the one studied by Allen in Ref. 8, Eq. (10).

²¹By parallel dipole and quadrupole moments we mean that the quadrupoles have a unique symmetry axis which is parallel to the dipole moments.

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High-Temperature Series Expansions for a Spin-1 Model of Ferromagnetism^{*}

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High-temperature series expansions are derived up to terms in T^{-4} for the dipole and quadrupole susceptibilities for arbitrary lattices. The expansions are evaluated for a spin-1 isotropic Hamiltonian with bilinear and biquadratic pair interactions. We compare the dipole and quadrupole phase transition temperatures determined from these series to those obtained by the molecular-field and constant-coupling approximations. There are large uncertainties in the estimates of the quadrupole transition temperatures because of the few terms in the series.

The Hamiltonian for a magnetic system with isotropic bilinear and biquadratic pair interactions between nearest-neighbor ions on an arbitrary lattice is given by

$$\mathcal{C} = -J \sum_{\langle i_j, j \rangle} [\vec{\mathbf{S}}_i \cdot \vec{\mathbf{S}}_j + \alpha (\vec{\mathbf{S}}_i \cdot \vec{\mathbf{S}}_j)^2].$$
(1)

This system has been investigated mostly for spin-1, S=1, and when α is either very small or $\alpha = 1$. Recently, this Hamiltonian has been studied for S = 1 and for all values of α by using the molecular-field^{1,2} and constant-coupling³ approximations. It is generally felt that effective-field theories give only qualitative results and do not accurately predict the critical temperatures. We report in this paper on a study of the critical temperatures of the spin-1 Hamiltonian found by deriving and analyzing the high-temperature series expansions for the dipole and quadrupole susceptibilities.

For $\alpha \ll 1$ and for arbitrary spin the high-temperature series expansions for the dipole suscepti-

bility have been calculated up to the term T^{-4} by Joseph⁴ by using a diagrammatic method. For $\alpha = 1$ and S = 1 the dipole susceptibility series expansions for terms through T^{-7} was obtained by Allan and Betts⁵ by using a cluster-expansion method together with group-theoretical techniques. Here we calculate the dipole and the quadrupole susceptibility series to terms through T^{-4} for S = 1 and for arbitrary α by using the cluster-expansion method.⁶ The estimates of the critical temperatures we obtain particularly those from the quadrupole series have large uncertainties because of the few terms in the series.

The zero-field dipole susceptibility χ_1 is proportional to the mean square fluctuation of the dipole moment $S_z = \sum_i S_{iz}$, i.e.,

$$\chi_1 = C_1 \beta \Delta(s_z), \tag{2}$$
 where

$$\Delta(\mathfrak{S}_{g}) = \langle \mathfrak{S}_{g}^{2} \rangle - \langle \mathfrak{S}_{g} \rangle^{2}$$