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Uniaxial and Biaxial Quadrupolar Ordering in Magnetic Crystals: Molecular-Field Theory*

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The single order parameter $Q = \langle (S^z)^2 - \frac{1}{3}S(S+1)\rangle$ is, in general, insufficient to describe ordering in low-symmetry magnetic crystals with quadrupolar coupling. After a brief discussion of the general situation, we study in detail the molecular-field theory of an array of quadrupoles coupled in pairs $\langle 12\rangle$ by the Hamiltonian $(J(12) > 0)$, $\mathcal{H} = -\sum_{\langle 12\rangle} J(12) [\![\frac{3}{2}\{[S^z(1)]^2 - \frac{1}{3}S(S+1)\}\{[S^z(2)]^2 - \frac{1}{3}S(S+1)\} + \frac{1}{2}\eta\{[S^x(1)]^2 - [S^y(1)]^2\}\{[S^x(2)]^2 - [S^y(2)]^2\}]\!]$. For $\eta > 1$, both Q and the biaxiality parameter $P = \langle (S^x)^2 - (S^y)^2\rangle$ become simultaneously nonzero at sufficiently low temperatures. We exhibit (η, T) phase diagrams and give the temperature dependence of the ordering for spins $S = 1, \frac{3}{2}, 2, \frac{5}{2}$, and ∞. The transitions in Q and P may be separated by introducing single-ion anisotropy into the Hamiltonian.

I. INTRODUCTION

Quadrupolar ordering in magnetic crystals has been investigated theoretically[1-5] in connection with experimental results on magnetic and crystallographic phase transitions in some rare-earth compounds such as[6] DyVO$_4$; however, with two exceptions,[4,5] previous authors have only considered the possibility of uniaxial order in the single order parameter $Q = \langle (S^z)^2 - \frac{1}{3}S(S+1)\rangle$. This restriction is both unnecessary and (except in special cases) incorrect. A general purely quadrupolar system may have up to $2l + 1 = 5$ independent, nonzero order parameters, though this number may often be reduced by a judicious choice of axes, when the system possesses appreciable symmetry. In particular, the asymmetry parameter ("biaxiality[7] parameter") $P = \langle (S^x)^2 - (S^y)^2\rangle$ does not, in general, vanish and both P and Q may well be necessary[4,5] to describe states of quadrupolar order in low-symmetry magnetic crystals such as the rare-earth vanadates, phosphates, and arsenates.

In this paper we study in considerable detail within the molecular-field approximation the ordering of an array of quadrupoles interacting in pairs via a coupling with a restricted axial symmetry. We do not introduce dipolar coupling[5] or any sublattice structure. This system is simple enough so that (at most) only the two order parameters P and Q are nonzero; however, it is still rich enough to exhibit phase diagrams of considerable complexity, including uniaxial and biaxial ordering, first- and second-order phase transitions, and tricritical points.

In Sec. II we discuss the various possible symmetries of the quadrupolar Hamiltonian, develop the molecular-field approximation, and extract a few analytic results at high and low temperatures. Section III describes specific numerical results for systems of spin $S = 1, \frac{3}{2}, 2, \frac{5}{2}$, and ∞, including both phase diagrams and a general study of the temperature-dependent ordering. Section IV suggests a few conclusions and extensions. The Appendix discusses symmetries in the molecular-field approximation.

II. FORMULATION AND THEORY

A. Hamiltonian

We consider a regular array of atomic or molecular quadrupoles described in a spin representation by the symmetric Hermitian operators,

$$Q^{\alpha\beta} = \tfrac{1}{2}(S^\alpha S^\beta + S^\beta S^\alpha) - \tfrac{1}{3}\delta^{\alpha\beta}S(S+1) . \tag{1}$$

α and β label Cartesian components. $\overleftrightarrow{\mathrm{Q}}$ is a traceless tensor of rank two. It is convenient to work with linear combinations of the five independent components of $\overleftrightarrow{\mathrm{Q}}$ which transform irreducibly under important symmetry groups. We therefore introduce (a) the $l = 2$ cubic harmonics[8] $(\mathcal{O}_i = \mathcal{O}_i^\dagger)$,

$$\mathcal{O}_1 = \sqrt{\tfrac{3}{2}}\, Q^{zz}, \quad \mathcal{O}_2 = (1/\sqrt{2})(Q^{xx} - Q^{yy}) , \tag{2a}$$

which belong to the representation E_g of the cubic group and

$$\mathcal{O}_3 = \sqrt{2}\, Q^{xy}, \quad \mathcal{O}_4 = \sqrt{2} Q^{xz}, \quad \mathcal{O}_5 = \sqrt{2}\, Q^{yz} , \tag{2b}$$

which belong to the representation T_{2g}; and (b) the $l = 2$ spin spherical harmonics[9] $[Y_{lm}^\dagger = (-1)^m Y_{l-m}]$,

$$\begin{aligned} Y_{20} &= \tfrac{3}{2}(5/4\pi)^{1/2} Q^{zz} , \\ Y_{2\pm1} &= \mp \tfrac{1}{2}(15/2\pi)^{1/2}(Q^{zx} \pm iQ^{zy}) , \\ Y_{2\pm2} &= \tfrac{1}{4}(15/2\pi)^{1/2} Q^{xx} - (Q^{yy} \pm 2iQ^{xy}) . \end{aligned} \tag{3}$$

The most general possible symmetric bilinear coupling between two fixed quadrupoles is

$$\mathcal{H}(12) = -\sum_{i,j} J_{ij}\mathcal{O}_i(1)\mathcal{O}_j(2), \quad J_{ij} = J_{ij}^* = J_{ji} \tag{4}$$

where numerical arguments label the atomic quadrupoles. The 5×5 matrix J_{ij} of quadrupolar "exchange" constants may depend on the atomic separation $(\vec{r}_1 - \vec{r}_2)$ and can contain as many as 15 independent nonvanishing elements.[10] When symmetries are present, the number of independent elements is greatly reduced, as shown in Table I for some important cases. For spherical symmetry the interaction is proportional to the manifestly isotropic operator $\sum_{m=-2}^{2}(-1)^m Y_{2m}(1)Y_{2-m}(2)$. For axial symmetry (about the z axis) the pairs $\mathcal{O}_2 \leftrightarrow \mathcal{O}_3, \mathcal{O}_4 \leftrightarrow \mathcal{O}_5$ transform into one another, and the interaction is equivalent to $\sum_{m=-2}^{2} a_{|m|}(-1)^m Y_{2m}(1) \times Y_{2-m}(2)$. "Restricted" axial symmetry, with which our calculations will primarily be concerned, denotes the special case $a_1 \equiv 0$. "Uniaxial" coupling refers to the situation $a_1 = a_2 = 0$.

Thorpe and Blume[11] and Liu and Joseph[12] have solved exactly for the statistical mechanics of a linear chain of isotropically interacting classical $(S=\infty)$ quadrupoles. Blume and Hsieh[1,2] have studied the $S=1$ isotropic quadrupolar interaction in the molecular-field approximation (MFA). Rys[13] and Hintermann and Rys[14] have treated the uniaxial $S=1$ system (including a variety of dipolar and single-ion interactions) exactly in one dimension and more generally in MFA. Griffiths[15] has shown that the $S=1$ uniaxial system with certain single-ion terms can be mapped rigorously onto the $S=\frac{1}{2}$ Ising model. Sivardière and Blume[3] have studied the $S=\frac{3}{2}$ uniaxial case with additional dipolar terms in MFA. Chen and Levy[4] performed similar calculations with $S=1$ and $S=\frac{3}{2}$. They considered uniaxial symmetry and (for $S=1$) special cases of cubic and axial symmetry. In addition, the classical $(S=\infty)$ isotropic Hamiltonian forms a model for orientational interactions in uniaxial nematic liquids[16,17] and has been treated by Krieger and James[18] and Maier and Saupe[19] via MFA, in which context it is fully equivalent (see below) to the uniaxial case. In all of these special cases of the Hamiltonian (4), the quadrupolar order is entirely uniaxial $(\langle\mathcal{O}_i\rangle = 0,\ i=2,3,4,5)$. Freiser[16,17] and, more recently, Alben, McColl, and Shih[20] have found biaxial order $(\langle\mathcal{O}_1\rangle, \langle\mathcal{O}_2\rangle \neq 0)$ within MFA for nonuniaxial nematics; however, the applicable Hamiltonian is not of the form (4), as we now discuss.

It is worth commenting on the connection between the general biquadrupolar pair Hamiltonian (4) and the interactions among rigid molecular quadrupoles as, for example, in nematic liquids.[16,17] In nematics the existence of local quadrupoles is due to strong *intra*molecular forces which fix the "shape" of the molecules. The much weaker *inter*molecular orientational forces depend on the relative alignment of molecular quadrupolar axes and involve[17] the rotation matrix $D^{(2)}(R)$ for the rotation R which brings these axes into alignment. This interaction is *not*, in general, of the form (4) but reduces to our classical isotropic case when the elementary molecular quadrupoles are uniaxial. By contrast, in the problem we treat the existence of the local quadrupoles *and* their alignment arise *together* from the intermolecular interaction.[21]

B. Molecular-Field Approximation

Consider an array of quadrupoles interacting in pairs according to the Hamiltonian (4). The effective single-ion Hamiltonian for the quadrupole 1 is

$$\mathcal{H}_{\mathrm{MFA}}(1) = -\sum_{i=1}^{5} T_i(1)\mathcal{O}_i(1), \quad T_i(1) = \sum_{2,j} J_{ij}(12)\langle\mathcal{O}_j(2)\rangle, \tag{5}$$

where $T_i(1)$ is the effective quadrupolar field and $\langle\mathcal{O}_j(2)\rangle$ denotes the thermal average of $\mathcal{O}_j(2)$. The effective partition function is

$$Z(1) = \mathrm{Tr}_1 e^{-\beta\mathcal{H}_{\mathrm{MFA}}(1)}, \tag{6}$$

and we define the variational function

$$W \equiv \sum_{1} \ln Z(1) - \tfrac{1}{2}\beta \sum_{\substack{1,2\\ i,j}} J_{ij}(12)\langle\mathcal{O}_i(1)\rangle\langle\mathcal{O}_j(2)\rangle. \tag{7}$$

In Eq. (7), $\ln Z(1)$ is to be regarded as a function of the set of expectation values $\langle\mathcal{O}_j(2)\rangle$ via the molecular field $T_i(1)$. Molecular-field theory[22] then requires that $W(\{\langle\mathcal{O}_i(1)\rangle\})$ be maximized with respect to variations of all the parameters $\langle\mathcal{O}_i(1)\rangle$. The maximum value $W_{\max} = -\beta A(T,N)$ gives the MFA (Helmholtz) free energy, and the corresponding $\langle\mathcal{O}_i(1)\rangle$'s are the MFA quadrupole moments at each site.

For attractive interactions, which we assume henceforth, the variational solution is expected to be translationally invariant, so we may drop the site dependence[23] and maximize

$$w[\langle\mathcal{O}_i\rangle] \equiv \frac{W}{N} = \ln Z - \frac{1}{2}\sum_{i,j} v_{ij}\langle\mathcal{O}_i\rangle\langle\mathcal{O}_j\rangle,$$
$$v_{ij} \equiv \beta\sum_{2} J_{ij}(12), \tag{8}$$

TABLE I. Nonvanishing coupling constants consistent with various symmetries. When there is one preferred axis, z has been chosen.

Symmetry	Nonvanishing J_{ij}
Spherical (isotropic)	$J_{11}=J_{22}=J_{33}=J_{44}=J_{55}$
Cubic (O)	$J_{11}=J_{22},\ J_{33}=J_{44}=J_{55}$
Axial $(C_\infty,\ D_\infty)$	$J_{11},\ J_{22}=J_{33},\ J_{44}=J_{55}$
"Restricted" axial	$J_{11},\ J_{22}=J_{33}$
"Uniaxial"	J_{11}
Quadratic, with reflection (D_4)	$J_{11},\ J_{22},\ J_{33},\ J_{44}=J_{55}$
Quadratic, without reflection (C_4)	$J_{11},\ J_{22},\ J_{33},\ J_{23}=J_{32},\ J_{44}=J_{55}$
Orthorhombic (D_2)	$J_{11},\ J_{22},\ J_{12}=J_{21},\ J_{33},\ J_{44},\ J_{55}$

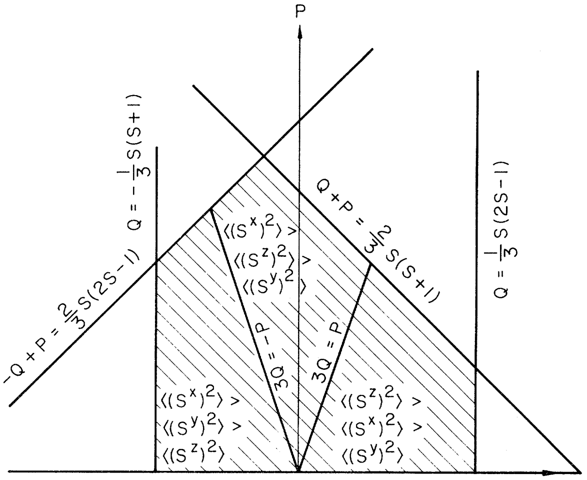

FIG. 1. Physical region of the Q, P plane. The maximum of $w(Q, P)$ lies in the shaded area. The diagram is drawn to scale for $S=3$ but remains qualitatively similar for other spins.

with respect to the five parameters $\langle \mathcal{O}_i \rangle$. A necessary but not sufficient condition for the (global) maximum is the *self-consistent equations* (local extremum conditions)

$$\frac{\partial \ln Z}{\partial \langle \mathcal{O}_i \rangle} = \sum_j v_{ij} \langle \mathcal{O}_j \rangle \ . \tag{9}$$

There are, in general, several solutions of (9), so the maximal solution must be selected by hand.

For general v_{ij} all five potential order parameters $\langle \mathcal{O}_i \rangle$ may be nonzero at the maximum and the situation is complicated. Of course, at any *fixed* T, $\langle Q^{\alpha\beta} \rangle$ can be diagonalized, so $\langle \mathcal{O}_3 \rangle = \langle \mathcal{O}_4 \rangle = \langle \mathcal{O}_5 \rangle = 0$ in the appropriate coordinate system; however, we have been able to find no argument which excludes the possibility that the orientation of the principal axes may be temperature dependent.[24] On the other hand, when symmetries such as those shown in Table I exist, it is often possible to show that several of the order parameters may be chosen to vanish with no loss of generality.

In what follows we shall study in detail the case of "restricted" axial symmetry. While this problem by no means exhibits the most general possible features of the full maximization problem (8), nevertheless, within MFA it subsumes both the spherical and "uniaxial" problems as special cases and, in addition, as we show in the Appendix, it is fully equivalent to the cubic problem. Finally, we note that because of the variational structure of MFA, *small* changes in those v_{ij} which do not contribute to the dominant maximum will leave the symmetries of the solution intact. For example, we expect that for sufficiently small v_{44} and v_{55} (relative to v_{11} and $v_{22}=v_{33}$) the full axial problem will reduce to the "restricted" axial problem. The symmetry of the solution only changes when local maxima pass one another; however, the precise crossover point cannot, in general, be predicted on grounds of symmetry alone.

For "restricted" axial symmetry, $\langle \mathcal{O}_4 \rangle = \langle \mathcal{O}_5 \rangle = 0$ immediately. The Hamiltonian is invariant with respect to rotations about the z axis, so $\langle \mathcal{O}_3 \rangle$ may be set to zero by an appropriate choice of axes in the x-y plane with no loss of generality. These simplifications reduce (8) to

$$w(Q,P) = \ln Z - \tfrac{3}{4} v Q^2 - \tfrac{1}{4} \eta v P^2, \quad v \equiv v_{11}, \quad \eta v \equiv v_{22} \ , \tag{10}$$

where

$$Q \equiv \langle Q^{zz} \rangle = \sqrt{\tfrac{2}{3}} \langle \mathcal{O}_1 \rangle, \qquad P \equiv \langle Q^{xx} - Q^{yy} \rangle = \sqrt{2} \langle \mathcal{O}_2 \rangle,$$

$$\begin{aligned} \langle (S^z)^2 \rangle &= \tfrac{1}{3}[S(S+1)] + Q \ , \\ \langle (S^x)^2 \rangle &= \tfrac{1}{3}[S(S+1)] - \tfrac{1}{2} Q + \tfrac{1}{2} P \ , \\ \langle (S^y)^2 \rangle &= \tfrac{1}{3}[S(S+1)] - \tfrac{1}{2} Q - \tfrac{1}{2} P \ . \end{aligned} \tag{11}$$

The molecular-field partition function is now

$$Z = \mathrm{Tr}\, e^{-\beta \mathcal{H}_{\mathrm{MFA}}} = \sum_{n=1}^{2S+1} e^{v\lambda_n(Q,P)} \ , \tag{12}$$

where λ_n are the $(2S+1)$ eigenvalues of the matrix,

$$-\beta v^{-1} \mathcal{H}_{\mathrm{MFA}} = \tfrac{3}{2} Q \{ (S^z)^2 - \tfrac{1}{3}[S(S+1)] \} + \tfrac{1}{4} P \eta [(S^+)^2 + (S^-)^2],$$

$$S^{\pm} = S^x \pm i S^y \ . \tag{13}$$

Note that the nonuniaxial (second) term only couples M values differing by 2. Thus, for $S=\frac{3}{2}, \frac{5}{2}, \frac{7}{2}$, etc., there are at most $(S+\frac{1}{2})$ different levels, each doubly degenerate, while for integer S the problem factors into an S-tuplet and an $(S+1)$-tuplet.

Since $w(Q,P) = w(Q,-P)$, we may take $P \geq 0$ without loss of generality. In addition $0 \leq \langle (S^\alpha)^2 \rangle \leq S^2$, so the search for the maximum of $w(Q,P)$ may be restricted to the shaded regions shown in Fig. 1. In the calculations reported in Sec. III, we have used two techniques for locating the maximum. For each value of η and v we either (i) directly maximize $w(Q,P)$ or (ii) find all solutions of the self-consistent equations $\partial w / \partial Q = \partial w / \partial P = 0$ and select the one which maximizes w. Both methods require a computer. In addition, analytic work may be done when the order parameters Q and P are both small (Sec. II C) and at low temperatures, where v is large (Sec. II D).

C. Second-Order Transitions: Landau Development

When the factor $e^{-\beta\mathcal{H}_{\mathrm{MFA}}}$ in (12) is expanded in powers of v, standard tables[25] make it easy to evaluate the traces of the first few terms. One finds for small Q and P the expression

$$w-\ln(2S+1)=\frac{vQ^2}{40}\,[vX(4X-3)-30]+\frac{\eta vP^2}{120}[\eta vX(4X-3)-30]$$
$$+\frac{(vQ)^3X}{2^4\times3\times5\times7}\,(4X-3)\,(4X-15)-\frac{\eta^2v^3QP^2X}{2^4\times3\times5\times7}\,(4X-3)\,(4X-15)$$
$$-\frac{(\eta vP)^4X}{2^7\times3^2\times5^2\times7}\,(4X-3)(8X^2+54X-105)+\cdots, \quad (14)$$

where $X\equiv S(S+1)$.

When the bracketed expressions in the first two terms of (14) are both negative, the origin of the Q-P plane is a local maximum. If the origin is a global maximum, the system undergoes a second-order transition of the Landau type[26] when the normalized temperature $t\equiv 1/v$ decreases through a critical value which makes one or both brackets vanish. The locus of these incipient transitions is sketched in Fig. 2. For $0\le\eta<1$ the Landau transition is (except when $S=\frac{3}{2}$) preempted (Sec. III) by a first-order transition at a higher temperature; however, for sufficiently large η, the second-order transition is realized at

$$t_c(\eta)\equiv 1/v_c(\eta)=\tfrac{1}{30}\eta X(4X-3)\ . \quad (15)$$

Just below the transition, $P\propto(t_c-t)^{1/2}$ and $Q\propto(t_c-t)$. As η is decreased, the second-order transition terminates in a tricritical point.[27] On examining the self-consistent equations at temperatures t just greater than $t_c(\eta)$, one finds that a first-order transition (to a state with small but finite Q and P) occurs just below the tricritical value

$$\eta_t=\frac{2}{7}\left(\frac{68X^2-111X+195}{8X^2+54X-105}\right), \quad (16)$$

as indicated in Fig. 2.

D. Low Temperatures

v is large at low temperatures, and analytic solution of MFA is again possible, provided the eigenvalues $\lambda_n(Q,P)$ of (13) are available. This is useful, since it provides a direct understanding of the ordering in the low-temperature phase.

At low temperatures,

$$w(Q,P)=v[\lambda_{\max}(Q,P)-\tfrac{3}{4}Q^2-\tfrac{1}{4}\eta P^2]$$
$$+\ln g(Q,P)+O(e^{-v})\ , \quad (17)$$

where $\lambda_{\max}$ is the maximum eigenvalue λ_n and $g(Q,P)$ is its degeneracy. For each eigenvalue, the (Q,P) which maximizes w is determined. Then the magnitudes of the maxima must be compared.

We illustrate by studying the particularly interesting example $S=2$. The doublet $(M=\pm1)$ gives eigenvalues $\lambda_{1,2}=-\frac{3}{2}Q\pm\frac{3}{2}\eta P$. The triplet $(M=0,\pm2)$ gives $\lambda_3=3Q$ and $\lambda_{4,5}=\pm(9Q^2+3\eta^2P^2)^{1/2}$. Local maxima in w for various λ_n occur at points (Q,P) as follows: $(-1,\pm3)$ for $\lambda_{1,2}$, $(2,0)$ for λ_3, and for λ_4 both $(\pm2,0)$ and $(0,\pm2\sqrt{3})$. The η dependence of the associated values of ω is shown in Fig. 3. For $0\le\eta<1$ the points $(\pm2,0)$ are degenerate to order v; however, λ_3 and λ_4 are degenerate at $(+2,0)$, giving an extra contribution ln2 to (17), so by (11) the low-temperature phase is uniaxially elongated along $\hat{z}$, with $\langle(S^z)^2\rangle=4$, $\langle(S^x)^2\rangle=\langle(S^y)^2\rangle=1$ at $t=0$. When $\eta>1$, the global maximum is at $(0,\pm2\sqrt{3})$, so the ground state is always biaxial, elongated along $\hat{x}$ and squeezed along $\hat{y}$ or conversely. A special situation (unique to $S=2$) develops for $\eta\gtrsim1$ at low but finite temperature. For $\eta\ne1$ the eigenvalues are nondegenerate at both $(0,\pm2\sqrt{3})$ and $(-1,\pm3)$; however,

$$\lambda_4(-1,\pm3)=3(1+3\eta^2)^{1/2}=6+\tfrac{9}{2}(\eta-1)+O((\eta-1)^2)\ ,$$

which is degenerate with $\lambda_{1,2}$ except for terms $O((\eta-1)^2)$. This accidental degeneracy allows $(-1,\pm3)$ to compete (entropically) with $(0,\pm2\sqrt{3})$; and, for $\eta\gtrsim1$, as t increases, the system undergoes a first-order transition at $t_f=\frac{3}{4}(\eta-1)/\ln2$ to a nearly uniaxial state, $\langle(S^x)^2\rangle\approx4$, $\langle(S^y)^2\rangle\approx\langle(S^z)^2\rangle\approx1$ (or with $x\leftrightarrow y$). The full phase diagram is shown in Fig. 4.

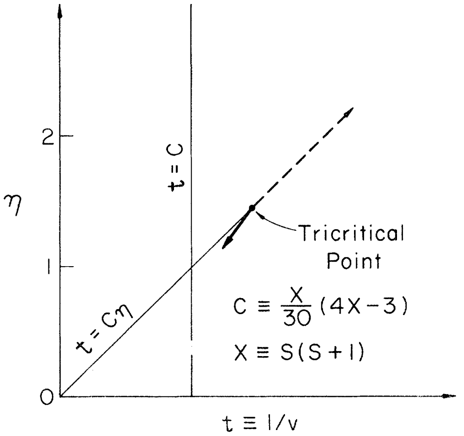

FIG. 2. Potential second-order phase transitions in MFA. The plot is to scale for $S=3$. The position of the tricritical point is given by (16). Only the dashed portion of the second-order phase boundary is actually realized. The heavy line shows the beginning of the first-order phase boundary.

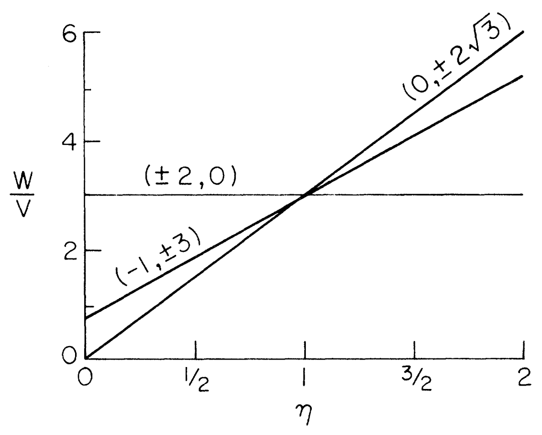

FIG. 3. Local maximum values of $\omega(\eta)$ at low temperatures for $S=2$. Plots are labeled by the position (Q, P) of the maximum.

E. $\eta = 1$, Uniaxial-Biaxial Transition

When $\eta = 1$, the "restricted" axial problem defined by (10)–(13) becomes a special case ($J_{33} = J_{44} = J_{55} = 0$) of cubic symmetry (see Table I). Under the cubic operations regions of the MFA free-energy surface map into one another; i.e., $w(Q, P)$ is the same at the following six equivalent points in the (Q, P) plane: $(Q, \pm P)$, $(-\frac{1}{2}Q + \frac{1}{2}P, \pm(\frac{3}{2}Q + \frac{1}{2}P))$, and $(-\frac{1}{2}Q - \frac{1}{2}P, \pm(\frac{3}{2}Q - \frac{1}{2}P))$. For $0 \leq \eta < 1$ the dominant maximum in the ordered phase is always at[28] $(Q_0(t), P = 0)$, corresponding to uniaxial order in the z direction. As η approaches unity, equivalent maxima develop near the points $(-\frac{1}{2}Q_0(t), \pm\frac{3}{2}Q_0(t))$, corresponding to uniaxial order in the x or y directions. Beyond $\eta = 1$ these new maxima take over, and the system undergoes a first-order transition to a state which becomes increasingly biaxial as η increases. It will sometimes be convenient for $\eta > 1$ to plot variables such as

$$
\begin{aligned}
Q_y &\equiv \langle Q^{yy} \rangle = -\tfrac{1}{2}Q - \tfrac{1}{2}P \,, \\
P_y &\equiv \langle Q^{zz} - Q^{xx} \rangle = \tfrac{3}{2}Q - \tfrac{1}{2}P \,,
\end{aligned}
\tag{18}
$$

which directly exhibit the development of biaxiality in the departure of P_y from zero.

TABLE II. Important parameters of the molecular-field solutions. $t_f \equiv 1/v_f$ [see (8)] is the reduced transition temperature (first order, except for $S=\frac{3}{2}$) for $0 \leq \eta \leq 1$. ΔQ is the corresponding discontinuity in Q. η_t and t_t are the tricritical-point parameters from (15) and (16). $S=\infty$ data are specially normalized, as explained in the text.

Spin	t_f	ΔQ	η_t	t_t
1	0.361	−0.333	2	$\frac{2}{3}$
$\frac{3}{2}$	$\frac{3}{2}$	0	...	...
2	4.251	0.473	1.114	4.679
$\frac{5}{2}$	9.80	1.10	1.292	12.054
∞	0.147 (Ref. 15)	0.286 (Ref. 15)	2.429	0.324

III. RESULTS

Molecular-field phase diagrams are shown for $S = 1$, $\frac{3}{2}$, 2, $\frac{5}{2}$, and ∞ in Fig. 4. Table II gives numerical values for several of the principal features. First- and second-order phase boundaries are shown as full and dashed lines, respectively. Between $\eta = 1$ and η_t the transition remains first order, but the discontinuity ΔQ in Q decreases from its $\eta = 1$ value to zero at the tricritical point. The discontinuity in P vanishes at both ends of the interval. For $0 \leq \eta \leq 1$ the ordering is always uniaxial; for $\eta > 1$ it is biaxial. We comment briefly on the special features of each spin value.

A. $S = 1$

The three eigenvalues of (13) and their corresponding eigenfunctions are $\lambda = -Q$ ($|M=0\rangle$), $\frac{1}{2}Q \pm \frac{1}{2}\eta P$ ($(1/\sqrt{2})(|1\rangle \pm |-1\rangle)$). The single-ion molecular-field energy levels are (in our notation) $E_n = -kTv\lambda_n$, which are shown schematically in Fig. 5. The uniaxial ($P=0$) ordering for $0 \leq \eta < 1$ involves compression along $\hat{z}$ with dilation along $\hat{x}$ and $\hat{y}$ (Fig. 6). The ground state is the singlet $|0\rangle$, and at $t=0$ one finds $Q = -\frac{2}{3}$, so $\langle (S^z)^2 \rangle = 0$,

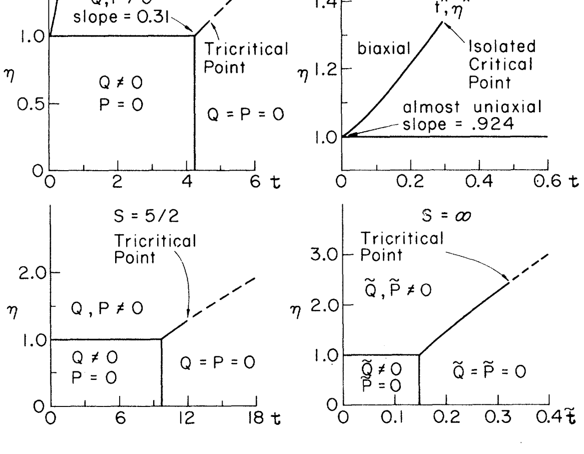

FIG. 4. Phase diagrams for spins $S=1$, $\frac{3}{2}$, 2, $\frac{5}{2}$, and ∞. $t = 1/v$ is the reduced temperature and η measures the anistropy. First- and second-order phase boundaries are shown as full and dashed lines, respectively.

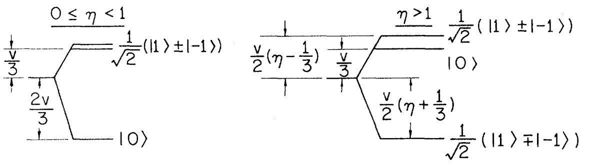

FIG. 5. Single-ion molecular-field energy levels for $S=1$. Because of the self-consistency the splittings vary with both temperature $t=1/v$ and anisotropy η.

$\langle (S^x)^2\rangle = \langle (S^y)^2\rangle = 1$. At $\eta=1$ the three axes become equivalent.

Above $\eta=1$ the ground state belongs to the $M=\pm 1$ doublet. At $t=0$ the ordering is uniaxial, shaped as for $0 \le \eta < 1$, only with the "pancake's" axis now along $\hat{x}$ or $\hat{y}$. For $t>0$ the ordering is weakly biaxial. Variation of Q_y and P_y [Eq. (18)] is shown in Fig. 7.

Note that for $\eta > 1$ transitions in the two parameters Q and P occur simultaneously. The transitions in Q and P can be separated by adding to the Hamiltonian a single-ion anisotropy term $D\sum_1 [S^z(1)]^2$, which modifies the phase boundary along $\eta=1$ by shifting its low-temperature end to $\eta = 1+4\delta$, $\delta \equiv \beta D/v$, and by diverting its high-temperature end from the horizontal (see Fig. 8). Thus for $D>0$, inside a range of η just above $\eta=1+4\delta$, a first-order transition in Q at $P=0$ is followed at lower temperature by another first-order transition into the fully biaxial state, as long as $\delta < 0.010$. For $\delta > 0.010$ the high-temperature transition disappears and $Q(t)$ is continuous at low η. A similar range exists just below $\eta = 1+4\delta$ for $D<0$: A second-order transition in P with Q smooth is followed at a lower temperature by a first-order transition out of the fully biaxial state (as shown, for example, in Fig. 8 for $\delta = -0.1$).

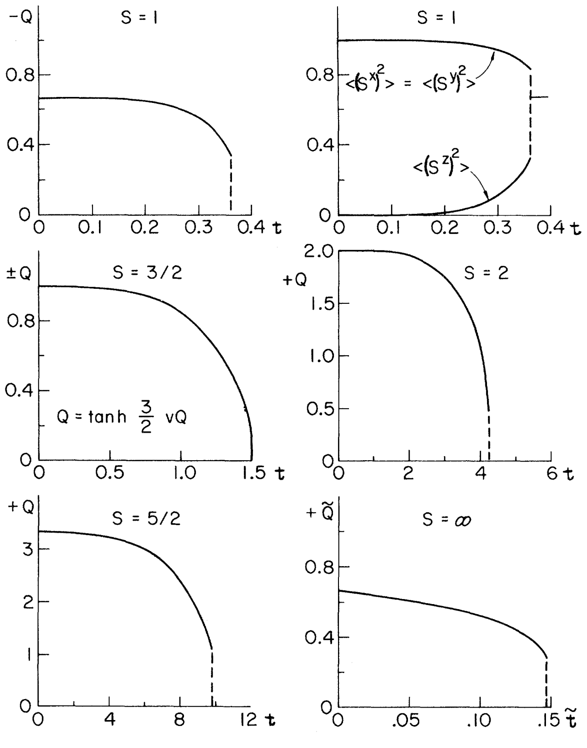

FIG. 6. Thermal variation of the order parameter Q in the uniaxial regime $0 \le \eta \le 1$. The corresponding variation of $\langle (S^\alpha)^2\rangle$, $\alpha = x, y, z$, is shown for $S=1$. Dashed lines indicate the discontinuities at first-order transitions.

B. $S=\frac{3}{2}$

This is a very special case.[29] The eigenvalues of (13) are $\lambda = \pm\frac{1}{2}(9Q^2 + 3\eta^2 P^2)^{1/2}$. There are only two energy levels (each doubly degenerate), so the system is quite Ising-like. Furthermore, the single-ion energies (and, therefore, w) depend

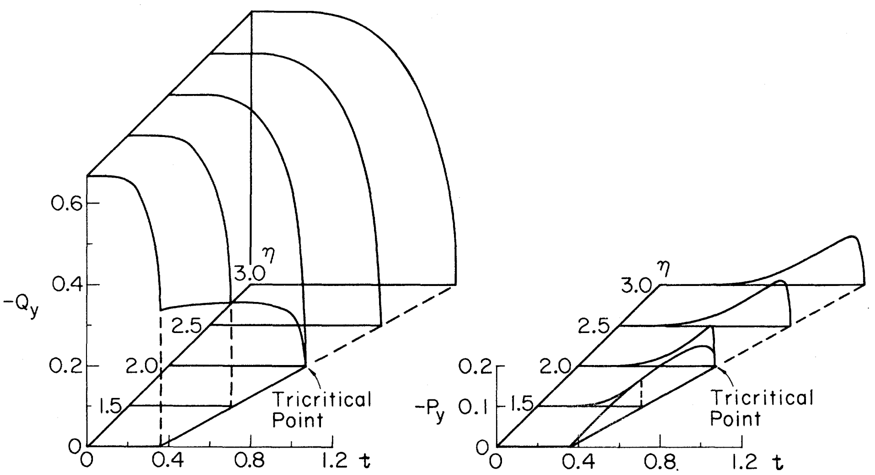

FIG. 7. $S=1$; the variation of the quadrupolar order parameters Q_y and P_y [Eq. (18)] with temperature t and anistropy η. Note that $P_y = 0$ at $\eta = 1$.

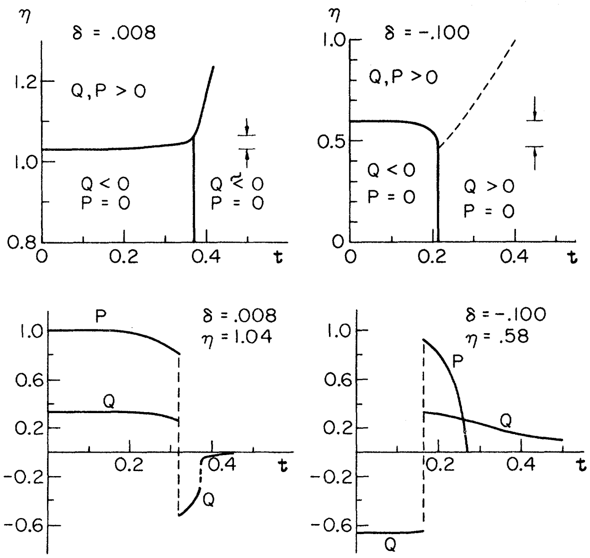

FIG. 8. Phase diagrams and thermal variations of the order parameters for $S=1$ in the presence of single-ion anisotropy. Arrows on the phase diagrams show the ranges of η corresponding to successive transitions. Positive (negative) δ shifts the tricritical point in the $+\eta$, $+t$ direction ($-\eta$, $-t$ direction); for $\delta=-0.1$, the tricritical point has disappeared.

only on Q^2 and P^2, so $w(\pm Q, \pm P)$ are all degenerate. All transitions in t are second order and can be located by the methods of Sec. IIC. For $t=0$ and $0 \leq \eta < 1$ the uniaxial ground state is $Q=\pm 1$, $P=0$, i.e., either $\langle (S^x)^2\rangle = \langle (S^y)^2\rangle = \frac{3}{4}$, $\langle (S^z)^2\rangle = \frac{9}{4}$ or $\langle (S^x)^2\rangle = \langle (S^y)^2\rangle = \frac{7}{4}$, $\langle (S^z)^2\rangle = \frac{1}{4}$. These two alternative orderings are rigorously degenerate within MFA and remain so at finite t because of the Q^2 dependence noted above.

At $\eta=1$ the system is even more degenerate, because $w(Q,P)$ becomes a function of the single variable $R \equiv \frac{1}{2}(9Q^2+3P^2)^{1/2}$, which must satisfy the single self-consistent equation $R=\frac{3}{4}\tanh vR$, so $R(t)$ corresponds to a whole family of solutions $Q(t)$, $P(t)$ at each temperature.

Above $\eta=1$ the ordering is biaxial. At $t=0$, we find $Q=0$, $P=\pm\sqrt{3}$, which represents a dilation along $\hat{x}$ and a compression along $\hat{y}$ (or vice versa) with $\hat{z}$ remaining fixed.

C. $S=2$

The eigenvalues were given in Sec. IID, where the low-temperature properties are discussed in detail. The low-η phase is uniaxially elongated along $\hat{z}$. At $\eta=1$ for any finite t there is a first-order phase transition (with increasing η) to a state which is elongated along one of the transverse axes. Biaxiality develops away from $\eta=1$. At low temperatures and $\eta \gtrsim 1$ there is another first-order phase boundary, separating the nearly uniaxial state (η near 1) from the fully biaxial state, which always dominates as $t\rightarrow 0$. This phase boundary terminates in a critical point at $t^*=0.294$, $\eta^*=1.34$, beyond which the shape of the ordering changes continuously. Figure 9 shows the variation of Q and P.

D. $S=\frac{5}{2}$

As for $S=2$, the low-η phase is uniaxially elongated in the z direction. Biaxiality develops above $\eta=1$. The phase diagram is represented in Fig. 4, and the thermal variation of Q for $\eta=1$ is given in Fig. 6. The thermal variation of Q and P for $\eta>1$ is qualitatively similar to that found for $S=\infty$ and shown in Fig. 10.

E. $S=\infty$

It is convenient to normalize the $S\rightarrow\infty$ limit in such a way that the fundamental variable is $\vec{S}/S$, which becomes a classical unit vector as $S\rightarrow\infty$. To do this, we write in (4) $J=\tilde{J}/S^4$, $\mathcal{O}=S^2\tilde{\mathcal{O}}$, and interpret $\mathrm{Tr}\rightarrow\int(d\Omega)/4\pi$, dropping the irrelevant

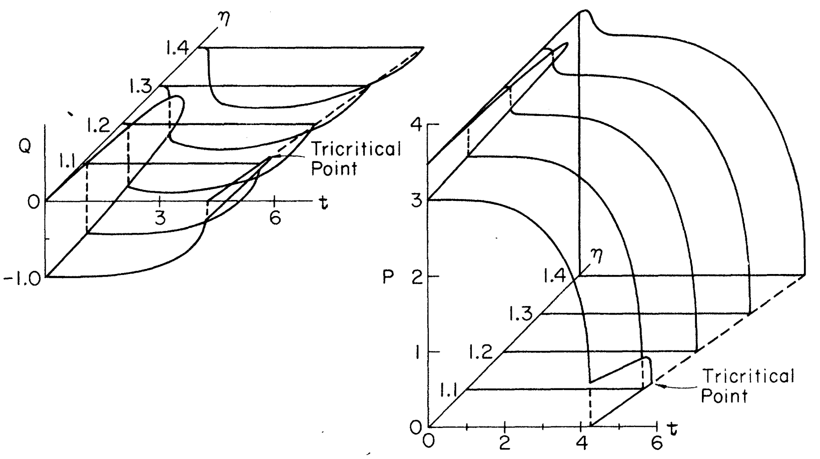

FIG. 9. $S=2$; the variation of the quadrupolar order parameters Q and P with temperature t and anistropy η.

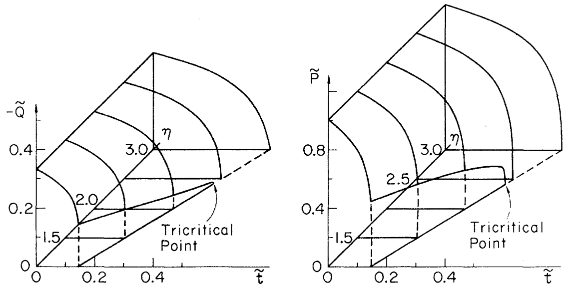

FIG. 10. $S=\infty$; the variation of the (normalized) quadrupolar order parameters $\tilde{Q}$ and $\tilde{P}$ with the (normalized) temperature $\tilde{t}$ and the anisotropy η. The normalized variables are defined in the text.

constant $\ln(2S+1)$ which appears in w [e.g., (14)]. Thus, $\tilde{v}=S^4 v$ and $\tilde{t}=t/S^4$. In place of (11) one finds

$$\langle (S^z/S)^2\rangle = \tfrac{1}{3}+\tilde{Q}, \quad \langle (S^x/S)^2\rangle = \tfrac{1}{3}-\tfrac{1}{2}\tilde{Q}+\tfrac{1}{2}\tilde{P},$$
$$\langle (S^y/S)^2\rangle = \tfrac{1}{3}-\tfrac{1}{2}\tilde{Q}-\tfrac{1}{2}\tilde{P}\,. \tag{19}$$

We plot the normalized variables $\tilde{t}$, $\tilde{Q}$, and $\tilde{P}$.

The behavior is entirely analogous to that of $S=\frac{5}{2}$ and we expect qualitatively similar results for all $\frac{5}{2}<S<\infty$. For $0\le\eta<1$ the quadrupoles[19] are uniaxially elongated along $\hat{z}$, with $\langle (S^z/S)^2\rangle=1$, $\langle (S^x/S)^2\rangle=\langle (S^y/S)^2\rangle=0$ at $t=0$. At $\eta=1$ the long axis shifts to $\hat{x}$ or $\hat{y}$. See Fig. 10.

IV. CONCLUSION

We have shown that the description of quadrupolar ordering in magnetic crystals involves at least two order parameters, $Q=\langle (S^z)^2-\frac{1}{3}S(S+1)\rangle$ and $P=\langle (S^x)^2-(S^y)^2\rangle$. The restricted axial situation has been investigated in detail within the molecular-field approximation. Two separate phase transitions in Q and P appear only if uniaxial single-ion anisotropy is introduced into the Hamiltonian (dipolar interactions might produce a third transition).

One may speculate on the ways in which exact results for the quadrupolar system might differ from the molecular-field results which we have studied. Extensive experience[30] suggests that the MFA phase diagram is likely to be qualitatively correct; however, quantitative changes may well be appreciable. The disordering effects of fluctuations (neglected in MFA) will certainly reduce all transition temperatures. In addition, the influence of low-energy collective excitations will render the behavior of the order parameters at low temperatures much "softer" than in MFA, particularly near $\eta=1$. It is quite likely, for example, that the special $S=2$ behavior is reduced in scope or entirely suppressed.

It should be interesting to consider multipolar interactions of orders higher than $l=2$ [e.g., octupolar ($l=3$) or hexadecapolar ($l=4$)][31] and to determine the number of independent parameters necessary to describe the most general multipolar ordered state. (When symmetries are present, a proper choice of coordinate axes may reduce the number appreciably from $2l+1$.) It seems likely that the onset of ordering in these new parameters will tend to drive ordering in order parameters of lower l. For instance, ordering in a nontetrahedral octupolar order parameter will drive quadrupolar ordering.

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APPENDIX: SYMMETRIES IN THE MOLECULAR-FIELD PROBLEM

Within the context of Eq. (8),

$$Z=\mathrm{Tr}\,\exp\sum_{i=i}^{5} V_i\mathcal{O}_i\,, \quad V_i=\sum_j v_{ij}\langle \mathcal{O}_j\rangle\,. \tag{A1}$$

Z is scalar under rotations and must be a function of the two spherical invariants which can be constructed from the quadrupolar field V.[32] These are[33]

$$I_1=\tfrac{1}{2}\sum_{i=i}^{5} V_i^2\,,$$
$$I_2=(2/\sqrt{3})V_1(\tfrac{1}{3}V_1^2-V_2^2)-(2/\sqrt{3})V_1V_3^2+2V_3V_4V_5$$
$$+V_4^2[(1/\sqrt{3})V_1+V_2]+V_5^2[(1/\sqrt{3})V_1-V_2]\,. \tag{A2}$$

The self-consistent equations (9) can then be written

$$F_1\frac{\partial I_1}{\partial\langle \mathcal{O}_i\rangle}+F_2\frac{\partial I_2}{\partial\langle \mathcal{O}_i\rangle}=\sum_j v_{ij}\langle \mathcal{O}_j\rangle\,, \tag{A3}$$

where $\partial\ln Z/\partial I_k=F_k(I_1,I_2)$, $k=1,2$. The structure of the five equations (A3), $i=1,\ldots,5$, can often be exploited without reference to the explicit form of F_1 and F_2.

As an example, we sketch the reduction of the cubic problem ($v_{11}=v_{22}=v$, $v_{33}=v_{44}=v_{55}=v'$, $v_{ij}=0$ for $i\ne j$) to the "restricted" axial problem solved in the text. We assume for simplicity that $v, v'\ne 0$ and $v\ne v'$. (These special cases are easily reduced to the uniaxial problem by proper choice of axes.) The following propositions are easily proved by manipulation of the equations (A3):

(i) If $\langle \mathcal{O}_3\rangle$, $\langle \mathcal{O}_4\rangle$, and $\langle \mathcal{O}_5\rangle\ne 0$, then $\langle \mathcal{O}_1\rangle=\langle \mathcal{O}_2\rangle=0$, and the solution has uniaxial structure along a (111) direction.

(ii) It is not possible for only one $\langle \mathcal{O}_i\rangle$, $i=3,4,5$, to vanish.

(iii) If $\langle \mathcal{O}_3\rangle = \langle \mathcal{O}_4\rangle = \langle \mathcal{O}_5\rangle = 0$, then the solution reduces to the $\eta = 1$ case of the text; i.e., the solution is uniaxial along a (100) direction.

(iv) If $\langle \mathcal{O}_3\rangle = \sqrt{2}\,\langle Q^{xy}\rangle \neq 0$, $\langle \mathcal{O}_4\rangle = \langle \mathcal{O}_5\rangle = 0$, then the solutions reduce to "restricted" axial solutions, referred to axes $(1/\sqrt{2})\,(\hat{x}\pm\hat{y}), \hat{z}$. The cases $\langle Q^{zx}\rangle \neq 0$ and $\langle Q^{yz}\rangle \neq 0$ follow by cyclic permutation.

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[7] The terminology "triaxial" is in some ways more appropriate, since, when both Q and P are nonzero, the quadrupole tensor has three distinct principal moments and the over-all symmetry is orthorhombic. On the other hand, nematic liquids are optically "biaxial" when $P \neq 0$, and it seems useful to stress this correspondence. See Refs. 16 and 17.

[8] Except for an over-all normalization factor, these are just the "Kubic Harmonics" $(\gamma_2)_1$, $(\gamma_2)_2$, $(\epsilon_2)_z$, $(\epsilon_2)_y$, and $(\epsilon_2)_x$, introduced by F. C. Von der Lage and H. A. Bethe, Phys. Rev. 71, 612 (1947).

[9] L. R. Walker, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1963), Vol. I, pp. 307–308.

[10] The corresponding 3×3 matrix J_{ij} for dipolar coupling $(l = 1)$ contains at most six independent elements and can always be diagonalized by a proper choice of axes. This result is *not* true for $l = 2$. Note that the diagonalization of J has nothing to do with the diagonalization of $\langle \overleftrightarrow{Q}\rangle$ discussed in Ref. 21.

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[21] The quadrupole operators $\overleftrightarrow{Q}$ are entirely isotropic and average to zero in the absence of interactions; however, the average $\langle \overleftrightarrow{Q}\rangle_\psi$ in any particular state ψ does not in general vanish. The 3×3 matrix $\langle Q^{\alpha\beta}\rangle_\psi$ may be diagonalized by a proper choice of "molecular axes" (depending on ψ). In the absence of external forces, the intramolecular Hamiltonian is isotropic and picks out energetically not a single state ψ but a set of states $\{R\psi\}$, all with the *same* eigenvalues $\langle \overleftrightarrow{Q}\rangle_{R\psi}$, which transform into one another under rotations R. One can model this structure with a spin Hamiltonian by either (i) putting in the (isotropic) intramolecular forces (single-ion terms in the Hamiltonian) or (ii) directly restricting thermal averages to the states $\{R\psi\}$.

[22] M. Blume *et al.*, Phys. Rev. A 4, 1071 (1971); H. Falk, Am. J. Phys. 38, 858 (1970).

[23] We neglect hereby the possibility of spatially more complicated order, such as occurs for example in antiferromagnets.

[24] By contrast, for dipolar coupling $(l = 1)$ in MFA it is easy to construct such an argument.

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[26] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, London, 1958), pp. 434ff.

[27] R. B. Griffiths, Phys. Rev. Letters 24, 715 (1970).

[28] Since $P = 0$, η disappears from the problem, and the MFA solution is fixed and strictly unaxial for $0 \leq \eta < 1$.

[29] When $\eta = 0$, the system is rigorously (i.e., *not* just in MFA) equivalent to an $S = \frac{1}{2}$ Ising model. See Ref. 3.

[30] J. S. Smart, *Effective Field Theories of Magnetism* (Saunders, Philadelphia, Pa., 1966).

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[32] The corresponding statement for the dipolar case $l = 1$ is that $Z = \mathrm{Tr}\,\exp\vec{h}\cdot\vec{S}$ is a function of the invariant h^2. See also Ref. 24.

[33] In the Cartesian representation these are $\frac{1}{4}\mathrm{Tr}V^2$ and $\det V$. See Ref. 17.