Quantum quadrupolar magnetism and phase transitions in the presence of biquadratic exchange

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A Hamiltonian with biquadratic exchange permits new types of magnetic order. In particular, a quantum quadrupolar structure is possible, i.e., order in which $S_f^z=0$ for all atoms to within the zero-point oscillations. A spin-wave approximation is derived for the case $S=1$ by employing a special representation for the spin operators. This permits one to determine the stability range for such structures. It is shown in the molecular field approximation that the transition from the ferromagnetic to the paramagnetic state at finite temperatures can be not only first order but, for $S\geq 2$, can occur via an intermediate quadrupolar phase of statistical nature; this is a semi-ordered state with $\langle S_f^z\rangle = 0$ and $\langle (S_f^z)^2\rangle \sim S^2$. The phase transition from the ferromagnetic to the semi-ordered state can be of either first or second order; the destruction of this state, like that of the quantum quadrupolar structure, occurs in a discontinuous manner.

There exist materials whose magnetic properties are determined by localized moments but for which the Heisenberg Hamiltonian is certainly inapplicable. This is the situation, e.g., in the case of magnetic conductors that can be described by the s-d-model if the Fermi energy of the charge carriers is comparable with or less than the s-d exchange energy; superexchange in insulators can also lead to an effective non-Heisenberg exchange Hamiltonian.

A number of authors, e.g., in the papers[1-5], take the non-Heisenberg character of the exchange into account by adding a biquadratic term to the Heisenberg Hamiltonian:

$$H=-\frac{1}{2}\sum J(f-g)\,(\mathbf{S}_f\mathbf{S}_g)-\frac{1}{2}\sum K(f-g)\,(\mathbf{S}_f\mathbf{S}_g)^2. \qquad (1)$$

The lattice is assumed to consist of identical atoms with spin $S \geq 1$, and $\mathbf{S}_g$ is the spin operator of the atom with label g.

This simplest isotropic non-Heisenberg Hamiltonian enables us to describe a wider range of phenomena than can be described by the Heisenberg model. In particular, it was pointed out in the papers[3-5] that for certain values of the parameters of the Hamiltonian (1) both ferromagnetic and antiferromagnetic structures are unstable against the formation of a new quadrupolar phase with $\langle S_j^z \rangle = 0$, but since the molecular-field approximation was used the authors were not able to prove that a structure of this type can correspond to the ground state of the system.

It is shown in the present paper that at low temperatures this phase represents a new type of magnetic order—a quantum quadrupolar structure in which, for each atom, $S_f^z = 0$ to within the zero-point oscillations. In this case, long range magnetic order exists in the system and all correlators of the type $\langle S_f^i S_g^j \rangle_{f\neq g}$ are equal to zero.

The main result of the paper is the quantum-mechanical proof of this structure. A spin-wave approximation (with the usual small parameter $1/Z$) is derived by means of a special representation for the spin operators in the case $S = 1$, and this has made it possible to indicate the range of stability of the quantum quadrupolar structure. The existence of such a structure is a specifically quantum effect, generally speaking, which vanishes in the transition to classical spins.

At finite temperatures, a quadrupolar phase of a statistical type is possible, viz., an intermediate semi-ordered state with $\langle S_f^z \rangle = 0$ and $\langle (S_f^z)^2 \rangle \sim S^2$ which arises on heating of the ferromagnetic (or antiferromagnetic) crystal and goes over into the paramagnetic state on further heating. The process of destruction of the ferromagnetic order is studied in the present paper in the molecular-field approximation for arbitrary S and it has been possible to obtain part of the results analytically, whereas the analogous calculations of Nauciel-Bloch, Sarma and Castets[4] were performed for $S = 1$ only, and results of numerical calculations for the cases $S = 1$ and $S = 5/2$ are given in the paper by Chen and Levy[5].

It is shown below that the phase transition from the ferromagnetic to the semi-ordered state can be either first- or second-order (the character of this transition was not elucidated in[5]), while the destruction of the semi-ordered state, like that of the quantum quadrupolar structure, occurs discontinuously.

1. THE GROUND STATE AND MAGNON SPECTRUM

As in[4,5], here and below we confine ourselves to the approximation of nearest neighbors and to magnetic structures that can be represented by one sublattice, i.e., to the ferromagnetic structure and the quadrupolar structures (the extension of the results to the case of an antiferromagnet is trivial).

The Hamiltonian (1) can be written conveniently by choosing the direction of the magnetic moment of the system as the quantization axis z:

$$\begin{aligned}H=&-\frac{1}{2}\left(J-\frac{K}{2}\right)\sum S_f^zS_g^z-\frac{J}{2}\sum S_f^+S_g^--\frac{S^2(S+1)^2}{4}KNZ\\&-\frac{1}{2}K\sum\Big[\frac{3}{2}(S_f^z)^2(S_g^z)^2-S(S+1)(S_f^z)^2\\&+\frac{1}{2}(S_f^+)^2(S_g^-)^2+S_f^zS_f^+S_g^zS_g^-+S_f^+S_f^zS_g^-S_g^z\Big]\end{aligned} \qquad (2)$$

where $S_f^{\pm} = S_f^x \pm iS_f^y$, and Z is the number of nearest neighbors.

For J > 0 and K > 0, in addition to ordinary ferromagnetic order this Hamiltonian also permits quantum quadrupolar order. As will be shown below, in the molecular-field approximation the energy as a function of the parameters $m = \langle S_f^z \rangle$ and $y = \langle (S_f^z)^2 \rangle - S(S+1)/3$ has a local minimum for a wavefunction $|0\rangle$ such that $\langle 0 | S_f^z | 0 \rangle = 0$, and $\langle 0 | (S_f^z)^2 | 0 \rangle = 0$ for integer S and $\langle 0 | (S_f^z)^2 | 0 \rangle = 1/4$ for half-integer S. In the case S = 1, for K > J > 0 this minimum lies below the energies of the ferromagnetic and antiferromagnetic states.

We shall establish the stability of such a structure. For this we must show that the energy of excitations from the state assumed to be the ground state is positive. Usually, this can be done for weakly-excited states by obtaining a spin-wave spectrum with positive frequencies. For a quantum quadrupolar structure, however, it does not make sense to use a representation of the Holstein-Primakoff-Izyumov type to introduce the second-quantization operators and derive the spin-wave approximation.

We shall confine ourselves to the case S = 1. It is clear from the symmetry of the problem that if an atom is in a state with zero spin component along the z axis, then, in the case of a quantum quadrupolar structure, it can go over into a state with component +1 or into a state with component −1. It seems reasonable, therefore, to introduce two different types of operator for a single site with label f: b_{f1}^+, b_{f1} are the operators of the spin deviation from the value $S_f^x = 0$, which describe transitions between states with spin components +1 and 0:

$$b_{f1}^+\delta(S_f^z)=\delta(S_f^z-1),\ b_{f1}\delta(S_f^z-1)=\delta(S_f^z); \tag{3}$$

b_{f2}^+, b_{f2} are the analogous operators describing transitions between states with spin components 0 and −1:

$$b_{f2}^+\delta(S_f^z)=\delta(S_f^z+1),\ b_{f2}\delta(S_f^z+1)=\delta(S_f^z). \tag{4}$$

In the terminology of second quantization, b_{f1}^+ and b_{f2}^+ are creation operators and b_{f1} and b_{f2} annihilation operators for the corresponding spin deviations; the vacuum wavefunction corresponds to the case when all the atoms are in the state with zero spin component along the z axis, i.e., to the ground state in the molecular-field approximation.

These operators can be related to the spins as follows:

$$\begin{gathered} S_f^+=\sqrt{2}(b_{f1}^++b_{f2}),\quad S_f^-=\sqrt{2}(b_{f1}+b_{f2}^+),\\ S_f^z=b_{f1}^+b_{f1}-b_{f2}^+b_{f2},\quad (S_f^z)^2=b_{f1}^+b_{f1}+b_{f2}^+b_{f2}. \end{gathered} \tag{5}$$

Since only states with atomic-spin components 0 and ±1 have physical meaning, it is necessary to introduce restrictions on the occupation numbers, i.e., to take commutation relations describing the kinematic interaction:

$$b_{fi}^+b_{fi}^+=b_{fi}b_{fi}=0. \tag{6}$$

In order to ensure the uniqueness of the physical states arising from the vacuum state under the action of the operators introduced above, we must also put

$$b_{f1}b_{f2}=b_{f2}b_{f1}=b_{f1}^+b_{f2}^+=b_{f2}^+b_{f1}^+=b_{f1}b_{f2}^+=b_{f2}b_{f1}^+=0. \tag{7}$$

In addition, the commutation relations for the spin operators expressed in terms of the second-quantization operators must be satisfied. The latter condition gives Bose relations for operators referring to different sites, and, for diagonal operators, the relation

$$b_{f1}b_{f1}^+=1-b_{f1}^+b_{f1}-b_{f2}^+b_{f2}=b_{f2}b_{f2}^+. \tag{8}$$

Using (5) and the commutation relations (6)–(8), we can write the Hamiltonian (2) in the second-quantization representation:

$$\begin{aligned} H={}&-KNZ+KZ\sum(n_{f1}+n_{f2})+(K-J)\sum(b_{f1}^+b_{g2}^++b_{f1}b_{g2})\\ &-J\sum(b_{f1}^+b_{g1}+b_{f2}^+b_{g2})-\frac{3}{4}K\sum(n_{f1}+n_{f2})(n_{g1}+n_{g2})\\ &-\frac{1}{2}\left(J-\frac{K}{2}\right)\sum(n_{f1}-n_{f2})(n_{g1}-n_{g2})-K\sum b_{f1}^+b_{f2}b_{g2}^+b_{g1}\equiv E_0+H_2+H_4, \end{aligned} \tag{9}$$

where E_0 is the vacuum-state energy, and H_2 and H_4 are expressions of second and fourth order respectively in the second-quantization operators; $n_{fi} = b_{fi}^+b_{fi}$.

It does not seem possible to diagonalize the Hamiltonian (9) exactly; therefore, in the spirit of the formalism of the spin-wave approximation, we attempt to approximate the lower part of the spectrum of the full Hamiltonian (9) by the spectrum of the quadratic form H_2, assuming b_{fi}^+ and b_{fi} to be operators of the Bose type. For this, we assume that the probability of encountering a value $(S_f^z)^2 \neq 0$ is small, i.e., that the true ground state differs little from that obtained by means of the variational principle. In accordance with this, we shall regard the mean values of products of spin operators as quantities of decreasing order of magnitude (the subsequent calculation confirms this assumption):

$$\begin{gathered} 1\gg\{\langle(S_f^z)^2\rangle\}\sim\{\langle(S_f^{\pm})^2\rangle\}\gg\{\langle(S_f^z)^2(S_g^z)^2\rangle_{f\neq g}\}\\ \sim\{\langle(S_f^{\pm})^2(S_g^{\mp})^2\rangle_{f\neq g}\}\gg\ldots \end{gathered} \tag{10}$$

Under this condition, the form H_2 will be the principal term in the Hamiltonian and the spectrum will be determined approximately by the expression $H = E_0 + H_2$.

In addition, if in accordance with the assumption of the small mathematical expectations of the spin deviations we neglect the deviations of the corresponding commutators for the operators b_{fi} and b_{ji}^+ from their values for the ground state, then these operators can be regarded as Bose operators (these differences, as can easily be shown directly from (5)–(8), are $\sim\langle (S_f^z)^2 \rangle$ in order of magnitude).

The quadratic form in the Bose operators is diagonalized by the usual Fourier transformation with respect to the site label and by interchanging the two types of creation and annihilation operators. As in an ordinary antiferromagnet, the magnon spectrum is found to be doubly degenerate with a linear dispersion law at small quasi-momenta q:

$$\omega_{\mathbf{q}}^2=K^2Z^2(1-\gamma_{\mathbf{q}})\left(1+\gamma_{\mathbf{q}}-\frac{2J}{K}\gamma_{\mathbf{q}}\right),\quad \gamma_{\mathbf{q}}=\frac{1}{Z}\sum_{\boldsymbol{\delta}}e^{i\mathbf{q}\boldsymbol{\delta}}, \tag{11}$$

and the vector $\boldsymbol{\delta}$ connects neighboring sites. However, in this case, unlike that of the antiferromagnet, the equality $\omega(q) = \omega(\pi/a - q)$ is not valid, i.e., the magnetic period of the crystal coincides with the crystallographic period.

For the renormalized energy of the ground state, we obtain the expression

$$E_0=-KNZ\left[1+\frac{1}{2Z}\left(\frac{K-J}{K}\right)^2+o\left(\frac{1}{Z}\right)\right]. \tag{12}$$

As can be seen from formula (11) the magnon frequencies are positive, signifying that the quantum quadrupolar structure is stable (this is a necessary but by no means sufficient condition) for $0 < J < K$.

We now estimate how well the condition $\langle (S_f^z)^2\rangle \ll 1$ is fulfilled. Using the transformation that diagonalizes H_2, for $T = 0$ we obtain

$$\langle (S_f^z)^2\rangle = \langle n_{f1}\rangle + \langle n_{f2}\rangle = D \equiv \frac{1}{N}\sum_q \frac{\Gamma_q^2}{\sqrt{1-\Gamma_q^2}\,[1+\sqrt{1-\Gamma_q^2}]},$$
$$\Gamma_q \equiv \frac{(K-J)\gamma_q}{K-J\gamma_q}. \tag{13}$$

For $K = J$, as can be seen from (13), $D = 0$ identically (i.e., on the boundary with the ferromagnetic solution, the quantum quadrupolar solution is as exact as the ferromagnetic solution). By virtue of the continuity of D as a function of $K - J$, we also have $D \ll 1$ for $K - J \ll K$. The situation near the other stability boundary, with $J \approx 0$, is somewhat more complicated. In this case, we obtain from (13)

$$\varepsilon/2 < D_0 < \varepsilon, \quad \varepsilon = \frac{1}{N}\sum_q \frac{\gamma_q^2}{(1-\gamma_q^2)^{1/2}}. \tag{14}$$

We assume, as usual[6], that in order of magnitude $\epsilon \sim 1/Z$, i.e., $D_0 \sim 1/Z$, which gives in general a favorable estimate for the possibility of applying the spin-wave approximation. Inside the interval $0 < J < K$, the quantity D takes intermediate values $0 < D < D_0$. Analogous estimates hold for the other products of spin operators, i.e., the single small parameter $D \sim 1/Z$ occurs in (10).

Thus, in the approximation of noninteracting spin waves, a doubly degenerate spectrum is obtained and the estimated accuracy is 1/Z. In more exact calculations, it is necessary to take into account the dynamic interaction (the form H_4), and the kinematic interaction described by the non-Bose commutation relations. The cumbersome technique proposed by Haley and Erdös[7] may turn out to be useful for this purpose.

For comparison, we now give the results of the calculation in the spin-wave approximation for the ferromagnetic and antiferromagnetic order. In the case of a ferromagnet, these are the obvious result for the ground-state energy:

$$E_F = -\tfrac{1}{2}NZ(JS^2+KS^4), \tag{15}$$

and the usual magnon dispersion law (with a renormalized energy constant):

$$\omega_q = [J+2S(S-1)K]SZ(1-\gamma_q). \tag{16}$$

Analogously, for the antiferromagnet,

$$E_{AF} = -\frac{NZ}{2}\left[KS^4-(J-K)S^2-\frac{(J-K)S}{Z}+o\left(\frac{1}{Z}\right)\right], \tag{17}$$

$$\omega_q = [(K-J)+2S(S-1)K]SZ\sqrt{1-\gamma_q^2}. \tag{18}$$

Comparing (12) with (15) and (17), we convince ourselves that, in the stability range $0 < J < K$, quantum quadrupolar order for $S = 1$ is energetically more favorable than either ferromagnetic or antiferromagnetic order.

We note, incidentally, that the spectra (16) and (18) were first obtained in a paper by Lines and Jones[8], but without a sufficiently rigorous proof. A feature of Hamiltonians of the type (1) that are nonlinear in spin operators referring to the same atom is that, after application of the Holstein-Primakoff-Izyumov transformation from the spin operators to the "almost-Bose" operators a_f^+ and a_f[6], the Hamiltonian must be brought to normal form, in which, in order of action upon the wave function, all annihilation operators stand ahead of the creation operators. To obtain, in the final form, an expression quadratic in the operators a_f and a_f^+ for the Hamiltonian reduced to normal form, it is convenient, before going over to the second-quantization representation, to rearrange the operators $S_f^\pm$ and S_f^z in (2) in such a way that their products appear only in the combinations $S_f^zS_f^+$ and $S_f^-S_f^z$. In the case of collinear structures, diagonalization of the corresponding quadratic forms leads to the relations (15)—(18). The approach used in[8] is thereby justified. However, in the study of noncollinear structures, the terms with $(S_f^\pm)^2$, which were discarded in[8], are important, and in this case the arguments given in[8] for the derivation of the magnon spectrum are insufficient.

2. BEHAVIOR OF THE MAGNET AT FINITE TEMPERATURES

To investigate the behavior of the magnet at finite temperatures we use the molecular-field approximation, based on the variational principle for the free energy. The variational parameters m and y are proportional to the effective fields acting on S_f^z and $(S_f^z)^2$ respectively. The Hamiltonian (2) can be represented in the form

$$H = H_0 + H_1, \tag{19}$$

where H_0 is the Hamiltonian of the molecular field:

$$H_0 = -j\left[m\sum_f S_f^z + \varkappa y\sum_f (S_f^z)^2\right], \quad j = Z\left(J-\frac{K}{2}\right), \quad j\varkappa = \frac{3}{2}K. \tag{20}$$

The quantities j and κ must be assumed positive, since for any other choice of their signs one-sublattice ordering may turn out to be energetically unfavorable.

The variational principle is formulated in the form of an inequality[6]

$$F \leqslant F_M = F_0 + \langle H_1\rangle, \tag{21}$$

$$F_0 = -Nj\tau\ln\left[\sum_{l=-S}^{S}\exp\frac{ml+\varkappa yl^2}{\tau}\right], \tag{22}$$

where F_0 is the free energy corresponding to the Hamiltonian H_0; the angular brackets denote thermal averaging with the Hamiltonian H_0; $\tau = T/j$ is the dimensionless temperature;

$$\langle H_1\rangle = Nj\left\{\left(m-\frac{\langle S_f^z\rangle}{2}\right)\langle S_f^z\rangle - \varkappa\frac{S^2(S+1)^2}{6} + \varkappa\left[y+\frac{S(S+1)}{3}-\frac{\langle (S_f^z)^2\rangle}{2}\right]\langle (S_f^z)^2\rangle\right\}. \tag{23}$$

The stationary values m_0 and y_0 of the parameters m and y are found from the extremum conditions for the modelfree energy F_M (21) with respect to these parameters:

$$\langle S_f^z\rangle = m_0 = \left\{\sum_{l=-S}^{S}\exp\frac{m_0l+\varkappa y_0l^2}{\tau}\right\}^{-1}\sum_{l=-S}^{S} l\exp\frac{m_0l+\varkappa y_0l^2}{\tau}, \tag{24}$$

$$\langle (S_f^z)^2\rangle = y_0 + \frac{S(S+1)}{3} = \left\{\sum_{l=-S}^{S}\exp\frac{m_0l+\varkappa y_0l^2}{\tau}\right\}^{-1}\sum_{l=-S}^{S} l^2\exp\frac{m_0l+\varkappa y_0l^2}{\tau}. \tag{25}$$

Apart from the trivial solution ($m_0 = 0$, $y_0 = 0$), the system (24), (25) has two solutions corresponding to ordered states. For $T \to 0$, these are the ferromagnetic solution ($m_0 = S$, $y_0 + S(S+1)/3 = S^2$) and the quantum quadrupolar solution ($m_0 = 0$, $y_0 = -S(S+1)/3$

in the case of integer S, or the corresponding solution for half-integer S, viz., $m_0 = 0$, $y_0 = \frac{1}{4} - S(S+1)/3$).

For sufficiently large κ, yet another possibility must be taken into account—a semi-ordered state. In fact, if $\langle (S_f^z)^2 \rangle = S^2$, this still does not imply that $\langle S_f^z \rangle = S$, since $S_f^z = S$ or $S_f^z = -S$ follows from $(S_f^z)^2 = S^2$. Thus, a situation is possible in which the system is almost completely ordered in the parameter y (for all f, we have $(S_f^z)^2 \approx S^2$), but order is absent in m, i.e., a state resembling the disordered state in the spin-$\frac{1}{2}$ Ising model is possible. Naturally, this semi-ordered state ($m_0 = 0$, $y_0(T) > 0$) cannot be the ground state, since an energy of order jS^2N is associated with order in the parameter m; however, for $\kappa \gg 1/S^2$, when this energy is relatively small, at finite temperatures it becomes thermodynamically favorable as a result of the gain in entropy.

In addition to the four physically meaningful solutions mentioned, there exists one other solution of the system (24) and (25) ($m_0(T) < S$, $y_0(T) < 0$), which corresponds to a saddle-point of the function $F_M(m, y)$ and always vanishes at a lower temperature than the ferromagnetic solution. These five solutions exhaust the solutions of the system (24) and (25).

Substituting (24) and (25) into (21), for $T \to 0$ we obtain an expression for the model energy:

$$E_M = -\tfrac{1}{2}Nj[m_0^2 + \varkappa y_0^2 + \tfrac{2}{9}\varkappa S^2(S+1)^2]. \tag{26}$$

It is easy to see from (26) that, for positive j and κ, both ordered states—ferromagnetic and quantum quadrupolar—correspond to local energy minima, with, in the case $S = 1$, the quantum quadrupolar state corresponding to the absolute minimum for $\kappa > 3$.

Suppose that the parameter κ representing the deviation from Heisenberg-like behavior is not too great and the ground state is ferromagnetic. We shall investigate how the biquadratic exchange affects the destruction of the ferromagnetic order.

Expanding (24) and (25) in series in powers of m_0, for small m_0 we obtain the solution of the system in the form

$$\tau_c - \tau = \frac{m_0^2}{2\langle l^2\rangle} \frac{2\varkappa\langle l^4\rangle(\langle l^2\rangle^2 - \langle l^4\rangle) + 3\langle l^2\rangle^3 - \langle l^4\rangle\langle l^2\rangle}{\varkappa S(S+1)(\langle l^2\rangle^2 - \langle l^4\rangle) + 3\langle l^2\rangle^2}, \tag{27}$$

$$y_0 - y_1 = \frac{m_0^2}{2} \frac{2[\langle l^4\rangle - \frac{1}{3}S(S+1)\langle l^2\rangle] + S(S+1)(\langle l^4\rangle - \langle l^2\rangle^2)}{\varkappa S(S+1)(\langle l^2\rangle^2 - \langle l^4\rangle) + 3\langle l^2\rangle^2}, \tag{28}$$

where we have used the notation: $\tau_c = \langle l^2 \rangle = y_1 + S(S+1)/3$,

$$\langle l^n\rangle = \left\{\sum_{l=-S}^{S} \exp\frac{\varkappa y_1 l^2}{\tau_c}\right\}^{-1} \sum_{l=-S}^{S} l^n \exp\frac{\varkappa y_1 l^2}{\tau_c},$$

and the constant y_1 for each value of κ and S should be found by solving the following equation:

$$y_1 + \frac{S(S+1)}{3} = \left\{\sum_{l=-S}^{S} \exp\frac{\varkappa y_1 l^2}{y_1 + S(S+1)/3}\right\}^{-1} \sum_{l=-S}^{S} l^2 \exp\frac{\varkappa y_1 l^2}{y_1 + S(S+1)/3}. \tag{29}$$

In addition to the trivial solution $y_1 = 0$ with the corresponding value $\tau_c = S(S+1)/3$, Eq. (29) has another solution for all $\kappa > 0$. On increase of κ from zero to ∞, the constant $\tau_c = y_1 + S(S+1)/3$, which has the meaning of the critical temperature for the transition to the state with $m_0 = 0$, varies, for the second solution of (29), from zero (from $\frac{1}{4}$ for half-integer S) to S^2. For $\kappa = \kappa_0 \equiv 15/(4S^2 + 4S - 3)$, the two roots of Eq. (29) coincide.

Since the solution of the system (24), (25) with $m_0 > 0$, having the lower transition temperature τ_c of the two, corresponds to a saddle-point of the function $F_M(m, y)$ for all $\tau \leq \tau_c$, the root $\{y_1 < 0$ for $\kappa < \kappa_0$, $y_1 = 0$ for $\kappa > \kappa_0\}$ of Eq. (29) refers to a solution that has no physical meaning.

Thus, the set of constants y_1, τ_c and $\langle l^n \rangle$, with $y_1 = 0$ for $\kappa < \kappa_0$ and $y_1 > 0$ for $\kappa > \kappa_0$, corresponds to ferromagnetic order.

Thus, for small κ, in a ferromagnetic crystal a second-order phase transition to the paramagnetic state occurs on heating to a temperature $\tau_{cp} = S(S+1)/3$. Near the Curie point, when m_0 and y_0 are small ($\tau \lesssim \tau_{cp}$), we obtain from (27) and (28)

$$m_0^2 = (\tau_{cp} - \tau)\frac{4S(S+1)}{3} \frac{15 - (4S^2+4S-3)\varkappa}{15(2S^2+2S+1) - 2(3S^2+3S-1)(4S^2+4S-3)\varkappa}$$

$$y_0 = \frac{m_0^2}{2S(S+1)} \frac{4S^2+4S-3}{15 - (4S^2+4S-3)\varkappa}. \tag{30}$$

As can be seen from the expression (30), such a transition, with $m_0 \sim \sqrt{\tau_{cp} - \tau}$ is possible only when

$$\varkappa < \varkappa_1 \equiv \frac{15(2S^2+2S+1)}{2(3S^2+3S-1)(4S^2+4S-3)} \leqslant \frac{\varkappa_0}{2}. \tag{31}$$

On further increase of the parameter κ representing the deviation from Heisenberg-like behavior, the value of m_0^2 becomes negative, i.e., on decrease of m_0 the curve $m_0(\tau)$ describes a loop and comes back. This implies that the transition to the paramagnetic state should occur discontinuously when $\tau > \tau_{cp}$.

For yet higher values of $\kappa > \kappa_2 \sim \kappa_0$, systems with $S = 1$ and $S \geq 2$ behave differently.

1. First we shall consider the case $S \geq 2$. In this case, for $\kappa > \kappa_0$ the solution with $y_1 > 0$ corresponds to ferromagnetic order. It then follows from (27) that, if the right-hand side of (27) is positive, then, at a temperature $\tau_{cq} = y_1 + S(S+1)/3$ (it is clear from (29) that $S(S+1)/3 < \tau_{cq} < S^2$), a second-order phase transition occurs not to the paramagnetic state ($m_0 = 0$, $y_0 = 0$) but to the semi-ordered state ($m_0 = 0$, $y_0 = y_1 > 0$), since the usual temperature dependence of the order parameter for second-order phase transitions is obtained: $m_0 \sim \sqrt{\tau_{cq} - \tau}$. According to numerical calculations, for $\kappa > \kappa_0$ the denominator of the right-hand side of (27) is always positive, but the numerator, which is positive for large κ, changes sign at a certain point $\kappa = \kappa_3(S) > \kappa_0$ (the ratio κ_3/κ_1 increases monotonically from 1.74 for $S = 2$ to 1.91 for $S = 10$).

Thus, for large $\kappa > \kappa_3$, a smooth transition from the ferromagnetic to the semi-ordered state does indeed occur at $\tau = \tau_{cq}$. For $\kappa_3 > \kappa > \kappa_0$, as for $\kappa_0 > \kappa > \kappa_1$, m_0^2 is found to be negative and the destruction of the ferromagnetic structure should occur discontinuously.

It can be shown that, near κ_0, there exists yet another characteristic value $\kappa = \kappa_2$ of the parameter describing the deviation from Heisenberg-like behavior; this value corresponds to a triple point on the $\kappa - \tau$ phase diagram. For $\kappa_3 > \kappa > \kappa_2$, a jump from the ferromagnetic to the semi-ordered state occurs; for $\kappa_2 > \kappa > \kappa_1$, the semi-ordered state is not realized and the jump occurs directly to the paramagnetic state.

We shall consider in more detail the solution of the system (24), (25) that corresponds to the semi-ordered state ($m_0 = 0$, $y_0(\tau)$). The condition (24) is satisfied in this case when the sum over l is performed, and from

(25) we obtain the dependence $y_0 = y_0(\tau)$ in parametric form:

$$y_0 = -\frac{S(S+1)}{3} + \left\{ \sum_{l=-S}^{S} \exp(xl^2) \right\}^{-1} \sum_{l=-S}^{S} l^2 \exp(xl^2),$$
$$\tau = \frac{\varkappa}{x}\left[-\frac{S(S+1)}{3} + \left\{ \sum_{l=-S}^{S} \exp(xl^2) \right\}^{-1} \sum_{l=-S}^{S} l^2 \exp(xl^2) \right], \tag{32}$$

where the branch with $x > 0$ in (32) corresponds to the semi-ordered state (the branch with $x < 0$ refers to the quadrupolar order with $y_0(\tau) < 0$, i.e., to quantum quadrupolar order for integer S).

The expression (21) for the free energy has the form, for $m = 0$,

$$\frac{F_M}{Nj\varkappa} = \text{const} + \frac{y^2}{2} + \frac{S(S+1)}{3} y - \frac{\tau}{\varkappa} \ln \sum_{l=-S}^{S} \exp \frac{\varkappa y l^2}{\tau}. \tag{33}$$

Expanding (33) in powers of y, we obtain

$$\frac{F_M}{Nj\varkappa} = \text{const} + \frac{\tau}{\varkappa} \ln(2S+1) - \frac{y^2}{2} \frac{\tau_0 - \tau}{\tau} - \left(S - \frac{3}{2}\right) a_3 y^3 \left(\frac{\varkappa}{\tau}\right)^2 + a_4 y^4 \left(\frac{\varkappa}{\tau}\right)^3 + \ldots, \tag{34}$$

where

$$\tau_0 = \frac{S(S+1)}{3} \frac{4S^2+4S-3}{15} \varkappa$$

is a characteristic temperature. Explicit expressions for the coefficients a_3 and a_4 will not be given. For our purposes, it is sufficient to know that they are positive.

As can be seen from (34), for small y the solution with $y_0(\tau) > 0$ has a lower F_M than the branch $y_0(\tau) < 0$ (it can be shown that this is true for all $\tau > 0$), i.e., in the approximation under consideration, quadrupolar order with the lowest possible value of $\langle (S_f^z)^2 \rangle$ is not thermodynamically favorable at finite temperatures in the case $S \geq 2$.

It follows from (32) that, for the semi-ordered state, the parameter y_0 monotonically decreases with increasing temperature. Since $a_3 \neq 0$, in accordance with the Landau theory of phase transitions the destruction of this state proceeds discontinuously at $\tau = \tau_q > \tau_0$. A numerical calculation shows that the ratio $(\tau_q - \tau_0)/\tau_0$ increases monotonically with increasing S, from 1.4% for $S = 2$ to 9.3% for $S = 10$.

2. In the case $S = 1$ with $\varkappa_1 < \varkappa < \varkappa_0 = 3$, the ground state, as was shown above, is a ferromagnetic state which goes over discontinuously to the disordered state on heating. For $\varkappa > 3$, the ground state is the quantum quadrupolar structure. Calculation confirms that in this case quantum quadrupolar order is thermodynamically more favorable than ferromagnetic order at all temperatures. According to (32)–(33), the parameter $y_0(\tau)$ for the quantum quadrupolar structure increases monotonically from $-2/3$ at $\tau = 0$ to $-1/3$ at the transition temperature $\tau_d = \varkappa/6 \ln 2$. Since $a_3 \neq 0$, the destruction of this structure proceeds discontinuously, i.e., a first-order phase transition to the paramagnetic state occurs.

3. In the case $S = 3/2$ with $m = 0$, degeneracy exists in the sign of y, i.e., as can be seen easily from (33), $F_M(0, y)$ is a function of y^2. But since there are terms in (2) of the form $S_f^+ S_g^-$ and $(S_f^+)^2 (S_g^-)^2$, which can lift the degeneracy, for $S = 3/2$ the molecular-field approximation (21) for the system (2) is too crude and, apparently, does not even qualitatively yield the features of the behavior of the magnet at large $\varkappa$.

The behavior of anisotropic systems with a Hamiltonian analogous to the diagonal part of (2), for which the approximation (21) makes sense, has been analyzed in detail for $S = 3/2$ in[9].

3. DISCUSSION OF THE RESULTS

The main result of the present paper is the construction of a spin-wave approximation for a new type of magnetic order with a quantum quadrupolar structure, and the proof of its stability in the framework of a model with biquadratic exchange.

Such a structure can be substantially more favorable than other types of magnetic order for $S = 1$. It should not be thought, however, that it is possible only for $S = 1$. In fact, it can be seen from formula (26) that, in the molecular-field approximation with $2J = K > 0$, the states with $\langle S_f^z \rangle = 0$ and $\langle (S_f^z)^2 \rangle = 1/4$ for $S = 3/2$, and with $\langle S_f^z \rangle = 0$ and $\langle (S_f^z)^2 \rangle = 0$ for $S = 2$, have the same energy as the states corresponding to ferromagnetic (and antiferromagnetic) order. As is well known, the energy of the ferromagnetic state in (26) is exact, while the true energy of states with $\langle S_f^z \rangle = 0$ is lower than the energy (26) found by the variational method. By generalizing the spin-wave approximation (7)–(14), it can be shown, at least for $S = 2$, that in a certain range $|J - \frac{1}{2}K|/K < \Delta$, where $\Delta \sim 1/Z$, the energy of the quantum quadrupolar structure is strictly less than the energy of the ferromagnetic (and antiferromagnetic) order.

It should be noted that, for $S > 1$, terms up to $(\mathbf{S}_f \cdot \mathbf{S}_g)^n$, where $n = 2S$, can occur in the Hamiltonian of the system. In models which take such terms into account, the quantum quadrupolar structure can evidently be even more favorable.

In addition to the quantum quadrupolar structure, the model (1) also permits another quadrupolar state—the semi-ordered state, and although both states are described by the same formula (32) in the molecular-field approximation, their natures are completely different. This fact was not noticed by Chen and Levy[5], who carried out a numerical investigation of the molecular-field equations in systems with biquadratic exchange. The results given in[5] for the cases $S = 1$ and $S = 5/2$ are analogous to those obtained in the present paper. The case $S = 1$ was considered in more detail in[4].

In the present paper, as compared with[4,5], we have succeeded in obtaining part of the results analytically for arbitrary S, and also in elucidating the character of the phase transitions in such a system for $S \geq 2$.

Experimental data on the first-order phase transitions from an ordered to a disordered state that are possible in the model considered here are given in the review by Grazhdankina[10]. A number of authors[11,12] explain the results of their experiments by a transition from the ordered to the paramagnetic state via a semi-ordered state. Quantum quadrupolar order has apparently not been observed experimentally.

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