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Dipolar and quadrupolar phase transitions in the spin $S=2$ cubic crystal-field system

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The dipolar and quadrupolar ordering in the spin $S=2$ cubic crystal-field system of localized magnetic moments interacting via exchange (dipolar) and biquadratic (quadrupolar) interaction are studied in the molecular-field approximation. One obtains pure quadrupolar ordering (paramagnetic state) or both dipolar and quadrupolar ordering (ferromagnetic state). The phase transition between these states is of second order, whereas the phase transition between the ferromagnetic and disordered phase may be of first or second order. A first-order phase transition also exists between the disordered and paramagnetic states.

Quadrupolar ordering in magnetic crystal has been investigated theoretically in connection with experimental results on magnetic and crystallographic phase transitions in some rare-earth compounds.[1,2] It is well known that the character of the phase transitions depends on the value of spin S and the symmetry of the system.[3-5]

In this paper, we discuss the magnetic system with spin $S=2$ of which Hamiltonian contains the cubic single-ion term. A similar but not identical model has been considered in Ref. 5 where it has been shown that the paramagnetic state is stable at low temperatures and for large quadrupole interaction constants as in the cases of $S=1$ and $S=\frac{3}{2}$. It has also been shown in Refs. 4 and 5 that for $S=1$, 2, and for any other value of S except $S=\frac{3}{2}$, the (dipolar) transitions between ferromagnetic and paramagnetic states are of the first or second order whereas the vanishing of quadrupolar ordering indicates the first-order phase (quadrupolar) transition. The Ising-type model for $S=\frac{3}{2}$ is exceptional and exhibits a second-order phase transition in quadrupolar ordering. In this paper we show that for $S=2$ there is a possible second-order phase transition in quadrupolar ordering and that at low temperature the large quadrupole interactions do not destroy ferromagnetic ordering as in the model considered in Ref. 5.

The Hamiltonian under consideration is

$$\mathcal{H}=-I\sum_{\alpha,i,j}S_i^\alpha S_j^\alpha-\sum_{\alpha,\beta,i,j}A^{\alpha\beta}(S_i^\alpha)^2(S_j^\beta)^2+\tfrac{1}{3}V\sum_{i,\alpha}(S_i^\alpha)^4\ , \tag{1}$$

where I (>0) stands for the exchange integral, $A^{\alpha\alpha}=A$ (>0), and $A^{\alpha\beta}=B$ (>0) are biquadratic interaction constants. By applying the molecular-field approximation which involves the substitution of operators S_i with their average value we find that the Hamiltonian (1) is expressed as

$$\mathcal{H}=E_0+\mathcal{H}_1\ , \tag{2}$$

where

$$E_0=I\sum_\alpha(M_\alpha)^2+A\sum_{\alpha,i,j}\langle(S_i^\alpha)^2\rangle\langle(S_j^\alpha)^2\rangle+B\sum_{i,j,\alpha,\beta}\langle(S_i^\alpha)^2\rangle\langle(S_j^\beta)^2\rangle\ , \tag{3}$$

$$\mathcal{H}_1=-2I\sum_\alpha M_\alpha S^\alpha-2\sum_{\alpha,\beta}[A^\alpha(S^\alpha)^2+B^\alpha(S^\alpha)^2]+\tfrac{1}{3}V\sum_\alpha(S^\alpha)^4\ , \tag{4}$$

and

$$I\sum_i\langle S_i^\alpha\rangle\equiv IM_\alpha;\ A^\alpha\equiv\sum_i A\langle(S_i^\alpha)^2\rangle;\ B^\alpha\equiv\sum_i B\langle(S_i^\beta)^2\rangle\ . \tag{5}$$

We consider the system with spin $S=2$, and therefore the energy eigenvalues of $\mathcal{H}_1$ are the roots of the secular equation which cannot be solved, of course, by the standard analytical methods. However, we can solve this equation when $M_x=M_y=0$, $M_z=M$. In other words, we reduce our problem to the Ising-type model as in Refs. 3 and 5. This is, of course, related to reducing of the symmetry of the system under consideration. According to Ref. 6 such a procedure is dependent on the constant $V\leq 0$. Without a loss of generalization we can assume $M_x=M_y=0$, $M_z=M$. In this case the secular equation yields the following energy levels:

$$\lambda_1=a_{22}+2[(IM)^2+\tfrac{9}{16}b^2]^{1/2}\ , \tag{6a}$$

$$\lambda_2=a_{22}-2[(IM)^2+\tfrac{9}{16}b^2]^{1/2}\ , \tag{6b}$$

$$\lambda_3=\tfrac{1}{3}(a_{11}+a_3)+(Z_1)^{1/3}+(Z_2)^{1/3}\ , \tag{6c}$$

$$\lambda_4=\tfrac{1}{3}(a_{11}+a_3)+\varepsilon(Z_1)^{1/3}+\varepsilon^2(Z_2)^{1/3}\ , \tag{6d}$$

$$\lambda_5=\tfrac{1}{3}(a_{11}+a_3)+\varepsilon^2(Z_1)^{1/3}+\varepsilon(Z_2)^{1/3}\ , \tag{6e}$$

where

$$Z_{1,2}=(-q\pm\sqrt{\Delta_1})/2\ , \tag{7a}$$

$$\Delta_1=q^2+\tfrac{4}{27}p^3\ , \tag{7b}$$

$$p=-[\tfrac{1}{2}(a_{11}-a_3)^2+V^2+16(IM)^2+3b^2]\ , \tag{7c}$$

$$q=\tfrac{2}{3}(a_{11}-a_3)[\tfrac{1}{9}(a_{11}-a_3)^2-V^2-16(IM)^2+\tfrac{3}{2}b^2]-3Vb^2\ , \tag{7d}$$

$$\varepsilon=(1)^{1/3}\ , \tag{7e}$$

$$b=-2[(A^x-A^y)-(B^x-B^y)]\ , \tag{7f}$$

$$a_{11}=7V-8A^z-2(A^x+A^y)-4B^z-10(B^x+B^y)\ , \tag{7g}$$

$$a_{22}=6V-2A^z-5(A^x+A^y)-10B^z-7(B^x-B^y)\ , \tag{7h}$$

$$a_3=8V-6(A^x+A^y)-12B^z-6(B^x+B^y)\ . \tag{7i}$$

We introduce new variables α instead of $\langle (S^\alpha)^2\rangle$:

$$\langle (S^\alpha)^2\rangle=\tfrac{1}{3}S(S+1)+\alpha,\ \sum_\alpha \alpha=x+y+z=0\ . \tag{8}$$

For the sake of (8), A^α and B^α in (5) are

$$A^\alpha=2A+A\alpha,\ B^\alpha=2B+B\alpha\ . \tag{9}$$

The appropriate free energy for (6a)–(6e) in new variables has the form

$$F=-2OD+IM^2+\tfrac{1}{2}E(3X^2+Y^2)-\frac{1}{\beta}\ln Z\ , \tag{10}$$

where

$$\beta=\frac{1}{kT},\ Z=\sum_i^5 e^{-\beta\lambda_i}\ , \tag{11}$$

$$X=x+y,\ Y=x-y,\ D=A+2B,\ E=A-B\ . \tag{12}$$

The equilibrium condition $\partial F/\partial Y=0$ has only one solution,

$$Y=x-y=0\ , \tag{13}$$

which justifies the assumption $P=(I^x)^2-(I^y)^2=Y=0$ that has been given in Ref. 5, in order to solve the problem.

The stability configurations and their stability range may be obtained by solving the necessary conditions and conditions sufficient for a minimum (10) with respect to $M=\langle S^z\rangle$ and $X=x+y$:

$$\frac{\partial F}{\partial M}=0,\ \frac{\partial F}{\partial X}=0\ , \tag{14}$$

$$\Delta=\frac{\partial^2F}{\partial M^2}\frac{\partial^2F}{\partial X^2}-\left(\frac{\partial^2F}{\partial M\partial X}\right)^2\geq 0,\ \frac{\partial^2F}{\partial M^2}\geq 0\ . \tag{15}$$

In order to obtain analytical solutions of (14) and (15) we perform the Landau development of the free energy (10)

$$F=IM^2+\tfrac{3}{2}EX^2-\frac{1}{\beta}\ln Z_0-Z_0^{-2}[9\beta EZ_0(2+Z_0)X^2-27\beta^2\alpha Z_0E^3X^3-\tfrac{27}{4}\beta^3A_2E^4X^4+12\beta Z_0\gamma EI^2M^2X-18\beta^2E^2\delta I^2M^2X^2+4Z_0\phi I^2M^2-4B_1I^4M^4]\ , \tag{16}$$

where

$$\alpha=\exp(2\beta V)\ , \tag{17a}$$

$$Z_0=2+3\alpha\ , \tag{17b}$$

$$A_2=6(2+Z_0)-Z_0(16+9\alpha)\ , \tag{17c}$$

$$\phi=\beta\alpha-\frac{2}{V}(1-\alpha)\ , \tag{17d}$$

$$\gamma=\beta\alpha+\frac{4}{V}(1-\alpha)\ , \tag{17e}$$

$$\delta=Z_0\gamma+4\phi\ , \tag{17f}$$

$$B_1=2\beta\phi^2-Z_0\left[\frac{\beta^3\alpha}{3}+\frac{8}{V^2}\left(\beta(1+\alpha)+\frac{1}{V}(1-\alpha)\right)\right]\ . \tag{17g}$$

Now, the condition (14) $\partial F/\partial M=0$, leads to

$$M=0\ , \tag{18}$$

$$M^2=-F^0_{MM}/8B_1I^3\ , \tag{19}$$

where

$$F^0_{MM}=Z_0^2-2I(2Z_0\phi+6\beta EZ_0\gamma X-9\beta^2E^2\delta X^2)\ . \tag{20}$$

Solution (18) and the condition $\partial F/\partial X=0$ yields

$$X_0=0\ , \tag{21}$$

$$X_{1,2}=\frac{-9\beta E\alpha Z_0\pm(\beta EZ_0\{81\beta E\alpha^2Z_0-4A_2[Z_0-6\beta E(2+Z_0)]\})^{1/2}}{6\beta^2E^2A_2}\ . \tag{22}$$

The solutions (18) and (21) correspond to the so-called disordered state, the solutions (18) and (23) $|X_2<0|$ to the paramagnetic state, and those for (18) and (22) $|X_1\geq 0|$ to the metastable paramagnetic state which is metastable everywhere and therefore out of our interest. From the sufficient conditions (15) for the solutions (18) and (21) and

(22), the stability boundaries are as follows. For the disordered state and paramagnetic one they are, respectively,

$$Z_0-4I\phi\geq 0\ , \tag{23}$$

$$\beta E\leq \frac{Z_0}{6(2+Z_0)}\ , \tag{24}$$

and

$$\beta E\geq \frac{4A_2Z_0}{81\alpha^2Z_0+24A_2(2+Z_0)}\ , \tag{25}$$

$$\beta E\leq \frac{2Z_0\{\delta[A_2(Z_0-4\phi)+12\delta(2+Z_0)]-[2A_2\gamma+9\delta\alpha]2\gamma Z_0+\sqrt{2Z_0[2Z_0\gamma^2-\delta(Z_0-4\phi)]}\}}{[A_2(Z_0-4\phi)+12\delta(2+Z_0)]^2+6Z_0[2A_2\gamma+9\delta\alpha][3\alpha(Z_0-4\phi)-8\gamma(2+Z_0)]}\ . \tag{26}$$

The phase diagrams for $M=0$ presented in Figs. 1 and 2 are obtained from inequalities (23)–(26). The region between the stability curve (straight line) described by Eq. (25) and the stability curve described by Eq. (26) corresponds to that in which paramagnetic state ($M=0$, $X_2<0$) fulfills conditions for a minimum free energy. The region between the straight lines [Eqs. (23) and (24)] corresponds to that in which disordered state ($M=0$, $X_0=0$) ensures a minimum of free energy. As seen in Figs. 1 and 2 there is a region between straight lines [Eqs. (24) and (25)] in which the paramagnetic state and disordered one can coexist as metastable states.

Let us consider now the solution (19) $M^2=F^0_{MM}/8B_1I^3$ which concerns the ferromagnetic state. In order to obtain a stability curve for Eqs. (16) and (19) we insert $\partial^2F/\partial M^2\geq 0$ ($F^0_{MM}\leq 0$) into $\partial F/\partial X=0$. It turns out

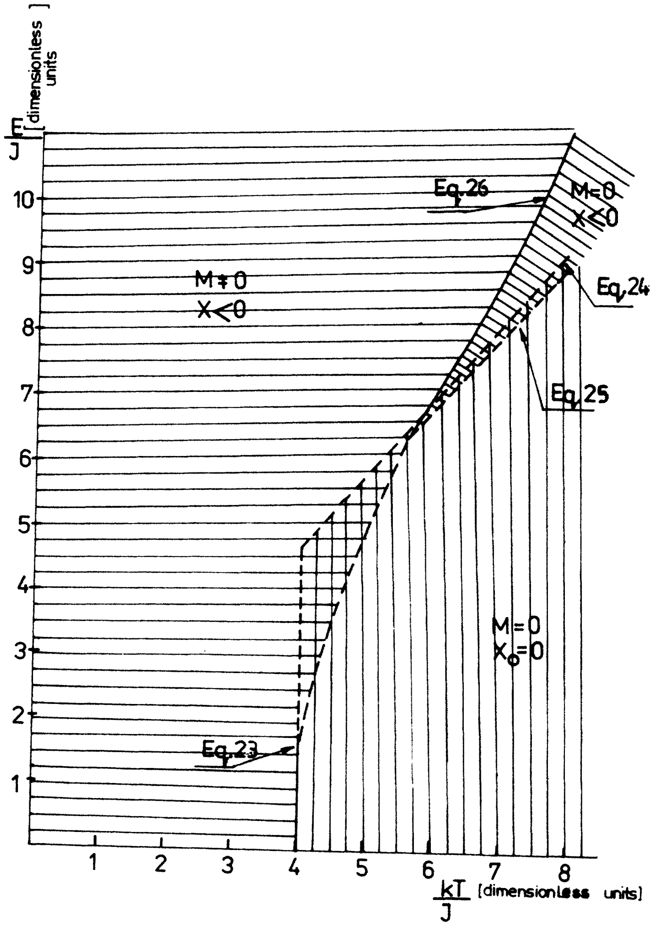

FIG. 1. Phase diagram for $V=0$. The first-order phase-transition line is marked with broken line.

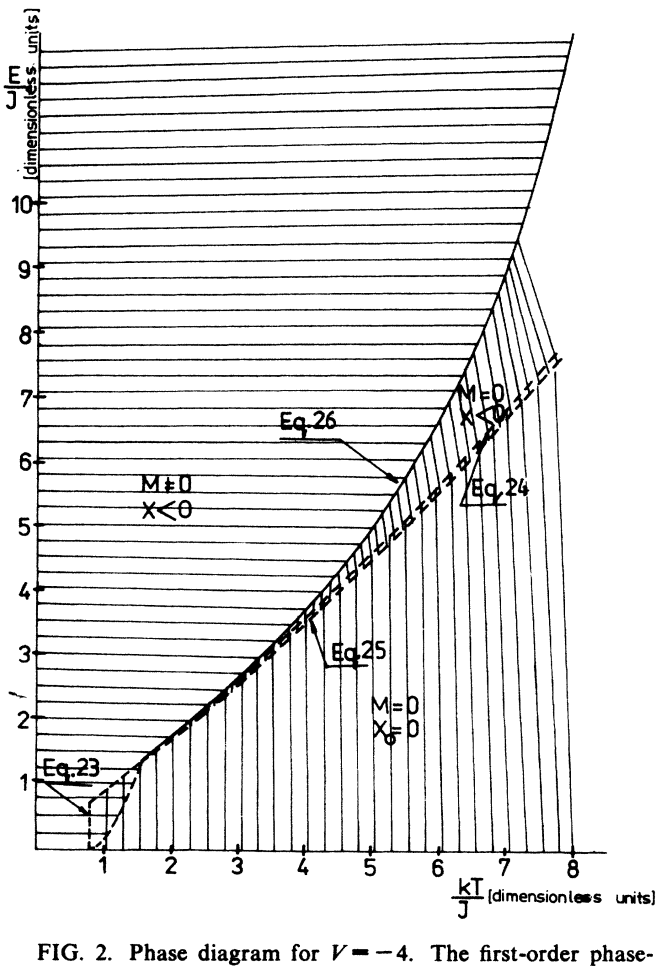

FIG. 2. Phase diagram for $V=-4$. The first-order phase-transition line is marked with broken line.

that the stability boundary of the ferromagnetic phase is described by two equations already known [(23) and (26)] and therefore is the second-order phase-transition line. It is essential that the inequality $\Delta \geq 0$ [Eq. (15)] is satisfied everywhere on the curve (26), but not everywhere on the curve (23). This means that the inequality $\Delta \geq 0$ cuts off the line of the second-order phase transition (23). From Eq. (23) and the condition $\Delta \geq 0$, the point where the second-order phase transition ends may be obtained:

$$E \leq \frac{B_1 Z_0}{6\beta[B_1(2+Z_0)-\beta Z_0 \gamma^2]} , \qquad (27)$$

where Eq. (23) holds.

In order to obtain a full description we ought to find the curve which represents the points of the first-order phase transitions from ferromagnetic ($M \neq 0$, $X < 0$) to disordered phase ($M = 0$, $X_0 = 0$). Definitely this curve represents the stability boundary of ferromagnetic order, and it may be obtained from $\partial F / \partial X = 0$ and $\Delta \geq 0$ [Eq. (16)]. This procedure leads to a third-order equation, which ought to be solved numerically. Therefore we choose another way. Varying X from -2 to 2 and M between 0 and 1.5 for chosen V and E we made a map of free energy. From this map the end of the ferromagnetic order is seen as the minimum. Phase diagrams for the single-ion cubic anisotropy constants $V = 0, -4$ are presented in Figs. 1 and 2. It follows from this that the ferromagnetic state at low temperatures is stable, which is in contradiction to previous results.[5]

As follows from Eq. (27), the second-order phase transition along line (23) vanishes for single-ion cubic anisotropy constant V equal to -4 (see Fig. 2). This is related to the fact that the coefficient B_1 at M^4 term becomes 0 when $V \rightarrow -4$ and changes its sign.

As has been shown in Ref. 3, the quadrupolar ordering induces, in general, a distortion of the lattice and therefore the quadrupolar phase transitions can be identified with structural transitions.

We have studied here the possible phase transitions in the spin $S = 2$ system involving dipolar and quadrupolar interactions. This system exhibits the second-order transition between ferromagnetic and paramagnetic states. The quadrupolar variable $-X = z = \langle (S^z)^2 \rangle - 2$ does not change in this transition. On the other hand, the quadrupolar variable changes in the first-order phase transition between paramagnetic and disordered states, whereas magnetization is constant. The phase transition between the ferromagnetic ordering and disordered state may be of both first or second order.

The pure dipolar phase transition is of second order whereas the pure quadrupolar phase transition has to be of first order. Such a remark explains why the pure quadrupolar transition must be of first order: The free energy $F(M = 0, X)$ contains a third-order term in quadrupolar variable X whereas there are only even powers of magnetization M in the free-energy expansion. On the other hand, the free energy $F(M \neq 0, X)$ contains both first- and third-order terms of variable X, and therefore the phase transition may be of first or second order, respectively, because these terms may mutually compensate at phase-transition points. The second-order phase transition occurs when two minima and one maximum become identical. For the function $F(X) = aX^4 + bX^3 + cX^2 + dX$, two minima degenerate to one minimum if $bd = -\frac{2}{3}c^2$. In our case this condition is fulfilled only by the straight line defined by Eq. (23) up to the line defined by Eq. (27).

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