Quadrupole Phase Transitions in Magnetic Solids*

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We have studied the phase transitions of magnetic systems with large biquadratic interactions in the molecular-field approximation. Quadrupole and dipole phase transitions occur at different temperatures whenever the biquadratic interactions are greater than the bilinear terms for effective spin interactions with $\mathcal{S} \geq \frac{3}{2}$. For isotropic or Ising-like interactions with $\mathcal{S}=1$ there is only a quadrupole phase transition when the biquadratic interactions are larger.

We have identified a series of compounds, the rare-earth pnictides, which display a unique property: two separate, but closely coupled, phase transitions.[1] To our knowledge no explanation exists for the origins of the separate phase transitions. Most of the pnictides which have the two phase transitions are type-2 antiferromagnets; for this type of ordering the contributions of the nearest-neighbor bilinear exchange interactions cancel one another, while the biquadratic terms reinforce one another. For these systems the net quadrupole or electric multipole field at a rare-earth site is larger than the exchange field. In this Letter we present our results on the statistical mechanics of magnetic systems with large biquadratic interactions. In an accompanying Letter[2] we consider in detail dysprosium antimonide; by including crystal-field effects and the orbit-lattice interactions, we are able to explain the observed anisotropic distortions which precede the magnetic ordering of these compounds.[1]

To understand the origins of multiple phase transitions in rare-earth compounds, we made an extensive study of phase transitions in magnetic systems with large biquadratic interactions. We based our study on the molecular-field approximation and considered effective-spin Hamiltonians ($\mathcal{S} \geq 1$) with various symmetries. We find that for effective-spin interactions with $\mathcal{S} \geq \frac{3}{2}$, quadrupole and dipole phase transitions occur at different temperatures whenever the biquadratic interactions are larger than the bilinear ones; this result is true for all symmetries of the pair interactions. On the contrary for $\mathcal{S}=1$, we find that two distinct phase transitions occur *only* for certain symmetries of the Hamiltonian for the magnetic system. For example, when the biquadratic interactions are larger than the bilinear ones, a system with overall cubic or tetragonal symmetry will have two distinct phase transitions[3]; however, for isotropic or Ising-like Hamiltonians, there is only a quadrupole phase transition. This result disagrees with previous work on the isotropic spin-1 model.[4]

For systems with large orbital contributions to their magnetic moments, the interactions between ions i and j can be described by the Hamiltonian[5]

$$\mathcal{H}_{ij} = \sum_{k_1,k_2,q_1,q_2} \Gamma_{q_1q_2}{}^{k_1k_2} O_{q_1}{}^{[k_1]} O_{q_2}{}^{[k_2]}. \qquad (1)$$

The operators $O_q{}^{[k]}$, which transform under proper rotations as the spherical harmonics, act on a degenerate set of states of multiplicity $2\mathcal{S}+1$. The ranks and components are limited to $0 \leq k \leq 2\mathcal{S}$, $-k \leq q \leq k$, and $k_1+k_2=$even. The exact calculation of the thermodynamic properties is intractable for a many-body system containing these pair interactions; therefore, to arrive at some conclusions we used the molecular-field approximation.

In the present analysis we consider only the bilinear and biquadratic interactions. For a system with effective-spin interaction with $\mathcal{S}=1$, they describe the spin interactions completely. The molecular-field Hamiltonian for Eq. (1) including only the bilinear and biquadratic terms is given by

$$\mathcal{H} = -(I_x\langle \mathcal{S}_x\rangle \mathcal{S}_x + I_y\langle \mathcal{S}_y\rangle \mathcal{S}_y + I_z\langle \mathcal{S}_z\rangle \mathcal{S}_z + \tfrac{1}{3}I_{20}\langle O_0{}^{[2]}\rangle O_0{}^{[2]} + I_{22}\langle O_2{}^{[2]}\rangle O_2{}^{[2]} + I_{xy}\langle O_{xy}\rangle O_{xy} + I_{yz}\langle O_{yz}\rangle O_{yz} + I_{xz}\langle O_{xz}\rangle O_{xz}), \quad (2)$$

where

$$O_0{}^{[2]} = 3\mathcal{S}_z{}^2 - \mathcal{S}(\mathcal{S}+1), \quad O_2{}^{[2]} = \mathcal{S}_x{}^2 - \mathcal{S}_y{}^2,$$

and

$$O_{xy} = \mathcal{S}_x\mathcal{S}_y + \mathcal{S}_y\mathcal{S}_x, \text{ etc.}$$

The thermal averages $\langle \mathcal{S}_x\rangle$, $\langle O_0{}^{[2]}\rangle$, $\langle O_{xy}\rangle$, etc. are the set of values which minimize the Gibbs free energy

$$G = -kT\ln(\mathrm{tr}\, e^{-\mathcal{H}/kT}) + \tfrac{1}{2}\langle\mathcal{H}\rangle, \qquad (3)$$

where the Hamiltonian $\mathcal{H}$ is given by Eq. (2). We have studied the Hamiltonian, Eq. (2), for various values of the exchange interaction constants, I_x, I_y, I_{20}, $\cdots$, and for effective spin values $\mathcal{S} \geq 1$. In this Letter we report only the results for negative biquadratic interactions, i.e., I_{20}, I_{22}, I_{xy}, I_{yz}, $I_{xz} \geq 0$. In this case each ion has the same quadrupole alignment; the dipole moments may be parallel or antiparallel depending on the signs of I_x, I_y, and I_z.

The main results are as follows:

(a) For effective-spin interactions with $\mathcal{S}=1$ and for an isotropic Hamiltonian, $I_x = I_y = I_z$, $I_{20} = I_{22} = I_{xy} = I_{yz} = I_{xz}$, or an Ising-like Hamiltonian, $I_x = I_y = I_{22} = I_{xy} = I_{yz} = I_{xz} = 0$, the dipole and quadrupole phase transitions occur simultaneously when $|I_z| > I_{20}$. when $I_{20} > |I_z|$, there is only one phase transition—a quadrupole ordering; the system does not have any magnetic ordering. This result disagrees with previous work which predicted that the dipoles and quadrupoles may order at different temperatures for an isotropic spin-1 Hamiltonian.[4] The phase diagram for isotropic systems with $\mathcal{S}=1$ is shown in Fig. 1(a).

(b) For effective-spin interactions with $\mathcal{S} \geq \frac{3}{2}$, two separate phase transitions are found for isotropic and Ising-like Hamiltonians whenever the biquadratic interactions are larger than the bilinear ones. Figure 1(b) is the phase diagram for an $\mathcal{S}=\frac{5}{2}$ Ising system. We consider this system in particular because it applies to the two phase transitions in the rare-earth pnictides.[2] Phase diagrams for Ising systems with $\mathcal{S} \geq \frac{3}{2}$ are similar to Fig. 1(b). In contrast to the spin-1 case, see Fig. 1(a), magnetic ordering occurs in these systems for an arbitrarily small bilinear interaction.

(c) In order to have two separate phase transitions, the spin-1 system must have either cubic or some lower symmetry. In a special case when $I_{20} = I_{22} = 0$, $I_x = I_y = I_z$, and $I_{xy} = I_{yz} = I_{xz}$, the Hamiltonian, Eq. (2), reduces to the form studied by Allen.[3] As shown in Fig. 1(c), two phase transitions occur for the values of I_x/I_{xy} from 0.5 to 0.88.[6] We have also considered a Hamiltonian with tetragonal symmetry, $I_x = I_y \neq I_z$, $I_{20} \neq I_{22}$, $I_{xy} = I_{yz} = I_{xz} = 0$; we find that two separate phase transitions do occur for this anisotropic spin-1 system. The phase diagram for this case is similar to Fig. 1(c) for each value of I_{22}; however, it has a very narrow range of I_x/I_{20} for which two separate phase transitions occur.

(d) The peculiar behavior of isotropic and Ising-like spin-1 systems, i.e., no magnetic ordering when $I_{20} > |I_z|$, can be understood on the basis of the following inequality for $\mathcal{S}=1$:

$$\sum_{q=x,y,z} \langle \mathcal{S}_q \rangle^2 + \sum_{q=xy,yz,xz} \langle O_q \rangle^2 + \langle O_2^{[2]} \rangle^2 + \tfrac{1}{3} \langle O_0^{[2]} \rangle^2 \leq \tfrac{4}{3}. \quad (4)$$

If the biquadratic interaction constant I_{20} is greater than other interaction constants, $|I_x|$, $|I_y|$, $|I_z|$, I_{22}, I_{xy}, etc., the minimum energy of the system at absolute zero temperature is $E_0 = -\frac{4}{3} I_{20}$.

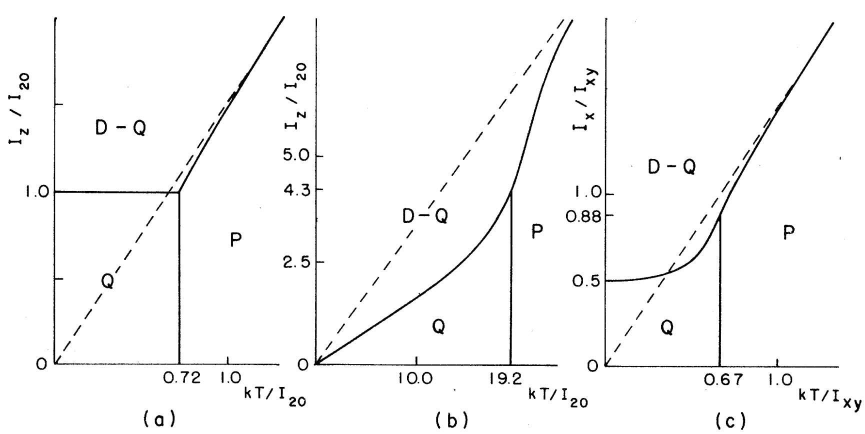

FIG. 1. The phase diagrams for magnetic systems with bilinear I_x, I_z and biquadratic I_{20}, I_{xy} interactions. The solid lines are the boundaries of the various phases of the systems: paramagnetic (P), ordered dipole and quadrupole (D-Q), and nonmagnetic quadrupole (Q) phases. The dashed lines represent the boundaries between the paramagnetic and ordered dipole-quadrupole regions when the biquadratic interactions vanish. The interaction constants refer to the Hamiltonian, Eq. (2). (a) For isotropic effective spin interactions with $\mathcal{S}=1$ ($I_x = I_y = I_z$, $I_{20} = I_{22} = I_{xy} = I_{yz} = I_{xz}$); (b) for Ising-like interactions with $\mathcal{S}=\frac{5}{2}$ ($I_x = I_y = 0$, $I_{22}=0$, $I_{xy} = I_{yz} = I_{xz} = 0$); and (c) for systems with $\mathcal{S}=1$ and overall cubic symmetry ($I_x = I_y = I_z$, $I_{xy} = I_{yz} = I_{xz}$, $I_{20} = I_{22} = 0$).

This energy is obtained only when $\langle O_0^{[2]}\rangle = -2$, and all other moments are equal to zero. Therefore, the system does not have a magnetic moment at $T=0$°K. At finite temperatures our numerical results confirm that the nonmagnetic state has the lowest free energy when $I_{20} > |I_z|$.

(e) From the phase diagrams we see that biquadratic interactions raise the magnetic-ordering temperature for effective-spin interactions with $\mathcal{S}>1$. For example, in Fig. 1(b) the magnetic-ordering temperature for a fixed I_z is higher for a finite biquadratic interaction I_{20} (solid curve) than it is when $I_{20}=0$ (dashed line). This is just the opposite of the spin-1 model where the biquadratic interactions preclude magnetic ordering altogether when the bilinear interactions are small.

The high-temperature behavior of the quadrupoles has not been considered because we have used the molecular field approximation. However, we can rigorously state that there is no macroscopic quadrupole polarization for $T > T_Q$ for all systems with at least cubic symmetry, where T_Q is the quadrupole-ordering temperature, by using symmetry arguments similar to those used by Priest.[7] Even though macroscopic polarization, i.e., long-range order, is not present above the ordering temperature, short-range order does exist. This short-range order is not included in the molecular-field approximation. Regions exist in a solid for $T \gtrsim T_Q$ in which all the quadrupoles are locally aligned; these regions are equally partitioned among the crystallographically equivalent directions. For example, for a system with cubic symmetry, the regions of ordered quadrupoles align themselves equally along the three cubic edges, four body diagonals, or six face diagonals above T_Q. At the quadrupole-ordering temperature one of the easy axes is singled out, and the entire crystal forms a single domain.

In summary, the salient feature of magnetic systems with large biquadratic interactions is the separate quadrupole and dipole phase transitions. For systems with $\mathcal{S}=1$ the region of the phase diagram for separate transitions to occur is small; it is more probable to find these transitions for models with $\mathcal{S}\geq\frac{3}{2}$, e.g., the rare-earth pnictides which have low-lying states described by effective spins of $\mathcal{S}\geq\frac{5}{2}$.

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Structural and Magnetic Phase Transitions in the Rare-Earth Pnictides*

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The pnictides, a series of rare-earth group-V intermetallic compounds, have the unique property that these cubic materials distort 2–3°K above the Néel point. We are able to explain this unusual behavior by using a model in which the lattice distortions are driven by quadrupole phase transitions which occur at higher temperatures than the magnetic phase transitions.

A recent study of the magnetic susceptibilities and lattice distortions of a series of rare-earth group-V intermetallic compounds, the pnictides, has revealed a unique property. These cubic materials distort 2–3°K *above* the Néel temperature,[1] e.g., DySb has a very abrupt tetragonal distortion ($c/a=0.993$) at $T^*=11.5$°K, and orders magnetically at $T_N=9.5$°K. The differences in