First-order magnetic phase transitions and metamagnetism of quantum origin

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Quantum spin fluctuations can induce phase transitions in Heisenberg magnets with competing exchange interactions. Quantum effects can lead to the formation of a specific metamagnetic state and long-lived induced magnetization in such magnets.

First-order magnetic phase transitions are usually attributed either to non-Heisenberg exchange (spin-lattice interaction reduces to it; see, for example, Ref. 1) or critical fluctuations, which transform the order-disorder transition in crystals of certain symmetry into a jump-like transition.[2] In this paper we propose a new mechanism for magnetic field-order phase transitions which should operate in Heisenberg magnets near the boundaries of magnetic phases. In contrast to the mechanisms indicated above, this mechanism is based on the quantum nature of spins and, therefore, it cannot occur in magnets with classically large spins. The same physics leading to such phase transitions also leads to the existence of metamagnetism of a specifically quantum nature. It differs from the usual metamagnetism by the fact that, first of all, it is caused by isotropic Heisenberg exchange, rather than by magnetic anisotropy, and second, quantum metamagnetism is characterized by the presence of magnetic memory in the crystals: at low temperatures the crystal can remain in the magnetized state even after the external magnetic field is removed.

We are examining crystals in which the magnetic ordering changes from ferromagnetic (FM) to antiferromagnetic (AF) ordering as the parameters of the competing exchange interactions change. It is assumed, for simplicity, that the magnetic atoms form a simple cubic lattice and that the exchange integral I_1 between nearest neighbors is positive, whereas the exchange integral I_2 between the second nearest neighbors is negative. The Fourier components of the exchange integral are given by

$$I_{\mathbf{k}} = 2I_1 \left[\sum_i \cos k_i - \frac{l}{2} \sum_{i \neq j} \cos k_i \cos k_j \right], \quad l = \frac{2|I_2|}{I_1}, \tag{1}$$

where $\mathbf{k}$ is a reciprocal lattice vector, and $i = x, y, z$.

The standard procedure for finding the ordering at $T = 0$ consists of replacing the spin operators in the Heisenberg Hamiltonian by classical vectors and looking for a vector $\mathbf{k}$ that minimizes the energy produced in this manner. The condition of minimum energy will then be equivalent to the condition of maximum $I_{\mathbf{k}}$ with the same $\mathbf{k}$. The theory of phase transitions also leads to the same criterion for the magnetic ordering: In the paramagnetic region, as the temperature is reduced, fluctuations with $\mathbf{k}$ for which $I_{\mathbf{k}}$ is maximum grow most strongly, and a long-range order with this $\mathbf{k}$ is

established at the critical point. Correspondingly, according to (1), FM ordering should be realized for small l, and $l_c = 0.5$ is the boundary between FM and a layered AF phase with $\mathbf{k} = (0,0,\pi) \equiv \mathbf{P}$.

However, if the quantum nature of the spins is taken into account, then the investigation of low-temperature and critical properties leads to different positions of the boundaries between the phases. In contrast to the FM state, the classical AF state is not a characteristic state of the Heisenberg Hamiltonian. For this reason, the true energy of the antiferromagnet E_{AF} is lower than its classical energy by an amount $\sim 1/zS$, where S is the spin, and z is the number of nearest neighbors:

$$E_{FM} = -\frac{I_0 S^2}{2}, \quad E_{AF} = -\frac{I_P S}{2}(S+\alpha) \qquad \alpha \cong 0.14. \tag{2}$$

Correspondingly, at the classical boundary of phases $l_c = 0.5$, where $I_0 = I_P$, E_{AF} is lower by the same amount than the energy of the FM state E_{FM}. For this reason, the quantum value l_q, which bounds the region of stability of the FM phase, must also be less than l_c by an amount $\sim 1/zS$.

However, the zero-point oscillations of the spins, which lower the energy of the AF state relative to the energy of the FM state, are the strongest oscillations at $T = 0$. As the temperature is increased, their relative contribution to the thermodynamic quantities must decrease, because the degree of antiparallel orientation of spins from different sublattices decreases. For this reason, the quantum corrections to the criterion, according to which a structure with maximum $I_{\mathbf{k}}$ must be established in T_c, must also be small. In the relatively rough molecular-field approximation, as is evident from the expression for the susceptibility, we would have

$$\chi_{\mathbf{k}} \sim [3T - I_k S(S+1)]^{-1}. \tag{3}$$

In spite of the fact that the quantum nature of the spins is taken into account, such quantum corrections are missing in the criterion under discussion. In contrast to the energy (2), according to (3), the spin enters into both T_c for FM and into T_N for AF in the same manner: in the form of the combination $S(S+1)$. The smallness of corrections to the classical criterion is also indicated by the most accurate results of the high-temperature expansions[3]: T_c for FM includes the spin in the form of the combination $[S(S+1) - 0.09]$, i.e., in essentially the same way as in the molecular-field approximation.

Thus, although in the interval $l_q < l < l_c$, above T_c FM short-range order develops most intensively as the temperature is reduced, it cannot exist at $T = 0$, since $E_{FM} > E_{AF}$. However, the AF state is also classically unstable in this interval. For this reason, there arises the question of whether it would be stable when quantum effects are taken into account. To answer this question it is necessary to calculate the magnon frequencies $\omega_{\mathbf{k}}$ in the second order with respect to $1/S$. Separating the cubic terms in the magnon Hamiltonian into products of pairs of operators and their averages over the ground state and performing a Bogolyubov (u,v) transformation, we obtain

$$\omega_{\mathbf{k}} = \sqrt{B_{\mathbf{k}}^2 - C_{\mathbf{k}}^2}, \tag{4}$$

$$B_{\mathbf{k}} = 2I_1 S[1 - \cos k_x - \cos k_y + l(1 + \cos k_x \cos k_y) + \frac{1}{S}(\nu_{100} - \nu_{000})(2 - \cos k_x - \cos k_y) - \frac{l}{S}(\nu_{110} - \nu_{000})(1 - \cos k_x \cos k_y) + \frac{1}{S}(\nu_{000} - \mu_{001}) - \frac{2l}{S}(\nu_{000} - \mu_{110})],$$

$$C_{\mathbf{k}} = 2I_1 S \cos k_z \{l(\cos k_x + \cos k_y)[1 - \frac{1}{S}(\nu_{000} - \mu_{110})] - 1 + \frac{1}{S}(\nu_{000} - \mu_{001})\},$$

$$\nu_{pqr} = \frac{1}{2N}\Sigma(\frac{B_k}{\omega_k} - 1)\cos^p k_x \cos^q k_y \cos^r k_z, \mu_{pqr} = \frac{1}{2N}\Sigma\frac{C_k}{\omega_k}\cos^p k_x \cos^q k_y \cos^r k_z.$$

As follows from (4), the AF state, at least, is also stable relative to small fluctuations for $l < l_c$, since the frequencies remain real up to $l_q = 0.5 - (0.14/S)$. It is highly unlikely that some other state would have a lower energy than the AF state at the boundary between the AF and FM phases. For this reason, it is natural to conclude that in the classically forbidden interval from l_q to l_c a specifically quantum AF ordering should be realized. For small spins this interval is quite wide: It is comparable to the interval of stability of the FM phase.

The fact that in this interval short-range order in the paramagnetic region is of a different type than long-range order at $T = 0$ (FM in the first case and AF in the second) requires that the type of magnetic order change in a jump-like manner. There are two possibilities. 1) As the temperature is reduced, at first there is a second-order phase transition from the paramagnetic state to the FM state, which is accompanied by a first-order phase transition from the FM to the AF state. 2) There is a first-order phase transition from the paramagnetic state to the antiferromagnetic state, i.e., the phase transition is of a "order-foreign disorder" type. Thus far we have proved the possibility of such phase transitions only in non-Heisenberg magnets.[1]

It is important that in the interval $l_q < l < l_c$ FM ordering corresponds to a local minimum of the energy. This follows from the fact that the magnon frequencies $\tilde{\omega}_{\mathbf{k}} = I_0 - I_{\mathbf{k}}$, according to (1), are non-negative in this interval. This follows from the fact that the external magnetic field must give rise to a jump-like transition from the AF state to the FM state and, in addition, the magnitude of the field required for this transition decreases as l approaches l_q. If the field is removed, then as $T \to 0$ the crystal must remain for an arbitrarily long time in the metastable FM state. Isotropic metamagnets, in principle, are also possible with Heisenberg exchange (1), but they do not have a magnetic memory.

As regards the experimental observation of quantum first-order phase transitions, they should be sought in AF with small spins and with strong FM exchange which competes with the AF exchange. The fact that they compete strongly is indicated by the large shift in the paramagnetic Curie temperature Θ from $(-T_N)$ toward positive values. For many AF, Θ is even positive. Among magnets with small spins, such materials include, for example, $CoCl_2$, $CuCl_2 \cdot 2H_2O$, $NiBr_2$, MnF_3, UP, UP_2, and

others. It is also possible to approach the boundary between the AF and FM phases by applying a pressure to the crystals.

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