New type of magnetic phase transitions of the first kind

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The possibility of phase transitions of the first kind (PT1) of the type "long-range order—foreign short-range order" is shown. A new mechanism for the VT1 type ferromagnetic-antiferromagnetic transition is proposed.

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A number of magnetic crystals exhibit phase transitions of the first kind (PT1) when the type of long-range order changes or when it vanishes. These transitions may sometimes be explained by an interaction between the magnetic subsystem and the crystal lattice.[1] Certain PT1 may be fully determined by the specifics of magnetic interactions. For instance, ferromagnetic-paramagnetic (FM-PM) PT1 may result from a significant contribution of the biquadratic terms $\sim(S_1S_2)^2$ to the exchange interaction, where S_g is the spin of atom g.[2] PT1's with disappearing long-range order, which occurs in accordance with mechanisms in Refs. 1 and 2, are characterized by the fact that the short-range order after a transition remains of the same type as the long-range order was before a transition. The type of short-range order that is determined by the correlating function $\Sigma_{g\neq 0}\langle S_0S_g\rangle/S(S+1)=\Theta/(T-\Theta)$, where $S(S+1)=S_g^2$, may be judged from the sign of the PM Curie temperature Θ. For

example, Θ is negative in an antiferromagnet (AF) after PT1 in accordance with Refs. 1 and 2.

We shall show below that, first, PTls of the type "long-range order–foreign short-range order" are also possible (for example, from an AF state to a PM state with FM short-range order, i.e., with $\Theta > 0$). Second, type AF-FM PT1s which were earlier explained by a change of sign of the exchange integral in the case of thermal expansion of the lattice,[1] may also be explained by purely magnetic effects which is more realistic for low-temperature PTls.

Phase transitions with a changing order type in isotropic magnetics occur provided the exchange integral is sufficiently small. But, under these conditions, alongside the Heisenberg exchange, non-Heisenberg terms become significant. The analysis below is based on a Hamiltonian which contains three-spin terms in addition to the Heisenberg two-spin terms (i.e., of the (S_1S_2) (S_1S_3) type).

$$H = -\frac{J}{2}\sum_{\Delta g}(S_g S_{g+\Delta}) - \frac{K}{2}\sum_{\substack{g \\ \Delta\Delta'}}\left(S_g S_{g+\Delta}\right)\left[(S_{g+\Delta'} S_{g+\Delta}) + (S_g S_{g+\Delta+\Delta'})\right], \quad \Delta' \neq \pm\Delta \tag{1}$$

where the vector Δ indexes z of the nearest neighbors and the vectors Δ' satisfy the condition that the atoms $g+\Delta+\Delta'$ and $g+\Delta'$ be the second nearest neighbors with respect to range of the atoms g and $g+\Delta$, respectively. The crystal lattice was assumed to be cubic.

The Hamiltonian (Eq. (1)) permits only collinear magnetic structures. For the sake of definition, we shall assume that at $T=0$ AF ordering of the chessboard structure type is the most energetically favorable. The Heisenberg exchange integral J is considered positive and the non-Heisenberg exchange integral K, negative.

Qualitatively the nature of the dependence of magnetic properties on T may be understood from the following considerations. The nature of the ordering is determined by the sign of the effective exchange integral $\tilde{J}(T) = J + 8K\overline{(S^z)^2}$, where the bar indicates temperature averaging. The value of $(S^z)^2$ decreases with increasing T, converging to $S^2/3$ as $T\to\infty$ (the spins are considered to be classical vectors). If $J < 8|K|S^2 < 3J$, $J(0)$ is negative. As the temperature increases, its sign is inverted and the AF ordering becomes unstable. However, the positiveness of $J(T)$ does not yet guarantee stability of FM ordering: instead of a transition from an AF state into a FM state, a transition into a PM state with an FM short-range order may occur.

Quantitative analysis is made in a self-consistent field (SCF) approximation; moreover, two SCFs must be introduced here due to the non-Heisenberg structure of the Hamiltonian (Eq. (1)). One of the fields, h, as a rule appears in the SCF Hamiltonian H_0 as an operator on a spin projection, and the second—$\sim k$—operates on the square of a spin projection

$$H_0^{\pm} = \mp(hx + 1/2\, ks^2x^2), \quad x = S^z/S,$$

$$h = (km^2 - 1)s, \quad k = 8|K|S^2/J, \quad s = |\overline{S^z}|/S, \quad m^2 = \overline{(S^z)^2}/S^2, \tag{2}$$

where the upper sign corresponds to AF and the lower to FM ordering. All the energies here and below are measured in the units $6JS^2$.

The free energies of these two types of ordering calculated, as usual, in the SCF theory using the variational principle are given by the respective expressions (per atom):

$$F_{\pm} = \pm (km^2 - 1/2)s^2 - \tau \ln Z_{\pm}, \quad \tau = T/6JS^2,$$
$$Z_{\pm} = \sum_x \exp\{\pm \tau^{-1}[(km^2 - 1)sx + 1/2\, ks^2x^2]\}, \tag{3}$$

(the calculation is with respect to the free energy of PM state $-\tau\ln(2S+1)$). The variational parameters s (average magnetization) and m^2 are determined from the following conditions

$$\frac{\partial F}{\partial s} = \frac{\partial F}{\partial m^2} = 0. \tag{4}$$

The results of the numercial solution of Eq. (4) are shown graphically (Fig. 1) for $k = 1.5$ (solid lines) and $k = 1.8$ (dotted lines). The upper of the two lines, corresponding to a given k, represents the temperature dependence of parameter AF of order S_A, the lower—the same for an FM of order S_F. At all the temperatures at which FM ordering is possible, its free energy F_- is negative. The free energy of AF ordering F_+ is negative only in a portion of the $S_A(T)$ curve to the left of the arrow. To the right, the AF state is known to be unstable.

If the arrow corresponds to a temperature τ_p which is below the FM Curie point τ_c, a transition from an AF state to FM should occur as a result of a phase transition of the first kind at a temperature τ_0 when the free energies of both are comparable. This is exactly what occurs at $k = 1.5$ ($\tau_0 = 0.12$ was obtained). Upon transition into an FM state, a phase transition of the second kind into a PM state takes place. If, however, τ_p is greater than τ_c, an AF-FM transition is not obligatory; a phase transition from AF directly into a PM state may occur at a temperature τ_p. Such is the

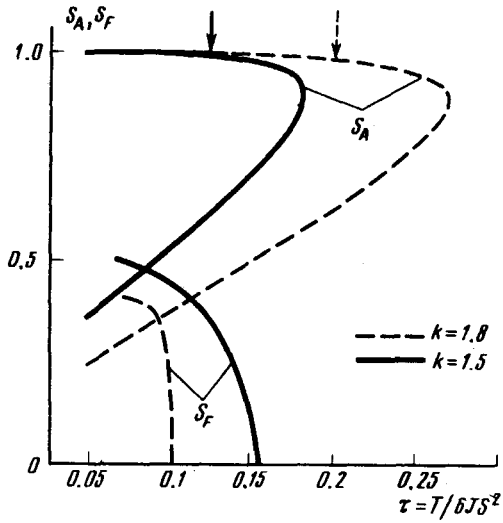

FIG 1.

situation at $k = 1.8$. A value of k_c corresponding to a triple point $\tau_p = \tau_0$ lies in an interval from 1.5 to 1.8. In order to prove that the PM state is characterized by short-range order FM, and at $k > k_c$—when a transition from AF directly into PM state occurs—it suffices to calculate the PM Curie temperature Θ by standard methods. The value of the latter is $1/3(1 - k/3)$ and it is positive for all values of k under consideration.

The above results are confirmed by experimental analysis of EuSe. The phase transition from the AF to PM state in EuSe at 4.6 °K is of the first kind (all the experimental data and references to original works are cited in Ref. 3). The fact that an FM short-range order is realized in the PM state affirms, above all, that Θ is positive at 9 °K. The same is also attested to by the occurrence of a strong red shift of the optical absorption edge as the temperature decreases. It is observed at temperatures somewhat exceeding $T_N = 4.6$ °K but it disappears below 4.6 °K. This shift is typical for FM semiconductors, but it is absent in AF semiconductors. Thus, above T_N EuSe behaves like FM semiconductors. In the latter the red shift in the PM region depends on a lowering of the conduction band bottom when the short-range FM order is established. The same should also occur in EuSe.

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