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# *CONCENTRATION-DEPENDENT PHASE TRANSITIONS TO A NONCOLLINEAR MAGNETIC STATE*

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Noncollinear antiferromagnetism is also possible when the thermodynamic potential lacks a term that is linear in the magnetic moment. The required conditions are then an anomalously small negative coefficient $A_2$ of the quadratic term and a positive fourth-order term. This situation is possible in heavily doped antiferromagnetic semiconductors because of competition between direct antiferromagnetic exchange and the indirect exchange via conduction electrons that tends to establish ferromagnetic order. The coefficient $A_2$ is positive for small concentrations, but a sign reversal occurs with increase of the latter. Transition to the noncollinear state near the vanishing point of $A_2$ can be interpreted as a second-order isothermal phase transition. The derivative of the electron chemical potential with respect to the concentration is discontinuous at the transition point, with resulting singularities of electrical quantities (a jump of the thermoelectromotive force, etc.). These phenomenological considerations are confirmed by a microscopic calculation for the case $T = 0$, and the critical concentration is calculated.

It is well known that the noncollinear magnetic structure found in some antiferromagnetic dielectrics is associated with the fact that their symmetry allows the thermodynamic potential to include terms that are linear in the magnetic moment.[1,2] In the present work noncollinear structures of a different type are investigated. These are possible even when the thermodynamic potential lacks terms containing odd powers of the moment, if the coefficient of the fourth-order term is positive and the coefficient of the quadratic term is negative but anomalously small. This situation is realized in heavily doped antiferromagnetic semiconductors as a result of competition between direct antiferromagnetic exchange and the indirect exchange via conduction electrons that tend to establish ferromagnetic order. No special crystal symmetry properties of a crystal are presupposed here. It is only essential that the current carriers should not be in a magnetic polaron state.[3] The theoretical possibility of noncollinear structures resulting from competition between direct and indirect exchange has been discussed by de Gennes[4] on the basis of experimental data in [5]. However, the analysis in [4] was incorrect, as it included unjustified limitations on the type of the initial antiferromagnetic ordering as well as a conflict between the result of the quantum-mechanical calculation and the symmetry properties of the system.

We assume that the transition of an isotropic antiferromagnet to the ferromagnetic state with increasing carrier concentration n proceeds via a gradual increase of the angle $\theta$ between the moments of the two sublattices. Neglecting magnetic anisotropy, the thermodynamic potential $\Phi$ depends only on $\theta$, of which it must be an even function, and on the angle $\alpha = (\pi - \theta)/2$, which is proportional to the moment:

$$\Phi(n, T, \alpha) = \Phi_0(n, T) + A_2(n, T)\alpha^2 + A_4(n, T)\alpha^4. \qquad (1)$$

Here $\Phi$ is always an extremum when $\alpha = 0$.

For low concentrations n the antiferromagnetic state is stable, i.e., $A_2(n, T) > 0$. Thus noncollinearity can appear only beginning at some critical concentration $n_A$ when the sign of $A_2(n, T)$ is reversed while $A_4(n_A, T)$ remains positive. If $A_2$ is analytic in n near $n_A$ and the linear term of the expansion does not vanish, the uncompensated magnetic moment should be proportional to $\sqrt{n - n_A}$. The derivative of the electron chemical potential with respect to the concentration will be discontinuous at the critical point $n_A$; this should be manifested by singularities of the electric properties of the crystal as functions of the concentration. We thus find here essentially a second-order isothermal phase transition of the second kind, characterized by the fact that it is realized not in an individual sample, but in an ensemble of samples having different concentrations. With further increase of the concentration another phase transition of the same kind occurs—from the noncollinear to a completely ferromagnetic state.

To confirm the foregoing phenomenological analysis and to calculate the critical concentrations at $T = 0$, we shall now perform a calculation on a microscopic model. We consider a simple cubic lattice of magnetic atoms with spin S that interact with the conduction electrons. The system is described by the customary Hamiltonian for the s–d model:

$$\begin{aligned}\mathcal{H} = &-A \sum (\mathbf{s}\mathbf{S}_g)_{\sigma\sigma'} a^*(g\sigma) a(g\sigma') \\ &+ B \sum a^*(g\sigma) a(g + \Delta\sigma) - \frac{J}{2} \sum (\mathbf{S}_g \mathbf{S}_{g+\Delta}).\end{aligned} \qquad (2)$$

Here $\mathbf{s}$ and $\mathbf{S}_g$ are the spin operators of a conduction electron and an atom having the index g; $a^*(g\sigma)$ and $a(g\sigma)$ are the creation and annihilation operators of a conduction electron with spin projection $\sigma$ on the atom of index g. The index $\Delta$ represents the numbering of the nearest neighbors of the given atom. It is assumed that the integral of exchange between a conduction electron and magnetic atom (A) considerably exceeds the half-width $6|B|$ of the electronic band. The Bloch integral B, in turn, considerably exceeds the exchange integral J between magnetic atoms. We consider only the case $A > 0$, since the conditions for the production of magnetic polarons are then less favorable than for $A < 0$.[3]

In the principal approximation with respect to $B/A$ the wave function of an electron interacting with a magnetic subsystem is obtained in the form of an expansion in the eigenfunctions of the Hamiltonian of intratomic exchange [the first term in (2)]:

$$\psi=\sum_{(\pm)gJ} c_g(J)\sqrt{\frac{S+{}^1\!/\!_2\pm J}{2S+1}}\,\delta\Big(S_g^z,J\pm\frac{1}{2}\Big)\,a^*(g,\pm 1_g)\,|0|\prod_{f\neq g}\delta(S_f^z,S). \tag{3}$$

Here $\delta(x, y)$ is a delta function representing a discrete argument having the value 0 or 1, and $|0\rangle$ is the vacuum electron function. The magnetic state of atom g is described by the variable $S_g^z$, which is the spin projection of this atom on the direction of its average moment. The symbols $\pm 1_g$ designate the the possible values of the conduction-electron spin projection on the average moment of atom g. The projection J of the combined (atom plus electron) moment appears in Clebsch–Gordan coefficients of (3), and can have only the values $J_+ = S + {}^1\!/\!_2$ and $J = S - {}^1\!/\!_2$.

The selection of (3) as the wave function signifies, first, that we neglect zeroth spin oscillations, which are unessential for the present problem. Secondly, it is implied that for atoms which are free of conduction electrons the spin projection corresponds to the ground state of the magnetic subsystem ($S_f = S$). From a rigorous point of view, when a conduction electron passes through an atom the spin projection of the latter can be changed. Therefore the true wave function should contain fluctuating terms as well as terms describing electronic translational motion that does not affect the magnetic ordering. The additional terms would describe the motion of a quasi-oscillator electron[6] accompanied by the destruction of magnetic order in a very small region and the subsequent restoration of this order when the motion is reversed. However, a calculation shows that the quasi-oscillator states contribute only a small admixture and can actually be neglected.

When we assume that the x axes of all local systems of coordinates coincide while the z axes of neighboring atoms form an angle $\theta$, then we have the following relations between the electron operators in the different coordinate systems:[7]

$$\begin{aligned} a^*(g+\Delta,1_{g+\Delta})&=\cos\frac{\theta}{2}a^*(g+\Delta,1_g)+i\sin\frac{\theta}{2}a^*(g+\Delta,-1_g),\\ a^*(g+\Delta,-1_{g+\Delta})&=i\sin\frac{\theta}{2}a^*(g+\Delta,1_g)+\cos\frac{\theta}{2}a^*(g+\Delta,-1_g).\end{aligned} \tag{4}$$

We take $+\theta$ as the angle through which the z axis of the second magnetic sublattice is rotated with respect to the z axis of the first sublattice. Then $-\theta$ is the angle through which the z axis of the first sublattice is rotated with respect to the z axis of the second sublattice.

We assign to each atom an "isotopic spin" with the projection $\tau = +1$ or $-1$, depending on whether the atom belongs to the first or second sublattice. The coefficients $c_g$ of the wave function (3) are obtained in the form

$$c_g(J_m)=e^{ikg}c(\tau_g,m),\quad m=\pm. \tag{5}$$

With the aid of (2)–(5) we derive the following "bispinor" Schrödinger equations:

$$\begin{aligned} Ec(\tau,+)&=B\cos\frac{\theta}{2}\gamma_k c(-\tau,+)+\frac{i\tau B\gamma_k}{\sqrt{2S+1}}\sin\frac{\theta}{2}c(-\tau,-),\\ Ec(\tau,-)&=i\tau B\sin\frac{\theta}{2}\gamma_k c(-\tau,+)+\frac{B\gamma_k}{2S+1}\cos\frac{\theta}{2}c(-\tau,-),\end{aligned} \tag{6}$$

$$\gamma_k=\sum_\Delta e^{ik\Delta}.$$

In writing (6) we have used the condition $|B| \gg |J|$. The energy spectrum of a moving electron consists of two bands with an identical dependence of energy on the quasimomentum:

$$E_\pm(k)=-\tilde{E}_\pm\gamma_k$$

$$\tilde{B}_\pm=|B|\left\{\frac{b_1^2+2b_2^2+b_3^2}{2}\pm\frac{1}{2}(b_1-b_3)[(b_1+b_3)^2+4b_2^2]^{1/2}\right\}^{1/2},$$

$$b_1=\cos\frac{\theta}{2},\quad b_2=(2S+1)^{-1/2}\sin\frac{\theta}{2},\quad b_3=(2S+1)^{-1}\cos\frac{\theta}{2}. \tag{7}$$

If $\theta = \pi$ (in collinear antiferromagnetism) these bands are degenerate. Each bandwidth is $1/\sqrt{2S+1}$ of the maximum electronic bandwidth that is attainable in ferromagnetic ordering. As the angle $\theta$ diminishes one of the bands is broadened while the other contracts, so that the narrower band may be neglected at small values of $\theta$.

In accordance with the condition $|B| \gg |J|$ a magnetic moment should begin to appear when the number n of electrons per magnetic atom is much smaller than unity. In our investigation of the electronic spectrum we are thus able to limit ourselves to a quadratic dispersion law. The angle $\alpha$ is assumed to be so small that the bottom of the narrower band lies below the Fermi level. The carrier concentrations in the broad band ($n_+$) and in the narrow band ($n_-$) are determined from the condition that the electron chemical potentials in these bands are equal:

$$6(\tilde{B}_+-\tilde{B}_-)+\tilde{B}_-(6\pi^2n_-)^{2/3}=\tilde{B}_+(6\pi^2n_+)^{2/3},\quad n=n_++n_-. \tag{8}$$

The total energy of the system consisting of magnetic atoms and conduction electrons is given for a single unit cell by

$$E_t(\alpha)\approx-6|J|S^2\cos 2\alpha-6[\tilde{B}_+n_++\tilde{B}_-n_-]. \tag{9}$$

For small angles $\alpha$ (9) in conjunction with (7) and (8) reduces to a series that is represented by (1), with the following coefficients:

$$A_2(n)\approx-\frac{8|B|S^2(n-n_A)}{n_A^{1/3}(2S+1)^{3/2}},\quad A_4(n_A)\approx\frac{40|J|S^4}{n_A^{1/3}(2S+1)},$$

$$n_A\approx 0{,}15\left[\left|\frac{J}{B}\right|(2S+1)\right]^3. \tag{10}$$

Equation (1) is also valid for states close to collinear ferromagnetism when $\alpha$ is replaced by $\theta/2$:

$$A_2(n)=\frac{3|B|S}{S+1}(n-n_F),\quad A_4(n_F)\approx 2|J|S^2,$$

$$n_F=\frac{4|J|S(S+1)}{|B|}. \tag{11}$$

Equations (10) and (11) show clearly that $n_A$ and $n_F$ are critical concentrations for transitions from a noncollinear to a pure antiferromagnetic and a pure ferromagnetic state, respectively. In accordance with $|B| \gg |J|$ the first of these concentrations is considerably smaller than the second. If we assume $S = 1$ and

$|B/J| = 10$ (in which case magnetic polarons are evidently not realized[3]), we obtain $n_A \approx 4 \times 10^{-3}$, while $n_F$ cannot be attained within the applicability limits of the present model.

Equations (10) and (11) show that at the critical points the derivative of the electron chemical potential $\mu$ with respect to concentration is discontinuous. The value of the derivative is lower in the noncollinear region than in the collinear region, because in the former the bottom of the broader carrier band is lowered as n increases, with a corresponding effect on the chemical potential. A calculation shows that for reasonable values of B/J the relative discontinuities of $d\mu/dn$ are of the order of unity at the critical points.

The discontinuities of $d\mu/dn$ lead to analogous discontinuities of the thermoelectromotive force, which according to the Mott relation is proportional to

$$\frac{d}{dn} \ln \sigma \frac{dn}{d\mu}.$$

At the critical points the sign of the thermoelectromotive force can be reversed along with that of $d\mu/dn$. The curves representing the dependence of the work function and of the conductivity $\sigma$ on n should exhibit "breaks" at the critical points. In the case of the conductivity this effect is accounted for by the direct dependence of the effective mass on concentration and by the dependence of the relaxation time on the difference between the Fermi level and the bottom of the band.

An external electric field will enhance the carrier concentration in a surface layer having thickness of the order of the screening length, so that if the concentration is below $n_A$ in the bulk it can exceed $n_A$ at the surface. Since indirect exchange is of short-range character in narrow bands,[8] an electric field can generate a surface layer having a non-zero magnetic moment.

The foregoing considerations can be extended directly to noncollinear structures of other (e.g., helicoidal) types. Our model, which is based on the nearest-neighbor approximation, does not enable a decision as to which of two structures—weakly ferromagnetic or helicoidal—is favored energetically. This question can be answered easily by including interactions with next-nearest neighbors. For example, if the corresponding Bloch integral is negative while the exchange integral is positive, a weakly ferromagnetic structure is favored.

It is extremely important that, according to the foregoing results, a transition to the noncollinear state is possible only beginning at a certain critical concentration of current carriers, whereas according to [4] any small concentration should permit noncollinearity. The data given in Goodenough's book[9] show that we can now consider that experimental work has established reliably the transition of the antiferromagnetic crystal $LaMnO_3$ to a weakly ferromagnetic state for sufficiently heavy doping with electrically active impurities. A weakly ferromagnetic transition has been observed in doped $FeS_2$ and $NiS_2$.[10] The data in [9] show that $NiS_2$ is antiferromagnetic. Investigations of several other materials have not detected noncollinear structures even in cases of heavy doping. We can account for these negative results by assuming that the critical carrier concentration at which such structures begin to be possible are practically unattainable (or had not been attained) in these materials.

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149