Inhomogeneous ferromagnetism of conducting magnets with ions in a singlet ground state

O. I. Zavaritskiĭ and É. L. Nagaev

(Submitted April 6, 1977)
Pis'ma Zh. Eksp. Teor. Fiz. **25**, No. 11, 505–509 (5 June 1977)

The low-temperature small-angle scattering of neutrons in materials such as HoN, which is usually attributed to their complicated magnetic ordering, is ascribed to the existence in these materials of increased-magnetization regions that are stabilized by the conduction electrons.

PACS numbers: 75.25.+z, 75.50.Dd

In some rare-earth compounds (HoN etc.), the crystal field lifts completely the energy degeneracy of the magnetic ions with respect to the directions of their angular momentum **J**. The mean value $\langle J^z \rangle$ of its projection in the ground state of the ions would be equal to zero were it not for the exchange interaction of the ions with their neighbors, as a result of which $\langle J^z \rangle$ becomes different from zero, although it does not reach $\pm J$. As a result, such a magnet reveals one type of magnet order or another, with unsaturated magnetic moments.

A neutron diffraction investigation of nitrides of rare earths (HoN etc.) has shown that when the temperature is lowered, a clearly pronounced small-angle scattering appears even before the scattering corresponding to the long-range ferromagnetic order sets in, and increases monotonically with decreasing temperature.[1]

Such scattering in ferromagnets is usually connected with the short-range ferromagnetic order and therefore goes through a maximum at the Curie point T_c. In nitrides, the maximum of small angle scattering turns out to be at $T=0$. This has prompted Child *et al.*[1] to suggest that the maximum is the result of a superposition of higher-order reflections from an exceedingly complicated magnetic structure with nonzero average magnetization. The reason why such a complicated magnetic structure can be produced in crystals with a very simple lattice (of the NaCl type) is not clear.

We propose in this article a simpler interpretation of the results of[1]. Judging from the presence of a gap in their optical spectrum when their conductivity is metallic, these nitrides, since their composition is not stoichiometric, are strongly doped semiconductors.[2] The conduction electrons are coupled by *s-f* exchange interaction with the localized *f* moments. Just as the *f-f* exchange with the neighbors, the *s-f* exchange also tends to increase the localized moment. If the electron concentration were high enough, saturated ferromagnetic order would be produced in the entire crystal. At lower concentrations, an energywise more favored state may be an inhomogeneous crystal state, wherein the crystal is broken up at $T=0$ into regions having larger and smaller magnetizations. An excess of electron density is produced in the former and it is this density which maintains the increased value of the local magnetization. This state is the analog of the inhomogeneous

ferro-antiferromagnetic state of strongly doped antiferromagnetic semiconductors. Owing to the increase of the Coulomb energy when the regions with excess charge are produced, their radius is small (~ 10—100 Å).[3]

The superiority of this interpretation over that given in[1], besides the clarity of the physical mechanism of the phenomenon, lies also in the following. It is capable of explaining why a noticable small-angle scattering appears above the Curie point T_c, and does not go through a maximum at the Curie point itself. Indeed, the regions of increased magnetization, in which the conduction electrons are concentrated, arise with decreasing temperature even before T_c is reached. At T_c, their formation has already terminated and therefore the intensity of neutron scattering from these regions is comparable at T_c with the maximum value (i.e., at $T=0$). No critical small-angle scattering appears against the background of the intense small-angle scattering due to the regions with the increased magnetization.

We consider a very simple model of a magnet with ions in a singlet ground state: the ion level $|1\rangle$, which is closest to the ground level $|0\rangle$, is also singlet, so that $\langle 0|J^z|0\rangle = \langle 1|J^z|1\rangle = 0$, but the matrix element J^z for the exciton transition $|0\rangle \to |1\rangle$, $\langle 0|J^z|1\rangle = c$ is different from zero. Taking the f-f exchange and the s-f exchange into account, the Hamiltonian of the system takes the form

$$H = \omega \Sigma b_g^* b_g - \frac{K}{2} \Sigma < 0|J_g|1> < 1|J_g|0> (b_g^* + b_g)(b_{g+\Delta}^* + b_{g+\Delta}),$$
$$- A \Sigma < 0|J_g|1> (s)_{\sigma\sigma'} a_{g\sigma}^* a_{g\sigma'} + B \Sigma a_{g\sigma}^* a_{g+\Delta\sigma}, \qquad (1)$$

where b_g^* and b_g (and $a_{g\sigma}^*$ and $a_{g\sigma}$ respectively) are the creation and annihilation operators for a magnetic exciton on the atom g and on the conduction electron, $(s)_{\sigma\sigma'}$, are Pauli matrices, and Δ is the nearest-neighbor symbol (the number of nearest neighbors is z).

That the homogeneous unsaturated ferromagnetic states of degenerate semiconductors can be unstable is easiest to verify by calculating their statistic dielectric constant $\epsilon(q)$. Assume that the magnetic ordering is entirely realized as a result of indirect exchange via s electrons, which are assumed to be completely spin-polarized. From the Hamiltonian (1) with $K=0$ it follows in the self-consistent field approximation that as a result of the s-f exchange the s electrons gain an energy equal to

$$V = -M(\nu)\frac{|A|}{2}; \quad M(\nu) = \frac{\gamma \nu c}{\sqrt{\gamma^2 \nu^2 + \omega^2/4}}; \quad \gamma = \frac{|A|c}{2}, \qquad (2)$$

where $M(\nu)$ is the moment induced by the conduction electrons. The electric field, by changing the local value of the number ν of electrons per atom, changes by the same token also $M(\nu)$ (the magneto-electric effect). By a calculation analogous to that given in[3] for a ferromagnet at $T=0$, it is easy to verify that the dielectric constant of the homogeneously saturated ferromagnets at $q>0$ is given by

$$\frac{\epsilon(q)}{\epsilon} = 1 + \frac{\lambda^2}{q^2(1-\Gamma_0)}; \qquad \lambda^2 = \frac{6\pi e^2 n}{\mu \epsilon_0};$$

$$\Gamma_0 = \frac{3}{8\mu\nu} \frac{(\gamma\nu\omega)^2}{\left[\gamma^2\nu^2 + \omega^2/4\right]^{3/2}}; \qquad \mu = \frac{(b\omega^2 n)^{2/3}}{2m}, \tag{3}$$

where ϵ_0 is the dielectric constant of a pure semiconductor, μ is the Fermi energy of the electrons, and $n = \nu/a^3$ is their concentration.

The quantity Γ_0 [Eq. (3)] as a function of ν goes through a maximum at $\nu = \omega/4\sqrt{2}\gamma$. At $n \sim 10^{20}$ cm^{-3} and $\omega = 10^{-3}$ eV, at an effective mass m on the order of the true mass, at $AJ \sim 0.5$ eV, and $c \sim J/2$, the maximum value of the feedback function Γ_0 can exceed unity. In the assumed approximation, this is sufficient (but not necessary) for the stability of the homogeneous state. If the crystal breaks up into regions $\nu < \nu_m$ and $\nu > \nu_m$, in which $\Gamma_0 < 1$, then the necessary conditions for the stability of this inhomogeneous ferromagnetic state will in any case be satisfied.

To gain an idea of the properties of the inhomogeneous state, we consider a very simple case, when the electron density is low and each electron produces a region of increased magnetization independently of the others. Accordingly, the direct f-f exchange is predominant ($K > AJ\nu$). In the molecular-field approximation, the free energy of such a magnet per atom is given by

$$F_M = \frac{\omega}{2} - T \ln\left\{2\mathrm{ch}\left[\frac{\omega}{2T}\sqrt{1+\left(\frac{aM}{c}\right)^2}\right]\right\} + \frac{KzM^2}{2}; \qquad a = \frac{2Kzc^2}{\omega}, \tag{4}$$

where the induced moment is determined from the self-consistency condition

$$\sqrt{1+\left(\frac{aM}{c}\right)^2} = a\,\mathrm{th}\left(\sqrt{1+\left(\frac{aM}{c}\right)^2}\,\frac{\omega}{2T}\right). \tag{5}$$

If in some microscopic region of radius R the localized f spins are transferred into a state in which their average projections J^z are equal to the limiting value J, then such a region will constitute a potential well for the conduction electrons, with a depth $A(J-M)/2$. On the other hand, the free energy (per atom) consumed in the production of the saturated ferromagnetic order is $D_F = \omega_F - F_M$, where $\omega = \delta - KzJ/2$, and δ is the difference between the average ion energy in the state with $J^z = J$ and its ground state energy $|0\rangle$. Performing the calculation by the same variational method as for the ferronic state in an antiferromagnet[3] with the radius R as the variational parameter, we obtain the condition under which this state is thermodynamically favored in an unsaturated ferromagnet, when the electron is localized in the increased-magnetization region produced by itself

$$D^* = \left[1 - \frac{M(T)}{J}\right]^{-5/2} D_F < 0.2\,W\left(\frac{AJ}{2W}\right)^{5/2} = D_c, \tag{6}$$

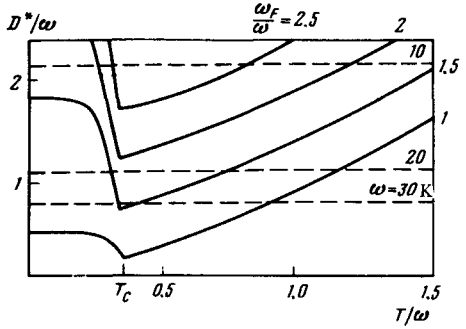

FIG. 1.

where $W = b/Ma^3$ is the width of the electron conduction band.

Figure 1 shows the results of a numerical calculation of D^* with the aid of formulas (1)—(3), for certain values of ω_F/ω, using for the parameters the numerical values $AJ/2W = 0.1$, $c/J = 0.6$, and $\alpha = 1.2$ (this value of α corresponds to a moment of $0.55c$ at $T = 0$). Given the value of ω, the self-localized state of the electron in the region with the increased magnetization is stable when the corresponding curve lies below the straight line D^*/ω. As seen from Fig. 1, at $\omega_F/\omega = 1.5$ and $\omega = 10$ K the state with the increased magnetization is stable from $T = 0$ to $T_d = 17$ K, i.e., T_d is much higher than $T_c = 3.3$ K [T_c obtained in accordance with formula (5) from the condition $M(T_c) = 0$].

[1]H. Child, M. Wilkinson, J. Cable, W. Koehler, and E. Wollan, Phys. Rev. 131, 922 (1963).
[2]N. Selar, J. Appl. Phys. 35, 1534 (1964).
[3]E. L. Nagaev, Usp. Fiz. Nauk 117, 437 (1975) [Sov. Phys. Usp. 18, 863 (1975)].