

NONLINEAR MAGNETOELECTRIC EFFECT

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We show in this paper that in a ferroelectric antiferromagnet with nonequivalent magnetic ions it is possible to have a quadratic dependence of the spontaneous polarization on the sublattice magnetization. We also point out the physical effects ensuing from this dependence.

It is shown in [1] that in antiferromagnets without symmetry centers between the magnetic ions, the matrix elements of the dipole moment for the spin-wave states differ from zero, if account is taken of the electronic transitions to the excited ionic states together with the Coulomb exchange of the electrons of the nonequivalent ions. These dipole-moment matrix elements, which are responsible for the two-magnon absorption [2], are determined by the effective dipole-moment operator

$$D_{\text{eff}} = \sum_{m, m'} d_{m, m'} (S_m S_{m'}) \quad (1)$$

We note that relation (1) results not only from the mechanism considered in [1], but also from indirect exchange between nonequivalent ions, which is responsible for the antiferromagnetic ordering [3]. The Hamiltonian with allowance for the Coulomb repulsion of the electrons of the unfilled shell and for the indirect exchange is given by

$$H = H_0 + H'; \quad H_0 = 1/2 \sum_{m_1 m_2} I_{m_1 m_2} n_{m_1} n_{m_2}, \quad (2)$$

$$H' = \sum_{m_1 m_2 \sigma} \beta_{m_1 m_2} a_{m_1 \sigma}^+ a_{m_2 \sigma} + \sum_{m_1 m_2 \sigma} \beta_{m_1 m_2} a_{m_1 \sigma} a_{m_2 \sigma}^+; \quad n_m = \sum_{\sigma} a_{m \sigma}^+ a_{m \sigma}$$

where  $I_{m_1 m_2}$  is the Coulomb repulsion of the electrons at sites  $m_1$  and  $m_2$ ,  $\beta_{mm'}$  is the parameter of indirect exchange between the ions  $m$  and  $m'$ , and it is assumed that there is one electron in the unfilled shell of the magnetic ion. In the same representation of the localized electrons, the dipole moment operator is

$$D = \sum_{m_1 m_2 \sigma} X_{m_1 m_2} (a_{m_1 \sigma}^+ a_{m_2 \sigma} - a_{m_1 \sigma} a_{m_2 \sigma}^+), \quad (3)$$

$$X_{m_1 m_2} = \int w_{m_1}(r) r w_{m_2}(r) d^3 r,$$

where  $w_m(r)$  is the Wannier function at site  $m$ . From (2) and (3) we obtain, in the first and second order of perturbation theory in terms of the indirect exchange  $H'$ , the effective dipole-moment operator

$$D_{\text{eff}} = P(1 - H')(1/H_0)D(1 - (1/H_0)H')P = \sum_{m, m'} d_{mm'} (S_m S_{m'} - 1/4), \quad (4)$$

where  $P$  is the operator of projection on the degenerate states with one electron at the center, and

$$d_{mm'} = 2X_{mm'}\beta_{mm'} \frac{1}{u_{mm'}} - \frac{1}{u_{m'm}} - (m - m')e\beta_{mm'}^2 \left[ \frac{1}{u_{mm'}^2} - \frac{1}{u_{m'm}^2} \right], \quad u_{mm'} = l_{mm} - l_{m'm}. \quad (5)$$

For the nonequivalent ions  $m$  and  $m'$  we have  $X_{mm'} \neq 0$ ,  $u_{mm'} \neq u_{m'm}$ , and  $d_{mm'} \sim e|m - m'|(\beta/u)^2$ , i.e., the contribution of the indirect exchange to the parameters  $d_{mm'}$  is  $10^{-2} - 10^{-5}$  of the atomic dipole moment  $d_0$ .

It follows from (1) that in antiferromagnets whose symmetry admits of a vector (ferroelectrics below  $T_c$ ) there can exist a macroscopic polarization  $P$  that depends on the magnetic state of the system. Indeed,

$$P = P_0 + \frac{1}{V} \langle D_{\text{eff}} \rangle = P_0 + \frac{1}{V} \sum_{m,m'} d_{mm'} \langle S_m S_{m'} \rangle, \quad (6)$$

where  $P_0$  is the spin-independent part of the polarization and  $V$  is the volume. Below the Neel point  $T_N$  we have, in the molecular-field approximation,

$$P = P_0 + D(S_1 S_2); \quad D = \frac{1}{V} \sum_{m,m'} d_{mm'}, \quad (7)$$

where  $S_{1,2}$  is the average spin in the sites of sublattice 1 or 2, and the directions of  $P_0$  and  $D$  coincide if the symmetry admits of a vector with one direction only.

The coexistence of a ferroelectric and antiferromagnetic phase was observed, for example, in boracides [4, 5], in which it is apparently possible to observe the following effects based on the spin dependence of the polarization.

It follows from (6) that in crystals with  $T_N < T_c$  (apparently in nickel-chloride boracide) the polarization will vary with the temperature in the region of  $T_N$  just as the magnetic energy. In the Landau model of second-order phase transitions, the temperature variation of the polarization will be linear, with a coefficient

$$D/T_N, \quad D \sim d_0 N (\beta/u)^2 \sim (10^{-2} - 10^{-5}) d_0 N,$$

where  $N$  is the density of the magnetic ions.

Relation (1) leads to a frequency-doubling effect in a ferroelectric antiferromagnet. Indeed, when antiferromagnetic resonance is excited by an alternating magnetic field

$$h e^{i\omega t} + h^* e^{-i\omega t}$$

there appear in the polarization terms proportional to the square of the alternating field

$$\begin{aligned} \Delta P &= \frac{1}{2} D [(S_{1x} + S_{2x})^2 + (S_{1y} + S_{2y})^2] = \\ &= 2D\gamma^2 \omega_\sigma^2 \frac{h_+ h_-^*}{|A(\omega)|^2} + \frac{h_+ h_-^*}{|A(-\omega)|^2} + \frac{(h_+)^2 e^{2i\omega t}}{A(\omega) A^*(-\omega)} + \\ &+ \frac{(h_-^*)^2 e^{-2i\omega t}}{A(-\omega) A^*(\omega)}, \quad A(\omega) = (\omega_\sigma + \omega_\sigma)^2 - \omega_\sigma^2 - (\omega + \omega_H - i\omega_r)^2, \end{aligned} \quad (8)$$

where  $h_{\pm} = h_x \pm ih_y$ ,  $\omega_e$ ,  $\omega_a$ , and  $\omega_H$  are the frequencies corresponding to the exchange field, the anisotropy field, and the constant magnetic field, respectively,  $\omega_r$  is the relaxation frequency, and  $\gamma$  is the gyromagnetic ratio. It is seen from (8) that  $\Delta P$  contains terms that do not depend on the time, as well as terms oscillating at double the frequency  $2\omega$ , which lead to magnetoelectric frequency doubling. Estimate of the effect off resonance yields  $\Delta P = \gamma^2 D |h|^2 / \omega_e^2$ .

We note also that two-magnon absorption at double the antiferromagnetic-resonance frequency, i.e., production of magnons with  $k = 0$ , is possible in ferroelectric-antiferromagnets. Magnons with nonzero quasimomenta  $k$  and  $-k$  appear in fluorides of iron-group transition elements in two-magnon absorption, since the symmetry group of the crystal contains an inversion and  $\sum_m d_{mm} = 0$ .

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#### INDUCED FERROELECTRIC MAGNETISM IN MAGNETICALLY ORDERED PIEZOELECTRICS

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The crystallographic symmetry group of a magnet is determined from its magnetic group if the transformation  $R$  [1], which consists of the reversal of the signs of all the currents and magnetic field, is formally regarded as identical. Such a symmetry group is as a rule lower than the symmetry of the paramagnetic phase, i.e., a realignment of the electric structure of the crystal takes place in the magnetic transition as a result of interactions of the spin-orbit or magnetostriction type. This means that the thermodynamic potential is in the region of the transition point a functional not only of the microscopic spin density, but also of a certain electric ordering parameter. We are interested in the case when this parameter can be chosen to be the spontaneous electric polarization  $\vec{P}$  of the crystal, i.e., when the crystallographic group resulting from the magnetic transition belongs to the pyroelectric class. To describe the magnetic phase transition we introduce, following Dyaloshinskii [2], the vectors  $\vec{S}_{n\alpha}$ . The connection between  $\vec{S}_{n\alpha}$  and the microscopic spin density  $s(r)$  inside the unit cell was considered in detail in [2], and there is no need to repeat the conclusion derived there. We note only that when the symmetry operations are applied, the  $S_{n\alpha}$  with different  $\alpha$  and specified  $n$  are transformed in terms of one another, realizing a crystallographic-representation which is a direct product of the representation of the realized pseudovector and the  $n$ -th reducible one. The thermodynamic potential can be expanded in the region of the transition point in a power series in the projections of  $\vec{S}_{n\alpha}$  and  $\vec{P}$  (and not a functional series, as when  $\vec{s}(r)$  is used). The terms of the series are determined as invariants relative to the symmetry group of the paramagnetic phase. Since the paramagnetic phase as an operation  $R$  by itself, and the  $\vec{S}_{n\alpha}$  are invariant with respect to