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Electric-field effects on the spin-density wave in magnetic ferroelectrics

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A profound analogy exists between the modulate structures in magnetic materials and in nematic liquid crystals, especially for the behavior in an external field. Starting from this point, we study the influence of an electric field on the spatially modulated spin structure (spin-density-wave state) of the magnetic ferroelectric $BiFeO_3$, discovering and investigating the possibility of a transition between the spin-density-wave state into a homogeneous antiferromagnetic configuration.

I. INTRODUCTION

In the physics of the long-range order phenomena, the contributions to the free-energy density of the terms linear in the derivatives of the order parameter are of great importance: such a kind of terms have been recognized to be fundamental in governing the appearance of spatially modulated spin structures (helicoidal and fan) in magnetic materials[1,2] and the arising of the periodic patterns in liquid crystals. In fact, in liquid-crystalline films the presence of the periodic domains is due to the competition among the elastic and anchoring torques, biased by the possible external field interaction.[3-10] In all the situations showing modulated structures, there is a term, responsible for the transition from the undistorted alignment to the modulated one, containing the first derivatives of the director field, that is of the local mean molecular orientation of the liquid crystal.

It is actually possible to find phenomena in magnetic materials and in liquid crystals that can be explained by a term of the same structure in the free energy. Let us for instance, consider one case that is connected with a new phase transition, induced by a magnetic field, between a spatially modulated spin structure (spin-density wave—SDW) and a homogeneous antiferromagnetic state. Such a transition was recently discovered in the magnetic ferroelectric material $BiFeO_3$.[11] Here, the space-modulated spin structure is due to the coupling of the spontaneous electric polarization with the magnetic order parameter, taking the form of a Lifshitz invariant.[12,13] In the same manner, the linear coupling between the flexoelectric induced polarization in nematic liquid crystals and an external electric field can substantially influence a transition between an undistorted state and a periodic pattern.[4,14]

Another general feature is achieved both in antiferromagnetic materials and in liquid crystals and it is connected to the presence of linear and quadratic terms concerning the electric-field interaction. The quadratic terms are always present, but, when the symmetry with respect to an inversion point is broken, then linear terms appear and become dominant for producing the change of the material order parameter. In conclusion, the similar behavior of magnetic materials and liquid crystals is due to a profound analogy between the free-energy density for magnetic ferroelectric materials, whose distribution is assumed to be continuous,[15] and the Nehring and Saupe free-energy density for nematic liquid crystals.[16]

The aim of this paper is to understand more deeply the properties of the spin-density-wave state in antiferromagnetics and to find common features between these structures and those observed in liquid crystals. In analogy with the behavior of liquid crystals in electric field, the effect of a constant electric field on the transition from the spin-density wave to the homogeneous state will be investigated. Also the effect of a magnetic field on such a threshold will be considered.

II. FREE ENERGY

The magnetic-field-induced phase transition between space-modulated spin structure and homogeneous antiferromagnetic state has been discovered in the magnetic ferroelectric $BiFeO_3$.[11] $BiFeO_3$ is an antiferromagnet with high electric and antiferromagnetic ordering temperature, $T_c = 1083$ K and $T_N = 673$ K.[17-19] The crystal structure of this material is a rhombohedrally distorted perovskite and the space group is $R3c$. The magnetoelectric and magnetic properties of this material are very interesting from an experimental and theoretical point of view: in fact, while the crystal symmetry allows linear magnetoelectric phenomena, they are not observed due to the presence of the spatially modulated structure.[20] The magnetic order can be characterized by the antiferromagnetic vector:

$$\mathbf{L} = \nu_0^{-1} \sum (-1)^i \mathbf{M}_i \ , \tag{1}$$

where $\mathbf{M}_i$ are the magnetic moments of the six Fe ions of a unit cell, and ν_0 is the unit-cell volume. The sum index is running over all Fe ions of the unit volume. The vector $\mathbf{L}$ is the principal order parameter of $BiFeO_3$, and thus the free-energy density of the system, assumed as continuously distributed, is written as

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$$f = A \sum_{i=x,y,z} (\nabla L_i)^2 + \tilde{\alpha} P_z \sum_{j=x,y} L_j L_{z,j} - K_u L_z^2 , \quad (2)$$

where **A** is the exchange stiffness of magnetic material and $\tilde{\alpha}$ is the nonhomogeneous relativistic constant. P_z is the polarization and K_u the constant of uniaxial anisotropy. The notation $L_{i,j}$ indicates the derivatives of the i component with respect to the j variable. The second term in the free energy (2) is a Lifshitz-type invariant responsible for the modulated structure in this material.[12] The leading contribution to the free energy is given by the exchange energy

$$A \sum_i (\nabla L_i)^2 = A \sum_{i,j} (L_{i,j})^2 . \quad (3)$$

This kind of term is analogous to the bulk term in the Nehring and Saupe form[16] of the free-energy density for nematic liquid crystal in the case of the isotropic approximation with the fundamental elastic constants related in the following way:

$$K_{11} = K_{22} = K_{33}; \quad K_{24} = -\tfrac{1}{2} K_{22} , \quad (4)$$

that is,

$$K\{(\mathrm{div}\mathbf{n})^2 + (\mathbf{n}\cdot\mathrm{rot}\mathbf{n})^2 + (\mathbf{n}\times\mathrm{rot}\mathbf{n})^2 - \mathrm{div}(\mathbf{n}\,\mathrm{div}\mathbf{n} + \mathbf{n}\times\mathrm{rot}\mathbf{n})\} , \quad (5)$$

where **n** is the mean molecular direction of the long axis of molecules (in the statistical average sense),[21] that is the so-called director.

In materials without an inversion center in the crystal structure (such as $BiFeO_3$), special contributions into the free energy, linear on first derivatives of the order parameter, come from the Lifshitz invariant terms. The second contribution in the free energy (2) is a term of this form and is responsible for the appearance of the modulate structure.[13] In analogy with the nematic liquid crystals we can call this term the spin-flexoelectricity term because it has a striking similarity to the flexoelectric term for the nematic liquid crystal

$$\Delta F = -\mathbf{E}\cdot\mathbf{P} = e_1(\mathbf{E}\cdot\mathbf{n})(\mathrm{div}\mathbf{n}) + e_3\mathbf{E}(\mathbf{n}\times\mathrm{rot}\mathbf{n}) . \quad (6)$$

The important role played here by the vector

$$\mathbf{A} = \mathbf{L}\,\mathrm{div}\mathbf{L} + \mathbf{L}\times\mathrm{rot}\mathbf{L} \quad (7)$$

is due to the fact that it transforms like an electric field under action of elements of the crystal symmetry group. Then the second term in the free energy (2), that is the Lifshitz invariant, can be represented by

$$\Delta f_{\mathrm{LI}} = \tilde{\alpha}\mathbf{P}_S\cdot\mathbf{A} , \quad (8)$$

where $\mathbf{P}_S$ is the spontaneous polarization of crystal. In the bismuth ferrite $BiFeO_3$, $\mathbf{P}_S = (0,0,P_z)$.

The last term of the free energy (2) represents the energy of magnetic anisotropy for uniaxial crystals and this term can be put into relation with the action of an external magnetic field on the nematic director in the case of liquid crystals.

III. EULER-LAGRANGE EQUATIONS

The components of the antiferromagnetic vector, in a polar reference frame, can be written as

$$\begin{aligned} L_x &= L\sin\theta\cos\phi , \\ L_y &= L\sin\theta\sin\phi , \\ L_z &= L\cos\theta , \end{aligned} \quad (9)$$

and the free-energy density assumes the following form:

$$f = A[(\nabla\theta)^2 + \sin^2\theta(\nabla\phi)^2] + \tilde{\alpha}P_z\sin^2\theta(\theta'_x\cos\phi + \theta'_y\sin\phi) + K_u\sin^2\theta . \quad (10)$$

As we can see from (10), the phase with $\theta = 0$ can be stable only if $K_u > 0$. The Euler-Lagrange equations are

$$\begin{cases} 2A\nabla^2\theta - \tilde{\alpha}P_z\sin^2\theta(-\phi'_x\sin\phi + \phi'_y\cos\phi) \\ \qquad - 2\sin\theta\cos\theta[2A(\nabla\phi)^2 + K_u] = 0 , \\ 2A\,\mathrm{div}[\sin^2\theta\nabla\phi] + \tilde{\alpha}P_z(-\theta'_x\sin\phi + \theta'_y\cos\phi) = 0 . \end{cases} \quad (11)$$

From the last equation of system (11), it follows that $\phi = \mathrm{const}$ is a solution, when $\tan\phi = \theta'_y/\theta'_x = q_x/q_y = \mathrm{const}$. With $\phi = \mathrm{const}$, the Euler-Lagrange equations can be rewritten as

$$\begin{aligned} &2A\nabla^2\theta - 2K_u\sin\theta\cos\theta = 0 , \\ &-\theta'_x\sin\phi + \theta'_y\cos\phi = 0 . \end{aligned} \quad (12)$$

From the first equation of system (12), we can see that an homogeneous (antiferromagnetic) orientation and a periodic structure (spatially modulated spin structure or spin-density wave—SDW) can exist. Let us compare the free energies and study the transition between these two phases. After integration, this equation becomes

$$A(\nabla\theta)^2 - K_u\sin^2\theta = \mathrm{const} = \varepsilon , \quad (13)$$

which can be solved by elliptic functions: but it is possible to assume

$$\varepsilon \gg K_u\sin^2\theta . \quad (14)$$

This means that, in the phase space (θ', θ) (see Fig. 1), we are far from the separatrix of Eq. (13). The assumption (14) is confirmed from the experimental observations with neutron diffraction[22–24] in which one sees only one harmonic behavior and higher reflexions are absent.

Thus

$$\nabla\theta = \left[\frac{\varepsilon}{A}\right]^{-1/2} , \quad (15)$$

so that

$$\theta = \mathbf{q}\cdot\mathbf{r} + O(K_u/\varepsilon)_0 \quad (16)$$

The spin-density-wave solution is thus given by $\theta = \mathbf{q}\cdot\mathbf{r}$. Substituting into the second equation of system (12), we have the following relation:

$$-(q_x x)\sin\phi + (q_y y)\cos\phi = 0 . \quad (17)$$

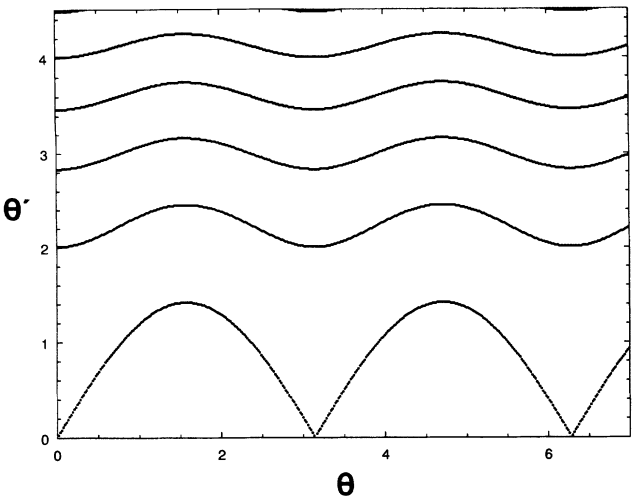

FIG. 1. Phase space (θ,θ') of Eq. (13).

Actually, **q** has a well-defined direction: in fact, the in-plane degeneracy is removed by a term into the free energy of the form

$$K_I\cos(6\phi+\beta) \tag{18}$$

in the case of $BiFeO_3$. This term represents the anisotropy for a uniaxial system with an axis of the third and sixth orders. For the sake of simplicity we do not include this term and assume the in-plane degeneracy: this assumption will not have further influence on the main results.

Let us now compare the free energy for the unit volume of the SDW state with the homogeneous one with $\theta=0$. Starting from expression (10) for the free energy, we substitute solution (16) and, averaging over the volume, we obtain

$$\begin{aligned} F_{\rm SDW}=\frac{1}{V}\int dV\{ A(\nabla\theta)^2+\sin^2\theta(\nabla\phi)^2 \\ +\tilde{\alpha}P_z\sin^2\theta(\theta'_x\cos\phi+\theta'_y\sin\phi)+K_u\sin^2\theta\} \\ =Aq^2-\frac{\alpha}{2}q+\frac{K_u}{2}\ , \end{aligned} \tag{19}$$

where $\alpha=\tilde{\alpha}P_z$. The value of q, minimizing the free energy, is then

$$q_0=\alpha/(4A)\ . \tag{20}$$

For the homogeneous state with **L** directed along the z axis, that is $\theta=0$, which according to (10) also minimizes the free energy, we have

$$F_{\rm HS}(\theta=0)=0\ .$$

Evidently,

$$-Aq_0^2+\frac{K_u}{2}<0 \tag{21}$$

because the stable SDW is realized in the $BiFeO_3$: this relation imposes a finite wave vector q_0 to the the SDW state.

IV. COUPLING BETWEEN ELECTRIC FIELD AND INTERNAL MAGNETIC FIELD

A. Electric field parallel to z axis

The coupling between an external electric field **E** and a spatial uniform inner field of the Dzyaloshinski-Moriya-type $\mathbf{H}_{\rm DM}$ has the following form:

$$\Delta F_{\rm ME}=-\mathbf{E}\tilde{\alpha}\mathbf{H}_{\rm DM}\ , \tag{22}$$

where $\tilde{\alpha}$ is the magnetoelectric susceptibility tensor of the second rank.[25] For the ferrite of bismuth $BiFeO_3$ this tensor is given by[12]

$$\tilde{\alpha}=\begin{vmatrix} -a_1L_x & -a_4L_z+a_1L_y & -a_2L_y \\ a_1L_y+a_4L_z & a_1L_x & a_2L_x \\ -a_3L_y & a_3L_x & 0 \end{vmatrix}\ . \tag{23}$$

The resulting interaction is spatially uniform in the sense that it does not depend on the derivatives of the antiferromagnetic vector **L**, unlike the Lifshitz invariant term previously discussed.

The in-plane DM field can be determined here as (see, for instance, Refs. 26 and 27)

$$\mathbf{H}_{\rm DM}=\mathbf{d}\times\mathbf{L}\ , \tag{24}$$

where $\mathbf{d}=(0,0,d)$, with $d=bP_z$. Assuming, for instance, **E** parallel to the z axis, we have a contribution to the free energy of the type

$$\Delta F=-a_3E_zd\sin^2\theta=-E_zP_3\sin^2\theta\ . \tag{25}$$

B. Electrical-field-induced phase transition between SDW and HS states

Evaluating the free energy for unit volume, that is averaging on this volume, as the same in (19), we have

$$\begin{aligned} F_{\rm SDW}&=Aq^2-\frac{\alpha}{2}q+\frac{K_u}{2}-\frac{1}{2}a_3E_zd\ , \\ F_{\rm HS}&\left[\theta=\frac{\pi}{2}\right]=K_u-a_3E_zd\ . \end{aligned} \tag{26}$$

Comparing $F_{\rm SDW}$ and $F_{\rm HS}(\theta=\pi/2)$ yields the field threshold for the SDW→HS transition:

$$E_c=-\frac{2}{a_3d}\left\{Aq^2-\frac{\alpha}{2}q-\frac{K_u}{2}\right\}=\frac{2}{a_3d}Aq^2\ . \tag{27}$$

Taking into account the inequality (21) it is not difficult to see that in a field $E\approx E_c$ the homogeneous phase $\theta=\pi/2$ is actually stable and the phase $\theta=0$ is unstable. So we can conclude that, in principle, it is possible to have a spin flop from the SDW state into the in-plane homogeneous one by applying an external electric field. Estimating the value of the threshold field we find that it is of the order of 10^7–10^8 V/cm. Of course, the critical field E_c can be lowered by decreasing the constant of uniaxial anisotropy by means, for instance, of the technological method: doping the material by ions.[28] But here we

will discuss a different possibility based on the use of an external magnetic field. We know[11,12] that the magnetic field can produce phase transition from the SDW to HS state. It means that magnetic field can decrease the difference of energy between SDW and HS ($\theta=\pi/2$) states.

C. Combined action of electric and magnetic field

Let us now assume **E** perpendicular to the z axis (it can be easily shown that in the case with **E** parallel to **H** parallel to the z-axis $\Delta F=0$):

$$\Delta F=-\mathbf{E}\tilde{\alpha}(\mathbf{d}\times\mathbf{L})$$
$$=-a_1 Ed\sin^2\theta\sin(2\phi+\psi)+\tfrac{1}{2}a_4 Ed\sin 2\theta\cos(\psi-\phi)\ , \tag{28}$$

where ψ is the azimuthal angle of the electric field. After averaging on θ, we have

$$\Delta F_{\mathrm{SDW}}=-\tfrac{1}{2}a_1 Ed\sin(2\phi+\psi)\ . \tag{29}$$

It is clear that the minimum of the free energy is reached when $2\phi+\psi=\pi/2$ or $3\pi/2$ in dependence on the sign of the combination $a_1 Ed$.

The contribution due to the electric field of the free energy of the homogeneous phase is

$$\Delta F_{\mathrm{HS}}=-a_1 Ed\ . \tag{30}$$

Let us study the effect of the combined action of a magnetic and an electric field. We have also to add to the free energy the contribution coming from the interaction of a magnetic field with the antiferromagnetic vector **L** that it is given by[27]

$$\Delta F_{\mathrm{Hz}}=-\frac{\chi}{2}[\mathbf{H}^2-(\mathbf{H}\cdot\mathbf{L})^2]$$
$$=-\frac{\chi}{2}H^2+\frac{\chi}{2}(HL\cos\theta)^2 \tag{31}$$

where χ is the magnetic susceptibility of the antiferromagnetic. If the temperature is lower than the Néel temperature T_N of the antiferromagnet, the parallel contribution $\chi_\parallel$ of the magnetic susceptibility is negligible. Calling from now on χ the perpendicular contribution $\chi_\perp$, we have that the contribution to the free energy in the SDW state is given by

$$\Delta F=Aq^2-\frac{\alpha}{2}q+\frac{K_u}{2}-\frac{\chi}{2}H^2+\frac{\chi}{2}\langle\cos^2\theta\rangle H^2$$
$$=Aq^2-\frac{\alpha}{2}q+\frac{K_u}{2}-\frac{\chi}{2}\frac{H^2}{2}$$
$$=Aq^2-\frac{\alpha}{2}q+\tilde{K}_u=-A\frac{q^2}{2}+\frac{\tilde{K}_u}{2}\ , \tag{32}$$

where we have defined $\tilde{K}_u=K_u-\chi H^2/2$.

For the homogeneous state with $\theta=\pi/2$ the dependence of the free energy on the magnetic field is

$$F=K_u-\frac{\chi}{2}H^2=\tilde{K}_u\ . \tag{33}$$

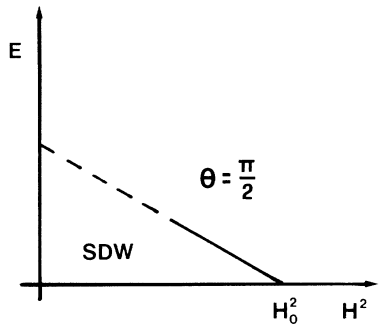

FIG. 2. Critical electric field E as a function of H^2. The value of H_0^2 is $\sim 2\times 10^5$ Oe.

So, inserting the contributions from the magnetoelectric interaction into the energy of the SDW and HS states we have

$$F_{\mathrm{SDW}}=-A\frac{q^2}{2}+\frac{\tilde{K}_u}{2}-\left|\frac{a_1 Ed}{2}\right|\ ,$$
$$F_{\mathrm{HS}}\left[\theta=\frac{\pi}{2}\right]=\tilde{K}_u-|a_1 Ed|\ . \tag{34}$$

Comparing the two free energies we obtain the equation for the critical fields

$$\frac{A}{2}q^2+\frac{\tilde{K}_u}{2}=\frac{|a_1 d|}{2}E_c+\frac{\chi H_c^2}{4}\ . \tag{35}$$

In Fig. 2 one can see the phase diagram with the transition line between the antiferromagnetic state and the SDW state. The presence of the magnetic field lowers the value of the critical field. The broken piece of the threshold line refers to a zone in which the approximation of low electric field $E\ll E_c$ is not valid: E_c is the critical field determined by Eq. (27), giving the field threshold for the SDW$\rightarrow$HS transition, due to the coupling of the electric field with the Dzyaloshinski-Moriya field. The value of the critical magnetic field H_o for $E=0$, can be estimated to be ~ 200 KOe.[11,12]

V. CONCLUSIONS

Starting from the analogy between modulate structures in magnetic materials and nematic liquid crystals, we studied the influence of an electric field on the magnetic structure of magnetic ferroelectric materials with spatially modulated spin structure (SDW state) and we showed that the electric field has a tendency to prefer the homogeneous state and so to induce a phase transition to this structure. We studied also the combined action of electric and magnetic fields and calculated the phase diagram of the system in order to estimate the possibility of such a transition.

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