Magnetoferroelectric and toroidal ordering

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The possible occurrence of a toroidal ordering of a nonintrinsic type in a magnetoferroelectric is discussed. This type of ordering should be manifested by an intensification of diamagnetic effects. Magnetostatic equations are formulated. They describe, in particular, a toroidal-state diamagnetism.

1. A new type of ordering in a solid has recently been predicted and studied theoretically: a toroidal current state.[1–3] The order parameter in this state is the density of the toroidal moment, $\mathbf{T}(\mathbf{r})$, and the conjugate field is the current density $\mathbf{j}(\mathbf{r})$. The response to $\mathbf{j}(\mathbf{r})$ diverges at the point of a second-order phase transition. The symmetry of the polar vector $\mathbf{T}(\mathbf{r})$, which changes sign upon time reversal (the existence of such a vector is allowed in the magnetic symmetry class 31; see Ref. 3, for example), leads to a magnetoelectric effect in the toroidal-current state. Analysis of a microscopic model (see the bibliography in Ref. 4) shows that in addition to the actual transition to the toroidal-current state there is a high probability that a toroidal-current state will arise in the domain walls of orbital magnetic materials and semiconducting ferroelectrics if the ferroelectricity arises from a Coulomb or electron-phonon interaction (the vibron model as a particular case). In the present letter we show that in a material that exhibits both ferroelectric and magnetic properties—a magnetoferroelectric material—the appearance of a toroidal moment is unavoidable, and this moment appears throughout the volume, not exclusively in domain walls. Evidence of a toroidal-current state against the background of ferroelectric magnetic ordering might be an intensification of diamagnetic effects. We formulate some magnetostatic equations and associated boundary conditions which also describe, in particular, the diamagnetism of a toroidal-current state.

2. The magnetic symmetry classes that allow a toroidal-moment vector in principle allow the existence of magnetic-order parameters of other types: the magnetic moment or the antiferromagnetic vector. For this reason, knowledge of the symmetry of a medium is not sufficient for unambiguously determining whether a toroidal current state occurs or whether some other type of magnetic ordering occurs. There is every reason to believe that ordering in terms of the toroidal moment coexists with ordering in terms of the magnetic moment in at least one class of media: magnetoferroelectrics (see, e.g., Ref. 5). In a magnetoferroelectric, a toroidal moment

$$\mathbf{T} \sim [\mathbf{P}\,\mathbf{M}]\,. \tag{1}$$

is induced in the system in proportion to the polarization vector **P** and the orbital component of the magnetic moment, **M**.

In this case the transition to the toroidal-current state is a nonintrinsic transition. A distinctive property of the toroidal-current state is its diamagnetic response to an external magnetic field. This result was established in Ref. 6 for the case of smooth spatial variations of $\mathbf{T}(\mathbf{r})$. We show in the present letter that the toroidal-current state is diamagnetic for arbitrarily sharp spatial changes in $\mathbf{T}(\mathbf{r})$ (discontinuities). The diamagnetic component of the magnetic response, which arises simultaneously with $\mathbf{T}(\mathbf{r})$ in (1), however, may be masked by the predominant paramagnetic component of the response, which is associated with the magnetic ordering of **M**. Nevertheless, at sufficiently low temperatures in a fixed external field, or in sufficiently strong fields at a given temperature, at which the induced paramagnetic moment reaches saturation, the toroidal diamagnetic component may become predominant, and the resultant moment of the sample may begin to decrease with decreasing temperature. The behavior in a strong magnetic field, which is characteristic of the toroidal-current state, has been observed experimentally in nickel iodide boracite[7] ($Ni_3B_7O_{13}I$). It was shown in Ref. 7 that when the external magnetic field is oriented in a certain way with respect to the crystallographic axes, the induced magnetic flux through the sample becomes negative at a certain critical value of the field. The existence of a critical magnetic field can be explained as follows. A high diamagnetic susceptibility requires a high concentration of regions of inhomogeneous toroidal moment. The role of these regions may be played by the boundaries of the ferroelectric domains in a magnetoferroelectric, whose density may increase with increasing magnetic field because of the term $|(\mathbf{H}^0\overrightarrow{\nabla}_{\mathbf{n}}P|^2$ in the free-energy functional ($\overrightarrow{\nabla}_{\mathbf{n}}$ is the gradient in a given symmetry direction **n** of the crystal).[8] A decrease in the induced magnetic moment with decreasing temperature has also been observed in nickel iodide boracite.[9] The magnetic susceptibility will behave in a similar way when the toriodal-current state forms only near a ferroelectric domain wall, rather than over the entire volume of the sample.[2]

The situation opposite (1) is also possible, i.e., a situation in which an ordering in the magnetic moment which arises from an intrinsic transition to a toroidal current state is nonintrinsic:

$$\mathbf{M} \sim [\,\mathbf{T}\mathbf{P}\,]\,. \tag{2}$$

The vector **P** is not necessarily the polarization vector. The role of the vector **P** could also be played by the displacement vector upon a structural transition involving the loss of an inversion center. If the transition accompanied by the formation of **P** occurs before the transition to the toroidal-current state, the invariant that is cubic in

T, and **H** will cause the magnetic susceptibility to vary in accordance with the Curie-Weiss law only below the temperature of the transition to the state with $\mathbf{P} \neq 0$, with a slope change at the transition point. This behavior of the magnetic susceptibility has been observed[10] in $GaMo_6S_8$, where the appearance of a ferromagnetic order is preceded by a structural transition. Since $GaMo_6S_8$ contains no magnetic ions, we would seek the reason for the ferromagnetism of this compound in the model of collectivized electrons. A spin ferromagnetism of collectivized electrons (see Ref. 11, for example) arises only to the extent that there is an excess of charge carriers; i.e., the ferromagnetic phase has a metallic conductivity. A nonintrinsic orbital ferromagnetism in a toroidal-current state, in contrast, does not require a doping of a semiconductor—an important point for an experimental identification of the toroidal-current state. To the best of our knowledge, the type of conductivity of $GaMo_6S_8$ is an open question.

3. *The toroidal-current state in a magnetic field is a situation whose description cannot ignore spatial dispersion.*

We write an expression for the change in the free energy density in an external field:

$$\delta\tilde{\mathscr{F}} = \delta\mathscr{F} - \mathbf{T}\,\delta\mathbf{j}^0 - \frac{1}{4\pi}\,\mathbf{H}^0\delta\mathbf{H}^0\,, \tag{3}$$

where $\mathbf{j}^0$ is the external current that produces the field $\mathbf{H}^0$. The first term in (3) is the variation of the free energy density $\mathscr{F}$, without allowance for the interaction with the field:

$$\mathscr{F} = \alpha|\,\mathbf{T}\,|^2 + \beta\,|\,\mathbf{T}\,|^4 + \gamma\,|\,\mathrm{rot}\,\mathbf{T}\,|^2 \tag{4}$$

where α, β, and γ are phenomenological parameters whose specific values are determined from the microscopic theory.[2] Here $\alpha = a(\theta - \theta_c)$, where θ is the temperature, and we have $a, \beta, \gamma > 0$. We are interested in temperatures below the transition to the toroidal-current state ($\theta < \theta_c$). Without any loss of generality we may assume $\mathrm{div}\mathbf{T} = 0$.

Varying (3) with respect to the external field, we find an expression for the magnetic induction in the sample:

$$\mathbf{B}(\mathbf{r}) = \mathbf{H}^0 + 4\pi\,\mathrm{rot}\,\mathbf{T} + \mathbf{M}_s - 4\pi\frac{\partial\mathscr{F}}{\partial\mathbf{H}^0} \tag{5}$$

where $\mathbf{M}_s = 4\pi[\mathbf{T}\vec{\nu}]\delta(\mathbf{r} - \mathbf{r}_s)$ is the surface moment, $\vec{\nu}$ is the vector normal to the surface, and $\mathbf{r}_s$ is the radius vector on the surface of the sample. The moment $\mathbf{M}_s$ is produced by currents which are concentrated in a surface layer with a thickness roughly equal to the correlation length for the order parameter, ξ_0. The structure of the surface contribution is of such a nature that it exactly cancels the paramagnetic second term in (5), integrated over the volume. The magnetization of the toroidal-current state is thus determined by the last term in (5) and is always diamagnetic. An expansion of the free energy density in powers of the gradients of $\mathbf{T}(\mathbf{r})$ [see (4)] is applicable only over scale lengths much larger than ξ_0. All the changes that occur over scale lengths on the order of ξ_0 are microscopic; at the macroscopic level, these changes are treated as abrupt and are described by introducing a surface magnetic moment density $\mathbf{M}_s$ and by means of a boundary condition on the magnetic induction.

The boundary condition on the induction **B**,

$$\mathbf{B}(\mathbf{r} = \mathbf{r}_s) - \mathbf{M}_s = \mathbf{H}^0 , \tag{6}$$

means that the smooth component of the magnetic moment formed by the macroscopic currents must vanish at the surface.

The equilibrium value of the order parameter is determined by minimizing the free-energy functional $\tilde{F} = (1/V)\int \tilde{\mathscr{F}}(\mathbf{r})d\mathbf{r}$

$$\delta \tilde{F} / \delta \mathbf{T} = 0. \tag{7}$$

Equations (5) and (7) with boundary condition (6) constitute a closed system of equations that describes the behavior of the toroidal-current state in a static magnetic field near the transition to the toroidal-current state. As an example, we consider a plane-parallel plate of thickness $2L$; this thickness models the typical size of a domain in an inhomogeneous toroidal-current state. We direct the normal to the plane of the plate along the y axis, the vector **T** along the x axis, and the external field $\mathbf{H}^0$ along the z axis. Solving (5)–(7), we find the following expression for the magnetic-induction flux:

$$\phi = \phi_0 \left[1 - \frac{\pi \xi_\theta}{L\gamma} \tanh\left(\frac{2L}{\xi_\theta}\right)\left(1 + \tanh^2\left(\frac{2L}{\xi_\theta}\right)\right)^{-2} \right], \qquad \xi_\theta = \frac{2\gamma}{|\alpha|} \tag{8}$$

where $\phi_0 = 2LH^0$ is the flux in the absence of the toroidal-current state (at $\theta > \theta_c$). The formation of a toroidal-current state leads to a partial repulsion of the flux because of the sharp decrease in the magnetic induction near the surface. The diamagnetic susceptibility of the toroidal-current state is proportional to L^{-1}, i.e., to the concentration of domains.

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