Magnetoelectric Effects in Gadolinium Iron Borate $GdFe_3(BO_3)_4$

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Magnetoelectric interactions have been investigated in a single crystal of gadolinium iron borate $GdFe_3(BO_3)_4$, whose macroscopic symmetry is characterized by the crystal class 32. Using the results of this study, the interplay of magnetic and electric orderings occurring in the system has been experimentally revealed and theoretically substantiated. The electric polarization and magnetostriction of this material that arise in spin-reorientation transitions induced by a magnetic field have been investigated experimentally. For $H \parallel c$ and $H \perp c$, H–T phase diagrams have been constructed, and a strict correlation between the changes in the magnetoelectric and magnetoelastic properties in the observed phase transitions has been ascertained. A mechanism of specific noncollinear antiferroelectric ordering at the structural phase transition point was proposed to interpret the magnetoelectric behavior of the system within the framework of the symmetry approach in the entire temperature range. This ordering provides the conservation of the crystal class of the system when the temperature decreases to the antiferroelectric ordering point. The expressions that have been obtained for the magnetoelectric and magnetoelastic energy describe reasonably well the behavior of gadolinium iron borate observed experimentally. © 2005 Pleiades Publishing, Inc.

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INTRODUCTION

In recent years, magnetoelectric materials (also known as multiferroics) have attracted much attention. These materials have been known for more than half a century, but they have been of only academic interest until recently, because the magnetoelectric effect that was observed in them was very weak. Only recently, new interesting materials have been found in which this effect is sufficiently strong [1–3]. In addition, recent investigations have revealed another manifestation of magnetoelectric interactions, namely, the possibility of controlling the magnetic state of a substance by an electric field and vice versa [4–9]. In particular, electric domains in such materials as $TbMnO_3$ and $GdMnO_3$ were switched by a magnetic field [4–6]. These new effects provide promising prospects for applications, but many fundamental questions concerning the nature of these effects have not been clarified so far.

Among new multiferroics, gadolinium iron borate $GdFe_3(BO_3)_4$ [10–20] (one of the representatives of a new family of multiferroics—rare-earth iron borates $RFe_3(BO_3)_4$) is of considerable interest. Its crystal structure is characterized by the space group $R32$ (D_3^7). At $T_C = 156$ K, a structural phase transition is observed in gadolinium iron borate at which the translational symmetry of the crystal changes presumably without a change in the crystal symmetry class. This transition is accompanied by characteristic dielectric anomalies [20], which may serve as indirect evidence for the occurrence of antiferroelectric ordering in the crystal.

According to [18], Fe^{3+} spins in gadolinium iron borate are ordered antiparallel in the basal plane at $T < T_N = 38$ K (AF1 phase). At $T_R = 10$ K, another phase transition occurs at which the Fe^{3+} spins are reoriented from the easy plane (AF1) to the easy axis c (AF2). For this reason, we expected a substantial manifestation of magnetoelectric interactions and their transformations in phase transitions accompanied by a change in the magnetic symmetry in gadolinium iron borate, which has a noncentrosymmetric symmetry group. Since information on this aspect in the behavior of rare-earth iron borates is unavailable in the literature, the magnetoelectric and magnetoelastic properties of $GdFe_3(BO_3)_4$ in phase transitions induced by a magnetic field have been studied both experimentally and theoretically in this work.

EXPERIMENTAL RESULTS

The longitudinal electric polarization and magnetostriction of a $GdFe_3(BO_3)_4$ single crystal were measured in magnetic fields up to 100 kOe for $H \parallel c$ and $H \perp c$ in the temperature range 4.2–50 K by the proce-

dure described in [21]. It was found that the magnetic field below T_N induced the rearrangement of the magnetic structure in this compound that was accompanied by the occurrence of the magnetoelectric effect and magnetoelastic deformations. The field dependences of the electric polarization and magnetostriction were drastically different for $H \parallel c$ and $H \perp c$. Thus, the magnetoelectric effect and magnetostriction for $H \parallel c$ were observed only at temperatures of $T < 10$ K, vanishing in the temperature range 10 K $< T <$ 38 K. This presumably indicates that a change in the symmetry occurred near T_R. For $H \perp c$, anomalies in the magnetoelectric effect and magnetostriction were observed for all temperatures below T_N.

The field dependences of the longitudinal magnetostriction and electric polarization in the low-temperature region for $H \parallel c$ are presented in Fig. 1. It is evident that jumps in the electric polarization $P_C(H_C)$ and magnetostriction $\lambda_C(H_C)$ occur in the vicinity of 5 K at a certain critical field $H_C^{crit} = 8$ kOe, where a magnetic field-induced spin reorientation from the c axis to the easy plane was observed according to [16]. With increasing temperature, the threshold fields decrease and they vanish at T_R. For temperatures 10 K $< T <$ 38 K, the longitudinal electric polarization and magnetostriction along the c axis exhibit no anomalies and depend monotonically (quadratically) on the field. The H_C^{crit}–T phase diagrams that are obtained from measurements of the magnetoelectric and magnetoelastic properties (Fig. 2) are in good agreement, which indicates that these properties evidently correlate with each other. For $H \perp c$, the character of the field dependences of the electric polarization and magnetostriction changes qualitatively.

The field dependences of the longitudinal magnetostriction and electric polarization for $H \parallel a$ are presented in Fig. 3. It is seen that, at $T = 4.5$ K, the electric polarization and magnetostriction in low fields depend weakly on the magnetic field. Then, they increase abruptly at $H_C^{crit} = 37$ kOe, and the polarization jump at 4.5 K for $H \parallel a$ exceeds the polarization jump for $H \parallel c$ by a factor of 20. With increasing temperature from 4.2 K to T_R, the threshold fields for the AF2 $\Rightarrow$ AF1 transition decrease strongly. Starting with T_R up to T_N, when the Fe^{3+} spins lie in the basal plane, the electric polarization and magnetostriction increase abruptly already in a relatively weak magnetic field of ~2 kOe and, then, vary monotonically when the field increases.

The H_a^{crit}–T phase diagrams for $H \perp c$ (Fig. 4) that are plotted using the electric polarization and magnetostriction isotherms (Fig. 3) in the same way as for $H \parallel c$ (Fig. 2) are in good agreement with each other. This indicates that the magnetoelectric and magnetoelastic properties that are measured for the $H \parallel c$ and $H \perp c$ orientations of the magnetic field strictly correlate with
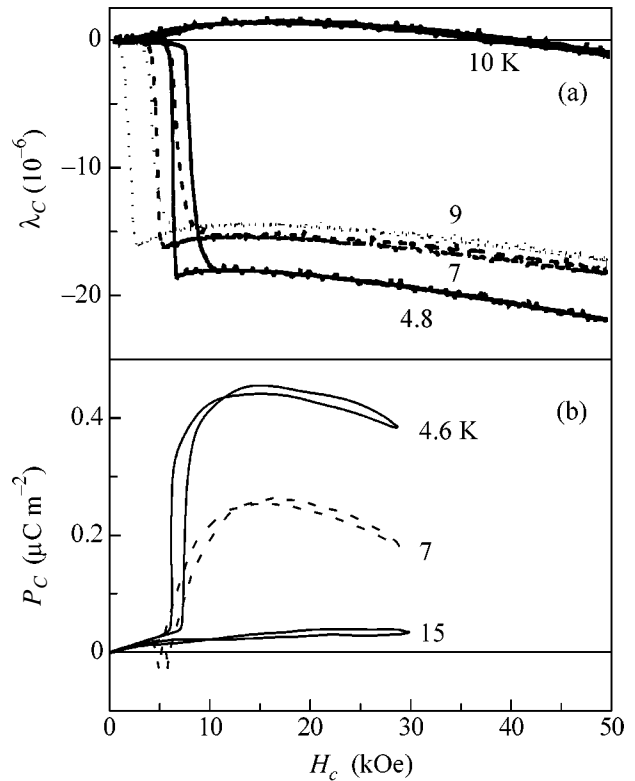

Fig. 1. Isotherms of longitudinal (a) magnetostriction and (b) electric polarization vs. the magnetic field directed along the c axis for the $GdFe_3(BO_3)_4$ single crystal.
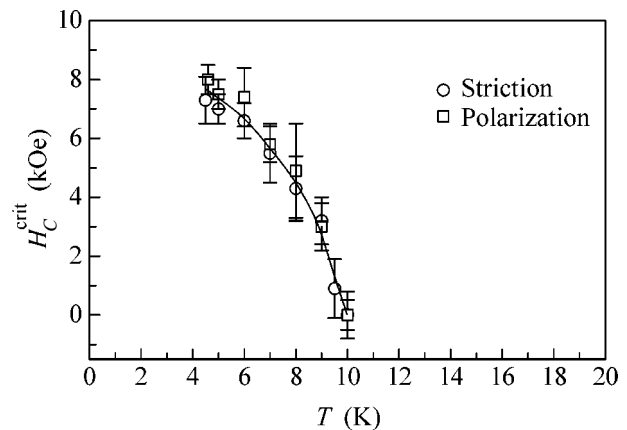

Fig. 2. H–T phase diagram obtained from measurements of magnetostriction and electric polarization in the $GdFe_3(BO_3)_4$ single crystal for $H \parallel c$.

each other. The experimental results indicate that jumps arise in the electric polarization vector **P** when the magnetic field reorients the $GdFe_3(BO_3)_4$ single crystal from the AF2 to AF1 phase. This behavior certainly points to the occurrence of ferroelectric properties in this crystal.
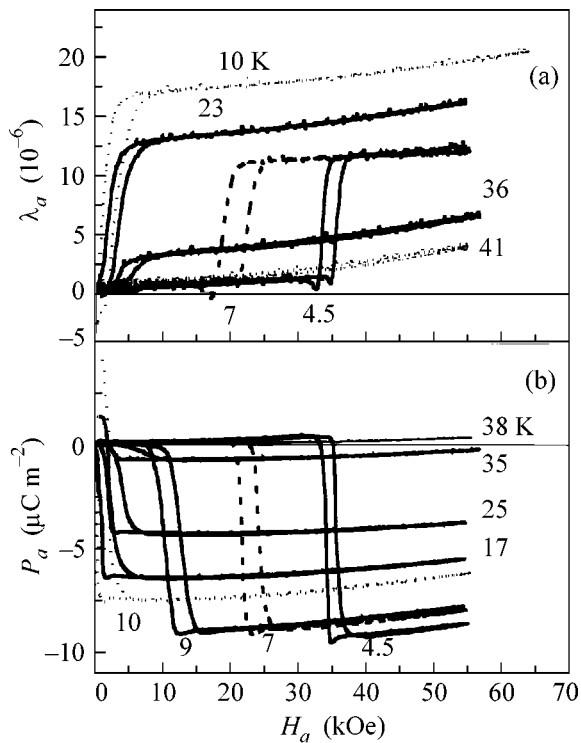
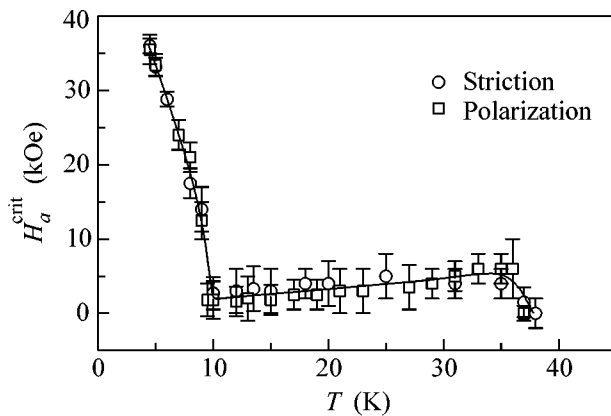**Fig. 3.** Same as in Fig. 1 but for the magnetic field directed along axis *a*.

Fig. 4. Same as in Fig. 2 but for $H \parallel a$.

THEORETICAL PART

In this work, a theoretical model for the magneto-electric structure of gadolinium iron borate is proposed to qualitatively explain the observed magnetoelectric properties of the material. Magnetic measurements and measurements of the antiferromagnetic resonance spectra [18] allow the conclusion that an antiferromagnetic collinear structure that is characterized by the antiferromagnetic vector **L** is realized in this material at $T < T_N$. Therefore, we will take the model proposed in [18] for the magnetic structure of gadolinium iron

borate as the basis for the subsequent analysis. Because the vector **L** for $T_R < T < T_N$ lies in the basal plane, the crystallographic symmetry in this case changes evidently due to the spin–orbit interaction. Actually, if **L** is parallel to a second-order axis, the third-order axis (element 3) is eliminated from the set of the class 32 symmetry elements. As a result, class 32 changes to monoclinic class 2 characterized by the point group with a second-order symmetry axis as the generator. If **L** departs from the second-order axis, symmetry element 2 also disappears. As a result, class 2 passes into trivial class 1. Both these classes (2 and 1), as distinct from 32, allow the occurrence of a polar vector, and this gives a clue to the problem of the magnetoelectricity of gadolinium iron borate.

At the same time, the dielectric anomaly at the point T_C (namely, the jump in the dielectric constant when passing through T_C in the direction of decreasing temperature but with the retention of the crystal class 32) points to the possibility of realizing a compensated ferroelectric state for $T < T_C$, i.e., forming an antiferroelectric structure.

A natural model describing the mechanism of the occurrence of electric polarization upon magnetic ordering is the decompensation of zero total electric polarization ($\mathbf{P}_S = \mathbf{P}_1 + \mathbf{P}_2 + \mathbf{P}_3 \neq 0$) of the antiferroelectric (triangular) state (when $\mathbf{P}_S = 0$ for $T_N < T < T_C$). Here, $\mathbf{P}_1$, $\mathbf{P}_2$, and $\mathbf{P}_3$ are the polarization vectors of neighboring atomic layers spaced by one third of the vertical lattice constant. These vectors appear at the point T_C, and they are directed along the corresponding axes 2. This decompensation is very small due to the smallness of the spin–orbit interaction in the system of Fe^{3+} ions (which are *s* ions; i.e., their orbital angular momentum in the ground state equals zero). It can be responsible for the small increase observed in the dielectric constant of gadolinium iron borate when T decreases from T_N to T_R [20]. It is reasonable to expect that P_s increases with increasing the absolute value of **L**, which is the case when decreasing T. For $T < T_R$, a spin-reorientation transition to the $\mathbf{L} \parallel c$ phase occurs [17]. This phase is characterized by the point crystal group 32, in which the polar vector **P** is absent. Therefore, it may be expected that the magnetic field-induced transitions AF2 $\longrightarrow$ AF1 will be accompanied by jumps in the electric polarization (and in the dielectric constant).

For deeper insight into the nature of the magnetoelectric interactions, the interplay between the electric polarization and the vector **L**, and the magnetic structure and orientational phase transitions of gadolinium iron borate, we consider the transformation properties of vector **L** and other quantities under the transformations of class 32. Note that the magnetic unit cell of gadolinium iron borate (in the direction of the *c* axis) is twice as large as the crystallographic one. This circumstance distinguishes the material under consideration

from typical objects in the symmetry theory of antiferromagnetism [22, 23], in which these cells are assumed to coincide. The evident way of overcoming this difficulty is to consider an extended (doubled) crystal unit cell of gadolinium iron borate and thus to return to the conventional approach. Following it, let us reduce the initial space group, assuming that the translations by the unit cell constants in the basal plane and the doubled translations along the c axis are equal to the identity transformation E. As a result, the reduced group $\tilde{G}_{32}$ can be characterized by the following generators: C_3, 2_x, and T_z where T_z is translation on the period of the unit cell along the c axis. The absolute values and orientations of these generators are completely determined by the state of the iron ions, because the other magnetic subsystem consisting of the Gd^{3+} ions is supposed to be paramagnetic. The generator T_z is odd; that is, this generator transforms one magnetic sublattice of the antiferromagnet into the other one $T_z\mathbf{L} = -\mathbf{L}$. At the same time, 2_x and C_3 are even; that is, they interchange atoms of the same sublattice $2_x\mathbf{L} = \mathbf{L}$, $C_3\mathbf{L} = \mathbf{L}$.

The transformation properties of the above reduced group offer the possibility of determining the symmetry of the magnetoelectric interaction and the desired interrelations between the magnetic structure and physical properties of the crystal. In Turov's terminology, the magnetic structure of gadolinium iron borate can be characterized by the code T_z^-, 3_z^-, 2_x^+. Note a certain analogy (but not the isomorphism!) of the structure under consideration with the magnetic structure of Cr_2O_3 with the code I^-, 3_z^-, 2_x^+ [22, 23], which has been comprehensively studied in the theory of antiferromagnetism.

The magnetoelectric interaction energy of the iron ion subsystem can be represented in the form[1]

$$E_{ME} = c_1 L_z (P_x L_y - P_y L_x)$$
$$+ c_2 [P_x (L_x^2 - L_y^2) + 2 P_y L_x L_y] + c_3 P_z L_x L_z (L_x^2 - 3L_y^2), \quad (1)$$

where c_1, c_2, and c_3 are the thermodynamic parameters of the symmetry theory. From Eq. (1), we will obtain the following equations determining the electric polarization vector $\mathbf{P}_s$, which spontaneously appears at the antiferromagnetic ordering point:

$$P_{sx} = c_1 L_y L_z + c_2 (L_x^2 - L_y^2)$$
$$= C_1 L^2 \sin\theta\cos\theta\sin\varphi + C_2 L^2 \sin^2\theta\cos 2\varphi, \quad (2a)$$

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[1] Rare-earth ions are paramagnetic and, in principle, do not change the equations given below (for $T \gg T_{RN}$, where T_{RN} is the ordering temperature of rare-earth elements). The inclusion of these ions leads only to the renormalization of coefficients. Therefore, having in mind a qualitative interpretation of the experiment, we will not complicate the equations by taking into account the rare-earth subsystem. Such a situation is typical for many d–f compounds with an antiferromagnetic d subsystem [24].

$$P_{sy} = -c_1 L_x L_z + 2 c_2 L_x L_y$$
$$= -C_1 L^2 \sin\theta\cos\theta\cos\varphi + C_2 L^2 \sin^2\theta\sin 2\varphi, \quad (2b)$$

$$P_{sz} = c_3 L_x L_z (L_x^2 - 3L_y^2) = C_3 L^4 \sin^3\theta\cos\theta\cos 3\varphi, \quad (2c)$$

where θ and φ are the polar and azimuth angles of the vector $\mathbf{L}$.

According to the $\tilde{G}_{32}$ symmetry, the linear magnetoelectric effect is forbidden in gadolinium iron borate, which is confirmed experimentally [19]. We emphasize a certain similarity (and distinctions!) between Eq. (2c) and the equation for P_z in the case of Cr_2O_3 [21], which reflects the similarity and distinction between the corresponding magnetic structures and between the groups 32 and $\bar{3}m$.

A symmetry analysis also provides the following expression for the magnetoelastic energy:

$$\Delta\Phi_{Mel} = \gamma_1 u_{zz} L_z^2 + \gamma_2 u_{zz} (L_X^2 + L_Y^2)$$
$$+ \gamma_3 [(u_{XX} - u_{YY})(L_X^2 - L_Y^2) + 2 u_{XY} L_X L_Y]$$
$$+ \gamma_4 (2 u_{XZ} L_X L_Z + u_{YZ} (L_X^2 - L_Y^2))$$
$$+ \gamma_5 (L_Y L_Z (u_{XX} - u_{YY}) + u_{XY} L_X L_Z)$$
$$+ \gamma_6 (L_X L_Z u_{XZ} + L_Y L_Z u_{YZ})$$
$$+ \gamma_7 u_{ZZ} ([L_X^2 - L_Y^2] + 2 L_x^2) L_Y L_Z, \quad (3)$$

from which the following formulas for magnetostriction can readily be obtained:

$$u_{zz} = \gamma_1 L_z^2 + \gamma_2 (L_X^2 + L_Y^2) + \gamma_7 ([L_X^2 - L_Y^2] + 2 L_X^2) L_Y L_Z;$$

$$u_{XX} - u_{YY} = \gamma_3 (L_X^2 - L_Y^2) + \gamma_5 L_Y L_Z;$$

$$u_{XY} = 2\gamma_3 L_X L_Y + \gamma_5 L_X L_Z; \quad (4)$$

$$u_{XZ} = \gamma_4 2 L_X L_Y + \gamma_6 L_X L_Z;$$

$$u_{YZ} = \gamma_6 L_Y L_Z + \gamma_4 (L_X^2 - L_Y^2).$$

Note that linear piezomagnetism, that is, the linear coupling between the elastic deformations and the external magnetic field, is forbidden in space group 32.

The above mechanism of symmetry breaking through magnetic ordering offers another view on Eqs. (2) for spontaneous electric polarization. Namely, the electric polarization in a crystal can be considered as a result of the double action: the spontaneous magnetostriction $u_{ik} = \delta_{iklm} L_l L_m$ and the piezoelectric effect $P_\alpha = \pi_{\alpha i} u_{ik}$, where δ_{iklm} and $\pi_{\alpha ik}$ are the magnetoelastic and piezoelectric tensors, respectively. Both tensors differ from zero in the crystals of class 32.

The multiplication of the tensors δ_{iklm} and $\pi_{\alpha ik}$ results in formulas for P_x and P_y that coincide with those given by Eqs. (2). Certainly, this coincidence does not mean that the coefficients are equal to the

products of the components of the tensors π and δ. These coefficients can also depend on intrinsic microscopic magnetoelectric interactions. The component P_z in this "piezoelastic" consideration is naturally equal to zero, because this component, according to more detailed Eqs. (2), is determined by the terms of the fourth order in **L**; i.e., it is a small value (in the spin–orbit coupling constant) as compared to P_x and P_y, and this relation is manifested experimentally.

Another fourth-order combination of the components L_i is $((L_x^2 - L_y^2) + 2L_x^2)L_yL_z = L^4\sin^3\theta\cos\theta\sin 3\varphi$. This combination is an invariant of the group $\tilde{G}_{32}$; that is, it transforms by the representation Γ_1. It is linear in L_z. Therefore, the spins in the AF1 phase can be departed from the basal plane at a small angle (because the corresponding invariant is of the fourth order in L_i). This fact in combination with Eq. (2c) can be used to explain the small jump in the P_z component of the electric polarization upon the AF2 $\longrightarrow$ AF1 reorientation.

The above consideration was mainly devoted to the magnetic ordering (and magnetic field) effect on the electric polarization in gadolinium iron borate. However, Eqs. (2) allow an interesting generalization to the reverse crossing effects, that is, the electric field effects on magnetism and magnetic transformations [7–9]. Actually, substituting E_i for P_i in Eq. (1), which is evidently allowed by symmetry, we obtain the energy of interaction between the external electric field and vector **L**. The new effects arising in this case will be considered in a separate paper.

Thus, the magnetic symmetry of gadolinium iron borate and the model of the collinear antiferromagnetic structure proposed in [18] offer the possibility of explaining the jumps observed in the electric polarization and magnetostriction as a manifestation of spin-reorientation transitions induced by the magnetic field in this material. Expression (3) for the magnetoelastic interaction in gadolinium iron borate has been obtained using symmetry theory.

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