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Investigation of the anomalies of the magnetoelectric and magnetoelastic properties of single crystals of the ferroborate $GdFe_3(BO_3)_4$ at phase transitions

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The transformation of various properties of gadolinium ferroborate single crystals at phase transitions, both spontaneous and induced by magnetic fields up to 200 kOe, is investigated theoretically and experimentally. Particular attention is paid to elucidating the role of magnetoelectric interactions and the change in them at spin-reorientation transitions accompanied by a change of magnetic symmetry. With that goal the magnetoelastic and magnetoelectric properties of the system are investigated over a wide range of temperatures for two orientations of the magnetic field, $H \| c$ and $H \perp c$, and a fundamental difference of the character of the field dependences of the magnetostriction and electric polarization is found. In the framework of a symmetry approach a description of the magnetic structures and their transformations in the system $GdFe_3(BO_3)_4$ is proposed, and an interpretation of the experimentally observed properties is given. © *2005 American Institute of Physics.* [DOI: 10.1063/1.2008142]

INTRODUCTION

Rare-earth ferroborates $RFe_3(BO_3)_4$, isostructural to the natural mineral huntite, have a rhombohedral structure and belong to the hexagonal space group $R32$ (D_3^7).

These compounds have attracted particular interest in recent years in connection with the prospects for their practical use, particularly in laser technique[1,2] and for optical second-harmonic generation,[3] and also because of the discovery of unusual magnetic properties and diverse phase transitions in them.[4–6] According to measurements of the temperature dependence of the magnetic susceptibility[7] and heat capacity,[8] three phase transitions are observed in gadolinium ferroborate: a structural phase transition at $T_C = 156$ K, a magnetic ordering of the Fe^{3+} ions at $T_N = 38$ K, and a spin-reorientation phase transition at $T_R = 10$ K.[7] The existing data in the literature nevertheless do not permit one to reach definite conclusions as to the nature of the phase transitions observed in these compounds.

In regard to the magnetic structure of gadolinium ferroborate the data in the literature are contradictory. In Ref. 9 it was stated on the basis of a study of antiferromagnetic (AFM) resonance that the magnetic phase transition of the Fe^{3+} ion subsystem at T_N corresponds to two-sublattice spin ordering of the easy-plane type, and, as the temperature is lowered below T_R, the interaction of the iron and gadolinium subsystems brings about a reorientation of the Fe^{3+} spins from easy-plane to easy-axis (the c axis). The magnetic unit cell of the system is doubled along the c axis in comparison with the crystalline unit cell in hexagonal coordinates.

In Ref. 7 the magnetic behavior of gadolinium ferroborate was investigated in the framework of three-sublattice ordering (of the triangular type) of the iron subsystem. The spins of the Fe^{3+} ions in the temperature interval $10\ \text{K} < T < 38$ K were found to lie in the "easy plane" at an angle of 120° to one another. Below 10 K, according to Ref. 7, under the influence of an interaction with the gadolinium subsystem, the Fe^{3+} spins are reoriented from the easy plane in the direction toward the c axis, forming a cone with axis along c. Since nothing was said about any change in the unit call at the magnetic phase transition, and the system remained antiferromagnetic over the whole temperature interval, the opening angle of the cone (the tilt angle of the Fe^{3+} spins toward the c axis for compensation of the magnetization of the gadolinium subsystem) should "follow" the increase of the magnetic moment of the Ge^{3+} ions with decreasing temperature. For an orientation of the external magnetic field $H \| c$ at $T < 10$ K a field-induced reorientation of the Fe^{3+} spins from the c axis to the easy plane was observed.[5,7]

We carried out additional experimental and theoretical investigations of the transformation of various properties of gadolinium ferroborate single crystals at the spontaneous and field-induced phase transitions at high magnetic fields up to 200 kOe. Particular attention was paid to investigation of the role of magnetoelectric interactions and their changes at the spin-reorientation transitions. An interpretation of the antiferromagnetic properties of the system was given in the framework of a thermodynamic approach. Studies of the magnetoelastic and magnetoelectric properties of the system for two

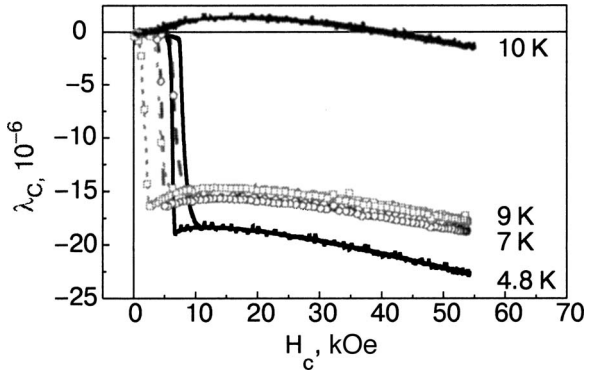

FIG. 1. Isotherms of the dependence of the longitudinal magnetostriction of the $GdFe_3(BO_3)_4$ single crystal for $H\|c$.

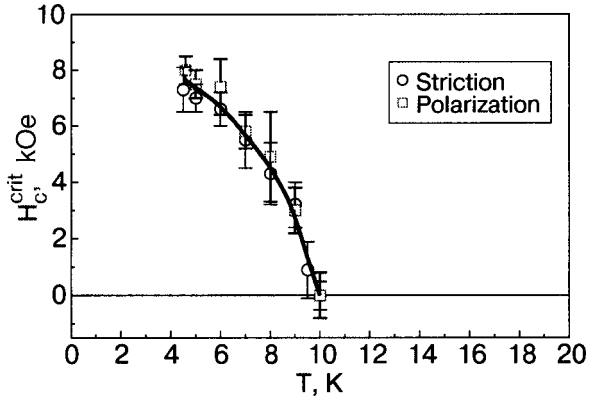

FIG. 3. H-T phase diagram obtained for $GdFe_3(BO_3)_4$ from measurements of the longitudinal magnetostriction and electric polarization for $H\|c$.

orientations of the magnetic field: $H\|c$ and $H\perp c$ (for which at present there is absolutely no information in the literature). We expected that gadolinium ferroborate, which has a noncentrosymmetric space group, would exhibit substantial manifestations of the magnetoelectric interactions and their change at the spin-reorientation transitions, which are accompanied by a change of magnetic symmetry.

EXPERIMENTAL RESULTS

We studied the electric polarization P_i and magnetostriction λ_i as functions of magnetic field up to 200 kOe in the temperature interval 4.2–50 K for $H\|c$ and $H\perp c$ by the technique described in Ref. 10, and also the temperature dependence of the thermal expansion of $GdFe_3(BO_3)_4$.

Figure 1 shows isotherms of the dependence of the longitudinal magnetostriction of the gadolinium ferroborate single crystal at $H\|c$. It is seen that in the low-temperature region $T<10$ K at a certain critical value of magnetic field $H=H^{crit}(H\|c)$ there are jumps in the magnetostriction, where, according to Refs. 7 and 9, a magnetic-field-induced spin reorientation from the c axis toward the easy plane was observed. At high temperatures $10<T<T_N=38$ K the magnetostriction does not exhibit anomalies and depends quadratically on the field. The threshold fields H^{crit} at which the magnetostriction jumps appear decrease with increasing temperature and agree with the fields at which the magnetization jumps were observed at the field-induced reorientation of the spins from the c axis to the easy plane.[7]

Our studies of the magnetoelectric properties of $GdFe_3(BO_3)_4$ single crystals have shown that in the course of the spin-reorientation transition at $T<10$ K for a field orientation $H\|c$ there are also jumps of the electric polarization (Fig. 2), evidently due to the change of the magnetoelectric interactions as a result of the change of magnetic symmetry. The spin-reorientation transition induced by a magnetic field $H\|c$ is accompanied by hysteresis with respect to the the field, which indicates that the transition is a first-order phase transition. Figure 3 shows the H-T phase diagrams obtained from measurements of the magnetoelectric and magnetoelastic properties for $H\|c$, which demonstrated good agreement with the values of the threshold fields. The character of the field dependence of the magnetostriction and electric polarization differs strongly for $H\|c$ and $H\perp c$. Figure 4 shows the dependence of the longitudinal magnetostriction for $H\|a$. It is seen that at $T\sim 5$ K the magnetostriction initially depends weakly on field, and then, at $H^{crit}\sim 37$ K, it increases in a jump to 1×10^{-5}. With increasing temperature the threshold field decreases monotonically. Starting at temperatures $T\sim 10$ K and on up to 38 K the magnetostriction increases in a sharp jump even in weak magnetic fields ~ 2 kOe and then behaves monotonically. The magnetic-field dependence of the electric polarization is of an analogous character (Fig. 5), and the threshold fields agree with each other, as is seen on the H-T phase diagrams (Fig. 6) constructed from the data of the $\lambda(H)$ and $P(H)$ measurements. Thus for $H\|c$ and $H\perp c$ a strict correlation of

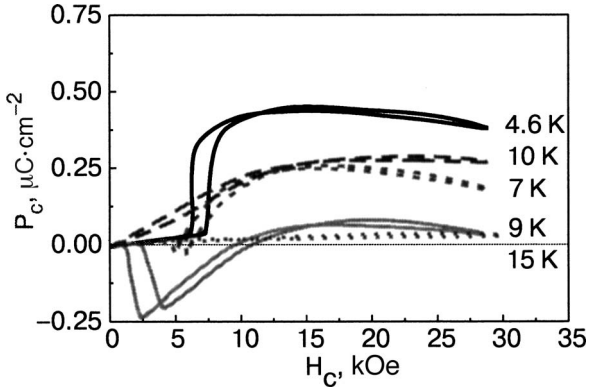

FIG. 2. Isotherms of the longitudinal electric polarization in a gadolinium ferroborate single crystal for $H\|c$.

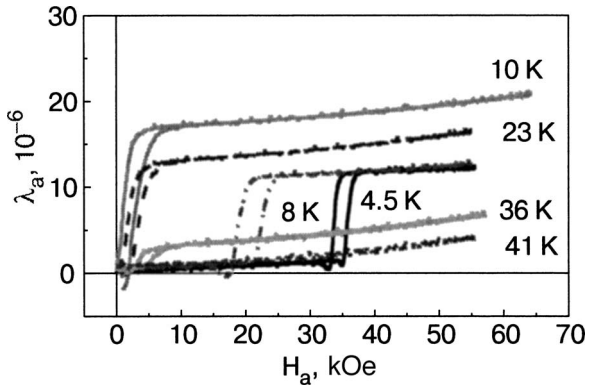

FIG. 4. Isotherms of the longitudinal magnetostriction for a $GdFe_3(BO_3)_4$ single crystal at $H\|a$.

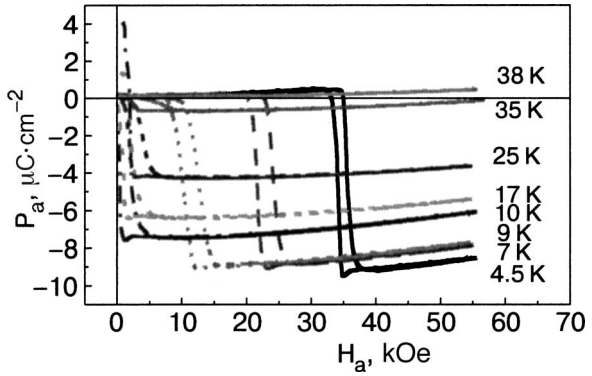

FIG. 5. Curves of the dependence of the electric polarization on magnetic field $H\|a$ for a $GdFe_3(BO_3)_4$ single crystal at various temperatures.

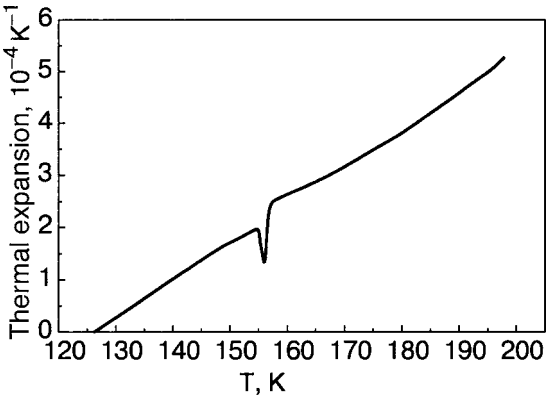

FIG. 7. Dependence of the thermal expansion for a $GdFe_3(BO_3)_4$ single crystal along the c axis in the region of the structural transition $T_C = 156$ K.

the magnetoelectric and magnetoelastic properties is established. It should be noted that in measurements of the temperature dependence of the thermal expansion we observed a sharp λ-shaped anomaly at a temperature of 156 K (Fig. 7). Recent measurements[11] have shown that at $T=156$ K there is also a jumplike change of the dielectric constant, which apparently indicates the onset of spontaneous electric ordering at that temperature.

THEORETICAL PART

In view of what we have said above, it is best to take a symmetry approach to the theoretical description of the properties of the $GdFe_3(BO_3)_4$ system. On the one hand, it allows one to explain the behavior of that system in a unified way and to identify the active and passive degrees of freedom responsible for the change of its magnetic and crystalline symmetry, the corresponding order parameters, and the interactions of the latter both among themselves (leading to phenomena such as weak ferromagnetism, intrinsic magnetoelectric effect, etc.) and with external fields. At the same time, it is exceptionally efficient for predicting new effects (according to the "possible-impossible" principle from considerations of whether the space-time symmetry in the behavior of a particular system is broken or preserved).

The group-theoretical approach used here (in the spirit of the Landau theory of phase transitions) permits one to describe in an exhaustive way all the possible types of magnetic structures that, depending on the concrete form of the exchange interactions (and also the features of the anisotropic interactions) can appear in the ferroborate $GdFe_3(BO_3)_4$ below the magnetic ordering temperature. We begin with a discussion of the features of the magnetic phase transition at the temperature T_N (at which the moments of the Fe^{3+} ions order). We recall that the unit cell of $RFe_3(BO_3)_4$ in the rhombohedral scheme contains one R^{3+} ion (position $1a$) and three Fe^{3+} ions (position $3d$). If the space diagonal of the elementary rhombohedron is assumed to be directed vertically, then the crystal structure of the $RFe_3(BO_3)_4$ system will be a set of rhombohedrally shifted identical horizontal layers (oblique with respect to the vertical but parallel to each other) alternating along the vertical. The distance between two adjacent equivalent layers is one-third of the vertical period c of the structure, which is the height of the unit cell of $RFe_3(BO_3)_4$ in the hexagonal crystallographic coordinates (Fig. 8). But then the hexagonal unit cell of the $RFe_3(BO_3)_4$ system (which is doubly body-centered and tripled in volume as compared to the rhombohedral cell) contains three formula units ($Z=3$), or, in other words, three translationally equivalent R^{3+} ions (position $3a$) and, accordingly, nine Fe^{3+} ions (position $9d$). Since the rhombohedral (truly primitive) crystal cell of $GdFe_3(BO_3)_4$ contains

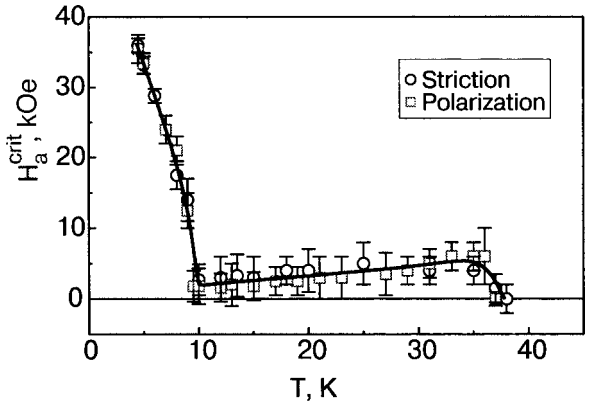

FIG. 6. H-T phase diagram obtained from measurements of the longitudinal magnetostriction and electric polarization for $H\|a$, for the single crystal $GdFe_3(BO_3)_4$.

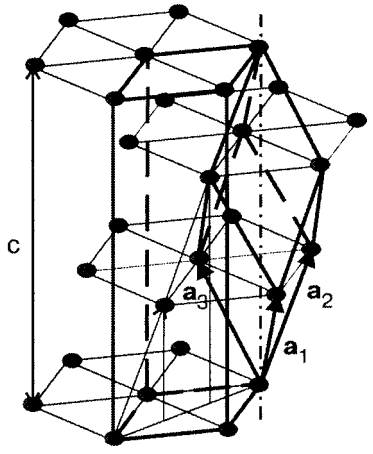

FIG. 8. Fragment of the Bravais lattice of the system $RFe_3(BO_3)_4$ with the rhombohedral (primitive) and hexagonal (unit) cells shown explicitly. The lattice sites (ellipses) correspond to the positions of the R^{3+} ions.

only one R^{3+} ion, which will be magnetic for R=Gd, Nd, and our system is antiferromagnetic at all temperatures below T_N, we shall assume that the elementary translations of the magnetic Bravais lattice $\mathbf{a}_1^m\mathbf{a}_2^m\mathbf{a}_3^m$ of the $GdFe_3(BO_3)_4$ system will be related to the elementary translations $\mathbf{a}_1,\mathbf{a}_2,\mathbf{a}_3$ of its crystal lattice (Fig. 8) by the relations

$$\mathbf{a}_1^m=\mathbf{a}_2+\mathbf{a}_3, \quad \mathbf{a}_2^m=\mathbf{a}_3+\mathbf{a}_1, \quad \mathbf{a}_3^m=\mathbf{a}_1+\mathbf{a}_2. \tag{1}$$

It follows from relations (1) that the magnetic primitive cell of $GdFe_3(BO_3)_4$ will be a rhombohedron doubled in volume in comparison with the high-temperature primitive crystal cell. In fact, the volume V^m of the magnetic cell is found from the relation $V^m=\mathbf{a}_1^m\cdot[\mathbf{a}_2^m\times\mathbf{a}_3^m]=(\mathbf{a}_2+\mathbf{a}_3)\cdot[(\mathbf{a}_3+\mathbf{a}_1)\times(\mathbf{a}_1+\mathbf{a}_2)]=2V^c$, where V^c is the volume of the primitive crystal cell. In principle, since in our case the appearance of antiferromagnetic order in the system from the standpoint of magnetic symmetry corresponds to a change of the Bravais lattice on account of the appearance of anti-translations in it (doubling of a certain number of primitive translations of the initial crystal lattice), besides the case (1) considered above, in terms of exchange symmetry there are two more possibilities, fundamentally different from the first: 1) when only one of the primitive translations is doubled, while the other two remain unchanged; 2) when some pair of the three translations doubles, while the third translation remains unchanged. One is readily convinced that the two cases mentioned would lead, as a result of a phase transition, to the "loss" of a threefold symmetry axis and, accordingly, to a change of the symmetry class of the system from hexagonal to monoclinic. For the existing ideas about the hierarchy of exchange interactions (intralayer and interlayer), in our system the realization of these possibilities is improbable. For that reason we shall restrict the discussion to case (1). If one is working with the hexagonal unit cell (which is more natural from an experimental standpoint) for this system, the change of magnetic symmetry (1) leads to doubling of the height of the $GdFe_3(BO_3)_4$ unit cell. Since no concrete change of the crystal symmetry (micro- and, accordingly, macroscopic) of the system at $T_C=156$ K has been established experimentally[1)] (while such a change could in principle occur with a doubling of the unit cell, as, e.g., in the case of $BiFeO_3$), we assume that the doubling of the unit cell of the $GdFe_3(BO_3)_4$ system occurs at the Néel temperature T_N.

As we have said, at high temperatures the rare-earth ferroborates belong to the rhombohedral space group $R32$ (D_3^7). Taking the change of the unit cell at T_N into account, for describing the magnetic properties of our system (construction of the corresponding irreducible representations of the group $R32$) we consider six Fe^{3+} magnetic moments characterized by spins $\mathbf{S}_1-\mathbf{S}_6$. The first three of them—$\mathbf{S}_1,\mathbf{S}_2,\mathbf{S}_3$—belong to one horizontal layer, and the other three—$\mathbf{S}_4,\mathbf{S}_5,\mathbf{S}_6$—lie in the adjacent layer parallel to the first at a distance of $c/3$ from it. As is done in Landau theory, in describing the magnetic phase transition it is necessary to go over from the individual spins $\mathbf{S}_1-\mathbf{S}_6$ to their symmetrized combinations (basis functions of the corresponding irreducible representations of the group $R32$), each of which describes one of the possible types of magnetic ordering—either collinear (in the case of a one-dimensional representation) or noncollinear (for two- and three-dimensional representations). Under the condition that in hexagonal coordinates the vector of the AFM structure appearing at the Néel point is equal to $\mathbf{k}=\{0,0,1/2\}$, we obtain the following relations:

TABLE I. Basis functions of the irreducible representations (structural, magnetic, and exchange) of the group $R32$.

D_3^7	Structure	Magnetic	Exchange
Γ_1	u_{ZZ} $u_{XX}+u_{YY}$	$\tilde{B}_{1Y}-\tilde{B}_{2X}$	
Γ_1'		$B_{1Y}-B_{2X}$	
Γ_2	P_Z	$F_Z,\ \tilde{B}_{1X}+\tilde{B}_{2Y}$	
Γ_2'		$L_Z,\ B_{1X}+B_{2Y}$	
Γ_3	$\begin{Bmatrix}P_X\\P_Y\end{Bmatrix}$ $\begin{Bmatrix}u_{XX}-u_{YY}\\-2u_{XY}\end{Bmatrix}$ $\begin{Bmatrix}u_{YZ}\\-u_{XZ}\end{Bmatrix}$	$\begin{Bmatrix}F_X\\F_Y\end{Bmatrix}, \begin{Bmatrix}L_X^2-L_Y^2\\-2L_XL_Y\end{Bmatrix}$ $\begin{Bmatrix}\tilde{B}_{1Z}\\\tilde{B}_{2Z}\end{Bmatrix}, \begin{Bmatrix}\tilde{B}_{1Y}+\tilde{B}_{2X}\\\tilde{B}_{1X}-\tilde{B}_{2Y}\end{Bmatrix}$	$\begin{Bmatrix}\mathbf{L}\cdot\mathbf{B}_2\\-\mathbf{L}\cdot\mathbf{B}_1\end{Bmatrix}$ $\begin{Bmatrix}\mathbf{F}\cdot\tilde{\mathbf{B}}_1\\-\mathbf{F}\cdot\tilde{\mathbf{B}}_2\end{Bmatrix}$
Γ_3'		$\begin{Bmatrix}L_X\\L_Y\end{Bmatrix}, \begin{Bmatrix}B_{1Z}\\B_{2Z}\end{Bmatrix}$ $\begin{Bmatrix}B_{1Y}+B_{2X}\\B_{1X}-B_{2Y}\end{Bmatrix}$	$\begin{Bmatrix}\mathbf{F}\cdot\mathbf{B}_2\\-\mathbf{F}\cdot\mathbf{B}_1\end{Bmatrix}, \begin{Bmatrix}\mathbf{L}\cdot\tilde{\mathbf{B}}_2\\-\mathbf{L}\cdot\tilde{\mathbf{B}}_1\end{Bmatrix}$

Note: The primed representations are odd with respect to translation along the c axis.

$$\mathbf{B}_1=\sqrt{3}(\mathbf{S}_1-\mathbf{S}_2)-\sqrt{3}(\mathbf{S}_4-\mathbf{S}_5),$$
$$\mathbf{B}_2=\mathbf{S}_1+\mathbf{S}_2-2\mathbf{S}_3-\mathbf{S}_4-\mathbf{S}_5+2\mathbf{S}_6,$$
$$\tilde{\mathbf{B}}_1=\sqrt{3}(\mathbf{S}_1-\mathbf{S}_2)+\sqrt{3}(\mathbf{S}_3-\mathbf{S}_5),$$
$$\tilde{\mathbf{B}}_2=\mathbf{S}_1+\mathbf{S}_2-2\mathbf{S}_3+\mathbf{S}_4+\mathbf{S}_5-2\mathbf{S}_6,$$
$$\mathbf{L}=\mathbf{S}_1+\mathbf{S}_2+\mathbf{S}_3-\mathbf{S}_4-\mathbf{S}_5-\mathbf{S}_6.$$
$$\mathbf{F}=\mathbf{S}_1+\mathbf{S}_2+\mathbf{S}_3+\mathbf{S}_4+\mathbf{S}_5-\mathbf{S}_6. \tag{2}$$

Since we are interested not only in the magnetic but also the magnetoelastic and magnetoelectric properties of the $GdFe_3(BO_3)_4$ system, in the corresponding column of the table of irreducible representations of the group $R32$ (Table I) we also give the basis functions of the "nonmagnetic" representations (corresponding to structural macro-variables of the system—to the components of the strain tensor and electric polarization vector).

In accordance with formulas (2), the pair of functions $\{\mathbf{B}_1,\mathbf{B}_2\}$, corresponding in the exchange approximation to a two-dimensional representation (odd with respect to a shift by a period along the c axis), will itself describe an exchange-noncollinear AFM structure of the triangular type, with the closest three moments, those belonging to the Fe^{3+} ions found at the center of the sides of the elementary triangle of Gd ions of one layer, directed at an angle of 120° to one another, and the moments of the next-nearest layer antiparallel to the moments of the first layer. Another pair of functions, $\{\tilde{\mathbf{B}}_1,\tilde{\mathbf{B}}_2\}$, corresponding in the exchange approximation to yet another two-dimensional representation (even with respect to vertical translation), will describe another exchange-noncollinear AFM structure, also of the triangular type, that is possible from the standpoint of symmetry. Being

ordered (as in pair of functions $\{\mathbf{B}_1,\mathbf{B}_2\}$) antiferromagnetically within each layer, the moments of adjacent layers will be coupled ferromagnetically, and the resulting magnetic structure will be antiferromagnetic, with coincident magnetic and crystal cells. If one goes by the magnetizations of the layers, the function **L** describes two-sublattice (and formally speaking, six-sublattice) collinear AFM ordering in which all the moments of one layer are coupled ferromagnetically and those of the next layer are also coupled ferromagnetically among themselves, but are opposite to the moments of the initial layer, etc. (this corresponds to the case $\mathbf{k}=\{0,0,1/2\}$). The function **F** is the magnetization vector of the magnetic unit cell. It follows from what we have said that the dominant role of the antiferromagnetic interlayer exchange (brought about by the interaction of nearest spins lying in neighboring layers) leads to the appearance, as the temperature is lowered, first of 1D magnetic ordering along the corresponding helical chains, parallel to the c axis, of iron ions surrounded by distorted oxygen octahedra.[6] Depending on the character of the intralayer exchange of nearest spins of the Fe^{3+} ions (and, hence, the exchange between individual ordered chains)—ferromagnetic or antiferromagnetic—our system on the whole in the exchange approximation will be either a collinear antiferromagnet (which, in the main approximation, exhibits traits of a two-sublattice antiferromagnet) or an exchange-noncollinear antiferromagnet of the triangular type. There are no other possibilities for the aforementioned change of magnetic symmetry (1).

Following Ref. 9, in our discussion below we shall give preference mainly to the case of collinear ordering. Then the magnetic ordering that appears at the temperature T_N will be characterized by a vector **L**. Nevertheless, for the sake of completeness (since more-detailed studies of the system are still warranted) we shall write the thermodynamic potential of the system (the subsystems of ordering moments of the Fe^{3+} ions) to second order in the exchange approximation with allowance for the characteristic energy of all possible magnetic modes of our system:

$$\Phi_{\text{ex}}^{(2)}=\frac{1}{2}\Lambda_1^{(2)}\mathbf{L}^2+\frac{1}{2}\Lambda_2^{(2)}(\mathbf{B}_1^2+\mathbf{B}_2^2)+\frac{1}{2}\Lambda_3^{(2)}\mathbf{F}^2+\frac{1}{2}\Lambda_4^{(2)}\times(\tilde{\mathbf{B}}_1^2+\tilde{\mathbf{B}}_2^2). \tag{3}$$

We obtain the relativistic (magnetically anisotropic) contribution taking into account not only the independent magnetic modes, after explicitly separating out the terms corresponding to the case $\mathbf{k}=\{0,0,1/2\}$,

$$\Phi_{\text{rel.ind}}^{(2)}=\frac{1}{2}\eta_1^{(2)}L_Z^2+\frac{1}{4}\eta_1^{(4)}L_Z^4+\frac{1}{2}\eta_2(B_{1Y}-B_{2X})^2+\frac{1}{2}\eta_3(B_{1X}+B_{2Y})^2+\frac{1}{2}\eta_4(B_{1Y}+B_{2X})^2+(B_{1X}-B_{2Y})^2, \tag{4}$$

[in Eq. (4) we have explicitly taken into account the anisotropic contributions of both second and fourth order only for the mode **L** of interest to us, which, as we know,[12] will be responsible for possible spin reorientation] but also the mixed contributions (''mixing'' the different magnetic modes) of second order, which describe the simplest characteristic interactions of the different magnetic modes of our system,

$$\Phi_{\text{rel.int.}}=\alpha_1[L_X(B_{1Y}+B_{2X})+L_Y(B_{1X}-B_{2Y})]+\alpha_2L_Z(B_{1X}+B_{2Y}). \tag{5}$$

Furthermore, we write the main intrinsic (in the absence of magnetic field) magnetoelectric contributions of both exchange and relativistic nature,

$$\Phi_{ME}=\beta_0\{P_X(\mathbf{L}\cdot\mathbf{B}_2)-P_Y(\mathbf{L}\cdot\mathbf{B}_1)\}+\beta_1\{P_X(L_x^2-L_Y^2)-2P_YL_XL_Y\}+\beta_2L_Z(P_XL_Y-P_YL_X)+\beta_3P_ZL_Z(B_{1Y}-B_{2X}). \tag{6}$$

We also take into account the simplest magnetoelastic contributions:

$$\Delta\Phi_{\text{Mel}}=\gamma_1^1u_{ZZ}L_Z^2+\gamma_1^2u_{ZZ}(L_X^2+L_Y^2)+\gamma_2^1(u_{XX}+u_{YY})L_Z^2+\gamma_2^2(u_{XX}+u_{YY})(L_X^2+L_Y^2)+\gamma_3[(u_{XX}-u_{YY})\times(L_X^2-L_Y^2)]+4u_{XY}L_XL_Y]+\gamma_4[u_{YZ}(L_X^2-L_Y^2)+2u_{XZ}L_XL_Y]. \tag{7}$$

The establishment of collinear AFM order in the system at the Néel temperature T_N means, in the ideology of the Landau theory, that the following inequalities hold:

$$\Lambda_1^{(2)}(T_N)=0,\quad \Lambda_2^{(2)}(T_N)>0,\quad \Lambda_3^{(2)}(T_N)>0,\quad \Lambda_4^{(4)}(T_N)>0. \tag{8}$$

Assuming that in the temperature region $10\text{ K}<T<38\text{ K}$ the system is an easy-plane antiferromagnet, we must assume that the inequality $\eta_1^{(2)}(T)>0$ holds in that temperature interval. Then the point of the spin-reorientation transition T_R will correspond to the condition $\eta_1^{(2)}(T_R)+\eta_1^{(4)}(T_R)=0$,[12] and the system goes from easy-plane to easy-axis at temperatures $T<T_R$, for which $\eta_1^{(2)}(T)+\eta_1^{(4)}(T)<0$.

It follows from the results of Ref. 8 that as the temperature is lowered in the region $T\sim 20$ K the subsystem of moments of the rare-earth ions Gd will begin to play a role in the magnetism, the interaction of the subsystem of Fe spins with it having a substantial influence on the spin-reorientation transition in our system, although no actual magnetic ordering occurs in the rare-earth subsystem itself. Let us give some special attention to this fact. We start for the temperature region $T>10$ K, i.e., where the system is still an easy-plane antiferromagnet. Since the magnetic unit cell of the $GdFe_3(BO_3)_4$ system is doubled at the phase transition at the Néel point (and then contains two Gd ions), for describing the interaction of the disordered subsystem of moments of the Gd ions with the ordered system of moments of the Fe ions, we introduce an antiferromagnetic vector $\tilde{\mathbf{L}}$ for the gadolinium subsystem also. Taking into account the symmetry of the sites of the two gadolinium ions in the magnetic unit cell of our system, we easily see that the vectors $\tilde{\mathbf{L}}$ and **L** correspond to equivalent representations of the exchange symmetry group of our system, and so the energy of the f-d exchange interaction, $E=\kappa\tilde{\mathbf{L}}\cdot\mathbf{L}$ will be an invariant of the

group $R32$. The mean energy of the f-d exchange, averaged over the vector $\tilde{\mathbf{L}}$, i.e., $\langle E\rangle = \kappa\langle\tilde{\mathbf{L}}\rangle\cdot\mathbf{L}$, because of the disordered nature of the gadolinium subsystem, does not itself contribute to the thermodynamic potential of the system. Nevertheless, the antiferromagnetic order induced by the f-d exchange in the gadolinium subsystem can give an effective contribution to the thermodynamic potential on account of the corresponding correlations of the longitudinal (lying in the easy plane) component of the vector $\tilde{\mathbf{L}}$ in the second order of perturbation theory:

$$\Delta\Phi_{\text{cor}} = \kappa^2\frac{1}{\varepsilon}\langle\tilde{L}^2\rangle(L_X^2+L_Y^2), \tag{9}$$

where ε is the characteristic mean energy of spin waves of the gadolinium subsystem. It is seen that the correlation contribution to the thermodynamic potential of the system will be positive independently of the sign of κ. The physical meaning of the energy $\Delta\Phi_{\text{cor}}$ is that the correlations tend to make it unfavorable for the vector $\mathbf{L}$ to lie in the horizontal plane. As the temperature is lowered and the antiferromagnetic vector of the gadolinium sublattice $\tilde{\mathbf{L}}$ induced by the f-d exchange increases, an anisotropic contribution of opposite sign will appear in the thermodynamic potential of the system and compete with the initial (easy-plane) one. Then at the corresponding temperature T_R the resultant anisotropy constant will change sign, and an "easy plane to easy axis" spin-reorientation transition will occur in the system (it is known[5] that this transition is not observed in the case of the nonmagnetic ions R=Y, La).

DISCUSSION OF THE RESULTS

Our proposed expression (7) for the magnetoelastic energy of the system allows an easy explanation of the experimentally observed behavior (Figs. 1 and 4) of the magnetostriction for the magnetic field directions $H\|c$ and $H\perp c$, both for the temperature region $T<10$ K and for 10 K$<T<$38 K. Indeed, at a temperature $T\leqslant 10$ K, when the vector $\mathbf{L}$ is directed along the c axis and the field $H\|c$, at a certain value of the field H_{cr} a spin-reorientation transition occurs, and the vector $\mathbf{L}$ lies in the plane without changing its length. The lower the temperature, the larger the value of the threshold field. Starting from formula (7), one can conclude that at that point the magnetostriction has a jump, and $\lambda_C\sim(\gamma_1^2-\gamma_1^1)L^2$.

At the same field orientation $H\|c$ but for $T>10$ K the vector $\mathbf{L}$ lies in the easy plane, and the magnetostriction behaves in a monotonic manner (quadratically in the field; Fig. 1). For the field direction $H\perp c$ in the temperature region $T<10$ K the magnetic field H acting on the gadolinium subsystem disrupts the mechanism of the spin reorientation that is observed at temperature T_R and tips the vector $\mathbf{L}$ over into the basal plane, but perpendicular to the field (the in-plane anisotropy is extremely small), so that in this case the magnetostriction λ_C will exhibit a jump $\Delta\lambda_C\sim(\gamma_2^2-\gamma_2^1)L^2$.

At temperatures $T>10$ K the vector $\mathbf{L}$ lies in the plane, and in the general case there will be six types of domains in the system (in accordance with the three equivalent easy directions in the plane), so that the mean magnetostriction over the sample will be equal to zero. At low magnetic fields, when the vectors $\mathbf{L}$ of all the domains align counter to the field, the magnetostriction exhibits jumplike behavior $\Delta\lambda_a\sim\gamma_3L^2$. For the field direction $H\|c$ the magnetostriction behaves monotonically, in accordance with expression (7).

Analysis of the magnetoelectric contributions (6) permits a detailed interpretation of the behavior of the planar component of the electric polarization vector (Fig. 5). On the whole, the theory [expression (6) and Table I] permits the assertion that a quadratic magnetoelectric effect should be observed in our system. It is noteworthy here that the discussion of the magnetoelectric effect in the framework of the symmetry space group $R32$ with the invariant contributions (6) taken into account does not permit a satisfactory description of the behavior of the vertical component of the electric polarization vector, P_C. The similarity of its behavior with that of the magnetostriction λ_C argues, in particular, that for the magnetically ordered state the vector P_C should be an invariant (i.e., our system belongs to a polar class). In the absence of unambiguous analysis of the change of the crystal symmetry of the system at the point of the structural phase transition $T_C=156$ K, this remains an open question.

It follows from expression (6) that the symmetry of the system admits yet another magnetoelectric contribution $\sim\beta_2$ (of a relativistic nature), which is responsible for the spin-reorientation transition in an electric field. Indeed, for the state in which the antiferromagnetic vector lies in the basal plane (for the region $T>T_R$) the transverse component of the electric field applied in the basal plane induces the appearance of a component of the vector $\mathbf{L}$ directed along the c axis and, accordingly, in the temperature region $T<T_R$ this contribution brings about a reorientation of the antiferromagnetic vector from the easy axis to the easy plane under the influence of a transverse electric field.

Finally, the features of the symmetry of our system are such that, in principle, under certain conditions (in particular, in the presence of antiferromagnetic intralayer exchange) an antiferromagnetic phase transition could occur at the Néel point with the formation of a fundamentally noncollinear structure of the triangular type, described by a two-dimensional representation (by the basis vectors $\mathbf{B}_1$ and $\mathbf{B}_2$ mentioned previously). In this case it would not require very much effort to describe the spin-reorientation transition and so forth in the framework of the thermodynamic approach. However, the realization of an easy-plane triangular AFM structure in the temperature interval 10 K$<T<$38 K would lead, for both the cases of weak and strong easy-plane anisotropy,[13] to the existence of yet another spin-reorientation phase transition in the high-temperature region at moderately high fields $H\perp c$ (completely achievable in our experiments). Since no such transformation was observed in principle in our studies, we shall assume, as in Ref. 8, that the features of our system are such that collinear AFM ordering is realized at the Néel point. We complete the discussion of the properties of the thermodynamic potential of the system (3) by calling attention to the presence of specific cross contributions in it that are capable of "admixing" exchange-noncollinear components to the fundamental collinear AFM mode both above and below the spin reorientation point. One can see that each of these noncollinear components corresponds to a different chirality (right or left

"handedness").[14] This, in particular, attests that the magnetooptical properties of our system will be different on different sides of the spin reorientation point.

On the whole, the above-mentioned features of the behavior of the system $GdFe_3(BO_3)_4$ permit the assumption that it is a multiferroic compound.

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[1)]After this article went to press, the preprint of an article entitled "Evidence for structure differentiation in the iron-helicoidal-chain in $GdFe_3(BO_3)_4$," by S. A. Klimin, D. Fausti, A. Meetsma, L. N. Besmaternykh, P. H. M. van Loosdrecht, and T. T. M. Palstra (to be published in Acta Cryst. B), came out, which contained a detailed description of the change of the crystal system at the point T_c; however, taking that change into account would not alter the basic conclusions found in our paper.

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