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Quantum theory of magnetoelectricity in rare-earth multiferroics: Nd, Sm, and Eu ferroborates

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The quantum theory of magnetoelectricity in rare-earth ferroborates is developed. It is shown that the electric polarization in the materials is induced by means of two single-ion mechanisms: effective magnetic and crystal fields produce the electric dipole moment directly in the electronic $4f$ shells of rare-earth ions (the electronic contribution) and also through displacement of oppositely charged ion sublattices (the ionic one). The magnetoelectrical properties are described in detail for the neodymium, samarium, and europium ferroborates. In particular, the field and temperature dependencies of polarization are obtained.

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I. INTRODUCTION

Recently, multiferroic (MF) materials have attracted considerable attention focused on both improved fundamental understanding and novel desirable applications. Challenging and promising visions emerged, for example, of how to switch magnetism with bare electric fields and thus overcome the overheating bottleneck in microelectronic devices.[1,2] Today, a rich variety of multiferroic materials is encountered. Despite its smallness, the linear magnetoelectric effect (MEE) has been shown to control spintronics devices very efficiently, for example, even by using the classic magnetoelectric (ME) antiferromagnet Cr_2O_3.[3] In recent years, it has also been shown that significantly larger values of MEE can be in multiferroic composites.[4,5]

Nevertheless, a problem of searching for new materials with substantial magnetoelectricity still remains highly topical. To handle the problem, profound understanding of MEE microscopic mechanisms is needed, since traditional phenomenological theories, based on the symmetry analysis approach, which can predict the presence (or the absence) of the effect, are not capable of giving exact temperature or field dependencies.

The conventional MEE is the result of the interaction between the two subsystems of an ionic crystal, namely electrical, consisting of charged ions, and magnetic, constituted of the uncompensated spin magnetic moments of the ions. The microscopic mechanisms of the magnetoelectric effect have not been sufficiently identified. The magnetoelectricity of transition d ions is usually explained in terms of the exchange striction and the inverse Dzyaloshinskii-Moriya mechanisms, which are both attributed to a modulation of interionic exchange interactions, which is quite strong for d ions. As for multiferroics, there exist two microscopic theories of magnetoelectric coupling in them, one theory based on the spin current model[6] and the other based on the model of an electric current compensation.[7]

In recent years, a new class of (improper) multiferroics, namely rare-earth (RE) ferroborates $RFe_3(BO_3)_4$, where $R = La–Lu$, is actively studied, both theoretically and experimentally.[8–11] The materials are attractive because of the huge MEE[9] and a possible effect of an electric polarization control with an external magnetic field.[10] The magnetoelectricity of rare-earth ferroborates is owed primarily to the presence of rare-earth f ions, which is convincingly proved by the minute MEE in yttrium ferroborate[9] and recently observed giant MEE in rare-earth alumoborates.[12] Weak exchange interaction between rare-earth f ions (compared with d-d and f-d exchange), large orbital moments together with weak orbital-moment quenching and a low-symmetry crystal field make the single-ion mechanisms of magnetoelectricity in rare-earth f ions dominate over double-ion mechanisms, which are typical for transition metal d ions.

In the present work, the quantum theory of the magnetoelectric effect in rare-earth ferroborates is worked out by the example of Nd, Sm, and Eu ferroborates. Two single-ion mechanisms are shown to underlie the magnetoelectricity of such compounds. These are the electronic mechanism (the electric dipole moment in the electronic $4f$ shell of a rare-earth ion is produced by an effective exchange and external magnetic fields combined with a low-symmetry crystal field) and ionic one (attributed to displacement of oppositely charged ion sublattices in a magnetic field). Prominently, the second-order contributions to polarization from both mechanisms coincide in the form. The field and temperature dependencies of the electric polarization induced with the magnetic field taking into account both the electronic and ionic contributions are obtained. A good agreement achieved between the theoretical predictions and the experimental data counts in favor of the validity of the theory developed.

II. THE ELECTRONIC MECHANISM

First of all, we consider the electronic mechanism of the magnetoelectricity in rare-earth ions, which was already outlined in Ref. 13. We would like to discuss it now somewhat closer in respect to rare-earth ferroborates.

Let a rare-earth ion be under the influence of magnetic and external electric fields. The actual perturbation Hamiltonian $\mathcal{V}$ of the ion then reads

$$\mathcal{V} = -\mathbf{dE} + \mathcal{H}_{cr}^{\mathrm{odd}}, \tag{1}$$

where $\mathbf{d} = -e\sum_{k=1}^{n}\mathbf{r}_k$ is the dipole moment operator of the ion with n electrons in the $4f$ shell. The crystal field (CF) operator $\mathcal{H}_{cr}^{\mathrm{odd}}$ in Eq. (1) contains only odd harmonics and can be expressed as a sum,

$$\mathcal{H}_{cr}^{\text{odd}} = \sum_{t\tau k} B_\tau^t \mathcal{C}_\tau^t(k),$$

where index t is odd and $\mathcal{C}_\tau^t(k) = \sqrt{\frac{4\pi}{2t+1}}\, Y_{t\tau}(\theta,\varphi)$ are the single-electron irreducible tensor operators, which are defined by the reduced matrix element $\langle l'||\mathcal{C}^t||l\rangle = \sqrt{2l+1}\, C_{l0t0}^{l'0}$. $Y_{t\tau}(\theta,\varphi)$ are spherical functions.

For rare-earth ferroborates this crystal field operator has the following form:

$$\mathcal{H}_{cr}^{\text{odd}} = \sum_k B_3^3\left(\mathcal{C}_{-3}^3(k) - \mathcal{C}_3^3(k)\right) + \sum_k B_3^5\left(\mathcal{C}_{-3}^5(k) - \mathcal{C}_3^5(k)\right). \tag{2}$$

The crystal field parameters B_τ^t used in Eq. (2) are found to be $B_3^3 = 2110\ \text{cm}^{-1}$ and $B_3^5 = 2170\ \text{cm}^{-1}$ for Pr^{3+} ions in the frame of the point charge model.[14] It will be shown below that the same parameters allow the description of the magnetoelectric properties of other rare-earth ferroborates with sufficient accuracy.

The linear on the strength of the applied electric field corrections to the ion energy levels arises in the second-order perturbation theory with small parameter $||\mathcal{V}||/W$, where $||\mathcal{V}||$ is the norm of the $\mathcal{V}$ operator in Eq. (1) and W is the energy difference between the ground states and the weight center of excited ion electronic configurations (typically, $W \sim 10^5\ \text{cm}^{-1}$ for rare-earth ions). For the sake of simplicity, we will take into account only the lowest $4f^{n-1}5d^1$ configuration.

Making use of the wave-function genealogical scheme construction and the quantum theory of angular momentum,[15] we derived the expression for the magnetoelectric operator of rare-earth ferroborates. Referring the reader to the Appendix for the details of calculations, we give here the final expression for the magnetoelectric Hamiltonian,

$$\begin{aligned}\mathcal{H}_{me} &= -\left(\frac{er_{fd}}{W}\right)\mathbf{ED} \\ &= -\left(\frac{er_{fd}}{W}\right)(E_+D_- + E_-D_+ + E_zD_z),\end{aligned} \tag{3}$$

where r_{fd} is the radial integral (see the Appendix) and D_α ($\alpha = x,y,z$) are the effective operators of the RE ion electric dipole moment components. For the sake of brevity, we use the notation of so called "cyclic" operators $E_\pm = (E_x \pm i\,E_y)/\sqrt{2}$ and $D_\pm = (D_x \pm i\,D_y)/\sqrt{2}$, where

$$\begin{aligned}D_\pm &= \sum_{p=2,4,6} b_2^p \mathcal{C}_{\mp 2}^p + \sum_{p=4,6} b_4^p \mathcal{C}_{\pm 4}^p, \\ D_z &= b_3^4\left(\mathcal{C}_3^4 - \mathcal{C}_{-3}^4\right) + b_3^6\left(\mathcal{C}_3^6 - \mathcal{C}_{-3}^6\right).\end{aligned} \tag{4}$$

Hereafter the summation over electrons is assumed but the summation symbol is omitted to avoid bulky expressions. Coefficients b_q^p in Eq. (4) can be expressed in the terms of the crystal field parameters,

$$b_2^2 = \frac{4\sqrt{3}}{7\sqrt{7}}B_3^3, \quad b_2^4 = -\frac{11}{21\sqrt{14}}B_3^3 + \frac{4\sqrt{5}}{7}B_3^5,$$

$$b_2^6 = -\frac{\sqrt{78}}{7\sqrt{11}}B_3^5,$$

$$b_4^4 = \frac{11\sqrt{2}}{21}B_3^3 - \frac{2\sqrt{5}}{7\sqrt{7}}B_3^5, \quad b_4^6 = \frac{3\sqrt{65}}{7\sqrt{11}}B_3^5,$$

$$b_3^4 = -\frac{11}{42}B_3^3 - \frac{4\sqrt{10}}{7\sqrt{7}}B_3^5, \quad b_3^6 = -\frac{3\sqrt{39}}{7\sqrt{22}}B_3^5.$$

In order to describe magnetoelectric properties of rare-earth materials, it is necessary to know the energy levels and eigenfunctions of rare-earth ions in the crystals. Rare-earth ferroborates consist of two exchange-coupled magnetic subsystems, one of which is formed by Fe^{3+} ions and the second is formed by rare-earth ions. At low temperatures $T < T_N$ ($T_N \sim 30\ldots40$ K is the Neel temperature) the iron subsystem consists of two antiferromagnetically ordered magnetic sublattices $\mathbf{M}_1$ and $\mathbf{M}_2$. The RE-Fe exchange interaction, considered under the molecular field approximation, is less by the order of magnitude than that of iron ions, which is responsible for the magnetic ordering of the magnetic moments of the iron ions. The exchange interaction between rare-earth ions is weaker by the order of magnitude than the RE-Fe exchange and thus can be neglected. While there is the magnetic ordering of iron ions in ferroborates, rare-earth ions are divided into two subsystems. The first one is coupled by the exchange interaction mainly with iron ions of sublattice $\mathbf{M}_1$; the second one interacts with ions of sublattice $\mathbf{M}_2$. In the presence of external magnetic field $\mathbf{H}$ the rare-earth ions in sublattices 1 and 2 are under the action of effective magnetic field,

$$\mathbf{h}_q = \mathbf{H} + \mathbf{H}_{\text{mol},q}, \tag{5}$$

where index $q = 1,2$ and $\mathbf{H}_{\text{mol},q} = \lambda\mathbf{M}_q$ is the molecular field and λ is the constant of the molecular field.

The magnetoelectric contribution to the free energy of the crystal then reads

$$\mathcal{F}_{me} = -Q\left(\mathbf{E}\sum_{q=1,2}\langle\mathbf{D}\rangle_q\right), \tag{6}$$

where $Q = (N/2)(er_{fd}/W)$ and N is the number of rare-earth ions in the sample. Symbol $\langle\ldots\rangle$ means the thermodynamics averaging over wave functions of a rare-earth ion. Equation (6) allows us to analyze magnetoelectric properties (the field and temperature dependencies of the polarization components) in rare-earth ferroborates:

$$P_\alpha = -\frac{\partial\mathcal{F}_{me}}{\partial E_\alpha} = Q\sum_{q=1,2}\langle D_\alpha\rangle_q, \quad \alpha = x,y,z. \tag{7}$$

In order to calculate the dependencies, the energy levels and wave functions of rare-earth ions in crystal and magnetic fields are required.

III. THE CRYSTAL FIELD

At the R^{3+} sites in rare-earth ferroborates with D_3 symmetry, in the Cartesian system of coordinates with the z and x axes along the crystallographic c and a (which is of the C_2 symmetry) axes, the containing even harmonics crystal field Hamiltonian can be described by six independent real crystal field parameters,

$$\begin{aligned}\mathcal{H}_{\text{CF}} &= B_0^2\mathcal{C}_0^2 + B_0^4\mathcal{C}_0^4 + B_0^6\mathcal{C}_0^6 + i\,B_{-3}^4\left(\mathcal{C}_{-3}^4 + \mathcal{C}_3^4\right) \\ &\quad + i\,B_{-3}^6\left(\mathcal{C}_{-3}^6 + \mathcal{C}_3^6\right) + B_6^6\left(\mathcal{C}_6^6 + \mathcal{C}_{-6}^6\right).\end{aligned} \tag{8}$$

TABLE I. The Nd^{3+} ground multiplet split by the crystal field into the five Kramers doublets.

k	E_k (cm^{-1})	$\vert\psi_k\rangle$, $\vert\bar{\psi}_k\rangle$
0	0	$\pm 0.498\vert \pm \frac{7}{2}\rangle \pm 0.129i\vert \pm \frac{1}{2}\rangle \pm 0.858\vert \mp \frac{5}{2}\rangle$
1	72	$(-0.276 \pm 0.454i)(\vert + \frac{9}{2}\rangle \pm \vert - \frac{9}{2}\rangle) - 0.660(\vert - \frac{3}{2}\rangle \pm \vert + \frac{3}{2}\rangle)$
2	146	$\pm 0.840\vert \pm \frac{7}{2}\rangle \pm 0.174i\vert \pm \frac{1}{2}\rangle \mp 0.514\vert \mp \frac{5}{2}\rangle$
3	229	$(-0.242 \pm 0.399i)(\vert + \frac{9}{2}\rangle \pm \vert - \frac{9}{2}\rangle) + 0.531(\vert - \frac{3}{2}\rangle \pm \vert + \frac{3}{2}\rangle)$
4	326	$\pm 0.215\vert \pm \frac{7}{2}\rangle \mp 0.174i\vert \pm \frac{1}{2}\rangle \pm 0.022\vert \mp \frac{5}{2}\rangle$

We should here remind, that the summation over $4f$ electrons is assumed in Eq. (8). The numerical values of the crystal-field parameters are obtained by the fitting the CF levels of the CF Hamiltonian in Eq. (8) to the high-resolution polarized optical absorption spectra.[14,16] Currently, the neodymium crystal field parameters are determined with a high degree of reliability: $B_0^2 = 551\ \mathrm{cm}^{-1}$, $B_0^4 = -1239\ \mathrm{cm}^{-1}$, $B_0^6 = 519\ \mathrm{cm}^{-1}$, $B_{-3}^4 = 697\ \mathrm{cm}^{-1}$, $B_{-3}^6 = 105\ \mathrm{cm}^{-1}$, and $B_6^6 = 339\ \mathrm{cm}^{-1}$. Unfortunately, the crystal field of the Sm^{3+} ion is not known in such detail, but, given the proximity between samarium and neodymium, we can calculate the Sm^{3+} spectrum on the base of the neodymium CF data. The results of the calculations are represented in Table I for Nd^{3+} and in Table II for Sm^{3+} ions.

Obviously, the averaging of the $\mathbf{D}$ operator (see Sec. II) in a zero magnetic field over the states that are combinations of the harmonics differing in the magnetic quantum number by 3, 6, or 9 is equal to zero. In an effective magnetic field, the ground Kramers doublet ($|\psi_0\rangle,|\bar{\psi}_0\rangle$) of an ion is split by the field into the two close-lying levels,

$$|\psi_{1,2}^0(q)\rangle = C_{1,2}^{(1)}(q)|\psi_0\rangle \pm C_{1,2}^{(2)}(q)|\bar{\psi}_0\rangle,$$

with energies,

$$E_{1,2}(q) = \pm g_J \mu_B h_q \Delta_q,$$

where $\Delta_q = \sqrt{g_\parallel^2 \gamma_{q_\parallel}^2 + g_\perp^2 \gamma_{q_\perp}^2}$, unit vector $\vec{\gamma}_q = \mathbf{h}_q/h_q$, g_J is the Lande factor, and μ_B is the Bohr magneton. The nonzero magnetic spectroscopic factors are only $g_{xx} = g_{yy} = g_\perp$ and $g_{zz} = g_\parallel$ (for neodymium $g_{||} = 0.964$, $g_\perp = 1.751$, and $g_J = 8/11$; for samarium $g_{||} = 0.379$, $g_\perp = 1.441$, and $g_J = 2/7$). Coefficients $C_m^{(n)}(q)$ read

$$C_m^{(n)}(q) = \frac{1}{\sqrt{2}}\left(1 - (-1)^{n+m}\frac{g_\parallel \gamma_{q_\parallel}}{\Delta_q}\right)^{1/2} e^{-i(-1)^n(\pi+\varphi_q)/2},$$

where φ_q are defined by the expression $\tan\varphi_q = \gamma_{qy}/\gamma_{qx}$.

The contribution of the higher levels to the wave function of the rare-earth ion in the magnetic field can be taken into account by the perturbation theory,

$$|\psi_{1,2}(q)\rangle = \left|\psi_{1,2}^0\right\rangle + \sum_k \frac{\langle\psi_k|\mathcal{V}_Z(q)|\psi_{1,2}^0\rangle}{E_0 - E_k}\left|\psi_k^0\right\rangle, \tag{9}$$

where operator $\mathcal{V}_Z(q) = g_J \mu_B \mathbf{J}\mathbf{h}_q$ represents the Zeeman interaction of the ion magnetic moment in the qth subsystem with the effective magnetic field. The energies E_k and the wave functions ($|\psi_k\rangle$, $|\bar{\psi}_k\rangle$) of the Kramers doublets for the neodymium and samarium ground multiplets split by the crystal field are given in Tables I and II, respectively. It should also be noted that the applicability of the perturbation theory is limited to the range of not too strong magnetic fields $H \ll E_k/\mu_B \sim 10^6$ Oe.

TABLE II. The Sm^{3+} ground multiplet split by the crystal field into the three Kramers doublets ($\cos\alpha = 0.980$, $\sin\alpha = 0.201$).

k	E_k (cm^{-1})	$\vert\psi_k\rangle$, $\vert\bar{\psi}_k\rangle$
0	0	$\mp i \sin\alpha\vert \pm \frac{5}{2}\rangle \pm \cos\alpha\vert \mp \frac{1}{2}\rangle$
1	247	$\mp i \cos\alpha\vert \pm \frac{5}{2}\rangle \pm \sin\alpha\vert \mp \frac{1}{2}\rangle$
2	194	$\pm\vert \pm \frac{3}{2}\rangle$

In the most interesting case of the low temperatures $kT \ll \Delta$, where Δ is the energy difference between the first excited and the ground doublets, the magnetoelectric contribution to the free energy can be found as follows:

$$\mathcal{F}_{me} = \frac{N}{2}\sum_{q=1,2}\frac{\sum_{i=1,2}\langle\psi_i(q)|\mathcal{H}_{me}|\psi_i(q)\rangle e^{-E_i(q)/kT}}{\sum_{i=1,2} e^{-E_i(q)/kT}}, \tag{10}$$

where magnetoelectric Hamiltonian $\mathcal{H}_{me}$ is given by Eq. (3). In Eq. (10), we have neglected the population of all levels with the exception of the ground doublet levels. Calculating the matrix elements in Eq. (10) and taking into account Eq. (9) we find that

$$\mathcal{F}_{me} = Q g_J \mu_B \sum_{q=1,2} h_q \chi(\mathbf{h}_q, T)(C_1 I_1(q) + C_2 I_2(q)), \tag{11}$$

where

$$\chi(\mathbf{h}_q, T) = \frac{1}{\Delta_q}\tanh\left(\frac{g_J \mu_B h_q}{kT}\Delta_q\right),$$

$I_1(q) = E_x(\gamma_{qx}^2 - \gamma_{qy}^2) - 2E_y\gamma_{qx}\gamma_{qy}$, and $I_2(q) = E_x\gamma_{qy}\gamma_{qz} - E_y\gamma_{qx}\gamma_{qz}$.

Coefficients C_1 and C_2 are given by the following quite complicated expressions:

$$C_1 = 2g_\perp \sum_{q=1,3}\frac{\mathrm{Re}[\langle\psi_0|\hat{D}_x|\psi_q\rangle\langle\psi_q|\hat{J}_+|\psi_0\rangle]}{E_q} = 2.952,$$

$$\begin{aligned} C_2 = {} & -2g_{||}\sum_{q=1,3}\frac{\mathrm{Im}[\langle\psi_0|\hat{D}_x|\psi_q\rangle\langle\psi_q|\hat{J}_+|\psi_0\rangle]}{E_q} \\ & - \sum_{q=2,4}\frac{2g_\perp\langle\psi_q|\hat{J}_z|\psi_0\rangle - g_{||}\langle\psi_q|\hat{J}_+|\bar{\psi}_0\rangle}{2E_q}\mathrm{Im}\langle\bar{\psi}_0|\hat{D}_x|\psi_q\rangle \\ = {} & 1.164, \end{aligned}$$

for neodymium and

$$\begin{aligned} C_1 = &-\frac{g_\perp}{E_2}(\langle\psi_2|\hat{J}_+|\bar{\psi}_0\rangle\langle\psi_0|\hat{D}_x|\psi_2\rangle \\ &+\langle\bar{\psi}_0|\hat{D}_x|\psi_2\rangle\langle\psi_2|\hat{J}_-|\psi_0\rangle) = 4.92, \\ C_2 = &-\frac{i\langle\bar{\psi}_0|\hat{D}_x|\psi_1\rangle}{E_1}\left(2g_\perp\langle\psi_1|\hat{J}_z|\psi_0\rangle - g_{||}\langle\psi_1|\hat{J}_-|\bar{\psi}_0\rangle\right) \\ &+\frac{ig_{||}}{E_2}(\langle\psi_0|\hat{J}_+|\psi_2\rangle\langle\psi_2|\hat{D}_x|\psi_0\rangle \\ &-\langle\psi_2|\hat{J}_+|\bar{\psi}_0\rangle\langle\bar{\psi}_0|\hat{D}_x|\psi_2\rangle) = 7.09, \end{aligned}$$

for samarium ions. Operator $\hat{D}_x = (\hat{D}_+ + \hat{D}_-)/\sqrt{2}$ is defined by Eq. (4).

The components P_x and P_y of the induced electric polarization can easily be obtained from Eq. (11) as

$$\begin{aligned} P_x &= -\frac{\partial\mathcal{F}_{me}}{\partial E_x} \\ &= Qg_J\mu_B\sum_{q=1,2}h_q\chi(\mathbf{h}_q,T)(C_1(\gamma_{qy}^2-\gamma_{qx}^2)-C_2\gamma_{qy}\gamma_{qz}), \end{aligned} \tag{12}$$

and

$$\begin{aligned} P_y &= -\frac{\partial\mathcal{F}_{me}}{\partial E_y} \\ &= Qg_J\mu_B\sum_{q=1,2}h_q\chi(\mathbf{h}_q,T)(2C_1\gamma_{qx}\gamma_{qy}+C_2\gamma_{qx}\gamma_{qz}). \end{aligned} \tag{13}$$

Equations (12) and (13) determine the polarization behavior of ferroborates with rare-earth ions with the doublet or quasidoublet ground state (Kramers ions) depending on the magnitude and the orientation of an external magnetic field as well as on the temperature. It is to be remarked that the z component of the polarization equals to zero in the frame of the above described approximation. Actually, the component arises out of Eq. (9) only when the higher order terms in the perturbation theory are considered (starting at the third-order terms).

IV. THE EFFECTIVE MAGNETIC FIELD

In this section we proceed to the direct calculation of the field and temperature dependencies of the polarization for neodymium, samarium, and europium ferroborates. To obtain a quantitative description, one has to know the dependencies of effective field $\mathbf{h}_q = \mathbf{H} + \mathbf{H}_{\text{mol},q}$ ($q = 1,2$) on external field $\mathbf{H}$ and temperature T. With this purpose in mind, we consider the model of the magnetic structure for the ferroborate crystals.

Neodymium ions enhance the stability of the crystal ab plane for the iron ion spins, thus the antiferromagnetic $\mathbf{L}$ vector is in the ab plane ($0 < T < T_N$, $T_N = 32$ K is the Neel temperature). In relatively weak magnetic fields (up to 10 kOe) magnetic and domain structures of the sample are changed so that the $\mathbf{L}$ vector becomes uniform over the sample and perpendicular to the external magnetic field. In fields exceeding 10 kOe, the magnetization process is determined by the rare-earth subsystem and the spin-flip of the iron sublattices.

If the external magnetic field is directed along the a crystallographic axis [i.e., $\mathbf{H}_a = H\mathbf{e}_x$ ($H > H_{\text{flop}} = 10$ kOe)], then the effective magnetic field,[11]

$$\mathbf{h}_q = \left(1+\frac{H_{\text{mol}}}{H_{\text{flip}}}\right)H\mathbf{e}_x + (-1)^q H_{\text{mol}}\sqrt{1-\left(\frac{H}{H_{\text{flip}}}\right)^2}\,\mathbf{e}_y, \tag{14}$$

where $H_{\text{mol}} = 50$ kOe and $H_{\text{flip}} \sim 10^6$ Oe are the Fe-Nd molecular field and the iron spin-flip field, relatively. The temperature dependence of the molecular field can be accounted for in the frame of the molecular field theory. Given the proximity between samarium and neodymium, we can extend the foregoing theory to the case of samarium ferroborate with reasonable accuracy. The Fe-Sm molecular field is $H_{\text{mol}} = 330$ kOe. Figures 1 and 2 shows the field and temperature dependencies of the polarization induced in neodymium and samarium ferroborates. The dependencies are described by Eqs. (12) and (14).

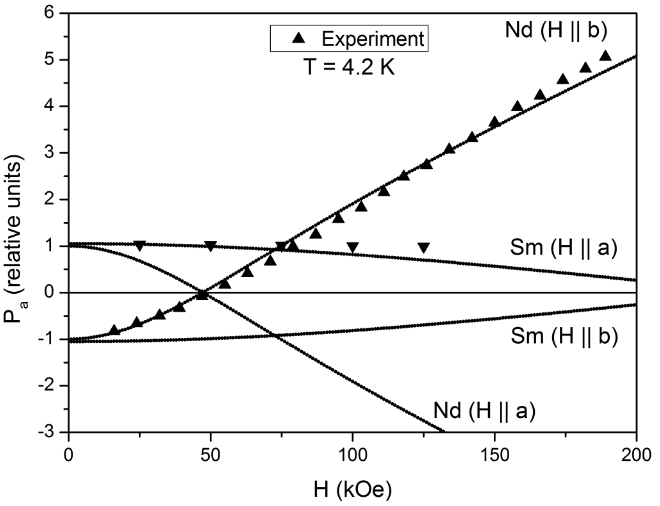

FIG. 1. The field dependencies of the polarization induced in the samarium and neodymium ferroborates at $T = 4.2$ K for different directions of the external magnetic field. The experimental data are given from Ref. 9.

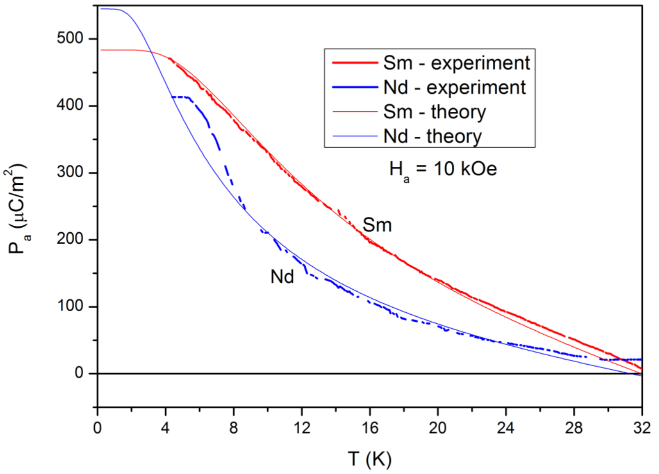

FIG. 2. (Color online) The temperature dependence of the polarization induced in the samarium and neodymium ferroborates. The binding of the theoretical curves to the experimental ones[9] is given at the point of the largest polarization ($T = 4.2$ K).

V. THE IONIC MECHANISM

In this section we consider the ionic contribution to the polarization. We use an approach based on the model of point charges. If the coordinate system is chosen so that the kth electron of a rare-earth ion is in the origin, then the potential produced by the environment ions is

$$V(k) = \sum_n \frac{q_n}{|\mathbf{r}_k - \mathbf{R}_n|},$$

where q_n and $\mathbf{R}_n$ are the charge and the radius vector of the nth ion. With this we can write the unperturbed crystal field Hamiltonian in the form,

$$\mathcal{H}_{cr}^{(0)} = \sum_{t\tau k} A_\tau^t P_\tau^t(\mathbf{r}_k) = \sum_{t\tau k} B_\tau^t \mathcal{C}_\tau^t(k). \tag{15}$$

Here $P_\tau^t(\mathbf{r}) = \sqrt{\frac{4\pi}{2t+1}}\, r^t Y_{t\tau}(\theta,\varphi)$ are the polynomials of degree t and $B_\tau^t = \langle r^t\rangle A_\tau^t$. We will use a simplified model of the polarization (a "garlic squeezer" model), in which all rare-earth ions are displaced by the same vector $\mathbf{u}$. The model neglects the displacement of the other ions in the crystal, assuming that they remain at their original positions. Such a shift of the rare-earth ions results in the following modification of the Hamiltonian in Eq. (15),

$$\mathcal{H}_{cr}(\mathbf{u}) = \sum_{t\tau k} A_\tau^t P_\tau^t(\mathbf{r}_k - \mathbf{u}). \tag{16}$$

In this equation, the ions of the rare-earth sublattice are removed from the summation, because the shift $\mathbf{u} = 0$ for them. Under the linear approximation the crystal field perturbations can be expressed as

$$\delta\mathcal{H}_{cr} = \mathcal{H}_{cr}(\mathbf{u}) - \mathcal{H}_{cr}^{(0)} = -\sum_{k\alpha} u_\alpha \frac{\partial \mathcal{H}_{cr}^{(0)}}{\partial r_{k\alpha}}. \tag{17}$$

In fact, Eq. (17) gives the magnetoelectric Hamiltonian, which can be reduced to the form,

$$\mathcal{H}_{me} = \sum_{t\tau k\alpha} b_{\tau\alpha}^t \mathcal{C}_\tau^t(k). \tag{18}$$

The crystal field Hamiltonian in Eq. (15) of rare-earth ferroborates contains the odd harmonics [see Eq. (2)]. Equation (2) can be rewritten in a polynomial form (the summation over k is implied),

$$\mathcal{H}_{cr}^{\text{odd}} = \frac{A_3^3\sqrt{5}}{2}(x^3 - 3xy^2) + \frac{A_3^5\sqrt{35}}{8}(9z^2 - r^2)(x^3 - 3xy^2). \tag{19}$$

Calculating the derivatives in Eq. (19) will give polynomials of even degree. As a result, the ionic mechanism results in the Hamiltonian of the magnetoelectric interaction in the form similar to that of the Hamiltonian in Eq. (3), in which the $\mathbf{E}$ vector is replaced by the $\mathbf{u}$ vector and parameters $b_{\tau\alpha}^t$ [see Eq. (18)], like the parameters in Eqs. (3) and (4), are defined by the B_3^3 and B_3^5 parameters of the odd crystal field.

The second-order contribution into magnetoelectric Hamiltonian is obtained from Eqs. (17) and (19):

$$\mathcal{H}_{me}^{(2)} = \frac{\langle r^2\rangle}{\langle r^3\rangle}(u_x D_x + u_y D_y) = \frac{\langle r^2\rangle}{\langle r^3\rangle} b\big(u_- \mathcal{C}_{-2}^2 + u_+ \mathcal{C}_2^2\big), \tag{20}$$

where operators of the effective dipole moment induced in the ion $D_x = b(C_{-2}^2 + C_2^2)$ and $D_y = -ib(C_{-2}^2 - C_2^2)$ and coefficient $b = -B_3^3\sqrt{\frac{15}{2}} = 5780\ \text{cm}^{-1}$. The value of r in Eq. (20) is $\langle r\rangle \sim 0.05$ nm.

The thermodynamic potential per ion is

$$\begin{aligned}\mathcal{F} &= \sum_\alpha \frac{c_\alpha u_\alpha^2}{2} + \langle \mathcal{H}_{me}\rangle \\ &= \sum_\alpha \frac{c_\alpha u_\alpha^2}{2} + \frac{1}{2r}\sum_{q=1,2}\big(u_-\langle D_+\rangle_q + u_+\langle D_-\rangle_q + u_z\langle D_z\rangle_q\big),\end{aligned}$$

where c_α stands for an effective stiffness coefficient. Operators $D_\pm$ and D_z are given by Eq. (4) with coefficients b_τ^t calculated from Eq. (17). From the equilibrium condition $\partial\mathcal{F}/\partial u_\alpha = 0$, we find that the equilibrium shift is $u_\alpha = -\sum_q \langle D_\alpha\rangle_q/(2rc_\alpha)$. The electric polarization is then given by $P_\alpha = -3eu_\alpha$, where $3e$ is the charge of a rare-earth ion, therefore,

$$P_\alpha = \frac{3e}{2rc_\alpha}\sum_{q=1,2}\langle D_\alpha\rangle_q. \tag{21}$$

Finally, it should be noted that this equation coincides in form with Eq. (7).

VI. THE MEE IN EUROPIUM FERROBORATE

Now we consider the magnetoelectricity of europium ferroborate. The ground state of a Eu^{3+} ion is described by the quantum number of total momentum $J = 0$, separated from states with $J = 1$ and $J = 2$ by energies $\Delta_1 = 350\ \text{cm}^{-1}$ and $\Delta_2 = 1050\ \text{cm}^{-1}$, relatively. The wave function of the ground state in external effective magnetic field $\mathbf{h}_q$ is

$$\begin{aligned}|\psi_0(q)\rangle = {} & \left(1 - \frac{2\mu_B^2 h_q^2}{\Delta_1^2}\right)|0,0\rangle - \frac{2\mu_B}{\Delta_1}\sum_{\nu=0,\pm1} h_{q\nu}|1,-\nu\rangle \\ & + \frac{\mu_B^2\sqrt{3}}{\Delta_1\Delta_2}\big(3h_{q0}^2 - h_q^2\big)|2,0\rangle \\ & - \frac{6\mu_B^2 h_{q0}}{\Delta_1\Delta_2}\sum_{\nu=\pm1} h_{q\nu}|2,-\nu\rangle \\ & + \frac{\mu_B^2\sqrt{3}}{\Delta_1\Delta_2}\sum_{\nu=\pm1} h_{q\nu}^2|2,-2\nu\rangle,\end{aligned} \tag{22}$$

where $h_{q0} = h_{qz}$, $h_{q,\pm1} = \mp(h_{qx} \pm ih_{qy})/\sqrt{2}$. If external field $\mathbf{H}$ is directed along crystallographic axis a, then effective magnetic field $\mathbf{h}_q$ is given by Eq. (14) with $H_{\text{mol}} = 134$ kOe.

In order to obtain the P_x component of the induced polarization $P_x = -(e/2rc_x)\sum_q\langle\psi_0(q)|D_x|\psi_0(q)\rangle$, we calculate the matrix elements,

$$\langle\psi_0(q)|D_x|\psi_0(q)\rangle = \frac{4\mu_B^2}{5\Delta_1^2}\left(\frac{\Delta_1}{\Delta_2} + \sqrt{\frac{3}{2}}\right)\left(h_{qx}^2 - h_{qy}^2\right), \tag{23}$$

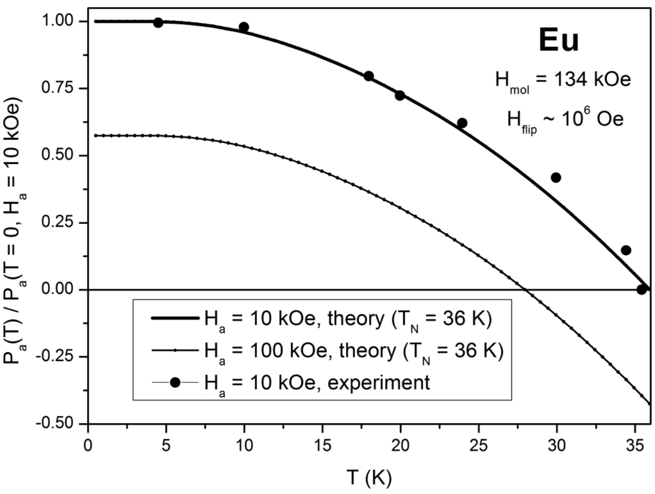

FIG. 3. The temperature dependence of the polarization induced in the europium ferroborate.

and finally arrive at the following expression for the polarization,

$$P_x(H,T) = A\left\{H_{\text{mol}}^2 - H^2\left[\left(\frac{H_{\text{mol}}}{H_{\text{flip}}}\right)^2 + \left(1 - \frac{H_{\text{mol}}}{H_{\text{flip}}}\right)^2\right]\right\}. \tag{24}$$

The temperature dependence of the molecular field can be accounted for in the frame of molecular field theory, as in Sec. III. The best possible fit with the experimental data[9] has been achieved with the Neel temperature $T_N = 36$ K. The plot of polarization vs temperature is shown in Fig. 3. The comparison between the theoretical calculations and the experimental data opens a possibility to estimate the value of the effective stiffness c_x. According to Eq. (24), $P_x = 1.6 \times 10^{-26} \cdot N/c_x$ C $\cdot$ erg/cm, where $N = 10^{22}$ is the number of ions per volume unit. The experiment gives $P_x = 70\ \mu\text{C/m}^2$, therefore $c_x \sim 10^4$ erg/cm^2.

VII. CONCLUSION

Thus, the quantum theory of magnetoelectricity in rare-earth ferroborates is developed and the mechanisms of magnetoelectricity in them is explained in detail. It is shown, that single-ion mechanisms dominate in the case of rare-earth ions, which leads to the large values of the polarization induced in the materials. The dependencies of the electrical polarization on the magnitude and direction of an external magnetic field and temperature are calculated. Comparison of the theoretical results obtained in this work with all experimental data shows their good quantitative agreement and indicates that the crystal field parameters obtained from spectroscopic data allow us to accurately describe magnetoelectric phenomena in the rare-earth ferroborates. Although we concentrate on the neodymium, samarium, and europium ferroborates, the theory developed can be applied with minor modifications not only to rare-earth ferroborates but also to other rare-earth compounds.

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APPENDIX

The purpose of this additional section is the detailed derivation of the magnetoelectric Hamiltonian of rare-earth ferroborates. As already mentioned in Sec. II, the analysis is based on the perturbation theory. The second-order corrections to the rare-earth ion energy levels read

$$E_g^{(2)} = \sum_{l',e_{l'}} \frac{\langle g|\mathbf{dE}|e_{l'}\rangle\langle e_{l'}|\mathcal{V}_{cr}^{\text{odd}}|g\rangle + \langle g|\mathcal{V}_{cr}^{\text{odd}}|e_{l'}\rangle\langle e_{l'}|\mathbf{dE}|g\rangle}{W_{l'}}. \tag{A1}$$

Here $|g\rangle$ are the rare-earth ion states of the ground l^n configuration in a magnetic field ($l = 3$ is the orbital quantum number of rare-earth ions with n electrons in the ion $4f$ shell), $|e_{l'}\rangle$ are the states from the excited $l^{n-1}l'$ configuration with $l' = l \pm 1$, and $W_{l'}$ is the energy difference between the $|e_{l'}\rangle$ and $|g\rangle$ states. The splitting of the $l^{n-1}l'$ configuration levels is neglected. The configuration with $l' = l - 1 = 2$ (typically $W_{l-1} \sim 10^5$ cm^{-1}) is closer to the ground levels than the configuration with $l' = l + 1 = 4$.

The operator describing the interaction of the ion dipole moment $\mathbf{d}$ with an electric field $\mathbf{E}$ can be written in terms of irreducible tensor operators,

$$\mathbf{dE} = \sum_{\mu=0,\pm1} (-1)^\mu E_{-\mu} d_{1\mu},$$

where $d_{1,\pm1} = \mp(d_x \pm i d_y)/\sqrt{2}$, $d_{10} = d_z$, $E_{\pm1} = \mp(E_x \pm i E_y)/\sqrt{2}$, and $E_0 = E_z$.

In order to construct the wave functions $|g\rangle$ and $|e_{l'}\rangle$ we use the genealogical scheme. The wave function $|g\rangle$ is expanded as $|g\rangle = \sum_M a_M |JM\rangle$, where J and M are the quantum numbers of the ion ground multiplet and a_M are the numerical coefficients given by the following equations:

$$\begin{aligned} |JM\rangle &= \sum_{M_L M_S} C_{LM_L SM_S}^{JM} |l^n SLM_S M_L\rangle, \\ |l^n SLM_S M_L\rangle &= \sum_{S_1 L_1 m} \sum_{M_{S_1} M_{L_1} \mu} G_{S_1 L_1}^{SL} C_{L_1 M_{L_1} lm}^{LM_L} C_{S_1 M_{S_1} \frac{1}{2}\mu}^{SM_S} \\ &\quad \times \Psi_{S_1 L_1 M_{S_1} M_{L_1}} (-1)^{n-m} \psi_{lm\frac{1}{2}\mu}(\xi), \\ |e_{l'}\rangle &= \frac{1}{\sqrt{n}} \sum_{m'} (-1)^{n-m'} \Psi_{S_1 L_1 M_{S_1} M_{L_1}} \psi_{l'm'\frac{1}{2}\mu'}(\xi). \end{aligned}$$

Here symbols $G_{S_1 L_1}^{SL}$ and $C_{j_1 m_1 j_2 m_2}^{jm}$ stand for the genealogical and Clebsch-Gordan coefficients, respectively, and L_1, S_1, M_{L_1}, M_{S_1} are the quantum numbers of the initial therm.

The known identity $\sum_{nm} C_{1\mu tp}^{nm} C_{1\nu tq}^{nm} = \delta_{\mu\nu}\delta_{pq}$[15] yields

$$\sum_{e_{l'}} \langle g|d_{1\mu}|e_{l'}\rangle\langle e_{l'}|C_\tau^t|g\rangle = \sum_{nm} C_{1\mu t\tau}^{nm} \langle g|\{d_1 \otimes C^t\}_{nm}|g\rangle,$$

where the matrix element of the direct product is

$$\langle g|\{d_1 \otimes C^t\}_{nm}|g\rangle = \sum_{e_{l'}\nu q} C^{nm}_{1\nu tq}\langle g|d_{1\nu}|e_{l'}\rangle\langle e_{l'}|C^t_q|g\rangle. \quad \text{(A2)}$$

Equation (A2) contains matrix elements of irreducible tensor operators $T_{pq} = \sum_k t_{pq}(k)$ which can be expanded as

$$\langle g|T_{pq}|e_{l'}\rangle = \sqrt{n} \sum_{M,M_L,M_S} \sum_{S_1,L_1,M_{S_1},M_{L_1}} \sum_{m_l,m_{l'},\mu} a^*_M C^{JM}_{LM_LSM_S} \times G^{SL}_{S_1L_1} C^{LM_L}_{L_1M_{L_1}lm_l} C^{SM_S}_{S_1M_{S_1}\frac{1}{2}\mu}\langle lm_l|t_{pq}|l'm_{l'}\rangle, \quad \text{(A3)}$$

where $\langle lm_l|t_{pq}|l'm_{l'}\rangle = C^{lm_l}_{l'm_{l'}pq}\langle l||t_{pq}||l'\rangle/\sqrt{2l+1}$ and $\langle l||t_{pq}||l'\rangle$ is the reduced matrix element.

Substituting Eq. (A3) into Eq. (A2) we obtain

$$\langle g|\{d_1 \otimes C^t\}_{nm}|g\rangle = -en\sum C^{nm}_{1\nu tq}C^{lm_l}_{l'm_{l'}1\nu}C^{l'm_{l'}}_{lm'_ltq}a^*_M a_{M'}C^{JM}_{LM_LSM_S}C^{JM'}_{LM'_LSM_S} \times C^{LM_L}_{L_1M_{L_1}lm_l}C^{LM'_L}_{L_1M'_{L_1}lm'_l}\left(G^{SL}_{S_1L_1}\right)^2\frac{\langle l||r_1||l'\rangle\langle l'||C^t||l\rangle}{\sqrt{(2l+1)(2l'+1)}}. \quad \text{(A4)}$$

According to the theory of angular momentum,[15] the reduced matrix elements in Eq. (A4) can be rewritten as $\langle l||r_1||l'\rangle = r_{ll'}\sqrt{2l'+1}C^{l0}_{l'010}$ and $\langle l'||C^t||l\rangle = (r^t)_{ll'}\sqrt{2l+1}C^{l'0}_{l0t0}$, where $(r^t)_{ll'} = \langle l|r^t|l'\rangle$ are the radial integrals. Summing up the first three factors in Eq. (A4) over ν, q, and $m_{l'}$ results in (see Ref. 15)

$$\sum_{\nu q m_{l'}} C^{nm}_{1\nu tq}C^{lm_l}_{l'm_{l'}1\nu}C^{l'm_{l'}}_{lm'_ltq} = (-1)^n\sqrt{(2n+1)(2l'+1)}C^{lm_l}_{lm'_lnm}\begin{Bmatrix} t & 1 & n \\ l & l & l' \end{Bmatrix},$$

where $\{\begin{smallmatrix} t & 1 & n \\ l & l & l' \end{smallmatrix}\}$ are the $6j$ symbols with even index n. Introducing the coefficient,

$$A(ll',tn) = -er_{ll'}\frac{C^{l0}_{l'010}C^{l'0}_{l0t0}}{C^{l0}_{l0n0}}\begin{Bmatrix} t & 1 & n \\ l & l & l' \end{Bmatrix}\sqrt{(2l'+1)(2l+1)},$$

and substituting Eq. (A1) into Eq. (A2) we arrive at the contribution of an ion to the magnetoelectric operator projected onto the space of the ion ground multiplet functions,

$$\mathcal{H}_{me} = 2\sum_{\mu t\tau}\sum_{nm}(-1)^\mu E_{-\mu}B^t_\tau A(ll',tn)W^{-1}_{l'}C^{nm}_{1\mu t\tau}C^n_m. \quad \text{(A5)}$$

The effective magnetoelectric operator can be obtained as the result of the summation over all indices in Eq. (A5) [see Eq. (3) in the text].

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