

Magnetoelectric effect in dysprosium orthoferrite due to dopant bismuth ions

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When dysprosium orthoferrite is doped with bismuth ions, a magnetoelectric effect quadratic in the magnetic field arises. This effect was studied in pulsed fields up to 120 kOe. The temperature dependence of the magnetoelectric susceptibility was determined over the range 4.2–150 K.

A quadratic magnetoelectric effect $\vec{P} = \hat{H}\hat{\beta}\vec{H}$, is not observed in the rare-earth orthoferrites $RFeO_3$ whose symmetry is described by the orthorhombic space group $D_{2h}^{16} - P_{bnm}$. The reason is that the independent symmetry elements of this group (E , $\hat{2}_x$, $\hat{2}_y$, I) include an inversion center (Ref. 1). We have observed that doping dysprosium orthoferrite with bismuth ions gives rise to an electric polarization quadratic in the magnetic field.

We studied the magnetic properties and magnetoelectric effect of $Dy_{1-x}Bi_xFeO_3$ single crystals ($x = 0.025$ and 0.14) grown from a molten solution of lead compounds. The quantitative concentration of Bi^{3+} ions was determined within $\sim 4\%$ by an x-ray spectral method. The magnetic properties were measured on a vibration magnetometer in fields up to 50 kOe, generated by a superconducting solenoid. The magnetoelectric effect was measured in pulsed magnetic fields up to 120 kOe, with a pulse length of 10 ms, on an apparatus similar to that described in Ref. 2. Electrodes were deposited on (110) parallel planes of the single crystal with the help of epoxy resin with a conducting filler. A signal taken from these electrodes was fed to an electrometer cascade and then to the y input of an oscilloscope. A signal proportional to the magnetic field was fed to the x input. The inverse problem has been solved previously in Ref. 3, i.e., the effect of the replacement of Bi^{3+} ions by a rare earth in $BiFeO_3$ on the magnetoelectric properties has been studied. In contrast with Ref. 3, we found that doping dysprosium orthoferrite with Bi^{3+} in a concentration x of 0.14 or 0.025 gives rise to a quadratic magnetoelectric effect $\vec{P} = \hat{H}\hat{\beta}\vec{H}$. We studied this effect over the temperature range 4.2–150 K.

Figure 1 shows the longitudinal and transverse electric polarizations $P_{(110)}$ versus the field, applied along the [110] and [001] directions, respectively, for the composition $x = 0.14$. We see from Fig. 1 that the transverse electric polarization $P_{(110)}^\perp$ varies quadratically with increasing field, while the longitudinal electric polarization $P_{(110)}^\parallel$ has a more complex field dependence, with a change in the slope of $P_{(110)}^\parallel$ in a strong field. For the composition $x = 0.14$ the components of the transverse and longitudinal magnetoelectric susceptibility are $\beta_{(110)}^\perp = 8 \times 10^{-20}$ and $\beta_{(110)}^\parallel = 6 \times 10^{-20}$ s/A, respectively, at $T = 11$ K.

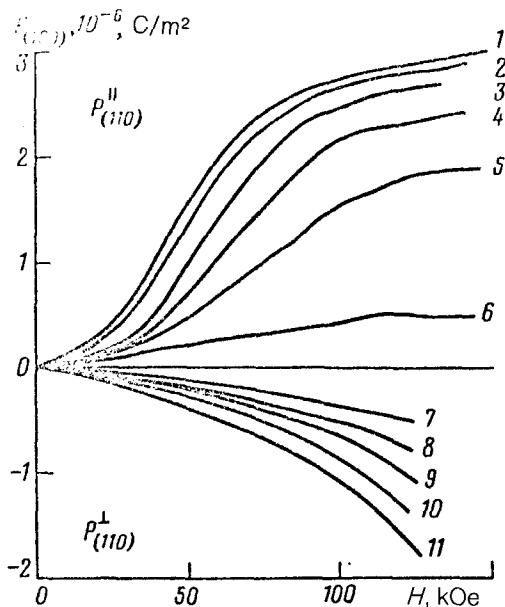


FIG. 1. Isotherms of the field dependence of the electric polarization for the composition $\text{Dy}_{0.86}\text{Bi}_{0.14}\text{FeO}_3$. 1-6: $P_{(110)}^{\parallel}(H)$. 1—11 K; 2—26; 3—43; 4—55; 5—83; 6—100 K. 7-11: $P_{(110)}^{\perp}(H)$. 7—92 K; 8—62; 9—44; 10—26; 11—11 K.

The difference in the behavior of the longitudinal and transverse magnetoelectric effects as a function of the magnetic field can be explained in the following way. The magnetic measurements showed that the slight ferromagnetic moment in $\text{Dy}_{0.86}\text{Bi}_{0.14}\text{FeO}_3$ is directed along the c axis of the orthorhombic crystal (along the $[001]$ direction). Consequently, the magnetic structure of the crystal does not change when a magnetic field is applied along the $[001]$ direction, as in the measurements of $P_{(110)}^{\perp}$. When the magnetic field is directed along $[110]$, and the projection of the magnetic field onto the a axis of the orthorhombic crystal (the $[100]$ direction) is large, the slight ferromagnetic moment undergoes a reorientation from the c axis to the a axis of the crystal.⁴ This reorientation apparently leads to the change in the slope of the $P_{(110)}^{\parallel}(H)$ curve (Fig. 1).

Figure 2 shows the temperature dependence of the magnetoelectric susceptibility. Above 105 K the magnetoelectric effect essentially disappears. As the temperature is lowered, it rises rapidly, apparently because of a magnetoelectric-susceptibility component from the Dy^{3+} ions, which have a strong spin-orbit coupling.

For the composition $x = 0.025$, we again observe a quadratic magnetoelectric effect in fields up to 20 kOe, with a magnetoelectric susceptibility $\beta_{(110)}^{\parallel} = 5 \times 10^{-18}$ s/A at $T = 7$ K. This susceptibility is greater than that observed at $x = 0.14$. As the field is raised further, the slope of the $P_{(110)}^{\parallel}(H)$ curve changes, because of a change in the magnetic structure in the field.

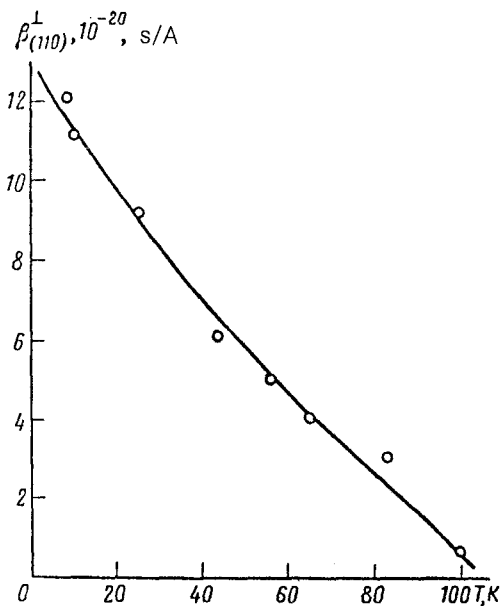


FIG. 2. Temperature dependence of the magnetolectric susceptibility $\beta_{(110)}^\perp$ for the composition $\text{Dy}_{0.86}\text{Bi}_{0.14}\text{FeO}_3$.

The appearance of a magnetolectric effect at such a low concentration of Bi^{3+} ions in DyFeO_3 is evidently due to particular features of the electronic structure of the Bi^{3+} ions. The completely filled $6s$ outer shell of Bi^{3+} is separated by a small "gap" (~ 4 eV in the various oxides) from the vacant $6p$ orbital. Since the energy of the $6s^2$ configuration (even) and that of the $6s^16p^1$ configuration (odd) are nearly the same, the Bi^{3+} dopant ion tends to set up a "cloud" of electric dipole polarization near itself (a local "ferroelectric phase"!) in crystals. This cloud arises from local displacements of the surrounding ions. The associated increase in the lattice energy is offset by a decrease in the electronic energy of Bi^{3+} as the result of a $6s$ - $6p$ hybridization. Here we are actually dealing with the ordinary pseudo-Jahn-Teller effect.

In view of the long-range nature of dipole forces, we might expect these local ferroelectric phases associated with the Bi^{3+} ions to be relatively large, and we might expect an effective interaction between them (an overlap), even at a relatively low bismuth concentration ($\sim 1\%$). In this case, macroscopic regions with a spontaneous polarization might arise in a sample, or the entire sample might have a uniform although small polarization. Everything depends on just how the Bi^{3+} ions are distributed over the volume of the sample: in a uniform or nonuniform way. In the case of the Bi^{3+} ions one sees a tendency toward an ordering of a pairing type (particularly in iron garnets). This tendency might lead to the appearance of a superstructure in the distribution of the Bi^{3+} ions in $\text{Dy}_{1-x}\text{Bi}_x\text{FeO}_3$ and to a change in the symmetry of the crystal, in particular, to a loss of the inversion center. The disappearance of the inversion center is a necessary condition for the onset of a quadratic magnetolectric effect.

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