Article

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Abstract

Ferroelectricity and weak ferromagnetism have been found to set in simultaneously in Ni3B7O13I at ~64°K. This is evidenced by dielectric hysteresis, spontaneous Faraday effect, quadratic magnetoelectric hysteresis, etc. The strong coupling between the mutually perpendicular spontaneous polarization--[001]--and spontaneous magnetization--[110]--is such that, when the former is reversed, the latter turns by 90°. The magnetic point group is most probably m'm2'. Dielectric constant, magnetic, and magnetoelectric susceptibilities and magnetic coercive field are shown as a function of temperature.

Reference

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Some Properties of Ferromagnetoelectric Nickel–Iodine Boracite, $Ni_3B_7O_{13}I$

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Ferroelectricity and weak ferromagnetism have been found to set on simultaneously in $Ni_3B_7O_{13}I$ at about 64°K. This is evidenced by dielectric hysteresis, spontaneous Faraday effect, quadratic magnetoelectric hysteresis, etc. The strong coupling between the mutually perpendicular spontaneous polarization—[001]—and spontaneous magnetization—[110]—is such that, when the former is reversed, the latter turns by 90°. The magnetic point group is most probably $m'm2'$. Dielectric constant, magnetic, and magnetoelectric susceptibilities and magnetic coercive field are shown as a function of temperature.

IN this paper we report on the discovery of ferromagnetoelectricity—simultaneous ferroelectricity and (weak) ferromagnetism—in $Ni_3B_7O_{13}I$. This compound is essentially isostructural with the mineral boracite, $Mg_3B_7O_{13}Cl$, that has a piezoelectric high-temperature phase (T_d^5) and a pyroelectric low-temperature phase (C_{2v}^5).[1,2]

Ni–Cl–boracite was shown to be ferroelectric[3]; the other paramagnetic boracites were expected to behave similarly. Since 3-dimensionally linked metal–halogen–metal chains occur in the boracite structure, it was anticipated that collective magnetic phenomena would occur at sufficiently low temperatures, and that there would be interactions with the electric polarization. Magnetic susceptibility measurements on powders of 3d-metal boracites indicate that these become antiferromagnetic at low temperature.[4] $Ni_3B_7O_{13}I$ shows the highest magnetic ordering temperature (broad maximum of the susceptibility at ~120°K); there is furthermore a sharp minimum at 64°K and a sharp maximum at 60°K (Fig. 1).[4] The dielectric constant—measured on a (100) platelet[5]—shows a very small peak at 60°K (Fig. 1). Observation in polarized light (transmission approximately between 5300 and 7000 Å) reveals a spontaneous Faraday effect, and hence a spontaneous magnetization M^s, below 64°K. The simultaneous onset of ferroelectricity is evidenced by dielectric hysteresis (Fig. 2). The displaced loop reveals a unidirectional anisotropy (due to growth condition) of the spontaneous polarization P^s. Optical observations and symmetry considerations show that the magnetic point group below 64°K is $m'm2'$, and that P^s is parallel to one of the cube edges, e.g. [001]; then M^s is either [110] or [$\bar{1}\bar{1}0$].[6]

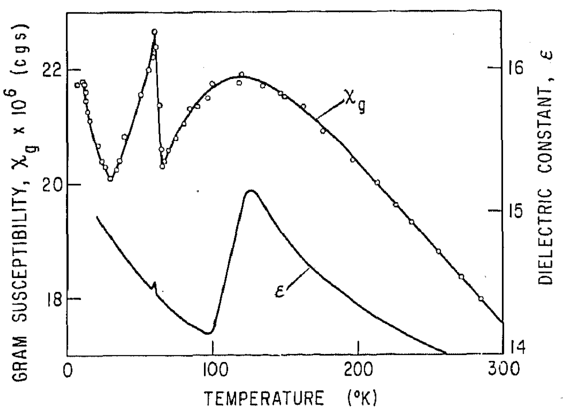

FIG. 1. Dielectric constant ϵ and gram susceptibility $\chi_g(H=2700$ Oe) versus temperature.

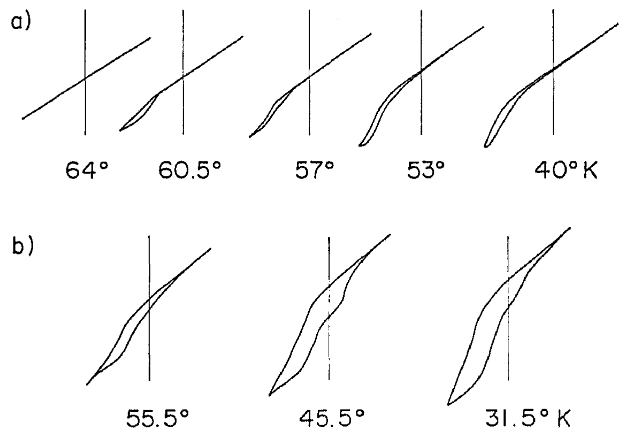

FIG. 2. Examples of ferroelectric hysteresis loops (a) 15 kV/cm; (b) 30 kV/cm, at 200 Hz.

(1) Electrical switching of P^s from [001] to [00$\bar{1}$]—by application of, e.g., 5 kV/cm at 56°K—results in a 90° change of M^s from [110] to [1$\bar{1}$0]; a magnetic field of a few oersted in the [100] direction prevents the new ferroelectric domain from splitting in several magnetic 180° domains. As a consequence of this cou-

[1] T. Ito, N. Morimoto and R. Sadanaga, Acta Cryst. 4, 310 (1951).
[2] The low-temperature space group seems to be inadequate; see Ref. 3.
[3] E. Ascher, H. Schmid, and D. Tar, Solid State Commun. 2, 45 (1964).
[4] H. Schmid, H. Rieder, and E. Ascher, Solid State Commun. 3, 327 (1965).
[5] H. Schmid, J. Phys. Chem. Solids 26, 973 (1965).
[6] Pseudocubic indices.

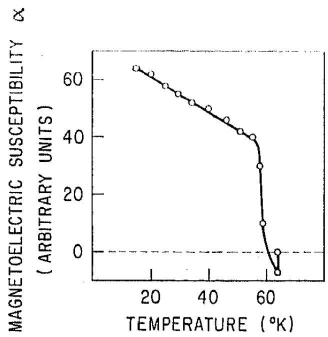

FIG. 3. Magnetoelectric susceptibility α versus temperature. Measured after cooling from above 65°K in H=7.6 kOe//[110] and E=10 kV/cm//[001].

pling, reversal of P^s in the plane of a (100) plate reverses the Faraday rotation for light propagating in the [100] direction from $+\rho$ to $-\rho$; reversal of P^s in the plane of a (110) plate changes the Faraday rotation for light propagating in the [110] direction from $\pm\rho$ to 0 (and vice versa).

(2) When an external magnetic field—e.g., 6 kOe at 56°K—is rotated from [110] to [$1\bar{1}0$], the polarization P^s is reversed from [001] to [$00\bar{1}$].

Denoting the direction of P^s by z, and that of M^s by y (point group $m_x'm_y2_z'$), we obtain the following equations for the linear magnetoelectric effects: $P_z=\alpha_{zy}H^y$, $M_y=\alpha_{zy}E^z$, $P_y=\alpha_{yz}H^z$, $M_z=\alpha_{yz}E^y$. We have measured the temperature dependence of α (as defined by the first equation) by a static method[7] in a field annealed sample (Fig. 3). The value of α_{zy} at, e.g. 15°K, is 3.3×10^{-4}. The sign reversal of α_{zy} at about 60°K may be explained by the fact that, in about 1% of the sample, the magnetization assumes the direction of the applied field only close to the Curie point (this results in a change of polarization opposite to the magnetoelectric effect). The presence of ferromagnetism gives rise to a quadratic magnetoelectric

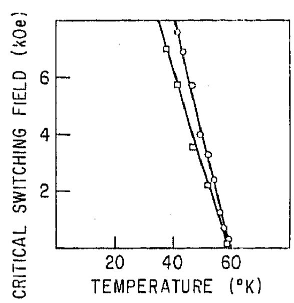

FIG. 5. Optically determined switching field versus temperature for the 180° magnetization reversal of two different ferromagnetic single domains of the same ferroelectric domain.

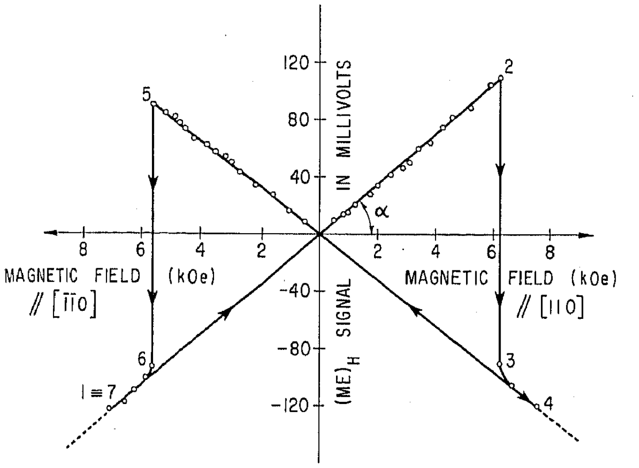

FIG. 4. Example of a quadratic magnetoelectric hysteresis loop with H along $\pm$[110] and P along [001] at 46°K. After annealing as in Fig. 3.

hysteresis loop (Fig. 4). The coercive field of these loops rises abruptly with falling temperature (Fig. 5) (as is typical for weak ferromagnets).

To summarize, it may be stated that $Ni_3B_7O_{13}I$ is a piezoelectric paramagnet above ~120°K, a piezoelectric-antiferromagnet from 64° to ~120°K, and a ferroelectric weak ferromagnet below 64°K.

ACKNOWLEDGMENTS

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[7] G. T. Rado and V. J. Folen, Phys. Rev. Letters 7, 310 (1961).