Magnetic properties of nickel-iodine boracite

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(Submitted May 28, 1974)
ZhETF Pis. Red. **20**, No. 5, 289–292 (September 5, 1974)

The magnetic properties of nickel-iodine boracite were investigated in the paramagnetic and weakly ferromagnetic states. A decrease and a reversal of the sign of the magnetization with increasing field were observed below 68 °K in a magnetic field exceeding 3 kOe along the axis perpendicular to the spontaneous magnetization direction, and when the sample vibrated along the magnetizing field.

Boracite crystals with the general formula $Me_3B_7O_{13}X$ (Me is a divalent ion of a metal from chromium to copper, X is one of the halogens—chlorine, bromine, or iodine) are ferroelectric.[1] Nickel-iodine broacite $Ni_3B_7O_{13}I$ (NIB) has a cubic high-temperature phase with space group T_d^5 (point symmetry $\bar{4}3m$) and a low-temperature phase with point symmetry $m'm2'$.

Faraday-effect investigations have shown[2] that a spontaneous magnetization appears in NIB along the [110] axis below 64 °K, and a spontaneous electric polarization appears in the perpendicular direction [001]. The presence of a broad magnetic-susceptibility maximum at 120 °K has suggested to the authors of[1] that an antiferromagnetic spin ordering is observed in NIB below this temperature. These investigations of the magnetic properties were carried out on polycrystalline samples. It was also found in[1] that below 64 °K the magnetoelectric effect is also produced in NIB. It was shown on the basis of an investigation of the Faraday effect that the magnetoelectric polarization reverses sign in a magnetic field H close to 6 kOe, and the magnetization is rotated at the same time into one of the directions $[1\bar{1}0]$ or $[\bar{1}10]$.

The present paper is devoted to the magnetic properties of single-crystal NIB in the temperature interval from 4.2 to 300 °K. The single crystals were grown by the method of chemical gas-transport reaction. The crystals were oriented in the magnetic field on the basis of their natural faceting. The crystal shape was such that measurements could be performed in two directions, parallel to [110] and in the direction perpendicular to it $[1\bar{1}1]$.

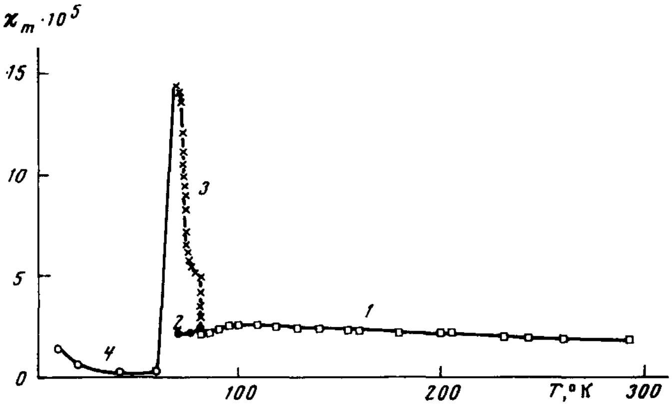

FIG. 1. Temperature dependence of the susceptibility of $Ni_3B_7O_{13}I$: 1—isotropic part of χ_m, 2—$H \parallel [1\bar{1}1]$, 3 and 4—$H \parallel [110]$.

The paramagnetic susceptibility χ_m of three NIB single crystals was investigated in the temperature interval from 70 to 300 °K at $H \parallel [1\bar{1}1]$ and from 80 to 300 °K at $H \parallel [110]$ by the magnetic-balance method in helium vapor and in nitrogen vapor. The measurements have shown that above 82 °K the susceptibility χ_m is isotropic, does not depend on the intensity of the applied field, and does not obey the Curie-Weiss law. In one of the three samples, a very broad maximum of χ_m was observed at 120 °K. This maximum was not observed for the other two samples (Fig. 1, curve 1), so that there are no grounds for assuming that antiferromagnetic spin ordering sets in below 120 °K.

The magnetization of NIB was investigated in an electromagnetic field up to 15 kOe, in the interval 69—82 °K, by the vibration-magnetometer method. The sample was in liquid air and the temperature was varied by pumping off the liquid-air vapor. The magnetic susceptibility calculated on the basis of the measurements is shown in the same figure (curve 2 for $H \parallel [1\bar{1}1]$ and curve 3 for $H \parallel [\bar{1}10]$). Measurements made by both methods along the $[1\bar{1}1]$ axis are in good agreement. The sharp increase of χ_m at $H \parallel [110]$ with decreasing temperature suggests that a magnetic phase transition takes place in these crystals near 68 °K.

The magnetization σ was measured in the interval 4.2—60 °K by the vibration-magnetometer method in a

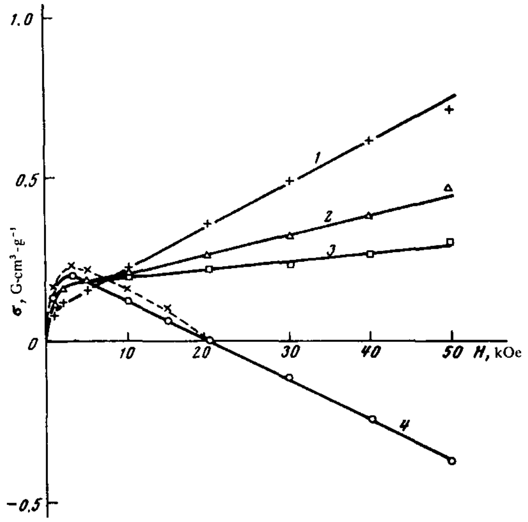

FIG. 2. Magnetization curves: $H \parallel [110]$; 1—10 °K, 2—20 °K, 3—40 and 60 °K; $H \parallel [1\bar{1}1]$: 4—20, 30, 40, and 60 °K; ○—increase of H, ×—decrease of H.

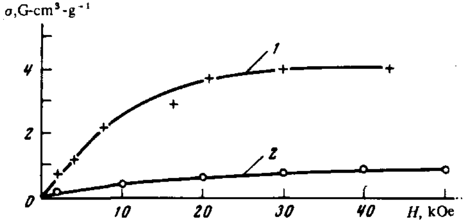

FIG. 3. Magnetization curves of $Ni_3B_7O_{13}I$ at 4.2 °K: 1—$H \parallel [1\bar{1}1]$, 2—$H \parallel [110]$.

superconducting solenoid in magnetic fields up to 50 kOe. Figure 2 shows the magnetization curves of NIB above 10 °K. The course of the curves at $H \parallel [110]$ shows that at $10 < T < 60$ °K the investigated crystals are weak ferromagnets with spontaneous magnetization 0.1—0.2 G-cm³/g. The value of χ_m calculated from the slopes of the linear part of the magnetization curves is shown in Fig. 1 (curve 4). Figure 3 shows the measured magnetization curves at 4.2 °K. At this temperature, the $\sigma(H)$ plot is reminiscent of the magnetization curve of ordinary ferromagnets or ferrimagnets.

An unusual behavior of $\sigma(H)$ is observed in the temperature interval 20—60 °K in a magnetic field directed along the $[1\bar{1}1]$ axis. Curve 4 of Fig. 2 shows that the magnetization in a field stronger than 3 kOe decreases with increasing field, and reverses sign above 20 kOe. The measurements of the magnetization curves were repeated by the usual ballistic method. The curves confirm qualitatively the behavior represented by curve 4 of Fig. 2, although no quantitative agreement of the curves was reached. This feature of the $\sigma(H)$ curves appears when the vibration of the sample in the vibration-magnetometer method, or the motion of the sample through the ballistic coil in the ballistic method, is parallel to the applied magnetic field. If the experiment is performed with the sample vibrating perpendicular to the magnetic field, the resultant magnetization curves are those customarily obtained for weak ferromagnetism.

To ascertain whether the observed effect is a consequence of screening of the magnetic field, we measured the qualitative temperature dependence of the electric resistance of NIB along the $[1\bar{1}1]$ axis. The measurements have shown that when the temperature is lowered from 300 to 4.2 °K the sample resistance increases from 10^5 to 10^{13} Ω. One cannot exclude the possibility that curve 4 of Fig. 2 is the consequence of the magnetoelectric effect.[2]

The authors are grateful to R. Z. Levitin, V. I. Sokolov, O. S. Galkina, and A. N. Bazhan for practical help and to A. P. Levanyuk for constant interest in the work.

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