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R. P. Chaudhury, B. Lorenz, Y. Y. Sun, L. N. Bezmaternykh, V. L. Temerov, and C. W. Chu

Magnetic phase diagram and magnetoelectric properties of $Ho_{0.25}Nd_{0.75}Fe_3(BO_3)_4$

R. P. Chaudhury,[1,a)] B. Lorenz,[1] Y. Y. Sun,[1] L. N. Bezmaternykh,[2] V. L. Temerov,[2] and C. W. Chu[1,3]
[1]*Department of Physics and TCSUH, University of Houston, Houston, Texas 77204-5002, USA*
[2]*Institute of Physics, Siberian Division, Russian Academy of Sciences, Krasnoyarsk 660036, Russia*
[3]*Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720, USA*

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The magnetic and magnetoelectric properties of a single crystal of $Ho_{0.25}Nd_{0.75}Fe_3(BO_3)_4$ have been investigated along the main crystallographic directions. The spontaneous polarization starts increasing below the Neel temperature $T_N \sim 32$ K and it displays a sudden drop at 4.8 K. This sharp decrease suggests the existence of a spin reorientation phase transition. In this compound, both spontaneous polarization and the polarization due to the magnetoelectric effect exist. Detailed study of the effect of magnetic field on the polarization and the spin rotation transition has been performed. Specific heat and magnetization measurements show characteristic anomalies at both magnetic transitions. The magnetic field (H)-temperature phase diagram has completely been resolved for $H \| c$ and $H \| a$ axes. © *2010 American Institute of Physics*. [doi:10.1063/1.3362915]

The magnetoelectric (ME) effect is the induction of electric polarization (magnetization) by magnetic (electric) field.[1] Because of such cross correlation of magnetic and dielectric properties, these ME materials have attracted much attention since they bear the potential to be used as a memory or sensor device. Some of the rare earth iron borates [$RFe_3(BO_3)_4$] show ME properties.[2–4] Therefore, this class of compounds has attracted significant interest.

In the family of $RFe_3(BO_3)_4$, neodymium iron borate $NdFe_3(BO_3)_4$ (Ref. 4) and holmium iron borate $HoFe_3(BO_3)_4$ (Refs. 5 and 6) have attracted recent attention. Both of these compounds posses rhombohedral structure with the space group $R32$. $HoFe_3(BO_3)_4$ is unique among the $RFe_3(BO_3)_4$ since it shows spontaneous polarization, $P(T)$ (polarization that appears upon changing temperature even at zero magnetic and electric fields) below T_N which increases with decreasing temperature and suddenly drops to zero at the spin reorientation transition $T_{SR} \sim 5$ K. This kind of spontaneous polarization was not observed in other rare earth iron borates. On the other hand, $NdFe_3(BO_3)_4$ shows large polarization in external magnetic field; however, no spontaneous polarization and spin reorientation transition exists in this compound. It is interesting to look for the ME properties of the solid solution $Ho_{1-x}Nd_xFe_3(BO_3)_4$.

Large $Ho_{0.25}Nd_{0.75}Fe_3(BO_3)_4$ single crystals have been grown using $Bi_2Mo_3O_{12}$ flux.[7] Small pieces of samples were cut and oriented using single crystal x-ray spectroscopy. The pyroelectric current was measured by the electrometer K6517. Temperature and field control were provided by the Physical Property Measurement System (Quantum Design). Magnetic measurements were done in the superconducting quantum interference device magnetometer (Quantum Design).

Low field susceptibility data along the a axis (χ_a) is shown in Fig. 1. It clearly shows two distinct anomalies. The Neel transition is visible as a change in slope at $T_N \sim 32$ K. At low temperature, χ_a shows a sharp change near $T_{SR} \sim 5$ K. In analogy to similar magnetic transitions observed in $GdFe_3(BO_3)_4$ and $HoFe_3(BO_3)_4$ that have been identified as spin rotation transitions, we suggest that the anomalies at T_{SR} in $Ho_{0.25}Nd_{0.75}Fe_3(BO_3)_4$ indicate a spin reorientation. The thermodynamic signature of both transitions was also investigated by heat capacity (C_P) measurement (shown in the inset of Fig. 1). The λ shaped peak at T_N indicates the second order phase transition, whereas the sharp peak of $C_P(T)$ at the spin reorientation transition as well as the 0.1 K temperature hysteresis of the magnetic susceptibility indicates the first-order nature of the phase transition at T_{SR}. Both χ_a and χ_c show a very sharp change in magnetization at T_{SR} (Fig. 2). The step of χ_a is positive with decreasing T at low magnetic field, whereas it turns negative for 3 kOe

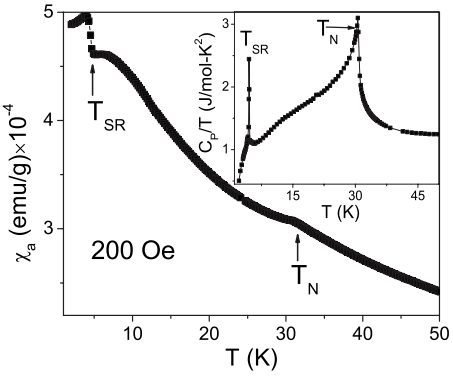

FIG. 1. Magnetic susceptibility of $Ho_{0.25}Nd_{0.75}Fe_3(BO_3)_4$ measured with field applied along a axis (χ_a). Inset shows the heat capacity and C_P data.

[a)]Electronic mail: rajit.chaudhury@mail.uh.edu. Also at Department of Physics, University of Houston, Houston, Texas 77204-5002, USA.

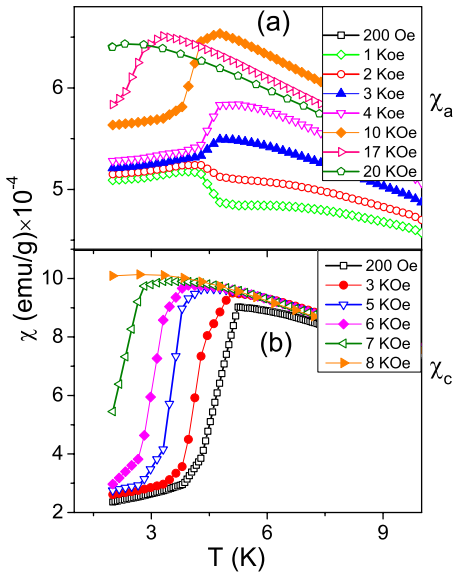

FIG. 2. (Color online) Susceptibility at different magnetic fields applied along (a) a axis (χ_a) and (b) c axis (χ_c).

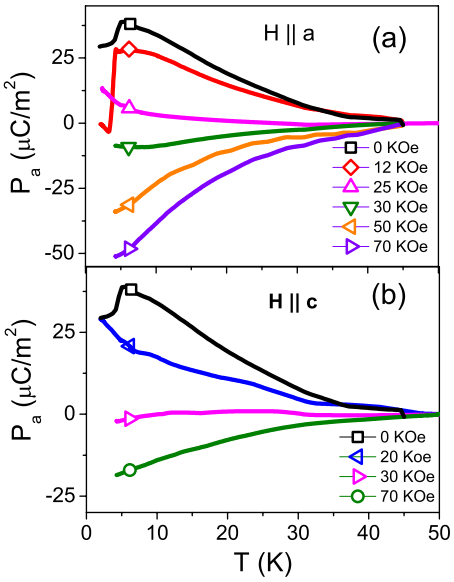

FIG. 4. (Color online) Temperature dependence of $P_a(T)$ at different magnetic fields: (a) $H \| a$ and (b) $H \| c$.

$< H_a < 17$ kOe. The evolution of T_{SR} with magnetic field (H) applied along the a and c axes are shown in Fig. 2. Both of the susceptibility measurements (χ_a and χ_c) clearly show the shift in T_{SR} to lower temperature with increasing H. From these magnetization data, the H-T phase diagram shown in Fig. 3 is constructed. The magnetic phases above and below T_{SR} are designated as AFM2 and AFM1, respectively.

Upon decreasing temperature, $Ho_{0.25}Nd_{0.75}Fe_3(BO_3)_4$ shows a spontaneous polarization measured along the a axis, $P_a(T)$, at zero magnetic field. $P_a(T)$ starts increasing below 40 K and reaches a maximum at T_{SR} and then suddenly drops to a finite value at 2 K (Fig. 4). If a magnetic field is applied during cooling the polarization below T_N decreases and becomes negative at fields above 25 kOe (Fig. 4). This can be attributed to the quadratic ME coupling which has been discussed recently.[4] At higher field, the ME coupling dominates over the spontaneous polarization and that causes $P_a(T)$ to change sign. This complex behavior of the polarization is unusual and not common to the majority of ME compounds. Isothermal polarization data $\Delta P_a(H)$ are displayed at different temperatures in Fig. 5, showing the change in P with H, $\Delta P = P(H) - P(0)$. When the field is applied along the a axis, $\Delta P_a(H_a)$ shows a steplike change at temperatures below 5 K [Fig. 5(a)], which is consistent with the anomalies observed in $P_a(T)$, $\chi(T)$, and $C_P(T)$ at T_{SR}. With the magnetic field applied along the c axis, $\Delta P_a(H_c)$ displays a similar complex behavior. Below 5 K $\Delta P_a(H_c)$ increases first but decreases quickly at higher fields with the transition from the AFM1 into the AFM2 phase. The field-induced ME effect results in negative values of ΔP_a with increasing field. The ME effect becomes negligibly small at temperatures above 80 K.

The ME polarization along the c axis in fields parallel to c, shown in Fig. 6(b), qualitatively shows the same field dependence as the a axis polarization [Fig. 5(b)]. However, in a axis magnetic fields, $\Delta P_c(H)$ decreases first, passes through a minimum, and increases with further increasing H_a [Fig. 6(a)]. The sharp change in the polarization across the

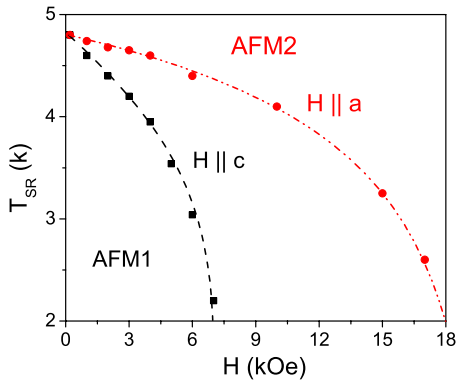

FIG. 3. (Color online) Magnetic phase diagram of $Ho_{0.25}Nd_{0.75}Fe_3(BO_3)_4$ at low temperature.

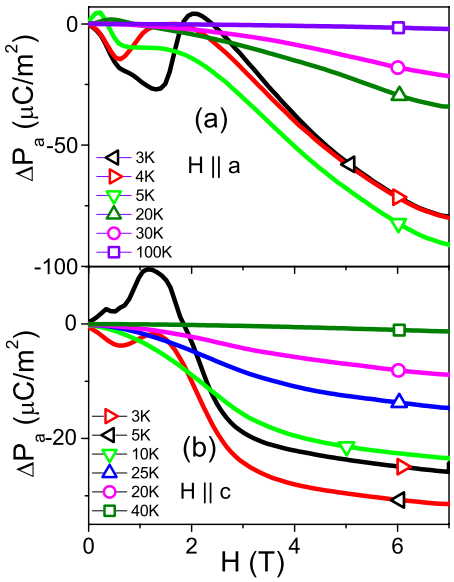

FIG. 5. (Color online) Change in isothermal polarization $\Delta P_a(H) = P(H) - P(0)$, with field at different temperatures. (a) $H \| a$ and (b) $H \| c$ axis.

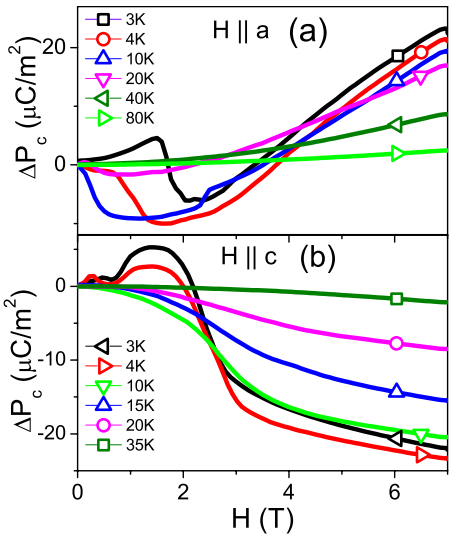

FIG. 6. (Color online) Change in isothermal polarization $\Delta P_c(H) = P(H) - P(0)$, with field at different temperatures. (a) $H \| a$ and (b) $H \| c$ axis.

spin reorientation transition is also resolved in the field dependence of $\Delta P_c(H)$. The complex field dependence of the ME polarization along both crystalline orientations is apparently due to the superposition of a spontaneous contribution, possibly due to the internal magnetic field originating from the magnetic order, and a ME contribution due to the external fields. Further investigations are necessary to fully understand the ME properties of this compound.

In summary, we have studied the thermodynamic, magnetic, and ME properties of $Ho_{0.25}Nd_{0.75}Fe_3(BO_3)_4$. A spin rotation transition is observed below 5 K and it is suppressed by the external magnetic fields oriented along *a* and *c* axes. Magnetic phase diagram is completely resolved. The complex temperature and field dependence of polarization indicates the intricate interaction of internal and external magnetic fields and their effects on the ME response. The solid solution $Ho_{0.25}Nd_{0.75}Fe_3(BO_3)_4$ exhibits typical features of pure $NdFe_3(BO_3)_4$ and $HoFe_3(BO_3)_4$. A detailed study of the magnetic structure of this compound is needed to understand the complex ME behavior.

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