Magnetic properties and phase transitions of iron boracites, Fe$_3$B$_7$O$_{13}$X (X = Cl, Br or I)

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Abstract

Magnetic measurements for Fe-X (X = Cl, Br, and I) boracites at 3.6-300 K were performed. Temp. dependence of the magnetization and magnetic susceptibility for all compds. shows an antiferromagnetic order with Neel temps. of 11.5 K, 18.5 K, and 31 K, resp. The Curie-Weiss law holds for the temp. dependence of the magnetic susceptibility up to room temp. The effective magnetic moment obtained from the inverse susceptibility slope, for all compds., is higher than but close to the spin only value of the Fe$^{2+}$ ion. From hysteresis measurements the temp. dependence of the coercive field was obtained, the 4 K value of the coercive field of Fe-Cl being approx. 5 times smaller than that of Fe-Br boracite and 25 times smaller than that of Fe-I boracite. For Fe-I the mm21' $\square$ mL' $\square$3 mL' phase transitions were evidenced by magnetic measurements, as a small thermal hysteresis in the temp. dependence of the reciprocal magnetization. [on SciFinder(R)]

Reference

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Magnetic properties and phase transitions of iron boracites, Fe$_3$B$_7$O$_{13}$X (X = Cl, Br or I)

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MAGNETIC PROPERTIES AND PHASE TRANSITIONS OF IRON BORACITES, 
Fe₃B₇O₁₃X (X = Cl, Br OR I)

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Magnetic measurements for Fe-X (X = Cl, Br and I) boracites in the temperature range of 3.6–300K have been performed. Temperature dependence of the magnetization and magnetic susceptibility for all compounds shows an antiferromagnetic order with Neél temperatures of 11.5K, 18.5K and 31K, respectively. The Curie-Weiss law holds for the temperature dependence of the magnetic susceptibility up to room temperature. The effective magnetic moment obtained from the inverse susceptibility slope, for all compounds, is higher than but close to the spin only value of the Fe²⁺ ion. From hysteresis measurements the temperature dependence of the coercive field was obtained, the 4K value of the coercive field of Fe-Cl being approximately 5 times smaller than that of Fe-Br boracite and 25 times smaller than that of Fe-I boracite. For Fe-I the mm21' ⇔ ml' ⇔ 3ml' phase transitions have been evidenced by magnetic measurements, as a small thermal hysteresis in the temperature dependence of the reciprocal magnetization.

Keywords: Magnetic measurements; Fe-Cl; Fe-Br; Fe-I; boracites

1. INTRODUCTION

Boracites, described by the general chemical formula M₃B₇O₁₃X (abbreviated M-X), where M stands for a divalent metal ion and X for a halogen, have intensively been studied over the past 30 years because of their interesting multiferroic properties. Most of the boracites transform from a cubic high temperature phase (Shubnikov point group 43 ml') to a fully

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ferroelectric/fully ferroelastic orthorhombic low temperature phase (except
for Cr-Cl boracite, with an intermediate non-polar 42 ml' phase [2]) or to a
sequence of phases with point groups mm2'1', 3ml' (for some boracites an
intermediate ml' phase is formed between mm2'1' and 3ml'). These latter
boracites are usually referred to in the literature as “trigonal boracites”. [3]

At low temperatures, in most of the boracite homologues containing 3d-
transition metal ions one can observe the coexistence of ferroelectricity and
ferromagnetism in the same phase, giving necessarily rise - for symmetry
reasons - to the linear magnetoelectric effect.[4] The knowledge of the
magnetic properties of those compounds is therefore very important for a
better understanding of the multiferroic properties.

So far magnetic susceptibility measurements on Fe-Cl and Fe-I above
80K,[4] on Fe-Cl above 4K [5] and hysteresis loops on Fe-Cl, Fe-Br and
Fe-I at 4K[6] have been reported. With a view to magnetoelectric measure-
ments on ferroelectric single domain crystals of Fe-Cl, Fe-Br and Fe-I, the
present study aimed at the determination of the coercive field and
magnetization versus temperature. In particular, it appeared of interest to
know whether the magnetization versus temperature might possibly reflect
spin ordering phenomena analogous to those found for cobalt boracites by
magnetic measurements [7] and manifested for example also by “Schottky
type” specific heat anomalies.[8] Different from the Co-Br and Co-I
compositions, iron boracites only show a slight shoulder in the temperature
dependence of the specific heat, very close to the Néel transition temper-
analogous origin. Because of the large temperature intervals between two
successive measured points, such anomalies were not observed in previous
magnetic investigations of the iron boracites. [4,5,6] For Fe-I boracite the
influence of the mm2'1' ⇔ ml' ⇔ 3 ml' phase transitions on the magnetic
properties in the paramagnetic range was also studied.

2. EXPERIMENT

The powder samples were obtained by crushing ferroelectric polydomain
single crystals of 1 – 3 mm size, obtained by gas phase transport reactions with
the starting constituents MeO, B2O3 and the metal halides[10] (this method has
permitted to obtain almost all members of the boracite series). The mass of
the powder used for magnetic measurements was about 70 mg. The magnetic
properties were measured in the temperature range of 3.6K – 300K with a
vibrating sample magnetometer (Model 155, Princeton Applied Research),
using fields up to 18.5kOe. Hysteresis loops for different temperatures were registered with a HP7090A Measurement Plotting System.

Three different procedures methods were used to measure the temperature dependence of magnetization in different magnetic fields:

1. zero field cooling down to 3.6K, "saturation" at 18.5kOe at 3.6K
2. field cooling (H = 16kOe) down to 3.6K,
3. zero field cooling down to 3.6K,

All the measurements were performed upon heating (around 5K/min.) and for Fe-I also upon cooling in the temperature range of 230–170K.

3. RESULTS

The temperature dependence of the magnetization (for different magnetic fields; procedure 1) and the reciprocal susceptibility are presented in Figure 1 (for Fe-Cl), Figure 2 (for Fe-Br) and Figure 3 (for Fe-I). The inset on Figure 3 shows the detail for Fe-I in the interval of 170–230K. Figure 4 presents the temperature dependence of the magnetization for Fe-I in the temperature range of 6–40K. In Figure 5 the temperature dependence of the coercive field is presented for all investigated compounds.

FIGURE 1 Temperature dependence of the magnetization (up to $T_N$) and inverse susceptibility (from $T_N$ to room temperature) for Fe-Br boracite.
FIGURE 2 Temperature dependence of the magnetization (up to $T_N$) and inverse susceptibility (from $T_N$ to room temperature) for Fe-Br boracite.

FIGURE 3 Temperature dependence of the magnetization (up to $T_N$) and inverse susceptibility (from $T_N$ to room temperature) for Fe-I boracite. The inset enlarges the 170K – 230K temperature range for the $3m\gamma' \leftrightarrow m\gamma' \leftrightarrow nm2\gamma'$ phase transitions.
FIGURE 4 Temperature dependence of the magnetization of Fe-I boracite in the magnetic phase. The sample was cooled without magnetic field down to 3.6K, "saturated" at 18.5kOe, then the field was selected to 0.5kOe.

FIGURE 5 Temperature dependence of the magnetic coercive field for iron boracites.
4. DISCUSSION

4.1. Magnetic Phase Transitions

For all studied compounds the paramagnetic phases can be described by the Curie-Weiss law down to the Néel temperature $T_N$, in agreement with literature data for temperatures higher than 300K.$^{[4, 5, 6]}$ No extra peaks or changes of slope were detected in the range $T_N < T < 300$K except for Fe-I (see below and Fig. 3), and no anomaly in the temperature dependence of the magnetization up to $T_N$ was found (also except for Fe-I). Thus for Fe-Cl and Fe-Br boracites which show a weak, shoulder-like specific heat anomaly closely below $T_N$, no corresponding anomaly could be evidenced by magnetic measurements - procedures 1, 2, 3, probably because the Néel and anomaly temperatures are too close to one another or the effect on magnetization is too small to be distinguished from the noise. For Fe-I, we cannot be sure whether the small anomalies in the temperature dependence of the magnetization (marked by arrows 1, 2 and 3 in Fig. 4) have the same origin as the “Schottky type” anomaly in the specific heat or represent reorientation of the magnetic domains with increasing temperature. Similar anomalies were evidenced by the temperature dependence of the spontaneous polarization$^{[11]}$ and birefringence$^{[12]}$ but between 15K and 20K.

The negative Curie-Weiss temperatures (approximately $-16$K for Fe-Cl, $-36$K for Fe-Br and around $-86$K $-110$K for Fe-I) indicate a dominating antiferromagnetic coupling at low temperatures.

From hysteresis loop measurements in the magnetic phase, a weak ferromagnetism was found to be superposed on the antiferromagnetic order. The temperature dependence of the coercive field is presented in Figure 5. Starting from a coercive field of 0.4kOe for Fe-Cl, 2.4kOe for Fe-Br and more than 8kOe for Fe-I at 3.6K, an exponential decrease was found for all compounds with rising temperature except for Fe-I where a nearly linear increase of the coercive field is observed with decreasing temperature, similar to Ni-I boracite.$^{[13]}$ These values may be affected by some small negative errors because of the relatively long response time of magnetization to the change in magnetic field strength (sweep rate: 40 min. per loop).

From the $M(T')$ curves in different fields and $T$ close to $T_N$ the spontaneous magnetic moment was obtained by zero field extrapolation, as well as the magnetic transition temperatures, $T_N$ (approximately $11.5$K, $18.5$K and $31$K for Fe-Cl, Fe-Br and Fe-I, respectively).
4.2. Effective Magnetic Moments

The effective magnetic moments (around 5.6\(\mu_B\)) obtained from the slope of the temperature dependence of the inverse susceptibility are larger than – but of the same order of magnitude as – the spin only value of the Fe\(^{2+}\) ion (4.9\(\mu_B\)) and very close to those reported in the literature.\[^4,6\]

In the case of Fe-I the effective magnetic moment value for the Fe\(^{2+}\) ions decreases very slightly from 5.7\(\mu_B\) in the 3ml' phase to 5.6\(\mu_B\) in the mm 21' phase. However, the much smaller slope of the temperature dependence of the reciprocal susceptibility between 190K and 213K in the ml' phase region cannot reasonably be attributed to a pure ml' phase with a change in magnetic moment of Fe\(^{2+}\), but is probably due to a mixture of phases, consistent with the extremely large thermal hysteresis behavior of the 3ml' \(\leftrightarrow\) ml' \(\leftrightarrow\) mm 21' transitions observed on a single crystal by X-rays\[^14\] and on powders around 200K by the Mössbauer effect.\[^15\]

4.3. Structure Phase Transitions in Fe-I

In the paramagnetic range between 170K and 230K, a change of slope of the reciprocal susceptibility was found for Fe-I. The same phenomenon was also evidenced upon cooling but at lower temperatures, giving rise to a hysteresis loop in the temperature dependence of reciprocal susceptibility (inset of Fig. 3).

This behavior can be correlated with the ferroelectric/ferroelastic 3ml' \(\leftrightarrow\) ml' \(\leftrightarrow\) mm 21' phase transitions found by Kobayashi \emph{et al.}\[^14\] by X-ray analysis and by Ye \emph{et al.}\[^11\] by optical domain examination, dielectric and polarization measurements. The reported phase transition temperatures are summarised in the following together with the results of this work:

Upon cooling:

\begin{center}
\begin{tabular}{|c|c|c|}
\hline
Reference & 3ml' & ml' & 3ml' \\
\hline
this work & 191K & 181K & \\
\hline
\end{tabular}
\end{center}

Upon heating:

\begin{center}
\begin{tabular}{|c|c|c|}
\hline
Reference & 3ml' & ml' & mm 21' \\
\hline
[14] & 205K & 218K & \\
this work & 190K & 210K & \\
\hline
\end{tabular}
\end{center}
One can see that an unusually large thermal hysteresis for the phase transitions was observed by X-ray\textsuperscript{[14]} and magnetic measurements. However, the dielectric constant and the spontaneous polarization, measured under simultaneous optical control of the domain state, shows clear discontinuous variation of first-order character for both phase transitions with smaller thermal hysteresis.\textsuperscript{[11]}

4.4. Magnetic Domain Switching

The weakly ferromagnetic monoclinic phase of boracites with Shubnikov point group $m$ is known to be fully ferroelectric/fully ferroelastic and partially ferromagnetic.\textsuperscript{[1, 12]} Its domain behavior has extensively been described in the case of Fe-I\textsuperscript{[12]} and is similar to that of Co-Cl.\textsuperscript{[16]} For that $m$ phase, three types of ferromagnetic coercive field are imaginable:

First, by applying a magnetic field along a pseudo-rhombohedral (pseudo-cubic [111]) direction, i.e. quasi-parallel to the spontaneous polarization and quasi-perpendicular to the spontaneous magnetization vector, a ferroelastically fully coupled reorientation of the spontaneous polarization along one of the three other pseudo-cubic space diagonals is in principle possible, provided a very strong magnetic anisotropy (spin-lattice coupling) would exist. However, because of the known very high ferroelectric coercive fields (about 320 kV/cm and 50 kV/cm at 298K, for Fe-Cl and Fe-Br, respectively\textsuperscript{[17]}), such a coupling will be completely blocked at low temperatures and increasing the magnetic field will certainly lead first to a magnetic symmetry change induced by the magnetic field rather than to a displacement of the ferroelectrically active ions from their deep potential wells.

Second, a ferroelectric/ferroelastic single domain of the paramagnetic rhombohedral $3ml'$ phase can split up into three ferroelastic domains of the ferromagnetic monoclinic phase $m$ with their magnetization vector lying perpendicular to one of the mirrors having survived from the original $3ml'$ phase. For Fe-I\textsuperscript{[12]} and Co-Cl\textsuperscript{[16]} boracites it has been shown that weak magnetic fields are sufficient for reorienting these ferromagnetic/ferroelastic domains by 60° or 120° when rotating the field in the (111)$_c$-plane containing the magnetization vectors.

The temperature dependence of that “reorientation coercive field” could for example be determined magnetoelectrically - as has been done for Co-Cl boracite\textsuperscript{[16]} - or by means of a torque experiment on a pseudorhombohedral single domain platelet.\textsuperscript{[18]}
Third, a further coercive field can be defined, linked to the 180° magnetization reversal in one of the three previously described ferroelastic ferromagnetic domains.

Thus in the presented hysteresis loop experiments we can admit that both ferroelastic 60° and 120°-reorientation switching, as well as non-ferroelastic 180°-switching of the spontaneous magnetization, are operating.

The magnetoelectric properties of the iron boracites, using (1 1 l), and (1 lo),-cut ferroelectric/ferroelastic single domain platelets, are under study. Further investigation on the 3mI' ↔ ml' ↔ mm21' phase transition sequence and its potential influence on the MEH bilinear effects would be rewarding.

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