PHYSICAL PROPERTIES OF SOME FERROIC Me$_3$B$_7$O$_{13}$X BORACITES

A.G. Castellanos-Guzmán*, Laboratorio de Investigación en Materiales. DIP-Cucei,
Universidad de Guadalajara, Guadalajara, Jalisco, México
E. Muñoz Sandoval y R. Escudero, Instituto de Investigaciones en Materiales,
Universidad Nacional Autónoma de México, México D.F.

ABSTRACT

In this work a short overview is presented on various physical properties of ferroic boracites. Precise measurements of low and high applied field magnetization of single crystals of ferroic Mn$_3$B$_7$O$_{13}$Br boracite by SQUID magnetometer are reported. We found that at low temperatures (Tc < 15 K) the magnetic susceptibility is strongly dependent on the mode we cool the crystals. According to the Curie law the susceptibility of this compound is strongly antiferromagnetic, however, at about 15 K Mn$_3$B$_7$O$_{13}$Br boracite shows an increase in the dc-susceptibility which seems to be a ferromagnetic-like transition.

Key words: Boracite crystals, ferroelectric, magnetically ordered materials, phase transitions, spontaneous magnetization, weak ferromagnetism, antiferromagnetism.

RESUMEN

Se describen brevemente varias propiedades físicas de las boracitas ferroicas y se reportan mediciones precisas de la magnetización a campos bajo y alto de monocristales de la boracita Mn$_3$B$_7$O$_{13}$Br por medio de SQUID. Encontramos que a bajas temperaturas (T$_c$ < 15 K) la susceptibilidad magnética de estos cristales depende fuertemente del modo en que se enfrían. De acuerdo a la ley de Curie, este compuesto es fuertemente antiferromagnético, sin embargo a 15 K Mn$_3$B$_7$O$_{13}$Br muestra un incremento en la susceptibilidad que semeja una transición ferromagnética débil.

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1. INTRODUCTION

The crystalline family known as *halogen boracites*; with more than 25 isomorphous compounds all with general formula Me$_3$B$_7$O$_{13}$X, where Me is one of the divalent metals Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn or Cd and X is usually Cl, Br and I, is a very interesting one due to its unusual ferroelectric, ferroelastic, electro-optical and magnetoelectric properties[1]. Boracites have been intensively studied since Ascher **et al**. [2] gave indisputable demonstration of Ferroelectricity in Ni$_3$B$_7$O$_{13}$Cl. All halogen boracites have a piezo-electric high temperature phase of cubic prototype symmetry (space group F43c) and most display a phase transformation from the cubic phase to a *pyroelectric, fully ferroelastic/fully ferroelectric* ortho-rhombic phase (space group Pca2$_1$). Additional phase transitions have been reported for five compositions to point groups m and 3m[1]. The transition temperatures from a piezoelectric to a pyroelectric phase (T$_c$), vary amply from 60 K to 800 K depending on composition but follows the order Cl > Br > I.

The interplay of ferroelectricity and magnetism in materials has been an interesting topic since the first report by Smolensky and Joffe on the synthesis of antiferromagnetic-ferroelectric perovskites [3]. The discovery of both ferroelectricity and weak ferro-magnetism in Ni$_3$B$_7$O$_{13}$I boracite [4-5] attracted the attention of researchers on this large family of compounds, and since the first report of Ascher **et al**. [4] on magnetic susceptibility measurements of several boracites, the magnetic order has been confirmed in more than fourteen compositions of this interesting family and at least four different types of transitions from paramagnetic to ferro or antiferro-magnetic phases have been reported [5]. However, to our knowledgement very few attemps have been made to look for magnetic phase transitions in compositions with Mn as paramagnetic ion.

Manganese bromine boracite, Mn$_3$B$_7$O$_{13}$Br (hereafter abbreviated as Mn-Br) undergoes a first order phase transition at about 538 K from a paraelectric cubic phase (space group F43c) to an orthorhombic fully ferroelectric/fully ferroelastic phase (space group Pca2$_1$) which currently is associated with a doubling of the primitive cell and a threefold splitting of the Mn positions. The crystal structure of both phases have recently been determined by Crottaz **et al**. [6], and by Kubel **et al**. [7]. We have made careful measurements of the

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*__Email__:gcastel@cucea.udg.mx

spontaneous magnetization of Mn-Br single crystals as a function of temperature and applied magnetic field. Measurements of magnetic susceptibility versus temperature, and as a function of the applied field are also reported.

2. EXPERIMENTAL

Single crystals of Mn-Br were grown by the three-crucibles method of Schmid[8] that yielded crystals with masses up to 50 mg in weight and dimensions up to 4x3x1 mm^3. For the synthesis work, the reactants are placed in three fused silica crucibles spatially separated by quartz rods (3 mm in diameter). The three crucibles contain boron oxide, metal oxide and metal bromide respectively. The crucibles are then inserted into a quartz ampoule which is sealed under a vacuum of approximately 0.02 mbar. Chemical transport reactions were carried out by heating the ampoule at about 900 Celsius in a vertical furnace resistance-heated, over a period of 72 hours and then cooling the ampoule freely down to room temperature. Two crystals, cut from as-grown crystals parallel to $(100)_{cub.}$ and $(101)_{cub.}$ facets and masses of 42.7 mg. and 10.2 mg. respectively were selected for this study. Temperature and field-dependent magnetization data were measured using a Quantum Design Superconducting Interference Device magnetometer (MPMS-SQUID). Because the Mn-Br samples had well developed facets we could easily align them in the MPMS with different orientations. Zero-field-cooled (ZFC) and field-cooled (FC) scans were used for magnetization measurements from 2 K to 300 K and from 300 K down to 2 K respectively.

3. RESULTS AND DISCUSSION

Figure 1 shows results of all our initial measurements of the magnetization as a function of temperature in two Mn-Br single crystals under an applied field of 100 G, in a ZFC and FC sequences.
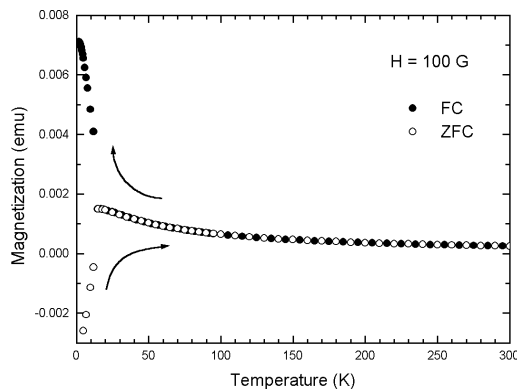
Figure 1. Temperature dependence of magnetization in Mn-Br single crystals.

A negative value of magnetization was found after ZFC measurements which was suspicious to us. Previous magnetic measurements made also by means of a SQUID magnetometer on Mn-I single crystals[9] reported that *for ZFC scans the magnetization adopted a preferred direction opposite to that enforced by FC scans*.

In order to clarify this behaviour we made careful measurements of magnetization at low applied magnetic fields on Mn-Br crystals. The results of this study showed that Mn-Br boracite is rather sensitive to remanent fields present in SQUIDs, which has an opposite direction to the magnetization and thus the latter increases in the direction of the field. The residual magnetic fields present in the MPMS system are one of the most common problems found in low field SQUID measurements. These fields can lead to spurious results such as, for example, a negative value of magnetization which is absolutely false. In order to test if this was the case for Mn-Br, as well as to eliminate the remanent fields from our measurements, we performed a fluxgate operation on the MPMS and magnetization measurements, on the same samples of Mn-Br as in Figure 1, were repeated. Results of these measurements at zero applied magnetic field and at different cooling rates are shown in Figure 2.
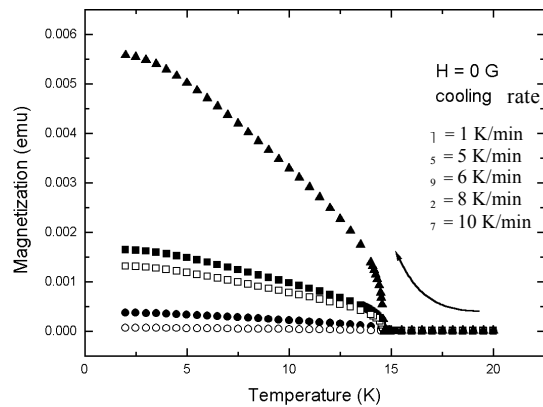
Figure 2. SQUID measurements of magnetization in Mn-Br with different cooling rates.

Figure 2 shows the thermal behaviour of magnetization (zero applied magnetic field) at different cooling rates in Mn-Br in the temperature region between 20 and 2 K, after having applied a fluxgate operation to the measuring system. These results confirm that the remanent fields in the SQUID caused a negative value of magnetization. It is also seen in this figure that the magnitude of magnetization in Mn-Br depends on the cooling rate. We believe that by cooling the Mn-Br crystals below the transition temperature (T_c = 14.5 K in Mn-Br) without an applied field its magnetic properties are determined in a metastable zone whose order

parameter depends on the cooling rate. It also could be that the exchange interactions between the Mn atoms are very sensitive to the way the sample is cooled. Such an explanation seems to be supported by the results of three different ZFC susceptibility measurements made on the same Mn-Br sample (Figure 3) at three different cooling rates. Previous to the ZFC sequence a magnetic field of 100 G was applied to the samples. In figure 3, three different types of behaviour are observed. In order to interpret the magnetic behaviour of Mn-Br it is necessary to recall that previous studies on boracites [4-5,9-10] have shown that among the three metal sites the Mn ions can form only two types of magnetic moments: One in mutually perpendicular Mn(2)-X-Mn(3) chains in the (001)-orthorhombic plane and another in the Mn(1)-X-Mn(1) chains along the [001] orthorhombic direction. and the magnitude of the magnetic effective moments is $3.8(2)\mu_B$ /atom and $5.4\ (2)\mu_B$/atom respectively [9].
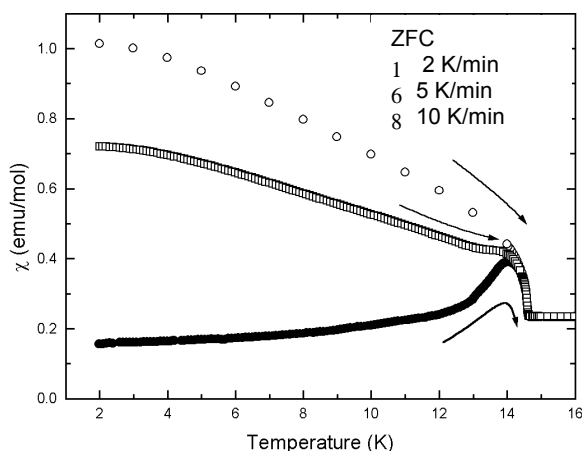

Figure 3. ZFC susceptibility measurements on Mn-Br boracite.

In Mn-Br, we believe that the interaction between Mn(i) and Mn(i) (i = 1, 2 or 3) is strongly antiferromagnetic. The Mn(2) and Mn(3) atoms feel a ferromagnetic interaction when they are near-neighbors and an antiferromagnetic one if they are next-near neighbors in the plane ab. The situation is different with Mn(1) and Mn(2) or Mn(3) atoms, since in this case there should be an antiferromagnetic interaction, situation which is frustrated. In Mn-I boracite, Crottaz et. al.[9] found that Mn(1) is canted by 12.0(3)° from the a axis in the (101) orthorhombic plane, so these authors deduced that such an arrangement is related to the two-steps onset of magnetic order at higher temperatures due to the frustration of the antiferromagnetic interactions between metal (2) and metal (3). In Mn-Br we think that a strong frustration produces a great instability below T_c and the direction of Mn(1) is really determined by the way the sample is cooled (rate of cooling). It is also clear that if a very small magnetic field is applied to the sample, the antiferromagnetic order is also affected

by this frustration. It is also factible that when the sample is cooled from a temperature above the critical temperature, the position of the magnetic moments of some Mn(1) atoms is just frozen-in at the transition temperature and the other Mn atoms determine the ferromagnetic signal. If the cooling process is very fast all the magnetic moments on Mn(1) atoms are frozen and thus no ferromagnetic signal is obtained. Finally, if the rate of cooling is small some of the Mn(1) atoms order antiferro-magnetically and some others do not manifest an antiferromagnetic alignment and thus a ferro-magnetic signal is produced. This is a plausible explanation of the observed behaviour in Mn-Br under ZFC measurements.

The temperature dependence of the magnetic susceptibility of Mn-Br under different small magnetic fields is shown in Figure 4. Before measurements, the sample was cooled from 300 K down to 2 K with a cooling rate of 10 K/min. Under a field of 20 G an increase of the magnetic susceptibility is observed with a broad maximum at the transition temperature (T_c = 14.6 K) and it decreases after the transition. However, under a field of 2 G the magnitude of the magnetic susceptibility is much higher than in the former case, it decreases smoothly to a minimum at the vicinity of the transition, reaching a maximum at T_c, a temperature at which falls down abruptly.
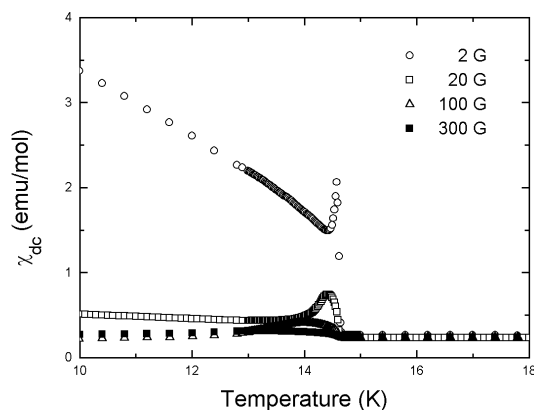

Figure 4. χ magnetic susceptibility versus temperature in Mn-Br.

The influence of the applied magnetic field on the susceptibility is dramatically shown in Figure 5. Figure 5a shows the ac-susceptibility for FC measurements whilst Figure 5b corresponds to ZFC measurements. By increasing the field the magnitude of the magnetic susceptibility in Mn-Br decreases below the transition temperature in both types of scan. However with fields higher than 0.5 T this effect disappears and the magnitude of the magnetic susceptibility is lower than in the previous cases, with a smooth kink at the transition temperature. There is a small influence of high applied magnetic fields on both types of scan as it should be expected for an antiferromagnetic system,

and there is hardly a difference between the two types of measurements. However, at low fields a great difference is observed between them. The shape of the susceptibility curve for magnetic fields higher than 0.5 T is typical of antiferromagnetics. We believe that there must be a kind of critical magnetic field at which Mn-Br experiences a transition from a weak ferromagnetism to a conventional antiferromagnetic ordering. However, we could not find such a value in our experiments on Mn-Br boracite.
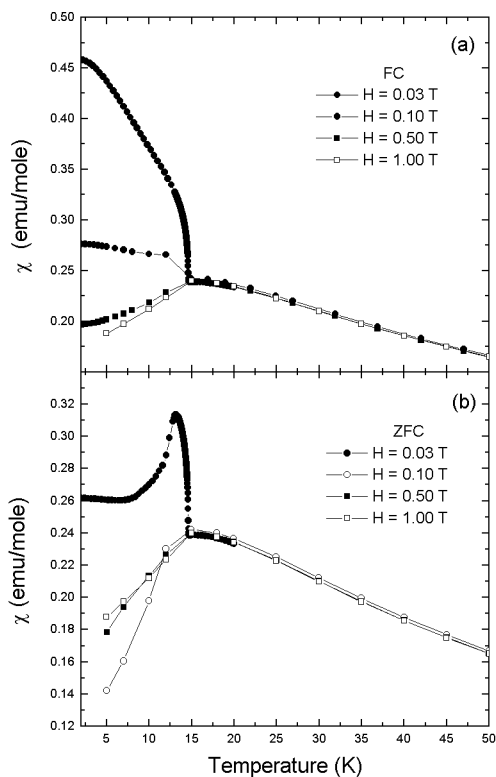

Figure 5. Magnetic susceptibility in Mn-Br under different applied magnetic fields.

As for most boracites Mn-Br follows a Curie-Weiss law (θ = -28.31 K) indicating antiferromagnetic inter-actions between the paramagnetic ions. The magnitude of the effective magnetic moment for Mn-Br (μ_{eff} = 5.919μ_B) obtained from the straight part of the Curie-Weiss region is very near to the values calculated from the magnitude of the spins and to that obtained from experimental data on powdered samples of the same composition[10].

Figure 6 shows the behaviour of the derivative of the susceptibility with respect to temperature under applied magnetic fields of 0.1 T (Figure 6a), and of 1 T (Figure 6b) for Mn-Br. Two completely different curves are obtained: in the one hand, under a low magnetic field, a strong and abrupt decrease in the magnetic susceptibility is present at the transition temperature. This is characteristic of a weak ferromagnetic transition. On the other hand, under a higher magnetic field the susceptibility increases

continuosly from the high temperature down to the transition temperature, a temperature a which it starts to drop. This behaviour is typical of an anti-ferromagnetic transition.
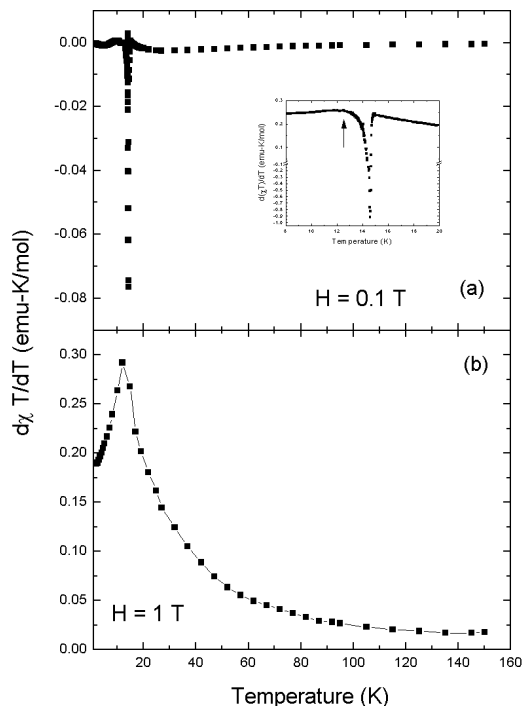

Figure 6. Derivative of the susceptibility as a function of temperature in Mn-Br.

The different behaviour of magnetic susceptibility and its derivative in Mn-Br, both depending on the applied magnetic field is a clear evidence of the presence of at least two transitions in the region around T_c in this boracite.

4. CONCLUSIONS

We have investigated magnetic properties of Mn-Br single crystals. We found that some of these properties are affected by the magnitude of the applied magnetic fields as well as for the rate of cooling the crystals. According to the Curie-Weiss and the high negative value of the Curie temperature observed in this composition its ordering at low temperature should be strongly antiferromagnetic, however what we observe from our experimental data is a weak ferromagnetic ordering in Mn-Br boracite. At 14.6~K approximately the field-cooled susceptibility increases as the temperature decreases which is an indication of a strong influence of ferromagnetic interactions in Mn-Br. The susceptibility versus temperature curve of Mn-Br under high applied magnetic fields exhibits a maximum before the antiferromagnetic transition, when the temperature decreases. Under low applied magnetic fields there is no maximum in the susceptibility curve for Mn-Br. The absence of such a maximum could be an indication of the presence of non-collinear antiferromagnetic interactions in relation

to the magnetic frustration. Further magnetic and structural studies are needed in order to clarify Mn-br properties at low temperatures.

ACKNOWLEDGMENTS

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