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Magnetism and charge ordering in $Fe_3O_2BO_3$ ludwigite

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Abstract

Features of the magnetic and charge ordering of the $Fe_3O_2BO_3$ ludwigite have been studied using Mössbauer spectroscopy in the range of $4\,K < T < 120\,K$. From the temperature dependence of the magnetic hyperfine fields (B_{hf}), associated to four different iron sites, three magnetic transitions, at 112, 73 and 40 K, can be distinguished in agreement with previous magnetization measurements. In the temperature region where a weak ferromagnetism appears, the B_{hf} of some Fe sites show two different values related with different canting angles.

Keywords: Charge fluctuations; Low-dimensional systems; Mössbauer spectroscopy

1. Introduction

The magnetic behavior of insulating transition metal oxides is related to the presence of low-dimensional units in their crystalline structure. The oxy-borate, known as *ludwigite* $Fe_3O_2BO_3$, has a '*zig–zag wall*' crystalline structure which consists of an array of sub-units, with four non-equivalent octahedral sites which are preferentially occupied by divalent or trivalent Fe ions [1].

A study of the temperature dependence of the Mössbauer spectra of this compound was reported by Swinnea et al. (1983) [1] giving a simple analysis of the paramagnetic spectra and proposing an electron hopping behavior. Here we extend these ^{57}Fe Mössbauer investigations to lower temperatures studying the magnetic properties of the $Fe_3O_2BO_3$. Previous magnetic studies on this compound revealed an anti-ferromagnetic transition around $T_N = 112\,K$, weak ferromagnetism below $T_{WF} = 73\,K$ and a reentrance to an antiferromagnetic state of the system at $T'_N = 40\,K$ [2]. Our aim is to use Mössbauer spectroscopy to understand how several Fe ions participate in these magnetic ordering processes.

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2. Results and discussion

In the paramagnetic regime above T_N the Mössbauer spectra consist of four doublets, which are attributed to sites 1 and 4, occupied by Fe^{2+} ($S = 2$) ions, and to triad sites 2 and 3. The triads form stripes along the *c*-axis and have three Fe^{3+} ($S = \frac{5}{2}$) sharing one electron. A very interesting temperature dependence of electron exchange can be traced from the observed valence of these Fe ions including intermediate valence behavior [3] and charge localization. These aspects will be discussed in another publication. In this paper we concentrate on the magnetic features below 120 K, where, according to our Mössbauer study, the triad contains two Fe^{3+} and a third Fe with intermediate valence (~ 2.5).

The ^{57}Fe Mössbauer spectra below $T_N \approx 112\,K$ reveal complex splittings which can be analyzed with four sextets, and a remaining paramagnetic doublet due to Fe at site 1 which orders only below about $T_{WF} = 74\,K$. All the spectra below T_N have been fitted using a hyperfine Hamiltonian including combined electrical and magnetic interactions. The variation of the normalized hyperfine fields $[B_{hf}(T)/B_{hf}(4\,K)]$ with a reduced temperature (T/T_N) as derived from this analysis can be seen in Figs. 1 and 2. The fits of the Mössbauer spectra near to the ordering temperatures are more complicated, therefore the curves were extrapolated as can be seen in both

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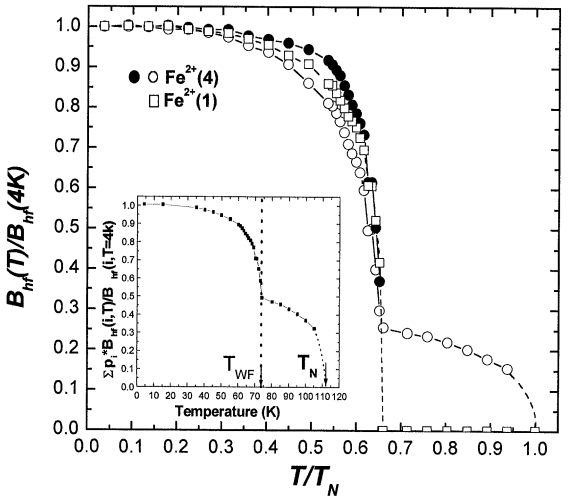

Fig. 1. Normalized magnetic hyperfine field $[B_{hf}(T)/B_{hf}(4\,K)]$ vs. reduced temperature (T/T_N) for the Fe ions at sites 1 and 4. The inset shows a total magnetization curve, where each Fe ion is contributing with a weight given by its relative intensity in the Mössbauer spectra.

figures. These curves are related to local magnetization of different sites. By adding them with a weight given by their relative intensities, we obtain a curve for the staggered magnetization, as seen in the inset of Fig. 1, where two transition temperatures at $\sim 112\,K$ and $\sim 73\,K$ can be clearly observed. To make our presentation more clear, we have separated the data corresponding to Fe^{2+} at sites 1 and 4 in Fig. 1 and the data for the irons located in the triads in Fig. 2.

From the analysis of both figures we can get the following information:

1. All the Fe ions belonging to the triads (sites 2 and 3) order at $T_N = 112\,K$ and follow a Brillouin-type curve up to $T_{WF} = 73\,K$, where an additional increase of B_{hf} occurs (see Fig. 2). In the range 73–40 K, where weak ferromagnetism occurs, each site reveals two different Fe components with the same isomer shift and quadrupole splitting but different B_{hf} and θ, θ being the angle between the directions of B_{hf} and the major axis of the electric field gradient. This separation into two separate Fe components (see inset in Fig. 2) is related to different canting angles.
2. The Fe^{2+}, which do not belong to the triads (sites 1 and 4), have different behavior (Fig. 1) which may be associated to their position with reference to the triads: site 4 which is close to the triads displays only a small $B_{hf,}$ below $T_{N,}$ and splits into two components at T_{WF}, this behavior is very similar to the Fe in the triads. The Fe^{2+} which is at site 1, on the contrary, only displays a B_{hf} below T_{WF} and remains as a single component.

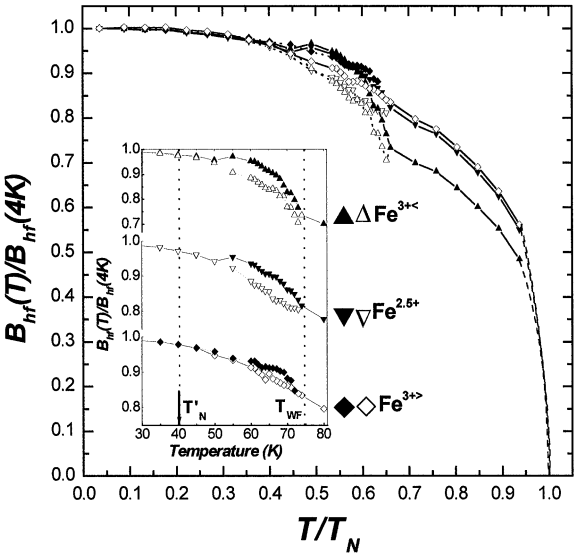

Fig. 2. Normalized magnetic hyperfine field $[B_{hf}(T)/B_{hf}(4\,K)]$ vs. reduced temperature (T/T_N) for the Fe ions in the triads. The inset gives an expanded view of the range with weak ferromagnetism where each of the Fe ions in the triads reveals two distinct magnetic hyperfine fields. The arrow indicates the temperature T'_N at which the system reenters the antiferromagnetic state.

The results described above can be best understood if the magnetic ludwigite is viewed as being formed by two sub-systems: one formed by the divalent irons and the other formed by triads. Between $112 \geqslant T \geqslant 74\,K$, one divalent iron (site 4) mediates the interaction between the triads (or is under the influence of a transferred field from them), while the other remains paramagnetic down to 74 K. Below this temperature this second divalent cation also orders magnetically making the interaction between the two sub-systems stronger and giving rise to an interesting magnetic behavior.

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