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LETTER TO THE EDITOR

Charge delocalization in the ludwigite $\text{Fe}_3\text{O}_2\text{BO}_3$ **J Larrea, D R Sánchez, F J Litterst¹ and E M Baggio-Saitovitch**

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Online at stacks.iop.org/JPhysCM/13/L949**Abstract**

⁵⁷Fe Mössbauer spectra of $\text{Fe}_3\text{O}_2\text{BO}_3$ reveal a combined effect of charge ordering and electron delocalization between 112 and 450 K. On the basis of the temperature dependence of the isomer shifts and quadrupole interactions, together with the information from previously obtained transport data, we are able to discuss the arrangement of Fe^{2+} and Fe^{3+} in the structure and the dynamics of the electronic configurations. We found a charge-delocalization transition around 300 K. Below this temperature, formation of pairs of Fe ions with mixed valence takes place in part of the crystalline structure.

Iron oxyborates of the chemical formula $\text{M}_2^{2+}\text{M}^{3+}\text{O}_2\text{BO}_3$ crystallize as *ludwigites*. The structure (figure 1) is basically formed from an assembly of subunits in the form of *zigzag walls* built from four kinds of edge-sharing nonequivalent oxygen octahedra [1–3]. The sites at their centres, labelled 1–4 in the following, are occupied by divalent (1, 4) or trivalent (2, 3) Fe ions. The sequence of 3–2–3 sites form a *triad* which can be described as three Fe^{3+} sharing an extra electron. The triads are linked closely along the *c*-axis yielding some precondition for charge delocalization along the walls formed by the triads. In contrast, sites 1 and 4, occupied by Fe^{2+} , have no neighbours of the same kind. Evidence for this distribution comes from x-ray diffraction and a first Mössbauer study of this compound [2]. The two classes of iron site will turn out to show different behaviour in the charge dynamics as well as in the magnetic ordering process [3]. An important question to answer is that of how the low-dimensional structural units affect the magnetic and electrical properties [1].

Transport measurements on Fe ludwigite can be explained by an activated behaviour with a strong change of the activation energy around 220 K indicating a crossover temperature. Magnetization measurements and our more recent Mössbauer data lead to the definition of three characteristic temperatures for changes in the magnetic behaviour, at 112, 74 and 50 K [1, 4].

The temperature dependencies of the isomer shift and of the quadrupole splitting can be very sensitive to transitions between ordered and disordered charge states. A transition of this kind has been proposed to occur in the Fe ludwigite, on the basis of transport

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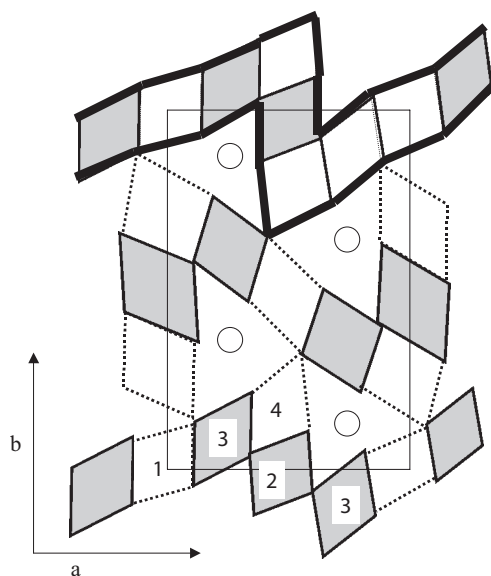


Figure 1. A schematic unit cell of the $\text{Fe}_3\text{O}_2\text{BO}_3$ structure viewed along the c -axis showing the four different iron sites. Sites 3–2–3 form the *triad*. Open circles represent the boron ions. One of the *walls* is bordered by bold lines.

measurements [3]. Therefore we have studied the temperature dependencies of the Mössbauer parameters, searching for further evidence of charge ordering in the Fe ludwigite.

Details of the sample preparation, the ^{57}Fe Mössbauer absorption experiments and the analysis of the spectra are described in [1] and [3], respectively.

From 113 to 450 K the Mössbauer spectra are typical for a paramagnetic regime revealing a superposition of several quadrupole doublets. In figure 2 some representative spectra around 300 K and at 116 K are shown. For $300 < T < 450$ K they consist of three quadrupole doublets, while below 300 K a fourth doublet appears. The isomer shifts and quadrupole splittings obtained from the fits are depicted in figure 3. The temperature dependence of the isomer shift values is corrected for second-order Doppler shift (SOD). For all temperatures the linewidths obtained remain relatively narrow (0.26 mm s^{-1}) and constant for each site. This speaks for well-defined hyperfine interactions without severe inhomogeneous broadening and for good quality of the sample. It also supports the chosen way of fitting the data. The relative absorption areas for the subspectra are in agreement with the simple charge balance per chemical formula for each site [3].

The isomer shifts of Fe^{2+} at positions 1 and 4 remain almost constant with temperature, indicating that the divalent irons outside of the triads 3–2–3 do not participate in the proposed charge-ordering process [3]. This is as expected from the distances between $\text{Fe}^{2+}(1)$ and $\text{Fe}^{2+}(4)$ and the trivalent iron neighbours in the triads which are $>3 \text{ \AA}$ [2, 6], thus impeding electron exchange. Therefore we will concentrate in our analysis on the Fe sites belonging to the triads.

From figure 3 we can clearly see the difference in electronic structure of the three iron sites of the triad. It is necessary to consider two ranges of temperatures: above 300 K the spectra contain a component with clear high-spin Fe^{2+} character which we attribute to $\text{Fe}^{2+}(2)$. The other has high-spin Fe^{3+} character with twice the absorption area; we can therefore conclude that the two $\text{Fe}^{3+}(3)$ are identical in this temperature range. Below 300 K the spectra contain

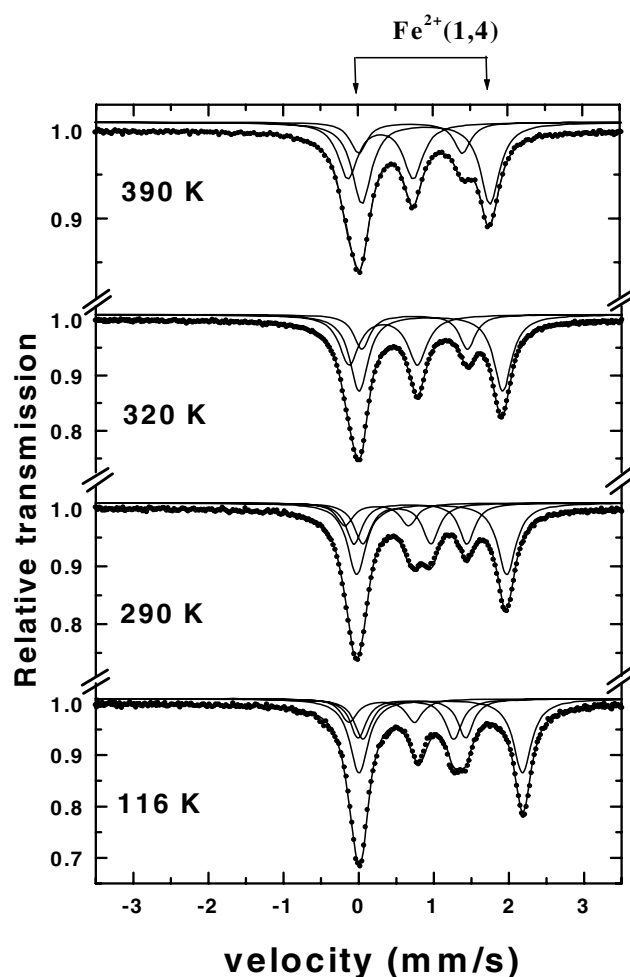


Figure 2. Some ^{57}Fe Mössbauer absorption spectra for different temperatures. The solid curves are least-squares fits.

three doublets with equal absorption areas. Two doublets correspond to two types of $\text{Fe}^{3+}(3)$ site named $\text{Fe}^{3+}(3)^*$ and $\text{Fe}^{3+}(3)^{**}$ with $\text{Fe}^{3+}(3)^{**}$ having a larger and $\text{Fe}^{3+}(3)^*$ a smaller isomer shift value. This means that $\text{Fe}^{3+}(3)^{**}$ has rather intermediate-valence character ($\text{Fe}^{2.5+}$) whereas $\text{Fe}^{3+}(3)^*$ is more trivalent (see figure 3(a)). Judging from its decreasing isomer shift below 300 K, the third component that we had labelled as $\text{Fe}^{2+}(2)$ becomes more trivalent, also approaching values typical for intermediate valency. This picture remains valid down to $T_N = 112$ K where magnetically split spectra appear [3, 4].

For the triads a series of combinations of intermediate-valence states can be expected exhibiting a rich variety of charge behaviour along the temperature range:

- If, e.g., the electron is localized at the Fe which is at the middle of the triad, it would be an Fe^{2+} and the remaining two Fe should have similar electronic structure close to Fe^{3+} .
- If, e.g., the electron is shared or tunnelling between two Fe (the middle one with one of the neighbouring ones), they can have similar charge, but this similarity as viewed by hyperfine spectroscopy will depend on the tunnelling frequency compared with the

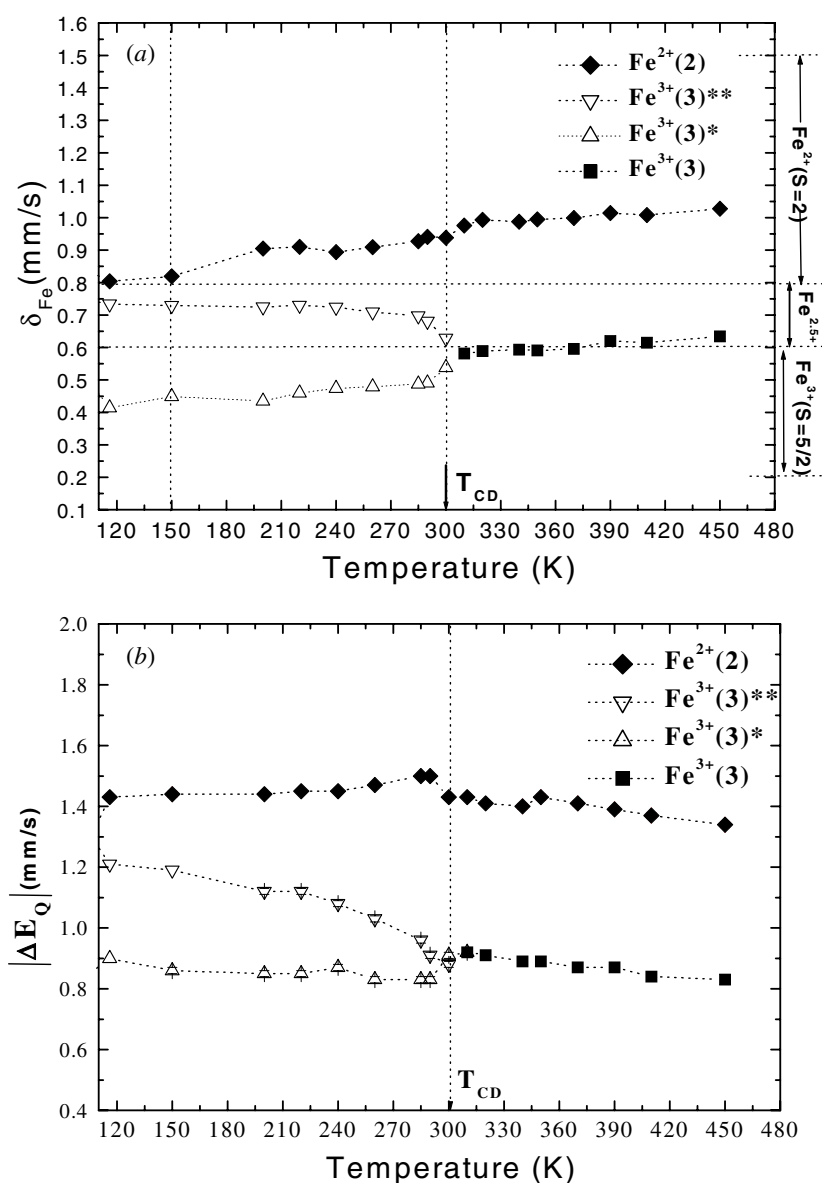


Figure 3. Variation of the isomer shift (a) and quadrupole splitting (b) for temperatures above 116 K, for the three iron sites belonging to the triads. T_{CD} is the charge-delocalization temperature.

hyperfine frequencies involved and will therefore also depend on temperature. This case applies for Fe²⁺(2) and Fe³⁺(3)**. The remaining Fe of the triad, which does not participate in this process, should be close to an Fe³⁺ since in this condition this ion can have more trivalent character (smaller isomer shift value). This is the case for Fe³⁺(3)*. Under these conditions one would expect slightly different bond lengths between the three irons in the triad.

From our Mössbauer data there is thus clear evidence for the formation of mixed-valence pairs in the triads.

The fact that the Fe^{2+} keeps a similar isomer shift and quadrupole splitting around the crossover of the activation behaviour in transport suggests that it stays at the same site, probably in the middle of the triad. The reason for the preference of the divalent iron for site 2 for all temperatures above 120 K may be found in its symmetric position which is stabilized for electrostatic reasons, probably due to the symmetric arrangements of the divalent sites 1 and 4 outside the triad.

We propose that the charge arrangement of the individual triads along the c -direction is not completely random when coming from low temperatures, but there may be correlated domains with coherent charge and also structural order with decreasing domain size upon going to higher temperatures. In this way a high degree of disorder is introduced which may be traced from the transport and the specific heat data [1, 5]. The correlation lengths are apparently so long that the Mössbauer parameters are not influenced by this kind of disorder but reflect only the short-range order.

This picture is compatible with the temperature-dependent behaviour of the Fe triad sites if we take into account neighbouring triads in the c -direction. These may allow electron hopping along the c -axis to be activated, adding to the tunnelling and hopping which takes place in the ab -plane within each *triad*. With the 2–2 and 3–3 distances between positions along the c -axes being close to 3.0 Å, electron exchange along the c -axes is permitted [6]. In parallel there occurs a dramatic change in the transport properties, revealing the above-mentioned drop of the activation energy. The higher activation energy found for low temperatures should however not be related to the electron tunnelling in the individual triads; it is instead connected to the disorder which at low temperatures is still frozen and becomes more dynamic above 150 K.

Our data clearly show the presence of mixed-valence ion pairs below 300 K. At around 300 K, however, a new charge configuration is reached where we can no longer distinguish $\text{Fe}^{3+}(3)^*$ and $\text{Fe}^{3+}(3)^{**}$ from their Mössbauer parameters. We therefore introduce as the characteristic charge-delocalization temperature $T_{CD} = 300$ K. This result may reflect that fast charge dynamics takes place above T_{CD} , meaning complete delocalization along the c -direction occurring mostly between sites 2 which are preferentially divalent. The fast electronic dynamics due the delocalization in sites 2 leads to a fast averaging of hyperfine interactions at sites 3, which therefore appear indistinguishable. In addition the fast electronic dynamics should also lead to a more uniform structure with equal distances between sites 2 and 3. From figure 3(b), the variation of the quadrupole interactions for the Fe sites belonging to triads supports the interpretation concerning the charge-delocalization transition and also gives evidence for the expected structural change around 300 K. Since the Mössbauer spectra can only indicate the changes in the surrounding of the Fe probe, the long-range details of this transition remain to be investigated.

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