Influence of Electron Delocalization on the Magnetic Properties of Iron Ludwigite $Fe_3O_2BO_3$

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Abstract. [57]Fe Mössbauer spectroscopic studies of iron ludwigite $Fe_3O_2BO_3$ performed between 4 and 450 K allow the discussion of magnetic spin arrangements and the dynamics of electronic configurations of iron. The observed magnetic transitions are related to charge ordering.

Key Words: antiferromagnetism, charge order, double exchange, iron oxyborate, Mössbauer spectroscopy, weak ferromagnetism.

1. Introduction

The homometallic iron ludwigite $Fe_3O_2BO_3$ is an oxyborate with orthorhombic structure (see Figure 1) [1–6]. It is basically formed from two subsystems. Firstly, there are three leg ladders (3LL) directed along the c axis (i.e., perpendicular to the plane shown in Figure 1), they are consisting of oxygen octahedra with iron in its centres. The rungs of the 3LL are formed by three iron sites (one site 2 and two sites 3) forming a so-called triad. Secondly, there are oxygen octahedra with iron site 4 and site 1, which together with the boron atoms (open circles in Figure 1) are connecting the 3LL. Neighbouring 3LL together with sites 1 and 4 between them can be conceived as zigzag walls extending along c.

Sites 1 and 4 are magnetically and also from charge state clearly distinct from sites 2 and 3 of the 3LL which are mainly determining the properties of the iron ludwigite. Reason is the mixed valent character of the iron ions in sites 2 and 3 in contrast to those in sites 1 and 4, which are clearly high-spin Fe^{2+}.

From formal stoichiometry considerations each triad can be considered as being formed by three Fe^{3+} with an extra electron added. These extra electrons
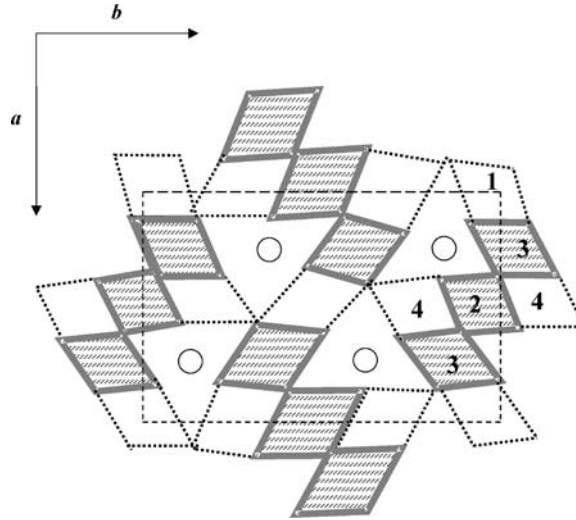
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Figure 1. Projection of $Fe_3O_2BO_3$ structure to *ab* plane. Iron sites 1 to 4 are in the centres of oxygen octahedra. The 3-2-3 marks the triads, which are the rungs of the 3LL running along the *c* direction (i.e. out of plane). *Circles* indicate boron.

are distributed along the 3LL and are strongly correlated. They are supposed to cause peculiar charge and spin dynamics. Macroscopic thermodynamic and transport properties have been studied [5] giving evidence for semiconducting behaviour with an activation energy corresponding to 60 and 1300 K for the temperature ranges below and above about 220 K, respectively, the supposed onset temperature for charge delocalization along the 3LL. Caloric data can be interpreted with 2d magnon excitations below about 40 K. Between about 110 and 200 K a linear specific heat is interpreted with excitations in a Wigner glass caused by tunnelling of the extra electrons.

Neutron diffraction indicates an antiferromagnetic state (called AF2) for the 3LL at 5 K with an up–down–up structure at sites 3, 2 and 3 of the triads [7] with an overall ferromagnetic behaviour which is in contradiction to magnetization which indicates an antiferromagnetic ground state [5]. Magnetization data show a weak ferromagnetic phase (WF) between about 50 and 74 K [5]. Mössbauer spectroscopy allows distinguishing in addition a third magnetically ordered phase between 74 and 112 K [8]. From magnetization it becomes clear that this is a second antiferromagnetic phase (AF1) [5].

Earlier Mössbauer results [4] have given evidence for the presence of mixed valent iron. We extended these studies [2] and detected a charge order transition at $T_{CO} \approx 300$ K, which afterwards also could be detected from X-ray diffraction [3]. The changes of charge states at lower temperatures and the magnetic behaviour are described in ref. [9]. Our data were mainly corroborated by the
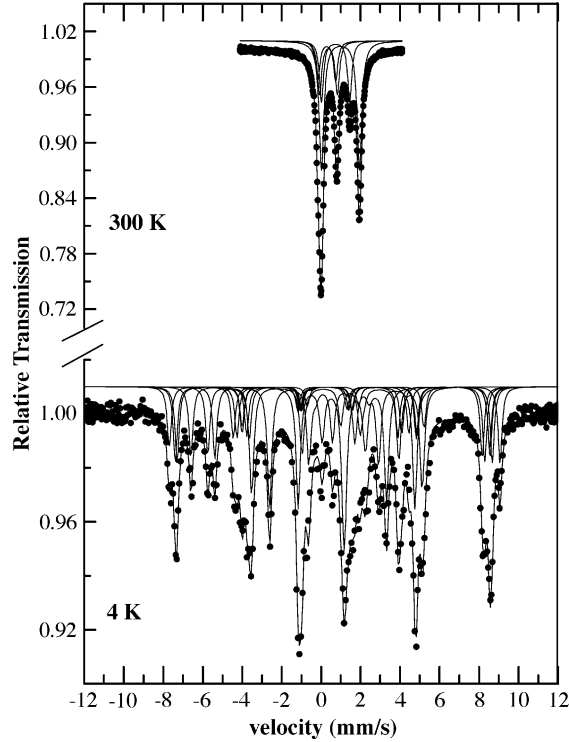
Figure 2. Typical ^{57}Fe Mössbauer absorption spectra in the paramagnetic (*upper*) and the magnetically ordered AF2 phase (*lower*).

studies of Douvalis et al. [10]. In contrast to our results their data cannot distinguish the transition between the low temperature AF2 and the WF phase which may be a problem of different data analysis [9].

Several interesting theoretical considerations concerning charge order and delocalization and the possible influence of the dimensionality have been presented [6, 11, 12]. In this present paper we want to give a critical résumé of Mössbauer data in relation with these models since we believe that hyperfine data provide essential information about the individual iron sites' charge states and their magnetic properties. Since sites 1 and 4 do not participate in charge dynamics and in charge order we will concentrate here on the properties of the 3LL.

2. Summary of Mössbauer spectroscopic results

We only want to give here a brief overview of the Mössbauer data. Detailed information is given elsewhere [9]. Typical spectra for the paramagnetic state and the low temperature ordered state are shown in Figure 2. The complex spectra
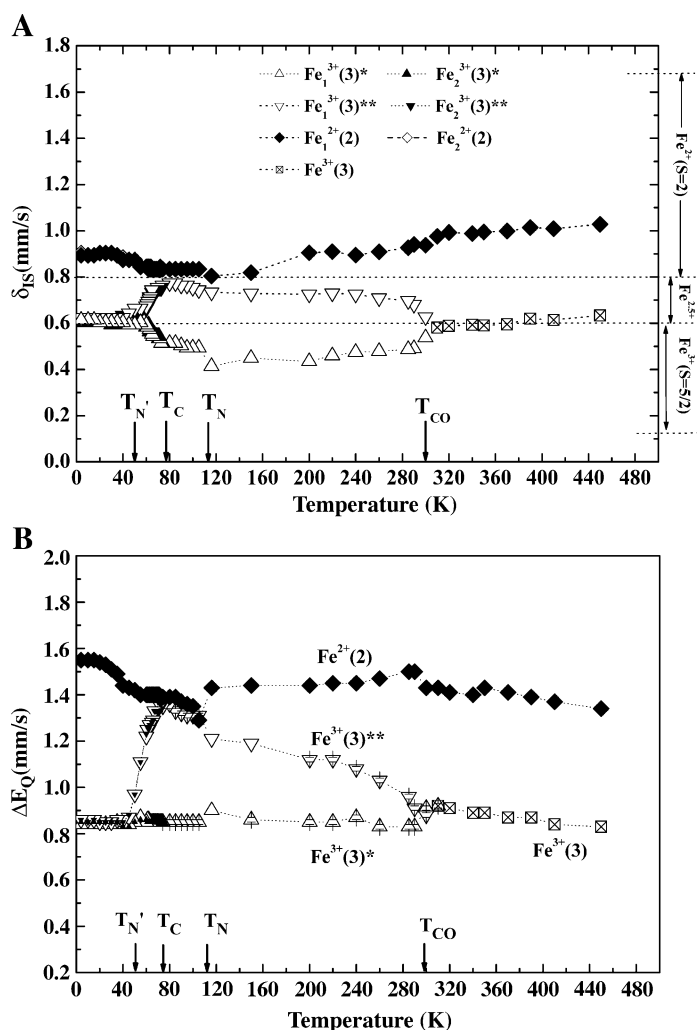
A

B

Figure 3. (A) Temperature dependence of isomer shifts of the triad sites. (B) Temperature dependence of the quadrupole splitting of the triad sites.

can be analyzed with the superposition of subspectra for individual sites 1 to 4. Isomer shifts and quadrupole splittings for sites 1 and 4 are typical for divalent iron without exceptional changes. For the triad sites, however, these parameters are revealing remarkable variations (Figure 3A and B). Above $T_{CO} \approx 300$ K sites 3 ($Fe^{3+}(3)$) have the same isomer shifts and quadrupole splittings indicating a charge state, which is not clearly trivalent but rather mixed valent; $Fe^{2+}(2)$ is divalent. Below T_{CO} sites 3 reveal two different isomer shifts and quadrupole interactions. We call these sites $Fe^{3+}(3)*$ and $Fe^{3+}(3)**$, the latter having even more mixed valent character than $Fe^{3+}(3)$, the other, however, is more trivalent
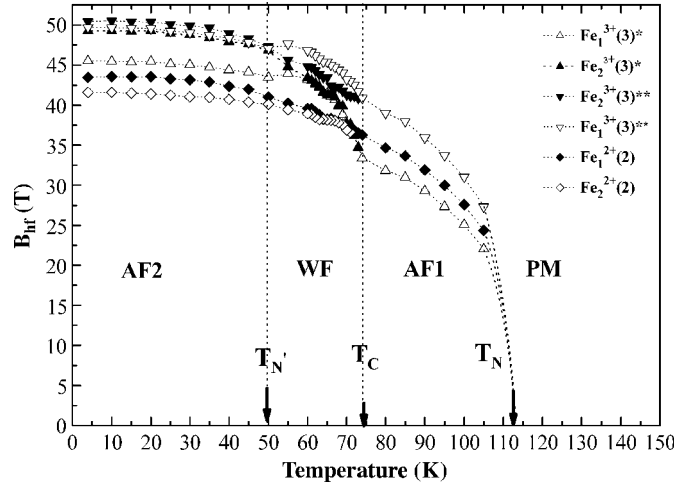
Figure 4. Temperature dependence of the magnetic hyperfine fields of the triad sites.

(see isomer shifts). Between about 120 and 75 K (the range of the AF1 phase) $Fe^{3+}(3)**$ and $Fe^{2+}(2)$ can hardly be distinguished from isomer shift and quadrupole interaction. Below 74 K (in the WF phase) $Fe^{3+}(3)**$ and $Fe^{3+}(3)*$ approach again in their charge states and below about 50 K (AF2 phase) both are close to the state found above T_{CO}. Site 2 then is divalent, yet still close to mixed valent character. The magnetic hyperfine fields for the triads are shown in Figure 4. They are revealing an increase of sublattice magnetizations below $T_N = 112$ K with a further increase below $T_C = 74$ K in the WF phase. In the WF phase a further complication appears: the spectra can only be fitted assuming two magnetically different subsites for each site revealing different magnetic hyperfine fields yet the same isomer shifts and quadrupole interactions. The same holds below $T'_N = 50$ K in AF2, there however with less deviations from the average for each site. Again this is in severe contrast to sites 1 and 4: whereas sites 4 only show a very small field in AF2, probably only of transferred nature, sites 1 reveal an onset of magnetic hyperfine field only below T_C. Below T_C the magnetic hyperfine fields for both sites show typical magnetization behaviour, however, with clearly smaller saturation fields compared to those of the triad sites. This indicates ordering of the 3LL below T_N, sites 1 and 4 which are between the 3LL, however, are still magnetically decoupled and order only at T_C. All sites exhibit considerable canting of the magnetic hyperfine field with respect to the main axis of the electrical field gradient. The canting angles are changing considerably when passing T'_N and T_C. We only want to give here some qualitative arguments since an unambiguous data analysis deriving both polar and azimuthal angles together with an eventually non-zero asymmetry parameter of the electrical field gradient is not possible for a nuclear spin 3/2 to 1/2 transition [13].

3. Discussion

We now will discuss the various regimes with special respect to the information we draw from the hyperfine data: up to T_N'; between T_N' and T_C; between T_C and T_N; between T_N and T_{CO}; above T_{CO}.

3.1. $T < T_N'$

Isomer shifts and quadrupole splittings of the triad sites in the AF2 phase indicate that sites 3 are identical from charge point of view, but they have different magnetic hyperfine fields and different canting. The isomer shift values of sites 2 and 3 indicate that the extra electron is mainly located at site 2, i.e., in the middle of the 3LL. From electrostatic consideration within a single 3LL one might expect to have the extra electron charge mainly located in the outer ladder. In fact the hyperfine parameters of sites 3 indicate that there is a non-negligible charge transfer to sites 3. This is also expected from the relatively short distances between sites 3 and 2 of about 2.79 Å with some overlap of their 3d wave functions allowing charge hopping at least at higher temperatures. One should, however, take into account also the charges outside the 3LL, namely the divalent ions in sites 1 and 4 favouring the localization of the extra charge in sites 2.

The distribution of values of magnetic hyperfine fields and also of angles points to a severely canted and probably modulated antiferromagnetic structure. This is not unexpected due to the just described overlap of 3d wave functions. As shown by de Gennes [14] under these conditions double exchange may lead to considerably canted, helical, or even disordered moment arrangements in the ground state. From our data a possible structure would be a probably incommensurate spiral structure for all three legs of the 3LL. The gross arrangement in one triad is up–down–up (in agreement with neutron results) or inverse, yet with considerable canting. Further reasons for canting are the different anisotropies due to the 3d orbitals in different symmetries of the iron states and the non-negligible interaction between neighbouring 3LL which is mediated via sites 1 and 4. A schematic view of charge distribution in the 3LL is shown in Figure 5. The charge distribution is ordered and at the time scale of Mössbauer spectroscopy (about microsecond) static. A possible moment arrangement is given in Figure 6 where the projection to the plane of a single 3LL is shown indicating also whether the moments are pointing into or out of this plane.

3.2. $T_N' < T < T_C$

In the WF regime one observes a gradual change of the charge distribution: one of sites 3 is turning more trivalent ($Fe^{3+}(3)^*$), the other tends to accept 3d charge coming closer with its hyperfine parameters to those of $Fe^{2+}(2)$. This shift of charge mainly from one side of the triad to the other marks a transition between AF2 and AF1 where $Fe^{3+}(3)^*$ and $Fe^{2+}(2)$ become indistinguishable from charge
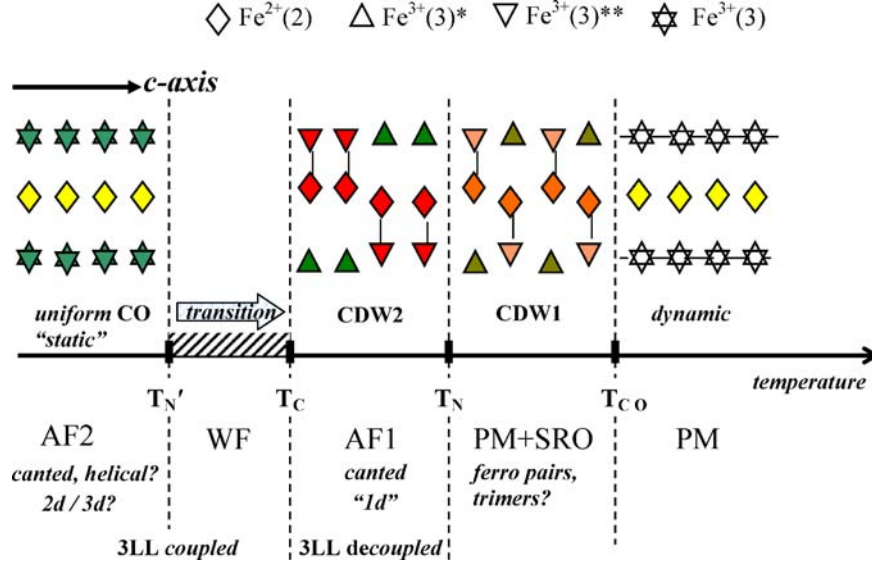
Figure 5. Proposed charge (*upper part*) and magnetic arrangement (*lower part*) of the 3LL running along *c*.

state. The magnetic patterns in the WF range reveal an even more complex arrangement than in AF2 mainly with still stronger canting and deviations of magnetic hyperfine fields from the average ones [9]. We cannot exclude that one has to deal with a mixture of AF1 and AF2 leading locally to frustration.

Another reason for the staggered magnetization of the WF could be an exchange mechanism of Dzialoshinski–Moriya type [15].

3.3. $T_C < T < T_N$

As mentioned above there is a clear formation of pairs in AF1 with equal mixed valent charge state and also symmetry as seen from quadrupole interaction whereas one site 3 is clearly trivalent. The major change concerning magnetic behaviour is that sites 1 and 4 turn non-(or nearly non-)magnetic, i.e., the coupling between neighbouring 3LL is vanishing. Each triad site now reveals one magnetic hyperfine field only. The temperature dependences of the hyperfine fields follow magnetization curves with clearly lower (extrapolated) saturation fields than for WF and AF2. In this situation with decoupled 3LL one can expect that the one- dimensional character of the ladders becomes pronounced and one might suspect the formation of non-magnetic singlets [9]. For this, however, no evidence is found. Reason may be the strongly correlated behaviour due to the mixed valent ions. We propose that the mixed valent pairs couple mainly ferromagnetically as expected from double exchange, with the second trivalent ion
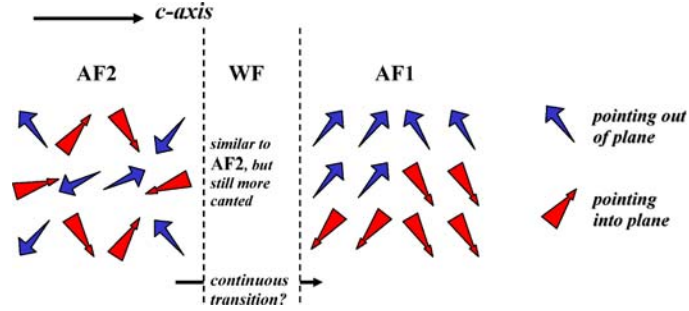
Figure 6. Proposed canted magnetic structures of 3LL.

in site 3 coupling antiparallel to the pair. A possible charge arrangement is given by a charge density wave (CDW2, see Figure 5). The moment orientation is still canted with main direction perpendicular to c close to the normal of the plane formed by each 3LL. A proposed magnetic structure is given in Figure 6.

3.4. $T_N < T < T_{CO}$

The magnetic hyperfine interaction has vanished and the charge distribution in the triads gradually relaxes, meaning that the two ions of the mixed valent pairs become again distinguishable. We believe that the structure is best characterized now by a different charge density wave (CDW1) for which evidence comes from X-ray diffraction [3].

Also in this regime there is no evidence for non-magnetic singlets from trivalent iron as suspected in theoretical considerations together with magnetization data yielding relatively small effective moments. Our Mössbauer spectra in applied magnetic field rather indicate short-range order (SRO) with moments around 10–15 μ_B from which one may suspect ferromagnetic dimers or trimers embedded in a paramagnetic (PM) surrounding. This finding is also compatible with the magnetization data. In contrast to [10] who assumed quenched orbital moments for all divalent iron ions we assume that the orbital moments of the divalent ions in the triad are quenched and also those in sites 1 and 4 are reduced. This is supported by the values of magnetic hyperfine fields.

Close to T_{CO} the hyperfine parameters of sites 3 approach each other indicating the transition from the CDW1 to a more uniform distribution.

3.5. $T_{CO} < T$

This is reached at T_{CO} where sites 3 become again indistinguishable from isomer shift and quadrupole interaction. The uniform charge distribution along sites 3 and sites 4, respectively, is reflected in the high temperature orthorhombic structure in contrast to the structure below T_{CO}, which possesses a doubled cell along c.

This transition was for the first time proposed from the Mössbauer data and indicates a fast charge delocalization along the c-direction of the 3LL.

4. Conclusions

As main results concerning charge order and magnetism in the 3LL of iron ludwigite and we can summarize:

- The extra 3d electrons of iron in the triads are mainly in sites 2, i.e., sites in the middle of the 3LL. We propose that this is due to the influence of Fe^{2+} in sites 1 and 4.
- For all temperatures the magnetic properties of the 3LL are controlled by electron (de-)localization.
- From the spectra in applied field above 112 K there is no evidence for non-magnetic singlets of antiferromagnetically coupled pairs of Fe^{3+}. However, there are indications for short-range order with effective moments of about 10–15 μ_B what is compatible with magnetization data. The moments can be interpreted with ferromagnetically coupled dimers of $Fe^{3+}(3)$**–$Fe^{2+}(2)$, or even trimers.
- Iron in sites 1 and 4 is not magnetically ordered down to 74 K, i.e., neighbouring 3LL are magnetically decoupled.
- The ordered magnetic structures below T_N are complex. We propose that they are related to different charge arrangements in charge density waves and that double exchange plays an important role for the details.
- The origin of the weak ferromagnetic phase remains unclear, also whether it is a magnetically and electronically homogeneous phase or a mixture of AF1 and AF2.
- Dimensionality does not primarily determine the magnetic properties of the ladders.
- There are indications from the Mössbauer data for additional structural changes which may occur at T_N and T_N and are related to charge order.

Acknowledgements

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