SPECIAL ISSUE ARTICLE

Mössbauer study of the temperature dependence of electron delocalization in mixed valence freudenbergite

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Abstract

The evolution of the electron delocalization in the ferrous subspectra in a sample of mixed valence ferrous-ferric freudenbergite has been followed by Mössbauer spectroscopy from 6 K to 650 K. The spectral changes do not involve the ferric component, leading to the conclusion that it is due to a thermally driven delocalization of the sixth d-electron on the ferrous ions. The phenomenon does not occur in samples of pure ferrous freudenbergite.

KEYWORDS

electron delocalization, freudenbergite, iron titanate, mixed valence, Mössbauer effect

1 | INTRODUCTION

The iron titanates have provided a rich source of structures and electron dynamics for what are loosely called charge transfer processes. Since both elements can exist in two stable valence states at room temperature, electron transfer processes can be between two atoms of the same type, or of different types or simply involve a single atom in events such as crystal field transitions or electron delocalization. Historically, all of these processes have been of great interest because of their effects in colouring well-known minerals. Iron-titanium minerals reported as having electron delocalization include sapphire, kyanite, fassaite, omphacite, aenigmatite, Ti andradite,[1] schorlomite,[2] taramelite, traskite, and neptunite.[3]

Freudenbergite has the general formula $Na_2Fe_xTi_{8-x}O_{16}$, and is ferric for $x = 2$ or ferrous for $x = 1$. The structures of both ferric and ferrous freudenbergite were determined by Ishiguro et al.[4,5] The ferric form is monoclinic and has edge-sharing $(Fe,Ti)O_6$ octahedra in double sheets parallel to (001) and corner-sharing perpendicular to this.[4] The charge compensating Na^+ ions are in the channels between the octahedra and are not necessarily completely filled. The ferrous form is orthorhombic[5] and also has edge-sharing $(Fe,Ti)O_6$ octahedra, but in double chains parallel to [010].

For the ferric freudenbergite, there is a preference by the Ti^{3+} ions for the M(2) site over the M(1) site.[4] For the ferrous freudenbergite, there is a stronger preference of Ti^{4+} ions for the M(2) site, so that the Fe^{2+} ions are now distributed quite asymmetrically in favour of the M(1) site.[5] Within the sites, the distribution of the iron and titanium ions is statistically random.[4,5]

The M(1) site is larger and more distorted so that in a previous Mössbauer experiment on a natural Nb-containing ferric freudenbergite,[6] the two doublets observed had nearly equal intensity and the doublet with the larger quadrupole splitting was assigned to the M(1) site.

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2 | SAMPLE PREPARATION AND CHARACTERIZATION

The sample was prepared from an aqueous mixture of $NaNO_3$, $Fe(NO_3)_3.9H_2O$, and Ti isopropoxide with the nominal composition $Na_2FeTi_7O_{16}$, appropriate for a ferrous freudenbergite. It was stir-dried, calcined in air for 1 hour at 700°C, hand-ground, ball-milled in cyclohexane for 3h and then sintered in argon for 2 hours at 1200°C. The sample was black in color.

A powder x-ray diffraction pattern was measured with a PANalytical X'Pert Pro diffractometer (Almelo, the Netherlands) using Cu Kα radiation (λ = 1.54060 Å) in the range 5° < 2θ < 80°, with a step size of 0.03° (2θ). Phase identification was performed with X'pert highscore plus combined with the ICSD data base.

An SEM scan was taken in a Zeiss Ultra Plus instrument (Carl Zeiss NTS GmbH) operating at an accelerating voltage of 15 kV and equipped with an Oxford Instruments X-Max 80 mm^2 SDD X-ray microanalysis system. The sample was set in epoxy resin and polished to a 1 μm diamond finish and coated with ~10 nm of carbon to avoid charging effects.

Neutron diffraction experiments were carried out on the C2 multi-wire powder diffractometer (DUALSPEC) at the NRU reactor, Canadian Neutron Beam Centre, Chalk River, Ontario using a wavelength of 1.3304 A. The scattering data were collected in two blocks: 2θ = 5°-85° and 37°-117° and the two patterns were co-fitted (Figure 1) using the GSAS/EXPGUI packages.[7,8]

The Mössbauer spectra were collected on a conventional spectrometer operated in constant acceleration mode using a 50 mCi ^{57}Co(Rh) source and calibrated against α-Fe at ambient temperature. For the low-temperature spectra, the sample was mounted on a vibration-isolated closed-cycle refrigerator, while the high-temperature spectra were obtained using a resistively heated oven with the sample in vacuum. The spectra were fitted to a sum of Lorentzian lines using a conventional least-squares minimization routine. Both lines of a given doublet were constrained to have equal areas and linewidths, while the linewidth of each doublet was treated as an independent variable.

3 | RESULTS

3.1 | Sample characterization

The XRD spectrum showed that the sample had the monoclinic freudenbergite structure[4] with lattice parameters a = 1.2253(4) nm, b = 0.3816(6) nm and c = 0.6483(8) nm, with β = 107.166(3) deg. The last three of these values agree with those of Ishiguro,[4] while the a-value is smaller by 0.1%. There were no detectable impurities.

The SEM scan (Figure 2) shows major freudenbergite matrix with minor iron-free $Na_2Ti_6O_{13}$ in the darker gray areas (the black spots are pores).

Analysis of the neutron diffraction pattern showed that the Ti: Fe distribution was 7.00 to 1.00(3), agreeing with the nominal composition. We found that the distribution of Ti: Fe on the two sites was markedly different, with the M(1) site being 0.816(5): 0.184(5) and the M(2) site being 0.933(7): 0.067(7). This gives a formula $Na_2(Ti_{3.26}Fe_{0.74})(Ti_{3.73}Fe_{0.27})O_{16}$, with the M(2) distribution agreeing almost perfectly with that of Ishigoru,[5] $Na_2(Ti_{3.16}Fe_{0.84})(Ti_{3.72}Fe_{0.28})O_{16}$. It would be expected that all the Fe ions on the M(2) site are the smaller Fe^{3+}ion.
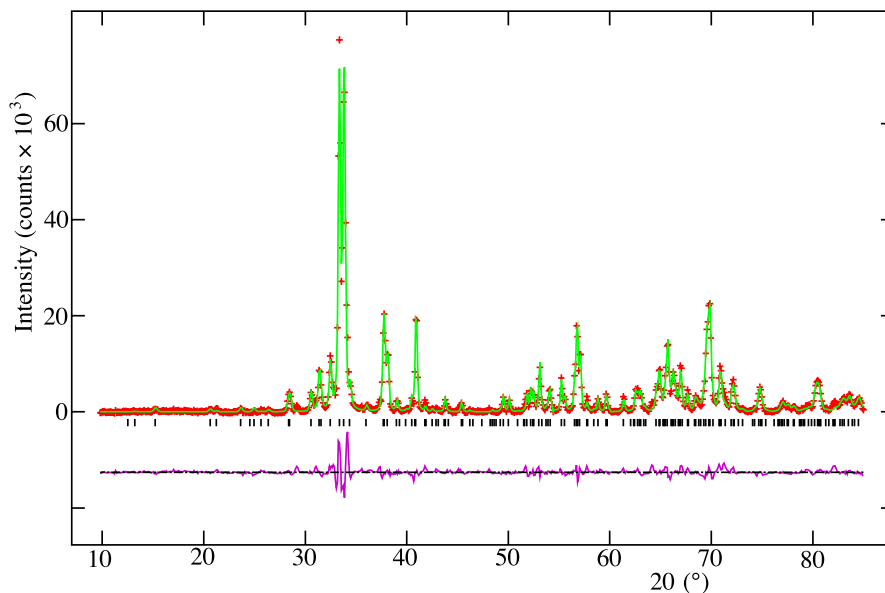

FIGURE 1 Neutron diffraction pattern of the freudenbergite sample [Color figure can be viewed at wileyonlinelibrary.com]
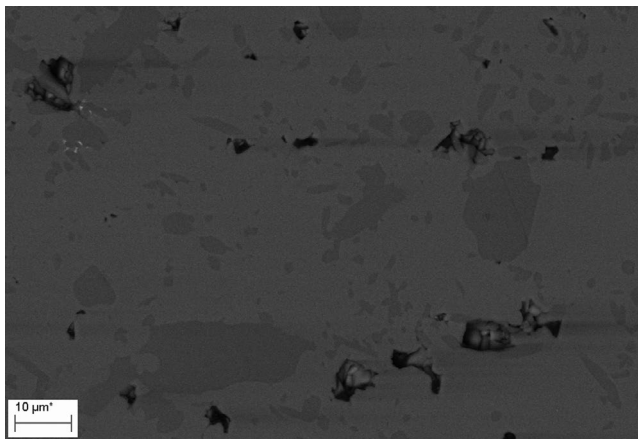
FIGURE 2   SEM image of the freudenbergite sample

3.2 | Mössbauer results and analysis

Spectra of the sample at 50K, 304 K, and 452 K were shown in reference 9.[1] We have now carried out the complete set of spectra from 6 K to 650 K illustrating the change in behavior as shown in Figure 3. In fitting the spectral series, the first problem was what model to use. The low temperature spectra could be fitted with one ferric doublet and two ferrous doublets, except for the two lowest temperatures where there is evidence of broadening. However, the spectra taken above room temperature all required three ferrous doublets, so it was decided to use this model for all the spectra in the interests of consistency. We do not interpret this as implying that there are three distinct ferrous arrangements, but rather that this is the minimum required to simulate a reasonably smooth profile for the observed spectra.

The lack of features in the envelope made it difficult to obtain absolute stability in the parameters. A consistent set of fits was obtained by fitting the spectra in the order of increasing temperatures with each fit using a slightly modified version of the preceding fit. It is clear from Figure 3, that there is considerable change in the ferrous contribution but it is not so clear whether the ferric contribution is also changing, either in shape or in fraction of the total area. Figure 4 shows the temperature dependence of the ferric area as a percentage of the total area and it can be seen that it remains reasonably stable, but with a small reduction with increasing temperature.

The variation in the quadrupole splittings is shown in Figure 5A with the ferrous value being a spectrum average, with the parameter values for each of the three doublets

weighted by the area of that doublet. The ferric ions do not appear to be affected by the behavior of the ferrous ions and we would attribute the apparent small reduction at the highest temperatures to the difficulty of fitting the spectrum. The ferric ions should, in principle, be fitted with two doublets for the M1 and M2 sites. However, we found it impossible to fit two doublets to a pure ferric freudenbergite[9] when the site occupancies were clear, and it is certainly not possible here in this more complex spectrum and with a ratio of 2.6:1 in the site populations.aaa

A spectrum of an almost pure ferrous freudenbergite was shown as Figure 1B in reference 9 and spectra of that sample at elevated temperatures show the common behavior of reduced quadrupole splitting due to thermal effects on the d-electron populations, but little change in the isomer shift except for the second-order Doppler shift. This is different from the behavior observed here where the ferrous isomer shift, given as the area weighted values for the three doublets, decreases more rapidly than predicted by the high temperature approximation for the second-order Doppler shift (Figure 5B).

The variation in the average Fe^{2+} linewidth is less straightforward and is shown in Figure 6A while the Fe^{3+} linewidth remains relatively constant. We believe that the increased line width for Fe^{2+} in the region 200-400 K is a manifestation of the electron dynamics and could be due to a modification to the time scale appropriate in the Heisenberg uncertainty principle or small fluctuations in either the isomer shift or the quadrupole splitting. The increase at the two lowest temperatures is likely to be due to the onset of magnetic ordering, but we are not aware of any determination of the magnetic ordering temperature, which will in any case be composition dependent.

The variation in the area, given relative to the baseline, is shown in Figure 6B. The high temperature part has been fitted to the Debye model with a Debye temperature of 352 ± 4 K. Note the apparent reduction in area for the two lowest temperatures which is also due to the onset of magnetic ordering.

4 | DISCUSSION

In our previous papers on freudenbergite,[9,10] we referred to the electron dynamics as electron hopping, whereas, using the scheme of Amthauer and Rossman,[11] it should be more correctly described as their system 3, thermally activated electron delocalization. There are many well documented mineral examples of this and minerals containing iron and titanium constitute a considerable proportion of such electron transition phases as detailed in the extensive review by Burns.[1]
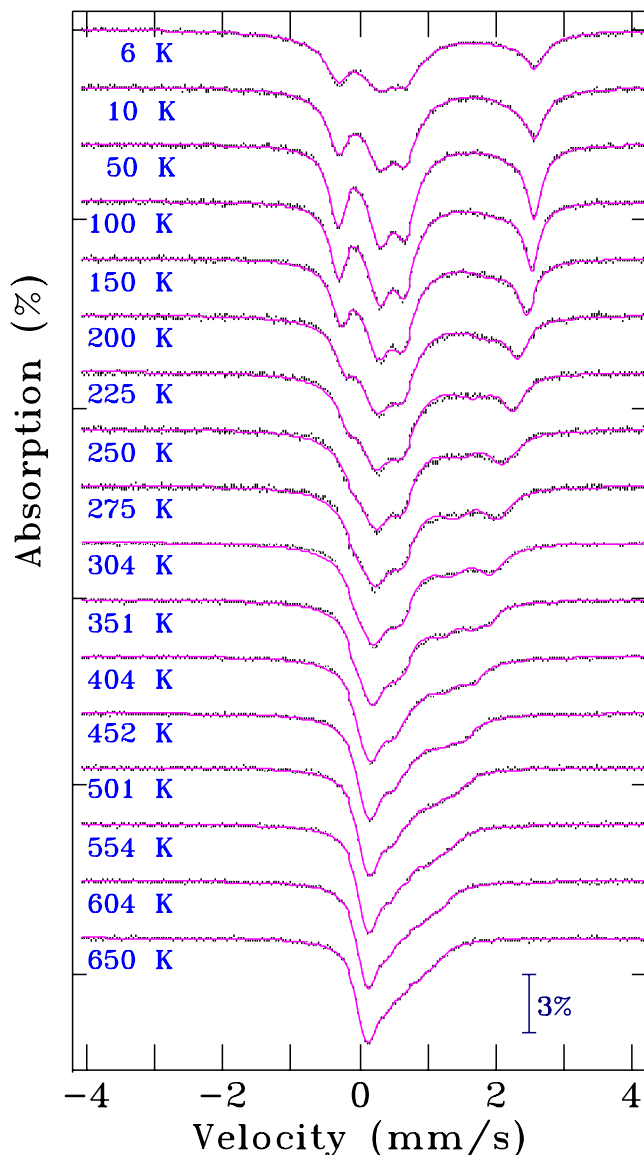
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[1]We note that there was an error in Section 3 of ref. 9, as pointed out in ref. 10. All the descriptions, Figures and Table in that section have the sample labels consistently reversed, **3 ↔ 2**. The present sample corresponds to sample **2** as described in Section 2 of ref. 9 and in ref. 10.

FIGURE 3 ^{57}Fe Mössbauer spectra of mixed valence freudenbergite sample [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 4 Ferric spectral area as a function of temperature

FIGURE 5 A, Ferric and average ferrous quadrupole splittings as functions of temperature. B, Ferric and average ferrous isomer shifts as functions of temperature [Color figure can be viewed at wileyonlinelibrary.com]

The spectra in Figure 3 have been fitted with static doublets quite successfully indicating that the time scale of the hopping must be slow on the Mössbauer time scale ($>10^{-7}$ s). The spectra at 6K and 10 K have broadened appreciably and could not be fitted to the same model as the other spectra. We attribute this to the onset of magnetic ordering, but it is not well enough defined at these temperatures to tell whether both valence states are participating. The changes in the linewidth and the area are also both consistent with the onset of magnetic ordering.

The EFG for the ferrous doublets is due principally to the sixth d-electron and any change in the behavior of this electron will cause a change in the Mössbauer spectrum. The decrease in the quadrupole splitting (Figure 5A) is much steeper than would be expected from crystal field effects. In contrast, the almost unchanging Fe^{3+} EFG is due to the lattice, which
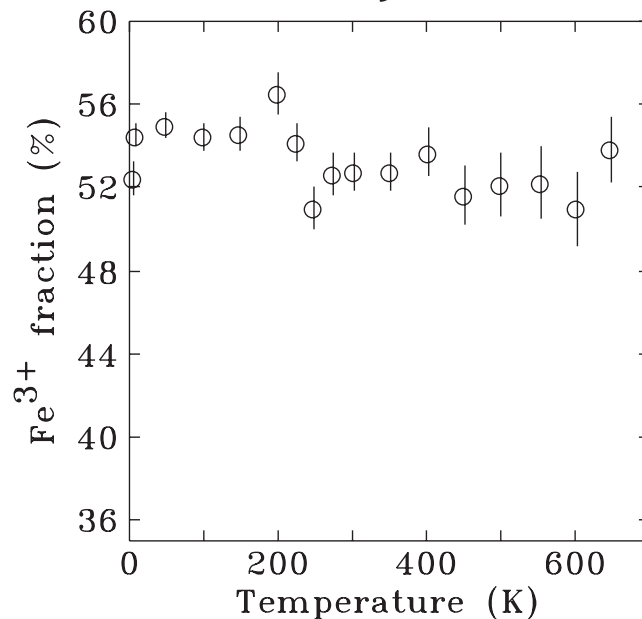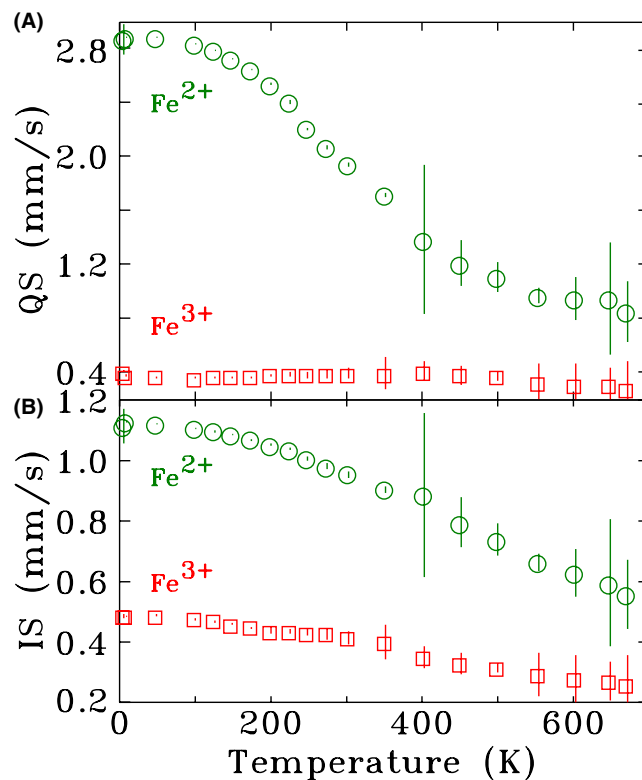
is relatively unaffected by the electron dynamics because it cannot relax sufficiently quickly.

From the concentrations as measured by neutron diffraction and the valence distribution from the Mössbauer
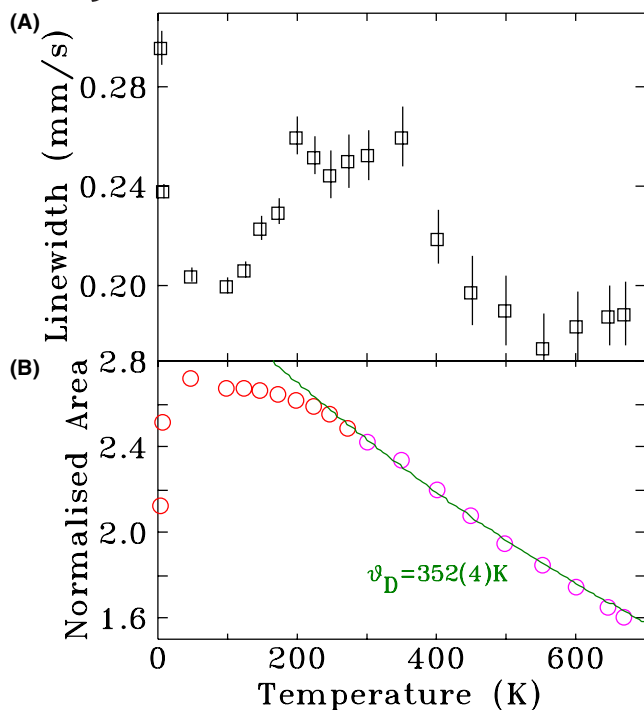
FIGURE 6 A, Mean ferrous HWHM as a function of temperature, (B) Total spectral area as a function of temperature [Color figure can be viewed at wileyonlinelibrary.com]

analyses (Figure 4), the valence sums of the iron and titanium add up to 30.5 if all the Ti is Ti^{4+}, instead of the expected 30. The neutron results showed no evidence for sodium deficiency, with an occupancy of 0.97(5). One possibility is that 0.5 of a Ti ion is in the Ti^{3+} state. This clearly has implications for whether the electron dynamics are really.

$$Fe^{2+} + Ti^{4+} \leftrightarrow Fe^{3+} + Ti^{3+},$$
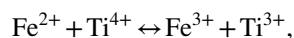
instead of the electron delocalization so far assumed. At this stage we have no evidence for a titanium contribution. Another possibility is a cation deficiency of 2% in the titanium, which is within the uncertainty of the analysis.

We can draw on the similarity between our ferrous spectra and the spectra of the ferrous-ferric silicate mineral cronstedtite[12] where the ferrous quadrupole splitting shows a very similar collapse. However, in cronstedtite, the ferric quadrupole splitting also collapses, which is not the case here. A similar collapse of the ferrous and ferric doublets has also been observed in ilvaite,[13-16] with differing interpretations. Similar spectral behavior to freudenbergite has also been observed in schorlomite[2] and Ti-andradite.[17]

It is noteworthy that we have made more than ten different compositions of freudenbergite, some of which were explicitly tailored to try to obtain more examples of the

delocalization, including by adding Al to stabilize some 3+ valence. In spite of annealing in air and argon, the electron delocalization was only observed in two cases with approximately equal ferrous-ferric proportions, even though mixed valence was observed in other samples (see, for example, Figure 2 in reference 10).

5 | CONCLUSIONS

We have shown the temperature evolution of the Mössbauer spectra of a mixed valence freudenbergite from 6 K to 650 K. The changes have been dominated by a thermally induced delocalization of the sixth d-electron in the ferrous component of the spectrum. Although the ferric ions were unaffected by these changes, it appears to be essential to have the approximately equal ferrous/ferric mixture to obtain the delocalization effects. At this stage we are unable to determine whether the titanium ions are also participating in the electron transfers.

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