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Electron hopping in the Mössbauer spectrum of mixed valence freudenbergite

J. D. Cashion · A. Lashtabeg · E. R. Vance · D. H. Ryan

Abstract Samples of pure ferric, ferrous and mixed valence freudenbergite were prepared by different techniques. The ^{57}Fe Mössbauer spectra of the single valence samples showed poorly resolved quadrupole splittings for the ferric sample, two well-resolved quadrupole splittings for the ferrous sample and electron hopping at, and above, room temperature for the mixed valence sample, which disappeared on lowering the temperature to 50 K.

Keywords Freudenbergite · Iron titanate · Mixed valence · Electron hopping

1 Introduction

There are four quaternary oxide structures in the M_2O-Fe_2O_3-TiO_2 system, where M is a monovalent ion: spinel, calcium ferrite, hollandite and freudenbergite. Freudenbergite is most commonly ferric with composition $Na_2Fe_2^{3+}Ti_6O_{16}$, but can be ferrous, $Na_2Fe^{2+}Ti_7O_{16}$, with a complete solid solution possible between these end-members. Its structure has edge-sharing (Fe,Ti)O_6 octahedra in double sheets parallel to (001) and corner-sharing perpendicular to this [1]. The charge compensating Na^+ ions are in the channels between the octahedra. The iron titanates have a rich history of interesting Mössbauer results

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J. D. Cashion (✉)
School of Physics, Monash University, Melbourne, Vic 3800, Australia
e-mail: john.cashion@monash.edu

A. Lashtabeg
Nanolytical, PO Box 21, The Gap, Brisbane, Qld 4061, Australia

E. R. Vance
Australian Nuclear Science and Technology Organisation, Menai, NSW 2234, Australia

D. H. Ryan
Physics Department, McGill University, Montreal, Québec H3A 2T8, Canada

[2], with freudenbergite the least studied. Freudenbergite has been investigated as a potential mineral for SYNROC because of its ability to retain sodium [3].

The Fe and Ti atoms are randomly distributed between the octahedral M(1) and M(2) sites. A previous Mössbauer experiment on a natural ferric freudenbergite [4] showed that the Fe was nearly equally distributed between the two sites, with the subspectrum with the larger quadrupole splitting being assigned to the crystallographically more distorted M(1) site. Samples of ferrous freudenbergite have been described by Patchen et al. [5], but the crystals are inconveniently small for Mössbauer spectroscopy ($< 150 \times 40\mu$m) and there do not appear to be any Mössbauer spectra of ferrous freudenbergite in the literature.

2 Samples

Several different samples of freudenbergite were prepared, only three of which will be described here. Two were prepared [3] from aqueous mixtures of $NaNO_3$, $Fe(NO_3)_3.9H_2O$, and Ti isopropoxide with the nominal compositions for ferric and ferrous freudenbergite as given in the previous section. These were stir-dried, calcined in air for 1 h at 700 °C, hand-ground, ball-milled in cyclohexane for 3 h and then sintered for 2 h at 1200 °C in either air (sample 1) or argon (sample 2). In order to ensure a mixed valence, the same method was used to make a sample of $Na_2Al_{2-2x}Fe_xTi_{6+x}O_{16}$, with $x = 0.5$, and heated in argon (sample 3). The composition used 10 % excess of Na and 10 % excess of Ti to try to keep all the Fe in the freudenbergite. All the samples were checked by XRD and SEM. The XRD showed that Sample 1 had a few percent of the ferric brownmillerite Fe_2TiO_5, which has Mössbauer parameters very similar to those expected for freudenbergite [6]. Samples 2 and 3 had freudenbergite as the only iron-containing phase. These results were all confirmed by SEM.

It was noticeable that the air-fired samples were a greenish-brown colour, while the argon-fired and aluminium-containing samples were black. Diffuse reflectance spectroscopy was used to examine samples 1, 2 and 3 in the range 200–800 nm. The air-fired sample showed a very rapid drop-off in reflected intensity between 500–600 nm, while the other two samples showed a continuous increase from 500 nm up to 800 nm.

3 Mössbauer results and analysis

The spectrum of a pure ferric freudenbergite (sample 1) is shown in Fig. 1a. Fitting this spectrum to two doublets, as expected from the crystallography, proved to be very challenging and it was not possible to obtain an unambiguous fit. Constraining parameters such as equal areas and/or equal linewidths for the two components did not produce satisfactory results. The fit shown is to one Voigtian doublet, and although the χ^2 value is slightly higher than the other possibilities, it illustrates how little difference there is between the parameters of the M(1) and M(2) sites. The small misfit around 0.5 mm/s is evident. The blue line represents the difference between the fit and the data in all the figures.

As a test of symmetry about the mean δ of 0.36 mm/s, the left hand side was subtracted from the right hand side. For two different samples, each produced a very small negative peak initially, passing through zero at 0.17(2) mm/s from the doublet centre and then going briefly positive before decreasing to a statistical zero. This shows that there are two components there, but the difference in the parameters is smaller than we could unambiguously fit.

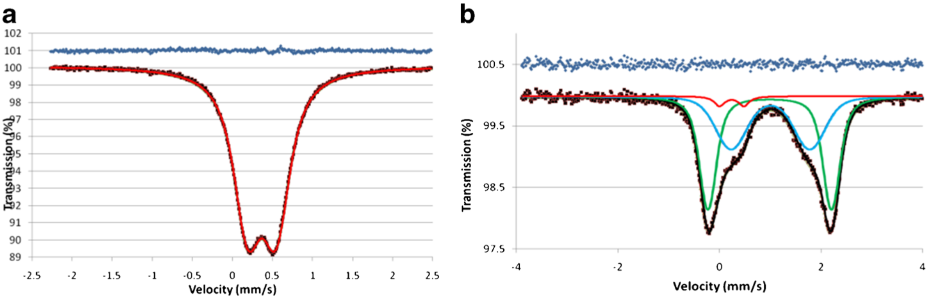

Fig. 1 **a** Room temperature spectrum of pure ferric freudenbergite (sample 1), fitted with one Voigtian doublet. **b** Room temperature spectrum of almost pure ferrous freudenbergite (sample 2), fitted to three Voigtian doublets

Table 1 Mössbauer parameters for fits to the spectra shown

Sample	Temp	Ferric site			Ferrous site		
	K	δ (mm/s)	Δ (mm/s)	Area (%)	δ (mm/s)	Δ (mm/s)	Area (%)
1	RT	0.36(1)	0.36(1)	100	–	–	–
2	RT	0.23(3)	0.48(5)	3	0.99(1)	2.43(1)	55
					1.00(1)	1.55(7)	42
3	50	0.49(1)	0.38(1)	53	1.12(2)	2.88(1)	40
					1.06(4)	2.12(23)	7
	304	0.42(1)	0.39(1)	43	0.96(2)	1.92(3)	24
					0.69(3)	1.08(6)	33
	452	0.33(2)	0.36(6)	35	0.74(3)	1.20(9)	40
					0.50(6)	0.68(13)	25
Ref [4]	RT	0.38(2)	0.45(5)	55(13)	–	–	–
		0.34(2)	0.21(5)	45(13)			

The spectrum of sample 2 is shown in Fig. 1b. The fit shown is to two Voigtian doublets for the ferrous component, and another Voigtian doublet for the weak ferric doublet. The parameters of the ferric component have not been constrained and do not match those from sample 1, nor the room temperature parameters of sample 3 (Table 1), although χ^2 was only marginally higher if the parameters were constrained to either of these parameter sets. While it is possible that it is due to an impurity, the 3 % intensity, in spite of the clean XRD and SEM analyses, suggests that the difference from the other ferric freudenberg parameters may be due to the increase of approximately 1 % in the lattice parameters of the ferrous sample relative to sample 1.

The spectrum of sample 3 at 304 K is shown in Fig. 2a and is clearly very different from either of the spectra in Fig. 1. There is a clean ferric doublet structure together with a relatively featureless absorption at higher velocities which is part of a ferrous contribution, the remainder of which is hidden under the ferric contribution. The ferric component has been fitted to a Voigtian doublet. The ferrous component has been fitted to a sum of two Voigtian doublets, after trying various alternatives including a correlation between the isomer shift,

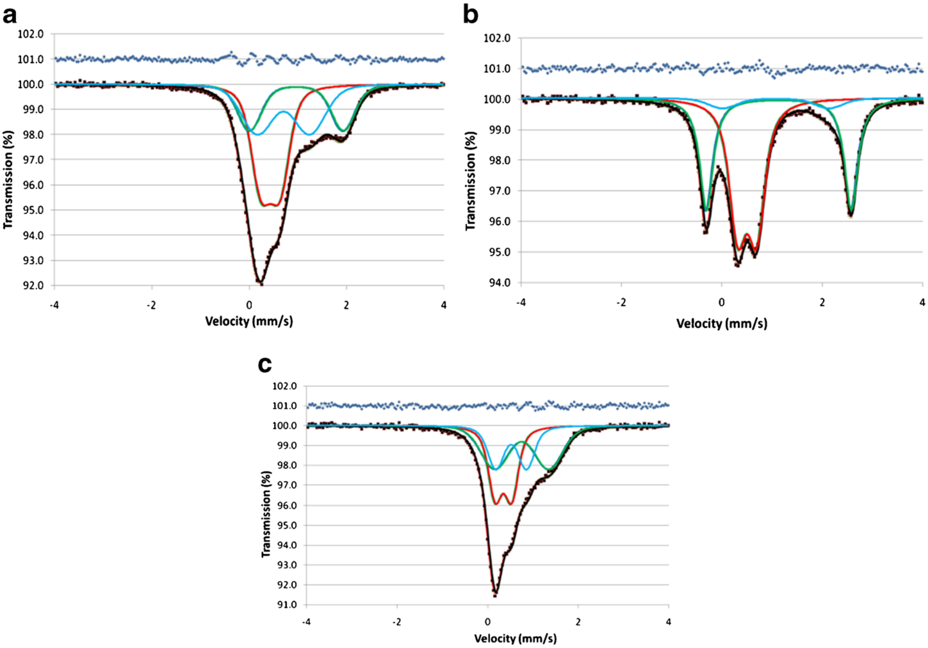

Fig. 2 **a** Mössbauer spectrum of mixed valence freudenbergite at room temperature. **b** Mössbauer spectrum of mixed valence freudenbergite at 50 K. **c** Mössbauer spectrum of mixed valence freudenbergite at 452 K

δ, and the quadrupole splitting, Δ. While the fit is not perfect, it is adequate to follow the behaviour of the ferrous component. All the parameters are given in Table 1.

Reducing the temperature to 50 K sharpened up the ferrous components (Fig. 2b), with the parameters also being given in Table 1. The percentage of the area fitted as ferrous had decreased from 54 % to 47 %. Raising the temperature to 452 K (Fig. 2c) resulted in a considerable narrowing of the envelope although the spectrum could still be fitted to the same model as before. The ferrous component had increased to 65 %.

4 Discussion

In contrast to our spectrum of sample 1, the freudenbergite spectrum of Stähle et al [4] is decidedly asymmetrical and has been fitted to two clear doublets. This spectrum is of a natural sample which contained, amongst other elements, 0.1 to 0.3 Nb^{5+} atoms per 16 oxygen atoms, which will replace some of the Ti^{4+} atoms. The resulting charge imbalance is compensated by corresponding Na^+ vacancies and we believe that these two changes have had the effect of increasing both the δ and Δ values on the M(2) site The corresponding values on the M(1) site are smaller than our one doublet mean fit.

The spectra of sample 3 at 50 K and 304 K are very similar to those of cronstedtite while undergoing electron hopping [7]. An interpretation of electron hopping is further supported by the different colours of the samples and the optical reflectance spectra, which will be discussed in a subsequent publication. It is apparent that the electron hopping predominantly affects the ferrous contribution to the spectrum while the ferric part is relatively unaffected. This is because the sixth d-electron is the major contributor to the Fe^{2+} EFG, so that its dynamics severely modify the EFG. In contrast, the Fe^{3+} EFG is due to the lattice, which is relatively unaffected by the electron hopping.

There are two possible mechanisms for the operation of the electron hopping. The first is

$$\mathrm{Fe}\,(1)^{2+} + \mathrm{Fe}\,(2)^{3+} \leftrightarrow \mathrm{Fe}\,(1)^{3+} + \mathrm{Fe}\,(2)^{2+}$$

as occurs, for example, in magnetite and many other minerals. However, given that the proportion of iron ions in the octahedral sheet in the mixed valence region is between 12.5 % and 25 %, we must also consider the second possibility of

$$\mathrm{Fe}^{2+} + \mathrm{Ti}^{4+} \leftrightarrow \mathrm{Fe}^{3+} + \mathrm{Ti}^{3+}.$$

We are currently undertaking further measurements to elucidate these possibilities.

5 Conclusions

We have taken ^{57}Fe Mössbauer spectra of pure ferric and pure ferrous freudenbergite. The spectrum of the former material comprised two very similar quadrupole doublets which we could not fit unambiguously, in contrast to the more resolved spectrum of a natural, but less pure, sample studied by Stähle et al. [4]. The spectrum of the ferrous sample showed two well-resolved, but slightly asymmetrical, doublets. Strong electron hopping was observed at room temperature and at 452 K for a mixed valence sample, but it had stopped by 50 K.

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