

^{57}Fe Mossbauer studies of Ba^{2+} -doped potassium ferrite

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1995 J. Phys.: Condens. Matter 7 5657

(<http://iopscience.iop.org/0953-8984/7/28/019>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 12/05/2010 at 21:43

Please note that [terms and conditions apply](#).

^{57}Fe Mössbauer studies of Ba^{2+} -doped potassium ferrite

Amani M Ghandour†, Lennart Häggström† and Kristina Edström‡

† Department of Physics, Uppsala University, Box 530, S-751 21 Uppsala, Sweden

‡ Institute of Chemistry, Uppsala University, Box 531, S-751 21 Uppsala, Sweden

Received 16 January 1995, in final form 16 March 1995

Abstract. Mössbauer spectroscopic study of the hexagonal β -ferrite $\text{Ba}_{0.45}\text{K}_{0.39}\text{Fe}_{11}\text{O}_{17}$ has been undertaken between 10 K and 743 K. Below the magnetic transition temperature ($T_N = 713 \pm 5$ K) six magnetically split Fe^{3+} components can be fitted to our experimental spectra. The broadening of the Fe(1) component is explained by three magnetically non-equivalent Fe(1) ions. The presence of Fe^{2+} could not be detected by the present study. A conduction electron picture is proposed to explain the results.

1. Introduction

Hexagonal β -ferrite compounds have received much less attention than the isomorphous aluminium analogues, β -aluminas, which have been extensively investigated because of their high ionic conductivity [1]. The β -ferrite exhibits electronic as well as ionic conductivity, which are of interest for industrial applications such as fuel cells, batteries and electrode materials [2, 3]. It has been suggested that the electronic conductivity is due to the presence of Fe^{2+} as well as Fe^{3+} in the structure [4], while analysis has shown that the electronic conductivity is greatest in samples with largest Fe^{2+} content [5]. Most work has been devoted to ferrites with different alkali metal additives or variations in stoichiometry (K^+ β -ferrite, $\text{K}_{1-x}\text{Fe}_{11}\text{O}_{17}$, $0 \leq x \leq 1$), on a relatively pure, well defined phase of $\text{KFe}_{11}\text{O}_{17}$. The results are consistent with the view that the excess alkali metal ions are charge compensated by charge reduction of Fe^{3+} to Fe^{2+} and/or vacancies statistically distributed over all Fe^{3+} sites [6].

In the present work, ^{57}Fe Mössbauer spectroscopy has been the tool to study the distribution of Fe between the lattice sites and the type of compensating defect accompanying the excess Ba^{2+} in a mixed ion $\text{Ba}^{2+}/\text{K}^+$ ferrite, namely $\text{Ba}_{0.45}\text{K}_{0.39}\text{Fe}_{11}\text{O}_{17}$. Two charge compensation mechanisms can be identified, a defect around Fe^{3+} ions indicating extra oxygen ions in the sample or vacancies at Fe^{3+} sites and/or the presence of Fe^{2+} . A double compensation mechanism is also possible. Mössbauer spectra at different temperatures (10 K, 295 K and 743 K) are here analysed and discussed in the light of the crystal structure study of this particular ferrite [7] and earlier Mössbauer studies on related β -ferrites [8].

2. Crystallographic data and magnetic structure

The basic lattice of the ferrite is isostructural with that of the hexagonal alkali metal β -alumina, space group $P6_3/mmc$. It is a layered structure with layers perpendicular to the c axis (figure 1) each layer consisting of blocks of Fe–O atoms sometimes called spinel

blocks. These blocks are connected via O bridges. Beside the bridging O, rows of K ions are located there in a rather isolated way. There are four crystallographically identifiable Fe sites in the lattice of the stoichiometric material. Within the unit cell of $K_2Fe_{22}O_{34}$, the Fe ions occupy 12 octahedral sites, Fe(1), and four tetrahedral sites, Fe(2), together with four tetrahedral sites, Fe(3), and two octahedral sites, Fe(4). Within each spinel block, containing 11 Fe atoms, the spins of all seven octahedral Fe ions are parallel, while being antiparallel to all four tetrahedral Fe ions, giving a net moment of $\sim 3.5\mu_B$ for each block [10]. Susceptibility measurements on single crystals of $KFe_{11}O_{17}$ show that the block moments are coupled antiparallel across that of the bridging O, giving a net antiferromagnetic behaviour (known also as antiferrimagnetism) [10]. The same author concluded that the magnetization lies on the c plane.

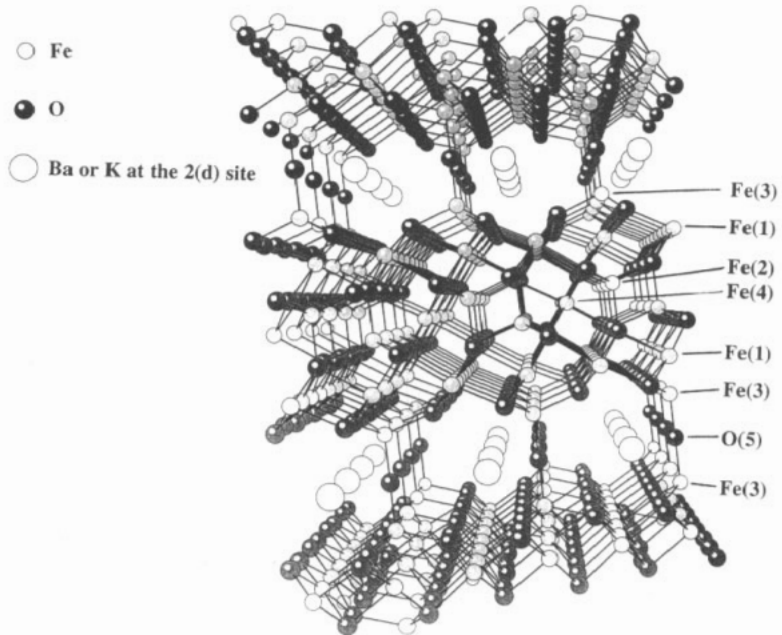


Figure 1. The crystal structure of $Ba_{0.45}K_{0.39}Fe_{11}O_{17}$ drawn using MOVIE MOL [9]. Note the positions of the different Fe ions in the block. The c axis is directed upwards.

Ba^{2+} β -ferrite is less well known and it has been pointed out [11] that Ba^{2+} ionic exchange for K^{+} results in the synthesis of the divalent β'' -ferrite, which is a metastable compound. The latter then converts to the thermodynamically more stable M-type hexagonal ferrite with the magnetoplumbite structure, $BaFe_{17}O_{19}$. The crystal structure of $Ba_{0.45}K_{0.39}Fe_{11}O_{17}$, however, has been determined by x-ray diffraction, and refined in the space group $P6_3/mmc$ [7]. A 2% impurity phase identified as M-type hexagonal structure was also detected. Its presence is an indication of the metastability of the Ba^{2+} β -ferrite.

3. Experimental details

Tiny particles, prepared by the ion exchange method [7], were crushed to fine powder in an agate mortar under alcohol to prevent oxidation and local heating. After drying, the

material was thoroughly mixed with hexagonal boron nitride (BN) and lightly pressed to a thin disc containing ~ 5 mg of natural iron per square centimetre, enclosed between thin iron-free aluminium foil.

The Mössbauer equipment was of conventional constant-acceleration type utilizing a vibrator with a $^{57}\text{CoRh}$ source mounted in the centre and radiating in both directions. One direction is used to simultaneously record calibration spectra using a natural iron foil at room temperature as a standard.

Mössbauer spectra were taken in the temperature range 10–800 K. In the low-temperature region, a liquid helium flow cryostat, with a temperature stability of ± 1 K, was used. A furnace was used for high-temperature measurements and the temperature stability was better than 5 K. The recorded spectra were folded and analysed using the least-squares fitting program MDA [12] to Lorentzian absorption lines, considering the absorbers to be thin.

4. Results and analysis

Representative Mössbauer spectra of $Ba_{0.45}K_{0.39}Fe_{11}O_{17}$ at different temperatures are shown in figure 2. Due to the crystallographic structure, Mössbauer spectra below the Néel temperature were expected to contain four sets of six lines (representing the Fe sites). Acceptable fitting of the spectra with only four sites turned out to be possible except for the intermediate-temperature-region spectra, as exemplified by the 295 K spectrum. A problem arises for the Fe(1) subspectra as directly seen in figure 2, the outer lines of Fe(1) at around -6.7 mm s^{-1} and at 7.2 mm s^{-1} having different heights and linewidths. This suggested a more detailed analysis of the magnetic structure.

Considering the fact that the magnetic field lies in the c plane, the Fe(1) site can be divided into three subsites. For Fe(1) sites, mirror planes formed by the nearby $2 \times O(3)$ and $2 \times O(4)$ atoms passing through the Fe site imply that one of the principal axes of the EFG tensor at the Fe nucleus is perpendicular to these planes. The other two principal axes must therefore be in the mirror plane but the exact direction is not known. In the unit cell the normal (principal axis) to the mirror planes forms an equiangular triangle with one side along the hexagonal a axis. With respect to a definite direction of the submagnetization in the c plane, there will in principle exist three different angles between the magnetization and this principal axis for the Fe(1) atoms. For Fe(2), Fe(3) and Fe(4) sites, a threefold axis passes through the Fe atom parallel to the c axis, which implies that for these sites the EFG tensor is axially symmetric ($\eta = 0$), with the principal z axis along the c axis. The angle θ between the principal z axis and the magnetic field would be 90° for all these latter sites.

Due to the considerations above, the magnetic spectra were fitted with six patterns having the fixed intensity ratio of their site occupation numbers with the first intensity divided into three equal groups belonging to the Fe(1) site. Further considerations in these fits were that the linewidths for all the Lorentzian lines were constrained to be equal and that the centroid shifts of the Fe(1) site patterns were the same.

Defining the transition temperature as the temperature where 50% antiferromagnetic ordering occurs on cooling, the Néel temperature T_N , obtained was (713 ± 5) K. The coexisting region of a paramagnetic pattern and a magnetic pattern in the Mössbauer spectra is between around 695 K and 730 K. The spectrum collected at 743 K (figure 2) was fitted with four doublets emanating from the four different crystallographic sites. The results of the fitting are presented in table 1.

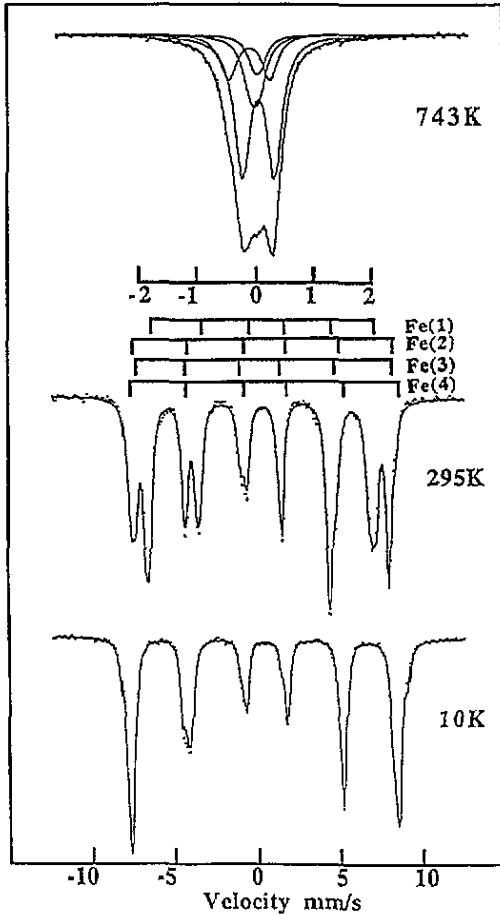


Figure 2. ^{57}Fe Mössbauer spectra of $\text{Ba}_{0.45}\text{K}_{0.39}\text{Fe}_{11}\text{O}_{17}$ recorded at 743 K, 295 K and 10 K.

5. Discussion

The centroid shift values at room temperature (table 1) are in the known range for Fe^{3+} ions in octahedral and tetrahedral sites. The magnetic hyperfine field values are compatible to the ones obtained before for $\text{KFe}_{11}\text{O}_{17}$ [8]. At $T = 10$ K, the magnetic hyperfine fields for Fe(1) approached the fields from the two tetrahedral sites (Fe(2) and Fe(3)); these were all ~ 50 T. The value for Fe(4) had risen to 54 T. All these field values show that all Fe atoms have a valence very near to 3+. The small differences, of the order of 2%, between the Fe(1) fields are due to the differences in the magnetic dipolar contributions to the magnetic hyperfine field. The increase in the magnetic field between 295 K and 10 K is much larger for Fe(1) as compared to the other Fe atoms. This may, in the localized model for magnetism, be taken as an indication of a larger spin value for Fe(1) as compared to the other Fe atoms. Assuming Fe(1) to have valence 3+ the other Fe atoms would have slightly lower valences.

From the brief Mössbauer report by Frankel *et al* [13], four hyperfine patterns were taken for granted for later studies of $\text{KFe}_{11}\text{O}_{17}$, and Howe and Dudley [8] used these to fit their spectra of $\text{KFe}_{11}\text{O}_{17}$. The width of the Lorentzian lines emanating from the Fe(1)

Table 1. Hyperfine parameters from the least-squares fitting to the spectra shown in figure 2. δ is the centroid shift, Δ denotes the electric quadrupole splitting (as defined in the text); both are in millimetres per second, and B_{hf} is the magnetic hyperfine field in tesla. The absorber line width (FWHM) Γ is in millimetres per second. The estimated limits of error are 0.001% mm s⁻¹ for δ , Δ and Γ , and 1 T for B_{hf} .

Temperature (K)	Fe(1) site									
	Fe(1)1, $I = \frac{2}{11}$			Fe(1)2, $I = \frac{2}{11}$			Fe(1)3, $I = \frac{2}{11}$			Γ
	δ	Δ	B_{hf}	δ	Δ	B_{hf}	δ	Δ	B_{hf}	
10	0.447	-0.279	49	0.447	-0.157	51	0.447	-0.193	50	0.147
295	0.364	-0.310	41	0.364	-0.146	44	0.364	-0.212	43	0.194
743	0.040	0.570	—	—	—	—	—	—	—	0.117

Temperature (K)	Fe(2), Fe(3) and Fe(4) sites									
	Fe(2), $I = \frac{2}{11}$			Fe(3), $I = \frac{2}{11}$			Fe(4), $I = \frac{1}{11}$			Γ
	δ	Δ	B_{hf}	δ	Δ	B_{hf}	δ	Δ	B_{hf}	
10	0.395	-0.067	52	0.342	0.352	51	0.455	-0.028	54	0.147
295	0.282	-0.046	49	0.229	0.309	48	0.342	0.019	51	0.194
743	-0.021	0.157	—	-0.110	0.726	—	0.024	0.093	—	0.117

site was broad and this feature was attributed to interaction between Fe and the alkali metal ions, although the shape of the fitted function was not shown. According to our results and analysis above, this interpretation of the line broadening seems not so probable. In our case the non-stoichiometry of the Ba/K ions would cause different near atomic surroundings for Fe(4). This could then give rise to line broadening for the corresponding Mössbauer pattern. This cannot however be verified in the present study.

The assignment of different Mössbauer patterns to definite tetrahedral sites need to be discussed. The atomic population for Fe(2) and Fe(3) is the same and both have near surroundings of four O atoms with a mean distance of 1.903 Å and 1.850 Å respectively [7]. The magnetic hyperfine field at 295 K and at 10 K is almost the same for the two tetrahedral sites indicating very small differences in the valence for Fe at these sites. Since larger s electron density at the Fe nucleus corresponds to smaller centroid shift, it is therefore tempting to ascribe the pattern with the smaller centroid shift to Fe(3) with a more compact near surrounding of O atoms.

The possibility of Fe²⁺, as a constituent and part of the charge compensation mechanism, was also considered. According to the chemical formula using the valences 2+ for Ba and 1+ for K and 2- for O the average valence for Fe would be 2.98+. The small proportion of the total iron as Fe²⁺ would then be 1.5%, which is at the limit of detection by Mössbauer spectroscopy if the Fe²⁺ resonance pattern is resolved from the Fe³⁺ pattern. Since the saturated magnetic hyperfine field for an Fe²⁺ atom is of the order of 40 T the search for an Fe²⁺ pattern at room temperature is greatly hindered by the overlap of the Fe(1) pattern having the same field. We found it therefore better to look for a Fe²⁺ pattern above the Néel temperature. The centroid shift at room temperature for a 4 O coordination lies around 0.82(13) mm s⁻¹ for Fe²⁺ and around 0.30(10) mm s⁻¹ for Fe³⁺, a difference of 0.52(23) mm s⁻¹. Corresponding values for 6 O coordination are around 1.00(10) mm s⁻¹ (Fe²⁺) and 0.45(10) mm s⁻¹ (Fe³⁺) or a difference of 0.55(20) mm s⁻¹ [14] (all values referring to high-spin states). Assuming the same Debye temperature for all Fe sites the centroid shift difference found at room temperature would be translated to higher temperature. The Fe²⁺ pattern would therefore be centred at around 0.5 mm s⁻¹ at 743 K.

Furthermore the electric quadrupole splitting for Fe^{2+} would be larger than $+2 \text{ mm s}^{-1}$ in both cases. This means that one of the lines in the doublet would be at or beyond 1.5 mm s^{-1} . As can be seen in figure 2 there is no resonance line at these velocities. We have tried to fit the Mössbauer spectra using a small Fe^{2+} component at around these velocities. The fitting of the spectra is however not improved by such a component, and the conclusion is that the amount of Fe^{2+} , if it exists, is lower than 1%.

On the other hand, β -ferrite is an electric conductor as well as an ionic conductor, which suggests that the material is not completely ionic and the average charge on the Fe ions is neither $2+$ nor $3+$. This view is further strengthened by the discussion above of a lower valence for Fe(2-4) as compared to Fe(1).

The possibility of Fe vacancies (0.7%) as a charge compensation mechanism is not possible to study with Mössbauer spectroscopy since the variation of the spectral intensities is larger than the intensity change caused by the vacancies.

In the paramagnetic state, the quadrupole splitting $|\Delta_{\text{PM}}|$ is defined as the peak separation in a doublet, i.e.,

$$\Delta_{\text{PM}} = (eQV_{zz}/2)\sqrt{1 + \eta^2/3}$$

where eQ is the nuclear electric quadrupole moment of the excited state. For a dominating magnetic hyperfine interaction, first-order perturbation theory gives for the electric quadrupole shift Δ_{M}

$$\Delta_{\text{M}} = (eQV_{zz}/2)(3 \cos^2 \theta - 1 + \eta \sin^2 \theta \cos 2\phi)/2.$$

θ and ϕ are the conventional angles governing the directions of the magnetic hyperfine field versus the principal components of the EFG. This Δ_{M} is the same as $[(v_5 - v_3) - (v_2 - v_1)]/2$ where v_i is the position of the i th peak in a sextet.

Adopting the result of Gorter [10] of the magnetization being in the c plane the angle θ for Fe(2), Fe(3) and Fe(4) sites would be 90° . Using also the fact that the asymmetry parameter $\eta = 0$ the ratio $|\Delta_{\text{M}}/\Delta_{\text{PM}}|$ can be calculated to be $\frac{1}{2}$, if there are no changes in V_{zz} below and above the magnetic transition temperature. In the present case the 295 K and 743 K values give the following ratios: $|\Delta_{\text{M}}/\Delta_{\text{PM}}| = 0.30, 0.43$ and 0.20 for Fe(2), Fe(3) and Fe(4) respectively. The values are lower than the expected value of 0.50. For a pure $3+$ state of the Fe atoms (half-filled shell) small temperature variations (a few per cent) of V_{zz} are expected. For $2+$ states however a relatively large decrease of $|V_{zz}|$ with increasing temperature is often found for the ferrites. The found decrease of V_{zz} is therefore an indication of an electronic contribution to V_{zz} . Furthermore the sign of V_{zz} for Fe(2) is positive but is negative for Fe(3) and Fe(4).

For Fe(1) the situation is more complex since the principal z axis can be either along the normal to the mirror planes or in the mirror planes as discussed above. In general the results for Δ_{M} and for Δ_{PM} can be used to determine the directions of the principal axis but, unfortunately, there exist several solutions so no definite directions can be given.

6. Conclusion

The search for an Fe^{2+} component in the Mössbauer spectra has given a negative result. The valence of the Fe ions is very near to $3+$ but differences in the valences have been found, with larger valence for Fe(1) as compared to the other Fe sites. Since the material is electronically conducting, 3d electrons from the Fe atoms may form electronic bands. In such a band picture the average 3d electron population at each Fe site may not be an integer.

Acknowledgment

The authors wish to thank Dr Shigeru Ito, University of Tokyo, for providing the crystals.

References

- [1] Yao F Y-F and Kummer J T 1967 *J. Inorg. Chem.* **29** 2453
- [2] Dudley G J, Steele B C H and Howe A T 1976 *J. Solid State Chem.* **18** 141
- [3] Dudley G J and Steele B C H 1977 *J. Solid State Chem.* **21** 1
- [4] Hever K O 1968 *J. Electrochem. Soc.* **115** 830
- [5] Roth W L and Romanczuk R J 1969 *J. Electrochem. Soc.* **116** 975
- [6] Boilot J P, Colomban Ph, Collin G and Comes R 1980 *Solid State Ion.* **1** 69
- [7] Edström K, Ito S and Thomas J 1995 *J. Mater. Chem.* at press
- [8] Howe A T and Dudley G J 1976 *J. Solid State Chem.* **18** 149
- [9] Hermansson K and Ojamae L 1993 *University of Uppsala, Institute of Chemistry Report UUIC-B94-500*
- [10] Gorter E W 1963 *J. Appl. Phys.* **34** 1253
- [11] Kalogirou O 1993 *J. Solid State Chem.* **102** 318
- [12] Jernberg P and Sundqvist T 1983 *Uppsala University International Report* 1090
- [13] Frankel R B, Schieber M and Blum N A 1966 *Bull. Am. Phys. Soc.* **11** 50
- [14] Bancroft G M, Maddock A G and Burns R G 1967 *Geochim. Cosmochim. Acta* **31** 2219