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Low-temperature dynamics of bipyramidal ions in $\text{SrFe}_{12}\text{O}_{19}$

J Fontcuberta†, W Reiff‡ and X Obradors§

† Departament de Física Fonamental, Universitat de Barcelona, Diagonal, 647, E-08028 Barcelona, Spain

‡ Chemistry Department, Northeastern University, Boston, MA, USA

§ ICMAB, Consejo Superior de Investigaciones Científicas Barcelona, Martí i Franquès, sin número, 08028 Barcelona, Spain

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Abstract. Low-temperature Mössbauer spectroscopy is used to study the dynamics of the bipyramidal ions in $\text{SrFe}_{12}\text{O}_{19}$ single crystals of magnetoplumbite structure. A photon self-interference model is used to analyse the Mössbauer data. This model allows us to show that the jumping distance of the Fe ions between the two pseudo-tetrahedral sites of the bipyramid decreases with increasing temperature from $R = 0.21 \text{ \AA}$ (300 K) to $R \approx 0.06 \text{ \AA}$ (4.2 K). X-ray diffraction data give excellent agreement with these results and reveals that at low temperatures, the pseudo-tetrahedral 4e sites transform to true bipyramidal sites.

1. Introduction

The magnetoplumbite M structure $\text{MFe}_{12}\text{O}_{19}$ can be described as the intergrowth of blocks R and S, where the R block contains an MO_3 layer hexagonally stacked between two oxide ion layers and the S block contains two oxide ion layers of a (111) slice of the cubic spinel structure. In this structure, the Fe atoms occupy five different sites, having different anion coordinations as indicated in table 1.

Below a critical temperature the spins of the Fe ion are fixed along the hexagonal c axis, giving rise to a ferrimagnetic structure (Albanese 1977).

The bipyramidal (4e) site existing in the R block is unusual for ferric ions; thus it has been studied using various techniques. For example from the analysis of x-ray diffraction data, Townes *et al* (1967) concluded that Fe^{3+} (4e) cations in $\text{BaFe}_{12}\text{O}_{19}$ are not placed

Table 1. Crystallographic characteristics for $\text{MFe}_{12}\text{O}_{19}$ ferrites.

Ion	Wyckoff position	Ions per formula unit	Block
Fe(1)	2a	1	S
Fe(2)	4e ($\frac{1}{2}$)	1	R
Fe(3)	4f	2	S
Fe(4)	4	2	R
Fe(5)	12k	6	R, S

at the mirror plane of the bipyramid but are randomly located at about 0.16 Å along the *c* axis, above and below this plane. Later Obradors *et al* (1985) refined the room-temperature structure of this oxide and showed that the x-ray diffraction data are consistent with fast diffusional motion of the bipyramidal ions between two minima of a bottle-shaped potential well.

Similar conclusions have also been suggested from the results obtained by Mössbauer spectroscopy (Rensen and Van Wieringen 1969, Rensen *et al* 1971, Kreber *et al* 1975, Mamalui *et al* 1979). It was argued that at room temperature the Fe³⁺(4e) ion makes fast jumps between both 4e positions at each side of the mirror plane, thus giving rise to a low *f*-factor along the *c* axis. In addition, it had been reported (Belozerskii and Khimich 1975) that the quadrupole splitting abruptly increases at a low temperature (80 K). This observation was interpreted as an indication that at this temperature the jumping process is inhibited, the Fe(4e) ions being trapped in one of the 4e sites.

However, the relative intensity of the Fe(4e) subspectrum remained much lower than the atomic occupancy of the 4e sites; so the existence of a blocking temperature still appeared to be inconsistent.

In some recent papers we have investigated the dynamics of the bipyramidal Fe ions in a number of hexagonal ferrites—both single-crystal and polycrystalline materials: SrFe₁₂O₁₉ (Fontcuberta and Obradors 1988), BaFe₁₂O₁₉, CaAl₁₁FeO₁₉ and La_{0.7}Na_{0.3}Fe₁₂O₁₉ (Fontcuberta *et al* 1988) in the temperature range 80–300 K. We have found that all the available data can be nicely explained in terms of a photon self-interference phenomenon between parts of a wave train emitted from both 4e sites at each side of the mirror plane. We did not observe any blocking temperature at *T* > 77 K, but the jumping distance that we were able to deduce from the analysis of the data was a decreasing function of temperature. Given that for all the investigated oxides, we obtained excellent agreement between the jumping distances and the 4e–4e distance deduced from structural x-ray diffraction (XRD) data when available, we found it convenient to extend the experimental work at the lowest temperatures, both XRD and Mössbauer spectroscopy, to test the validity and consistency of our model.

In this paper we present Mössbauer absorption data obtained from single-crystal specimens of SrFe₁₂O₁₉ in a temperature range from 4.2 up to 300 K. We shall demonstrate that at any temperature above 0 K there is a diffusive motion of the 4e ions, but the jumping distance decreases with decreasing temperature.

2. Experimental details

Single crystals of SrFe₁₂O₁₉ were grown by the flux method. The as-grown crystals have a platelet shape, with the hexagonal *c* axis perpendicular to the largest face. To prepare Mössbauer absorbers, some crystals were stacked together and polished down to 0.5 mm thickness.

Mössbauer spectra were recorded with a constant-acceleration drive system and a 512-channel analyser. In the first set of experiments (I) the sample was placed in a cryostat with the *c* axis parallel to the incoming γ -ray direction *k* ($\theta = 0^\circ$). The estimated error in the alignment angle was $\pm 3^\circ$ (see below). A number of Mössbauer spectra were recorded between 77 and 4.2 K.

In a second set of experiments (II), the sample was held at constant temperature (77 K) but the angle θ between *k* and *c* was varied. Spectra were recorded for $\theta = 0^\circ$, 20° and 45° .

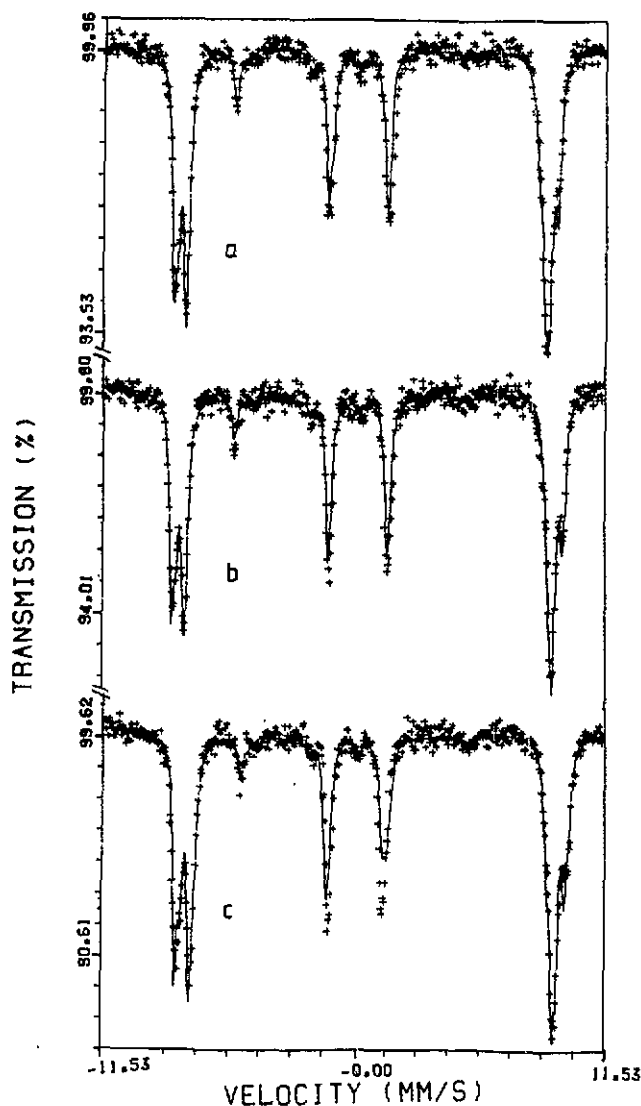


Figure 1. Mössbauer spectra recorded at 4.2 K (spectrum a), 47 K (spectrum b) and 77 K (spectrum c) for $\theta = 0^\circ$.

The fitting procedure was carried out using the standard least-squares method. Because of the close similarity between the hyperfine Mössbauer parameters of $\text{Fe}(f_{vi})$ and $\text{Fe}(2a)$ ions, it is difficult to reach a stable fit if the corresponding sets of Mössbauer parameters are allowed to vary independently. Therefore, we have assumed them to be identical and only four subspectra were included in the fit (Fontcuberta and Obradors 1988).

In order to include any misalignment effect, in the $\theta = 0^\circ$ experiments the intensity of each subspectrum was fitted using two different parameters (intensity ratio, 3:z:1:1:z:3). Of course, for the first set of experiments (I), $z = 0$ and the departure

from this ideal value provided us with an estimation of $\pm 3^\circ$ for the angular accuracy of our experimental set-up.

3. Results and discussion

In figure 1 we show some of the spectra recorded in the temperature range 77–4.2 K for $\theta = 0^\circ$. The spectra reveal the typical features of a magnetically ordered material somewhat simplified by the absence of the $\Delta m = 0$ transitions. These transitions are not allowed in the present configuration (k parallel to the c axis) because the magnetic structure is essentially axial, with all spins lying along the c axis. A small misalignment would be easily observed, as the $\Delta m = 0$ resonances will appear and would be clearly resolved in the 3–6 mm s⁻¹ velocity interval.

As mentioned in section 1, we have proposed a photon interference model to account for the observed small f -factor associated with the bipyramidal Fe ions. In essence, the model assumes that a photon (k) self-interference phenomenon can take place if an absorber atom can jump over a distance R with a characteristic time much shorter than the Mössbauer lifetime t_M . In such a case we have shown (Fontcuberta and Obradors 1988, Fontcuberta *et al* 1988) that the observed f -factor associated with the 4e sites is given by

$$f(k, R) = [f_0(4e)/2][1 + \cos(k \cdot R)] \quad (1)$$

where $f_0(4e)$ is the usual recoil-free fraction for a given lattice site.

Analysis of the room-temperature XRD data (Obradors *et al* 1985) revealed that, when the refinement is carried out with the bipyramidal Fe ions located at the pseudo-tetrahedral 4e sites, the thermal parameters are essentially isotropic and similar for all Fe sites in the unit cell. Therefore we assume that also $f_0(4e)$ is isotropic and it has the same value for any Fe site. With such an assumption, the relative intensity $I(4e)/I(\text{rem})$ ($I(\text{rem})$ is the resonant intensity associated with the Fe nuclei located in the remaining lattice sites) is independent of the actual f_0 -value. It is given by

$$I(4e)/I(\text{rem}) = \frac{1}{2} [1 + \cos(k \cdot R)]. \quad (2)$$

Equation (2) can be used to obtain the jumping distance R from the experimental values of the intensity ratio, determined at any temperature and for any orientation of the crystal with respect to the γ -ray direction k .

In table 2 we summarize the relative intensity values $I(4e)/I(\text{rem})$ as deduced from the fit of the spectra recorded at several temperatures and for $\theta = 0^\circ$. In figure 2, we show the calculated R -values. We also include, for completeness, the data already reported (Fontcuberta and Obradors 1988) for $T > 77$ K.

Within the context of this paper the more relevant result, revealed by the data in table 2 and figure 2, is that the jumping distance R decreases smoothly towards zero at the lowest temperature. As shown in table 2, at 4.2 K, $R < 0.06 \text{ \AA}$, thus signalling that the two minima of the wine-bottle potential will come closer together at low temperatures. Additional confirmation of this result can be obtained by recording Mössbauer spectra for other orientations. Some of the spectra are shown in figure 3. The data are also included in table 2 for $T = 4.2$ K ($\theta = 20^\circ$) and $T = 77$ K ($\theta = 20^\circ$ and 45°). By using equation (2) the jumping distance can now be evaluated for any angular configuration. It is remarkable that at any temperature the jumping distances (see table 1) are closely coincident with those obtained for the $\theta = 0^\circ$ case.

Table 2. Experimental values of the relative intensity $I(4e)/I(\text{rem})$ as deduced from the fit of the Mössbauer spectra at several temperatures and orientations of the crystal with respect to the incoming γ -ray direction. The R -values are the jumping distances computed by using equation (2).

T (K)	θ (deg)	$I(4e)/I(\text{rem})$	R (Å)
4.2	0	0.094 (4)	0.00 (6)
47	0	0.075 (4)	0.12 (1)
77	0	0.066 (4)	0.15 (1)
4.2	20	0.100 (9)	0.00 (-)
77	45	0.076 (4)	0.16 (3)
	20	0.056 (4)	0.19 (3)

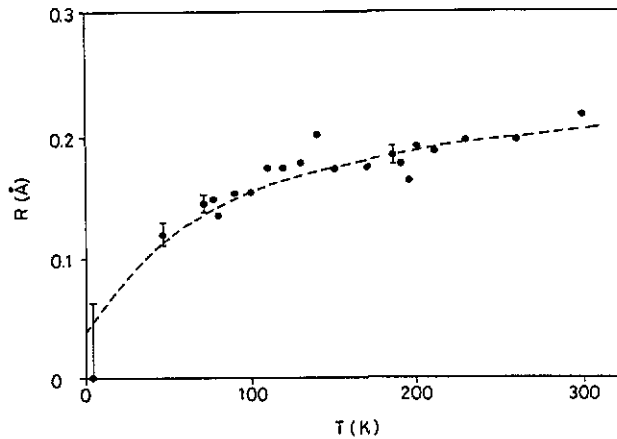


Figure 2. Jumping distances calculated by using equation (2) and the data in table 2. The data for $T > 77$ K are taken from Fontcuberta and Obradors (1988).

This progressive evolution of the double-well potential towards a single harmonic potential, corresponding to a true bipyramidal coordination should also be observed in diffraction experiments. Recent single-crystal x-ray diffraction experiments on $\text{SrFe}_{12}\text{O}_{19}$ appear to confirm this result. Extensive details of the structure refinement will be published elsewhere.

4. Conclusions

By using a photon self-interference model we have been able to deduce the jumping distance of the Fe ions in the bipyramidal sites of the magnetoplumbite structure. Our results show that there is a progressive, but smooth, reduction in the jumping distance, thus suggesting that at low temperatures there is a localization of the Fe ions on the mirror plane of the bipyramid. At higher temperatures a diffusive motion between the

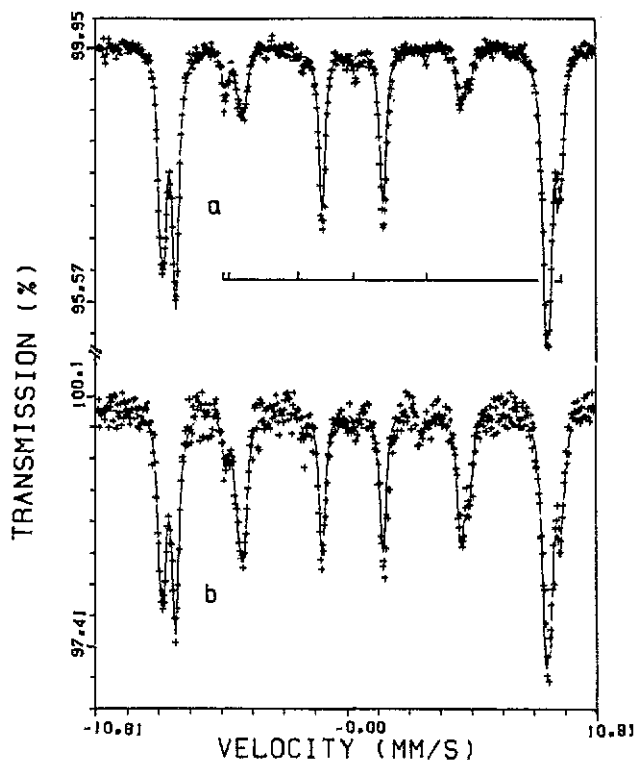


Figure 3. Mössbauer spectra recorded at 77 K for $\sigma = 20^\circ$ (spectrum a) and $\sigma = 45^\circ$ (spectrum b). The subspectrum corresponding to Fe(4e) is shown.

two pseudo-tetrahedral sites of the bipyramid leads to a lowering of the effective recoil-free fraction.

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