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# **$^{57}\text{Fe}$ Mössbauer spectroscopic examination of a single crystal of $\text{Fe}_3\text{O}_4$**

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**Abstract.**  $^{57}\text{Fe}$  Mössbauer spectra have been recorded in fields of up to 13 T from a single crystal of  $\text{Fe}_3\text{O}_4$  cut perpendicular to the [111] axis. The spectra were best fitted with five magnetic components complementing studies on a crystal cut normal to a [100] axis. One component corresponds to  $\text{Fe}^{3+}$  situated on the tetrahedral A sites of the inverse spinel-related structure whilst the other four correspond to  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  on two non-equivalent octahedral sites.

## **1. Introduction**

The iron oxide of composition  $\text{Fe}_3\text{O}_4$  adopts the inverse spinel structure in which  $\text{Fe}^{3+}$  occupies the tetrahedral A sites whilst the B sites are occupied by both  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions. Early studies of the material by  $^{57}\text{Fe}$  Mössbauer spectroscopy at 85 and 300 K [1–4] proposed that the two sextet components could be associated with the occupation by the iron ions of the A and B sites.

A subsequent study [5] suggested that the spectrum recorded below the Verwey transition at 77 K was best fitted to three components corresponding to two  $\text{Fe}^{3+}$  and one  $\text{Fe}^{2+}$  species. The application of an external magnetic field to a single crystal of  $\text{Fe}_3\text{O}_4$  at 85 K [6] gave a spectrum which was interpreted in terms of five magnetic components corresponding to one tetrahedral  $\text{Fe}^{3+}$  site, two octahedral  $\text{Fe}^{3+}$  sites, and two octahedral  $\text{Fe}^{2+}$  sites. More recently [7] the spectrum above the Verwey transition temperature has been suggested as being best fitted to two magnetically non-equivalent B site components and one A site component. Hence, despite long-term interest in this iron oxide, there is a lack of unanimity over the interpretation of the  $^{57}\text{Fe}$  Mössbauer spectrum. We report here on the examination of a single crystal of  $\text{Fe}_3\text{O}_4$  in the presence and absence of applied fields at low temperature and conclude that the spectrum is best fitted to five magnetic components which we interpret in terms of structural properties of the oxide.

## **2. Experimental details**

A single crystal of  $\text{Fe}_3\text{O}_4$  was obtained from the Natural History Museum, London. The crystal axes were identified using x-ray Laue diffraction and a sample was cut with a [111] direction normal to the plane. The sample was set in resin and thinned by abrasion until an optimum Mössbauer spectrum was obtained. Spectra were recorded using a 100 mCi  $^{57}\text{Co}$  in Rh source at 4.2 K in applied fields of 0, 2, 5, 9 and 13 T directed along the [111] direction. The chemical isomer shift data are quoted relative to  $\alpha$  iron at room temperature.

### 3. Results and discussion

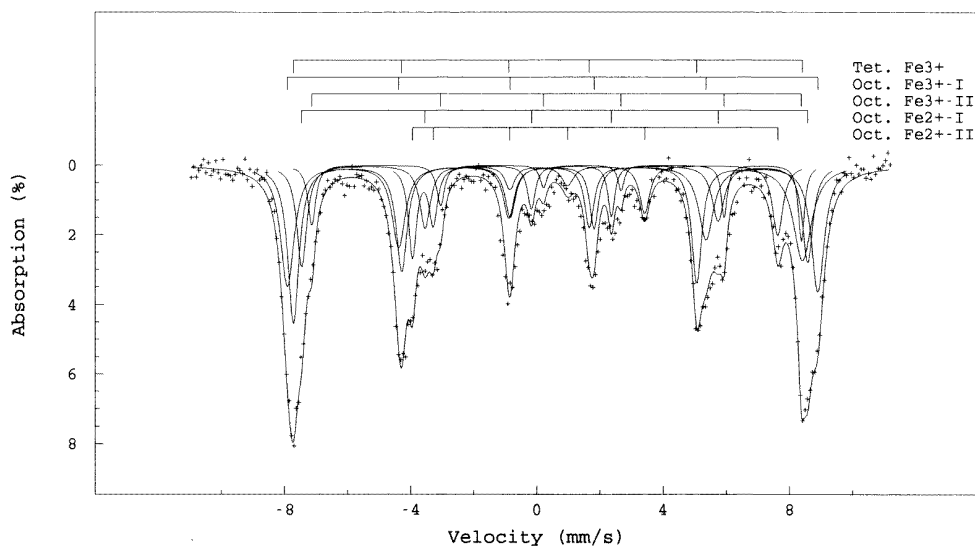
Difficulties in accounting for the behaviour of  $\text{Fe}_3\text{O}_4$  below the Verwey transition at  $T_v \sim 119$  K arise from

(i) the change from cubic crystal symmetry to a lower symmetry (this lower symmetry was initially thought [8,9] to be orthorhombic with a magnetic easy axis parallel to the  $a$  axis but subsequent neutron diffraction [10] and magnetoelectric measurements [11] have indicated a lower symmetry than orthorhombic).

(ii) the pattern of occupation of B sites by  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions and

(iii) the twinning of crystals that occurs on cooling through the Verwey transition.

In the work of Hargrove and Kundig [6] the  $\text{Fe}_3\text{O}_4$  crystal samples were cut so that the [100] direction was parallel to an external magnetic field. The field cooling of the sample through the Verwey transition selected the [001] direction as the orthorhombic  $c$  axis. It was found that a twinned (zero-field cooled) sample yielded a spectrum of broad unresolved lines but that field cooling sharpened the lines of the complex spectrum. In the work reported here the sample was not field cooled but the selected crystallographic orientation dictated that all the  $c$  axes made equivalent angles with the gamma ray beam directed along the [111] direction. The result was a spectrum, shown in figure 1, that is as sharp as the field cooled spectrum described previously [6].

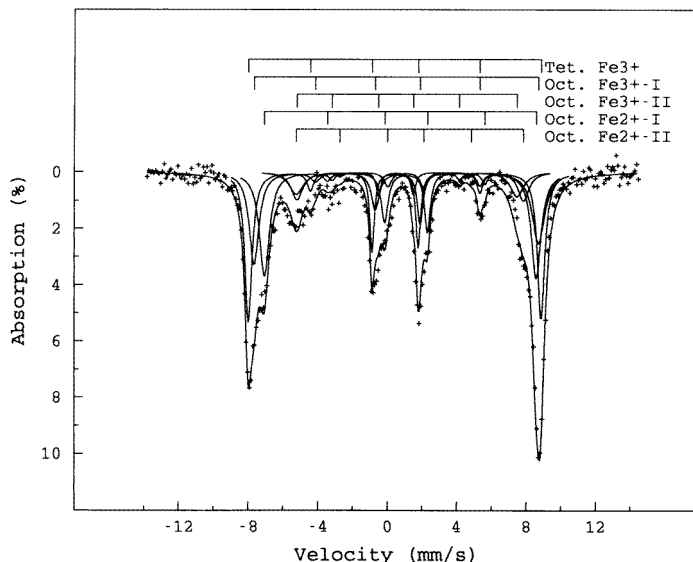


**Figure 1.**  $^{57}\text{Fe}$  Mössbauer spectrum recorded at 4.2 K and in zero applied field from a single crystal of  $\text{Fe}_3\text{O}_4$  cut perpendicular to the [111] axis.

This investigation has extended previous attempts to unravel the complex Mössbauer spectrum by utilizing the simplifying effects of large fields directed along the chosen [111] direction. All spectra were recorded at 4.2 K: that at applied field  $B_a = 2$  T is shown in figure 2 and spectra at applied fields  $B_a = 5, 9$  and 13 T are shown in figure 3. Good fits to these spectra required five magnetic sextet components; all the fitting parameters are listed in table 1. Qualitative equivalences can be seen with the fits reported by Hargrove and Kundig [6] but revealing differences of detail are also apparent which are discussed below.

**Table 1.** <sup>57</sup>Fe Mössbauer parameters recorded from a single crystal of Fe<sub>3</sub>O<sub>4</sub> oriented parallel to the [111] axis at 4.2 K.

Field (Tesla)	Tet. Fe <sup>3+</sup>			Oct. Fe <sup>3+</sup> – I			Oct. Fe <sup>3+</sup> – II			Oct. Fe <sup>2+</sup> – I			Oct. Fe <sup>2+</sup> – II		
	$\delta$ (mm s <sup>-1</sup> )	$\Delta$ (mm s <sup>-1</sup> )	$B$ (Tesla)	$\delta$ (mm s <sup>-1</sup> )	$\Delta$ (mm s <sup>-1</sup> )	$B$ (Tesla)	$\delta$ (mm s <sup>-1</sup> )	$\Delta$ (mm s <sup>-1</sup> )	$B$ (Tesla)	$\delta$ (mm s <sup>-1</sup> )	$\Delta$ (mm s <sup>-1</sup> )	$B$ (Tesla)	$\delta$ (mm s <sup>-1</sup> )	$\Delta$ (mm s <sup>-1</sup> )	$B$ (Tesla)
0	0.37	-0.02	50.1	0.49	0.00	52.2	0.83	-0.27	49.8	1.03	-0.41	48.2	0.96	0.89	35.9
2	0.42	0.00	52.3	0.53	-0.03	50.8	0.89	-0.16	48.6	0.78	0.32	39.3	1.15	0.12	40.6
5	0.39	-0.02	55.1	0.70	-0.29	47.4	0.69	0.17	46.7	0.85	-0.06	40.7	1.15	0.09	38.7
9	0.39	-0.02	58.9	0.74	-0.37	43.8	0.72	0.11	42.9	0.82	-0.03	37.7	1.16	0.01	35.4
13	0.39	-0.01	62.8	0.75	-0.40	40.0	0.74	0.11	39.3	0.82	-0.09	34.2	1.11	-0.05	32.4



**Figure 2.**  $^{57}\text{Fe}$  Mössbauer spectrum recorded at 4.2 K in an applied field of 2 T from a single crystal of  $\text{Fe}_3\text{O}_4$  cut perpendicular to the [111] axis.

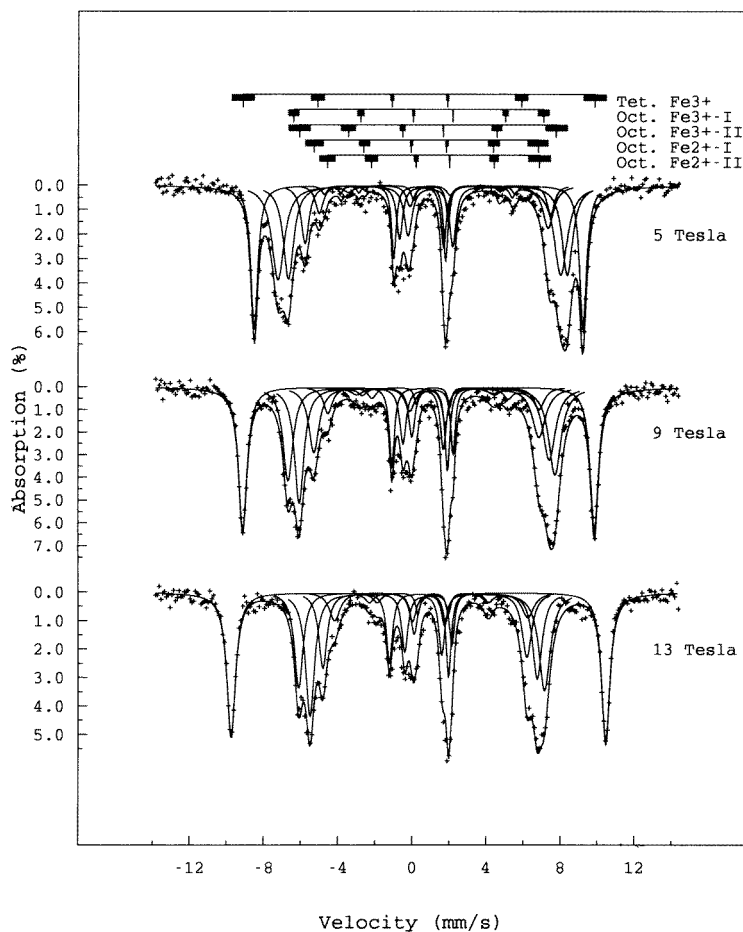
In the fits of [6] the tetrahedral site A component has a relative area fixed at 33% while the areas of all the B sites are fixed at half that value. However Sawatzky *et al* [12] report lower values of the recoilless fraction  $f$  for  $\text{Fe}^{2+}$  sites than for  $\text{Fe}^{3+}$ . Accordingly in our fits the areas were varied freely. The fits showed little variation in the relative areas with applied field and gave relative area values for  $\text{Fe}^{3+}(\text{A}) : \text{Fe}^{3+}(\text{I}) : \text{Fe}^{3+}(\text{II}) : \text{Fe}^{2+}(\text{I}) : \text{Fe}^{2+}(\text{II})$  of 28% : 24% : 23% : 15% : 10% with variations of  $\sim 2\%$ . These values exhibit smaller  $f$  values for  $\text{Fe}^{2+}$  sites though more strongly than the 6% reported in [7].

The simplification from the application of strong fields arises from the alignment of the ferrimagnetic moment parallel to the field along the [111] direction. For applied fields  $B_a > 2$  T full alignment is achieved as shown by the reduction to zero intensity of lines 2 and 5 ( $\Delta m = 0$ ) of each sextet component. In the  $B_a = 0$  spectrum of figure 1 the small peak at  $+3.8$  mm  $\text{s}^{-1}$  cannot be fitted without a fifth component. The extinction of this peak in the applied field spectra confirms that it is a  $\Delta m = 0$  transition and is important in determining the parameters of this  $\text{Fe}^{2+}(\text{II})$  component.

The fields listed in table 1 are effective fields  $B_e$  composed of identifiable contributions as

$$B_e = B_c - B_d \left( \frac{3 \cos^2 \theta - 1}{2} \right) \pm b_a \pm B_{dm}$$

where  $B_c$  and  $B_d$  represent contact and dipolar components of the hyperfine field and  $B_a$  and  $B_{dm}$  represent applied and demagnetizing fields respectively. The spectra and field values contained in table 1 show clearly the joint effect of the applied field and ferrimagnetic coupling in the increase of  $B_c$  with applied field for the tetrahedral  $\text{Fe}^{3+}$  component and the corresponding decrease in  $B_e$  for the octahedral B components as the applied field adds/subtracts collinearly with the hyperfine fields of the components. Small differences between the changes in  $B_e$  and  $B_a$  as  $B_a$  increases from 2 to 13 T in the well defined tetrahedral component are ascribed to the effect of the demagnetizing field  $B_{dm}$ . The



**Figure 3.** <sup>57</sup>Fe Mössbauer spectra recorded at 4.2 K in applied fields of 5, 9 and 13 T from a single crystal of Fe<sub>3</sub>O<sub>4</sub> cut perpendicular to the [111] axis.

hyperfine fields of the octahedral components are not so well defined but follow a definite pattern as  $B_a$  subtracts from the hyperfine field (directed oppositely to the aligned octahedral B site moment). This pattern is followed well in the range  $2 \text{ T} < B_a < 13 \text{ T}$  but additional perturbations are seen to occur in the range  $0 < B_a < 2 \text{ T}$ , most noticeably for the Fe<sup>2+</sup>(I) and Fe<sup>2+</sup>(II) sites. These perturbations arise from the anisotropic dipolar contribution  $B_d$  to the hyperfine fields. The equivalence of the angular variation of this component of the hyperfine field with that of the quadrupole shift links the change in the dipolar hyperfine field with the change in quadrupole shift as the spins are rotated to the [111] direction by the applied field. For the Fe<sup>2+</sup>(II) site the decrease in quadrupole shift from  $0.89 \text{ mm s}^{-1}$  at  $B_a = 0$  to  $0.12 \text{ mm s}^{-1}$  at  $B_a = 2 \text{ T}$  results in an increase in effective field  $B_e$  as the positive change in  $B_d$  outweighs the negative effect of  $B_a = 2 \text{ T}$  subtracting from the hyperfine field. The opposite effect is seen in site Fe<sup>2+</sup>(I) where the increase in quadrupole shift as  $B_a$  increases from 0 to 2 T causes the large decrease in  $B_e$  as the changes due to  $B_d$  and  $B_a$  add.

The obvious difference in the fitting parameters between the present study and the earlier fits to the field cooled single crystal of  $\text{Fe}_3\text{O}_4$  [6] occurs in the quadrupole shift of the  $\text{Fe}^{2+}(\text{I})$  and  $\text{Fe}^{2+}(\text{II})$  sites. In the earlier work [6] the spins were aligned along a [001] axis and quadrupole shifts  $\Delta$  of  $-1.15 \text{ mm s}^{-1}$  and  $2.29 \text{ mm s}^{-1}$  were reported for  $\text{Fe}^{2+}(\text{I})$  and  $\text{Fe}^{2+}(\text{II})$  sites respectively (the signs have been changed to conform to the sign convention used in this work). In the present study with  $B_a > 2 \text{ T}$  and spin alignment along a [111] direction the values in table 1 show  $\Delta = e^2qQ/4(3\cos^2\theta - 1) \approx 0$ —implying a value of  $\theta = 55^\circ$ . This angle is that between cubic [001] and [111] directions indicating that the principal axis of the electric field gradient  $V_{zz}$  lies along the [001] direction and the values of  $\Delta$  reported in [6] are those of the full quadrupole shift  $e^2qQ/2$ . In table 1 the values of  $\Delta$  for  $\text{Fe}^{2+}(\text{I})$  and  $\text{Fe}^{2+}(\text{II})$  sites for  $B_a = 0$  are seen to be  $-0.41 \text{ mm s}^{-1}$  and  $+0.89 \text{ mm s}^{-1}$  respectively. These intermediate values occur due to the action of the residual field in the magnet ( $< 0.03 \text{ T}$ ) causing a partial alignment of the spins toward the [111] direction. This partial alignment affects the hyperfine field value for site  $\text{Fe}^{2+}(\text{II})$  via the anisotropic dipolar component. This accounts for the lower value of  $35.9 \text{ T}$  compared to that in [6] where the spins lie along the [100] axis. A few details are not resolved in these fits—for example the  $\text{Fe}^{3+}(\text{I})$  isomer shift that changes from  $0.40 \pm 0.08 \text{ mm s}^{-1}$  at  $B_a = 0$  to  $0.75 \pm 0.08 \text{ mm s}^{-1}$  at  $B_a = 13 \text{ T}$ , but overall the model of five ferrimagnetically coupled components is seen to give good fits to spectra taken over a wide range of applied field. The fitting parameters evolve with applied field in a comprehensible manner and are compatible with those of earlier work carried out in different geometry. The study provides a stringent test of the  $\text{Fe}_3\text{O}_4$  magnetic structure in which a tetrahedral A  $\text{Fe}^{3+}$  site is ferrimagnetically coupled to two inequivalent octahedral B  $\text{Fe}^{3+}$  sites and two inequivalent octahedral B  $\text{Fe}^{2+}$  sites.

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