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1993 J. Phys.: Condens. Matter 5 3265

(http://iopscience.iop.org/0953-8984/5/19/022)

J. Phys.: Condens. Matter 5 (1993) 3265–3274. Printed in the UK

Field-induced phase transitions in neutron-irradiated haematite

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Received 4 March 1993

Abstract. Mössbauer spectra of three neutron-irradiated polycrystalline haematite (α-Fe_2O_3) samples have been recorded at 4.2 K in applied fields of up to 10 T. Field-induced phase transitions were observed, and were found to differ markedly from those that occur in non-irradiated haematite. In two lightly irradiated samples, transitions were detected from a state with Fe^{3+} spins near the [111] axis ('antiferromagnetic phase') to one where the spins are almost perpendicular to both the applied field and to the [111] axis ('weak ferromagnetic phase'). In the case of a heavily irradiated sample, in which the spins were initially in the weak ferromagnetic phase, the spins were observed to lie almost perpendicular to applied fields of greater than ~ 4.5 T. The difference in behaviour in irradiated and non-irradiated haematite is attributed to a smaller difference in anisotropy energy, in the irradiated samples, between the antiferromagnetic and weak ferromagnetic phases at 4.2 K.

1. Introduction

Phase transitions in haematite (α-Fe_2O_3), both those induced by temperature changes, and those induced by an applied magnetic field, have been the subject of many investigations. In the temperature-driven Morin transition, a phase transition occurs between a high temperature weak ferromagnetic state and a low temperature antiferromagnetic state at $T_M \sim 260$ K (in pure, non-irradiated haematite) [1]. Below T_M the Fe^{3+} spins align antiferromagnetically along the trigonal [111] axis, while above T_M the spins lie in the basal [111] plane but are not precisely antiparallel, being canted by $\sim 0.01°$ to produce a net moment in the basal plane. The origin of this weak canting lies in the symmetry of the haematite crystal structure, and has been described theoretically in terms of an antisymmetric exchange interaction between neighbouring spins of the form $\boldsymbol{D} \cdot \boldsymbol{S}_1 \times \boldsymbol{S}_2$ where $\boldsymbol{D}$ is the Dzyaloshinsky–Moriya anisotropy term, a constant vector parallel to the [111] axis [2,3].

Field-induced phase transitions in pure crystal haematite samples have also been extensively studied [4–8]. Below T_M the ferric spins can be made to undergo (i) a 'spin-flop' transition if the applied field is directed parallel to the [111] axis [4,7,8] and (ii) a 'screw rotation' transition if the applied field is directed perpendicular to the [111] axis [5,6,8]. In the spin-flop transition the spins reorient from the [111] axis to the (111) plane in an abrupt transition. At 4.2 K the applied field required to produce a spin-flop, B_{sf}, is in the range 6.3 T–6.8 T [4,7,8]. In the screw rotation transition the applied field perpendicular to the [111] axis produces a weak canting of the moments, and a weak ferromagnetic moment in the (111) plane. This in turn makes it energetically more favourable for the spins to effectively return to their $T > T_M$ state, with the antiferromagnetic axis of the spins in the (111) plane. Thus one observes a gradual rotation of the antiferromagnetic axis of the spins

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away from the [111] axis, towards the (111) plane, as well as a gradually increasing weak ferromagnetic moment in the (111) plane, as the applied field strength increases. The field at which this transition is complete, B_c, has been variously reported in the literature to be ~ 16.2 T at 100 K [5,6], ~ 5.4 T at 230 K and ~ 2.5 T at 245 K [5], and > 10 T at both 230 K and 245 K [8].

The spin configurations in the initial and final states of each of these three phase transitions (Morin, spin-flop and screw rotation) are shown schematically in figure 1.

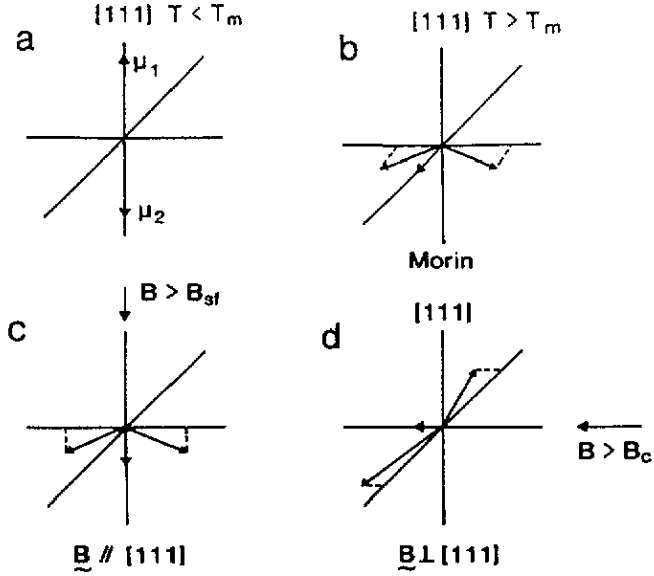

Figure 1. Schematic diagram of the spin configurations in non-irradiated haematite (a) below the Morin transition temperature T_M in zero applied field, (b) above T_M in zero applied field, (c) below T_M in a field exceeding the spin-flop field B_{sf} along the [111] axis, and (d) below T_M in a field exceeding the screw rotation critical field B_c perpendicular to the [111] axis.

In this paper we present the results of an ^{57}Fe Mössbauer effect study of the effect of neutron irradiation on the field-induced phase transitions in haematite. This work is a continuation of our earlier consideration of the effect of neutron bombardment on the Morin transition and on the low temperature magnetic state in haematite [9, 10]. In the previous work, we found that as the neutron-irradiation dosage increased, the Morin transition temperature decreased, and that in heavily irradiated samples a 'reverse Morin transition', from an antiferromagnetic state to a weak ferromagnetic state, was observed at low temperatures. This result was shown to be consistent with an irradiation-mediated change in the total magnetic anisotropy of the haematite samples [9, 10]. The logical extension of this work is to consider the effect of irradiation on the field-induced spin-flop and screw rotation transitions.

2. Experimental details

The powder samples used in this study comprise three of the four used in the previous temperature-dependent study of irradiated haematite [10]. The samples were subjected to

different degrees of irradiation from the neutron flux of a reactor. The degree of irradiation of each sample is characterized by the fraction of displaced atoms (FODA),

$$\text{FODA} = \int [\phi(E)\sigma_s(E)t\,dE]/[AE_d] \tag{1}$$

where $\phi(E)$ and $\sigma_s(E)$ are the neutron flux and the elastic scattering cross section at the neutron energy E, A and E_d are the relative atomic mass and the displacement energy of the atoms in the sample, and t is the time of irradiation. The FODA values for the irradiated samples 1, 2 and 3 used in this study were 0.9, 1.2 and 2.0×10^{-3} respectively.

Mössbauer spectra were recorded using a ^{57}Co in Rh source of initial strength 100 mCi and a conventional double-ramp constant acceleration spectrometer in transmission mode. The samples were cooled to 4.2 K by immersing them in a liquid helium bath cryostat. Fields of up to 10 T were applied perpendicular to the γ-ray beam using a pair of Helmholtz superconducting coils. Velocity calibration and reference isomer shift were obtained from the spectrum of a 25 μm α-Fe foil at room temperature.

3. Lightly irradiated haematite

3.1. Visual inspection

The applied field Mössbauer spectra of the two lightly irradiated samples, 1 and 2, were found to be very similar. The spectra recorded for sample 1 are shown in figure 2. Three features are apparent on visual inspection of the spectra. First, a small degree of line broadening is evident as the applied field B increases, with a maximum observed linewidth of ~ 0.4 mm s^{-1} for $B \simeq 2$ T. Second, the relative line positions change with increasing field. In zero field the separation of the left-most lines of the sextet (lines one and two) is smaller than the separation of lines five and six, whereas in the $B = 10$ T spectrum the opposite is the case. Third, the relative line intensities change with applied field. In zero field the ratio of the intensities of the outer:middle:inner pairs of lines is approximately 3:2:1, while in the $B = 10$ T spectrum the ratio is close to 3:4/3:1.

The small degree of line broadening observed is markedly different from that which has previously been seen in non-irradiated polycrystalline haematite at 4.2 K [11]. In that case a maximum linewidth ~ 1.3 mm^{-1} was obtained for $B = 6$ T, which was consistent with the contributions from those crystallites within the powder for which the [111] axis was nearly parallel to the applied field direction. (Those spins would therefore still be in the antiferromagnetic state, since the spin-flop transition field is ~ 6.5 T, and would exhibit a well split Mössbauer spectrum due to the vector addition of the applied field to the spin-up and spin-down sublattice hyperfine fields.) The applied field spectra seen here for the weakly irradiated haematite sample are more reminiscent of those recorded for non-irradiated haematite powders at temperatures above T_M, where the haematite is in the weak ferromagnetic state [12].

The relative line positions in an ^{57}Fe Mössbauer spectrum are governed by the combined electric quadrupole and magnetic hyperfine interactions at the Fe nuclei. When the quadrupole interaction is small compared to the magnetic interaction, as is the case in haematite, a 'quadrupole shift' of 2ϵ is observed in the line positions, where

$$2\epsilon = \tfrac{1}{2}(\Delta_{56} - \Delta_{12}) \tag{2}$$

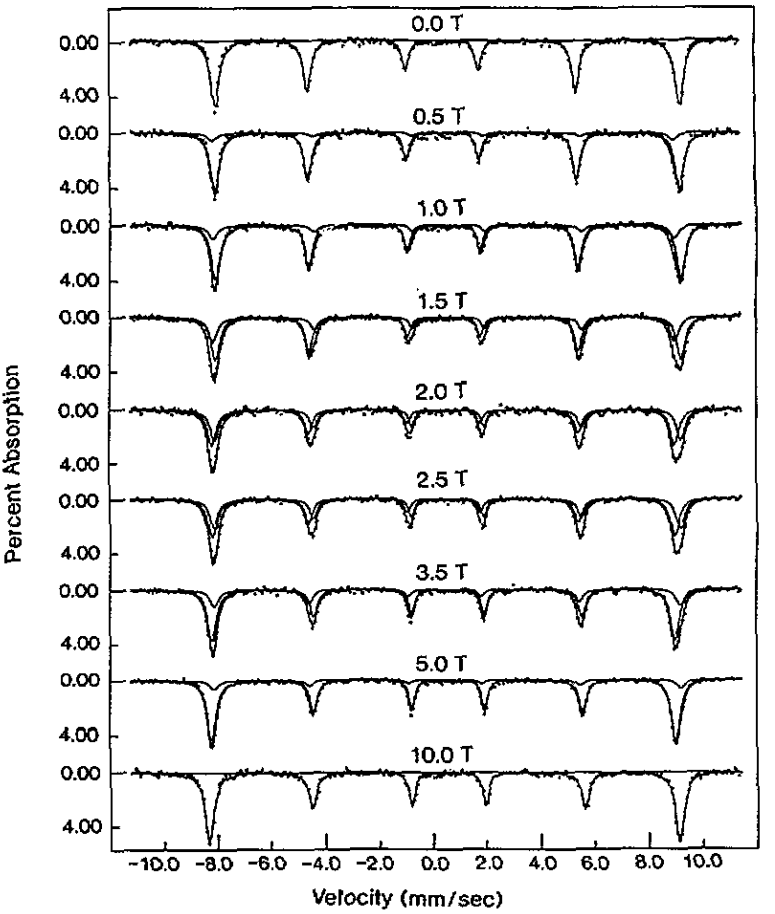

Figure 2. Mössbauer spectra of a polycrystalline sample of weakly irradiated haematite (sample 1) at 4.2 K, in applied fields of up to 10 T directed perpendicular to the γ-ray beam. The spectra are fitted with two components: an intermediate antiferromagnetic state, and a destination weak ferromagnetic state.

and Δ_{12} and Δ_{56} are the separations of lines one and two, and five and six, respectively. The quadrupole shift may also be related to the relative orientations of the major axes of the electric and magnetic interactions:

$$2\epsilon = \tfrac{1}{2}eQ|V_{zz}|\,\tfrac{1}{2}(3\cos^2\theta - 1) \tag{3}$$

where eQ is the nuclear quadrupole moment, V_{zz} is the principal component of the electric field gradient (EFG), and θ is the angle between the V_{zz} axis and the axis of the magnetic field at the nucleus.

It is known that in haematite the EFG principal axis is parallel to the [111] axis [13], and that this direction is temperature independent. Thus, the observation in the spectra of figure 2 that 2ϵ is positive in zero field and negative in a field of 10 T implies that the magnetic moments have reoriented from a position near the [111] axis, with $\theta < 54°$ in equation (3), to a position near the (111) plane, with $\theta > 54°$ in equation (3).

The relative line intensities of the outer:middle:inner pairs of lines in a magnetic ^{57}Fe Mössbauer spectrum are given by:

$$3(1+\cos^2\theta_\gamma) : 4\sin^2\theta_\gamma : (1+\cos^2\theta_\gamma) \tag{4}$$

where θ_γ is the angle between the γ-ray beam and the effective field which is the vector addition of the applied field $\boldsymbol{B}$ and the hyperfine field $\boldsymbol{B}_{\rm hf}$. The observation in the spectra of figure 2 of intensity ratios of 3:2:1 is in keeping with an isotopic distribution of spins over a sphere, with $\langle\cos^2\theta_\gamma\rangle = 1/3$, as is expected for a polycrystalline sample. Intensity ratios of 3:4/3:1, as seen in the $B = 10$ T spectrum, imply that the moments may be confined to a disc which is edge-on to the incident γ-ray beam, for which

$$\langle\cos^2\theta_\gamma\rangle = \tfrac{1}{2}.$$

3.2. *Quantitative analysis*

In order to proceed with a quantitative analysis of the data from samples 1 and 2, a number of different models were considered. First, it was assumed that the response was analogous to that observed in non-irradiated haematite above the Morin temperature, so that each of the applied field spectra comprised only a single well defined sextet of Lorentzian lines. Least-squares computer analysis of the spectra using this model gave poor quality fits, particularly in the $1.0\ \text{T} \leqslant B \leqslant 3.5\ \text{T}$ spectra, where both the line intensities and linewidths were significantly misfit.

Second, a model analogous to that used for non-irradiated haematite below the Morin temperature was used. Following the spin Hamiltonian procedure of Pankhurst and Pollard [11] the spectra were analysed in terms of a uniaxial anisotropy antiferromagnet, with the anisotropy field $B_{\rm A}$ and exchange field $B_{\rm E}$ included in the variable fitting parameters. Once again poor quality fits were obtained, particularly with respect to the line intensities in the $B \sim 2$ T spectra.

The third and last model comprised two component subspectra: a 'destination phase', defined by the Mössbauer spectrum obtained for $B = 10$ T, and an 'intermediate phase', which was taken to account for all of the spectral area that was not in the destination phase for $0\ \text{T} \leqslant B \leqslant 10\ \text{T}$. Several constraints were applied to this model to keep it physically rigorous; these are discussed below. The model gave high quality fits, as represented by the solid lines in figure 2. The proportion of the spectra area contained in the intermediate phase, as a function of applied field, is shown in figure 3.

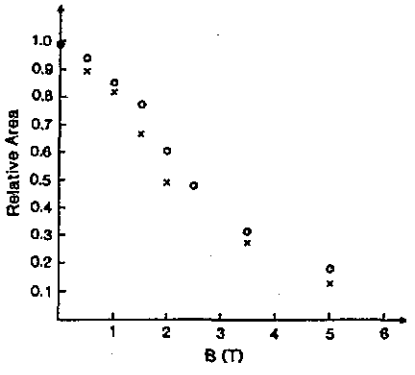

Figure 3. Relative spectral area of the intermediate state of the lightly irradiated sample 1 (×) and sample 2 (○) as a function of applied field.

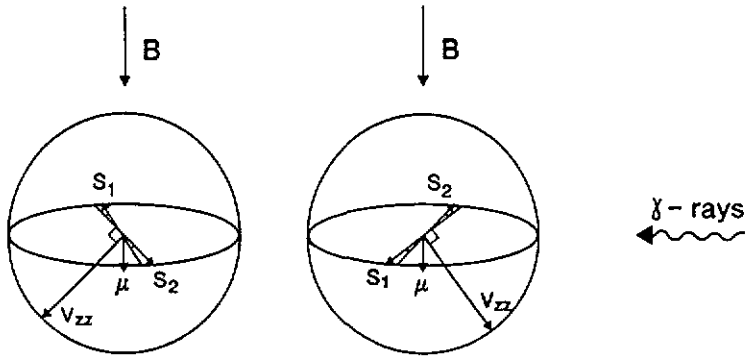

Figure 4. Diagram illustrating the spin configuration at high values of the applied field. The ferric spins are in the (111) plane, slightly canted to create a net magnetic moment oriented along the applied field B. In the polycrystalline samples the principal axes of the electric field gradient at the nucleus (the V_{zz} axes), which in haematite are parallel to the trigonal [111] axes, are randomly oriented in space. Two arbitrary directions for V_{zz} have been chosen here for the purpose of illustration.

The nature of the destination phase was determined by fitting the $B = 10$ T spectrum. The line intensity ratios are very close to 3:4/3:1, implying that all the spins lie in the plane perpendicular to the applied field direction. A single well defined quadrupole shift $2\epsilon = -0.20$ mm s^{-1} was measured. This value is the same as that observed in non-irradiated haematite above T_M, where the spins lie in the (111) plane, perpendicular to the EFG principal axis direction. Consequently, the destination phase may be identified with the weak ferromagnetic state in which the net moment is parallel to the applied field, and the antiferromagnetic axis of the spins lies both perpendicular to the applied field direction, and in the (111) plane. In other words, in the destination phase all the spins are in a weak ferromagnetic configuration, and have undergone a screw rotation transition so that they lie at the intersection of the planes perpendicular to the applied field B and the [111] axis. This state is illustrated in figure 4 for two of the different crystallite orientations within the polycrystalline haematite sample.

The nature of the initial state may be inferred from the measured quadrupole shift, $2\epsilon \sim +0.20$ mm s^{-1}, in the zero-applied-field spectrum. Using equation (3) a mean spin displacement of $\theta \simeq 32°$ from the [111] axis is obtained, since it is known from the measured quadrupole shift in the $B = 10$ T spectrum, where $\theta = 90°$, that $\frac{1}{2}eQ|V_{zz}| \approx +0.40$ mm s^{-1}. Thus the initial state is intermediate between the antiferromagnetic state in non-irradiated haematite, where the spins are parallel to the [111] axis, and the weak ferromagnetic state, where the spins lie in the (111) plane. In fact, the spins at 4.2 K in these lightly irradiated haematite samples are in the midst of a temperature driven 'reverse Morin transition' [10].

The 0 T $< B <$ 10 T spectra were fitted under the following constraints. For the destination phase the Mössbauer parameters isomer shift, quadrupole shift and hyperfine field were constrained to be the same for all applied fields, and the effective field at the nucleus was obtained by vector addition of the hyperfine and applied fields. It was also assumed that the spins in the destination phase were in all cases perpendicular to the applied field. For the intermediate phase, the isomer shift was taken to be the same for all applied fields. Both the quadrupole shift and the hyperfine field were allowed to vary with applied field, but they were constrained against each other to be consistent with a single angle θ

between the spins and the [111] axis. The relative line intensities of the intermediate phase were allowed to vary independently.

The quadrupole shifts, 2ϵ, for the intermediate phases of both sample 1 and sample 2, are shown in figure 5 as a function of applied field. The corresponding angles θ between the spins and the [111] axis are also shown on the same figure. It is notable that there does not appear to be a continuous motion of spins from the intermediate phase to the destination phase with increasing applied field, since such a rotation would require that the quadrupole shifts should approach the value -0.20 mm s^{-1} at higher fields.

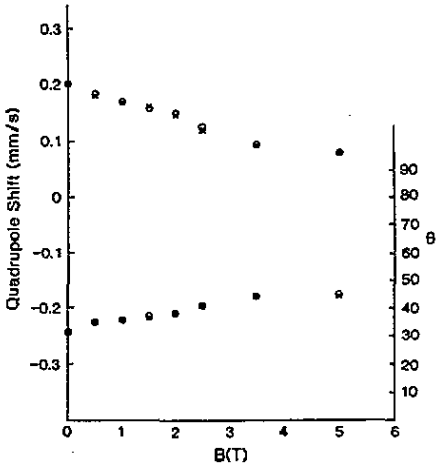

Figure 5. Variation of the quadrupole shift, 2ϵ, of sample 1 (×) and sample 2 (○) with applied field (upper curve), and the corresponding variation of the mean angle θ between the ferric spins and the V_{zz} axis (lower curve).

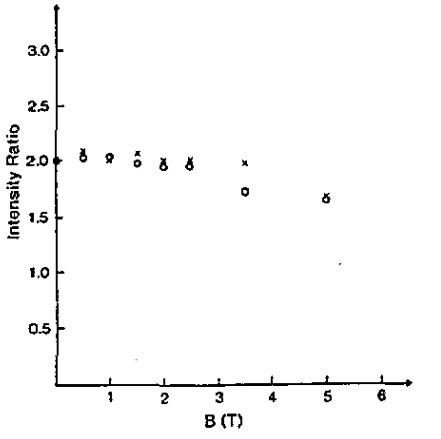

Figure 6. Applied field dependence of x in the relative line intensity ratio 3:x:1 of the outer:middle:inner pairs of lines in the Mössbauer spectra of the intermediate phase for sample 1 (×) and sample 2 (○).

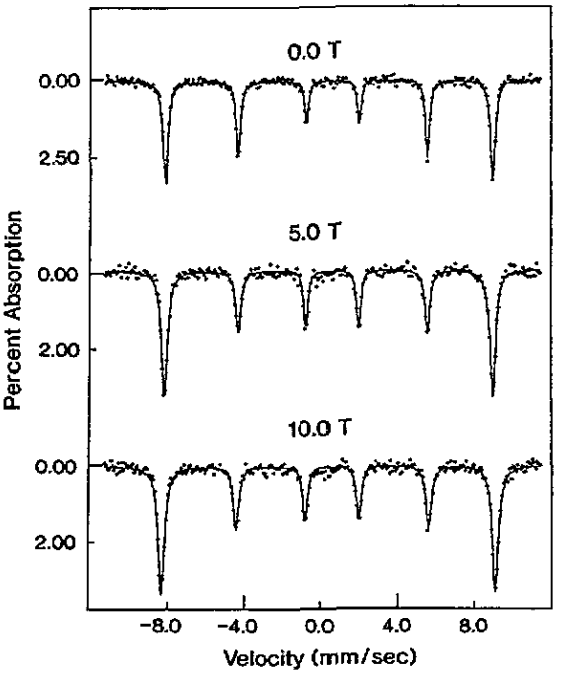

Figure 7. Mössbauer spectra of a polycrystalline sample of heavily irradiated haematite (sample 3) at 4.2 K in applied fields of the strength indicated, directed perpendicular to the γ-ray beam.

The relative line intensities of the intermediate phase in samples 1 and 2 show a similarly weak response to applied field (see figure 6). The intensity ratio falls gradully from 3:2:1 in zero field to approximately 3:1.6:1 at $B = 5$ T. If it were assumed that all the spins in this state were confined to the surface of a cone whose central axis was along the applied field direction, the latter line intensity ratio would correspond to an inclination axis for the cone of $\sim 68°$. This is well short of the 90° angle that characterizes the destination phase.

4. Heavily irradiated haematite

On the basis of earlier work, it is known that at 4.2 K the heavily irradiated haematite sample, sample 3, has completed a temperature driven 'reverse Morin transition', and has returned to a weak ferromagnetic state, with the spins in the basal plane [10]. This is seen in the zero-applied-field Mössbauer spectrum shown in figure 7, where a quadrupole shift of -0.20 mm s^{-1} is evident. As the external field is applied, the spins remain in the basal plane, as evidenced by a non-changing quadrupole shift, but reorient to a direction perpendicular to the applied field direction, as evidenced by a change in the relative line intensities from 3:2:1 in zero field to 3:4/3:1 for $B \geqslant 5$ T. This change in line intensity is apparent in the spectra in figure 7, and is also plotted in figure 8. This phase change is analogous to that seen in non-irradiated haematite above the Morin transition [12]. The final state is the same as the 'destination phase' observed in the lightly irradiated samples.

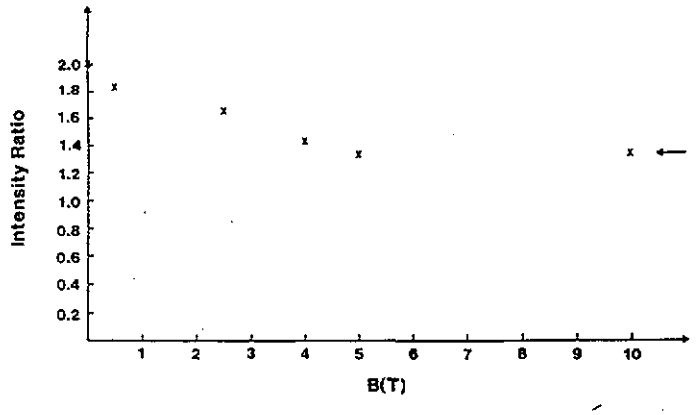

Figure 8. Applied field dependence of x in the relative line intensity ratio 3:x:1 of the outer:middle:inner pairs of lines in the Mössbauer spectra sample 3.

5. Conclusions

The field-induced phase transitions observed at 4.2 K in neutron-irradiated haematite differ markedly from those observed in non-irradiated haematite. These differences may be attributed to the effect of the neutron bombardment on the net magnetocrystalline anisotropy, which in haematite is a delicate balance of single-ion and magnetic dipolar contributions. (The single-ion anisotropy favours alignment of the spins along the [111] axis, while the magnetic dipolar anisotropy favours the (111) plane.) Earlier temperature-dependent measurements showed that the net anisotropy in the irradiated samples is smaller than in non-irradiated samples [10]. The current experiments confirm this result.

In the two lightly irradiated samples, the initial state at 4.2 K corresponds to the spins being caught in the midst of a 'reverse Morin transition', with the spins oriented at $\theta \simeq 32°$ to the [111] axis. If these samples were cooled below 4.2 K the spins would reorient further towards the (111) plane. The effect of an applied field is to promote a transition to a weak ferromagnetic state, corresponding to the final state observed in the 'screw rotation' transition in non-irradiated haematite, in which the spins lie perpendicular to both the applied field and the [111] axis. The fact that this state begins to be populated in applied fields $B \geqslant 0.5$ T is testament to the reduced anisotropy in these materials, given that in non-irradiated haematite a field of 16 T is required at 100 K to produce the same final state [5, 6]. It is also intriguing to note that the transition between the intermediate and final states in these irradiated samples appears to be quite abrupt, implying that despite the reduced anisotropy, some degree of the first-order nature of the phase transitions observed in non-irradiated samples has been retained.

In the heavily irradiated sample, the initial state at 4.2 K corresponds to the weak ferromagnetic state observed above the Morin transition in non-irradiated haematite. Applied fields of more than ~ 4.5 T are required to bring all the spins into the plane perpendicular to the applied field, while at the same time the spins stay within the basal (111) plane. This implies that in this sample the net anisotropy in favour of the (111) plane is rather high, and requires that the spins perform a 'screw rotation' type of reorientation, rather than respond directly to the applied field.

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