The magnetic-hyperfine-field distribution in aluminous haematite

S Bocquet†§ and E De Grave‡∥

† Department of Physics, Monash University, Clayton, Victoria 3168, Australia
‡ Laboratory of Magnetism, Department of Subatomic and Radiation Physics, University of Gent, Proeftuinstraat 86, B-9000 Gent, Belgium

Abstract. Mössbauer spectra of two synthetic aluminium-substituted haematites have been fitted with a model magnetic-hyperfine-field distribution which takes the form of a Boltzmann distribution for the z component of the sublattice magnetization. Good fits were obtained, and the hyperfine-field distribution is attributed to moment fluctuations on a longer timescale than the measurement time for ^{57}Fe Mössbauer spectroscopy. The fit parameters were compared with the predictions of a mean-field model for magnetic ordering in a diamagnetically substituted antiferromagnet.

1. Introduction

Mössbauer spectra of aluminium-substituted haematites exhibit a distinctive magnetic-hyperfine-field distribution. This distribution is asymmetric, being broader on the low-field side of the maximum. The asymmetry increases with increasing aluminium content, and with increasing sample temperature. The shape of the distribution, and its temperature dependence, are similar to those seen in Mössbauer spectra of fine-particle goethites. Mössbauer spectra of fine-particle goethites could be fitted using a model hyperfine-field distribution in the form of a Boltzmann distribution for the z component of the sublattice magnetization [1]. The presence of a Boltzmann distribution implies that there are fluctuations of the magnetization that occur on longer timescales than the Mössbauer measurement time. These fluctuations are separate from the antiferromagnetic spin waves. In goethite the maximum hyperfine field in the distributions follows the usual T^2 law for antiferromagnetic spin waves up to 80 K, whereas the average hyperfine field decreases linearly with increasing temperature due to the slow fluctuations. The aim of this work was to find out whether the model hyperfine-field distribution and magnetic-ordering model developed for fine-particle goethite could also be applied to aluminous haematite.

Two synthetic α-$(Fe_{1-c}Al_c)_2O_3$ compounds with $c = 0.18$ and 0.26, prepared by thermal decomposition of alumino-goethites at 500 °C [2], were investigated. ^{57}Fe Mössbauer spectra of both samples at temperatures from 80 to 480 K were obtained as part of a previous study [3], and these spectra were refitted for the present work.

§ Present address: Maritime Operations Division, Aeronautical and Maritime Research Laboratory, PO Box 4331, Melbourne, Victoria 3001, Australia.
∥ Research Director, National Fund for Scientific Research, Belgium.

2. Fitting procedure

All spectra were fitted with a model hyperfine-field distribution in the form of a Boltzmann distribution over an exchange potential [1]. The hyperfine field B is taken to be proportional to the z component of the iron magnetic moment, which is considered to be precessing rapidly about the z axis. The hyperfine-field distribution is then expressed as a Boltzmann distribution of precession angles θ:

$$B = B_0 \cos\theta$$
$$p(B) \propto \exp(E_c \cos\theta/kT) \qquad |B| \leqslant B_0 \qquad\qquad (1)$$
$$p(B) = 0 \qquad |B| > B_0$$

where B_0 is the hyperfine field for $\theta = 0$ and E_c is the height of a potential barrier in the form $E_c \cos\theta$.

For the $c = 0.18$ sample, good fits were obtained with a single model distribution with two variable parameters, B_0 and E_c (figure 1(a)). Spectra of the $c = 0.26$ sample (figure 1(b,c)) were initially fitted with a single distribution. However, good fits were obtained only up to 200 K. At 230 K and above, a second distribution was required for a good fit. Only the area and E_c/kT were allowed to vary independently for the second distribution; all other parameters were constrained to be equal for both components. At 390 K and above, it was necessary to introduce a Gaussian distribution in B_0, with standard deviation $\sigma(B_0)$.

Both samples are in the weakly ferromagnetic state at all temperatures, that is, the aluminium concentration is sufficient to completely suppress the Morin transition. Line positions for the individual subspectra in the distributions were calculated from the full Hamiltonian for an axially symmetric electric field gradient perpendicular to the magnetic hyperfine field.

In every case the isomer and quadrupole shifts obtained in the present work agree with those reported previously [3], within experimental uncertainties. Both of these parameters are independent of aluminium substitution; the quadrupole shift is also temperature independent.

The distribution parameters for both samples are plotted against temperature in figure 2. In the case of the $c = 0.26$ sample at 230 K and above, an area-weighted average of E_c from the two distributions is plotted, and this value was also used to calculate $\langle B \rangle$. The decrease in E_c at temperatures below 200 K is non-physical. At these temperatures the spectral lines are nearly symmetric, so that the spectrum is insensitive to E_c/kT. Symmetric line broadening due to absorber thickness saturation is dominant. This was not included in the calculations, so the fitting program tends to compensate with additional symmetric broadening by reducing E_c/kT. E_c is expected to increase monotonically with decreasing temperature.

3. Magnetic-ordering model

The model distribution parameters B_0 and E_c were plotted against temperature, along with the average hyperfine field $\langle B \rangle$ (figure 2). The average field is determined from the distribution parameters as $\langle B \rangle = B_0 L(E_c/kT)$, where L is the Langevin function. Note that the model hyperfine-field distribution includes negative field values, so the average
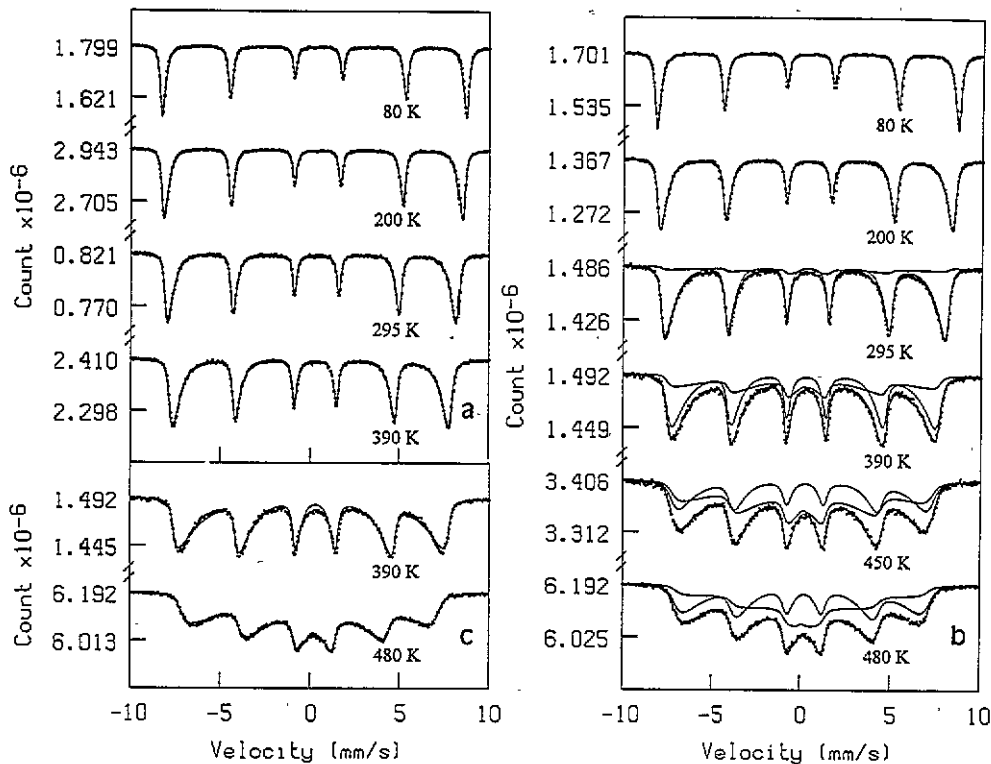
Figure 1. Mössbauer spectra of α-$(Fe_{1-c}Al_c)_2O_3$ at various temperatures, fitted with the model magnetic-hyperfine-field distribution. (a) $c = 0.18$, (b) $c = 0.26$; the lower four spectra have been fitted with two model distributions, and the component subspectra are shown. (c) Single-distribution fits to $c = 0.26$.

field differs from that obtained with a model-independent distribution, which is restricted to positive fields. In earlier work on goethite [1], $\langle B \rangle$ was obtained from model-independent distribution fits. However, the differences are small ($\leqslant$ 1 T), except close to T_N where $E_c/kT \sim 1$.

At low temperatures, $\langle B \rangle$ decreases linearly with increasing temperature in aluminous haematite, as with fine-particle goethite. The non-zero slope in $\langle B \rangle$ at $T = 0$ suggests that the ordering is best described by a Langevin function, appropriate for clusters with a large total spin, rather than the Brillouin function for individual spin $\frac{5}{2}$ Fe^{3+} ions, which is horizontal at $T = 0$. This suggests that a model based on the ordering of clusters is required. The average sublattice magnetization $M(T)$ for the clusters may be written

$$M(T) = M^b(T)L(x) \tag{2}$$

where $M^b(T)$ is the sublattice magnetization of unsubstituted haematite at temperature T, L is the Langevin function, and $x = J_c M(T)M^b(T)/kT$. J_c is the cluster exchange constant. This implicit equation for $M(T)$ may be solved for J_c in terms of T_N. Close to T_N, $x \ll 1$ and $L(x) \simeq x/3$, so (2) becomes

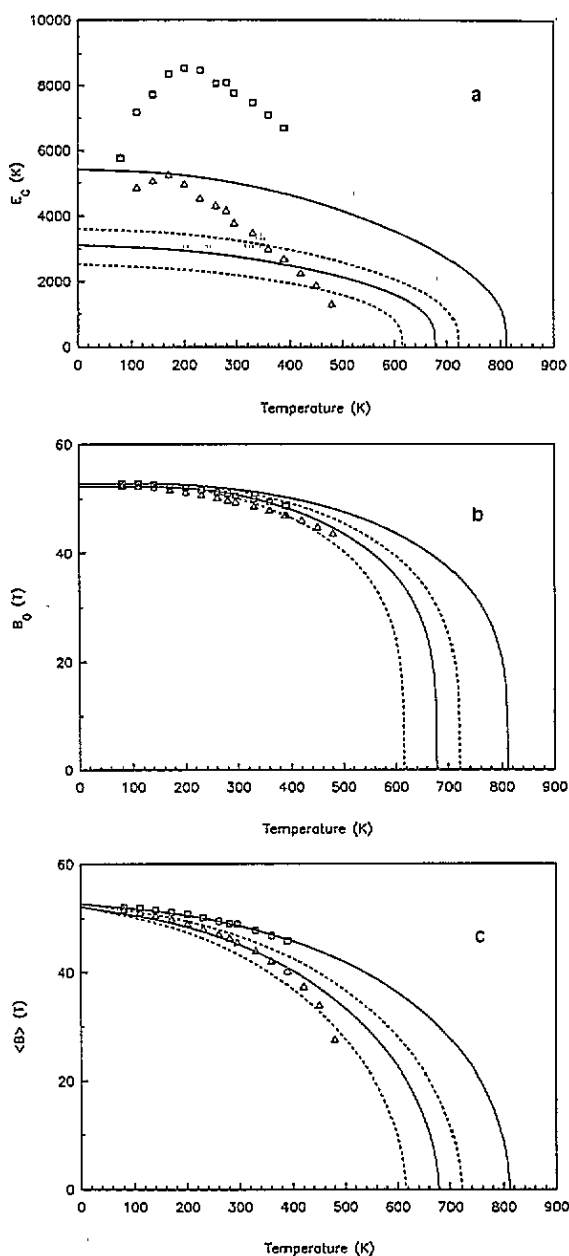$$M(T_N)/M^b(T_N) = J_c M(T_N)M^b(T_N)/3kT_N$$

Figure 2. The temperature variation of (*a*) the cluster exchange energy E_c, (*b*) the maximum hyperfine field B_0, and (*c*) the average hyperfine field $\langle B \rangle$ for the $c = 0.18$ ($\square$) and $c = 0.26$ ($\triangle$) samples. The solid curves are least-squares fits to the magnetic-ordering model, varying only T_N. The broken curves were calculated from the model using theoretical estimates of T_N.

and

$$J_c = 3kT_N/[M^b(T_N)]^2. \tag{3}$$

Substituting this equation for J_c into the expression for x gives

$$x = 3T_N M(T) M^b(T)/T[M^b(T_N)]^2. \tag{4}$$

$M(T)/M^b(T)$ is then replaced with $M(T)/M^b(0)$, so (2) becomes

$$M(T)/M^b(0) = L\{(3T_N/T)[M^b(T)/M^b(T_N)]^2 M(T)/M^b(0)\}. \tag{5}$$

The argument of the Langevin function in (5) is E_c/kT. When $M(T)$ is calculated from (5), $M(T)/M^b(0)$ is replaced by $[M(T)/M^b(0)]^{3/2}$. This changes the critical exponent from the usual mean-field value of $\frac{1}{2}$ to the more accurate value of $\frac{1}{3}$ [1]. The same procedure is followed in calculating $M^b(T)$. Equation (5) relates the magnetic ordering in a diamagnetically substituted sample to that of the unsubstituted material, via the sample ordering temperature T_N. This is similar to the virtual-crystal approximation [4] for the reduction in T_N due to diamagnetic substitution. B_0 is calculated from the model as

$$B_0(T) = B^b(T) B_s([s/(s+1)]E_c/kT) \tag{6}$$

where B_s is the Brillouin function for $s = \frac{5}{2}$. $B^b(T)$ is the magnetic hyperfine field for unsubstituted haematite, which is proportional to the sublattice magnetization $M^b(T)$ for the high-spin ferric iron.

The saturation hyperfine field was taken to be the value of B_0 obtained at 80 K for each sample. These will be good estimates, because the hyperfine fields in aluminium-substituted haematies change by less than 10^{-3} T between 4.2 K and 77 K [5]. The temperature variation of the average hyperfine field was then fitted to the model for each sample, with the Néel temperature T_N as a variable parameter (solid curves in figure 2(c)). Néel temperatures of 811 K and 678 K were obtained for the $c = 0.18$ and $c = 0.26$ samples respectively. In the case of the $c = 0.26$ sample, the three average-field points above 400 K were excluded from the fit because it was not possible to fit the data over the full temperature range. The two quantities, B_0 and E_c, could then be calculated as a function of temperature without introducing any other variable parameters (solid curves in figure 2(a, b)).

The decrease in T_N with decreasing magnetic-ion concentration $p = 1 - c$ may be approximated by a straight line, starting from the aluminium-free value of 955 K [5]. The limiting slope $dT_N/dp = 1.37T_N^{(p=1)}$ at $p = 1$ for a simple cubic lattice [6] was used as an estimate of the slope of this line. Estimates of 720 K and 615 K for T_N were obtained for $c = 0.18$ and $c = 0.26$ respectively, both significantly lower than those obtained from fits to the average hyperfine-field data. The broken lines in figure 2 are calculated from the mean-field model using the estimated values of T_N. Independent least-squares fits of the three parameters $\langle B\rangle$, B_0 and E_c were also tried, varying either T_N only, or both $B_0(0)$ and T_N, but consistent results could not be obtained.

4. Discussion

Mössbauer spectra of aluminium-substituted haematites have previously been analysed using a local-disorder model, and model-independent hyperfine-field distributions [3]. The local-disorder model gave good fits for sample temperatures below 200 K, but the strongly asymmetric distributions seen at higher temperatures could not be reproduced with this model. Good fits could be obtained at all temperatures with a model-independent distribution, but this method does not provide any physical interpretation. The effect of collective magnetic excitations was also considered. These are rapid fluctuations of the

magnetic moment of a small particle about its easy direction, which result in a reduction in the measured hyperfine field. The average hyperfine fields were found to decrease much more rapidly with increasing temperature than calculated from the effect of collective magnetic excitations. Moreover, the hyperfine-field distribution derived from the spectrum of the $c = 0.26$ sample at 480 K has a significant proportion of fields less than half the expected bulk value. This cannot be explained by collective magnetic excitations, which produce at most a 15% reduction in the hyperfine field from the bulk value [7].

The model distribution used in this work has just three parameters, B_0, $\sigma(B_0)$ and E_c, and is able to give good fits to the spectra at all temperatures. This is a significant improvement over the previous approaches, because the local-disorder model could only fit the spectra for sample temperatures below 200 K, and the model-independent distribution contains a large number of variable parameters (the individual field probabilities, typically 10–50 in number). The ability to fit the spectra with a small number of variable parameters is quite useful in itself, because it simplifies sample characterization, particularly in the case of samples containing several iron compounds. However, a proper understanding of the Mössbauer spectra demands a physical interpretation of the distribution parameters. In earlier work on fine-particle goethite, a mean-field model was devised for magnetic ordering in a diamagnetically substituted antiferromagnet. In goethite the diamagnetic substitution was attributed to vacancy defects, and the mean-field model was able to account quite well for the temperature variation of the magnetic-hyperfine-field distribution parameters. For aluminous haematite, the fit is not so good (figure 2). One reason for this may be the much higher diamagnetic substitutions in the two haematite samples, $c = 0.18$ and 0.26, compared with $c \sim 0.1$ in the goethites. Although the diamagnetic ion concentration does not appear explicitly in the model, the mean-field equation relating the magnetic ordering in a substituted sample to that in the unsubstituted material (5) is similar to the virtual-crystal approximation [4] for the percolation problem, which overestimates T_N for a given substitution. The model does however reproduce the general trends in the data, apart from the non-physical decrease in E_c at low temperatures discussed in section 2.

The greatest discrepancy between the model and the data occurs for E_c. The peak values of E_c obtained experimentally are almost twice the calculated saturation (0 K) values of this parameter. A similar discrepancy was found with the fine-particle goethites, but in that case it could be satisfactorily accounted for by one of the shortcomings of mean-field theory. Mean-field theory underestimates the exchange constant by about 40% for a given magnetic-ordering temperature [8]. This cannot by itself account for the much larger discrepancy seen here.

The cluster ordering model is essentially phenomenological. It is worth considering how the cluster exchange potential E_c may be interpreted. In both the aluminous haematites studied, the iron concentration is well above the percolation limit. Hence the clusters in the model must form part of the percolating cluster, and cannot be regarded as independent entities. The cluster magnetization represents an average over a large number of magnetic ions, so E_c is independent of any local variations in the sublattice magnetization. If the diamagnetic-ion concentration is low, most of the magnetic ions will have only one exchange path missing due to a diamagnetic neighbour. For a random distribution of diamagnetic ions, this corresponds to a random-exchange model with a two-valued exchange distribution. The random exchange may give rise to regions of oppositely directed staggered magnetization that persist to much longer timescales and lower temperatures than the critical fluctuations normally associated with a magnetic phase transition. The clusters possibly correspond to such regions, but it is likely that the true significance of E_c lies in its independence of local variations in the sublattice magnetization. From a theoretical viewpoint, a better

understanding of the moment fluctuations in aluminous haematite and other diamagnetically substituted antiferromagnets might be gained from the application of techniques developed for spin-glass dynamics [9] to a random-exchange model.

The need for a second model distribution to adequately fit the spectra of the $c = 0.26$ sample above 200 K may be due to non-random aluminium substitution. An applied-field Mössbauer study of aluminous goethite [10] revealed a strong tendency for aluminium substitution on one sublattice, making the material ferrimagnetic. This is likely to carry over to haematites made from the goethite. The relative areas of the two model distributions vary with temperature, the one with the lower value of E_c increasing in area with increasing temperature. This probably results from a distribution in E_c, so no particular significance can be attached to the two different values of E_c. Although two model distributions are needed to obtain a good fit, a single distribution reproduces the shape of the spectrum quite well (figure $1(c)$). The magnetic-ordering model assumes ideal antiferromagnetism, so an imbalance between the sublattices may also partly account for the discrepancy between the values of E_c obtained experimentally and those calculated from the model (figure $2(a)$).

A Gaussian distribution in B_0 was required to fit spectra of the $c = 0.26$ sample at 390 K and above. This probably reflects a distribution in T_N, as was the case for fine-particle goethite [1]. A Gaussian distribution in T_N would give rise to an asymmetric distribution in B_0, due to the non-linear behaviour of the hyperfine field as a function of temperature. However, the Gaussian distribution for B_0 is a reasonable approximation, with the Boltzmann distribution (1) accounting for any asymmetry.

A separate doublet component was needed in order to fit the spectra of the $c = 0.26$ sample at 295 K and above with the model-independent distribution [3]. No doublet was required in the model distribution fits. This is probably partly due to the use of two model distributions, and partly due to the use of a full Hamiltonian calculation for the perpendicular electric-field gradient. The model-independent distribution fits used a first-order perturbation treatment of the EFG, which breaks down when the magnetic hyperfine field is small.

5. Conclusion

Good fits to Mössbauer spectra of aluminous haematite were obtained using a model hyperfine-field distribution in the form of a Boltzmann distribution for the z component of the sublattice magnetization. The hyperfine-field distribution can thus be attributed to moment fluctuations on a slower timescale than the measurement time for ^{57}Fe Mössbauer spectroscopy ($\sim 10^{-8}$ s). A mean-field model for the magnetic ordering based on random diamagnetic-ion substitution was unable to fit the temperature dependence of the hyperfine-field distribution parameters, possibly because of preferential aluminium substitution on one magnetic sublattice. Nevertheless, the mean-field model does reproduce the general trends in these parameters, for two different aluminium concentrations.

References

[1] Bocquet S, Pollard R J and Cashion J D 1992 *Phys. Rev.* B **46** 11 657
[2] Golden D C 1978 *PhD Thesis* North Carolina State University
[3] De Grave E, Bowen L H, Amarasiriwardena D D and Vandenberghe R E 1988 *J. Magn. Magn. Mater.* **72** 129
[4] Stinchcombe R B 1983 *Phase Transitions and Critical Phenomena* vol 7, ed C Domb and J L Lebowitz (London: Academic) p 210

[5] Murad E and Johnston J H 1987 *Mössbauer Spectroscopy Applied to Inorganic Chemistry* vol 2, ed G J
       Long (New York: Plenum) ch 12
[6] Harris A B and Kirkpatrick S 1977 *Phys. Rev.* B **16** 542
[7] Mørup S 1983 *J. Magn. Magn. Mater.* **37** 39
[8] Smart J S 1966 *Effective Field Theories of Magnetism* (Philadelphia, PA: Saunders) ch 4
[9] Mezard M, Parisi G and Virasoro M 1987 *Spin Glass Theory and Beyond* (Singapore: World Scientific) ch 6
[10] Pollard R J, Pankhurst Q A and Zientek P 1991 *Phys. Chem. Miner.* **18** 259