Isotropic relaxation of the hyperfine field and intercluster interactions in ferrihydrite

1994 J. Phys.: Condens. Matter 6 2269

(http://iopscience.iop.org/0953-8984/6/11/015)

J. Phys.: Condens. Matter 6 (1994) 2269–2275. Printed in the UK

Isotropic relaxation of the hyperfine field and intercluster interactions in ferrihydrite

L Cianchi†, F Gulisano and G Spina
Dipartimento di Fisica, Università di Firenze, Firenze, Italy

Received 19 July 1993

Abstract. A theory for the fluctuations of the magnetic moment of the grains in ferrihydrite is developed, and their influence on the Mössbauer spectra is studied in the range of temperatures between 26 K and 65 K. The evolution of the spectra can be interpreted in terms of isotropic relaxation, in spite of the fact that they are not ordinary relaxation spectra. The results make it clear that superferromagnetic relaxation is present.

1. Introduction

In a previous work, the magnetic properties of ferrihydrite ($Fe_5HO_8{:}4H_2O$) were studied by Mössbauer spectroscopy [1]. In particular the evolution of the spectra above the blocking temperature T_B was explained by means of the isotropic relaxation of the hyperfine magnetic field. The relaxation time follows the Vogel–Fulcher law [2] with $T_B = 54$ K and $T_1 = 13$ K; as a consequence a superferromagnetic coupling constant $T_{SF} = 37$ K and a magnetic anisotropy constant $T_K = 26$ K result.

Below the blocking temperature the magnetization is different from zero. Each grain, which can be considered to be a microcrystal with quasi-cubic symmetry, is subject to a magnetic field, which will be denoted as 'molecular field' $\boldsymbol{H}_m$, proportional to the magnetization.

In the absence of the molecular field, the magnetic moment of the Fe^{3+} ion and of the grain, and hence the hyperfine magnetic field, may assume six equivalent directions along the edges of the cubic cell.

In the presence of the molecular field, the six orientations can correspond to different energies. Figure 1 shows the variation of the magnetic moment energy along the path A–M sketched on the cell for $\boldsymbol{H}_m = \boldsymbol{0}$ and $\boldsymbol{H}_m \neq \boldsymbol{0}$. The anisotropy energy T_K is indicated together with the energy difference $\Delta = \boldsymbol{\mu} \cdot \boldsymbol{H}_m$, where $\boldsymbol{\mu}$ is the magnetic moment of the grain.

Fitting the spectra with $T < T_B$ is a very complicated task. For this reason, in order to determine the mean hyperfine field, only the spectra with $T \ll T_B$ were considered in our previous work [1], as they can be represented fairly well by a Blume–Tjon sextet; moreover greater values were used there for the widths of the external rather than for the internal lines, in order to improve the fitting and to take into account possible inhomogeneous broadenings.

The analysis carried out for the temperature evolution of the hyperfine field for $T < T_B$ made it clear that the grains are oriented with an edge of the cell parallel to the molecular field.

† Present address: IROE, Consiglio Nazionale delle Ricerche, Firenze, Italy.

0953-8984/94/112269+07$19.50

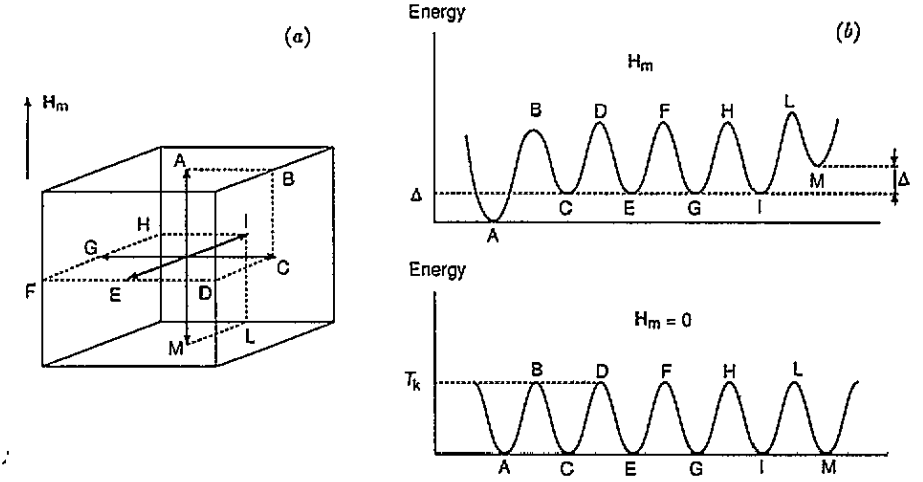


Figure 1. Qualitative representation of the variation of the magnetic moment energy along the path A–M sketched on the cubic cell (a) in the presence of a molecular field and (b) in the absence of a molecular field.

In the present work, on the basis of the previously described model, we have used a detailed theory for the hyperfine field relaxation in which the transitions among the six magnetic states in the molecular field are considered. As the characteristics of the spectra and their temperature evolution are quite peculiar, their faithful reproduction will give reliable assurance of the validity of our model and theory.

We shall first discuss the relative importance to the spectra of relaxation phenomena and hyperfine field distributions (section 2); then we shall describe the obtained spectra (section 3) and illustrate the theory for the analysis of the experimental data (section 4); and finally the fitting of the spectra and conclusions will be presented (section 5).

2. Relaxation phenomena and hyperfine field distribution

First we discuss the relative importance that must be attributed to inhomogeneous broadening and relaxation phenomena in the analysis of the spectra.

Relaxation phenomena are certainly active since the spectrum evolves from a broad sextet to a narrow doublet as the temperature increases. On the other hand the different size and packing of the grains yield a distribution in transition probabilities and characteristic parameters. However, even if each spectrum is a superposition of elementary spectra, they could not be simple 'classical' sextets corresponding to a hyperfine static field, but they would instead be relaxation spectra.

For this reason, as a first approach, the spectra of the compound will be studied in terms of relaxation only, and we shall take into account the superpositions of elementary spectra only if the parameter distribution will be so large that this procedure would be inadequate to account for the experimental data with reasonable values for the physical parameters.

3. Description of the spectra

Figure 2 shows some of the spectra from our collection up to 65 K. At low temperatures the spectra are magnetic sextets with zero quadrupole splitting; as the temperature increases

the outer lines broaden and tend to merge, while the two inner lines remain well separated. The last spectrum (T = 65 K) is recorded above the blocking temperature and consists of a quadrupolar doublet whose lines have equal widths and intensities, which indicates isotropic relaxation [3].

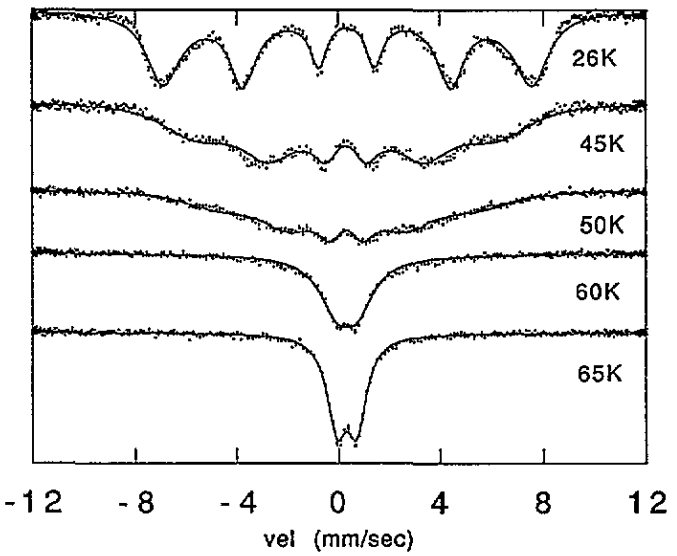
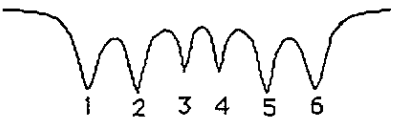


Figure 2. Mössbauer spectra of ferrihydrite for T = 26 K, 45 K, 50 K, 60 K, 65 K.

This kind of evolution is just the opposite to that studied by Blume and Tjon in their first work [4,5], to which we shall refer as the 'classical' case. There the broadening affects the inner lines first: at intermediate temperatures a central line originates from the collapse of the inner lines, with a background due to the external ones. As the temperature increases, the central line continues to emerge and also narrows, while the background tends to disappear. Therefore it might seem that in order to reproduce our spectra we ought to introduce the effect of inhomogeneities.

Nevertheless it is evident that the present physical situation is quite different from the 'classical' one, where the magnetic field on the nucleus is assumed to take only two values, which are opposite to one another. One could then think to approach the problem in the light of some earlier works [6–10] based on a stochastic relaxation theory but for a spin $\frac{5}{2}$ state with transitions between $+\frac{5}{2}$, $+\frac{3}{2}$ and $+\frac{1}{2}$ sublevels. However one can easily realize that this is not the case. The comparison with the spectra of [6] makes clear the differences between the two cases. There the low-temperature spectrum is unmistakably made up of *more than six lines, and moreover the intermediate line is more intense than the outer one.* This is explained by the fact that one is present there adiabatic relaxation of a spin $\frac{5}{2}$ state where the magnetic field assumes three distinct values but does not change in orientation. Therefore for small values of the transition probability the spectrum is a superposition of different sextets. In the present case, instead, the spectrum is a sextet with the outer lines more intense than the intermediate one. This suggests an interpretation in terms of a unique value of the magnetic field intensity and fluctuations among different orientations. Here six of them exist at right angles to each other. The most probable relaxation processes are then 90° rotations and not inversions of the field.

From a physical point of view the differences between our case and the classical Blume–Tjon case can be explained in the following way. In the absence of relaxation, spectral lines can be considered to be independent harmonic oscillators. Relaxation induces couplings among the oscillators. In figure 3, a table containing coefficients proportional to allowed couplings between line 1 and the others is shown for the two cases. These coupling coefficients have been calculated by diagonalizing the Liouville supermatrices that correspond to the different orientations of the magnetic field. As indicated, line 1 is connected only with line 6 in the Blume–Tjon case, while in the case examined here line 1 is connected with each of the remaining lines, particularly with the inner four.



Line	1	2	3	4	5	6
Classical case	0	0	0	0	0	1
Present case	0.06	0.19	0.19	0.19	0.19	0.06

Figure 3. Table of the coefficients proportional to the couplings between line 1 and the other lines in the classical relaxation case and in the present one.

Considering that the effects of relaxation become apparent when the transition probability W is comparable with the oscillator frequency differences, it becomes clear that lines 1 and 2 will be the first to mingle. It is thus understandable why in this case the spectrum loses its sextet structure starting from the outer and not from the inner lines.

4. Theory

The lineshape of Mössbauer spectra in the presence of relaxation is given by [4]

$$I(\omega) \propto \mathrm{Re} \sum_{\alpha} \frac{(\rho_1 A^{\dagger} \cdot U_{\alpha}) \cdot (V_{\alpha}^{\dagger} \cdot A)}{\mathrm{i}\omega - a_{\alpha}}$$

where U_α are the eigenvectors of the Liouville matrix $\mathbf{P} = \frac{1}{2}\Gamma\mathbf{I} + \mathbf{H}_1 + \mathbf{R}$, which corresponds to the eigenvalue a_α written on the basis $\{|\alpha, m_0; \beta, m_1\rangle\}$ where α denotes the electronic states and m_0, m_1 denote the nuclear states for the ground and excited state respectively; $\mathbf{I}$ is the unity matrix, $\mathbf{H}_1$ the hyperfine matrix and $\mathbf{R}$ the relaxation matrix whose non-zero elements are

$$\langle \alpha, m_0; \alpha m_1 | R | \alpha, m_0; \alpha m_1 \rangle = \sum_{\epsilon \neq \alpha} W_{\alpha\epsilon}$$

and

$$\langle \alpha, m_0; \alpha m_1 | R | \beta, m_0; \beta m_1 \rangle = W_{\alpha\beta} \qquad \alpha \neq \beta$$

where $W_{\alpha\beta}$ is the transition probability between the electronic states α and β. $V_\alpha^\dagger$ are the eigenvectors of the adjoint of the **P** matrix, and ρ_1 is the occupation probability of the electronuclear states. In figure 4 a scheme of the matrix that must be diagonalized is shown. The diagonal blocks represent the Liouville matrices, which correspond to the static orientations of the magnetic moment, while off diagonal blocks contain transition probabilities between electronic states. Finally, the A are Liouville vectors whose components are proportional to matrix elements of the magnetic dipole moment operator between nuclear states.

P_x		W	W	W	W
	P_x	W	W	W	W
W	W	P_y		W	W
W	W		P_y	W	W
W	W	W	W	P_z	
W	W	W	W		P_z

Figure 4. A scheme of the Liouville matrix **P**.

In the present case, there are six electronic states corresponding to the six orientations of the magnetic moments along the edges of the cubic cell, four nuclear states for the excited level $I = \frac{3}{2}$ and two nuclear states for the ground state $I = \frac{1}{2}$. Therefore a non-Hermitian matrix of order $(6 \times 4)(6 \times 2) = 288$ must be diagonalized, which reduces to a $6 \times 4 \times 2 = 48$ matrix because of the structure of **R**.

As previously stated, our previous work found that the grains are oriented with an edge of the quasi-cubic cell parallel to the 'molecular field'. The arrangement scheme of the electronic levels is sketched in figure 1. Moreover, the principal axis of the electric field gradient tensor is directed along a spatial diagonal of the quasi-cubic cell.

Taking into account the symmetry of the electronic states with respect to the molecular field and to the electric field gradient, the following relationships between transition

probabilities are assumed:

$$W_1 = W_{\pm x,\pm y} = W_{\pm y,\pm x}$$

$$W_3 = W_{+x,-y}$$

$$W_2 = W_{z,i} = \exp(-\Delta/T)W_{i,z} = W_{-z,i} = \exp(-\Delta T)W_{i,-z} \qquad i = \pm x, \pm y$$

$$W_{i,-i} = 0 \qquad i = \pm x, \pm y, \pm z.$$

5. Fitting of the data and conclusions

As mentioned previously, it was decided to perform the fitting while ignoring, at least initially, the effects of inhomogeneities, though our computer routine could provide for a distribution of the essential parameters. In addition, as in the absence of quadrupolar interaction, i.e. in perfect cubic symmetry, W_3 and W_1 should be equal; our system being quasi-cubic, the number of independent parameters was reduced by using $W_3 = W_1$ as a starting point. The independent parameters used in the fitting were W_1, W_2 and Δ.

The other important parameters include the quadrupole splitting Q, the hyperfine field B, and the energy difference Δ, which is related to the molecular field.

It turns out that the essential parameter for the evolution of the spectra is Δ/T. All spectra below T_B can be reproduced only by assuming a value of about 80 K for Δ, while for the spectrum above T_B it is necessary to assume $\Delta = 0$.

The hyperfine field B appears to change from 47 T at 26 K to 40 T at 50 K. This change can be attributed to the oscillations of the magnetic moment in the neighbourhood of the equilibrium position in each state, whose amplitude increases with T. The spectrum at 65 K falls within the range of fast relaxation, so that only one of the two parameters W and B can be determined, as the line width is proportional to W^2/B. For the fitting of this spectrum the value of 40 T for B, obtained from the spectrum at 50 K, was assumed. The quadrupole interaction can be revealed only for $T = 50$ K, when the effects of relaxation begin to destroy the magnetic structure of the spectra.

The experimental results can be interpreted as follows: for $T < T_B$ there is a T independent W_2, which is consistent with the fact that W_2 corresponds to a spontaneous transition, while W_1 slightly increases with T, in accordance to the expectations of a T_K barrier of about 26 K [1]. In figure 5 the continuous line is the exponential that fits the experimental data for W_1 from which this value for T_K results. For T well above T_B the spectra can be interpreted in terms of equal transition probabilities: a reasonable conclusion, all six states now being equivalent. The common value of the W is related to the value assumed for the magnetic field, and was obtained by assuming for H the value resulting from the fitting of the 50 K spectrum; for this reason it is probably an underestimate of the true value. Let us add that the conspicuous growth of transition probabilities above T_B is clearly related to the fact that Δ suddenly goes to zero, indicating destruction of the superferromagnetic order of the grains. In figure 5 the behaviour of transition probabilities as a function of the temperature T is shown.

The fitting of the spectra turned out to be unexpectedly satisfactory in spite of their complexity and of the simplifying assumptions previously made. We are then led to conclude that the physical properties of the compound show identical behaviour to those of a homogeneous sample, therefore making it unnecessary to invoke superpositions of spectra.

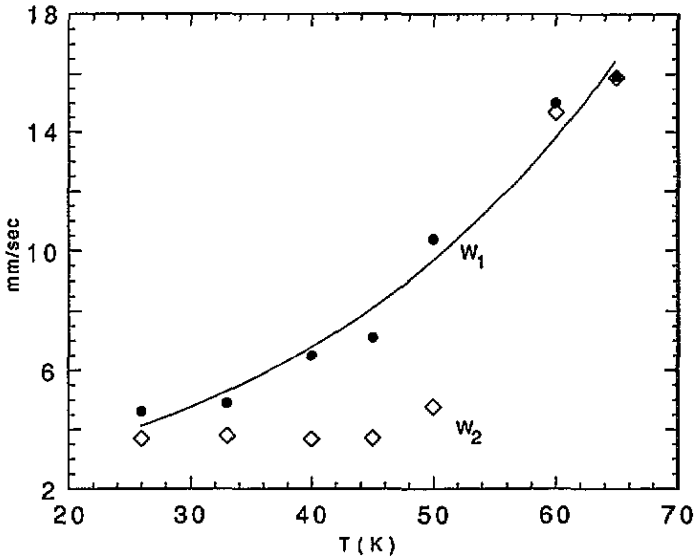


Figure 5. The behaviour of the transition probabilities as a function of the temperature. The continuous line represents the exponential that fits the W_1 data.

References

[1] Cianchi L, Mancini M, Spina G and Tang H 1992 *J. Phys.: Condens. Matter* **4** 1992
[2] Shtrikman S and Wohlfarth E P 1981 *Phys. Lett.* **85A** 467
[3] Afanasev A M and Gorobchenko V D 1974 *Sov. Phys.—JETP* **39** 690
[4] Blume M and Tjon J A 1968 *Phys. Rev.* **165** 446
[5] Cianchi L, Moretti P, Mancini M and Spina G 1986 *Rep. Prog. Phys.* **49** 1243
[6] de Waard H and Housley R M 1967 *Hyperfine Interactions* (New York: Academic) p 691
[7] Dekker A J 1967 *Hyperfine Interactions* (New York: Academic) p 679
[8] Van der Wood F and Dekker A J 1965 *Phys. Status Solidi* **9** 775
[9] Van der Wood F and Dekker A J 1966 *Phys. Status Solidi* **13** 181
[10] Van der Wood F and Dekker A J 1966 *Solid State Commun.* **3** 319