Mössbauer study of $Li_{0.5}Fe_{2.5}O_4$

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Abstract. $Li_{0.5}Fe_{2.5}O_4$ has been studied by means of Mössbauer spectroscopy and x-ray diffraction. The crystal is found to have a cubic spinel structure with the lattice constant $a_0 = 8.344 \pm 0.005$ Å. The iron ions are in ferric states. The temperature dependences of the magnetic hyperfine fields at the ^{57}Fe nuclei at the tetrahedral (A) and octahedral (B) sites are analysed using the Néel theory of ferrimagnetism. The inter-sublattice superexchange interaction is found to be antiferromagnetic with a strength of $J_{A-B} = -10.8k_B$ while the intra-sublattice superexchange interactions are ferromagnetic with strengths of $J_{A-A} = 17.6k_B$ and $J_{B-B} = 17.8k_B$. The Debye temperatures of the tetrahedral and octahedral sites are determined to be 398 ± 5 K and 362 ± 5 K, respectively.

1. Introduction

Mössbauer spectra of the oxyspinels and sulphospinels AB_2X_4 (X = O or S; A and B denote the cations at the tetrahedral and octahedral sites, respectively) have been reported by a number of authors [1]. However, many of them are complex spectra of ferrous ions from which it is very difficult to extract information on superexchange interactions, for the magnetic hyperfine field of a ferrous ion is not proportional [2] to the ionic spin, owing to the orbital contribution, and the electric field gradient due to the electrons of ferrous ions is usually quite large.

In an attempt to study superexchange interactions in ferrites using Mössbauer spectroscopy, we prepared a $Li_{0.5}Fe_{2.5}O_4$ sample in which the only magnetic ions are ferric ions. Two series of data—for example, magnetic hyperfine fields and magnetic moments—could be used to find correct superexchange integrals. However, the total spontaneous magnetic moment near the Néel temperature cannot be correctly determined under a high external magnetic field due to the induced magnetic moment. Thus, it would be desirable to obtain two series of data unaffected by the external magnetic field.

In the present study, superexchange interactions in the oxyferrite $Li_{0.5}Fe_{2.5}O_4$ have been studied using two series of undistorted data, namely, the magnetic hyperfine fields at the ^{57}Fe nuclei at the tetrahedral (A) and octahedral (B) sites. The magnetic hyperfine fields can be measured without any need for an external magnetic field by the Mössbauer technique.

$Li_{0.5}Fe_{2.5}O_4$ is known to crystallize into the spinel structure [3]. As a result of the strong preference of Li^{1+} for the octahedral site [4], the compound becomes an inverse spinel with iron ions at both the tetrahedral and the octahedral sites: $Fe[Li_{0.5}Fe_{1.5}]O_4$. Consequently, it is possible to measure magnetic hyperfine fields at ^{57}Fe nuclei at the tetrahedral (A) and octahedral (B) sites.
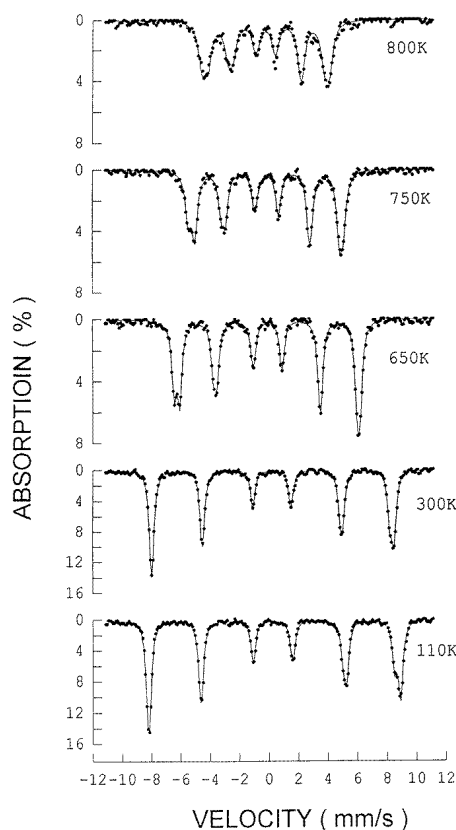
Figure 1. Mössbauer spectra of $Li_{0.5}Fe_{2.5}O_4$.

2. Experimental procedures

The $Li_{0.5}Fe_{2.5}O_4$ sample was prepared by the following ceramic method [5]. The starting materials were Li_2CO_3 and Fe_2O_3 of 99.995% and 99.999% purity, respectively. A mixture of the correct proportions of the compounds was pre-sintered in air at 700 °C for 2 h. The mixture was then ground and heated at 1040 °C for 4 h and at 930 °C for 1 h, and then cooled down to room temperature. In order to obtain homogeneous material, it was necessary to grind the sample after the first firing and press the powder into a pellet before heating it for a second time to 1040 °C for 5 h.

X-ray diffraction patterns for this sample were obtained with Cu Kα radiation. A Mössbauer spectrometer of the electromechanical type was used in the constant-acceleration mode. A ^{57}Co source in a rhodium matrix was used at room temperature.

3. Results

The x-ray diffraction measurements showed that the $Li_{0.5}Fe_{2.5}O_4$ sample had the cubic spinel structure. The lattice constant a_0 was found to be 8.344 ± 0.005 Å by plotting $a_0(\theta)$ versus the Nelson–Riley function [6] and extrapolating to $\theta = 90°$. No peaks for any secondary phase were found.

Mössbauer spectra of Li$_{0.5}$Fe$_{2.5}$O$_4$ have been taken at various absorber temperatures. Figure 1 illustrates some of the spectra, which are each composed of two six-line hyperfine patterns, A and B. Using a least-squares computer program, two sets of six Lorentzian lines were fitted to the Mössbauer spectra below the magnetic ordering temperature, under the well-known restraints [7] which are valid when the quadrupole interaction is much weaker than the magnetic hyperfine interaction.

Table 1. Magnetic hyperfine fields H and isomer shifts δ for tetrahedral (A) and octahedral (B) sites, and the ratio I_B/I_A of the area of the A pattern to that of the B pattern at various temperatures T for Li$_{0.5}$Fe$_{2.5}$O$_4$. δ is given relative to that of the metal.

T (K)	$H(A)$ (kOe)	$\delta(A)$ (mm s^{-1})	$H(B)$ (kOe)	$\delta(B)$ (mm s^{-1})	I_B/I_A
80	518	0.32	533	0.45	1.50
140	517	0.31	531	0.43	1.49
170	515	0.29	527	0.42	1.49
230	510	0.26	521	0.39	1.47
300	504	0.24	510	0.36	1.44
400	480	0.18	485	0.30	1.42
500	452	0.09	448	0.21	1.39
600	417	0.04	402	0.16	1.37
700	365	−0.03	344	0.09	1.35
800	273	−0.11	249	0.01	1.33
	(± 1)	(± 0.01)	(± 1)	(± 0.01)	(± 0.01)

Table 1 presents the magnetic hyperfine fields and isomer shifts for the A and B patterns for Li$_{0.5}$Fe$_{2.5}$O$_4$ at some typical temperatures. The isomer shifts at room temperature for the A and B patterns are found to be 0.24 ± 0.01 mm s^{-1} and 0.36 ± 0.01 mm s^{-1} relative to that of iron metal, which are consistent with the values for Fe^{3+} ($S = 5/2$) [8]. The ferric character of the Fe ions is also manifested by the magnitudes of the magnetic field given in table 1. It is also seen from table 1 that the ratio of the area of the B pattern to that of the A pattern at low temperatures is found to be 1.5. Therefore, the site distribution in Li$_{0.5}$Fe$_{2.5}$O$_4$ can be written as

$$\text{Fe}^A(\text{Li}_{0.5}\text{Fe}_{1.5})^B\text{O}_4$$
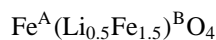
where the superscripts A and B denote the tetrahedral sites and octahedral sites, respectively. Since ferric ions provide neither orbital nor dipolar contributions [2] to the magnetic hyperfine field, it is proportional to the spin of the ferric ion.

Figures 2 and 3 show the reduced magnetic hyperfine fields $H(T)/H(0)$ for the A and B sites of Fe(Li$_{0.5}$Fe$_{1.5}$)O$_4$ as functions of the reduced temperature $\tau = T/T_N$, where the Néel temperature T_N of Li$_{0.5}$Fe$_{2.5}$O$_4$ is found to be 900 ± 2 K from Mössbauer measurements. In order to obtain information on the superexchange interactions from figures 2 and 3, we extend the Néel theory of ferrites [9] to the case of two sublattices each containing one kind of magnetic ion. The molecular field acting on each Fe ion at an A (tetrahedral) site is

$$H_A = \gamma\alpha M_A - \gamma M_B \tag{1a}$$

and that acting on each Fe ion at a B (octahedral) site is

$$H_B = -\gamma M_A + \gamma\beta M_B \tag{1b}$$

where M_A and M_B are the magnetizations of the A and B sublattices, respectively. $-\gamma$, $\gamma\alpha$, and $\gamma\beta$ are the molecular-field coefficients corresponding to A–B, A–A, and B–B
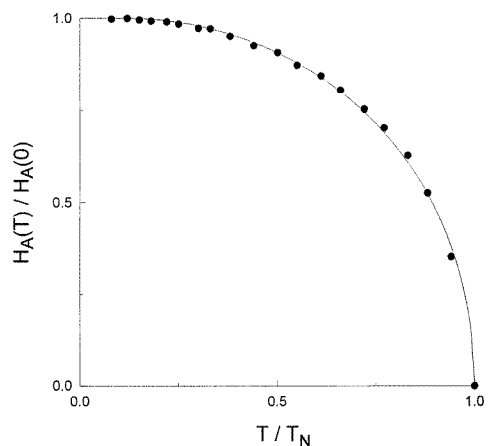
Figure 2. The reduced magnetic hyperfine field $H(T)/H(0)$ of ferric ions at the tetrahedral sites in $Li_{0.5}Fe_{2.5}O_4$ as a function of the reduced temperature $\tau = T/T_N$. The solid line represents σ_A calculated from equations (2) and (5).

Figure 3. The reduced magnetic hyperfine field $H(T)/H(0)$ of ferric ions at the octahedral sites in $Li_{0.5}Fe_{2.5}O_4$ as a function of the reduced temperature $\tau = T/T_N$. The solid line represents σ_B calculated from equations (2) and (5).

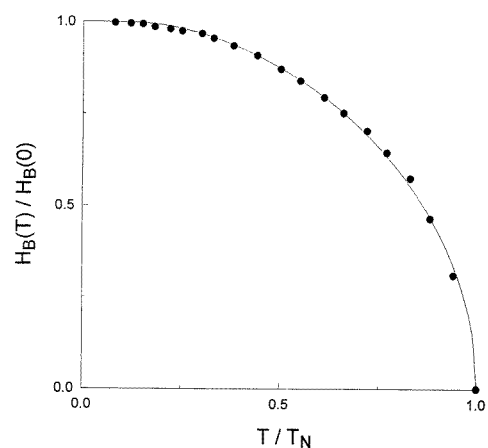superexchange interactions, respectively. The reduced magnetizations for the A and B sublattices are determined by

$$\sigma_A = B_S(x) \tag{2a}$$

and

$$\sigma_B = B_S(y) \tag{2b}$$

respectively. Here $B_S(x)$ and $B_S(y)$ denote, respectively, the Brillouin functions x and y defined by

$$x = \frac{g\mu_B S H_A}{k_B T} \tag{3a}$$

and

$$y = \frac{g\mu_B S H_B}{k_B T} \tag{3b}$$

where g is the g-factor of the Fe^{3+} $(S = 5/2)$. k_B is the Boltzmann constant, T is the absolute temperature, and μ_B is the Bohr magneton.
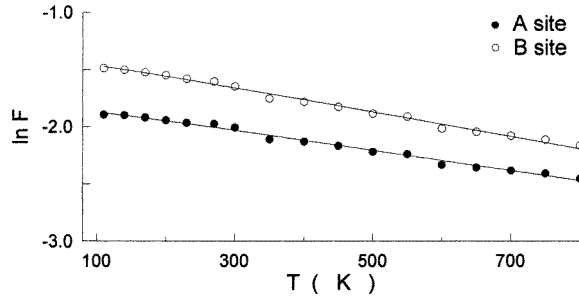

Figure 4. The temperature dependence of the natural logarithm of the resonant absorption area for the A and B sites of $Li_{0.5}Fe_{2.5}O_4$. The solid lines are calculated from equation (10).

The Néel temperature can be easily found from equations (1)–(3) to be

$$T_N = \frac{1}{2}\gamma[\alpha C + \beta C' + \sqrt{(\alpha C - \beta C')^2 + 4CC'}] \tag{4}$$

where C and C' are Curie constants for the A and B sublattices, respectively. Substituting equations (1) and (2) into equations (3) and solving for σ_A and σ_B, one can get the following equations:

$$\sigma_A = \frac{Q\tau}{(\alpha\beta - 1)g^2 S^2}(\beta x + y) \tag{5a}$$

and

$$\sigma_B = \frac{Q\tau}{1.5(\alpha\beta - 1)g^2 S^2}(\alpha y + x) \tag{5b}$$

where

$$Q = \frac{p}{6}[\alpha + 1.5\beta + \sqrt{(\alpha - 1.5\beta)^2 + 6}]. \tag{6}$$

Here $p = g^2 S(S + 1)$. For a set of (α, β) values, equations (2) and (5) are simultaneously solved to obtain σ_A and σ_B as functions of τ. Good agreement between the experimental data and the theoretical values of σ_A and σ_B was obtained for $(\alpha, \beta) = (1.09, 0.83)$ as shown by the solid lines in figures 2 and 3.

The inter-sublattice exchange integral for the Fe^{3+}(A) and Fe^{3+}(B) ions is calculated to be $(-10.8 \pm 0.5)k_B$ from the following equation:

$$J_{A-B} = -\frac{g^2 T_N k_B}{12Q}. \tag{7}$$

The exchange integral for the two nearest-neighbour Fe^{3+}(A) ions on the A sublattice is

$$J_{A-A} = -\frac{3\alpha J_{A-B}}{2} \tag{8}$$

and that of the two nearest-neighbour Fe^{3+} ions on the B sublattice is

$$J_{B-B} = -2\beta J_{A-B}. \tag{9}$$

J_{A-A} and J_{B-B} are calculated to be $(17.6 \pm 0.8)k_B$ and $(17.8 \pm 0.8)k_B$, respectively. It is noteworthy that the ferromagnetic intra-sublattice superexchange interactions between $Fe^{3+}(A)$ ions and between $Fe^{3+}(B)$ ions are stronger than the antiferromagnetic inter-sublattice superexchange interactions between $Fe^{3+}(A)$ ions and $Fe^{3+}(B)$ ions.

Figure 4 shows the temperature dependence of the resonant absorption area; the Debye model gives the following expression for the recoil-free fraction [10]:

$$f = \exp\left[-\frac{3E_R}{2k_B\Theta}\left(1 + \frac{4T^2}{\Theta^2}\int_0^{\Theta/T}\frac{x\,\mathrm{d}x}{\mathrm{e}^x - 1}\right)\right] \tag{10}$$

where E_R is the recoil energy of ^{57}Fe for the 14.4 keV gamma ray, and Θ represents the Debye temperature. The Debye temperature for each site can be calculated from the temperature dependence of the resonant absorption area of each subspectrum at low temperatures. The Debye temperatures of the tetrahedral and octahedral sites are found to be 398 ± 5 K and 362 ± 5 K, respectively. Thus, the Debye temperature Θ_A for the octahedral sites is almost as large as Θ_B for the tetrahedral sites, thereby suggesting similar inter-atomic binding forces for the A and B sites.

Acknowledgments

References

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