

Mössbauer Study and Atomic Migration in MgFe_2O_4

Seung Wha Lee, Sung Hyun Yoon¹, Sung Yong An², Woo Chul Kim² and Chul Sung Kim²

School of Electrical and Electronics Engineering, Chungbuk National University, Cheongju 631-763, Korea

¹*Department of Physics, Kunsan National University, Seoul 573-701, Korea*

²*Department of Physics, Kookmin University, Seoul 136-702, Korea*

(Received 22 November 1999)

MgFe_2O_4 has been studied with X-ray diffraction, Mössbauer spectroscopy and vibration sample magnetometer (VSM). The crystal structure of the sample is found to have a cubic spinel structure with a lattice constant of $a_0 = 8.390 \pm 0.005$ Å. The iron ions at both A (tetrahedral) and B (octahedral) sites are found to be in ferric high-spin states. Its Néel temperature T_N is found to be 710 ± 3 K. The Debye temperatures for the A and B sites found to be 417 ± 5 K and 331 ± 5 K, respectively. Atomic migration from the A to the B sites starts near 425 K and increases rapidly with increasing temperature to such a degree that 31% of the ferric ions at the A sites have moved over to the B sites by 600 K.

1. Introduction

A ferrimagnetic spinel can be represented by the formula AB_2O_4 , and the A-B magnetic interactions between the magnetic atoms on the A (tetrahedral) site and the on the B (octahedral) sites are stronger than the A-A interactions and the B-B interactions [1]. Metallic atoms are in an inverse distributions: half of the iron atoms are in the A sites and the other half, plus the magnetic atoms are in the B sites. However, MgFe_2O_4 is not completely inverse, and the degree of inversion depends on the heat treatment. The area ratio, $\text{Fe(A)}/\text{Fe(B)}$, has been found to vary from 0.60 ± 0.06 to 0.79 ± 0.06 in MgFe_2O_4 for two extreme heat treatments, quenched and slowly cooled, respectively, in an applied field of 45 kOe [2, 3]. In this article, we present our Mössbauer and X-ray results for slowly cooled MgFe_2O_4 with special emphasis on atomic migration as a function of temperature and on the Debye temperatures for the A and the B sites.

2. Experimental

The slowly cooled MgFe_2O_4 sample was synthesized by the usual ceramic method. A mixture of the proper proportions of Fe_2O_3 and MgO powders of 99.995% and 99.999% purities, respectively, was ground. The mixtures was heated at 1050 °C for 2 days and then slowly cooled to room temperature at a rate of 10 °C/h. In order to obtain a homogeneous material, the samples after the first firing were grounded and then pressed into pellet before annealing for a second time in evacuated.

The X-ray diffraction pattern of the samples was obtained

with $\text{CuK}\alpha$ radiation. A slow scanning speed of 0.25° advance in $2\theta/\text{min}$ was used in order to optimize the resolution of closely spaced reflections. The Mössbauer spectra of the electromechanical type was used with the constant-acceleration mode [4]. A 20-mCi ^{57}Co source in a Rh matrix was used at room temperature. Also, temperature dependence of saturation magnetization of the samples was measured by VSM from room temperature to 800 K with an external field of 5 kOe.

3. Results and Discussion

Results of the X-ray and the Mössbauer measurements showed that the sample had an inverse spinel structure. The lattice parameter $a_0(\theta)$ versus the Nelson-Riley [5] function and extrapolating to $\theta = 90^\circ$. The Mössbauer spectra of MgFe_2O_4 were measured at various temperatures from 12 to 750 K. The Mössbauer spectra are composed of two six-line hyperfine patterns, A and B. A least-squares computer program was used with the usual constraints [6], which are valid when the quadrupole interaction is much weaker than the magnetic hyperfine interaction. Some spectra are shown in Fig. 1 and 2. Just above the Néel temperature, $T_N = 710 \pm 3$ K, the Mössbauer spectrum becomes a sharp doublet. The results of the computer analysis are presented in Table 1. The isomer-shift values at room temperature for the A and the B patterns are found to be 0.11 ± 0.01 and 0.19 ± 0.01 mm/s relative to the Fe metal, respectively, which are consistent with high-spin Fe^{3+} charge state [7]. The smaller value of the A site isomer shift is due to a larger covalency at the A site. Above the Néel temperature, T_N the quadrupole splitting is given by

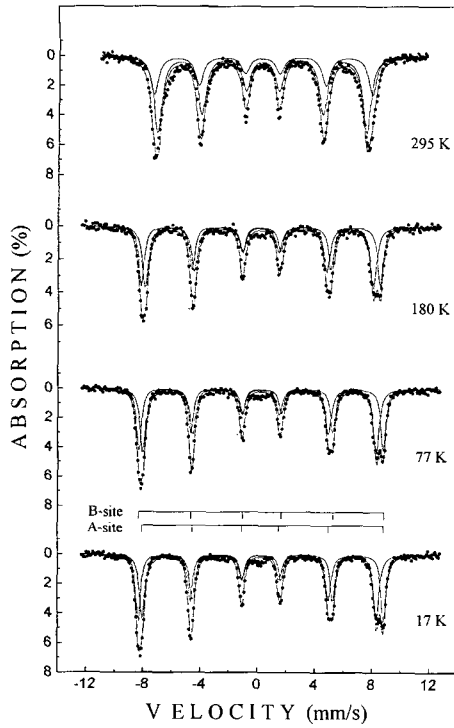


Fig. 1. Mössbauer spectra of MgFe_2O_4 within the temperature ranges of 17~295 K.

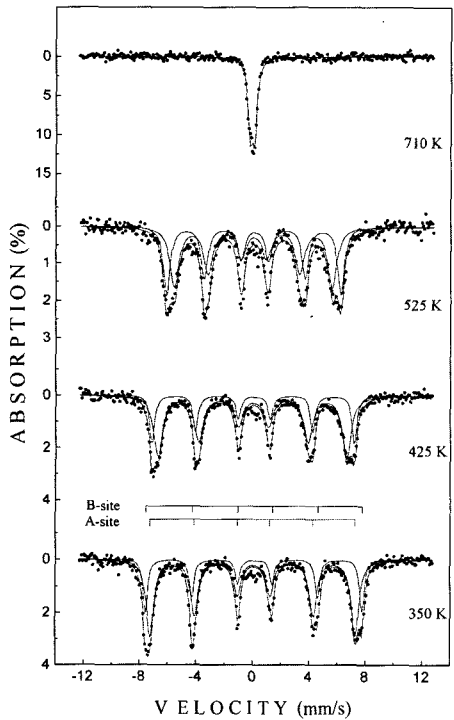


Fig. 2. Mössbauer spectra of MgFe_2O_4 from 350 K to near the Néel temperature.

$$\varepsilon = \frac{1}{2} e^2 q Q \left(1 + \frac{1}{3} \eta^2 \right)^{1/2}. \quad (1)$$

The value of ε was found to be 0.30 ± 0.01 mm/s at 710 K which is just above T_N . On the other hand, Table 1 shows

Table 1. Magnetic hyperfine field H_{hf} , quadrupole shift ΔE_Q , and isomer shift δ relative to the iron metal at various temperatures T for MgFe_2O_4

| T (K) | H_{hf} (kOe) | | ΔE_Q (mm/s) | | δ (mm/s) | |
|-------|-----------------------|-------------|---------------------|----------------|-----------------|----------------|
| | B | A | B | A | B | A |
| 17 | 533 | 510 | -0.02 | -0.03 | 0.41 | 0.20 |
| 77 | 531 | 507 | -0.02 | -0.03 | 0.29 | 0.19 |
| 180 | 520 | 496 | -0.02 | -0.02 | 0.25 | 0.16 |
| 290 | 494 | 468 | -0.02 | -0.03 | 0.19 | 0.11 |
| 350 | 477 | 452 | -0.03 | -0.03 | 0.16 | 0.08 |
| 425 | 446 | 416 | -0.03 | -0.03 | 0.09 | 0.04 |
| 525 | 381 | 348 | -0.03 | -0.02 | 0.04 | 0.00 |
| | (± 1) | (± 1) | (± 0.01) | (± 0.01) | (± 0.01) | (± 0.01) |

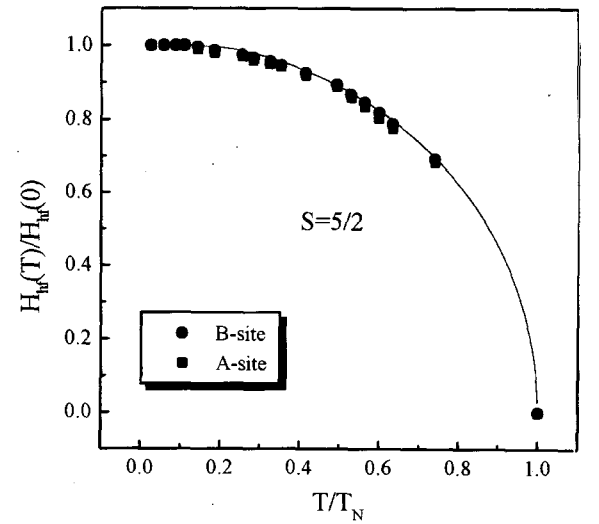
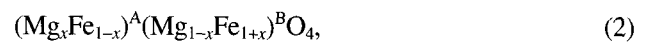


Fig. 3. Reduced magnetic hyperfine field $H_{\text{hf}}(T)/H_{\text{hf}}(0)$ versus reduced temperature T/T_N for the A and the B sites of MgFe_2O_4 . The marked points are the experimental values. The full curve is the Brillouin function for $S=5/2$.

that all the quadrupole shifts below T_N for both the A and the B sites are almost zero within experimental errors. Thus, the smaller magnitudes of the quadrupole shifts for MgFe_2O_4 are consistent with the cubic crystal structure. Plots of reduced magnetic hyperfine field $H_{\text{hf}}(T)/H_{\text{hf}}(0)$ against reduced temperature T/T_N for A and B sites of MgFe_2O_4 are given in Fig. 3 along with the Brillouin curve [8] $B(S)$ for $S = 5/2$.

Figure 4 shows the temperature dependence of the absorption area ratio of the A site to the B site. It is worth noting in Fig. 4 that at low temperatures, the area ratio increases with increasing temperature up to about 400 K and then decreases. The cation distribution [3] of MgFe_2O_4 is:



indicating that x Fe ions have migrated from A to B sites (the same number of Mg ions moved from B sites to A

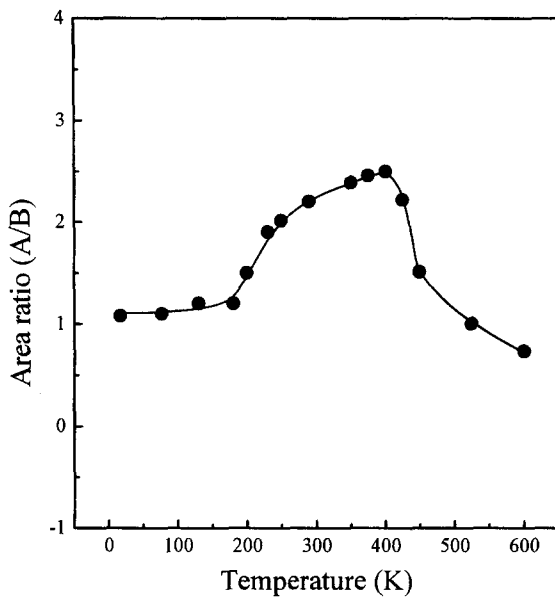


Fig. 4. Temperature dependence of the area ratio of A to B sites for MgFe_2O_4 .

sites). The area ratio of the A and the B subspectra for the above distribution [9] is:

$$\frac{I_A}{I_B} = \frac{(1-x)f_A}{(1+x)f_B}, \quad (3)$$

where f_A and f_B represent the recoil-free fractions of A-site and B-site Fe ions, respectively. The Debye model gives the following expression for the recoil-free fraction [10]:

$$f = \exp \left[-\frac{3E_R}{2k_B\theta} \left(1 + \frac{4T^2}{\theta^2} \int_0^{\theta/T} \frac{xdx}{e^x - 1} \right) \right], \quad (4)$$

Where E_R is the recoil energy of ^{57}Fe for the 14.4-keV γ ray, θ and k_B represent the Debye temperature and the Bolt-

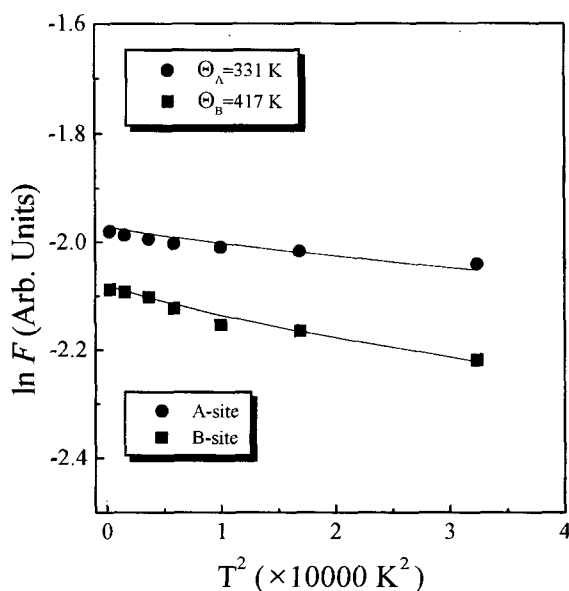


Fig. 5. Natural logarithm of the total resonance absorption area, $\ln F$ vs T^2 for the A and the B subspectra of MgFe_2O_4 .

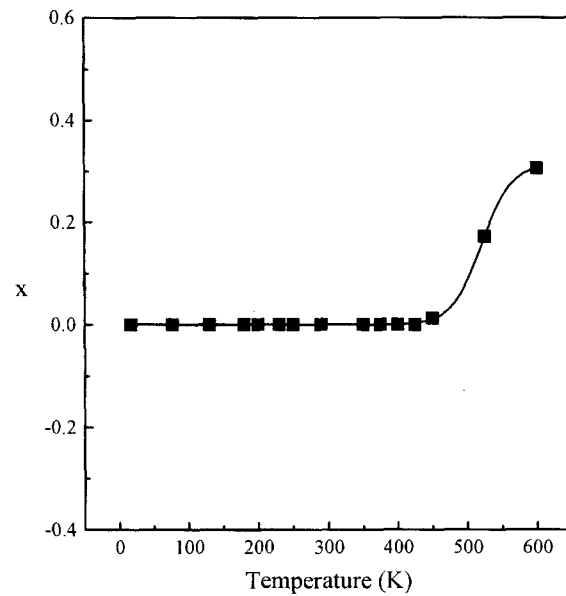


Fig. 6. Temperature dependence of the fraction x of the tetrahedral site Fe^{3+} ions that migrate to B sites.

zmann constant, respectively. The Debye temperature for each site can be calculated from the temperature dependence of the resonant absorption area of each subspectrum in the region of low temperatures.

Figure 5 shows $\ln F$ vs T^2 for MgFe_2O_4 where F stands for the total resonance absorption areas of A and B sites in a Mössbauer spectrum at T . F is proportional to the recoil-free fraction f . The curves are close to straight lines, and from the results the Debye temperatures, θ_A and θ_B of A and B site are determined to be 417 ± 5 K and 331 ± 5 K, respectively. Substituting the experimental area ratio I_A/I_B from Fig. 4 and the f values of Eq. (4) into Eq. (3), one can

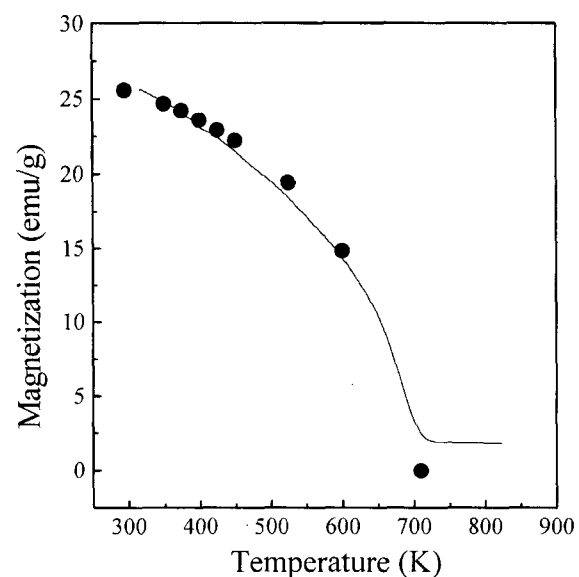


Fig. 7. Temperature dependence of the magnetization under an applied field of 5 kOe for MgFe_2O_4 . The solid circles are average values of normalized magnetic hyperfine fields taken from Mössbauer spectra.

get the x values as a function of temperature, as shown in Fig. 6. It can be seen in Fig. 6 that atomic migration starts near 425 K and increases rapidly with increasing temperature to such a degree that 31% of the iron ions at the A sites moves over to the B sites at 600 K. Bertaut [11] reported that 26% of the iron ions at the A sites in CuFe_2O_4 move over to the B sites at 700 °C. Comparison of the results for MgFe_2O_4 suggests that the Mg^{2+} ions can change the site preference of the Cu^{2+} and Fe^{3+} ions drastically. The temperature dependence of the magnetization of MgFe_2O_4 under an applied field $H=5$ kOe is shown in Fig. 7. The solid circle indicates the normalized magnetic hyperfine field taken from the Mössbauer spectra. The magnetization measured a function of temperatures with VSM are marked with a solid line. These data show the magnetization measured with Mössbauer spectroscopy and VSM agree with each other very well below the Néel temperature.

Acknowledgement

This work was supported by the Korea Science and Engineering Foundation (97-0702-0401-5).

References

- [1] C. M. Srivastava, G. Srinivasn and N. G. Nanaddikar, *Phys. Rev.*, **B 19**, 499 (1979).
- [2] G. A. Sawatzky, F. Van der Woude and A. H. Morrish, *Phys. Rev.*, **187**, 747 (1969).
- [3] G. De Grave, A. Govaert and D. Chambaere, *Physica B*, **96**, 1039 (1979).
- [4] H. N. Ok and Y. K. Kim, *Phys. Rev.*, **B 36**, 5120 (1987).
- [5] J. B. Nelson and D. P. Riley, *Proc. Phys. Soc.*, **57**, 160 (1945).
- [6] C. S. Kim, Y. J. Lee, S. W. Lee, Y. B. Kim and C. S. Kim, *J. Appl. Phys.*, **79**, 5428 (1996).
- [7] H. N. Ok, K. S. Baek and E. J. Choi, *Phys. Rev.*, **B 40**, 84 (1987).
- [8] C. S. Kim, S. W. Lee, S. I. Park, J. Y. Park and Y. J. Oh, *J. Appl. Phys.*, **79**, 5428 (1996).
- [9] S. W. Lee, S. I. Park, S. B. Kim, C. S. Kim and H. N. Ok, *J. Korean Phys. Soc.*, **31**, 504 (1997).
- [10] R. L. Mössbauer and W. H. Wiedermann, *Z. Phys.*, **159**, 33 (1960).
- [11] E. F. Bertaut, *J. Phys. Radium*, **12**, 252 (1951).