

## Mössbauer Study of $\text{Eu}_x\text{Fe}_{2-x}\text{O}_3$ ( $x=0.8$ and $0.7$ )

J. G. Kim

*Department of Physics, Hanyang University,  
Seoul, 133-791 Korea*

E. C. Kim

*Department of Physics, Yeungnam University,  
Kyousan, 712-749 Korea*

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The microscopic physical properties of nonstoichiometric garnet  $\text{Eu}_x\text{Fe}_{2-x}\text{O}_3$  ( $x=0.8$  and  $0.7$ ) have been studied by the methods of X-ray diffraction at room temperature and Mössbauer spectroscopy within the temperature range of 12~560 K. The X-ray diffraction patterns of the samples show coexistence of dominant garnet and a small portion of unknown crystal phase. But the Mössbauer spectra for the sample of EF08 and EF07 near Néel temperature determined to be equally  $549 \pm 5$  K show that there are no any other extra crystal phases within the experimental error. The results of which the temperature dependence of Mössbauer parameters was analyzed by the spin-wave theory and Debye model are in good agreement with the fact that the sample of EF08 has some vacancies at a- and/or d-sites.

### I. Introduction

Iron garnets have attracted much attention because of their interesting magnetic properties[1-7]. The general chemical structural formula for europium-iron garnet (EuIG) is  $\text{Eu}_3\text{Fe}_5\text{O}_{12}$  or  $\text{Eu}_x\text{Fe}_{2-x}\text{O}_3$  ( $x=0.75$ ). The X-ray diffraction data show that EuIG belongs to space group  $O_{10}^h-I_d3_d$  with the overall symmetry being cubic. The unit cell contains 8 formula units  $\{\text{Y}_3\}[\text{Fe}_2](\text{Fe}_3)\text{O}_{12}$ , where  $\{\}$ ,  $[\ ]$ , and  $( )$  represent a dodecahedral c-, octahedral a-, and tetrahedral d-site, respectively. Because the site preference for the different cations in the lattice is essentially determined by their ionic radius,  $\text{Eu}^{3+}$  and  $\text{Fe}^{3+}$  ions occupy the c-, a-, and d-sites, respectively[1,2]. The superexchange antiferromagnetic interaction between trivalent iron ion at a- and d-sites causes the garnet to be ferrimagnetism[3,4]. Accordingly it may be expected that the cation distribution of a- and d-site of garnet is the most important factor affecting the character of magnetic properties of the sample.

It is well known that the Mössbauer experiment is useful for obtaining the information about the microscopic environments affecting the physical properties of a system. The purpose of this study is to carry out X-ray and Mössbauer spectroscopic measurement on the

nonstoichiometric garnet  $\text{Eu}_x\text{Fe}_{2-x}\text{O}_3$  ( $x=0.7$  and  $0.8$ ) to observe the changes in Mössbauer parameters using some appropriate models and to examine the site preference of cations in the samples.

### II. Experimental Procedure

The sample was synthesized by the usual ceramic method in the same way as described in the previous work[7] with starting materials of purity better than 99.999 %  $\text{Fe}_2\text{O}_3$  and  $\text{Eu}_2\text{O}_3$ . The X-ray diffraction pattern of the samples at room temperature was obtained using a Japanese-made Rigaku diffractometer with  $\text{Cu}_{K\alpha}$  radiation. Mössbauer spectra were recorded using an Austin constant acceleration Mössbauer spectrometer with a 10 mCi  $^{57}\text{Co}$  source in Rh matrix and were measured at various absorber temperatures from 12 K to 560 K. To produce a uniform thickness over the area of the Mössbauer absorber, the sample was mixed with boron nitride powder and clamped between two thin boron nitride plates.

### III. Results and Discussion

As shown in Fig.1 the X-ray diffraction patterns of the

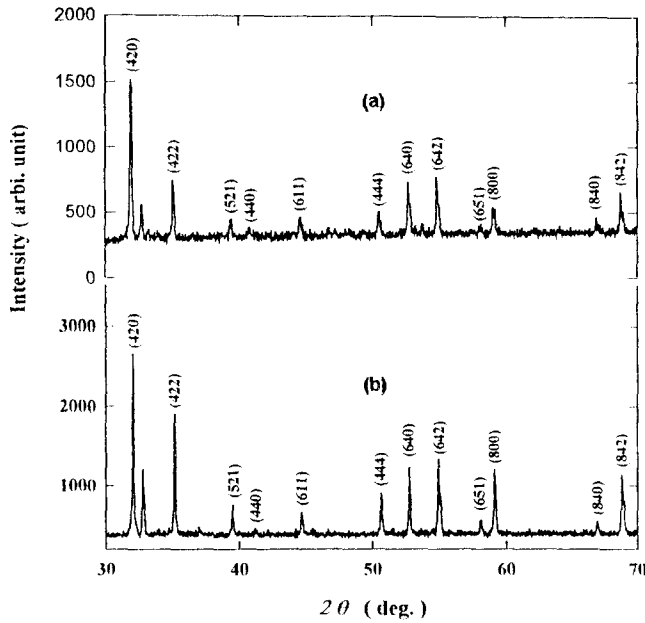


Fig.1. X-ray diffraction patterns of EF08(a) and EF07(b).

samples show the coexistence of dominant garnet and a small portion of unknown crystal phase. The lattice constants  $a_0$  of garnet phase for the sample of EF08( $x=0.8$ ) and EF07( $x=0.7$ ) were determined to be  $12.484\text{\AA}$  and  $12.498\text{\AA}$ , respectively. The lattice constants of garnet phase can be compared with the value of  $12.498\text{\AA}$  [2]. Fig.2 shows some of the Mössbauer spectra for the sample of EF08(a) and EF07(b) near Néel temperature  $T_N$  and indicates that there are no any other extra crystal phases appeared in the X-ray diffraction patterns. The Néel temperature for the samples were determined to be equally  $549\pm 5$  K. The values of the quadrupole interaction  $e^2qQ/2$  for the sample of EF08 and EF07 are  $0.386$  and  $0.392$  at a-site and  $0.900$  and  $0.885$  mm/s at d-site, respectively. They are compared with the values of  $0.408$  (a-site) and  $0.872$  mm/s (d-site) for EuIG[6].

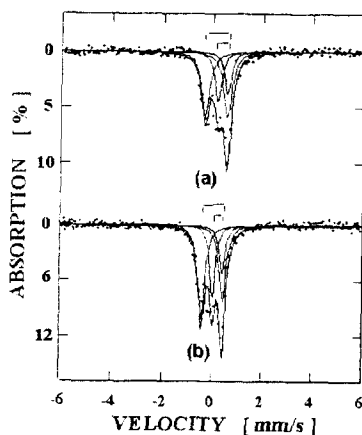


Fig.2. Mössbauer spectra near Néel temperature of EF08(a) and EF07(b) at 555 K.

Some of Mössbauer spectra for the sample of EF08(a) and EF07(b) below Néel temperature are shown in Fig.3.

The spectra of the samples below Néel temperature were fitted to a mixed-electric quadrupole plus magnetic hyperfine pattern. The widths that were assumed to be the same in respective subspectra and overall absorption areas of the spectra are independently varied as free parameters. However, within the subspectra the following constraints for the areas of spectrum were imposed:

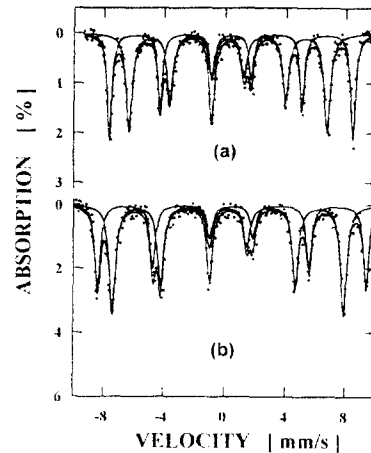


Fig.3. Mössbauer spectra of EF08(a) at room temperature and EF07(b) at 40 K.

$$A_{i,d} = b_d A_{i,d}, \quad A_i = A_{7,i} \quad (1)$$

where  $b_i$  is the best-fit parameter and a and d are termed the spectrum for a- and d-sites; and i goes from 1 to 3. The absorption area of subspectra for each site is proportional to the concentration of Fe ions using the value of the recoilless fractional ratio ( $f_a/f_d=0.99$ ) [5] of a- to d-subspectra for YIG at room temperature. An ideal value of area ratio of a- to d-site is  $0.667$ . The average ratio of the sample of EF08 and EF07 in the experimental temperature range were obtained to be  $0.758$  and  $0.658$ , respectively. The value of  $0.758$  for the sample of EF08 implies the possibility of existence of some vacancies at a- and/or d-sites.

Kubo[8] and Oguchi[9] have calculated the temperature dependence of the antiferromagnetic sublattice magnetization using the spin-wave theory neglecting anisotropy. Their result can be expressed as Eq.(2).

$$H(T) = H(0) / [1 - AT^2 - BT^3 - CT^4] \quad (2)$$

where  $H(0)$  is the magnetic hyperfine field at 0 K.  $A, B,$  and  $C$  are the best fit constants. The term of  $T^2$  in Eq.(2) represents the excitation of long-wavelength spin waves deduced from Kubo's "simple spin-wave theory" and the last two terms are given by Oguchi's corrections due to spin-

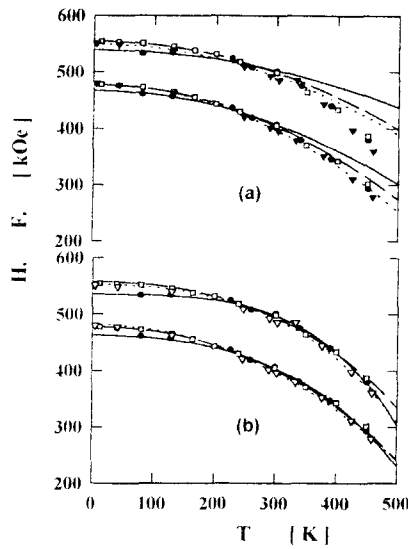


Fig.4. Temperature dependence of magnetic hyperfine fields analyzed by the sum of the terms to order  $T^2$ (a) and  $T^3$ (b). The data points of circle, square, and inverse triangle represent the sample of EF08, EF07, and DyIG, respectively.

wave interactions.

The experimental data of the fields at a- and d-site for the samples were analyzed by the sum of the terms to order  $T^2$ , to order  $T^3$ , and to order  $T^4$  of Eq.(2) using a least-square fitting program. The data of DyIG are those measured by G. Creelius et.al[10]. The analyzed results are listed in Table I. Fig.4(a) and (b) show the temperature dependence of the fields from the results of Table I. As shown in Fig.4 a good fit was obtained to the experimental values in the wide range of temperature to  $T/T_N < 0.6$  ( $\sim T^2$ ) and  $0.8$  ( $\sim T^3$ ). In Table I the ratios  $B/A$  at a- and d-site for the sample of DyIG is of order  $10^6$  and  $10^7$ . The sample of EF07 has similar values with that of DyIG except that of EF08. Following the fact that the ratio provides a measure of the range of the magnetic interaction[11,12], the results of smaller values of  $B/A$  suggest that the mean exchange interaction has a shorter range at d-site of EF07 and DyIG than that at a- and d-site of EF08 and a-site for all samples.

Table I. Results fitted the data of magnetic hyperfine fields to the spin-wave theory.

SAMPLE	TEMP.RANGE [K]	SITE	H(0)[kOe]	A[x10 <sup>6</sup> ]	B[x10 <sup>12</sup> ]	B/A[x10 <sup>6</sup> ]
EF08	80-300	a	539.189	0.755		
		d	466.899	1.417		
EF07	80-450	a	535.371	0.247	5.944	24.01
		d	462.932	1.066	3.763	3.530
	12-300	a	555.023	1.123		
		d	477.597	1.704		
DyIG	12-450	a	557.943	1.085	2.073	1.911
		d	481.312	1.860	0.141	0.075
	4.2-333	a	549.642	1.166		
		d	478.447	1.885		
4.2-458	a	552.988	0.924	3.437	3.720	
	d	482.053	1.912	0.331	0.173	

An elementary method applied for the analysis of the temperature dependence of Mössbauer parameters due to lattice dynamics is to assume that the phonon structure is based on Bose-Einstein populated states of independent harmonic oscillators. For a density of state  $g(\omega)$  populated by phonons with Bose-Einstein statistics, the expectation value of the energy will be the Eq.(3).

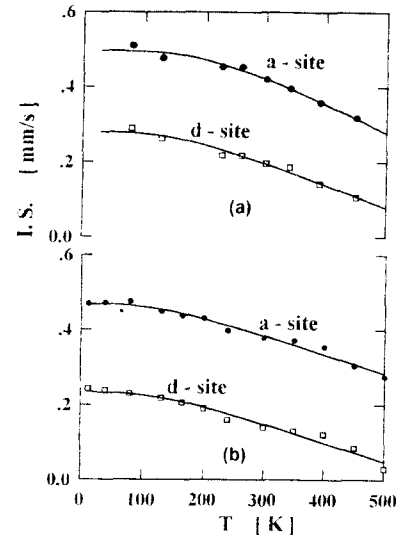


Fig.5. Analyzed result of temperature dependence of isomer shift of EF08(a) and EF07(b).

$$\langle E \rangle = \frac{\int \langle 1/2 + [\exp(\hbar\omega/kT) - 1]^{-1} \rangle \hbar\omega g(\omega) d\omega}{\int g(\omega) d\omega} \quad (3)$$

The quantized lattice energy levels can be explained by introducing the kinetic temperature  $T^*$  depending on the temperature. The  $\langle E \rangle$  and isomer shift  $I.S.$ , which is one of the Mössbauer parameters, can be defined by Eq.(4) and (5)[13].

$$\langle E \rangle = kT^*(T) \quad (4)$$

and

$$I.S. = A' + B'T^*(T) \quad (5)$$

The kinetic temperature  $T^*(T)$  can be easily calculated by Eq.(4) using a density of states  $g(\omega)$  in Debye model defined by Eq.(6).

$$g(\omega)d\omega = \begin{cases} 3\omega^2 / \omega_D^3, & \text{for } \omega \leq \omega_D \\ 0, & \text{for } \omega > \omega_D \end{cases} \quad (6)$$

where  $k$  is Boltzmann's constant and  $A'$  and  $B'$  are the best fit constants.  $\omega_D$  is defined by the relation of the Debye temperature  $\theta_D = \hbar \omega_D / k$ . From the data analysis the Debye

temperatures  $\theta$  were determined for the samples. The Debye temperatures and the ratio ( $\theta_a/\theta_d$ ) of the respective temperature at a- and d-site are listed in Table II. Fig.5 shows the temperature dependence of isomer shift (called the second order Doppler shift) of the samples and the values indicate  $\text{Fe}^{3+}$  at each site. In Table II the  $\theta_a$  and  $\theta_d$  represent Debye temperature at a- and d-site, respectively. As shown in Table II the ratio for the sample of EF08 is more than 1. This implies that the sample has some vacancies at d-site from the fact that  $\theta$  gives a measure of the strength with which the ion is bound to its equilibrium position.

Table II. Debye temperatures at each site of the sample

SAMPLE	$\theta_a$ [K]	$\theta_d$ [K]	$\theta_a/\theta_d$
EF08	465.25	311.72	1.49
EF07	336.20	390.05	0.86

#### IV. Conclusion

In spite of small portion of extra phases of the X-ray diffraction patterns, the Mössbauer spectra of the system  $\text{Eu}_x\text{Fe}_{2-x}\text{O}_3$  ( $x=0.7$  and  $0.8$ ) show the samples to be a single phase crystal. Considering the site preference of cations in the lattice, though further studies must be done, the results of which the temperature dependence of Mössbauer parameters was analyzed by the spin-wave theory and Debye model are in good agreement with the fact that the

sample of EF08 has some vacancies at at a- and/or d-sites.

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