MÖSSBAUER EFFECT STUDY OF MAGNETIC INTERACTIONS IN $Eu(Fe_{0.8}M_{0.2})O_3$ (M=Sc, Cr, Mn, Co)

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ABSTRACT

The solid state solutions of europium transition element oxides Eu $(Fe_{0.8}M_{0.2})O_3$ (M=Sc, Cr, Mn, Co) are synthesized. The X-ray diffraction of the compound shows that all the compounds possess the perovskite structures. Both the ^{151}Eu Mössbauer spectra and the ^{57}Fe Mössbauer spectra are measured. The hyperfine magnetic field and non-axisymmetric electric field gradient are observed in the ^{151}Eu Mössbauer spectrum. The ^{57}Fe Mössbauer spectrum shows that there are four components of hyperfine fields corresponding to four kinds of different neighbours of the Fe ion.

Keywords: Mössbauer effect Magnetic interaction Eu-Fe-M-O

1 INTRODUCTION

The rare earth iron perovskites $RFeO_3$ have been studied by ^{57}Fe Mössbauer spectroscopy[1,2,3]. The double rare earth ferrites have been investigated in our previous work[4]. Because the $EuFeO_3$ and $EuMO_3$ (M=other transition element) showed some of weak ferromagnetic properties, the significant researches on $EuFe_{1-x}Co_xO_3$ have been reported by Gibb[3]. In this paper, the solid state solutions $EuFe_{0.8}M_{0.2}O_3$ with different diamagnetic M ions (Sc, Cr, Co, Mn) were synthesized by a high-temperature (H-T) method and treated by a high-pressure and high-temperature method. The structures of the solutions were determined by X-ray diffraction. Both the ^{57}Fe and the ^{151}Eu Mössbauer spectra were measured. The magnetic exchange interaction in the ^{151}Eu and ^{57}Fe Mössbauer spectra was also studied.

2 EXPERIMENT

The Purities of Eu_2O_3, Fe_2O_3, Sc_2O_3, Cr_2O_3, Co_3O_4, MnO_2 used in the experiments were higher than 99.9% and original oxides were heated at 800 °C for 3 h before experiments. The sample was composed of three different kinds of oxides in a certain

stoichiometric ratio of Eu:Fe:M = 1:0.8:0.2. After fully mixed, the final mixture was pressed into a pellet and heated at 1300 °C for 10 h. Then, some of the samples were treated by a high-temperature and high-pressure method (1100 °C, 3.4 GPa).

The structures of these compounds at room temperature were determined by a Rigaku 12-kW copper rotating-anode X-ray diffractometer. The ^{151}Eu and ^{57}Fe Mössbauer spectra at room temperature were measured with an OXFORD MS-500 constant acceleration spectrometer. The velocity was calibrated with a α - Fe foil. The radiation sources were $^{151}Sm/SmF_3$ and $^{57}Co/Rh$. The thickness of absorber was 7 mg/cm^2 Eu in the measurement of ^{151}Eu spectra and 1 mg/cm^2 Fe in the measurement of ^{57}Fe spectra, respectively.

3 RESULTS AND DISCUSSION

The X-ray determination of $EuFe_{0.8}M_{0.2}O_3$ indicated that all the samples possessed

Table 1

The lattice parameters of $EuM_{0.2}Fe_{0.8}O_3$ (±0.0005nm)

Sample	a (nm)	b (nm)	c (nm)	V (nm^3)
$EuFeO_3$	0.5372	0.5608	0.7681	0.2313
$EuSc_{0.2}Fe_{0.8}O_3$	0.5395	0.5637	0.7723	0.2348
$EuCr_{0.2}Fe_{0.8}O_3$	0.5374	0.5588	0.7676	0.2305
$EuMn_{0.2}Fe_{0.8}O_3$	0.5371	0.5619	0.7668	0.2314
$EuCo_{0.2}Fe_{0.8}O_3$	0.5362	0.5568	0.7659	0.2287

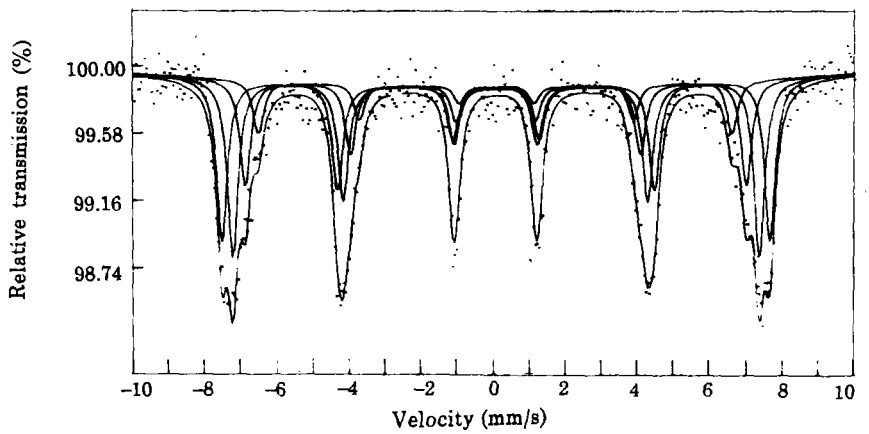

Fig.1 ^{57}Fe Mössbauer spectrum of $Eu(Fe_{0.8}Mn_{0.2})O_3$

an orthorhombic perovskite structure and were similar to that of $GdFeO_3$ reported by Geller[5]. The calculated lattice parameters of the compounds before being treated by a high-temperature and high-pressure method were listed in Table 1. It can be found that the lattice parameters a, b, c and the cell volume (V) showed a little variation

with different M in $EuFe_{1-x}M_xO_3$. The cell volume increased 1.4% when the Fe^{3+} was replaced by the larger Sc^{3+} ion and decreased 0.5% and 1.3% when the Fe^{3+} was replaced by the smaller Cr^{3+} and Co^{3+} ions, respectively. The samples treated by a high-temperature and high-pressure method possessed the same lattice parameters.

A complex magnetic structure was observed in the ^{57}Fe Mössbauer spectra. The spectrum of $EuFe_{0.8}Mn_{0.2}FeO_3$ was shown in Fig.1. The Mössbauer spectrum of the $EuFeO_3$ showed a single six-line pattern[2]. Because the Fe^{3+} was replaced by the diamagnetic cation M^{3+}, the hyperfine field decreased. It was known that the hyperfine field could vary with the different number of neighbour M ions of Fe ion. In solution, the probability of Fe^{3+} with n neighbour M ions can be calculated as a function of x, $P(n)=n!(1-x)^{6-n}x^n/(6-n)!n!$, given by Gibb[3]. In our case, the four components of each Mössbauer spectrum were assigned to the Fe^{3+} site with 6 Fe^{3+} neighbours (26.2%), to that with 1 M^{3+} and 5 Fe^{3+} neighbours (39.2%), to that with 2 M^{3+} and 4 Fe^{3+} neighbours (24.6%), to that with 3 M^{3+} and 3 Fe^{3+} neighbours (8.2%), respectively. The experimental spectra were fitted with four components of the hyperfine fields. The obtained parameters of $EuFe_{0.8}Mn_{0.2}O_3$ were listed in Table 2. The relative intensity obtained by fitting supported the above calculation.

Table 2

^{57}Fe Mössbauer parameters of $EuMn_{0.2}Fe_{0.8}O_3$ (IS is relative to α — Fe)

Components	IS (mm/s)(±0.01)	QS (mm/s)(±0.02)	H_{in} (A/m)(±4×10⁴)	Rate
1	0.35	0.00	3.744×10^7	32%
2	0.35	-0.01	3.598×10^7	36%
3	0.34	-0.01	3.423×10^7	22%
4	0.35	0.02	3.236×10^7	10%

It was found that the average field decreased when the Fe ion was replaced by the diamagnetic M ions, then the hyperfine field of the Fe^{3+} site with 6 Fe^{3+} neighbours in the solid state solution $EuFe_{0.8}Mn_{0.2}O_3$ was smaller than that in $EuFeO_3$. In the solid state solution mentioned above, the hyperfine field varied with the difference of the neighbour about the Fe^{3+}, the more the number of M ions about the Fe ion, the weaker the hyperfine field. The hyperfine field parameters were almost same when M was different kind of transition element, which showed the hyperfine field was not sensitive to the kind of M ion.

That the isomer shift of the different component was almost same showed that the electron density at the Fe nucleus was not sensitive to the nearest neighbour effect. The fact that the quadrupole splitting of the ^{57}Fe Mössbauer spectrum was very small and was not sensitive to the difference of M ion implied the distribution of the ligands about the Fe^{3+} ion was rather symmetrical.

The ^{151}Eu Mössbauer spectra showed a slight asymmetrical and very broad single

line with a half width 4–5mm/s (Fig.2). This anomalous broadening was because of the unresolved magnetic and quadrupole interaction[3]. The low symmetry at the Eu^{3+} sites lead to mixing of the $^7F_0$ ground state with the low-lying $^7F_1$ and $^7F_2$ excited states, then caused the quadrupole interaction. The Fe^{3+} spin could create an exchanged field at Eu^{3+} site due to the direct cation–cation or indirect cation–anion–cation exchange. In the pure $EuFeO_3$, the four pairs of equivalent Fe^{3+} spins caused the zero field at Eu site, but the substitution of an *M* ion for an Fe ion in the pairs of equivalant Fe ions could lead an imbalance in the exchange interaction. This might be the origin of magnetism of the Eu sites. Because the magnetic field was smaller, we assumed that the field at each Eu ion site possessed an approximate same value. Therefore the ^{151}Eu Mossbauer spectra were fitted to one set of magnetic subspectra with a quadrupole splitting by using the method Gibb[3] gave. The obtained parameters were listed in Table 3.

Table 3

^{151}Eu Mössbauer parameters of $EuFe_{0.8}M_{0.2}O_3$ synthesized by a H— T method

M	IS(mm/s) (vs Eu_2O_3)	eQVzz (mm/s)	Asymmetry	H_{in} (A/m)
Sc	−0.23 (0.01)	−7.2 (0.2)	0.7 (0.1)	7.96×10^5 (7.2×10^4)
Cr	−0.23 (0.01)	−5.9 (0.2)	0.7 (0.1)	1.36×10^6 (7.2×10^4)
Mn	−0.25 (0.01)	−6.0 (0.2)	0.8 (0.1)	1.22×10^6 (7.2×10^4)
Co	−0.15 (0.01)	−5.8 (0.2)	0.8 (0.1)	2.26×10^6 (7.2×10^4)

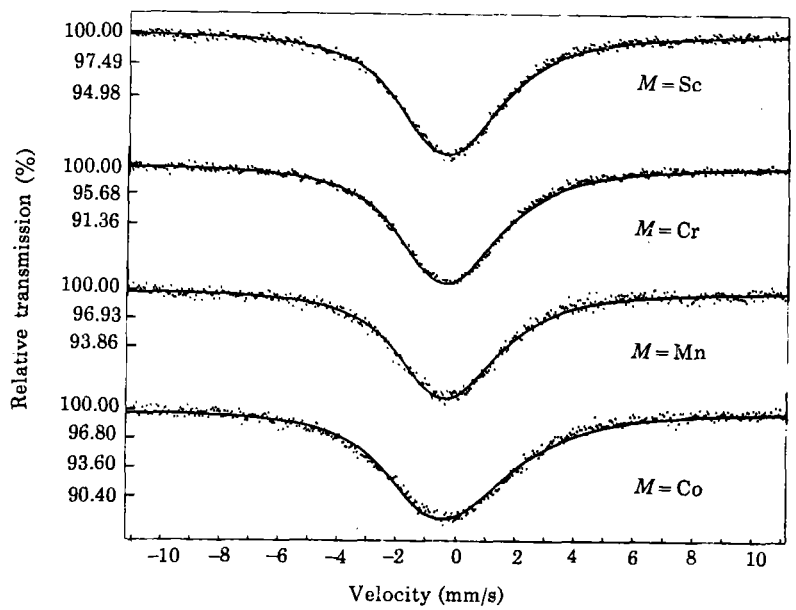

Fig.2 ^{151}Eu Mössbauer spectra of $EuFe_{0.8}M_{0.2}O_3$

The isomer shift of the Eu varied with different substitution of the M ion for the Fe ion. That no certain relationship between the isomer shift and a lattice parameter or a physical parameter of the M ion might imply the complex influence of the substitution of M ions. The hyperfine field was the largest as M = Co. Perhaps, this is related to the magnetic properties of M ion.

The ^{151}Eu spectra of the samples treated by a high-temperature and high-pressure method showed the same magnetic structure, but the quadrupole interaction decreased. This might indicate the local symmetry at the Eu ion site became better under the high-pressure.

REFERENCES

[1] Stadnik Z M, de Boer E . *Solid State Communications*, 1984, 50(4):335.

[2] Treves D. *J Appl Phys*, 1965, 36(3):1033.

[3] Gibb T C. *J Chem Soc Dalton Trans*, 1983:873.

[4] Liu Xuewu, Jin Mingzhi, Zhang Cailing. *J Appl Phys*, to be published.

[5] Geller S, Wood E A. *Acta Cryst*, 1956, 9:563.