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Iron-57 Mössbauer Studies on the $La_{1-x}Eu_xFeO_3$ Solid Solution System*

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Regarding the covalent character of the iron–oxygen bonds in iron compounds, namely in the ferrites, valuable information can be obtained by studying the hyperfine interactions. Several papers have dealt extensively with the rare earth orthoferrites, $LnFeO_3$, perovskite type; however, solid solutions with two different rare earth ions (on A sites), have so far received less attention. Therefore in this work ^{57}Fe Mössbauer experiments have been performed on the $La_{1-x}Eu_xFeO_3$ solid solution system at 295 K and it was shown that the magnitude of the magnetic hyperfine field varies linearly with x, depending on the Fe–O–Fe bond angle within the series.

Experimental

Samples of the solid solution $La_{1-x}Eu_xFeO_3$ were prepared for $x = 0$–1.0 in increments of 0.1, as follows. Accurately weighed samples of high-purity oxides in the appropriate proportions were ground together in a ball-mill, preheated in air to *ca.* 1000 °C for 24 h, and subsequently were fired to 1200 °C for 3–4 days with two intermediate grindings. The products were characterized by X-ray diffraction using a Philips diffractometer using Cu Kα radiation. All samples revealed patterns characteristic of the orthorhombic perovskite type with no other phases evident.

The parameters for $LaFeO_3$ and $EuFeO_3$ agreed well with published data [1, 2]. The lattice parameters a, b, c and cell volume for the solid solution showed a linear variation with composition. The ^{57}Fe Mössbauer spectra were obtained at room temperature using established techniques and a source matrix of ^{57}Co (Rh). Sampling time was usually *ca.* 2 days to achieve a good signal-to-noise ratio. Internal calibration was made to the spectrum of metallic α-iron. Absorbers were made according to the principles established in the recent literature [3].

Results and Discussion

Structural Characteristics of $La_{1-x}Eu_xFeO_3$

The end members $LaFeO_3$ and $EuFeO_3$ have been shown [1, 2] to belong to the orthorhombic space group *Pbnm* with the cell parameters $a = 555.3$, $b = 556.3$, $c = 786.7$ pm and $a = 537.2$, $b = 560.6$, $c = 768.5$ pm, respectively.

All the prepared compounds of the $La_{1-x}Eu_xFeO_3$ series with $0 < x < 1$ were isotypic and their unit cell parameters vary linearly with x (Table I), as is expected for ideal solid solution behaviour [4]. Considering this fact, the average Fe–O distance along the series should remain between the 200.6 and 201.3 pm values observed for $LaFeO_3$ and $EuFeO_3$, respectively [5]. In the same way the average Fe–O–Fe bond angle at the octahedral site is expected to decrease gradually from 156.8° to 147.9° [5], on going from $LaFeO_3$ to $EuFeO_3$. In Table II we have listed the weighted mean of the cosines squared of the Fe–O–Fe bond angles, calculated from ref. 6.

TABLE I. Crystallographic Data on $La_{1-x}Eu_xFeO_3$

x	a (pm)	b (pm)	c (pm)	$V \times 10^{30}$ (m^3)
0.0	555.5	556.8	786.0	243.1
0.2	552.3	557.4	783.4	241.2
0.4	547.8	558.3	780.2	238.6
0.5	545.0	558.7	777.1	236.6
0.6	544.8	559.1	776.0	236.4
0.8	541.1	560.1	772.2	234.0
1.0	537.3	560.5	768.4	231.4

TABLE II. ^{57}Fe Mössbauer Parameters at Room Temperature and $\cos^2\theta$ for $La_{1-x}Eu_xFeO_3$

x	δ (mm s^{-1})	Magnetic flux density (kG)	$\cos^2\theta$
0.0	0.374	531	0.854
0.2	0.371	527	0.820
0.4	0.371	522	0.782
0.5	0.382	521	0.766
0.6	0.378	518	0.767
0.8	0.368	515	0.742
1.0	0.373	513	0.719

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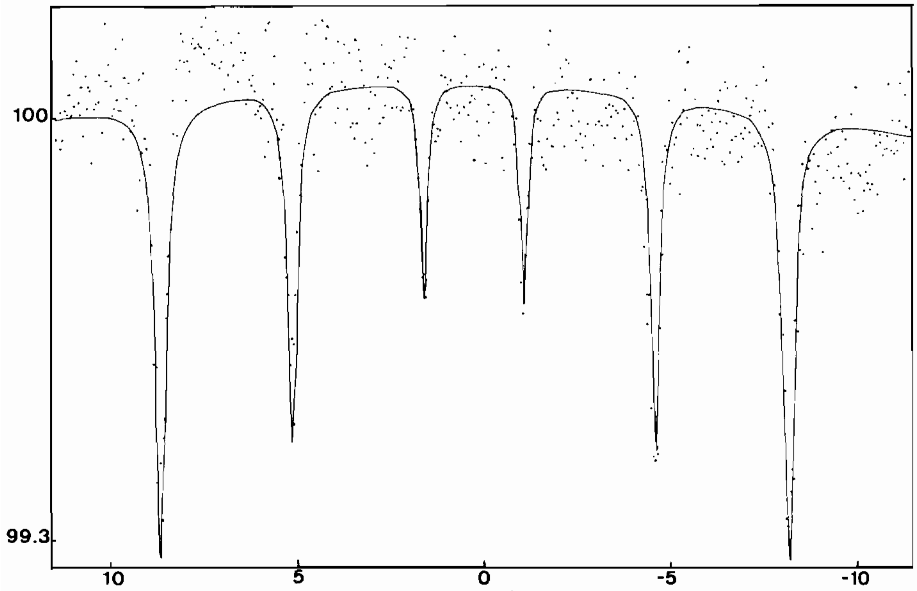

Fig. 1. ^{57}Fe Mössbauer spectrum for $La_{0.5}Eu_{0.5}FeO_3$ at 295 K.

^{57}*Fe Mössbauer Spectra*

The ^{57}Fe Mössbauer spectra were recorded at 295 K for all the samples. Detailed analyses of the spectra were carried out and the results are presented in Table II. The spectra for pure $LaFeO_3$ and $EuFeO_3$ comprised a single hyperfine pattern with a magnetic flux density of 531 kG and 513 kG, respectively, at 295 K, which is in accordance with the published data [5, 7].

All the compounds studied have similar Mössbauer spectra and Fig. 1 presents the spectrum of an intermediate member. The observations are summarized in Table II. Due to the relative constancy of the Fe–O distances, the isomer shift remains constant. This also shows that the degree of covalency of the Fe–O bonds is not affected by the possible inductive effect of the antagonistic bonds [8] when part of the La^{3+} ions are replaced by Eu^{3+} ions along the series. The quadrupole interactions are very small at 295 K, *i.e.* variations are insignificant.

For the magnetic flux density, it is known [5] that only the supertransfer hyperfine field (s.t.h.f.) contribution has a significant dependence on $\cos^2\theta$, considering θ to be the Fe–O–Fe bond angle (Fig. 2). The s.t.h.f. at the nucleus is produced by the 3d spins of the first neighbouring magnetic cations. The antiparallel spin of the six Fe^{3+} results in the s.t.h.f. and the intrinsic hyperfine field being additive, so we conclude that in the perovskite series studied the hyperfine magnetic field varies with the Fe–O–Fe bond angle.

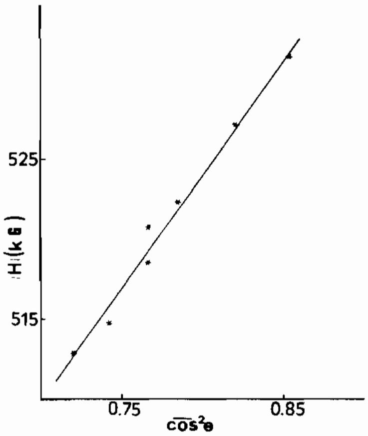

Fig. 2. Measured hyperfine fields *vs.* $\cos^2\theta$ for the series $La_{1-x}Eu_xFeO_3$.

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