CATION DISTRIBUTION IN Eu–Sc–Fe GARNETS

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Abstract—The cation distribution has been studied with \(^57\)Fe Mössbauer spectroscopy in the garnet system

\[
\text{Eu}_{3-x} \text{Sc}_x \text{Fe}_2 \text{O}_12
\]

with \(y = 0.0, 0.2, 0.5\) and 0.7. It is shown that the previously proposed cation distribution is not correct. The problem of possible impurities in the investigated system is discussed in detail. Several possible cation distributions are considered compatible with Mössbauer data. Mössbauer results combined with the composition dependence of lattice constants show that the tetrahedral sites are accessible to Sc\(^{3+}\) ions. The system studied is a second example of a garnet structure in which Sc\(^{3+}\) ions are found at the tetrahedral sites. A small fraction of Sc\(^{3+}\) ions for the samples \(y = 0.2\) and 0.5 is also found at the dodecahedral sites.

I. INTRODUCTION

The chemical formula of compounds with the garnet structure is written symbolically \([A]_3[B]_2[C]_6[O]_{12}\), where the curly braces represent a dodecahedral or \(c\) site, the square brackets—an octahedral or a \(d\) site, and the parentheses—a tetrahedral or \(A\) site[1]. \(A,\ B\) and \(C\) designate cations that can be both magnetic and non-magnetic ones. The exact knowledge of the cation distribution in garnets is of crucial importance since the physical properties of these materials essentially depend on it. Some of the experimental methods used for studies of cation distribution in garnets are described in[2].

The generally accepted idea concerning a site preference of a given ion in garnets is based on its ionic radius, i.e. ions with large radii are expected to enter eight-fold coordinated \(c\) sites, whereas those with small radii—four-fold coordinated \(d\) sites[3]. There are, however, several exceptions[2, 4, 5] which show that one should be very cautious when using ionic radius considerations. A site preference is also determined by other factors, in particular, by the site stabilization energy[4, 6].

It has been believed for many years that diamagnetic Sc\(^{3+}\) ions show exclusive preference for octahedral sites[1, 3, 7–10]. The possibility of Sc\(^{3+}\) ions entering the tetrahedral sites was considered in[7]. However, this could not explain the experimental results[7]. An indication of a small fraction of Sc\(^{3+}\) ions at the tetrahedral sites in the \(\text{Y}_3\text{Fe}_5\text{Sc}_2\text{O}_{12}\) system was given in a study by Coey[11]. From an analysis of Mössbauer spectra of this system with \(t = 0.5\), the author concluded that the fraction of Sc\(^{3+}\) ions on their preferred, i.e. octahedral, site is 0.97(0.05). This is equivalent to the cation distribution \([\text{Y}]_3[\text{Fe}_{2.95}\text{Sc}_{0.05}]\text{O}_{12}\). Experimental confirmation of small amounts of Sc\(^{3+}\) ions being at the tetrahedral site in Sc substituted YIG single crystals stemmed from recently reported magnetization measurements by Röschmann et al.[12, 13].

There are also reports of Sc\(^{3+}\) ions substituting rare-earth (RE) ions on the dodecahedral sites in \([\text{RE}_{3-x}\text{Sc}_x][\text{Sc}_{2}]\text{Al}_3\text{O}_{12}\)[14] and \([\text{RE}_{3-x}\text{Sc}_x][\text{Sc}_{2}]\text{Fe}_2\text{O}_{12}\)[15, 16]. These reports are based on the analysis of the values of the lattice constants for different values of \(y\) and different rare-earth ions. Values of lattice constants depend on the actual cation distribution and therefore can be used in the determination of it[17–19]. However, the cation distribution based on such analysis only may lead, as it is shown in this paper, to incorrect results. Thus, although Sc\(^{3+}\) ions have very strong octahedral preference, their presence at tetrahedral and dodecahedral sites cannot be excluded.

The \(\text{Eu}_{3-x}\text{Sc}_x\text{Fe}_2\text{O}_{12}\) system was studied previously with X-ray diffraction and magnetometric methods[15, 16]. It was found that single phase garnets were obtained for \(0 < y < 0.7\). From the linear dependence of the lattice constant with composition \(y\) it was concluded that the cation distribution is

\[
[\text{Eu}_{3-x}\text{Sc}_x][\text{Sc}_{2}]\text{Fe}_2\text{O}_{12}\tag{1}
\]

For the nominal composition \(y = 0\) one gets from (1) the cation distribution \([\text{Eu}_3][\text{Sc}_{2}](\text{Fe}_3)\text{O}_{12}\). This is an interesting result because in studying the series \([\text{RE}_{3-x}\text{Sc}_x][\text{Sc}_{2}]\text{Fe}_2\text{O}_{12}\) with RE = Sm or Gd it was found that the maximum value of \(x\) is 1.67 (RE = Sm) and 1.68 (RE = Gd)[8, 20]. The ionic radius of eight-fold coordinated Eu\(^{3+}\) is equal to 1.066 Å, whereas the ionic radii of eight-fold coordinated Sm\(^{3+}\) and Gd\(^{3+}\) are 1.079 and 1.053 Å, respectively[21]. One might expect therefore that the maximum value of \(x\) in the system \([\text{Eu}_3][\text{Sc}_{2}]\text{Fe}_2\text{O}_{12}\) should not exceed 1.68. An indication that the cation distribution is different from (1) comes from an analysis of the linear relationship between the lattice constant and the composition \(a(y)\) (Fig. 1 in [15]). Assuming the cation distribution (1) and using an equation from[15] relating the lattice constant with the garnet composition, one gets a linear relationship, however, with a slope much steeper than the experimental one. This may indicate that the cation distribution (1) predicts too many Sc\(^{3+}\) ions entering the \(c\) sites.

The aim of the present work is to elucidate the prob-
lem of the cation distribution in the Eu_{3-y}Sc_{2+y}Fe_{3}O_{12} garnet system. It is shown that the Sc^{3+} ions can occupy not only the octahedral, but also the dodecahedral and the tetrahedral sites.

2. EXPERIMENTAL

The polycrystalline specimens of a series Eu_{3-y}Sc_{2+y}Fe_{3}O_{12} used in this study had nominal compositions y = 0.0, 0.2 and 0.5. They were the same as those used in[15,16]. According to X-ray diffraction studies, they are all single phase[15]. Mössbauer absorbers with thicknesses 20-32 mg cm^{-2} were prepared by mixing garnet powders with boron nitride and pressing the mixture into lucite containers, which were covered with iron-free Al foils.

Mössbauer effect studies were carried out in the temperature range 1.5-300 K using 14.41 keV transition in $^{57}$Fe and 21.53 keV transition in $^{151}$Eu. The Mössbauer spectra were obtained using a standard constant acceleration spectrometer which was calibrated with a Michelson interferometer. The sources used were $^{57}$Co(Rh) and $^{151}$Sm(SmF3). All spectra were obtained in transmission geometry. The γ-rays were detected with a proportional counter filled with Xe-CO$_2$. In order to identify possible impurities in the investigated compounds which could not be detected by means of X-ray studies, $^{57}$Fe and $^{151}$Eu Mössbauer spectra of α-Fe$_2$O$_3$, EuFeO$_3$, EuScO$_3$ and Eu$_2$O$_3$ were measured at selected temperatures.

3. RESULTS AND DISCUSSION

$^{57}$Fe Mössbauer spectra of all investigated samples above their ordering temperatures can be fitted with two Lorentzian symmetric quadrupole doublets (Fig. 1). The

![](image_url)

Fig. 1. $^{57}$Fe Mössbauer spectra of the (a) y = 0.0; (b) y = 0.5 samples measured at 294 K, with the source at the same temperature. The full line is a least-squares computer fit with two quadrupole doublets which are also shown.
doubles} are unequivocally assigned to Fe$^{3+}$ ions at the $a$ and $d$ sites on the basis of the values of their isomer shifts and quadrupole splittings[22]. The area under a quadrupole doublet corresponding to a given site is proportional for a thin absorber to the product of the recoilless fraction and the amount of iron ions at that site[23]. It has been shown in[22] that recoilless fractions are equal and at the $a$ and $d$ sites in RE$_3$Fe$_5$O$_{12}$ garnets measured above their Néel temperatures. Assuming that the same is valid for the investigated series, one gets from the relative areas of the doubles a ratio $r$ for the number of Fe$^{3+}$ ions at the $a$ and $d$ sites. The values of $r$ for $y = 0.0$, 0.2 and 0.5 samples are 0.1007(0.0052), 0.1242(0.0072) and 0.2270(0.0089), respectively.

In consequence of the non-zero values of $r$ the cation distribution (1) cannot be correct. If we assume that the actual compositions of the samples are the same as the nominal ones, then the Mössbauer results lead to the following cation distribution

$$[\text{Eu}_{3-y} \text{Sc}_y][\text{Sc}_{2-y/3} \text{Fe}_{y/3+1}] (\text{Sc}_{3y/11} \text{Fe}_{3y/11+1})\text{O}_{12}. \quad (2)$$

If, however, the actual and nominal compositions of the samples differ, then other cation distributions are conceivable which are compatible with the Mössbauer results. In this case one could expect the existence of small amounts of impurities. Although such impurities were not found with X ray studies[15], their presence could be detected in principle with the Mössbauer effect method. It is known that in the preparation of scandium-substituted garnets, small amounts of extraneous phases of the perovskite-like and the Mn$_2$O$_3$-like type can be formed[7,8,20]. Also the presence of small amounts of starting oxides (Eu$_2$O$_3$, Sc$_2$O$_3$ and $\alpha$-Fe$_2$O$_3$) cannot be excluded.

$^{57}$Fe Mössbauer spectra of the $y = 0.0$ sample in the temperature range from about 15 K up to 78 K show the presence of a Zeeman pattern of an impurity superimposed on the patterns characteristic for the garnet phase of the sample. This is illustrated in Fig. 2, where apart from the $a$ and $d$ site quadrupole doublets, also a weak Zeeman pattern $z$ of an impurity can be seen. The area under the $z$ pattern constitutes 5.7% of the area under the two quadrupole doublets. Below 15 K the $z$ pattern cannot be seen because it is overshadowed by the Zeeman patterns corresponding to the $a$ and $d$ sites. The Zeeman pattern $z$ could not be detected at room temperature. It should be stressed that in order to detect the pattern $z$, spectra were necessary with a large number of counts per channel. The hyperfine magnetic field corresponding to the pattern $z$ and measured in the temperature range 15-78 K is lower and decreases faster with temperature than the corresponding fields in EuFeO$_3$ and $\alpha$-Fe$_2$O$_3$. This indicates that the impurity cannot be identified with EuFeO$_3$ and $\alpha$-Fe$_2$O$_3$. It was shown that in the preparation of some scandium-substituted garnets a solid solution of Sc$_{1-x}$Fe$_x$O$_3$ is formed[8,20]. This, together with the fact that the ordering temperature of ScFeO$_3$ is 39(2) K[24], suggests that the impurity in the $y = 0.0$ sample might be Sc$_{1.5}$Fe$_3$O$_5$ with $x > 1$. An impurity phase can also be seen in the $^{57}$Fe Mössbauer spectra of the $y = 0.5$ sample measured at temperatures up to the ordering temperature. The impurity spectrum consists of two lines, located in the middle of the spectrum, superimposed on
the Zeeman patterns corresponding to the a and d sites (Fig. 3a). The area under the two lines is equal to 5.4% of the area corresponding to the Zeeman patterns of the a and d sites. When a weak external magnetic field of 3 kOe is applied, the two lines cannot be observed anymore because the presence of the Zeeman patterns of the a and d sites makes their separate detection impossible (Fig. 3b). This indicates that the impurity lines originate from iron atoms in superparamagnetic particles\[25\].

 Mössbauer spectra of the y = 0.2 sample at liquid helium temperatures revealed an impurity phase too. Its spectrum is similar to the one detected in the y = 0.5 sample. The area under two impurity lines of the y = 0.2 sample is 1.5% of the area corresponding to the Zeeman patterns of the a and d sites. The nature of this impurity is the same as mentioned for the impurity in the y = 0.5 sample.

$^{151}$Eu Mössbauer studies shed no light on the nature of the impurities. The reason is that $^{151}$Eu spectra of Eu$^{3+}$-containing oxides, such as Eu$_2$O$_3$, EuScO$_3$, etc. measured in the paramagnetic region are to a first approximation single lines. Thus, they cannot be distinguished from the $^{151}$Eu spectra of the investigated samples in which the Eu ions are also in the trivalent oxidation state.

We conclude that all samples contain some impurity. The $^{57}$Fe spectra of the y = 0.0, 0.2 and 0.5 samples above their ordering temperatures were refitted taking into account the areas under the impurity lines. The corrected values of $r$ are 0.0853(0.0064), 0.1172(0.0086) and 0.1881(0.0080), respectively.

The results presented above indicate that the actual sample composition may be different from the nominal one. Thus, one should also consider the following cation...
with the condition $\alpha + \beta = \gamma + \delta = 3$. The chemical composition corresponding to the cation distribution (4) belongs to the general formula $\text{Eu}_{x-\delta} \text{Sc}_{3+x} \text{Fe}_{30+1} \text{O}_{3-\delta}$ of the studied series, however, with the nominal parameter $\gamma$, replaced by an effective parameter $\delta$. In contrast, the distribution (3) is not compatible with the formula $\text{Eu}_{x-\delta} \text{Sc}_{3+x} \text{Fe}_{30+1} \text{O}_{3-\delta}$.

It should be noticed that the cation distributions (2)-(4) are particular cases of a more general distribution

$$
\text{Eu}_{x-\delta} \text{Sc}_{3+x} \text{Fe}_{30+1} \text{O}_{3-\delta}.
$$

with $\xi + \eta = 3$ and an additional unknown parameter $q$. The distribution (5) reduces to (2) for $\xi = 3 - \gamma$ and $q = 3(1 + r)$, to (3) for $\xi = \alpha$ and $q = 3 - \gamma$, and to (4) for $\xi = \gamma$ and $q = 3(1 + r)$.

To determine the values of $\alpha$, $\beta$, and $\gamma$, $\delta$ in the cation distributions (3) and (4), and to decide which of the cation distributions (2)-(4) is the correct one, we proceed as follows. The cubic lattice constant of a garnet depends upon the average cation radii $r_{\text{VIII}}$, $r_{\text{VI}}$, and $r_{\text{IV}}$ referring to the dodecahedral, octahedral and tetrahedral sites, respectively. The average radii are a function of the actual cation distribution. Thus, an equation relating the lattice constant with the average radii can be used to test different possible cation distributions [19, 26]. Recently, there have been published two such equations. Stroock et al. [27] developed an equation based on the analysis of lattice constants of YIG and GdIG substituted by different cations, and using the values of cation radii published by Shannon and Prewitt [28, 29]. Another equation was found by Langley and Sturgeon [30] who analysed 333 garnet compositions using revised ion radii of Shannon [21]. In order to test the usefulness of both equations in the prediction of lattice constants we have calculated the lattice constants for many garnets of known cation distributions. Table 1 shows the experimental $a_{\text{exp}}$ and calculated $a_{\text{th}}$ values of lattice constants for selected garnets. It can be seen that for the majority of the garnets considered the values of $a_{\text{th}}$ calculated with the equation of Stroock et al. [27] give better agreement with the values of $a_{\text{exp}}$ than those calculated with the equation of Langley and Sturgeon [30]. Therefore, the equation of Stroock et al. [27] given by

$$
a = b_1 + b_2 r_{\text{VIII}} + b_3 r_{\text{VI}} + b_4 r_{\text{IV}} + b_5 r_{\text{VIII}} r_{\text{VI}} + b_6 r_{\text{VIII}} r_{\text{IV}} + b_7 r_{\text{VI}} r_{\text{IV}},
$$

where $b_i (i = 1, 2, \ldots, 6)$ are constants, will be used [27].

On applying (6) one needs the ionic radius $r_{\text{Sc}^{3+}}$, for which no experimental values are known. Assuming that the change in coordination number is the same as that of $\text{In}^{3+}$, of which ionic radii for eight-fold and six-fold coordination are very close to those of $\text{Sc}^{3+}$ (Fig. 2c in [21]), one can calculate $r_{\text{Sc}^{3+}}$, from the relation $r_{\text{Sc}^{3+}} = r_{\text{In}^{3+}} - (r_{\text{Sc}^{3+}} - r_{\text{In}^{3+}})$. The value of $r_{\text{Sc}^{3+}}$ thus obtained is equal $0.565 \text{Å}$. In order to calculate the unknown values of $\alpha$, $\beta$, and $\gamma$, $\delta$ appearing in cation distributions (3) and (4), the following procedure has been employed. From the cation distributions (3) and (4) one finds that $\alpha$ and $\gamma$ are equal to

$$
\alpha, \gamma = 3(r_{\text{VIII}} - r_{\text{Sc}^{3+}})/(r_{\text{In}^{3+}} - r_{\text{Sc}^{3+}}).
$$

where $r_{\text{VIII}}$ and $r_{\text{Sc}^{3+}}$ are the ionic radii for eight-fold coordination of $\text{Eu}^{3+}$ and $\text{Sc}^{3+}$, respectively. The value of $r_{\text{VIII}}$ can be obtained from (6) substituting the experimental value $a_{\text{exp}}$ for $a$. The values of $r_{\text{VIII}}$ and $r_{\text{Sc}^{3+}}$ are known [21] and thus $\alpha$ and $\gamma$ can be calculated from (7). It turned out that the values of $\alpha$ were larger than 3 for the cation distribution (3) for all values of nominal composition $y$. This means that the $\text{Sc}^{3+}$ ions do not substitute $\text{Eu}^{3+}$ ions at the c site. The cation distribution (3) would then lead to a paradoxical result: the increase in $y$, which corresponds to an increase of $r$, leads to a decrease in the actual content of $\text{Sc}^{3+}$ ions in the investigated series. The calculated values of $\gamma$ for the cation distribution (4) are 2.997 and 2.937 for the nominal compositions $y = 0.2$ and 0.5, respectively. For $y = 0.0$, the $\gamma$ value was larger than 3. For that nominal composition we therefore assumed $\gamma = 3.0$. In Fig. 4 the values of $a_{\text{th}}$ calculated with (6) for the cation distributions (1)-(4) are compared with those of $a_{\text{exp}}$ for nominal compositions $y = 0.0, 0.2$ and 0.5. As it can be seen, the best agreement between $a_{\text{exp}}$ and $a_{\text{th}}$ is obtained for the cation distribution (4). We, therefore, conclude that the most probable cation distribution in the investigated Eu–Sc–Fe garnet series is

$$
\text{Eu}_{y} \text{Sc}_{1.76} \text{Fe}_{0.23} \text{O}_{12}.
$$

Fig. 4. Comparison of experimental lattice constants (O) with calculated ones (f) for cation distributions (1)-(4), for nominal compositions $y = 0.0, 0.2$ and 0.5. The straight lines are guides for the eye.
Table 1. Comparison of experimental and calculated lattice constants for selected garnet compounds

<table>
<thead>
<tr>
<th>Composition</th>
<th>(a_{\text{exp}})</th>
<th>(a_{\text{th}})</th>
<th>(\Delta a)</th>
<th>(b_{\text{exp}})</th>
<th>(b_{\text{th}})</th>
<th>(\Delta b)</th>
</tr>
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<tbody>
<tr>
<td>([\text{Ga}_3][\text{Fe}_2] (\text{Fe}<em>3)\text{O}</em>{12})</td>
<td>12.529</td>
<td>12.528</td>
<td>0.001</td>
<td>12.476</td>
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<td>([\text{Eu}_3][\text{Fe}_2] (\text{Fe}<em>3)\text{O}</em>{12})</td>
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<td>0.011</td>
<td>12.433</td>
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<td>0.005</td>
<td>12.432</td>
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<td>12.410</td>
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<td>12.404</td>
<td>0.001</td>
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<td>([\text{Y}_3][\text{Fe}_2] (\text{Fe}<em>3)\text{O}</em>{12})</td>
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<td>12.373</td>
<td>0.003</td>
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<td>12.199</td>
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<td>([\text{Ga}<em>3][\text{Sc}</em>{0.5}\text{Fe}_{1.5}] (\text{Fe}<em>3)\text{O}</em>{12})</td>
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<td>12.344</td>
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<td>12.583</td>
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<td>12.556</td>
<td>0.036</td>
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</tr>
<tr>
<td>([\text{Gd}<em>2][\text{Y}] (\text{Sc}</em>{0.75}\text{Fe}_{1.25} (\text{Fe}<em>3)\text{O}</em>{12})</td>
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<td>0.008</td>
<td>12.475</td>
<td>0.027</td>
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<td>12.522</td>
<td>12.511</td>
<td>0.010</td>
<td>12.485</td>
<td>0.029</td>
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<td>12.562</td>
<td>12.553</td>
<td>0.009</td>
<td>12.537</td>
<td>0.025</td>
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\(a\) calculated from the equation of Strocka et al. [27].
\(b\) calculated from the equation of Langley and Sturgeon [30].
\(c\) from [31].
\(d\) from [32].
\(e\) average value from [33].
\(f\) average value from [32].
\(g\) from [33].
\(h\) from [20].

The above cation distribution implies the non-collinearity of \(\text{Fe}^{3+}\) spins at the \(a\) and \(d\) sites [34]. This has been confirmed and reported elsewhere [35].

The studied Eu–Sc–Fe series is the second garnet system, after that of Sc-substituted YIG [11–13], in which Sc\(^{3+}\) ions are found present at the tetrahedral sites. Recent investigations show that Fe\(^{2+}\) ions, which are even larger than Sc\(^{3+}\) ions (\(r_{\text{Sc}^{3+}} = 0.63 \AA\) [21]), as com-
pared with \( r_{\text{Fe}^{3+}}^\text{tetra} = 0.565 \text{ Å} \) can enter the tetrahedral sites. This was found by Antonini et al.\cite{5} with optical absorption and magnetic circular dichroism methods, and by Amthauer et al.\cite{36} and Huggins et al.\cite{37} with \( ^{57}\text{Fe} \) Mössbauer spectroscopy. Another characteristic of the investigated Eu–Sc–Fe garnets is the presence of \( \text{Sc}^{3+} \) ions at all three crystallographic sites in the \( y = 0.2 \) and 0.5 samples. Similar situation was found in schorlomite garnets\cite{36,37} in which \( \text{Fe}^{2+} \) ions were found at all three sites.

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REFERENCES