Formation of Icosahedral Clusters and Spin Freezing in RE(Fe_{1-x}Al_x)_{13} Amorphous Alloys

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The formation of icosahedral clusters in RE(Fe_{1-x}Al_x)_{13} (RE : La, Y, Ce and Lu) amorphous alloys have systematically been investigated. The spin-glass behavior and the magnetic phase diagrams are closely related with the interatomic distance of Fe-Fe pair in the icosahedral clusters formed in the amorphous phases. The existence of icosahedral clusters in the RE(Fe_{1-x}Al_x)_{13} amorphous alloys was confirmed by X-ray diffraction, although the formation in the crystalline state restricts to only RE = La. Mössbauer spectra were also found to be consistent with the occurrence of antiferromagnetic interactions, and the spin freezing temperature is scarcely affected by the variety of RE elements. On the other hand, the Curie temperature depends on the atomic size of RE.

1. Introduction

Because of a positive heat of mixing of Fe with La, no stable crystalline Fe-La compounds are formed. However, the cubic compounds with the NaZn_{13}-type having the Fm\overline{3}c(O_{6}) \textsuperscript{6} space-group symmetry have been prepared by substitution of Al for a part of Fe, that is, La(Fe_{1-x}Al_{x})_{13} compounds can be stabilized in the concentration range 0.08 \leq x \leq 0.54.\textsuperscript{1,2}

The conventional cubic cell of La(Fe_{1-x}Al_{x})_{13} compounds with the NaZn_{13}-type structure is composed of 112 atoms. That is, La on 8a, Fe on 8b and Fe(Al) on 96i sites. Since the conventional cubic cell consists of eight small cubes, and there are two La(Fe_{1-x}Al_{x})_{13} formula units in a primitive unit cell, i.e., 28 atoms with one kind of 2La atoms and two kinds of Fe atoms, that is, 2Fe\textsuperscript{I} and 24Fe\textsuperscript{II}(Fe(Al)) atoms. The Fe\textsuperscript{I} atom is located at the center of the icosahedron and the Fe\textsuperscript{II} atom sites are located at the vertices of the icosahedron and composed of Fe and Al atoms.\textsuperscript{3,4} The Fe\textsuperscript{II} atoms are surrounded by 9 near Fe\textsuperscript{II} atoms and 1 Fe\textsuperscript{I} atom. The local environment of a Fe\textsuperscript{I} is very similar to that of an fcc Fe, because it is surrounded by 12 Fe\textsuperscript{II} atoms.\textsuperscript{5} The La and Fe\textsuperscript{I} atoms form a cubic CsCl(B2) structure, in which 4 Fe\textsuperscript{II} atoms are located in each face of a cube. The La atoms occupy the (1/4, 1/4, 1/4) sites plus their symmetry operations.

The shortest Fe-Fe distance in La(Fe_{0.9}Al_{0.1})_{13} compound is the distance between Fe\textsuperscript{I} and Fe\textsuperscript{II}. This distance is about 4\% shorter than those between Fe\textsuperscript{II} and Fe\textsuperscript{III}.\textsuperscript{6} The results of the least-squares variational analysis for La(Fe_{1-x}Al_{x})_{13} amorphous alloys clearly suggest that the appearance of the icosahedral clusters.\textsuperscript{6,7} It should be noted that the structural parameters are the average values for all Fe atoms in the icosahedral cluster. In addition, the distance of the nearest-neighbor Fe-Fe pair is about 0.255 nm, coinciding with the Fe-Fe averaged distance in the corresponding crystal. Furthermore, it is noteworthy that this distance hardly depends on the Fe concentration.\textsuperscript{4}

The magnetization curves for La(Fe_{1-x}Al_{x})_{13} amorphous alloys are not easily saturated in high magnetic fields in the concentration range 0.05 \leq x \leq 0.10, and the high-field susceptibility \chi_{hf} increases remarkably with increasing Fe content.\textsuperscript{6} These results suggest that these alloys exhibit spin-glass behavior at low temperatures in this concentration range. In fact, the amorphous alloys in this range indicate a characteristic hysteresis between the zero-field-cooled (ZFC) and field-cooled (FC) states. The hysteresis of the field-cooling effect at low temperatures becomes more significant with increasing Fe content.\textsuperscript{7}

In the crystalline state, no existence of RE(Fe_{1-x}Al_{x})_{13} (RE : La, Y, Ce and Lu) compounds is confirmed, except for RE = La. It should be noted that the number of the icosahedral clusters around La atom is very different between the crystalline and amorphous states in La(Fe_{1-x}Al_{x})_{13} system.\textsuperscript{4} Accordingly, in the present paper, the possibility of the formation of icosahedral clusters is examined for other RE systems. A brief report of RE(Fe_{1-x}Al_{x})_{13} amorphous alloys has been published elsewhere.\textsuperscript{8} The present paper is extended into detailed and systematic analyses with discussions. The atomic structures of RE(Fe_{1-x}Al_{x})_{13} amorphous alloys are analyzed by X-ray diffraction at room temperature, and the interatomic distance and coordination numbers are compared with those of La(Fe_{1-x}Al_{x})_{13} amorphous alloys. Mössbauer spectroscopy is sensitive to local physical properties. In particular, the local symmetry around an Fe atom in amorphous alloys can be determined through the interaction between the nuclear quadrupole moment and the electric field gradient created by the electric charges distributed around the Fe nucleus. Mössbauer effect measurements, therefore, are useful in shedding some light on the local atomic environment in the amorphous alloys. Furthermore, magnetic properties of Fe-based amorphous alloys are...
very sensitive to the environment such as the interatomic distance and the coordination number. Therefore, the atomic structures of $\text{RE(Fe}_{1-x}\text{Al}_x)_{13}$ amorphous alloys are closely correlated with their magnetic properties.

2. Experiments

Alloying for $\text{RE(Fe}_{1-x}\text{Al}_x)_{13}$ targets was made by arc-melting in an argon gas atmosphere. The amorphous alloy specimens were prepared by high-rate DC sputtering on a water-cooled Cu substrate. The target voltage and the anode current were 1.0 kV and 6.0 A, respectively. The argon gas pressure during sputtering was 40 mTorr. The Cu substrate was removed by mechanical grinding.

The scattering intensity was measured with a Mo X-ray target and a flat Ge111 single crystal monochromator in incident beam. Since the sample thickness of about 0.3 mm is large enough to be regarded as an finite thickness, the ordinary $\theta$-29 coupling geometry was used for scattering intensity measurements with a scintillation counter. Fluorescent radiations of Fe and La atoms from the specimen were eliminated with a pulse height analyzer. The mass density of the specimen was examined by an Archimedes method using toluene as a working fluid.

The film specimens were sputtered on polyimide substrates, and Mössbauer effect measurements were made at 290 K with a constant acceleration-type spectrometer using a $^{57}$Co source doped with Rh. Magnetic cooling effects were measured with a superconducting quantum interference (SQUID) magnetometer. The temperature dependence of AC magnetic susceptibility was measured by an induction method at 0.1 mT and 80 Hz.

3. Method for Structural Analysis

It has been pointed out that the atomic structures of $\text{La(Fe}_{1-x}\text{Al}_x)_{13}$ amorphous alloys are remarkably different from those of other metallic amorphous alloys. Therefore, we need the least-squares variational method employed in the structural study for SiO$_2$ and BeF$_2$ glasses, because their intensity profiles are similar to the present amorphous alloy case. Therefore, a brief description for this method is given below.

The observed intensities were corrected for air scattering, absorption and polarization, followed by the conversion to absolute units per atom using the generalized Krogh-Moe-Norman method with the X-ray atomic scattering factors including the anomalous dispersion terms calculated by Cromer and Lieberman’s scheme and the Compton scattering intensity with the Breit-Dirac recoil factors. From the resultant coherent intensity in absolute units, $I_{\text{rel}}(Q)$, the following interference function $Q_i(Q)$ of the sample was evaluated by using the following expression.

$$Q_i(Q) = \frac{I_{\text{rel}}(Q) - \sum_{i=1}^{N} c_i f_i^2}{\left(\sum_{i=1}^{N} c_i f_i\right)^2}$$

where $Q = 4\pi \sin \theta / \lambda$, $\theta$ is the half of the angle between incident and diffracted beams, $\lambda$ is the wavelength and $N$ is the total number of the constituent elements. $c_i$ and $f_i$ are the atomic fraction and the atomic scattering factor of the $j$-th element, respectively. The RDF is calculated by the Fourier transformation of the interference functions.

$$2\pi^2 r \rho(r) = 2\pi^2 r \rho_0 + \int_{Q_{\text{min}}}^{Q_{\text{max}}} Q_i(Q) \sin(Qr)dQ,$$

where $\rho(r)$ is the radial number density function, $\rho_0$ is the average number density of the sample and $Q_{\text{max}}$ is the maximum scattering vector determined from the experimental condition. On the basis of the successful results applied to determining the local unit structure in SiO$_2$ and BeF$_2$ glasses, the interatomic distances and the coordination numbers of these amorphous alloys were evaluated using the least-squares variational method for the interference function. The non-linear least-squares program was slightly modified for the present analyses. The interference function $Q_i(Q)$ may be given by

$$Q_i(Q) = \sum_{j=1}^{N} \sum_{i=1}^{N} N_{ij} \exp(-b_{ij}Q^2) f_i(Q)f_j(Q) \left(\frac{\sin(Qrij)}{Qrij}\right)^2$$

$$+ \sum_{\alpha=1}^{N} \sum_{\beta=1}^{N} 4\pi \rho_0 c_\alpha c_\beta \exp(-b_{\alpha\beta}Q^2)$$

$$\times f_\alpha(Q)f_\beta(Q) Q_{\alpha\beta}^0 \cos(Q_{\alpha\beta}) - \sin(Q_{\alpha\beta})$$

$$\left(\frac{\sin(Q_{\alpha\beta})}{Q_{\alpha\beta}}\right)^2,$$

where $N$ is the number of near-neighbor atoms for a type-j atom, $N_{ij}$ and $r_{ij}$ are the coordination number and the average distance of the $i$-$j$ pairs, respectively. The value of $b_{ij}$ is the mean squared variation. In this relation, the average number of the nearest $j$ atoms around any origin atom of the type-$i$, $N_{ij}$ is assumed to be separated by an average distance $r_{ij}$ and the distributions with respect to each correlation are expressed as a discrete Gaussian-like function with a mean square width 2$b_{ij}$. The distributions of higher neighbor correlations are approximated by a continuous distribution with an average number density $\rho_0$. The quantities of $r_{\alpha\beta}^0$ and $b_{\alpha\beta}$, respectively, represent the average size and the variation of the boundary region. The parameters distinguished by $\alpha$ and $\beta$ have the same meanings but for $\alpha$ and $\beta$ atoms in the boundary region of the continuous distributions.

4. Results and Discussion

4.1 X-ray diffraction

The reduced interference functions ($R$IFs) $Q_i(Q)$ of $\text{RE(Fe}_{0.90}\text{Al}_{1.01})_{13}$ (RE: La, Y and Ce) and $\text{Lu(Fe}_{0.80}\text{Al}_{1.20})_{13}$ amorphous alloys are shown by the solid lines in Fig. 1. The prefixal a- of the specimens stands for the amorphous state. One of the notable features of the structural profiles is fairly distinct oscillations present even in the high-$Q$ region. This kind of intensity profile is scarcely observed in metallic amorphous alloys and rather resembles that for oxide glasses, implying the presence of chemical short-range ordering (hereafter referred to as SRO) clusters with definite bond...
Fe
Fe
Fe
Fe
Fe

squares variations were set by calculating the average parts. Accordingly, the starting parameters for the least-amorphous alloys resemble to those in crystalline counter-isotropic and dense clusters, and the atomic potential energy interference functions obtained in this procedure are shown to reproduce the experimental interference function data. The obtained by the least-squares calculation of eq. (3) so as to reproduce the observed and calculated results, respectively. The interatomic distance \( r \) in the amorphous state corresponds to the average value in the crystalline state. The correlations of the intra- and inter-icosahedral clusters are given with and without the underline, respectively. The number in the parenthesis gives the coordination number. It should be noted that there are four kinds of the nearest-neighbor correlations for Fe-Fe pairs ranging from 0.247 to 0.286 nm. Fe and Al atoms randomly share the FeII sites in the crystal structure, so the coordination numbers for Fe-Al pairs are readily calculated by multiplying the ratio of the atomic fractions of Al and Fe, \( x/(1 - x) \), to the coordination number for Fe-Fe pairs in Table 1. In the La(Fe0.90Al0.10)13 crystal, the icosahedral clusters formed by Fe and Al atoms located at their vertices and Fe atoms located at the center are present at the corner of the cubic cell and the La atom is located at its body-centered position. Since the coordination numbers and the interatomic distances of Fe-Fe pairs found in the amorphous state are rather close to the crystalline case as shown in Table 1, it is plausible that the local SRO clusters in the amorphous alloys are the same as those in the crystalline state. The RDFs for the RE(Fe0.90Al0.10)13 (RE: La, Y and Ce) and Lu(Fe0.80Al0.20)13 amorphous alloys are shown in Fig. 2. The solid and dotted curves are respectively the experimental and calculated RDFs obtained from Fourier transformation of RIF evaluated from eqs. (2) and (3). The formation of icosahedral clusters gives noble characteristics in the radial distribution function (RDF). The first peak composed of two peaks at about 0.25 and 0.32 nm is isolated from other peaks and fairly distinct oscillations are present even up to the middle distance range. These features also indicate the appearance of the SRO clusters in the RE(Fe1-xAlx)13 amorphous alloys.

Table 1 The interatomic distance \( r \), the coordination number \( CN \) in La(Fe0.90Al0.10)13 crystalline compound and La(Fe0.90Al0.10)13 amorphous alloy.

<table>
<thead>
<tr>
<th>Pair and CN</th>
<th>a-La(Fe0.90Al0.10)13</th>
<th>c-La(Fe0.90Al0.10)13</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Fe</td>
<td>0.247 ~ 0.286</td>
<td>FeI-FeII(12), FeII-FeI(1), FeII-FeII(4), FeI-FeII(5)</td>
</tr>
<tr>
<td>La-Fe</td>
<td>0.339</td>
<td>La-FeII(24)</td>
</tr>
<tr>
<td>Fe-Fe</td>
<td>0.352</td>
<td>FeII-FeII(1)</td>
</tr>
<tr>
<td>Fe-Fe</td>
<td>0.396 ~ 0.423</td>
<td>FeII-FeII(12), FeII-FeII(1), FeII-FeII(5), FeII-FeII(8)</td>
</tr>
<tr>
<td>Fe-Fe</td>
<td>0.462 ~ 0.465</td>
<td>FeII-FeII(8)</td>
</tr>
<tr>
<td>Fe-Fe</td>
<td>0.491 ~ 0.511</td>
<td>FeII-FeII(12), FeII-FeII(1), FeII-FeII(1), FeII-FeII(6)</td>
</tr>
<tr>
<td>La-Fe</td>
<td>0.510 ~ 0.520</td>
<td>La-FeII(8), La-FeII(24)</td>
</tr>
<tr>
<td>Fe-Fe</td>
<td>0.545</td>
<td>FeII-FeII(4)</td>
</tr>
<tr>
<td>La-La</td>
<td>0.579</td>
<td>La-La(8)</td>
</tr>
<tr>
<td>Fe-Fe</td>
<td>0.579 ~ 0.588</td>
<td>FeI-FeII(6), FeI-FeII(12), FeII-FeII(1), FeII-FeII(6)</td>
</tr>
</tbody>
</table>
The coordination numbers of the nearest-neighbor RE-Fe pairs will provide us the structural information on the configuration of the icosahedral clusters around the RE atom. In the case of RE = La, the experimental results indicate that the distribution of the icosahedral clusters around the La atom in amorphous alloy is extremely different from that of crystal. Therefore, it should be emphasized that the structure of amorphous alloys is not considered simply to be an assembly of microcrystals of La(Fe\textsubscript{1-\textit{x}}Al\textsubscript{\textit{x}}\textsubscript{13}). That is, the coordination numbers of La-Fe pairs in amorphous alloys are much smaller than those in the crystalline state. Thus, the change in the coordination numbers of the nearest-neighbor Fe-Fe pairs in these amorphous alloys may be attributed not to any change in the internal structure of the icosahedral clusters but to the increase in the Fe concentration. The coordination number of La-Fe\textsuperscript{41}, or La-Fe(Al) pairs in the amorphous state, is smaller than the crystalline case, and the interatomic distance of the nearest-neighbor La-Fe(Al) pairs in the amorphous state is shorter than that in the crystalline state.\textsuperscript{4} The La atom is totally surrounded by 8 icosahedra, i.e., 24 Fe atoms. From the ratio of the coordination numbers CNs for La-Fe pairs in the amorphous state, it is found that the number of the clusters around the La atom decreases to about three quarters of that in the crystal(see Table 1). Thus, by dividing the coordination number of the La-Fe pairs in Table 1 by a factor of 3, it is found that the La atom is surrounded by about 6 icosahedral clusters.

The structure parameters of \( r \) and \( CN \) of RE(Fe\textsubscript{1-\textit{x}}Al\textsubscript{\textit{x}}\textsubscript{13}) amorphous alloys are given in Table 2. The Fe-Fe interatomic distance hardly depends on the variety of REs, whereas the RE-Fe distance is different, corresponding to the difference in the RE-Fe distance. The average radius of the RE atom in amorphous alloys calculated from the nearest-neighbor Fe-Fe and RE-Fe pairs in Table 2 is about 0.192 nm for RE = La, 0.182 for Y, 0.179 for Ce, 0.175 for Lu. In Table 3, the radius of each RE atom is compared with each corresponding value given by Pauling under the condition of the coordination number \( CN = 12 \). The atomic radius may be counting on \( CN \). However, all of the present RE elements have the same number of \( CN = 12 \). The estimated radii in the experiment are slightly larger than the values given by Pauling, except for the value of RE = Ce. It should be noted that Ce atom tends to behave as a tetravalent state and decreases in its own atomic volume in Fe. In fact, Ce-Fe amorphous alloys exhibit no significantly large coercive force originated from random field anisotropy in a trivalent state.\textsuperscript{19} In addition, the mass density of Ce-Fe in amorphous alloys is larger than the value evaluated from Vegard’s law, suggesting a smaller volume of

![RDF](image)

Fig. 2 Radial distribution functions of RE(Fe\textsubscript{0.90}Al\textsubscript{0.10})\textsubscript{13} and Lu(Fe\textsubscript{0.90}Al\textsubscript{0.10})\textsubscript{13} amorphous alloys. The solid and dotted lines stand for the observed and calculated results, respectively.

<table>
<thead>
<tr>
<th>RE</th>
<th>Atomic radius/nm</th>
<th>Pauling</th>
<th>Present data</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>0.1871</td>
<td>0.192</td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>0.1797</td>
<td>0.182</td>
<td></td>
</tr>
<tr>
<td>Ce</td>
<td>0.1818</td>
<td>0.179</td>
<td></td>
</tr>
<tr>
<td>Lu</td>
<td>0.1738</td>
<td>0.175</td>
<td></td>
</tr>
</tbody>
</table>

Table 3 The estimated RE size in the RE(Fe\textsubscript{1-\textit{x}}Al\textsubscript{\textit{x}}\textsubscript{13}) (RE: La, Y, Ce and Lu) amorphous alloys, together with the atomic size given by Pauling.\textsuperscript{18}

<table>
<thead>
<tr>
<th>Pair</th>
<th>RE-Fe</th>
<th>a-Y(Fe\textsubscript{0.90}Al\textsubscript{0.10})\textsubscript{13}</th>
<th>a-Ce(Fe\textsubscript{0.90}Al\textsubscript{0.10})\textsubscript{13}</th>
<th>a-Lu(Fe\textsubscript{0.90}Al\textsubscript{0.10})\textsubscript{13}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( r/\text{nm} )</td>
<td>( CN )</td>
<td>( r/\text{nm} )</td>
<td>( CN )</td>
</tr>
<tr>
<td>Fe-Fe</td>
<td>0.254 ± 0.002</td>
<td>9.3 ± 0.2</td>
<td>0.254 ± 0.002</td>
<td>9.7 ± 0.2</td>
</tr>
<tr>
<td>RE-Fe</td>
<td>0.309 ± 0.002</td>
<td>18.1 ± 0.9</td>
<td>0.306 ± 0.002</td>
<td>18.9 ± 0.5</td>
</tr>
<tr>
<td>Fe-Fe</td>
<td>0.378 ± 0.004</td>
<td>1.6 ± 0.3</td>
<td>0.360 ± 0.003</td>
<td>2.0 ± 0.2</td>
</tr>
<tr>
<td>Fe-Fe</td>
<td>0.420 ± 0.002</td>
<td>11.7 ± 0.3</td>
<td>0.421 ± 0.002</td>
<td>12.1 ± 0.3</td>
</tr>
<tr>
<td>Fe-Fe</td>
<td>0.465 ± 0.002</td>
<td>9.0 ± 0.3</td>
<td>0.465 ± 0.002</td>
<td>9.6 ± 0.3</td>
</tr>
<tr>
<td>Fe-Fe</td>
<td>0.500 ± 0.002</td>
<td>8.0 ± 0.4</td>
<td>0.502 ± 0.002</td>
<td>7.6 ± 0.3</td>
</tr>
<tr>
<td>RE-Fe</td>
<td>0.513 ± 0.002</td>
<td>24.5 ± 1.6</td>
<td>0.505 ± 0.002</td>
<td>25.7 ± 0.9</td>
</tr>
<tr>
<td>Fe-Fe</td>
<td>0.548 ± 0.002</td>
<td>6.9 ± 0.4</td>
<td>0.545 ± 0.002</td>
<td>8.1 ± 0.4</td>
</tr>
<tr>
<td>RE-Fe</td>
<td>0.554 ± 0.006</td>
<td>8.6 ± 2.2</td>
<td>0.553 ± 0.002</td>
<td>8.3 ± 0.8</td>
</tr>
<tr>
<td>Fe-Fe</td>
<td>0.591 ± 0.002</td>
<td>8.2 ± 0.9</td>
<td>0.590 ± 0.002</td>
<td>7.3 ± 0.4</td>
</tr>
</tbody>
</table>
Ce in the tetravalent state.\textsuperscript{20} Therefore, it is concluded that such valence change takes places in the present amorphous alloys.

As discussed in connection with Figs. 1 and 2, it is strongly suggested that the icosahedral clusters similar to those in the crystalline compounds exist in the RE(Fe\textsubscript{1-x}Al\textsubscript{x})\textsubscript{13} amorphous alloys. It has been theoretically discussed that 3d metals with an fcc structure against volume exhibit instability of magnetic state. Note that a calculated result of amorphous Fe\textsuperscript{21} and antiferromagnetic fcc Fe\textsuperscript{22} also exhibit a remarkable distance dependence in analogy with fcc Fe. The local symmetry of fcc structure resembles to that of the icosahedral cluster. Furthermore, the critical distance of the magnetic state for fcc Fe is close to the average distance of nearest-neighbor Fe-Fe pair given in Table 2. Consequently, the structural fluctuations around the average distance and the coordination number (CN) cause the variety of the local magnetic state.

4.2 Mössbauer spectroscopy

The similarity of SRO between the crystalline and amorphous states can also be detected by Mössbauer spectroscopy for 57Fe atoms. Namely, the isomer shift (IS) and the quadrupole splitting (QS) of the paramagnetic Mössbauer spectra are sensitive to the s-electron special density and local electric field gradients, respectively, which are changed by local environment of Fe nucleus. The paramagnetic Mössbauer spectra at 290 K for RE(Fe\textsubscript{0.90}Al\textsubscript{0.10})\textsubscript{13} amorphous alloys and La(Fe\textsubscript{0.90}Al\textsubscript{0.10})\textsubscript{13} crystalline compound are shown in Fig. 3. The line width of the Mössbauer spectra is much wider than the natural line width of 57Fe, which is ascribed to the distribution of the quadrupole interactions. The low-velocity absorption peak is slightly larger than the high-velocity peak. This asymmetric spectrum is attributed to the correlation between the distribution of IS and that of the quadrupole interactions. The average values of IS and QS of RE(Fe\textsubscript{0.90}Al\textsubscript{0.10})\textsubscript{13} (RE: La, Y and Ce) and Lu(Fe\textsubscript{0.80}Al\textsubscript{0.20})\textsubscript{13} amorphous alloys are summarized in Table 4, together with those of several kinds of Fe-based binary amorphous alloys\textsuperscript{23,24} for comparison. These two values for La(Fe\textsubscript{0.90}Al\textsubscript{0.10})\textsubscript{13} are identical with those in the amorphous and crystalline states. This implies that the local environment around the Fe atoms in two states is very similar to each other, consistent with the results obtained by X-ray diffractions. Furthermore, the value of average QS for RE(Fe\textsubscript{0.90}Al\textsubscript{0.10})\textsubscript{13} amorphous alloys is smaller than that of binary amorphous alloys, although the Fe content in both series is not so different. The difference between the local atomic arrangements in RE(Fe\textsubscript{0.90}Al\textsubscript{0.10})\textsubscript{13} and Fe-based binary amorphous alloys is explained as the presence of the icosahedral clusters in the former alloy systems and suppress the fluctuation in the local atomic arrangements. The average values of IS for RE(Fe\textsubscript{0.90}Al\textsubscript{0.10})\textsubscript{13} amorphous alloys (RE: La, Ce and Y) coincide with one another, suggesting a similar electronic structure. A slight difference in QS among RE(Fe\textsubscript{0.90}Al\textsubscript{0.10})\textsubscript{13} amorphous alloys probably arises from the atomic size difference between RE elements.

4.3 Magnetic susceptibility

In La(Fe\textsubscript{1-x}Al\textsubscript{x})\textsubscript{13} amorphous alloys, the magnetization for $x \geq 0.15$ is easily saturated in an external magnetic field less than 0.5 T, varying linearly in the high-field ranges in analogy with conventional ferromagnetic alloys. On the other hand, the curves in the concentration range 0.05 $\leq x \leq 0.10$ are not easily saturated even in a field of 6 T. Such a phenomenon becomes more significant with increasing Fe content.\textsuperscript{6} It has been confirmed that the frustrated antiferromagnetic interactions caused by the structural disorder in the amorphous state appear in the Fe-rich concentration range, resulting in a re-entrant spin-glass state.\textsuperscript{25,26} It is well known that the magnetic moment of Fe is significantly affected by the environment effects such as the atomic distance $r$ of Fe-Fe pairs and the coordination number CN. Therefore, the difference in the magnetic properties would originate from

![Mössbauer spectra at 290 K for RE(Fe\textsubscript{0.90}Al\textsubscript{0.10})\textsubscript{13} amorphous alloys (a-La, a-Y and a-Ce), together with the result of La(Fe\textsubscript{0.90}Al\textsubscript{0.10})\textsubscript{13} in the crystalline state (c-La).](image)

Table 4 The average isomer shift (IS) and the average quadrupole splitting (QS) of RE(Fe\textsubscript{0.90}Al\textsubscript{0.10})\textsubscript{13} amorphous alloys, together with the results of RE-Fe binary amorphous alloys\textsuperscript{23,24} and La(Fe\textsubscript{0.90}Al\textsubscript{0.10})\textsubscript{13} in the crystalline state.\textsuperscript{56} The prefixal a- and c- stand for the amorphous and crystalline states, respectively.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>IS/mm s\textsuperscript{-1}</th>
<th>QS/mm s\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-La(Fe\textsubscript{0.90}Al\textsubscript{0.10})\textsubscript{13}</td>
<td>-0.04</td>
<td>0.39</td>
</tr>
<tr>
<td>a-La(Fe\textsubscript{0.90}Al\textsubscript{0.10})\textsubscript{13}</td>
<td>-0.04</td>
<td>0.39</td>
</tr>
<tr>
<td>a-Y(Fe\textsubscript{0.90}Al\textsubscript{0.10})\textsubscript{13}</td>
<td>-0.04</td>
<td>0.36</td>
</tr>
<tr>
<td>a-Ce(Fe\textsubscript{0.90}Al\textsubscript{0.10})\textsubscript{13}</td>
<td>-0.04</td>
<td>0.36</td>
</tr>
<tr>
<td>a-La\textsubscript{10}Fe\textsubscript{82}</td>
<td>-0.09</td>
<td>-</td>
</tr>
<tr>
<td>a-Ce\textsubscript{13}Fe\textsubscript{88}</td>
<td>-0.08</td>
<td>0.40</td>
</tr>
<tr>
<td>a-Ce\textsubscript{90}Fe\textsubscript{90}</td>
<td>-0.09</td>
<td>0.44</td>
</tr>
</tbody>
</table>
the difference between the above-mentioned environment effects in the amorphous and crystalline states. The correlation between the magnetic properties and the structure of Fe-rich La-Fe amorphous alloys has been investigated by using small-angle and large-angle X-ray scatterings.27) With increasing Fe content, the interatomic distance of Fe-Fe atoms is slightly shortened and the mean Fe-Fe coordination number is increased. Under such circumstances, the frustrated local antiferromagnetic exchange interactions are considered to be developed with increasing Fe content, resulting in a re-entrant spin-glass behavior at low temperatures. It has been reported that the ferromagnetic interaction becomes unstable when the Fe-Fe coordination number in the nearest-neighbor shell of the pair distribution function is larger than 6 and antiferromagnetic interactions prevail.28) The FeI atoms are surrounded by an icosahedron of 12 FeII atoms and the FeII atoms by nine nearest FeII atoms and one FeI atom. Furthermore, the FeI-FeII distance is shorter by about 4% that of the FeII-FeII.4) It is worth noting that the FeII-FeII distance in the La(Fe1-xAlx)13 crystalline compounds is much smaller than Fe-Fe distance of La2Fe1-x-y amorphous alloys.27)

The Curie temperature \( T_C \) was determined from the inflection point at high temperature ranges of the thermomagnetization curves. The re-entrant spin freezing temperature \( T_f \) was defined as the branch of these curves or the inflection point at low temperature ranges. The temperature \( T_f \) thus determined correspond to the point of the steepest increase of AC susceptibility curve measured in 0.1 mT at 80 Hz. Strictly speaking, \( T_f \) and \( T_C \) may slightly be higher and lower, respectively, because these temperatures are sensitive to the strength of the applied magnetic field (see Fig. 6). The point to observe is that the Curie temperature of the amorphous alloys is higher than the Curie temperature of La2Fe1-x-y amorphous alloy obtained at various DC fields.29) Therefore, the magnetic cooling effect accompanied by a clear hysteresis between the zero-field cooling (ZFC) and field cooling (FC) processes is affected by the strength of the applied magnetic field as shown in Fig. 6 for La(Fe0.95Al0.05)13 amorphous alloy. The ZFC and FC processes are given by the right and left direction arrows, respectively. The field dependence of the spin freezing \( T_f \) and the Curie temperature \( T_C \) of La(Fe0.95Al0.05)13 amorphous alloy obtained at various DC fields is shown in the inset in Fig. 6. With increasing external magnetic field, \( T_f \) shifts to lower temperatures. From these results, it should be emphasized that \( T_f \) is drastically decreased by relatively low magnetic fields, whereas \( T_C \) is slightly increased on applying magnetic field. Therefore, the temperatures \( T_C \) and \( T_f \) are extrapolated to \( H \to 0 \).

4.4 Magnetic phase diagram

The magnetic phase diagrams for RE(Fe1-xAlx)13 (RE: Y, Ce and Lu) amorphous alloys are given in Fig. 7. The results for La(Fe1-xAlx)13 in the crystalline state are given by the
solid line in the same figure for comparison. In the amorphous state, it should be noted that a re-entrant spin-glass behavior appears in the concentration range, below $x = 0.15$ in the antiferromagnetic state in the crystalline state. The antiferromagnetic order in the crystalline state is stabilized with increasing the Fe coordination number and with decreasing the atomic distance in the Fe-rich concentration range, and then the Néel temperature $T_N$ increases with increasing Fe content. Therefore, the antiferromagnetic interaction in the Fe-rich region is ascribed to high Fe-Fe coordination numbers, such as 12 for Fe$^2$ and 10 for Fe$^3$. Furthermore, the nearest-neighbor distance of the Fe-Fe pair is very close to 0.25 nm where the antiferromagnetic interaction dominates. However, the antiferromagnetic long-range ordering is not easy in the amorphous alloys because of the structural disorder. Therefore, the origin of the re-entrant spin-glass behavior at low temperatures for the amorphous alloys would be due to the frustrated antiferromagnetic interactions caused by the structural disorder. All these alloys exhibit RSG behavior below $x = 0.15$. The important point to note is that the spin freezing temperature $T_f$ is scarcely changed by the kind of REs. This behavior is correlated to the icosahedral clusters because the nearest-neighbor distance of the Fe-Fe pair hardly depends on the variety of REs (see Table 2). On the other hand, the Curie temperature $T_C$ exhibits a systematic tendency; that is, the larger the atomic size of RE, the higher $T_C$. Note that the coordination number $CN$ of RE-Fe pair in the amorphous state is large as given in Table 2. In addition, for RE = La, $T_C$ in the amorphous state is much higher than that in the crystalline state as seen from Fig. 7. Both the magnetic moment and the Curie temperature of Fe-based alloys are strongly affected by the local environments of the Fe atoms characterized by the coordination number and the interatomic distance of Fe-Fe nearest-neighboring pairs. On the other hand, the long-range antiferromagnetic order is not feasible in amorphous alloys. As a result, the appearance of the spin-glass state due to the frustrated antiferromagnetic interactions is expected at sufficiently low temperatures in the concentration range where the antiferromagnetic order appears in the crystalline state. The increase in $T_f$ with decreasing $x$ is related to increase in the Fe-Fe coordination number.

5. Summary

The formation of icosahedral clusters brings about unique magnetic properties. In order to investigate the existence of icosahedral clusters in Fe-based amorphous alloys, therefore, RE(Fe$_{1-x}$Fe$_x$)$_{13}$ (RE = La, Y, Ce and Lu) amorphous alloys have been prepared by high-rate DC sputtering. The atomic structures obtained by X-ray diffraction were found closely related with the magnetic properties. Main results are summarized as follows.

(1) Icosahedral clusters are formed in the present RE(Fe$_{1-x}$Fe$_x$)$_{13}$ amorphous alloy systems, though only the compounds with RE = La are formed in the crystalline state.

(2) The nearest Fe-Fe interatomic distance of Fe-Fe pair in the icosahedral clusters is hardly affected by the kind of RE and this value is very close to 0.25 nm where the antiferromagnetic interaction emerges.

(3) Contrary to RE-Fe binary amorphous alloys, similarity of the local environments around Fe atoms in RE(Fe$_{0.90}$Al$_{0.10}$)$_{13}$ amorphous alloys is confirmed by Mössbauer spectroscopy.

(4) The spin freezing temperature hardly depends on the kind of REs in accordance with no change in the structural parameters of the icosahedral clusters, although the Curie temperature depends on the size of REs.

REFERENCES