Structural Study of Amorphous $\text{La}(\text{Co}_{1-x}\text{TM}_x)_{13}$ Alloys by X-ray Diffraction

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The concentration dependence of transition metals Cr and Mn on atomic structures in amorphous $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ and $\text{La}(\text{Co}_{1-x}\text{Mn}_x)_{13}$ alloys has been studied by X-ray diffraction. The concentrations x are varied from 0.05 to 0.30 and from 0.05 to 0.40 in amorphous $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ and $\text{La}(\text{Co}_{1-x}\text{Mn}_x)_{13}$ alloys, respectively. The fundamental unit structure is a Co(Cr) icosahedron in the amorphous $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ alloys, which consists of 12Co(Cr) atoms at its vertices and a Co atom at its center. The distribution of the icosahedra around a La atom in the near neighbor region resembles that in the crystalline LaCo_{13} phase and is gradually changed at longer distance. The atomic structure shows no significant change up to $x=0.30$ in the amorphous $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ alloys. The atomic structure is also composed of the Co(Mn) icosahedra randomly distributed around a La atom in the amorphous $\text{La}(\text{Co}_{1-x}\text{Mn}_x)_{13}$ alloy. The atomic distance of the first neighbor Co-Co pairs, however, increases and the icosahedral cluster is gradually deformed with the Mn concentration. The difference of the concentration dependence of the atomic structure between the amorphous $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ and $\text{La}(\text{Co}_{1-x}\text{Mn}_x)_{13}$ alloys is understood by a balance of the size difference between Cr and Mn atoms, and the allowed size of an atom substituting for Co atoms located at the vertices of the icosahedron without any significant deformation.

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I. Introduction

Ferromagnetic LaCo_{13} ⁽¹⁾ contains the highest Co content among several binary La-Co compounds. Many studies on its magnetic properties have been carried out⁽¹⁾⁻⁽³⁾. Substitution of other transition metals for a part of Co atoms in the crystalline LaCo_{13} alloy changes the magnetic properties. The Curie temperature decreases and the magnetization increases with increase in Fe concentration x in $\text{La}(\text{Co}_{1-x}\text{Fe}_x)_{13}$ alloys⁽³⁾. Both Curie temperature and magnetization decrease with x in $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ alloys⁽⁴⁾. The magnetic properties in the binary Fe-Co and Cr-Co alloys are changed in a similar manner⁽⁵⁾. In $\text{La}(\text{Co}_{1-x}\text{Mn}_x)_{13}$ alloys, the magnetization shows the maximum at around $x=0.1$ ⁽⁶⁾, while it decreases monotonically with Mn concentration in the binary Co-Mn alloy⁽⁷⁾. This concentration dependence of $\text{La}(\text{Co}_{1-x}\text{Mn}_x)_{13}$ is explained by a virtual bound state⁽⁶⁾.

The LaCo_{13} compound is the cubic NaZn_{13} -type structure⁽⁸⁾. In this compound, a La atom is at the center of the cubic lattice and surrounded by 8 icosahedral clusters

located at the vertices of the cubic lattice. This icosahedral cluster consists of a Co atom at its center and 12Co atoms at its vertices. The compounds in which a part of Co atoms are replaced by Cr or Mn atoms also show the NaZn_{13} -type structure⁽⁴⁾⁽⁶⁾. $\text{La}(\text{Fe}, \text{Al})_{13}$ and $\text{La}(\text{Fe}, \text{Si})_{13}$ alloys have the same atomic structure though they contain Al or Si as well as La and Fe atoms. Thus, the LaCo_{13} alloy is more appropriate to study the effect of an additional element on its atomic structure as well as its magnetic properties.

The amorphous $\text{La}(\text{Fe}, \text{Al})_{13}$ alloy obtained by sputtering is also composed of Fe(Al) icosahedral clusters which resemble those in the crystalline $\text{La}(\text{Fe}, \text{Al})_{13}$ alloy⁽⁹⁾. Due to this particular structure in the amorphous state, the magnetic properties are quite different from those in ordinary Fe-based amorphous alloys⁽¹⁰⁾. It is expected that the similar atomic structure will be observed in the amorphous LaCo_{13} , $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ and $\text{La}(\text{Co}_{1-x}\text{Mn}_x)_{13}$ alloys. According to the previous reports⁽⁴⁾⁽⁶⁾, the dependence of magnetic properties on the concentration x in these amorphous alloys resembles that in the crystalline phase. Accordingly, in the present study, we prepared a series of amorphous $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ and $\text{La}(\text{Co}_{1-x}\text{Mn}_x)_{13}$ alloys and determined their atomic structures by X-ray diffraction method. This will provide us an important clue to understand the magnetic properties of these amorphous alloys.

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II. Experimental

Amorphous LaCo_{13} , $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ ($x=0.05, 0.10, 0.20, 0.25$ and 0.30) and $\text{La}(\text{Co}_{1-x}\text{Mn}_x)_{13}$ ($x=0.05, 0.10, 0.20, 0.30$ and 0.40) alloys of about 0.3 mm thick were prepared on a water-cooled Cu substrate by high-rate DC sputtering using the targets of the alloys with the same compositions. The targets of about 50 mm in diameter were prepared by arc-melting high purity metallic elements of 99.9%La, 99.9%Co, 99.9%Cr and 99.9%Mn in an argon atmosphere. The argon gas pressure during sputtering was 5.3 Pa (40 mTorr). The target voltage and the anode current were 1.0 kV and 6.0 A, respectively. The obtained amorphous samples were cut into a 10 mm by 20 mm plate with the substrate for X-ray diffraction measurement. Just before the X-ray measurements, the sample surface was carefully polished with 1 μm diamond paste. The densities of the amorphous samples in Table 1 were evaluated by the Archimedes' principle, using a piece of the original sputtered sample.

The scattering intensity was measured with a molybdenum X-ray target and a singly-bent pyrolytic graphite monochromator in a diffracted beam. Since the sample thickness of about 0.3 mm is large enough to be regarded as an infinite thickness, the ordinary $\theta-2\theta$ coupling geometry was used for measurements. The scattering intensity was collected with a scintillation counter and the fluorescent radiations of La and transition metals in the samples were eliminated with a pulse height analyzer. Observed intensities were corrected for air scattering, absorption and polarization, and converted to absolute unites per atom using the generalized Krogh-Moe-Norman method⁽¹¹⁾ with the X-ray atomic scattering factors⁽¹²⁾ including the anomalous dispersion terms⁽¹³⁾ and the Compton scattering intensity⁽¹⁴⁾ with the Breit-Dirac recoil factors. The interference function $Qi(Q)$ was evaluated from the resultant coherent intensity in absolute units.

In the present study, the Warren-type radial distribution function⁽¹⁵⁾ (hereafter, it will be referred to as RDF)

was used. This RDF is obtained from the Fourier transformation of the interference function by

$$2\pi^2 r \rho(r) = 2\pi^2 r \rho_0 + \int_0^{Q_{\max}} Qi(Q) \sin(Qr) dQ. \quad (1)$$

The term Q is denoted by $Q = 4\pi \sin \theta / \lambda$, where 2θ is the scattering angle and λ is the wavelength. The upper limit of integral in eq. (1) $Q_{\max}$ corresponds to the upper limit of Q -range observed in the present experiment, *i.e.* 165.9 nm^{-1} , and ρ_0 is the average number density calculated from the densities in Table 1.

III. Results

The interference function of the amorphous LaCo_{13} alloy is shown in Fig. 1. Although its basic profile displays a typical character of the amorphous phase, its first peak is quite sharp and its oscillations are not attenuated even at high- Q region. This resembles a profile of an oxide glass. The oxide glass consists of a random network structure of a certain fundamental local unit, such as SiO_2 glass with the fundamental local unit of a SiO_4 tetrahedron⁽¹⁶⁾. The well-defined first peak of the RDF in Fig. 2 also indicates the presence of the fundamental local unit with certain bond length and angular relation. The similar profiles of interference function and RDF are observed in the amorphous $\text{La}(\text{Fe}_{0.9}\text{Al}_{0.1})_{13}$ alloy⁽⁹⁾. The fundamental local unit in this amorphous alloy is an icosahedral cluster consisting of 13Fe atoms located at its center and vertices. As previously discussed, the crystalline LaCo_{13} alloy shows the same structural type as the crystalline $\text{La}(\text{Fe}_{0.9}\text{Al}_{0.1})_{13}$ alloy. Thus, it is plausible that the amorphous LaCo_{13} alloy is composed of the Co icosahedral clusters. This has been verified by determining a local atomic structure in the near neighbor region in this amorphous alloy by the non-linear least squares method developed by Narten and Levy⁽¹⁷⁾.

In this method, the interference function is described by

Table 1 Densities of the amorphous LaCo_{13} , $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ ($x=0.05, 0.10, 0.20, 0.25$ and 0.30) and $\text{La}(\text{Co}_{1-x}\text{Mn}_x)_{13}$ ($x=0.05, 0.10, 0.20, 0.30$ and 0.40) alloys.

Amorphous alloy	Density/Mg/m ³
LaCo_{13}	8.30
$\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$	
$x=0.05$	8.18
$x=0.10$	8.15
$x=0.20$	8.09
$x=0.25$	8.06
$x=0.30$	7.67
$\text{La}(\text{Co}_{1-x}\text{Mn}_x)_{13}$	
$x=0.05$	8.02
$x=0.10$	7.71
$x=0.20$	7.17
$x=0.30$	6.60
$x=0.40$	6.09

Fig. 1 Interference function in amorphous LaCo_{13} alloy. The experimental and calculated curves are described with the solid and dotted curves, respectively.

Fig. 2 Warren-type radial distribution function (RDF) in amorphous LaCo_{13} alloy. The experimental and calculated curves are described with the solid and dotted curves, respectively.

$$Q_i(Q) = \sum_j^n \sum_k^{n'} N_{jk} \exp(-b_{jk}Q^2) f_j(Q) f_k(Q) \frac{\sin(Qr_{jk})}{r_{jk}} + \sum_l^n \sum_m^n 4\pi \rho_0 \exp(-b_m Q^2) f_l(Q) f_m(Q) \times \frac{Qr_{lm} \cos(Qr_{lm}) - \sin(Qr_{lm})}{Q^2} \quad (2)$$

where N_{jk} , r_{jk} and b_{jk} are the coordination number, atomic distance and mean-square variation for j - k pairs in the near neighbor region, respectively. The integers n and n' are the numbers of elements and near-neighbor atoms around a type- j atom. The values of r_{lm} and b_{lm} are the distance and variation of the boundary region. By fitting the interference function calculated in eq. (2) to the experimental function with the non-linear least squares method, the structural parameters of N_{jk} , r_{jk} and b_{jk} are determined. Using the coordination numbers N_{jk} and atomic distances r_{jk} , the atomic structure in a near-neighbor region is evaluated. The structural parameters calculated from the crystalline data of LaCo_{13} were used as initial parameters for fitting in the present analyses. The coordination numbers and atomic distances of the amorphous and crystalline LaCo_{13} alloys in the present analysis are summarized in **Table 2**. The dotted curves in Figs. 1 and 2 correspond to the resultant profiles by this analysis. These observed and calculated profiles give good agreement with each other, which shows the validity of structural parameters in **Table 2**. In **Table 2**, we notify that the structural parameters in both amorphous and crystalline LaCo_{13} alloys basically resemble each other. This points out the fundamental structural unit in the amorphous LaCo_{13} alloy is the icosahedral Co cluster which also exists in the crystal. The presence of these clusters is consistent with the characteristic profiles of interference function and RDF in Figs. 1 and 2. Furthermore, in **Table 2**, the structural parameters for the La-Co and La-La pairs as well as the Co-Co pairs in both of the amorphous and crystalline LaCo_{13} alloys resembles

Table 2 Coordination numbers and atomic distances of amorphous and crystalline LaCo_{13} alloys. Their experimental errors are ± 0.2 and ± 0.002 nm, respectively. The values in the crystalline phase were evaluated from the crystalline data⁽⁸⁾.

Pairs	Amorphous LaCo_{13}		Crystalline LaCo_{13}	
	r/nm	N	r/nm	N
Co-Co	0.248	9.3	0.251	10.2
Co-Co	0.371	1.7	0.333	0.9
Co-Co	0.417	16.4	0.411	13.9
Co-Co	0.466	9.7	0.456	9.2
Co-Co	0.523	10.3	0.510	10.2
Co-Co	0.556	5.3	0.568	7.9
Co-Co	0.599	7.9	0.599	14.8
La-Co	0.309	24.3	0.329	24.0
La-Co	0.492	29.8	0.509	32.0
La-La	0.561	5.1	0.567	6.0

each other. This is different from the local atomic structure in the amorphous $\text{La}(\text{Fe}_{0.9}\text{Al}_{0.1})_{13}$ alloy although the fundamental unit structure is the same in both amorphous alloys.

The interference functions and RDFs of the amorphous $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ alloys in which the Cr concentration x is varied from 0.05 to 0.30 are shown in **Figs. 3** and **4**. The profiles of the interference functions and RDFs show no significant change in various Cr concentrations. This indicates that the atomic structures of the amorphous $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ alloys are identical to that of the amorphous LaCo_{13} alloy even if Cr atoms are substituted for 30% of the total Co atoms. This is more clearly shown in **Table 3** where the coordination numbers and atomic distances in the amorphous $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ alloys are compared in the observed concentration range. Since

Fig. 3 Interference functions in amorphous $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ alloys of $x=0.05, 0.10, 0.20, 0.25$ and 0.30 . The experimental and calculated curves are described with the solid and dotted curves.

Fig. 4 Warren-type radial distribution functions (RDFs) in amorphous $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ alloys of $x=0.05, 0.10, 0.20, 0.25$ and 0.30 . The experimental and calculated curves are described with the solid and dotted curves, respectively.

the atomic number of Cr(24) is close to that of Co(27), they are hardly distinguished each other by the ordinary X-ray diffraction method. Furthermore, the increase in fitting parameters in the least squares method often leads to instability in solution and increase in an experimental error. Thus, only in the analyses by the least squares method, Cr atoms are included among Co atoms. Similarly, Mn atoms are regarded as Co atoms in the least squares analyses for the amorphous $\text{La}(\text{Co}_{1-x}\text{Mn}_x)_{13}$ alloys discussed below. The structural parameters in Table 3 indicates that the fundamental local unit structure is Co(Cr) icosahedral clusters in the amorphous $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ alloys.

The interference functions of the amorphous $\text{La}(\text{Co}_{1-x}\text{Mn}_x)_{13}$ alloys with the Mn concentration x from 0.05 to 0.40 are shown in Fig. 5. In the interference functions of the amorphous $\text{La}(\text{Co}_{1-x}\text{Mn}_x)_{13}$ alloys, no sig-

Fig. 5 Interference functions in amorphous $\text{La}(\text{Co}_{1-x}\text{Mn}_x)_{13}$ alloys of $x=0.05, 0.10, 0.20, 0.30$ and 0.40 . The experimental and calculated curves are described with the solid and dotted curves, respectively.

nificant change is observed up to $x=0.10$. A whole profile of the interference function is gradually shifted toward a smaller Q -value above $x=0.20$ to 0.40 . Furthermore, its oscillations in a high- Q region are slightly reduced in the alloys of $x=0.30$ and 0.40 . This denotes a change of a local atomic structure by the substitution of Mn atoms for Co atoms, which is dissimilar to those in the amorphous $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ alloys. The first peak of the RDF in Fig. 6 is shifted about a few percent towards a larger r -value in the amorphous $\text{La}(\text{Co}_{1-x}\text{Mn}_x)_{13}$ alloys above $x=0.20$. This profile change in the RDFs above 0.20 corresponds to that in the interference function. The coordination numbers and atomic distances obtained in the amorphous $\text{La}(\text{Co}_{1-x}\text{Mn}_x)_{13}$ alloys with the least squares method are summarized in Table 4. In this table, we notice that the atomic distance of the nearest neighbor Co-Co pairs gradually increases from 0.248 nm

Table 3 Coordination numbers and atomic distances of amorphous $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ alloys of $x=0.05, 0.10, 0.20, 0.25$ and 0.30 . Their experimental errors are ± 0.2 and ± 0.002 nm, respectively.

Pairs	$x=0.05$		$x=0.10$		$x=0.20$		$x=0.25$		$x=0.30$	
	r/nm	N	r/nm	N	r/nm	N	r/nm	N	r/nm	N
Co-Co	0.248	9.0	0.248	9.0	0.248	9.1	0.248	8.9	0.248	8.6
Co-Co	0.364	1.9	0.368	2.2	0.366	1.9	0.365	1.9	0.363	1.9
Co-Co	0.417	15.9	0.418	16.3	0.417	16.3	0.418	16.1	0.417	15.3
Co-Co	0.464	9.3	0.465	8.9	0.465	8.9	0.465	8.8	0.463	8.3
Co-Co	0.523	11.1	0.523	11.4	0.525	11.5	0.525	11.6	0.524	11.2
Co-Co	0.553	5.2	0.554	5.4	0.553	5.7	0.553	5.8	0.552	5.6
Co-Co	0.599	7.9	0.599	7.9	0.599	6.5	0.599	6.5	0.599	6.5
La-Co	0.309	24.1	0.308	23.8	0.309	24.2	0.310	23.8	0.309	24.1
La-Co	0.492	28.8	0.492	28.6	0.492	29.9	0.492	29.7	0.492	28.8
La-La	0.564	5.4	0.566	5.5	0.572	5.2	0.571	5.8	0.572	5.3

Fig. 6 Warren-type radial distribution functions (RDFs) in amorphous $\text{La}(\text{Co}_{1-x}\text{Mn}_x)_{13}$ alloys of $x=0.05, 0.10, 0.20, 0.30$ and 0.40 . The experimental and calculated curves are described with the solid and dotted curves, respectively.

for $x=0.05$ to 0.253 nm for 0.40 , which corresponds to the shift of the first peak in the RDFs in Fig. 6. In the amorphous $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ alloys, the atomic distance of the first neighbor Co-Co pairs is kept to 0.248 nm. Namely, a striking contrast of the concentration dependence of the local atomic structure is observed between the amorphous $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ and $\text{La}(\text{Co}_{1-x}\text{Mn}_x)_{13}$ alloys.

IV. Discussion

In the LaCo_{13} alloy, the coordination numbers of La-Co pairs in the amorphous and crystalline phases well coincide with each other. This is quite different from those of La-Fe pairs in the amorphous and crystalline $\text{La}(\text{Fe}_{0.9}\text{Al}_{0.1})_{13}$ alloys⁽⁹⁾. In the amorphous $\text{La}(\text{Fe}_{0.9}\text{Al}_{0.1})_{13}$

alloy, the coordination numbers of the first and second nearest neighbor La-Fe pairs are 16 ± 0.2 and 24 ± 0.2 , that is about 67 and 75% of the crystalline values. This indicates that about 5 to 6 icosahedral Fe clusters are randomly distributed around a La atom, while 8 icosahedral clusters are orderly located in the crystal. In the amorphous LaCo_{13} alloy, the coordination number of the first nearest neighbor La-Co pairs is 24.3 ± 0.2 , which is equal to the crystalline value of 24. This shows that the number of the icosahedral Co clusters around a La atom is equal to 8. The coordination number of the second nearest neighbor La-Co pairs at 0.492 nm is 29.8 ± 0.2 that is about 93% of the value of the crystal, and that of the first nearest neighbor La-La pairs at 0.561 nm is 5.1 ± 0.2 that is about 85% of the crystal. Due to random arrangements of icosahedral clusters around a La atom, the number of icosahedral clusters is reduced at a longer distance in the amorphous LaCo_{13} alloy. Consequently, the degree of randomness in the arrangements of the icosahedral clusters is much gentle in the amorphous LaCo_{13} alloy than in the amorphous $\text{La}(\text{Fe}_{0.9}\text{Al}_{0.1})_{13}$ alloy. A similar tendency is also observed in the amorphous $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ alloys.

The tabulated atomic radii of the elements Co, Cr and Mn are $0.125, 0.130$ and 0.135 nm, respectively. In spite of the size difference of 4% between Co and Cr, the atomic distance of the nearest neighbor Co-Co pairs is not changed by substitution of Cr for Co in the observed range of x from 0.05 to 0.30 in the amorphous $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ alloys. This is also true in the atomic distances of the La-Co pairs as well as the other Co-Co pairs. The coordination numbers do not show any significant change in the present range in the amorphous $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ alloys by taking its experimental error of ± 0.2 into consideration.

This is not a case in the amorphous $\text{La}(\text{Co}_{1-x}\text{Mn}_x)_{13}$ alloy. The atomic distance of the first nearest neighbor Co-Co pairs increases with the value of x . The linear relation between the Mn concentration x and the atomic distance of the first nearest neighbor Co-Co pairs in Table 4 has been evaluated. The atomic distance for $x=0$ calculated from the linear relation is 0.248 ± 0.001 nm that coincides with the atomic distance of the first neighbor Co-

Table 4 Coordination numbers and atomic distances of amorphous $\text{La}(\text{Co}_{1-x}\text{Mn}_x)_{13}$ alloys of $x=0.05, 0.10, 0.20, 0.30$ and 0.40 . Their experimental errors are ± 0.2 and ± 0.002 nm, respectively.

Pairs	$x=0.05$		$x=0.10$		$x=0.20$		$x=0.30$		$x=0.40$	
	r/nm	N	r/nm	N	r/nm	N	r/nm	N	r/nm	N
Co-Co	0.248	9.1	0.249	9.0	0.251	9.0	0.251	8.7	0.253	8.4
Co-Co	0.363	1.7	0.366	1.9	0.356	1.7	0.356	1.7	0.354	1.5
Co-Co	0.416	16.1	0.418	16.0	0.418	15.5	0.418	15.3	0.418	14.1
Co-Co	0.464	9.4	0.464	8.5	0.463	8.5	0.460	7.8	0.460	7.8
Co-Co	0.523	11.0	0.522	10.8	0.524	11.4	0.521	10.3	0.522	10.7
Co-Co	0.554	5.5	0.551	4.8	0.552	5.4	0.550	5.1	0.550	4.9
Co-Co	0.599	7.8	0.603	7.8	0.599	6.5	0.591	6.1	0.599	6.9
La-Co	0.310	23.7	0.309	24.0	0.308	22.5	0.308	21.6	0.310	22.7
La-Co	0.492	28.2	0.492	28.4	0.493	30.5	0.489	28.5	0.491	28.4
La-La	0.564	5.7	0.565	5.5	0.571	4.8	0.567	4.6	0.564	4.4

Co pairs in the amorphous LaCo_{13} alloy, 0.248 ± 0.02 nm. The slope of the linear relation 0.014 ± 0.002 nm is nearly equal to 0.02 nm, that is evaluated from the size difference between Co and Mn atoms. Thus, the expansion of the atomic distance of the first neighbor Co-Co pairs in the amorphous $\text{La}(\text{Co}_{1-x}\text{Mn}_x)_{13}$ alloy is explained by partial substitution of 8% larger Mn atoms for Co atoms. This causes a gradual deformation of the icosahedral clusters with x in the amorphous $\text{La}(\text{Co}_{1-x}\text{Mn}_x)_{13}$ alloys. Decrease in the coordination numbers of La-La pairs with x in Table 4 indicates that packing of icosahedral clusters around a La atom loosens with x . This is also clearly seen in the number densities of the amorphous $\text{La}(\text{Co}_{1-x}\text{Mn}_x)_{13}$ alloys, that is the number of atoms in unit volume evaluated from the densities in Table 1. The number densities in the amorphous $\text{La}(\text{Co}_{1-x}\text{Mn}_x)_{13}$ alloys are 77.3, 76.6, 75.6, 74.2, 72.3 and 70.8 nm^{-3} for $x=0.0, 0.05, 0.10, 0.20, 0.30$ and 0.40, respectively, and monotonically decrease with x . Incidentally, the number densities in the amorphous $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ alloys are 76.6, 76.7, 76.9, 77.0 and 73.7 nm^{-3} for $x=0.05, 0.10, 0.20, 0.25$ and 0.30, respectively. Except for $x=0.30$, they are almost constant in the observed range from 0.05 to 0.25. This is consistent with the fact that no prominent structural change is observed in the amorphous $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ alloys.

As explained above, the atomic distances of Co-Co pairs in the amorphous $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ alloys do not show such a systematic change although Cr is about 4% larger than Co. Let us assume that an icosahedron consists of 13 atoms of equal size. Namely, one atom is located at the center of the cluster and 12 atoms at its vertices. The atomic distance between the neighbor atoms at the vertices is about 4% longer than that between the atoms at the center and at the vertices. Therefore, it is convincing that an atom of a little larger size is easily placed without any significant distortion around its neighbor even if the icosahedral Co cluster in the amorphous LaCo_{13} alloy is not rigidly a regular icosahedron. According to the analysis of the atomic structure and magnetic property in the crystalline $\text{La}(\text{Fe}_{1-x}\text{Al}_x)_{13}$ alloy⁽¹⁸⁾, the added Al atoms are randomly substituted for Fe atoms at the vertices of the icosahedral clusters, but not for an Fe atom at its center. Thus, it is plausible that the transition metals of Cr and Mn are also randomly substituted for Co located at the vertices of the icosahedral clusters in the amorphous $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ and $\text{La}(\text{Co}_{1-x}\text{Mn}_x)_{13}$ alloys. Consequently, this is a reason why no significant change is observed in the atomic structure of the amor-

phous $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ alloys by substitution of Cr for Co although the atomic size of Cr is about 4% larger than that of Co. Substitution of Mn for Co is not a case since Mn is about 8% larger than Co.

V. Summary

X-ray diffraction analyses revealed the dependence of the atomic structure on the concentration of the substituted atoms Cr and Mn for Co in the amorphous $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ and $\text{La}(\text{Co}_{1-x}\text{Mn}_x)_{13}$ alloys. The fundamental local unit is the icosahedral clusters of Co (Cr or Mn). These icosahedra are randomly distributed around a La atom in these amorphous alloys. The atomic structure is not significantly changed up to $x=0.30$ in the amorphous $\text{La}(\text{Co}_{1-x}\text{Cr}_x)_{13}$ alloys. On the other hand, the icosahedral clusters are distorted with x and the number density is reduced with x in the amorphous $\text{La}(\text{Co}_{1-x}\text{Mn}_x)_{13}$ alloys. The different concentration dependence of the atomic structures in both of the amorphous alloys is attributed to the size difference between Co and Mn or Cr.

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