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ICOSAHEDRAL CLUSTERS AND MAGNETIC PROPERTIES OF $LaCo_{13}$ AMORPHOUS AND CRYSTALLINE ALLOYS

K. Fukamichi, A. Fujita, N. Ohashi, M. Hashimoto, E. Matsubara*) and Y. Waseda#)

Department of Materials Science, Faculty of Engineering, Tohoku University, Sendai 980, Japan

*) Department of Metallurgy, Faculty of Engineering, Kyoto University, Kyoto 606, Japan

#) Institute for Advanced Materials Processing, Tohoku University, Sendai 980, Japan

Abstract- The atomic structure and magnetic properties of $LaCo_{13}$ amorphous alloy have been investigated and compared with those of its crystalline counterpart. It has been confirmed that the amorphous alloy is composed of the icosahedral clusters with a $NaZn_{13}$-type structure. The magnetic moment and the spin-wave stiffness constant obtained from the magnetic measurements in the amorphous state are larger than those in the crystalline state. The Curie temperature estimated from the reduced magnetization curve for the former is much higher than the value for the latter. The localized magnetic moment character in the amorphous state is stronger than that in the crystalline state.

I. INTRODUCTION

$La(Fe_xAl_{1-x})_{13}$ compounds have a cubic $NaZn_{13}$-type structure composed icosahedral clusters. Recently, the structure of $La(Fe_xAl_{1-x})_{13}$ amorphous alloys ($0.80 \leq x \leq 0.95$) have been investigated and pointed out that these alloys contain the icosahedral clusters similar to those in the crystalline state[1]. This means that these amorphous alloys have a quite rigid local unit structure which is different from other metallic amorphous alloy structures. It should be noted that the magnetic moment and the Curie temperature in the amorphous state are enhanced, compared with those in the crystalline state[2]. Such enhancements are exceptional for Fe-based amorphous alloys.

The enhancement of the Curie temperature due to the structural disorder in Co-based amorphous alloys has been pointed out experimentally[3] and theoretically[4]. The magnetic properties of 3d transition metals and alloys are very sensitive to the local environments such as the coordination number and interatomic distance. $LaCo_{13}$ is the only rare-earth transition metal binary compound with the $NaZn_{13}$-type structure. Since the $LaCo_{13}$ contains no additional third element, it is useful in shedding light on the local atomic arrangement in the amorphous alloy and on the difference in magnetic properties between the amorphous and crystalline states.

In the present study, therefore, the atomic arrangement in the $LaCo_{13}$ amorphous alloy prepared by high-rate DC sputtering has been investigated, and its magnetic properties such as the magnetic moment, the Curie temperature, spin-wave stiffness constant and the nature of spin fluctuations have been compared with those of the crystalline counterpart.

II. EXPERIMENTAL

The alloy target about 50mm in diameter was

made by arc melting. The amorphous alloy was prepared by high-rate DC sputtering on a water-cooled Cu substrate. More detailed procedures were described elsewhere[2]. The X-ray diffraction measurement was carried out using the ordinary θ - 2θ coupling geometry. The scattering intensity from the sample was measured by a scintillation counter with a pulse height analyzer in order to eliminate Co and La fluorescent radiations. Measurements of magnetization at 4.2 K up to 55 kOe and thermomagnetization in a wide temperature range were made with a SQUID magnetometer. The nature of spin fluctuations was investigated through the magnetization process.

III. RESULTS AND DISCUSSION

Figure 1 shows the interference function Qi(Q) of the $LaCo_{13}$ amorphous alloy. The distances and coordination numbers of near-neighbor correlations are obtained by the least-squares calculation so as to reproduce the experimental interference function data. The dotted line is the calculated result. The starting parameters for the least-squares variations were set by calculating the average coordination numbers and atomic distances of the $LaCo_{13}$ crystal at 300 K. The detailed procedures for the crystalline and amorphous alloys composed of the icosahedral clusters were described elsewhere[1]. Since the coordination number and the atomic distance of the nearest neighbor Co-Co pairs for the amorphous alloy and for the crystal show little difference, it is plausible that the local short-range ordering clusters in the amorphous state are the same icosahedral clusters as those in the crystalline state[4]. The essential features in the structural profile are fairly distinct oscillations present even in the high-Q region, being similar to those for oxide glasses[5]. Therefore, this characteristic profile implies the presence of chemical short-range ordering clusters with definite bond lengths and angular relations[6].

Shown in Fig. 2 is the reduced radial distribution function(RDF). The solid and dotted curves were respectively obtained by the Fourier transformation of the experimental and calculated interference functions in Fig. 1. The first peak composed of two peaks is isolated from other peaks and fairly distinct oscillations are present even up to the middle distance range. These features also

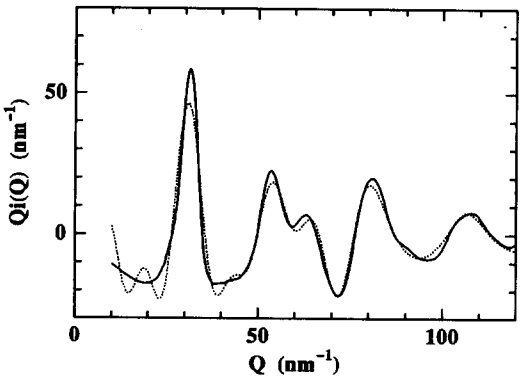

Fig. 1 Interference functions of the $LaCo_{13}$ amorphous alloy. The solid and dotted lines stand for the experimental and calculated results.

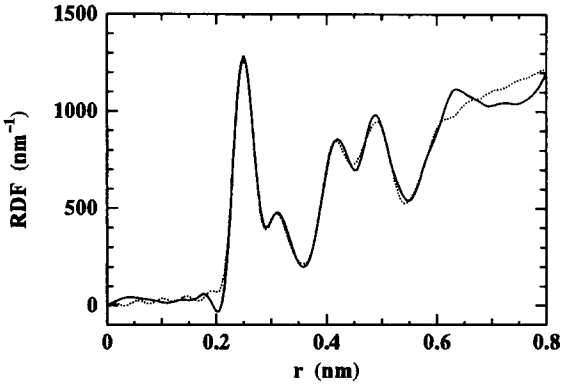

Fig. 2 Reduced radial distribution functions of the $LaCo_{13}$ amorphous alloy. The solid and dotted lines show the experimental and calculated results.

indicate the presence of the short-range ordering clusters in the present amorphous alloy. The Co atoms occupy two different sites, that is, Co(I) and Co(II). The shortest Co–Co distance is the distance between the Co(I) and Co(II) being several percent shorter than the Co(II)–Co(II) distance. The structural parameters determined in the present analysis are the average values for Co(I) and Co(II) although the result of the least-squares variational analysis for the amorphous alloy clearly suggests the presence of the icosahedral clusters. The nearest neighbor interatomic distances r's of the Co–Co and Co–La pairs are 0.250 and 0.311 ± 0.001, respectively. The coordination numbers N's for these two pairs are 10.0 ± 0.2 and 18.7 ± 0.9, respectively. The structure parameters r and N for the Co–Co pairs in the amorphous state are very similar to those in the crystalline state, but these for the Co–La paris are strikingly different.

The magnetization curves per Co atom are shown in Fig. 3. The saturation is easily achieved and the value in the amorphous state is larger than that in the crystalline state. The Curie temperature of

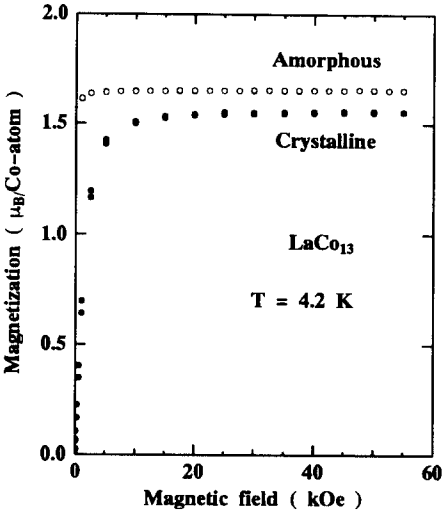

Fig. 3 Magnetization curves per Co atom for the $LaCo_{13}$ amorphous and crystalline alloys.

Co-based amorphous alloys is generally higher than the crystallization temperature in a high Co concentration range. Therefore, the Curie temperature of the $CoLa_{13}$ amorphous alloy is scaled by using the reduced magnetization curves of other amorphous Co-based alloys which have a higher crystallization temperature than the Curie temperature such as Y–Co amorphous alloys[3]. The Curie temperatures of the $LaCo_{13}$ in the amorphous and crystalline states are given in Table 1, together with other magnetic data. The Curie temperature T_C for the former is much higher than for the latter. According to the finite-temperature theory of the local environment effect, the ferromagnetism in the dense random packing of hard spheres for amorphous Co is enhanced because the main peak is near the Fermi level, so that the strong ferromagnetism is realized[7], and the calculation shows that the Curie temperature in the amorphous state becomes much higher than in an fcc structure of Co[7]. A drastic enhancement of the Curie temperature has been confirmed. The magnetic moment obtained from Fig. 3 for the $LaCo_{13}$ amorphous alloy is larger than that of the crystalline counterpart as given in Table 1. The magnetic moment for a Co amorphous calculated on the basis of the tight-binding LMTO-recursion method is 1.63 μ_B[8], which is slightly larger than 1.58 μ_B for an fcc Co[9, 10] and 1.55 μ_B for a hcp Co[9, 11]. In the present study, the value in the amorphous state is much larger than that in the crystalline state as shown in Table 1. The structural analysis for the amorphous alloy indicates that the average environment characteristics in the nearest neighbor range for the Co–Co pairs are not so different from those of the crystalline state. The $NaZn_{13}$-type atomic structure is very resemble to an fcc structure[12]. On the other hand, the interatomic distance and the coordination number for Co–La pairs are reduced about 5 % and 20 %, respectively, compared with those for the crystalline counterpart. Therefore, the different magnetic properties should be taken into consideration

the structural difference in the Co-La pairs.

Figure 4 shows the temperature dependence of magnetization M in the form M vs $T^{3/2}$ for the $LaCo_{13}$ amorphous and crystalline alloys. A linear relationship is observed in a wide range of temperature, and the spin-wave stiffness constants D is determined. The value of D/T_C is the measure of the exchange interaction range[13]. As seen from Table 1, the ratio of about 0.30 in the amorphous state is slightly smaller than the ratio of about 0.32 in the crystalline state, suggesting a shorter range of the exchange interaction.

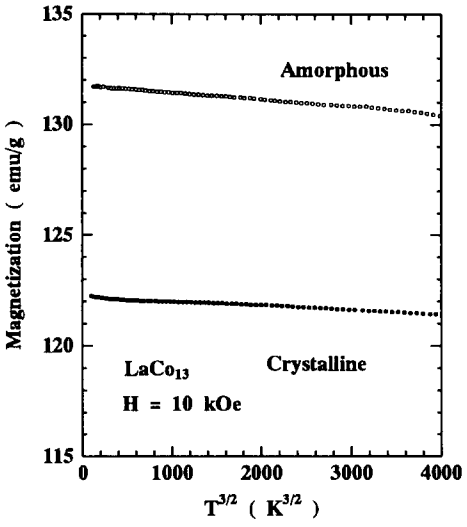

Fig. 4 Temperature dependence of magnetization in the form M vs $T^{3/2}$ for the $LaCo_{13}$ amorphous and crystalline alloys.

The formation of well defined icosahedral clusters reduces the concentration fluctuation in contrast with other binary amorphous alloys, favorable to discuss the nature of spin fluctuations[14]. Because of the enhancement of ferromagnetism in the amorphous state, the nature of spin fluctuations is expected to be different from that in the crystalline state. According to the theory of spin fluctuation[15], the nature of spin fluctuations is characterized by the spectral widths in both the wave-number q and the frequency ω spaces. Two characteristic temperatures T_A and T_0 are defined as the measures of the spectral width of spin fluctuations in the q and ω spaces, respectively. The intensity of the spin fluctuation spectrum in the large q and ω regions increases with increasing the magnetic moment and the Curie temperature. Therefore, the spectra of spin fluctuations are expected to be different between the $LaCo_{13}$ crystalline and amorphous alloys. The values of T_A and T_0 for the $LaCo_{13}$ crystalline and amorphous alloys are estimated from the Arrott plots at 4.2 K, referring to the correlation between these temperatures and magnetization process in low temperatures[15]. The values of T_A and T_0 are smaller than the Curie temperature T_C in weakly

Table 1 The Curie temperature T_C, magnetic moment μ per Co atom, spin-wave stiffness constant D, and the spin fluctuation parameters T_A and T_0 for the $LaCo_{13}$ crystalline and amorphous alloys.

State	T_C (K)	μ (μ_B /Co atom)	D (meVÅ^2)	T_A (K)	T_0 (K)
Crystalline	1290*	1.56	418	5655	8753
Amorphous	1660	1.66	491	7138	11135

*) K. H. J. Buschow and W. A. J. J. Velge, J. Less-Common Met., 13, 11(1976).

itinerant ferromagnets, while these temperatures are the same magnitude of T_C in the localized magnetic moment system. Although the correlation between these temperatures and the Arrott plots have some ambiguity in the region close to the localized magnetic moment system[15], the ratios of T_C/T_0 and T_C/T_A for the present alloys are the same order for the Y-Co amorphous alloys with a high concentration of Co[16], indicating that the magnetic properties are close to localized magnetic moment system. It is noteworthy that the ratio T_C/T_A is almost same value in both the crystalline and amorphous states. From these results, it is considered that the fluctuation of spin density in the real space is the same magnitude in both states, because T_A correlates with the static nature of spin fluctuations. On the contrary, the ratio T_C/T_0 in the amorphous state is larger than that in the crystalline state. The difference in the ratio of T_C/T_0 in both states means that the magnetic properties of the $LaCo_{13}$ amorphous alloy are closer to the localized system than the crystalline counterpart.

VI. SUMMARY

From the structural and magnetic studies for the $LaCo_{13}$ amorphous and crystalline alloys, the main results are summarized as follows.

(1) The $LaCo_{13}$ amorphous alloy is composed of the icosahedral clusters.
(2) The magnetic moment and the Curie temperature for the amorphous alloy are enhanced, compared with those for the crystalline counterpart.
(3) The range of the exchange interaction in the amorphous state is shorter than that in the crystalline state.
(4) The nature of spin fluctuations in the amorphous state is closer to the localized magnetic moment system than that in the crystalline state.

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