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Thermal expansion and elastic anomalies in $La(Fe_xAl_{1-x})_{13}$ amorphous alloys

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Abstract. $La(Fe_xAl_{1-x})_{13}$ ($0.80 \leqslant x \leqslant 0.95$) amorphous alloys have been prepared by high-rate DC sputtering to investigate the thermal expansion and elastic properties. A large thermal expansion anomaly has been observed in a wide temperature range. This anomaly is retained, even at high temperatures well above T_C. Such a peculiar phenomenon is associated with a large spontaneous volume magnetostriction. A significant ΔE effect has also been found in the temperature and field dependences of Young's modulus. The anomalous behaviour of Young's modulus can be explained in terms of the softening of elastic modulus caused by the anomalous thermal expansion. From these results, it is concluded that the anomalies in the thermal expansion and in Young's modulus for the $La(Fe_xAl_{1-x})_{13}$ amorphous alloys are caused by a large spontaneous volume magnetostriction associated with the large temperature variation in amplitude of the local moment.

1. Introduction

As is well known, Invar alloys exhibit various anomalies such as a low thermal expansion coefficient, a large forced volume magnetostriction and a marked ΔE effect. The study of these anomalous properties associated with the Invar effect is one of the most interesting fields of magnetism because it is closely related to the origin of ferromagnetism in transition metals and their alloys (Chikazumi 1979). The thermal expansion and the magnetoelastic behaviour of a number of Fe-based amorphous alloys have been investigated (Fukamichi *et al* 1979, Torok and Hausch 1979). It should be noted that a large magnetovolume effect is common to Fe-based amorphous alloys (Fukamichi 1983). Recently, the magnetoelastic properties of Fe–Ni and $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ crystalline alloys have been investigated intensively (Shiga *et al* 1990, 1991). These crystalline alloys exhibit Invar characteristics in a wide temperature range, accompanied by softening of the elastic constants. In recent years, in crystalline alloys, the magnetovolume effect has been successfully explained by taking into account spin fluctuation (Moriya and Usami 1980, Hasegawa 1981, Kakehashi 1981).

The intermetallic cubic compounds $La(Fe_xAl_{1-x})_{13}$ are attractive for basic research on Invar properties. They form a cubic $NaZn_{13}$ structure consisting of many icosahedral clusters, and the nearest neighbours of the two Fe sites are very similar to those in γ-Fe and FCC Fe–Ni Invar alloys (Ludorf *et al* 1989). These compounds exhibit a pronounced thermal expansion anomaly in a wide temperature range (Palstra *et al* 1985) in analogy with conventional crystalline Fe-based Invar alloys. Recently we have carried out systematic studies on the magnetic properties and structure of $La(Fe_xAl_{1-x})_{13}$ amorphous alloys. Above $x = 0.85$, re-entrant spin-glass behaviour has been observed in the concentration range where antiferromagnetic order occurs in the crystalline state (Chiang *et al* 1991). The local ordering characterized by the icosahedral clusters is present in these amorphous alloys (Matsubara *et al* 1992), in contrast with the other metallic amorphous alloys.

It has also been confirmed that these alloys show anomalous magnetic properties associated with the Invar effect such as a large high-field susceptibility and a small spin-wave stiffness constant (Chiang *et al* 1991). Since the marked magnetovolume effects are common to Fe-based amorphous alloys (Fukamichi 1983), it is expected that these amorphous counterparts will exhibit a large thermal expansion and elastic anomalies.

In the present paper, the thermal expansion properties of the $La(Fe_xAl_{1-x})_{13}$ amorphous alloy system have been investigated and compared with the corresponding $La(Fe_{0.8}Al_{0.2})_{13}$ crystalline compound. The temperature dependence of Young's modulus of $La(Fe_xAl_{1-x})_{13}$ amorphous alloys has also been measured in order to discuss the relationship between the anomalous thermal expansion and elastic properties in the amorphous state.

2. Experimental details

Alloy targets about 50 mm in diameter were made by arc melting in an argon atmosphere. The amorphous samples about 0.3 mm thick were prepared by high-rate DC sputtering for about 3 days on a Cu substrate. The argon gas pressure during sputtering was 40 mTorr; the target voltage and the anode current were 1.0 kV and 6.0 A, respectively. The samples were confirmed to be in an amorphous state by x-ray diffraction. The Cu substrate was dissolved away in a solvent of CrO_3 (500 g) $+H_2SO_4$ (27 cm^3) $+H_2O$ (1000 cm^3) at about 350 K.

In order to remove the structural relaxation effect, all samples were annealed for 30 min at 543 K in vacuum. The thermal expansion was measured with a differential transformer type of dilatometer from 4.2 to 600 K at a heating rate of 2.5 K min^{-1} in a helium gas atmosphere. The temperature dependence of Young's modulus was measured in zero and external magnetic fields from 4.2 to 400 K by an electrostatic driving method at 400–2000 Hz (Shirakawa and Oguma 1966).

The magnetization was measured with a SQUID magnetometer. The Curie temperature T_C and spin-freezing temperature T_f were determined from the AC susceptibility measurements which were carried out by a mutual inductance method in a field amplitude of 1 Oe at 80 Hz. Some magnetic data on $La(Fe_xAl_{1-x})_{13}$ amorphous alloys have already been reported in our previous paper (Chiang *et al* 1991).

3. Results and discussion

Figure 1 shows the thermal expansion curves of five $La(Fe_xAl_{1-x})_{13}$ amorphous alloys in the annealed state. The thermal expansion curve of the paramagnetic state estimated from the Grüneisen relation (Ziman 1964), assuming that the Debye temperature $\Theta_D = 300$ K, which is very close to the value estimated from Brillouin scattering (Chiang *et al* 1992), is shown by the broken curve in the same figure. A large anomaly associated with spontaneous volume magnetostriction ω_s is observed over a wide range of temperatures. The value of ω_s is obtained from

$$\omega_s \simeq 3 \int (\alpha_p - \alpha)\, dT \tag{1}$$

where α_p and α are the thermal expansion coefficients of the alloys in the paramagnetic state and in the ferromagnetic state, respectively. As seen from the figure, an anomalous behaviour appears in a wide temperature range and becomes much larger with increasing Fe content. All these curves show the so-called Invar characteristics. For the alloys with an Fe content above $x = 0.85$ a negative thermal expansion, i.e. a shrinkage, occurs even well above T_C. On the other hand, there is no additional anomaly at the spin-freezing temperature T_f.

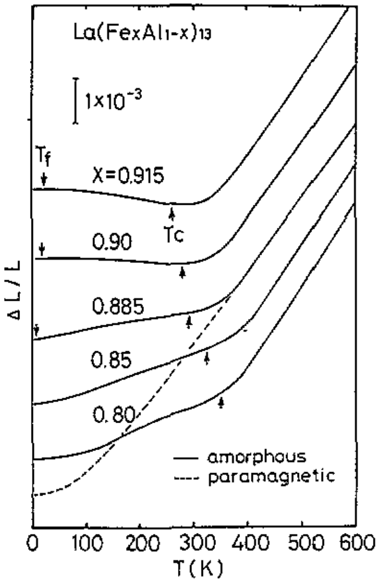

Figure 1. Thermal expansion curves of five $La(Fe_xAl_{1-x})_{13}$ amorphous alloys: – – –, paramagnetic state.

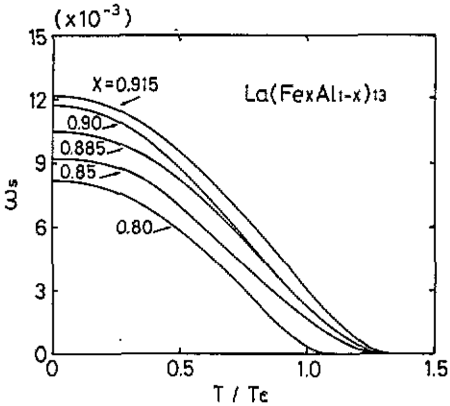

Figure 2. Spontaneous volume magnetostriction ω_s of $La(Fe_xAl_{1-x})_{13}$ amorphous alloys as a function of T/T_C.

Figure 2 shows the variation in the spontaneous volume magnetostriction ω_s of $La(Fe_xAl_{1-x})_{13}$ amorphous alloys with the reduced temperature T/T_C. The value of ω_s increases with increasing Fe content. Furthermore, it is clear that the marked thermal expansion anomaly still remains even well above the Curie temperature T_C. A similar behaviour has also been observed for many other Fe-based amorphous alloys (Fukamichi *et al* 1989).

Figure 3 shows the representative Arrott plots of $La(Fe_{0.9}Al_{0.1})_{13}$ amorphous alloy. The plots exhibit strong convex curves upwards, suggesting the existence of a magnetic inhomogeneity such as superparamagnetic clusters (Acker and Huguenin 1979). The Arrott plots for inhomogeneous ferromagnets have been discussed by taking into account cooperative spin fluctuations and a similar curve has been obtained (Herzer *et al* 1980). Such an inhomogeneity would, to a certain extent, be reflected in the thermal expansion anomaly. However, a distinct anomalous thermal expansion above T_C was also observed even in homogeneous $Fe_{72}Pt_{28}$ crystalline alloy (Nakamura *et al* 1979).

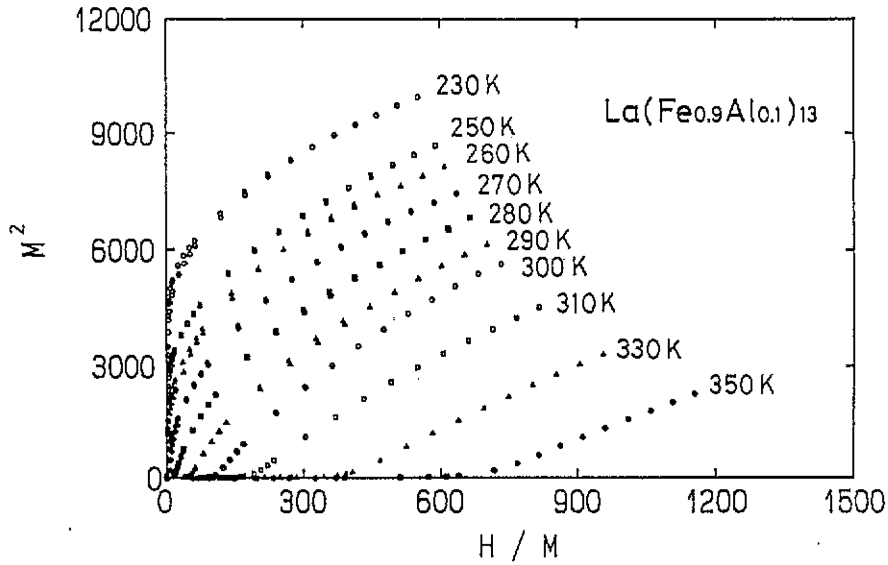

Figure 3. Arrott plots for $La(Fe_{0.9}Al_{0.1})_{13}$ amorphous alloy.

It has been pointed out that the anomalous thermal expansion in Fe–Ni Invar alloy is mainly caused by the large temperature variation in the amplitude of the Fe local moments (Kakehashi 1981). Because the Fe-rich Invar alloys are considered to be intermediate ferromagnets between the strong and weak ferromagnetic materials, the Coulomb interaction plays an important role. Therefore, when a large contraction in the amplitude of the local moment is caused by an increase in the temperature, negative thermal expansion can occur. In fact, this type of peculiar phenomenon has been presented in the calculation for Fe_cNi_{1-c} ($c = 0.8$) alloys despite the paramagnetic state (Kakehashi 1981). In the case of the present amorphous alloy system, a negative thermal expansion, i.e. a shrinkage, still exists even well above the Curie temperature for the alloys with an Fe content above $x = 0.85$. This behaviour is qualitatively explicable by analogy with the Fe–Ni Invar alloys described above.

Figure 4 shows the temperature dependence of the spontaneous volume magnetostriction ω_s for $La(Fe_{0.8}Al_{0.2})_{13}$ amorphous alloy, together with that for $La(Fe_{0.8}Al_{0.2})_{13}$ alloy crystallized from the amorphous state by annealing (sample (a)) and that of homogenized crystalline alloy (sample (b)). The samples (a) and (b) were confirmed by x-ray diffraction to be the same with the cubic $NaZn_{13}$-type structure. The values of ω_s for the two crystalline alloys have the same magnitude and exhibit the same temperature dependence. It has been reported that the value of ω_s for $La(Fe_{0.81}Al_{0.19})_{13}$ crystalline alloy is about 13.8×10^{-3} at 0 K (Palstra *et al* 1985). This is much larger by a factor of about 3 than that of $La(Fe_{0.8}Al_{0.2})_{13}$ alloy, as shown in figure 4, and also than the values of conventional Fe-based crystalline Invar alloys (Kussmann *et al* 1948, Tanji *et al* 1970). As seen from figures 2 and 4, the ω_s-value of 3.4×10^{-3} for $La(Fe_{0.8}Al_{0.2})_{13}$ crystalline alloy is lower than the ω_s-value of 8.3×10^{-3} for the amorphous alloy, which is consistent with the difference between the saturation magnetizations M_s and the Curie temperatures T_C of the amorphous and crystalline states. That is, the values of M_s and T_C of the amorphous alloys are, respectively, larger and higher than those of the crystalline alloys (Chiang *et al* 1991). Therefore, the values for other $La(Fe_xAl_{1-x})_{13}$ crystalline alloys (Palstra *et al* 1985) are also considered to be reduced to about one third of the values for the corresponding amorphous alloys.

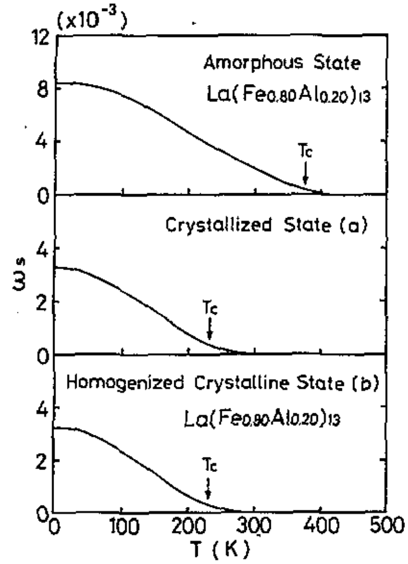

Figure 4. Temperature dependence of the spontaneous volume magnetostriction ω_s for $La(Fe_{0.8}Al_{0.2})_{13}$ amorphous alloy, together with that of $La(Fe_{0.8}Al_{0.2})_{13}$ alloy crystallized from the amorphous state by annealing (sample (a)) and that of homogenized crystalline alloy (sample (b)).

Figure 5 shows the concentration dependence of the spontaneous volume magnetostriction $\omega_s(0)$ at 0 K for $La(Fe_xAl_{1-x})_{13}$ amorphous alloys. The value of $\omega_s(0)$ increases with increasing Fe content and shows a marked increase above 0.85. These values are comparable with those for Fe–Ni crystalline alloys (Tanji *et al* 1970).

As is well known, the ΔE effect associated with the magnetic domain, internal stress and so on is common to ferromagnetic materials. It has been shown that Fe–Ni crystalline Invar alloys exhibit a pronounced elastic anomaly below the Curie temperature T_C, even in the saturated magnetic field. ΔE is described by three magnetic contributions using the following expression (Hausch and Warlimont 1973):

$$\Delta E = \Delta E_\lambda + \Delta E_\omega + \Delta E_A \tag{2}$$

with

$$\Delta E_\lambda = -2\lambda_s E^2/5\sigma_i \tag{3}$$

$$\Delta E_\omega = -E^2(\delta\omega/\delta H)^2/9\chi_{hf} \tag{4}$$

$$\Delta E_A \simeq -\omega_s \tag{5}$$

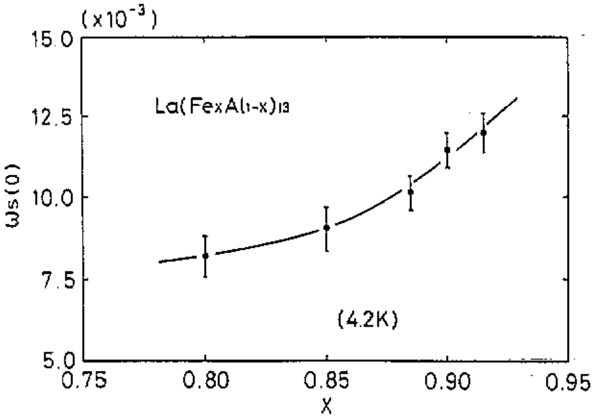

Figure 5. Concentration dependence of the spontaneous volume magnetostriction $\omega_s(0)$ at 0 K for the $La(Fe_xAl_{1-x})_{13}$ amorphous alloy system.

where ΔE_λ, ΔE_ω and ΔE_A are associated with the linear magnetostriction, the forced volume magnetostriction and the spontaneous volume magnetistriction, respectively. In equations (3)–(5), λ_s is the linear magnetostriction, σ_i the internal stress, $\delta\omega/\delta H$ the forced volume magnetostriction, χ_{hf} the high-field susceptibility and ω_s the spontaneous volume magnetostriction. Therefore, the anomalous thermal expansion shown in figure 1 would reflect the anomalous temperature dependence of Young's modulus.

Figure 6 shows the temperature dependence of $\Delta E/E$ for $La(Fe_xAl_{1-x})_{13}$ amorphous alloys, together with that of $Fe_{60}Hf_{40}$ amorphous alloy given by the short-dashed curves. The full and broken curves represent the results measured in magnetic fields of 0 kOe and 1.5 kOe, respectively. The external magnetic field of 1.5 kOe was applied in order to eliminate the magnetic domain effect. The temperature range of the paramagnetic state is too small to decide the slope of the elastic modulus. In order to estimate the paramagnetic Young's modulus, the temperature dependence of Young's modulus for $Fe_{60}Hf_{40}$ amorphous alloy was used as a reference and shown by the short-dashed curve because this sample has a wide paramagnetic temperature range. The signs of the ΔE effect given by equations (3)–(5) are negative. As seen from the figure, the temperature dependence of Young's modulus also shows a marked anomaly below T_C, reflecting the thermal expansion anomaly. It should be noted that Young's modulus measured in a magnetic field of 1.5 kOe is smaller than the paramagnetic Young's modulus, showing the softening with decreasing temperature. Such a peculiar phenomenon has also been observed for Fe–Zr and Fe–Hf amorphous alloys (Fukamichi *et al* 1984, 1989). The magnitude of the softening increases markedly with increasing Fe content. This behaviour is closely related to the Invar effect caused by the large spontaneous volume magnetostriction. It should be noted that the anomaly remains, even well above the Curie temperature. It has been reported that the temperature dependences of Young's modulus for Fe–Ni crystalline Invar alloys (Hausch and Warlimont 1973) and $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ crystalline alloys (Shiga *et al* 1990) also exhibit considerable softening in Young's modulus, even well above the Curie temperature. Poisson's ratio ν for these amorphous alloys has been confirmed to be about $\frac{1}{3}$ from Brillouin scattering (Chiang *et al* 1992). It is clear that the present amorphous alloys exhibit softening in the shear mode over a wide temperature range because the shear modulus is given by $E/2(1+\nu)$. The softening above the Curie temperature would be caused by the large spontaneous volume magnetostriction. Furthermore, it should be noted that a drastic increase in Young's modulus for the above-mentioned crystalline alloys is observed at very low temperatures (Hausch and Warlimont 1973, Shiga *et al* 1990), but the present amorphous alloys do not exhibit such an anomaly as seen from figure 6. In figures 1 and 6, furthermore, it is interesting to point out that no distinct anomaly is observed in the thermal expansion and Young's modulus curves at the spin-freezing temperature T_f.

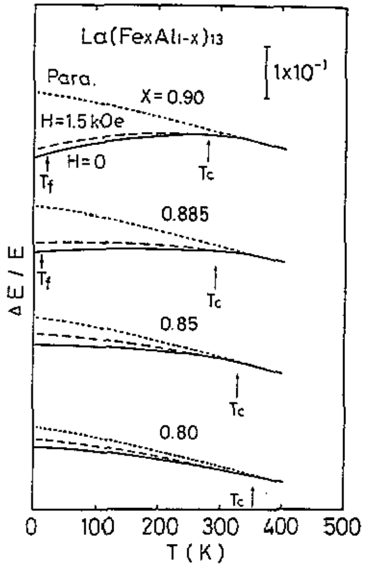

Figure 6. Relative change in Young's modulus versus temperature and external magnetic field for La(Fe$_x$Al$_{1-x}$)$_{13}$ amorphous alloys: the paramagnetic state is given by the short-dashed curves.

Figure 7 shows the concentration dependence of $|\Delta E_\lambda|/E$ for La(Fe$_x$Al$_{1-x}$)$_{13}$ amorphous alloys at 4.2 K, together with that of the squared magnetization M^2 in a magnetic field of 1.5 kOe at 4.2 K. These curves have a broad maximum at around $x = 0.85$. ΔE_λ is based on the magnetic domains which contribute to the linear magnetostriction λ_s. It is well known that the linear magnetostriction of Fe-based amorphous alloys is associated with the saturation magnetization M_s and can be written as (Ito *et al* 1980)

$$\lambda_s \propto M_s^2. \tag{6}$$

It is worth noting that the concentration dependence of the ratio $|\Delta E_\lambda|/E$ is very similar to that of the squared magnetization measured at 1.5 kOe. Therefore, it is expected that the linear magnetostriction λ_s of La(Fe$_x$Al$_{1-x}$)$_{13}$ amorphous alloys also exhibits a similar concentration dependence.

The concentration dependence of the ΔE effect associated with the spontaneous volume magnetostriction and the forced volume magnetostriction $|\Delta E_A + \Delta E_\omega|/E$, for La(Fe$_xAl_{1-x}$)$_{13}$ amorphous alloys is shown in figure 8. The concentration dependence of the spontaneous volume magnetostriction determined from the thermal

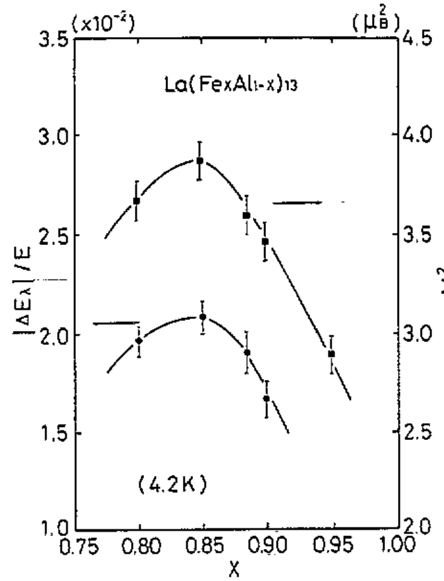

Figure 7. Concentration dependence of the linear magnetostriction term $|\Delta E_\lambda|$ of $La(Fe_xAl_{1-x})_{13}$ amorphous alloys at 4.2 K, together with that of the squared magnetization M^2 in a magnetic field of 1.5 kOe at the same temperature.

expansion measurements as shown in figure 5 is also presented in the same figure for comparison. Both of them increase dramatically with increasing Fe content. It should be noted that the concentration dependence of $|\Delta E_A + \Delta E_\omega|/E$ exhibits a similar tendency to that of the spontaneous volume magnetostriction $\omega_s(0)$. Strictly speaking, the increment in $|\Delta E_A + \Delta E_\omega|/E$ is much more pronounced than that in $\omega_s(0)$ at high x where the spin-glass state occurs (Chiang *et al* 1991). In Fe-rich Fe–Zr amorphous alloys exhibiting a spin-glass behaviour at low temperatures, the forced volume magnetostriction becomes very large (Tange *et al* 1989). This suggests that the ΔE_ω-term would increase markedly at high x.

It is expected that the present amorphous alloy system exhibits a large pressure effect on the Curie temperature $(\mathrm{d}T_C/\mathrm{d}P)$ because the spontaneous volume magnetostriction is directly reflected in the pressure effect on the Curie temperature associated with the magnetovolume effect. Furthermore, it would be expected that the present alloys also show a large compressibility due to the large magnetoelastic effects as shown in other Invar-type amorphous alloys (Fukamichi *et al* 1989). In fact, the compressibility of $La(Fe_{0.8}Al_{0.2})_{13}$ amorphous alloy is about twice that of pure crystalline Fe measured by the surface acoustic properties through Brillouin scattering (Chiang *et al* 1992). The data on the forced volume magnetostriction, Brillouin scattering and the pressure effect on magnetization of the present amorphous alloys will be presented in subsequent papers.

4. Conclusions

Several $La(Fe_xAl_{1-x})_{13}$ amorphous alloys have been prepared by high-rate DC sputtering in order to investigate the thermal expansion and elastic anomalies. Invar characteristics have been confirmed and the difference between the thermal expansions of the amorphous and crystalline states is also presented. Furthermore, the

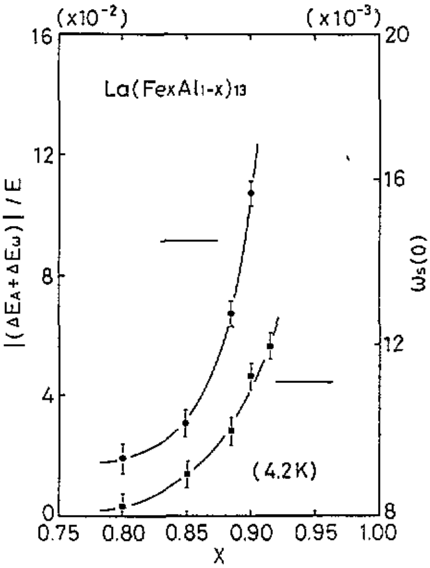

Figure 8. Concentration dependence of the ΔE effect associated with the spontaneous volume magnetostriction and forced volume magnetostriction $|\Delta E_A + \Delta E_\omega|/E$, for La(Fe$_xAl_{1-x}$)$_{13}$ amorphous alloys at 0 K, together with that of the spontaneous volume magnetostriction $\omega_s(0)$ determined from the thermal expansion measurement.

temperature and field dependences of Young's modulus have been investigated in a wide temperature range. The main results are summarized as follows.

(i) The thermal expansion anomaly due to the spontaneous volume magnetostriction ω_s is observed in a wide temperature range, and it becomes larger with increasing Fe content.

(ii) The thermal expansion anomaly above the Curie temperature T_C is closely associated with the large contraction of the amplitude of the local moment.

(iii) The spontaneous volume magnetostriction ω_s of La(Fe$_x$Al$_{1-x}$)$_{13}$ amorphous alloys is larger than that of the crystalline counterparts.

(iv) The temperature dependence of Young's modulus also shows a marked anomaly which coincides with the thermal expansion anomaly. The anomaly becomes pronounced with increasing Fe content and remains, even well above the Curie temperature.

(v) The concentration dependence of $|\Delta E_A + \Delta E_\omega|/E$ is similar to that of the spontaneous volume magnetostriction ω_s

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