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Magnetoelasticity of Fe–Ni and $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ Invar alloys: II. Low-temperature anomaly

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Abstract. The temperature dependence of the elastic constants of $Fe_{100-C}Ni_C$ and $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ alloys has been precisely measured at low temperatures by an ultrasonic pulse-echo technique. An anomalous increase in the longitudinal modulus C_L below around 40 K has been observed for $C \leqslant 40$ in $Fe_{100-C}Ni_C$ and for $x \leqslant 0.15$ in $Fe_{65}(Ni_{1-x}Mn_x)_{35}$. The onset temperature of this anomaly increases with increasing frequency of the ultra-sound, indicating a relaxation mechanism. The origin of this anomaly is discussed in connection with other low-temperature anomalies, especially with a rapid fall in the forced volume magnetostriction.

1. Introduction

In addition to the thermal expansion anomaly due to a large magnetovolume coupling, Invar alloys exhibit an anomalous temperature dependence on elastic constants. In a previous paper (Shiga *et al* 1990, hereafter referred to as I), we have discussed the origins of the softening of shear and bulk moduli in $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ Invar alloys. We have shown that the dominant mechanism of the softening of the bulk modulus is an inverse effect of the volume magnetostriction. In I, we did not refer to the sudden increase ΔC_L in the longitudinal modulus or the sudden increase ΔB in the bulk modulus at low temperatures.

The Fe–Ni Invar alloy exhibits many other anomalies at low temperatures, such as a decrease $\Delta\chi_{AC}$ in the AC susceptibility (Miyazaki *et al* 1986) and a decrease $\Delta\chi_i$ in the initial susceptibility (Rancourt *et al* 1989, 1990) in a very weak field, a decrease $\Delta\chi_{hf}$ in the high-field susceptibility (Kondorskii and Sedov 1959), a decrease $\Delta h'$ in the forced volume magnetostriction coefficient (Schlosser *et al* 1971, Zahres *et al* 1988) and long-time relaxation phenomena in magnetization and forced volume magnetostriction $d\omega/dH$ (Schlosser *et al* 1969). Of these, χ_{hf} and $h'(=\frac{1}{3}d\omega/dH)$ are correlated to each other through the following equation:

$$3h' = d\omega/dH = 2\kappa CM\chi_{hf}, \qquad (1)$$

where κ is the compressibility and C the magnetovolume coupling constant and, therefore, they can be ascribed to the same origin. These anomalies except for $\Delta\chi_{AC}$ appear

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below a certain characteristic temperature T_a of about 20 K for the $Fe_{65}Ni_{35}$ Invar. The microscopic mechanism of these anomalies has not been well understood although several models have been proposed mostly based on the assumption of partial antiferromagnetic ordering (Yamada *et al* 1980, Zahres *et al* 1988).

On the other hand, ΔC_L and ΔB occur below around 40 K (Fletcher 1969, Meincke and Litva 1969, Hausch 1976) which is much higher than T_a of the other anomalies. However, as discussed in I, the bulk modulus is correlated with the forced volume magnetostriction and the high-field susceptibility through a thermodynamical relation

$$1/B_H - 1/B_M = (\mathrm{d}\omega/\mathrm{d}H)^2/\chi_{\mathrm{hf}} \qquad (2)$$

where B_H and B_M are the bulk moduli under constant field and constant magnetization, respectively. Therefore, the ΔB effect probably has the same origin as the other anomalies. The difference between the characteristic temperatures may lie in the difference between the observation times for each measurement. The main purpose of the present paper is to study the relation between the anomalous increase ΔC_L in the longitudinal modulus, and other low-temperature anomalies and to discuss the origin of these anomalies. We have measured the temperature dependence of the elastic constants C_L, C' and C_{44} for $Fe_{100-C}Ni_C$ and $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ alloys at low temperatures under an applied field using an ultrasonic technique at several frequencies. We also measured the temperature dependence of forced volume magnetostriction of some of these alloys and analysed the effect of forced volume magnetostriction on the bulk modulus anomaly.

The $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ system undergoes a re-entrant spin-glass transition for $x \geqslant 0.1$ (Shiga *et al* 1985b). We investigate the effect of spin-glass freezing on elastic constants, which is clearly seen in some of re-entrant spin-glass systems (Shiga *et al* 1985a, 1986). Part of the present work has been published elsewhere (Shiga *et al* 1988).

2. Experimental details

Single-crystal samples for ultrasonic measurements are the same as used in I. In addition, we prepared single crystals of $Fe_{100-C}Ni_C$ alloys with $C = 33.6, 35, 37.5, 40$ and 45. The velocity of sound was measured by a standard pulse-echo overlapping technique at normally 10 MHz under an applied field of 5 kOe, which is high enough to get technical saturation and to avoid the softening due to the so-called ΔE effect caused by domain wall motions. In order to study the frequency dependence, we have carried out measurements at 20 and 30 MHz for some of the samples. The details of measurements and data analysis were the same as those described in I.

For measurements of the forced volume magnetostriction, polycrystalline samples of $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ with the same composition as those for ultrasonic measurements were prepared by argon arc melting. The ingots were subjected to homogenizing annealing at 1100 °C for 100 h. The forced magnetostriction was measured using a three-terminal capacitance bridge for the parallel direction to applied field.

3. Results

3.1. Concentration dependence of the low-temperature anomaly

Figures 1(*a*) and 1(*b*) show the temperature dependence of the longitudinal modulus C_L below 150 K of $Fe_{100-C}Ni_C$ and $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ alloys, respectively, at an applied field

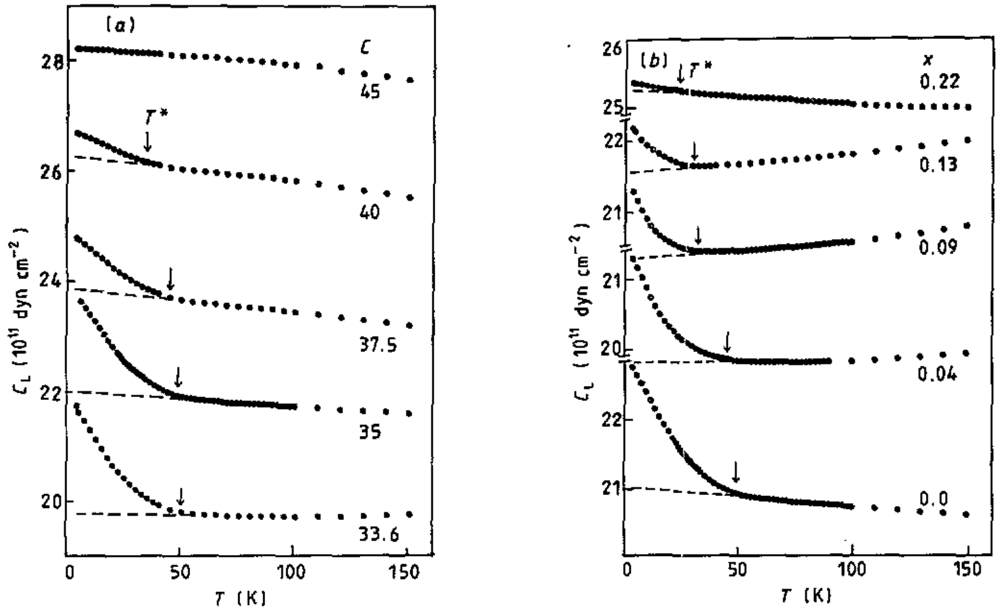

Figure 1. Temperature dependence of the longitudinal modulus C_L in a [110] direction of (*a*) $Fe_{100-C}Ni_C$ and (*b*) $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ at an external field of 5 kOe: ---, linear extrapolation of C_L from above T^*. The arrows indicate the onset temperature T^* of anomalous increase in C_L.

of 5 kOe. The results at higher temperatures have been given in I. An anomalous increase in C_L is clearly seen in each sample except $Fe_{55}Ni_{45}$ at low temperatures. We have estimated the magnitude of this anomalous increase ΔC_L at 4.2 K, by subtracting a simple linear extrapolation of the normal part at high temperatures to 0 K as shown by the broken lines. The onset temperature T^* of the anomaly was defined as the temperature where deviation from the linear line starts, as indicated by arrows in the figure. The concentration dependences of ΔC_L and T^* are plotted as a function of the mean electron concentration in figure 2. Both values exhibit a maximum near the classical Invar concentration and ΔC disappears at 45 at.% Ni in the $Fe_{100-C}Ni_C$ system and at $x = 0.23$ in the $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ system.

The temperature dependences of the shear moduli C' and C_{44} were also carefully measured at low temperatures. However, no appreciable anomaly was found at an applied field of 5 kOe although an anomaly was found in the C_{44} mode of $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ for zero-field measurements of a re-entrant spin-glass temperature system.

3.2. Frequency dependence of the low-temperature anomaly

The temperature dependence of C_L was measured at several frequencies. Since we have to change a quartz transducer for each measurement, the absolute values of C_L scatter somewhat for each run. However, the temperature dependence of C_L above T^* almost coincides after parallel displacement of curves. Therefore, C_L-values measured at frequencies higher than 10 MHz are normalized to C_L at 10 MHz at a temperature higher

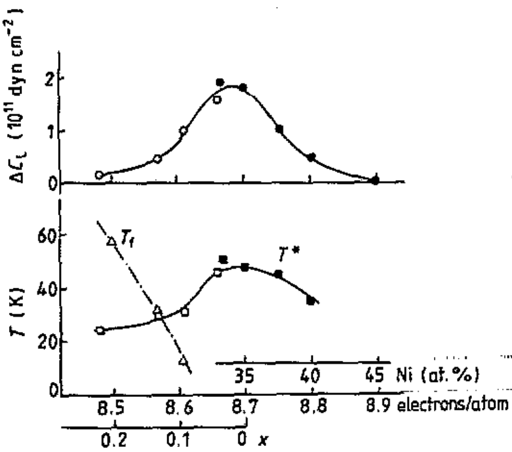

Figure 2. Magnitude of the anomalous increase ΔC_L (○, ●) in C_L, which is defined as the difference between the observed value and the extrapolated line at 4.2 K and the onset temperature T^* (□, ■) of the anomaly against concentration for $Fe_{100-C}Ni_C$, (○, □) and $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ (●, ■). The freezing temperatures T_f (△) of the re-entrant-type spin-glass state are also indicated.

enough than T^*, i.e. at 120 K for $Fe_{65}Ni_{35}$ and at 70 K for $x = 0.04$ and 0.09. The temperature dependence of C_L for several frequencies thus obtained are shown in figure 3. Both T^* and ΔC_L increase with increasing frequency, indicating the existence of a stress relaxation mechanism as suggested by Fletcher (1969). Since it is difficult to determine the onset temperature for each frequency precisely, we define an intersecting point of linear extrapolations of C_L from high- and low-temperature regions as a cross-over temperature $T^c(\nu)$ between the relaxed and unrelaxed states for each frequency as shown by arrows in figure 3. $T^c(\nu)$ for $Fe_{65}Ni_{35}$ for each frequency are given in table 1.

3.3. *Effects of spin-glass freezing on elastic constants*

Figure 4 shows the temperature dependence of C_{44} for $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ with $x = 0.09$ and 0.13 at zero field and 5 kOe. As described in a previous section, no anomaly is observed in shear moduli under an applied field. On the other hand, C_{44} at zero field is smaller than C_{44} at 5 kOe at high temperatures and increases at low temperatures with decreasing temperature, approaching the value under the applied field. Similar behaviour was found for Fe–Al and Au–Fe re-entrant spin-glass systems, which was interpreted as the result of suppression of the ΔE effect due to domain wall motions by the spin-glass freezing (Shiga *et al* 1986). The arrows in the figure indicate the spin-glass temperature T_f determined by AC susceptibility measurements (Shiga *et al* 1985b). The onset temperature of C_{44} hardening is higher than T_f determined by AC susceptibility measurements. This discrepancy may be ascribed to the difference between the observation times of measurements, namely 10 kHz for AC susceptibility and 10 MHz for

Figure 3. Temperature dependence of the longitudinal modulus C_L of $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ at an external field of 5 kOe for different frequencies with (*a*) $x = 0$ (△, 29 MHz; □, 22 MHz; ○, 10 MHz), (*b*) $x = 0.04$ (□, 23 MHz; ○, 10 MHz) and (*c*) $x = 0.09$ (△, 28 MHz; □, 18 MHz; ○, 10 MHz). The arrows in (*a*) indicate the crossover temperatures T^c between the relaxed and unrelaxed states for each frequency.

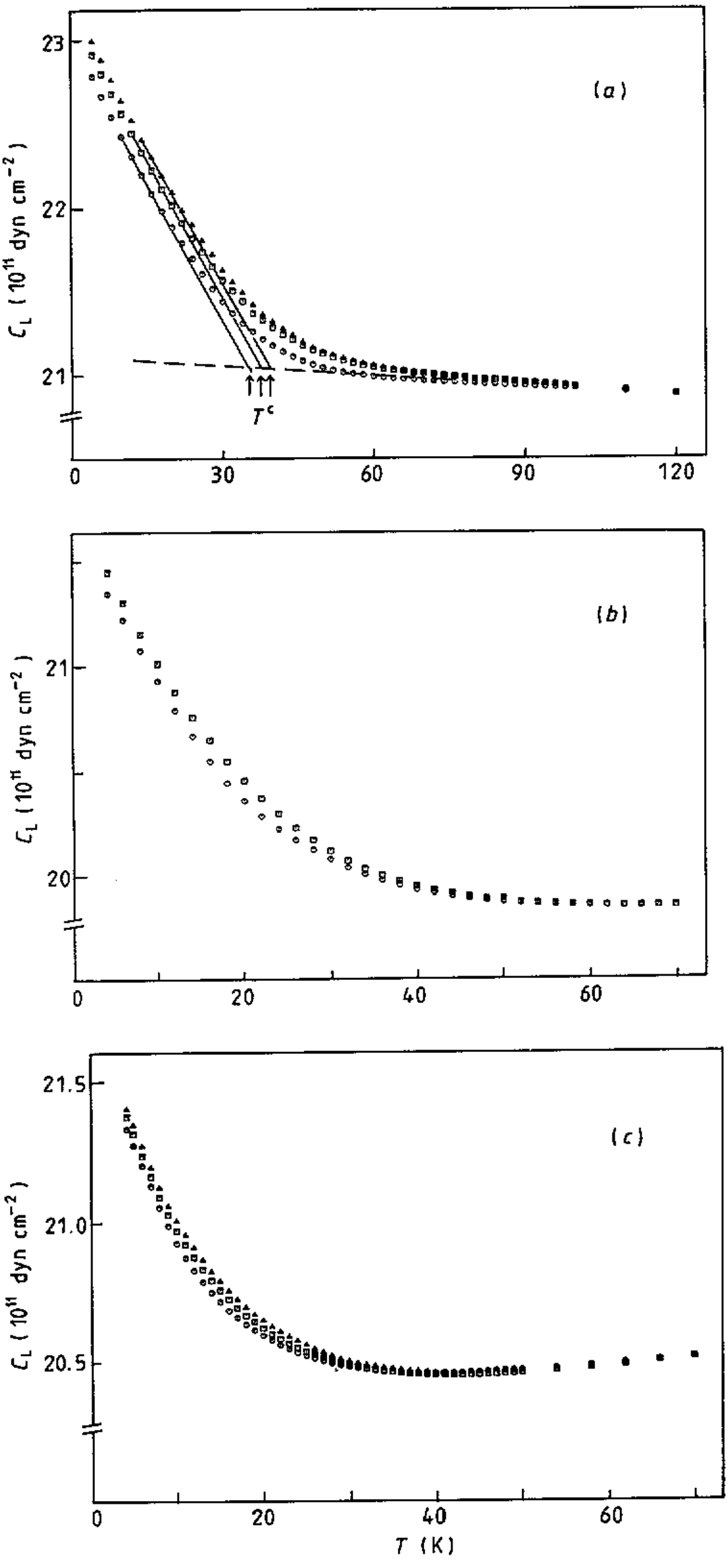
(a)
(b)
(c)
T^c
C_L (10^{11} dyn cm^{-2})
23
22
21
20
21.5
21.0
20.5
0
30
60
90
120
20
40
T (K)

Table 1. The crossover temperatures T^c between the relaxed and unrelaxed states in $Fe_{65}Ni_{35}$ for different frequencies.

Frequency (MHz)	T^c
10	35.5
22	37.8
29	39.6

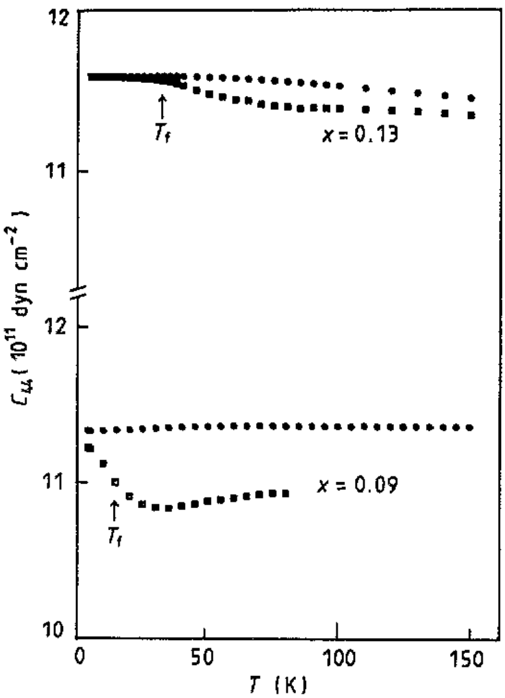

Figure 4. Temperature dependence of the shear modulus C_{44} of $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ at $H = 5$ kOe (⊙) and $H = 0$ (⊡). The arrows indicate the freezing temperature T_f of re-entrant-type spin-glass state determined by AC susceptibility.

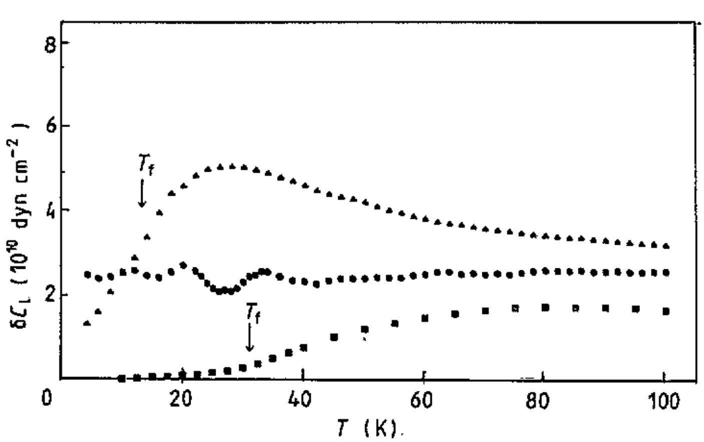

Figure 5. Temperature dependence of δC_L, which is defined as $\delta C_L = C_L(H = 5\,\text{kOe}) - C_L(H = 0)$: ⊙, $x = 0$; ▲, $x = 0.09$; ⊡, $x = 0.13$. The arrows indicate the freezing temperature T_f of the re-entrant-type spin-glass state determined by AC susceptibility.

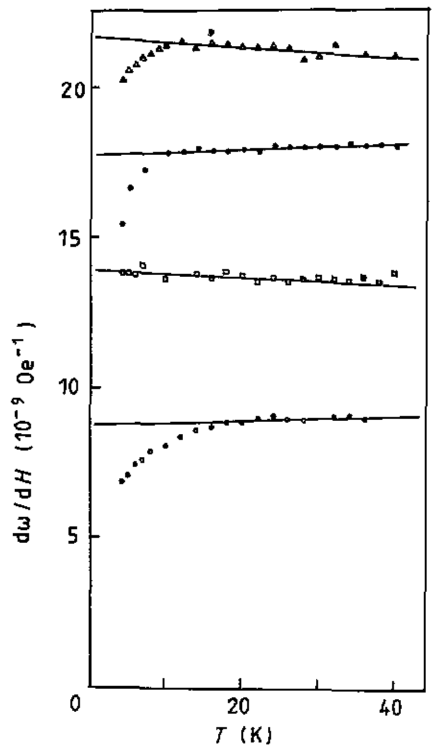

Figure 6. Temperature dependence of the forced volume magnetostriction of $Fe_{65}(Ni_{1-x}Mn_x)_{35}$: ○, $x = 0$; ●, $x = 0.05$; △, $x = 0.09$; □, $x = 0.21$; ———, fitted at high temperatures.

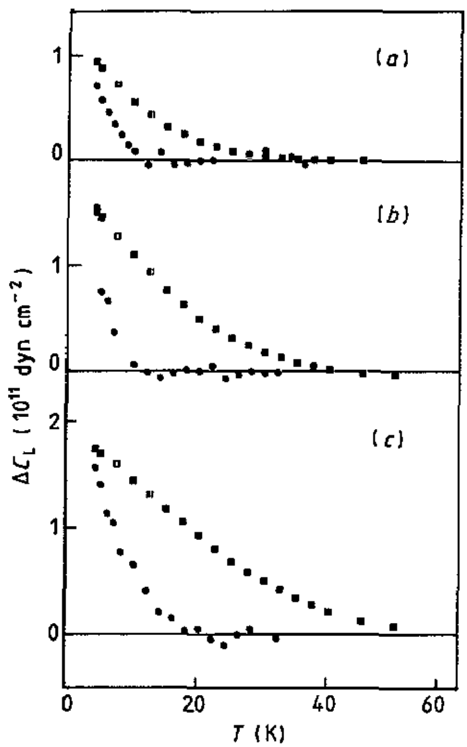

Figure 7. Temperature dependence of ΔC_L for $Fe_{65}(Ni_{1-x}Mn_x)_{35}$: (*a*) $x = 0.09$; (*b*) $x = 0.04$; (*c*) $x = 0.0$. ⊙, calculated values from anomalous decrease in the forced volume magnetostriction using equation (6); ⊡ observed values at 10 MHz.

ultrasonic measurements. The suppression of the ΔE effect is also observed in C_L but not in C'. Figure 5 shows the difference between C_L at $H = 0$ and $H = 5$ kOe, i.e. the ΔE effect of the C_L mode, for $x = 0$, 0.09 and 0.13. The ΔE effect in the C_L mode decreases with decreasing temperature from a temperature a little higher than the spin-freezing temperature T_f, indicated by arrows. However, for $x = 0$, namely for the classical Invar alloy, the ΔE effect remains constant down to 4.2 K, indicating the absence of spin-glass freezing. The irregular oscillations observed below 40 K may be a trivial phenomenon due to experimental error because of the strong temperature dependence of C_L itself.

3.4. *Temperature dependence of the forced magnetostriction*

The temperature dependence of the longitudinal forced magnetostriction coefficient $h'_{\parallel}$ for $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ is shown in figure 6. A rapid decrease in $h'_{\parallel}$ was observed at low temperatures for $x < 0.1$. It should be noted that the onset temperature of this anomaly is lower than T^* for ΔC_L. We have estimated the magnitude of this anomalous decrease $\Delta h'_{\parallel}$ by a simple linear extrapolation of the linear part at high temperatures to a low temperature as shown by the full lines. Since the longitudinal and the transverse forced volume magnetostriction coefficients, $h'_{\parallel}$ and $h'_{\perp}$, respectively, are almost the same in this system (Wada *et al* 1985), the forced volume magnetostriction $d\omega/dH$ can be obtained by multiplying $h_{\parallel}^{f}$ by a factor of 3. Then the anomalous decrease $\Delta(d\omega/dH)$ in the forced volume magnetostriction, is obtained from $\Delta(d\omega/dH) = 3\ \Delta h_{\parallel}^{f}$. The correlation between ΔC_L and $\Delta(d\omega/dH)$ will be discussed in the next section.

4. Discussion

4.1. Correlation between low-temperature anomalies of longitudinal modulus and forced volume magnetostriction

In I, we have shown that the decrease in the bulk modulus below the Curie temperature in Invar alloys can be ascribed to an inverse effect of the volume magnetostriction, which is given by a thermodynamic relation (equation (2)). Using the magnetovolume coupling constant, equation (2) can be written as

$$1/B_H - 1/B_M = 2\kappa CM(d\omega/dH) \tag{3}$$

(equation (11) of I). The observed bulk modulus B_H can be approximately given by

$$B_H \sim B_M - 2\kappa CMB_M^2(d\omega/dH). \tag{4}$$

Therefore, the anomalous decrease in $d\omega/dH$ at low temperatures gives rise to an increase in B_H provided that the temperature dependence of B_M and the magnetization M are normal. The longitudinal modulus C_L is given as a function of the bulk modulus and shear moduli by

$$C_L = B + C_{44} + C'/3. \tag{5}$$

Since no appreciable anomaly is detected in C_{44} and C' at low temperatures, the anomalous increase ΔC_L in the longitudinal modulus is correlated with the anomalous decrease $\Delta(d\omega/dH)$ in the forced volume magnetostriction by

$$\Delta C_L \simeq \Delta B = 2\kappa CMB_M^2\ \Delta(d\omega/dH). \tag{6}$$

ΔC_L thus estimated is shown in figure 7 as a function of temperature together with ΔC_L directly measured by the ultrasonic technique at 10 MHz. Here, the magnetovolume coupling constant $\kappa C = 1.3 \times 10^{-8}\ \text{emu}^2\ \text{cm}^{-6}$, which is taken from I, is used. As seen in the figure, ΔC_L at 4.2 K can be explained as an inverse effect of the anomalous decrease in the forced volume magnetostriction. However, the onset temperatures T^* of these anomalies are different from each other. Since the measurement of $d\omega/dH$ is nearly static while that of C_L is dynamic, this discrepancy may be attributed to the difference between the observation times. Precise static measurements of the bulk modulus or Young's modulus at low temperatures will probably give a lower T^* comparable with the present estimation from $d\omega/dH$.

4.2. Frequency dependence of the onset temperature of ΔC_L and relaxation process

The frequency dependence of T^* indicates a relaxation process in ΔC_L as suggested by Fletcher (1969). The mechanism will be following. Mechanical stress or pressure applied to the system gives rise to a change in the magnetic state, which relaxes stress, leading to softening of the lattice. In order to change the magnetic state, an activation energy and hence a relaxation time are necessary. Alternatively, a change in magnetization caused by an applied field is accompanied by a volume change. This process also needs

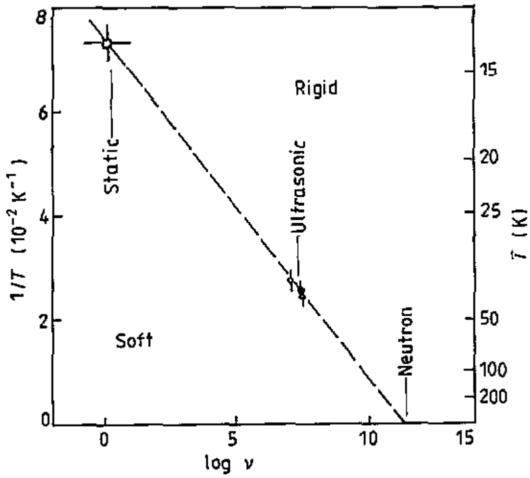

Figure 8. Inverse characteristic temperatures of the low-temperature anomalies for $Fe_{65}Ni_{35}$ against logarithm of the inverse observation time: -⌖-, onset temperature of anomalous decrease in forced volume magnetostriction; ⌽, crossover temperatures of the anomalous increase in C_L observed at different frequencies, which are indicated by arrows in figure 3(*a*). In the region above the broken line, the relaxation mechanism does not work and no lattice softening is observed.

the same relaxation time. According to Fletcher's analysis of Fe–Ni Invar alloys, the activation energy of the Arrhenius-type relaxation is widely distributed from 0 to 0.05 eV. For simplicity, however, we discuss the frequency dependence of the characteristic temperature of the relaxation process by assuming a single activation energy. On this assumption, the relaxation time τ is given by

$$\tau = \tau_0 \exp(\Delta E/kT) \tag{7}$$

where τ_0 is a constant and ΔE the activation energy. We define the crossover temperature $T^c(\nu)$ where the relaxation time becomes comparable with the observation time $1/\nu$ as

$$\tau = 1/\nu = 1/\nu_0 \exp[\Delta E/kT^c(\nu)] \tag{8}$$

where $\nu_0 = 1/\tau_0$. Therefore,

$$1/T^c(\nu) = -k(\log \nu - \log \nu_0)/\Delta E.$$

We plot $1/T^c(\nu)$ as a function of $\log \nu$ in figure 8. Although data points are not enough to give a definite conclusion, we may say that the crossover temperatures of low-temperature anomalies of the forced volume magnetostriction and of C_L for different frequencies lie on a common line, indicating the same relaxation mechanism for both anomalies. In this figure, the region above the line connecting the data points represents a rigid phase where the relaxation mechanism does not work. The extrapolation of the boundary line to $1/T \to 0$ intersects the horizontal axis at $\log \nu \sim 11$, which means that the lattice softening due to the relaxation process is not detected by a measurement faster than 10^{-11} s all over the temperature range. It is worthwhile noting that no softening is observed in the C_L mode by neutron scattering (Endoh 1979) whose characteristic time is faster than 10^{-11} s as indicated by an arrow in figure 8.

4.3. Origin of the low-temperature anomalies

As discussed in a previous section, it becomes evident that the rapid fall in the forced volume magnetostriction at a low temperature can be attributed to the same mechanism as the hardening of the lattice at low temperatures. In other words, the anomalous hardening is a result of reduction in the lattice softening due to the magnetovolume coupling at low temperatures. As seen in figure 6 of I, the degree of this reduction is 30–50% of the total magnetic softening, indicating that this anomaly is not a trivial phenomenon but that a substantial volume fraction of the crystal is concerned with the anomalous hardening.

It is reasonable to ascribe the decrease in the high-field susceptibility (Kondorskii and Sedov 1959) and the irreversible magnetization (Yamada *et al* 1980) at low temperatures to the same origin. It should be noted that these anomalies are observed at high magnetic fields. Therefore, it is difficult to ascribe them to re-entrant-type spin-glass freezing. As was discussed in section 3.3, the effect of spin-glass freezing is detected in both C_{44} and C_L at zero field as the suppression of the ΔE effect, which is not observed in $Fe_{65}Ni_{35}$ alloys. On the other hand, decreases in the AC susceptibility as well as the initial susceptibility of Fe–Ni Invar alloys under very weak fields may originate in a different mechanism as discussed by Miyazaki *et al* (1986) and Rancourt *et al* (1989, 1990).

One of the unsolved problems of the Invar effect is that the reduction in spontaneous magnetization with increasing temperature is much faster than that expected from spin-wave excitations (Ishikawa *et al* 1979). This discrepancy is removed on the same assumption that the response of the spin system to neutrons is possible only through the process without a volume change. On the other hand, another excitation, which causes a volume reduction, also contributes to the decrease in magnetization with increasing temperature. The mechanism of this excitation (hidden excitations (Ishikawa *et al* 1979)) is an essential problem of the Invar effect. The present analysis suggests that this excitation has a definite relaxation time, which is longer than the interaction time of thermal neutrons all over the temperature range. Therefore, neutron scattering measurements cannot detect this excitation.

4.4. Microscopic models to explain the low-temperature anomalies

As mentioned above, the rapid increase in C_L at low temperatures should be considered to be a result of the reduction in the magnetic softening of the bulk modulus. Accordingly we have a correct understanding of the low-temperature anomalies if we know the origin of the large magnetovolume coupling and the mechanism of its relaxation process in the Invar alloy, which is still a controversial problem. We make some comments on the models so far proposed.

A well known mechanism for explaining the low-temperature anomaly is partial antiferromagnetic ordering of Fe moments at low temperatures (Yamada *et al* 1980, Zahres *et al* 1988). However, this explanation is not satisfactory in many respects.

(i) Modern theories of spin glasses, which describe the magnetic state with mixed exchange interactions of both positive and negative signs, predict re-entrant-type spin-glass ordering below a critical temperature (Sherrington and Kirkpatrick 1975). This state is, however, very sensitive to the external magnetic field and the freezing temperature should decrease with increasing field (de Almeida and Thouless 1978) contrary to the present case.

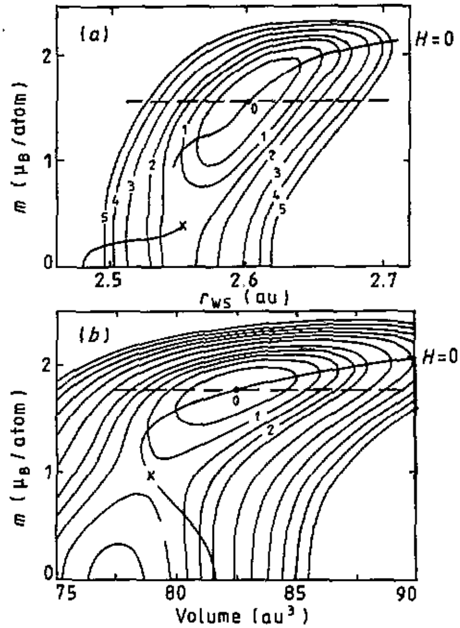

Figure 9. Total energy contours projected into the moment–volume (or the Wigner–Seitz radius r_{WS}) space for (*a*) Fe_3Ni (calculated by Moruzzi (1988)) and (*b*) Fe_3Pt (calculated by Entel and Schroter (1989)), where the contour lines are at 0.5 mRyd intervals for $E \leqslant 2.0$ mRyd and at 1 mRyd intervals for $E > 2.0$ mRyd: ——, $H = -dE/dM = 0$ solutions (the total energy along this curve gives E_{tot} versus volume curve, which is given in figure 10); – – –, $m = m_0$, the equilibrium moment (the total energy along this line gives the E_{tot} versus volume under a constant moment); ●, equilibrium position; ×, semiequilibrium position for the low-spin state.

(ii) From the magnetic phase diagram of $Fe_{65}(Ni_{1-x}Mn_x)_{35}$, it is expected that the substitution of Mn for Ni enhances the antiferromagnetic character of the system. On the contrary, both the onset temperature and the magnitude of ΔC_L decrease with increasing Mn content.

(iii) From analyses of the hyperfine field distribution (Shiga and Nakamura 1984), we have revealed that the ground state of the $Fe_{65}Ni_{35}$ alloy is almost purely ferromagnetic and the fraction of antiparallel coupled spins is at most 3% if they exist.

(iv) No anomalous decrease has been observed in the magnetization versus temperature curve of $Fe_{65}Ni_{35}$ around T_a (Ishikawa *et al* 1979), indicating that the number of antiparallel coupled spins is negligibly small if they existed. On the other hand, the increase in C_L at low temperatures is substantial as described in a previous section and, therefore, this increase can hardly be ascribed to the small amount of antiparallel spins.

The two γ-Fe states model of Weiss (1963) and its modified version (Chikazumi 1979) have been applied to explain the thermal expansion anomaly of the Invar alloy. Few attempts, however, have been made to explain the elastic anomalies on this basis. Hausch (1976) discussed qualitatively the origin of ΔC_L by introducing the third state of Fe atoms, i.e. the antiferromagnetic low-spin state. This assumption seems to be too artificial and not plausible because, from the hyperfine field distribution analysis, we observed a very small fraction of low-spin Fe for $x = 0$, which shows the largest ΔC_L effect.

Recently, precise total energy calculations have been carried out using a LSD approximation for Fe_3Ni (Moruzzi 1988) ordered alloys and the origin of thermal expansion anomaly of the Invar alloy is discussed on the basis of the total energy contours in the space of atomic radius r and the magnetic moment m which are shown in figure 9. We discuss the temperature dependence of the bulk modulus on this basis. If we neglect zero-point vibrations, the bulk modulus at 0 K is given by the second derivative

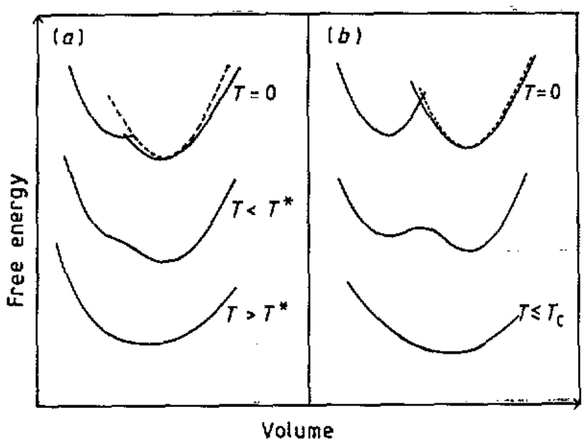

Figure 10. Schematic graphs of the free energy versus volume for (*a*) Fe_3Ni and (*b*) Fe_3Pt at $T = 0$ and at finite temperatures: – – –, E_{tot} versus volume curve for a constant magnetization B_M. The second derivative of these curves at the equilibrium position gives the bulk modulus.

of the total energy E_{tot} versus r curve plotted along the $H = 0$ line in the contour. On the other hand, the bulk modulus B_M under constant magnetization, which is shown in figure 6 of I, can be calculated in the same way from the E_{tot} versus r curve plotted along the $m = m_0$ line (horizontal line), in the contour. The E_{tot} versus r curves for both conditions are schematically shown in figure 10. It is clear that d^2E/dr^2 under constant m is larger than that at constant H at the equilibrium position. This explains the softening of the bulk modulus by an inverse effect of forced volume magnetostriction. A characteristic feature of the E_{tot} versus r curve is the existence of a non-magnetic branch at small r with a small energy difference. At low temperatures, this non-magnetic branch has no effect on $(d^2E/dr^2)_0$ but at elevated temperatures this part is thermally incorporated into the lattice distortion and an effective curvature of the free energy versus r curve becomes smaller. This may be a possible origin of the low-temperature elastic anomaly.

It is interesting to compare the temperature dependence of the bulk modulus of $Fe_{65}Ni_{35}$ with that of the Fe_3Pt alloy which is a typical Invar alloy with a chemically ordered structure. The bulk modulus of Fe_3Pt strongly softens below the Curie temperature but again increases rapidly with decreasing temperature and, at 0 K, the magnetic softening disappears as shown in figure 11 (Hausch 1974). This contrasting behaviour of Fe_3Pt may be explained by the features of the total energy contour for Fe_3Pt (Entel and Schroter 1989) which are different from those for Fe_3Ni. As seen in figure 9(*b*), the equilibrium curve for $H = 0$ is nearly horizontal, which means that the softening due to magnetovolume coupling is small at 0 K as observed in the experiments. In the E_{tot} versus r curve, there is also a non-magnetic branch. In this case, however, the non-magnetic curve is separated from the magnetic curve by a fairly-high-energy barrier. Therefore, it is understandable that the softening does not appear in the low-temperature region.

As discussed above, the total energy contours give a qualitative explanation of the effect of the magnetic state on the bulk modulus, including the low-temperature anomaly in Fe–Ni Invar and the different behaviours of Fe–Ni and Fe–Pt systems. However, they give neither the estimate of the relaxation time, which is essential in understanding of the low-temperature anomaly, nor the effect of spin fluctuations on the bulk modulus,

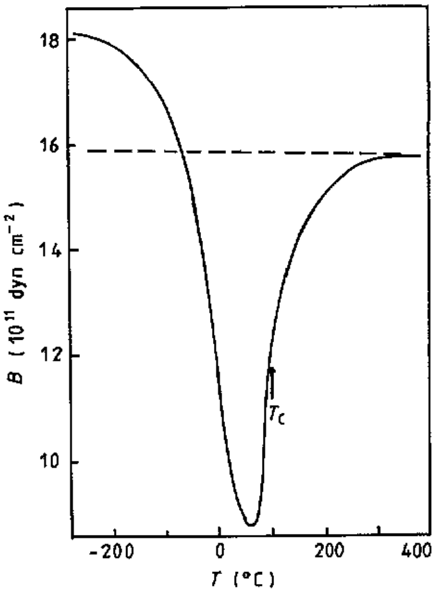

Figure 11. Temperature dependence of the bulk modulus of Fe–28 at.% Pt. (After Hausch 1974.)

which is important at high temperatures particularly near the Curie temperature. It is difficult to understand the existence of a long-time relaxation phenomenon observed in the forced volume magnetostriction (Schlosser *et al* 1969) only from the electronic process. There might be some other semimicroscopic processes which are accompanied by a volume change spread over a large spatial region. In this connection, we should note the magnetic inhomogeneous structure in the $Fe_{65}Ni_{35}$ Invar observed by small-angle neutron scattering (Takeda *et al* 1987, Menshikov 1979). Although the origin of this structure is not clear, the high sensitivity of the magnetic state of Fe atoms in the FCC lattice to their local environment may lead to the co-operative formation of magnetically weak regions with a small lattice constant. The volume fraction of these regions presumably changes by applying a magnetic field or a longitudinal stress with a short but definite time interval. We propose that such a process may play an important role in the magnetovolume coupling with a definite relaxation time in the Fe–Ni Invar alloys.

5. Concluding remarks

(1) An anomalous increase ΔC_L in the longitudinal modulus at low temperatures was observed in both $Fe_{100-C}Ni_C$ and $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ Invar alloys. ΔC_L and the onset temperature decrease with increasing C in $Fe_{100-C}Ni_C$ and with increasing x in $Fe_{65}(Ni_{1-x}Mn_x)_{35}$.

(2) ΔC_L depends upon the frequency of ultrasound for velocity measurements. The onset temperature of ΔC_L increases with increasing frequency, suggesting a relaxation mechanism in the magnetovolume coupling.

(3) ΔC_L can be explained by the same mechanism which causes a rapid decrease in the forced volume magnetostriction at low temperatures. The difference in the onset temperature is ascribed to the relaxation process. The absence of magnetic softening in

the longitudinal phonon measured by inelastic neutron scattering is also explained by assuming the relaxation process.

(4) The effect of re-entrant-type spin-glass freezing was detected in the shear modulus C_{44} and in the longitudinal modulus C_L of $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ for $x \geqslant 0.04$ as a suppression of the ΔE effect due to domain wall motions. Such a phenomenon was not observed in the Fe–Ni system, indicating that ΔC_L for the Invar alloy cannot be ascribed to the spin-glass freezing in the sense of the Sherrington–Kirkpatrick model but originates in an intrinsic electronic process.

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