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Magnetoelasticity of $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ invar alloys: I. Temperature and field dependences of the elastic constants

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Abstract. Temperature and field dependences of the elastic constants of $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ invar alloys have been measured by an ultrasonic pulse–echo technique from 4.2 up to 750 K. All of the elastic moduli, C_L, C_{44} and C', show softening due to magnetoelastic coupling. The softening of shear moduli, ΔC_{44} and $\Delta C'$, is proportional to the square of the magnetisation. The softening of the bulk modulus is mainly ascribed to an inverse effect of the volume magnetostriction, ΔB_ω. We have shown that magnetic ordering gives rise to an increase of the bulk modulus, ΔB_m. The large negative field dependence of shear moduli in the para-process is explained as a result of the increase of magnetisation caused by an external field. The positive field dependence of the bulk modulus for $x < 0.1$ and the negative one for $x > 0.1$ are also explained by taking into account the magnetic contributions to the bulk modulus, ΔB_ω and ΔB_m.

1. Introduction

Recent developments in the electron theory of magnetism give a deeper understanding of the so-called invar problem. Among them, the origin of the thermal expansion anomaly is most extensively discussed (Nakamura 1976) and successfully explained in terms of the itinerant electron model by taking accoung of spin fluctuations (Moriya and Usami 1980, Hasegawa 1981, Kakehashi 1981).

Another significant anomaly of invar-type alloys is observed in the temperature dependence of the elastic constants. All of the elastic moduli exhibit softening below the Curie temperature (Hausch and Warlimont 1973). The softening of the longitudinal modulus, C_L, or Young's modulus, E, may be explained as an inverse effect of the

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volume magnetostriction, $\mathrm{d}\omega/\mathrm{d}H$, which are connected to each other by a thermodynamic relation. For Young's modulus, the softening can be estimated by Döring's relation (Döring 1939),

$$\frac{\Delta E}{E^2} = \frac{1}{9}\frac{(\mathrm{d}\omega/\mathrm{d}H)^2}{\chi_{\mathrm{hf}}} \tag{1}$$

where χ_{hf} is the high-field susceptibility.

Many authors (Hausch 1973, 1974, Deryabin *et al* 1985) have claimed that this effect is not enough to explain the softening of Young's modulus below the Curie temperature and ascribed it to an intrinsic effect due to magnetic ordering. On the contrary, Schlosser (1973) has shown that the decrease of the bulk modulus is well explained as a result of magnetovolume coupling. It is still controversial whether the inverse effect of the volume magnetostriction is enough to explain the softening of the bulk modulus. In other words, it is not clear whether the intrinsic change of bulk modulus caused by magnetic ordering is positive or negative.

In this study, we have measured the temperature dependence of the elastic constants of invar-type $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ alloys with $0 \leqslant x \leqslant 0.23$ from 4.2 up to 750 K. This system shows distinct magnetovolume effects and has relatively low Curie temperatures. These characteristics are suitable to analyse the magnetoelastic coupling.

So far, little attention has been paid to the effect of external field on elastic constants beyond technical saturation, which may give fruitful information on the magnetoelastic coupling. We have measured the elastic constants as a function of applied field and found a very large field effect. Taking account of both temperature and field dependences of the elastic constants, we discuss the origin of the large magnetoelastic coupling in invar alloys.

In addition to the lattice softening below the Curie temperature, the Fe–Ni invar alloys exhibit a sharp increase of the longitudinal modulus at low temperatures (Fletcher 1969, Hausch 1976). We will discuss this low-temperature anomaly of elastic moduli in a separate paper.

2. Experimental details

Ingots of $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ alloys were prepared by argon arc melting from raw metals of 99.9% purity. Single crystals were grown by the Bridgman method in an induction furnace at a growth rate of about 1 cm h^{-1}. Cubes of about 10 mm length with (110) surfaces were cut from the single crystals. They were subjected to homogenising annealing at 1150 °C for two days and then quenched into ice-water. Two parallel (110) surfaces were subsequently polished by an automatic polishing machine with diamond paste. The difference in length between two (110) surfaces was maintained within 10 μm to obtain good quality of echo trains.

The composition of the specimens was determined by chemical analysis. For the ternary alloys, vaporisation of manganese during the growth of single crystals gives rise to inhomogeneity within 1 at.% for each element. The results of chemical analysis given in table 1 are the composition near to the cube sample for ultrasonic measurements.

Sound velocities were measured by a standard pulse–echo overlapping technique at 10 MHz in the temperature range from 4.2 up to 750 K under applied magnetic fields. Details of the equipments were given elsewhere (Shiga *et al* 1985). Appropriate adhesives were used to bond a quartz transducer on a surface of the single-crystal sample. A

Table 1. Result of chemical analysis of $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ alloys.

No	Fe (at. %)	Ni (at. %)	Mn (at. %)	x
00	65.05	34.95	–	0.0
04	65.76	32.93	1.31	0.038
09	65.01	31.79	3.20	0.091
13	64.99	30.31	4.70	0.134
22	65.26	27.07	7.67	0.221

thermoplastic adhesive was used for the measurements below room temperature. For high-temperature measurements, we have tried many adhesives and finally found that quasi-waterglass cement (Fisher and Renken 1963) is the most preferable for the present samples. During the heating process of the measurements, however, the cement occasionally becomes unstable around 400 K and appreciable attenuation was observed particularly for shear-wave measurements. Therefore, supplementary measurements were made from room temperature up to 400 K using Aron-alpha as the coupling agent.

The temperature of the sample cell was controlled within 1 K using a proportional-integral-derivative (PID) controller. The external magnetic field was applied by an electromagnet up to 20 kOe.

The three elastic constants were determined from the observed velocities using the following relations:

$$C_L = \rho V_l^2 \qquad C_{44} = \rho V_{t1}^2 \qquad C' = \rho V_{t2}^2 \tag{2}$$

where V_l is the velocity of longitudinal waves propagating along the [110] direction, V_{t1} and V_{t2} are the velocities of shear waves polarised in the [001] and [1$\bar{1}$0] directions, respectively, and ρ is the density. The bulk modulus, B, is calculated by the equation

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

The relative accuracy of velocity measurement is very high, one part in 10^5. However, the absolute value of elastic constants includes errors from several origins, for example, a decrease of velocity within the adhesives. In fact, the room-temperature value obtained in a series of measurements at lower temperatures differs slightly from that found in a series extending upwards from room temperature, usually by about 1%. Since the low-temperature coupling agent is more reliable, the high-temperature values were fitted to low-temperature values by adding a constant to obtain a smoothed curve. Corrections for the length change and the change of density due to thermal expansion have been made by using the thermal expansion curves of these alloys (Hayase *et al* 1971); however, this effect is not appreciable, at most 1% for C_L of the alloy with $x = 0.22$.

3. Results

3.1. Temperature dependence of elastic constants

The temperature dependence of the elastic constants C_L, C_{44} and C' of $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ was measured under external fields in steps of 5 kOe up to 20 kOe, applied along the

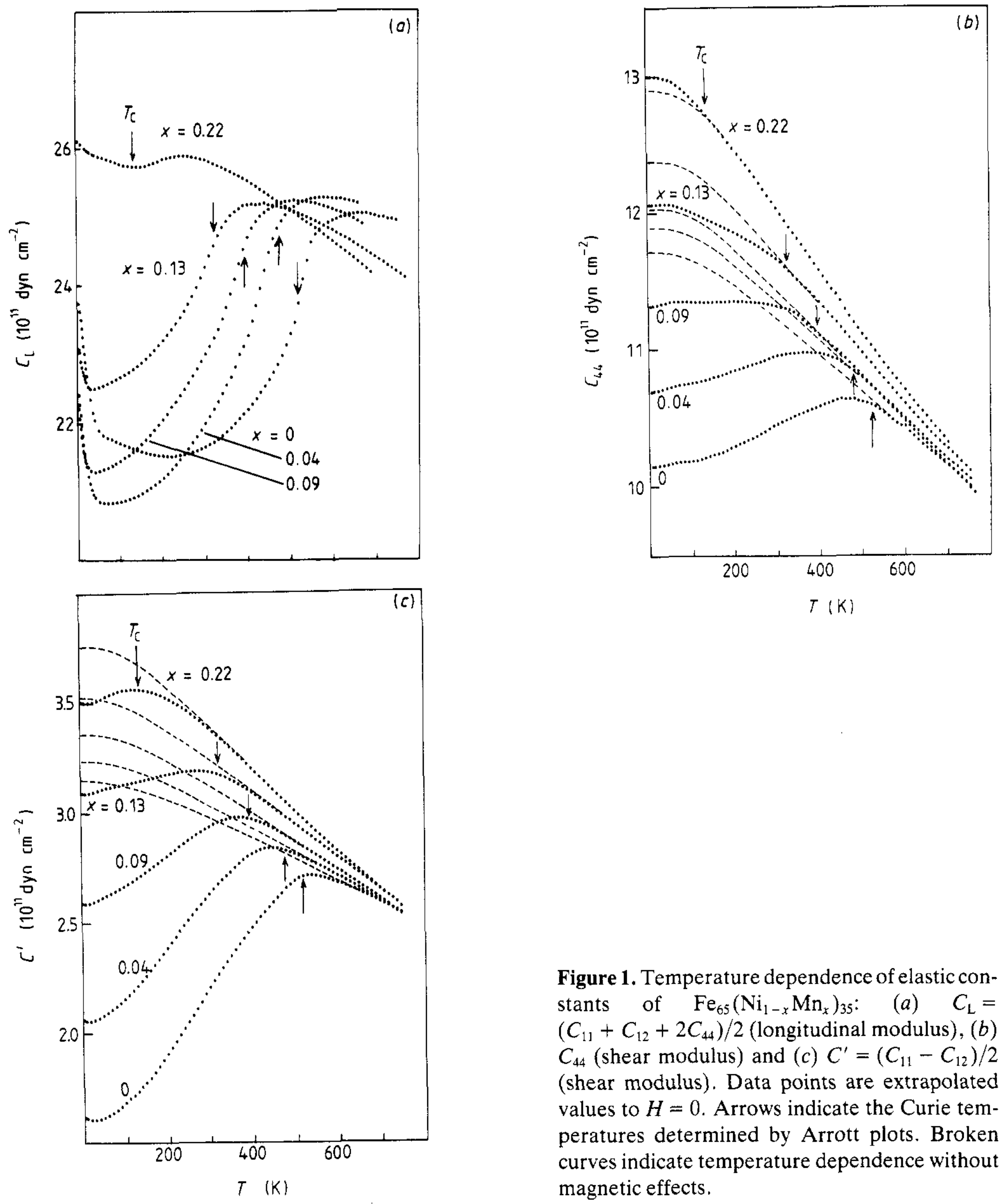

Figure 1. Temperature dependence of elastic constants of $Fe_{65}(Ni_{1-x}Mn_x)_{35}$: (*a*) $C_L = (C_{11} + C_{12} + 2C_{44})/2$ (longitudinal modulus), (*b*) C_{44} (shear modulus) and (*c*) $C' = (C_{11} - C_{12})/2$ (shear modulus). Data points are extrapolated values to $H = 0$. Arrows indicate the Curie temperatures determined by Arrott plots. Broken curves indicate temperature dependence without magnetic effects.

⟨1 1 0⟩ direction perpendicular to the direction of the wave propagation vector. The zero-field values were obtained by a linear extrapolation of the high-field data to zero field. Therefore, the temperature dependence of the elastic constants at $H \to 0$, which is shown in figure 1, is free from the ordinary ΔE effect.

The shear moduli, C_{44} and C', exhibit similar temperature dependences. Both moduli soften below the Curie temperature, which is indicated by arrows in the figures. The elastic constant of a normal crystal decreases with increasing temperature. The rate of decrease is proportional to the internal energy, which is given by the Debye model (Lakkad 1971) as

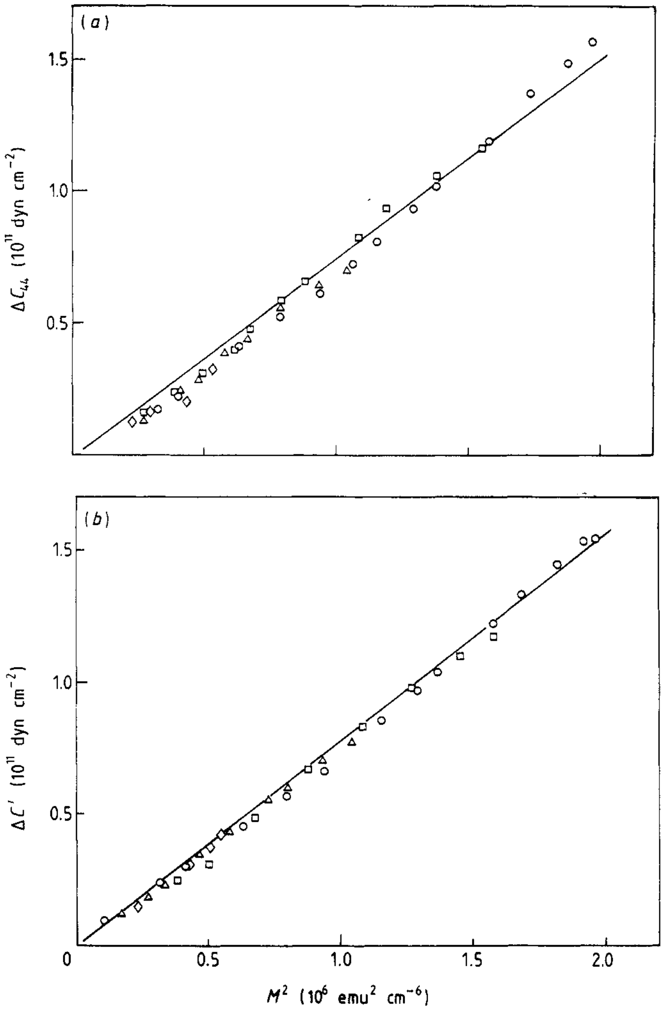

Figure 2. Magnetic softening ΔC versus M^2: (*a*) ΔC_{44} versus M^2 and (*b*) $\Delta C'$ versus M^2 of $Fe_{65}(Ni_{1-x}Mn_x)_{35}$. Symbols: (○) $x = 0$, (□) $x = 0.04$, (△) $x = 0.09$, (◇) $x = 0.13$. Data on spontaneous magnetisation, M, are after Shiga (1967).

$$C = C_0 - AF(T/\Theta_D) \qquad F(T/\Theta_D) = 3(T/\Theta_D)^4 \int_0^{\Theta/T} \frac{x^3\,dx}{e^x - 1} \tag{4}$$

where C_0 and A are constants and Θ_D is the Debye temperature.

We have estimated the elastic constants of this system in a hypothetical paramagnetic state by using this function where the constant A was chosen to fit the linear part of the observed curve above the Curie temperature. The Debye temperature was assumed to be 450 K for all samples, which is the value for Fe–50Ni alloy (Bower *et al* 1968). The results of this estimation are shown by broken curves in figures 1(*b*) and (*c*). The difference from the observed curve, which may be ascribed to a magnetic origin, is denoted as ΔC hereafter. In figure 2, ΔC_{44} and $\Delta C'$ are plotted against the square of the magnetisation, taken from Shiga (1967). As seen in the figure, both ΔC_{44} and $\Delta C'$

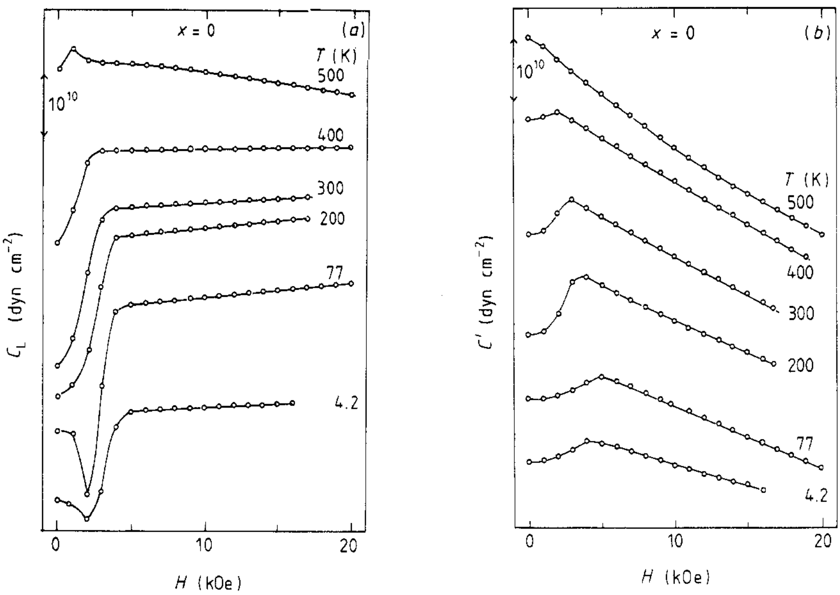

Figure 3. Field dependence of elastic constants of $Fe_{65}Ni_{35}$ at various temperatures: (*a*) C_L and (*b*) C'. Data are arranged in order of temperature. The absolute values of elastic constants at 5 kOe for each temperature are as follows (in units of 10^{12} dyn cm^{-2}): $C_L = 23.25$ (4.2 K), 21.87 (77 K), 21.54 (200 K), 21.67 (300 K), 22.20 (400 K), 23.30 (500 K); $C' = 1.57$ (4.2 K), 1.58 (77 K), 1.84 (200 K), 2.13 (300 K), 2.39 (400 K), 2.57 (500 K).

are proportional to M^2 with nearly the same coefficient. It should be noted that the proportionality coefficients are almost the same for both ΔC_{44} and $\Delta C'$ in spite of appreciable difference in the absolute values of moduli themselves.

The temperature dependence of the longitudinal modulus also exhibits considerable softening. In this case, however, the softening starts far above the Curie temperature. Therefore, it is difficult to estimate the modulus in the hypothetical non-magnetic state. Furthermore, at low temperatures, a sharp increase is observed. It is clear that the magnitude of the softening cannot be described by a linear function of M^2, in contrast to that of the shear modulus. An essential difference between longitudinal and transverse waves is that the former gives rise to a volume change but not the latter. In the next section, we discuss the softening of the bulk modulus, which is physically a more simple quantity.

3.2. Field dependence of elastic constants

The external field dependence of each elastic constant has been measured up to 500 K. Typical results are shown in figures 3 and 4. The strong field dependence at low fields is due to the ordinary ΔE effect caused by domain-wall motions. The field dependence above 5 kOe can be ascribed to the increase of domain magnetisation (para-process), with which we are concerned hereafter. For $x = 0$ (figure 3), dC_L/dH is positive at low temperatures and changes sign above 500 K. On the other hand, both shear moduli show negative field dependence at all temperatures. These results are consistent with a previous report by Hausch (1976). For $x = 0.09$ (figure 4) all elastic moduli exhibit large

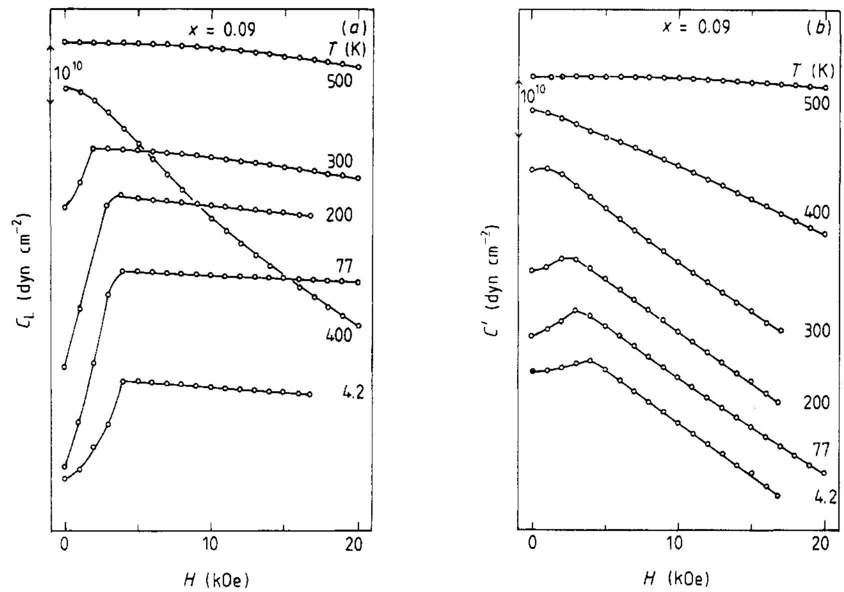

Figure 4. Field dependence of elastic constants of $Fe_{65}(Ni_{0.91}Mn_{0.09})_{35}$ at various temperatures: (*a*) C_L and (*b*) C'. Data are arranged in order of temperature. The absolute values of elastic constants at 5 kOe for each temperature are as follows (in units of 10^{12} dyn cm^{-2}): C_L = 22.18 (4.2 K), 21.38 (77 K), 22.04 (200 K), 22.99 (300 K), 24.60 (400 K), 25.24 (500 K); C' = 2.47 (4.2 K), 2.53 (77 K), 2.67 (200 K), 2.82 (300 K), 2.90 (400 K), 2.86 (500 K).

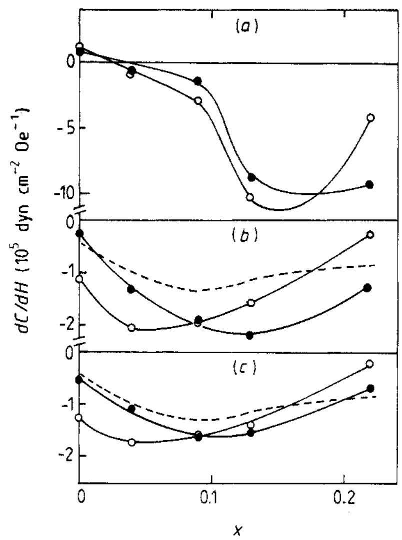

Figure 5. Field derivatives of elastic constants after saturation at 4.2 (●) and 300 K (○): (*a*) dC_L/dH, (*b*) dC_{44}/dH and (*c*) dC'/dH. Broken curves indicate calculated values for 4.2 K by using equation (14). Data on M and χ_{hf} are after Wada *et al* (1985).

negative field dependence. The extremely large negative field effect at 400 K is ascribed to a large susceptibility at this temperature, which is just above the Curie temperature (T_C = 390 K). The concentration dependence of dC/dH at 4.2 and 300 K is plotted in figure 5. Except C_L for $x = 0$, all of dC/dH are negative and show a minimum around

$x = 0.1$. As far as we know, the present system shows the largest field dependence of elastic constants in the para-process.

4. Discussion

4.1. Magnetic anomaly of shear moduli

Phenomenologically, the M^2 dependence of ΔC can be described on the basis of the Landau expansion of free energy, taking account of strain dependence as

$$F(M, \varepsilon) = F(0, 0) + A(\varepsilon)M^2 + \ldots. \tag{5}$$

The coefficient A may be expanded as

$$A(\varepsilon) = A(0) + \Sigma A'_{ij}\varepsilon_{ij} + \tfrac{1}{2}\Sigma A''_{ijkl}\varepsilon_{ij}\varepsilon_{kl} + \ldots \tag{6}$$

where ε_{ij} are strain tensors. Since the elastic modulus is the second derivative of the free energy with respect to strain, the magnetic contribution ΔC is proportional to M^2. Microscopic theories explaining ΔC have been developed by several authors. On the basis of the Heisenberg model, Hausch and Warlimont (1973) proposed a model assuming appropriate values of the first and second derivatives of the exchange integral with respect to strain. First-principle calculations, however, should be given on the basis of a band theory. Steinemann (1979) has formulated the magnetic effects on the shear moduli on the basis of the Stoner model and analysed the shear moduli of Fe–Ni alloys, giving parameters of deformation potentials. No theoretical estimation of ΔC based on band calculations has been performed so far.

The present results clearly show that both ΔC_{44} and $\Delta C'$ vary in proportion to M^2 up to near T_C. It should be noted that ΔC of shear moduli disappears just above T_C. This fact indicates that the softening of shear moduli correlates to long-range magnetic order, in contrast to that of the longitudinal modulus, which does not depend on M^2 and remains far above T_C.

4.2. Magnetic anomaly of bulk modulus

The bulk modulus, B, is the simplest elastic constant to discuss in terms of thermodynamics and microscopic theories, while it is difficult to measure directly. We can calculate it from the present data using equation (3). The results are shown in figures 6 and 7. The general shape of the temperature dependence is nearly the same as that of C_L. It should be noted that the softening of the bulk modulus starts from far above the Curie temperature. For $x \leqslant 0.09$, B still increases with increasing temperature at the highest temperature of our measurements. Therefore, it is not possible to estimate the bulk modulus in a hypothetical paramagnetic state from the present data only. Recently, Renaud and Steinemann (1989) have measured the elastic constants of Fe–Ni alloys at very high temperatures up to 1500 K. In figure 6, the calculated bulk modulus from their results for 36%Ni is shown with the present result for $x = 0$. Both data agree well in the temperature range of our measurements. As seen in the figure, B decreases almost linearly above 1000 K. Assuming no magnetic contribution above 1000 K, we have estimated the bulk modulus in the hypothetical paramagnetic state, $B_{M=0}$, by the same method used for shear moduli. The $B_{M=0}$ thus obtained is shown by a broken curve in figure 6. The difference between the observed bulk modulus $B_{H\to 0}$ and $B_{M=0}$,

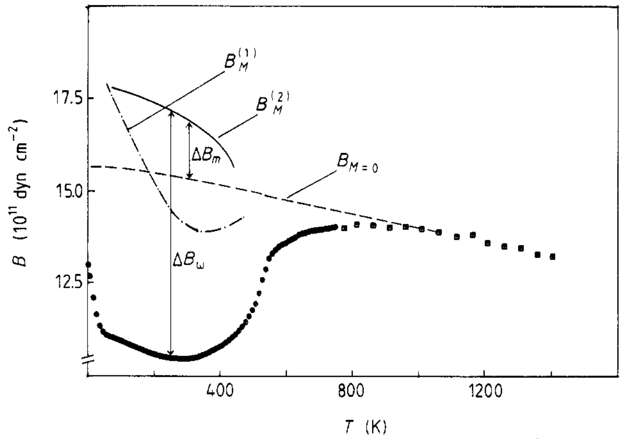

Figure 6. Temperature dependence of the bulk modulus of $Fe_{65}Ni_{35}$ (○) by present work and $Fe_{64}Ni_{36}$ (□) after Renaud and Steinemann (1989). Broken curve indicates the extrapolated bulk modulus from high temperatures corresponding to $B_{M=0}$. Chain curve is the bulk modulus under constant magnetisation, $B_M^{(1)}$, estimated by equation (8). Full curve represents $B_M^{(2)}$ estimated by equation (11). The difference from the broken curve corresponds to an intrinsic change of the bulk modulus due to magnetic ordering, ΔB_m. The difference between B_M and B_H corresponds to ΔB_ω.

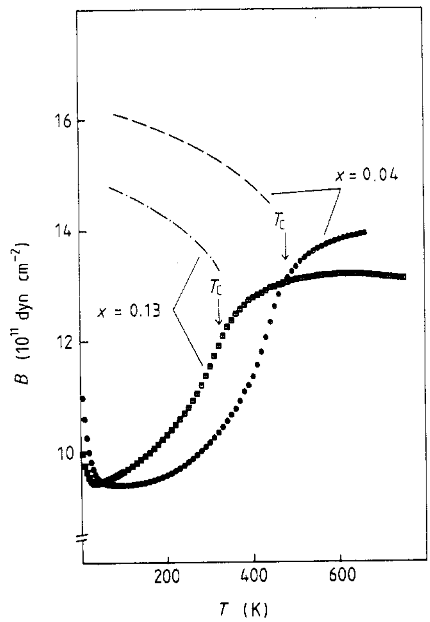

Figure 7. Temperature dependence of the bulk modulus of $Fe_{65}(Ni_{1-x}Mn_x)_{35}$: (○) $x = 0.04$, (□) $x = 0.13$. Broken and chain curves indicate calculated values of B_M for $x = 0.04$ and 0.13, respectively.

$\Delta B = B_{H\to 0} - B_{M=0}$, should be ascribed to a magnetic origin. However, it is clear that ΔB is not proportional to M^2, in contrast to shear moduli. The magnetic effects on ΔB may be divided into two contributory terms. One is a purely thermodynamic effect

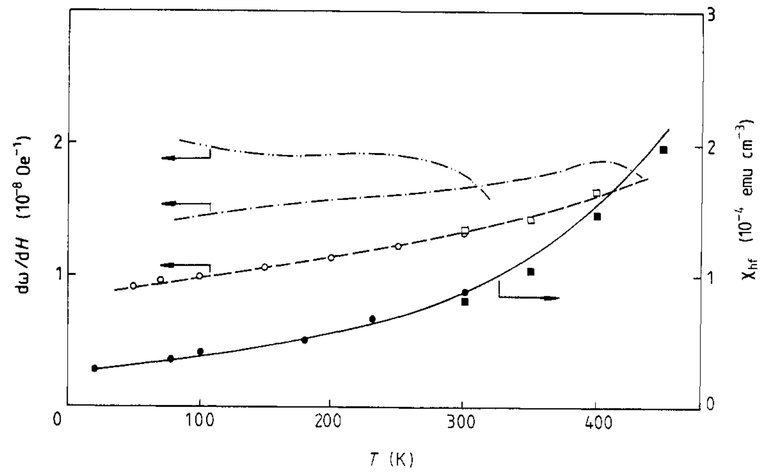

Figure 8. Temperature dependence of the high-field susceptibility, χ_{hf}, of $Fe_{65}Ni_{35}$ used in the estimation of B_ω. Data points: (●) after Yamada *et al* (1977), (■) after Yamada *et al* (1983). Temperature dependence of the forced volume magnetostriction $d\omega/dH$ of $Fe_{65}Ni_{35}$: (----) used for the estimation of B_ω, (○) after Zahres *et al* (1988), (□) after Ishio and Takahashi (1985). Temperature dependence of $d\omega/dH$ of $Fe_{65}(Ni_{1-x}Mn_x)_{35}$: (-·-·-) $x = 0.5$, (-··-··-) $x = 0.14$ (unpublished data after Hayase).

that originates in the volume magnetostriction, ΔB_ω, and the other an intrinsic effect accompanied by magnetic ordering, ΔB_m, as

$$\Delta B = \Delta B_\omega + \Delta B_m. \tag{7}$$

Strictly speaking, the magnetic ordering gives effects on the bulk modulus in two ways. First, as a result of the large positive spontaneous volume magnetostriction, the thermal expansion curve of invar alloys deviates upwards from the value expected through extrapolation from the paramagnetic region below the Curie temperature. This relative expansion of the lattice gives rise to a decrease in the bulk modulus, i.e. a negative ΔB_m, because of the non-harmonic term in the atomic potentials. Secondly, the intrinsic change in the bulk modulus accompanied by magnetic ordering is probably caused by 3d band polarisation. As discussed below, ΔB_m is positive in total and, therefore, the second effect should be positive and dominant. In the present analysis, we do not distinguish these two contributions and define the total effect as ΔB_m.

On the other hand, $\Delta B_\omega = B_M - B_H$ is given by the thermodynamic relation

$$1/B_H - 1/B_M = (d\omega/dH)^2/\chi_{hf} \tag{8}$$

where B_H and B_M are the bulk moduli under constant field and constant magnetisation, respectively, $d\omega/dH$ is the forced volume magnetostriction and χ_{hf} is the high-field susceptibility. It is possible to evaluate B_M from the observed value of $B_{H\to 0}$ and experimental data on $d\omega/dH$ and χ_{hf}.

There are several experimental data on $d\omega/dH$ and χ_{hf} for the invar alloys, but the concentrations are not exactly the same as the present alloy of 35 at.%Ni. Plots of $d\omega/dH$ and χ_{hf} for $x = 0$, and $d\omega/dH$ for $x = 0.05$ and $x = 0.13$, which we used for estimating B_M, are shown in figure 8. Using these values and equation (8), we have estimated B_M of $Fe_{65}N_{35}$ as shown by the chain curve in figure 6. We may regard the difference between

B_M and $B_{M=0}$ as the intrinsic change of the bulk modulus, ΔB_m. The value of ΔB_m estimated by equation (8) exhibits a somewhat peculiar temperature dependence, changing its sign from positive to negative around 200 K. It should be noted that χ_{hf} consists of several components. The total high-field susceptibility may be described by

$$\chi_{hf} = \chi_b + \chi_{sw} + \chi_{tech} \qquad (9)$$

where χ_b is the intrinsic susceptibility due to band polarisation, χ_{sw} the spin-wave susceptibility and χ_{tech} is that due to an incomplete technical saturation process. Among them, it is clear that χ_{tech} contributes neither to volume magnetostriction nor to ΔB_ω. We (Shiga 1981) have shown that the forced volume magnetostriction is mainly caused by the spin polarisation of 3d bands. Therefore, $d\omega/dH$ is given

$$d\omega/dH = 2\kappa CM\chi_b \qquad (10)$$

where κC is the magnetovolume coupling constant. It is reasonable to assume that only χ_b is responsible for ΔB_ω. Substituting equation (10) into equation (8), we have

$$1/B_H - 1/B_M = 2\kappa CM(d\omega/dH). \qquad (11)$$

The full curve in figure 6 indicates B_M calculated by equation (11), where we used $\kappa C = 1.3 \times 10^{-8}\,\mathrm{cm^6\,emu^{-2}}$, which was estimated by the analysis of magnetovolume effects (Shiga 1981). In figure 7, results of the same analysis for $x = 0.04$ and 0.13 are shown. These analyses have revealed a positive ΔB_m over all temperatures. A positive value of ΔB_m is consistent with the field dependence of the bulk modulus, as discussed later.

So far, many authors have claimed that the inverse effect of the volume magnetostriction is not enough to explain the softening of the elastic modulus of Fe–Ni invar alloys and the intrinsic magnetic contribution, ΔB_m, should be negative. However, most authors have discussed the softening of Young's modulus on the basis of the Döring relation (equation (1)). As pointed out by Wohlfarth (1974), equation (1) neglects the magnetic effect of the shear modulus on the softening of Young's modulus. He gave the correct relation as

$$\frac{\Delta E}{E} = \frac{1}{9}\frac{\Delta B}{B} + \frac{8}{9}\frac{\Delta G}{G}. \qquad (12)$$

We have shown in the previous section that the magnetic contributions to the shear moduli, ΔC_{44} and $\Delta C'$, are large and negative for invar alloys. It is likely that the negative ΔE mainly originates in the softening of the shear moduli. Furthermore, since there is uncertainty related to the choice of χ_{hf}, we believe that equation (11) gives the most reliable estimation of ΔB_ω. A similar claim was given by Schlosser (1973).

From a theoretical point of view, Wohlfarth (1976) and Hausch (1977) have given an itinerant electron description for the magnetic contribution to the bulk modulus. They derived an explicit formula for ΔB_m as

$$\Delta B_m = \tfrac{5}{3}(3 - 2I/I_b)\omega_m. \qquad (13)$$

Here, I and I_b are the effective and bare intra-atomic Coulomb interactions and ω_m is the spontaneous volume magnetostriction. Since I is always smaller than I_b and $\omega_m > 0$ for the invar alloy, ΔB_m should be positive. This means that the bulk modulus is expected to increase by magnetic ordering, as concluded in the present analysis. Sayers (1979) evaluated the effect of ferromagnetic order on the bulk modulus using a simple band model and has shown that ΔB_m is positive for the 3d band.

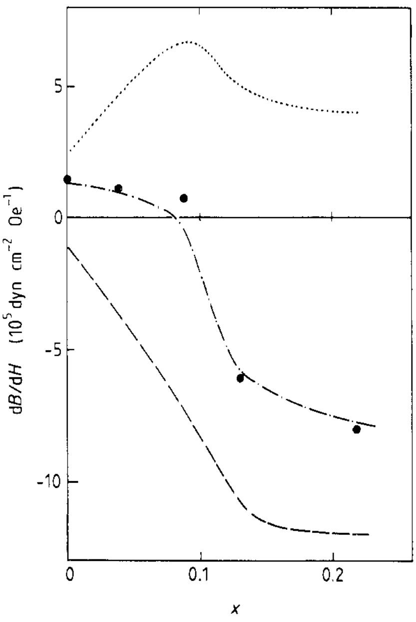

Figure 9. Concentration dependence of $\mathrm{d}B/\mathrm{d}H$ at 4.2 K of $Fe_{65}(Ni_{1-x}Mn_x)_{35}$: (●) observed values, (---) calculated value of $\mathrm{d}B_\omega/\mathrm{d}H$, (·········) calculated value of $\mathrm{d}B_m/\mathrm{d}H$, (—·—·—) $\mathrm{d}B_\omega/\mathrm{d}H + \mathrm{d}B_m/\mathrm{d}H$ for $k' = 4.5 \times 10^5$ dyn cm^4 emu^{-2}.

Finally, we point out the marked difference in the temperature dependences between shear and bulk moduli near the Curie temperature. The temperature dependence of the shear modulus exhibits a maximum at T_C determined by Arrott plots and the magnetic anomaly disappears just above T_C. In contrast, the bulk modulus sharply increases at T_C and the magnetic anomaly persists far above T_C. Therefore, it is likely that ΔB correlates with short-range magnetic order or spin fluctuations and ΔC_{44} and $\Delta C'$ with the long-range magnetic order parameter.

4.3. Field dependence of shear and bulk moduli

As seen in figure 5, the field dependence of both the shear moduli, $\mathrm{d}C_{44}/\mathrm{d}H$ and $\mathrm{d}C'/\mathrm{d}H$, is negative and their magnitudes increase markedly with increasing Mn content, x, up to $x = 0.1$. It is reasonable to consider that the softening of the shear moduli caused by an external field can be ascribed to the same origin as that caused by magnetic ordering, ΔC. Since ΔC is proportional to M^2, we may write

$$\mathrm{d}C/\mathrm{d}H = 2kM(\mathrm{d}M/\mathrm{d}H) = 2kM\chi_{\mathrm{hf}}. \tag{14}$$

Here, k is a constant. Using the constant k determined by the ΔC versus M^2 plot and experimental data on M and χ_{hf} (Wada *et al* 1985), we can estimate $\mathrm{d}C/\mathrm{d}H$. The results are shown by broken curves in figure 5. For C', the field dependence is almost explained as a result of the increase of magnetisation induced by the external field. On the other hand, the field dependence of the bulk modulus is positive for $x < 0.1$ and becomes negative for $x > 0.1$ (figure 9). We also discuss this on the same basis as the temperature effects. Since the magnetic contributions to the bulk modulus can be given by $\Delta B = \Delta B_\omega + \Delta B_m$, we may write

$$\mathrm{d}B/\mathrm{d}H = \mathrm{d}(\Delta B_\omega)/\mathrm{d}H + \mathrm{d}(\Delta B_m)/\mathrm{d}H. \tag{15}$$

From equation (11), we have

$$\mathrm{d}(\Delta B_\omega)/\mathrm{d}H = -2\kappa C B_H^2\left(\frac{\mathrm{d}M}{\mathrm{d}H}\frac{\mathrm{d}\omega}{\mathrm{d}H} + M\frac{\mathrm{d}^2\omega}{\mathrm{d}H^2}\right). \tag{16}$$

Neglecting the second derivative of ω and using equation (10), we have

$$\mathrm{d}(\Delta B_\omega)/\mathrm{d}H = -4(\kappa C)^2 B_H^2 M\chi_b^2. \tag{17}$$

Assuming $\Delta B_m = k'M^2$ and $\chi_b = \chi_{hf}$, we have

$$\mathrm{d}(\Delta B_m)/\mathrm{d}H = 2k'M\chi_{hf}. \tag{18}$$

Therefore,

$$\mathrm{d}B/\mathrm{d}H = -4(\kappa C)^2 B_H^2 M\chi_{hf}^2 + 2k'M\chi_{hf}. \tag{19}$$

Here, the first term is always negative and the second term is positive. It should be noted that the first term is proportional to χ_{hf}^2 and the second to χ_{hf}. We can expect a positive $\mathrm{d}B/\mathrm{d}H$ for a small χ_{hf} and negative for a large χ_{hf}. The first term, which was calculated from experimental data (Wada *et al* 1985) and the magnetovolume coupling constant, κC ($=1.3 \times 10^{-8}$ cm^6 emu^{-2}), is shown by the broken curve in figure 9. We have determined the magnetoelastic coupling constant, k', to fit the observed data of $\mathrm{d}B/\mathrm{d}H$. The contribution of the second term is shown by the dotted curve. The total effect is shown by the chain curve, being in good agreement with the experimental results. The value of k' determined here is larger than that expected from the temperature dependence of ΔB_m by about a factor of 3. The larger magnetoelastic coupling for the field effect at 4.2 K than that estimated by the ΔC versus M^2 plot is also observed in shear moduli as shown in figure 5. This trend may be explained as follows. The high-field susceptibility at 0 K is only due to 3d band polarisation. On the other hand, the decrease of the spontaneous magnetisation by raising the temperature does not mean the decrease of band polarisation because of spin fluctuations. Assuming that the elastic moduli couple to the degree of 3d band polarisation but not to the spontaneous magnetisation as seen in a magnetovolume coupling (Shiga 1981), we expect a larger coupling constant for $\mathrm{d}C/\mathrm{d}H$ and $\mathrm{d}B/\mathrm{d}H$ at 4.2 K. The large positive coupling constant estimated from $\mathrm{d}B/\mathrm{d}H$ strongly supports the positive contribution of ΔB_m.

5. Conclusions

The shear moduli C_{44} and C' soften just below the Curie temperature. The magnitude of the softening, ΔC, is proportional to the square of the spontaneous magnetisation, where the proportionality constant is common to all concentrations.

The bulk modulus is also reduced by effects of magnetic origin. The anomalous temperature dependence persists far above the Curie temperature, indicating that the softening correlates with magnetic short-range order or spin fluctuations. The dominant mechanism of the softening of the bulk modulus is the inverse effect of the volume magnetostriction, ΔB_ω, which was estimated by a thermodynamic equation. The estimated ΔB_ω is larger than the observed softening, suggesting that the intrinsic change of the bulk modulus caused by magnetic ordering, ΔB_m, is positive.

Both shear moduli C_{44} and C' exhibit a negative field dependence for all concentrations. The value of $-\mathrm{d}C/\mathrm{d}H$ is surprisingly large for $x = 0.09$ and 0.13. The negative field dependence of the shear moduli is well explained as a result of the increase of magnetisation by the external field.

The field dependence of the bulk modulus at 4.2 K is positive for small x and changes its sign around $x = 0.1$. The change of sign has been explained by taking into account the field effects on both ΔB_ω and ΔB_m.

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