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Longitudinal acoustic mode softening and Invar behaviour in $Fe_{72}Pt_{28}$

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Abstract. Pressure dependence measurements of ultrasound velocities in the monocrystalline Invar alloy $Fe_{72}Pt_{28}$ have revealed normal behaviour in the paramagnetic phase but marked longitudinal mode softening in the ferromagnetic phase: below T_C both $(\partial C_{11}/\partial P)_{P=0}$ and $(\partial B^S/\partial P)_{P=0}$ are negative due to the magnetoelastic interaction. This is the first experimental evidence for negative longitudinal acoustic mode Grüneisen parameters in the ferromagnetic phase—as recently suggested from itinerant electron magnetism theory—and accounts for the negative thermal expansion.

1. Introduction

The Invar problem, which stems from the discovery [1] of the thermal expansion anomaly in an FCC Fe–35%Ni alloy, is old. Yet the microscopic origin of Invar effects and their relationship to magnetoelasticity remains unresolved and an issue of controversial debate [2–7]. To establish the source of the negative thermal expansion in the Invar FePt alloys, we have measured the hydrostatic pressure dependences of ultrasonic wave velocities in both the ferromagnetic and paramagnetic states in monocrystalline $Fe_{72}Pt_{28}$. We have observed a previously unsuspected phenomenon central to an understanding of the complex of properties that constitute the Invar question: the longitudinal modes soften under pressure due to the magnetoelastic interaction and the bulk modulus decreases with pressure. The anomalous vibrational anharmonicity of the long-wavelength acoustic modes is shown to be largely responsible for the negative thermal expansion [8] of $Fe_{72}Pt_{28}$ between about 260 K and the Curie temperature T_C.

2. Experimental determination of the elastic stiffness tensor components

Ultrasonic pulse transit times were measured using the pulse–echo overlap technique, which having a sensitivity to changes of 1 part in 10^6 is particularly well suited to determination of pressure-induced variations in velocity; details of the experimental

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Table 1. The second-order elastic stiffness tensor components, their hydrostatic pressure derivatives (obtained from the best fit to the experimental data) and mean elastic Grüneisen parameter at selected temperatures.

	Elastic stiffness (GPa)						Hydrostatic pressure derivatives						
T (K)	C_{11}	C_L	C'	C_{12}	C_{44}	B	$\frac{\partial C_{11}}{\partial P}$	$\frac{\partial C_L}{\partial P}$	$\frac{\partial C'}{\partial P}$	$\frac{\partial C_{12}}{\partial P}$	$\frac{\partial C_{44}}{\partial P}$	$\frac{\partial B}{\partial P}$	γ^{el}
230	160.2	221.3	13.64	133	75	142	−6.0	−6.7	3.0	−12.0	2.3	−10.0	1.6
240	158.2	219.8	14.35	130	76	139	−6.2	−6.7	3.0	−12.2	2.5	−10.2	1.7
250	156.1	217.7	15.08	126	77	136	−8.0	−6.7	3.1	−14.2	4.4	−12.1	2.5
260	153.6	214.8	15.83	122	77	132	−10.7	−8.5	3.1	−16.9	5.3	−14.8	2.7
270	150.7	212.2	16.63	117	78	126	−14.0	−12.7	3.2	−20.4	4.5	−18.3	1.9
280	147.4	208.9	17.42	113	79	124	−17.0	−17.2	3.3	−23.6	3.1	−21.4	0.8
290	143.9	205.5	18.22	107	80	120	−19.2	−22.0	3.4	−26.0	0.6	−23.7	−0.6
300	139.3	201.3	19.08	101	81	114	−21.5	−26.5	3.4	−28.2	−1.6	−26.0	−1.9
310	136.8	197.2	19.88	97	80	110	−23.0	−29.7	3.5	−30	−3.2	−27.7	−2.9
320	131.5	192.1	20.78	90	81	104	−23.2	−30.0	3.5	−30.2	−3.3	−27.9	−2.9
330	127.6	187.8	21.86	84	82	99	−21.7	−22.5	3.6	−28.9	2.8	−26.5	0.1
340	123.7	184.8	22.84	78	84	97	−17.0	−13.7	3.7	−24.4	7.0	−21.9	2.6
350	121.6	182.4	24.01	74	85	97	−10.5	−5.0	3.7	−17.9	9.2	−15.4	4.4
360	120.7	181.8	25.34	70	86	87	−0.5	5.0	3.7	−7.9	9.2	−5.4	5.6

techniques used to obtain the hydrostatic pressure derivatives of the elastic stiffness tensor components can be found elsewhere [9]. Single crystals were grown by the Bridgman–Stockbarger process. The $Fe_{72}Pt_{28}$ crystal, for which results are reported, is in the disordered state, and it becomes ferromagnetic at T_C of 367 K [10]. Similar vibrational anharmonic properties have been found for other FePt and FePtNi alloys [11]. Inspection of the phase diagram for disordered FePt alloys shows that for a composition just below 28 at.%Pt there is an FCC–FCT martensitic phase transformation [12]. However, a 28 at.%Pt should remain FCC down to 4.2 K; the particular crystal whose results are discussed here does so [10]. The elastic stiffness tensor components (previously measured up to 330 K [10]) show the markedly anomalous elastic behaviour with temperature characteristic of these Invar alloys [3, 10, 13, 14]. Both shear moduli, C_{44} and C' $(=(C_{11} - C_{12})/2)$, decrease with reducing temperature, the shear anisotropy ratio C_{44}/C' increasing from 3.4 at 360 K to 5.5 at 230 K (table 1): the shear modes, especially that associated with C', soften. This decrease of C' to a small value is evidence that this $Fe_{72}Pt_{28}$ crystal shows incipient shear instability against the FCC–FCT transformation. This response to a shear in a $\langle 1\bar{1}0\rangle$ direction on a $\{110\}$ plane reveals that the low-temperature FCC–FCT transition has a ferroelastic mechanism at the atomic level with the soft mode being a $\langle 1\bar{1}0\rangle$-polarized long-wavelength shear acoustic phonon propagated in a $\langle 110\rangle$ direction and the order parameter being the associated strain tensor $(2\eta_{33} - \eta_{22} - \eta_{11})/\sqrt{3}$ (in Lagrangian strain tensor components η_{ij}) spanning a one-dimensional non-identical irreducible subspace [9, 15, 16]. This ferroelastic transition mechanism will be discussed fully elsewhere [11]. Extension of the temperature range of measurement of the velocities of longitudinal ultrasonic modes propagated along the [001] and [110] directions up to about 430 K confirms previous observations [3, 14] that C_{11} and C_L $(=(C_{11} + C_{12} + 2C_{44})/2$: the elastic modulus corresponding to a

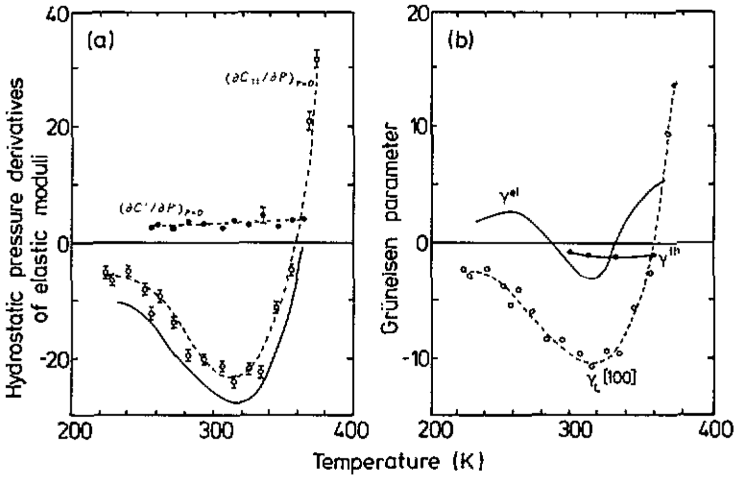

Figure 1. (*a*) Hydrostatic pressure derivatives of elastic stiffness tensor components of $Fe_{72}Pt_{28}$ as a function of temperature. Broken curves indicate best fits to experimental data. The full curve shows $(\partial B^S/\partial P)_{P=0}$. (*b*) The temperature dependences of the Grüneisen gamma γ_L [100] of the longitudinal mode propagated in a fourfold ⟨100⟩ direction (open circles), the mean elastic Grüneisen parameter γ^{el} (full curve) and the thermal Grüneisen parameter γ^{th} (full circles).

longitudinal mode propagated along a fourfold direction) decrease to a minimum just below the Curie temperature. The position of the minimum does not shift appreciably in a saturating magnetic field indicating that its source is an intrinsic magnetoelastic interaction rather than a domain wall stress effect [3]. This is confirmed by observation of the minimum in the bulk modulus determined from lattice parameter measurements which should not be much affected by domain wall effects [17].

3. Hydrostatic pressure dependences of the elastic stiffness tensor components

The effects of hydrostatic pressure on the elastic stiffnesses $(\partial C_{11}/\partial P)_{P=0}$ and $(\partial C'/\partial P)_{P=0}$ (figure 1(*a*)) are novel and instructive. In particular, in the ferromagnetic phase, pressure has the extremely unusual effect of reducing the longitudinal mode velocities and hence C_{11} and C_L. As a result the pressure derivative $(\partial B^S/\partial P)_{P=0}$ of the adiabatic bulk modulus B^S $(=(C_{11}+2C_{12})/3)$ is a large negative quantity (figure 1(*a*)): this alloy becomes easier to compress as pressure is applied! A negative $(\partial B^S/\partial P)_{P=0}$ (a newly recognized Invar property) relates directly to the negative thermal expansion because both properties involve the cubic term in the strain energy of the identical irreducible representation η_0, the volume strain $(\eta_{11}+\eta_{22}+\eta_{33})$ [15]. The elastic stiffnesses and their hydrostatic pressure derivatives are given in table 1. The shear modulus C' increases with pressure in the normal way. In the paramagnetic phase all the elastic stiffnesses, and hence the mode frequencies and energies, increase with pressure. Thus the negative values of $(\partial C_{11}/\partial P)_{P=0}$ and $(\partial B^S/\partial P)_{P=0}$ found only in the ferromagnetic phase are a consequence of a magnetovolume interaction.

A negative hydrostatic pressure derivative of an ultrasonic mode velocity implies the unusual attribute that under induced stress the long-wavelength acoustic mode frequencies $\omega_p(q)$ and energies decrease. The elastic mode vibrational anharmonicity

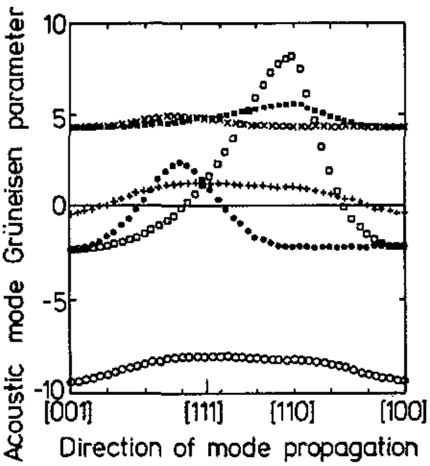

Figure 2. Long-wavelength acoustic mode Grüneisen parameters of $Fe_{72}Pt_{28}$ as a function of mode propagation direction (i) in the ferromagnetic state at 320 K: longitudinal (open circles), fast (full circles) and slow (open squares) shear modes; (ii) in the vicinity of T_C at 360 K: longitudinal (vertical crosses), fast (diagonal crosses) and slow (full squares) shear modes.

has been quantified by calculation of their Grüneisen parameters $\gamma(p, N)$ [18] from the measured elastic constants and hydrostatic pressure derivatives. The dependences upon propagation vector N of the $\gamma(p, N)$ for each acoustic branch p near $k = 0$ are shown in figure 2. In the paramagnetic state the $\gamma(p, N)$ are all positive. However, in the ferromagnetic state $Fe_{72}Pt_{28}$ shows the striking feature that all the longitudinal and quasi-longitudinal long-wavelength modes have negative gammas. In this respect $Fe_{72}Pt_{28}$ contrasts markedly with the FeNi alloys for which the pressure derivatives of the elastic constants, the mode Grüneisen parameters and the thermal expansion are all positive [19]. The temperature dependence of the Grüneisen gamma γ_L [100] of the longitudinal mode propagated in a ⟨100⟩ direction remains negative from 220 K up to T_C, passing through a minimum at about 315 K (figure 1(*b*)). As the temperature is raised, the hydrostatic pressure derivatives of the longitudinal mode velocities and hence their Grüneisen gammas decrease, and eventually at about 360 K (just below T_C) the diminishing magnetoelastic interaction, which leads to the longitudinal mode softening, is counterbalanced by the more usual positive contribution from vibrational anharmonicity; therefore the longitudinal mode gammas become positive close to the transition to the paramagnetic state.

4. Longitudinal acoustic mode softening and negative thermal expansion

There is a direct link between the longitudinal mode softening and the negative thermal expansion, which also is due to the anharmonicity of lattice vibrations but includes contributions from phonons of wavevectors spanning the entire Brillouin zone in all branches. In the quasiharmonic approximation the corresponding thermal Grüneisen parameter γ^{th} is the weighted average of all the individual excited mode (i) Grüneisen parameters γ_i $(= -\partial \ln \omega(p, N)/\partial \ln V)$ and is given by

$$\gamma^{th} = \sum_i C_i\gamma_i \Big/ \sum_i C_i = \beta V B^S/C_P = \beta V B^T/C_V \tag{1}$$

where β is the coefficient of volume thermal expansion. At high temperatures ($T \gg \theta_D$;

θ_D^{el} about 320 K) the heat capacity C_i per mode becomes equal to the Boltzmann constant. The thermal Grüneisen parameter γ^{th} (figure 1(*b*)) has been determined using thermal expansion [8] and specific heat (W Pepperhoff, communication) data. As temperature is reduced, optical phonons freeze out first and their contributions, and those of the population of large-wavevector-$\boldsymbol{k}$ acoustic mode phonons of higher energy, to γ^{th} and β decrease, and so the long-wavelength acoustic phonons, whose Grüneisen gammas are shown in figure 2, play an increasingly important role. The temperature dependence of the mean long-wavelength acoustic mode Grüneisen parameter γ^{el}, given by the sum

$$(1/12\pi)\sum\int\gamma(p,N)\,\mathrm{d}\Omega$$

over all zone centre modes, is shown in figure 1(*b*). The thermal expansion results from the mutual cancellation of effects from modes having some negative Grüneisen parameters and others of positive sign. In the summation (equation (1)) producing γ^{th}, the influence of the longitudinal modes, which have negative Grüneisen gammas in the ferromagnetic state, overrides that from the transverse modes, which have positive but numerically smaller $\gamma(p,N)$ (figure 2). Further confirmation that the negative thermal expansion does indeed result from the soft-longitudinal-mode contributions comes from consideration of the temperature range over which the effect occurs. The markedly sample-dependent thermal expansion in a $Fe_{72}Pt_{28}$ specimen was found to be negative between about 260 K and 376 K with a minimum at about 350 K [8]. Inspection of the temperature dependences of γ_L [100] and γ^{el} (figure 1(*b*)) shows why negative thermal expansion occurs only in this restricted range. While γ_L [100] remains negative down to 220 K, it has a comparatively small value at the lower temperatures, and so γ^{el}, which sums over both longitudinal and shear modes, becomes positive again. There is a range of temperature in which the contribution of the longitudinal acoustic modes causes the thermal expansion to be negative. The combination of reduction of the longitudinal Grüneisen parameters and freeze out of these modes at low temperature leads to domination by the lower-energy transverse acoustic modes with positive Grüneisen parameters, and so the thermal expansion resumes the normal positive sign.

While this work has been in progress there has been a relevant development in theoretical understanding of the anomalous volume behaviour of Invars in terms of a phenomenological model based on itinerant electron magnetism [5]. Throughout the long list of theoretical models trying to solve the Invar problem it has been customary to attribute the origin of the anomalous volume behaviour solely to the electron contribution β_{el}, while assuming that the lattice contribution β_{ph} behaves normally even in the ferromagnetic state. However, in general the volume thermal expansion coefficient β is given by $\beta_{el}+\beta_{ph}$; Kim [5] has assumed that the phonon free energy also depends upon magnetization, and examined in this context the role of the electron–phonon interaction on the volume and elastic behaviour of a ferromagnetic metal. For Fe_3Pt in particular a qualitative calculation based on a model density-of-states function with two maxima in the band and involving a number of experimentally undetermined quantities predicts a negative Grüneisen parameter, its actual value and hence that of β_{ph} being very sensitive to the electronic structure near the Fermi surface. This prediction applies to longitudinal acoustic phonons, the only modes that can propagate in his jellium model. The pressure dependences of longitudinal wave velocities measured here not only show that these modes do have negative Grüneisen parameters but also determine their values quantitatively. In themselves the data presented here do not render the standard viewpoint invalid (even though that has not yet been shown to accommodate negative acoustic mode Grüneisen parameters).

A negative thermal expansion leads to a negative thermal Grüneisen parameter γ^{th} (figure 1(*b*)). Since the thermal expansion is a volume effect, as is the bulk modulus, which has been found here to decrease anomalously with pressure, it could have been anticipated that longitudinal modes must be the source of these Invar properties. This has now been demonstrated experimentally. Ultrasonic measurements are confined to the long-wavelength limit; thus the present findings make it clear that phonons in the longitudinal branch near $k = 0$, where anharmonicities are dominated by the magnetoelastic interaction, provide an important contribution to the Invar behaviour.

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