Third-order elastic constants, vibrational anharmonicity, and the Invar behavior of the $Fe_{72}Pt_{28}$ alloy

G. A. Saunders, H. B. Senin, and H. A. A. Sidek*
School of Physics, University of Bath, Bath BA2 7AY, United Kingdom

J. Pelzl
Institut für Experimentalphysik, Ruhr-Universität Bochum, D-4630 Bochum 1, Germany
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In the ferromagnetic state the alloy $Fe_{72}Pt_{28}$ shows strong Invar effects governed by magnetoelastic interactions, including a negative hydrostatic pressure dependence of the bulk modulus: it becomes easier to squeeze under pressure. This remarkable behavior has prompted study of its nonlinear acoustic properties by determining its third-order elastic stiffness tensor components (TOEC) from measurements of the influence of uniaxial stress on the velocities of ultrasonic waves between 230 and 370 K, covering the range in which $Fe_{72}Pt_{28}$ has a negative thermal expansion, a property central to the Invar behavior. To obtain complete sets of the TOEC from 230 K up to the Curie point (367 K), the results have been combined with data for the hydrostatic pressure dependences of ultrasonic wave velocities. The TOEC quantify the first-order anharmonic terms in the interatomic potential and hence the long-wavelength acoustic phonon anharmonicities which are central to the Invar properties of this alloy. The tensor components C_{111}, C_{112}, and C_{123} are anomalously positive, in accord with the negative values previously determined for the hydrostatic pressure derivatives $(\partial C_{11}/\partial P)_{T,P=0}$ and $(\partial B^S/\partial P)_{T,P=0}$. Thus, the large stress-induced longitudinal-acoustic-mode softening in the ferromagnetic phase is confirmed, reinforcing the suggestion that the vibrational anharmonicities of the longitudinal acoustic modes, which have large negative mode Grüneisen parameters, play an important part in causing the thermal expansion of $Fe_{72}Pt_{28}$ to be negative.

I. INTRODUCTION

Recently the origin of the Invar effects shown by certain ferromagnetic alloys, an issue of much interesting, sometimes controversial debate,[1,2] has become much clearer. Invar behavior was discovered[3] as an almost invariant thermal expansion anomaly in a wide range of temperature around room temperature in fcc FeNi alloys at concentrations around Fe 35% Ni. To explain this remarkable effect, Weiss[4] proposed that Invar iron can exist in either of two states of quite different spin and volume. This has been confirmed by total-energy band calculations,[5–7] using a fixed-spin-moment procedure, which result in an energy-volume curve with a low-spin (LS) solution centered at low volume and a high-spin (HS) solution at high volume. The essential experimental features of Invar behavior in ferromagnetic alloys, encompassing a wide range of thermal and elastic effects, can be understood in terms of transition from the LS to the HS state. The observed pause in thermal expansion (or the contraction) of ferromagnetic alloys occurs as the low volume LS state becomes thermally populated at the expense of the higher volume HS state.

Invar effects are particularly pronounced in fcc FePt alloys with a composition in the vicinity of Fe_3Pt, which show negative thermal expansion in a range of temperature below the Curie point.[8] Another feature is that those second-order elastic stiffness tensor components, which correspond to a volume strain, show markedly anomalous behavior with temperature: C_{11} and $C_L[=(C_{11}+C_{12}+2C_{44})/2]$ decrease to a minimum just below the Curie temperature.[9,10] Lattice parameter and ultrasonic measurements have shown that there is a corresponding minimum in the bulk modulus.[11–13] A phenomenon central to understanding the negative thermal expansion has been recently found in ultrasonic studies of the Invar ferromagnetic alloy $Fe_{72}Pt_{28}$: The application of hydrostatic pressure induces a decrease in the velocities of longitudinal ultrasonic modes.[12,13] Both $(\partial C_{11}/\partial P)_{P=0}$ and $(\partial C_L/\partial P)_{P=0}$ are negative in the ferromagnetic phase, although they have the normal positive sign in the paramagnetic state. Hence, below the Curie temperature the hydrostatic pressure derivative $(\partial B/\partial P)_{P=0}$ of the bulk modulus is negative: $Fe_{72}Pt_{28}$ shows the extraordinary behavior of becoming easier to squeeze when pressure is applied to it. The ultrasonic studies under pressure provided the experimental evidence for negative longitudinal-acoustic-mode Grüneisen parameters in the ferromagnetic phase,[12,13] a feature indicated in the results of itinerant electron magnetism theory calculations.[14] The observation of negative Grüeisen mode γ's accounts[12] directly for the negative thermal expansion observed[8] from about 260 K up towards the Curie temperature for $Fe_{72}Pt_{28}$.

The root of Invar behavior lies in the effects on physical properties of strain induced by changing temperature or applying a pressure. But little is known about the influence of a uniaxial stress of Invars. A complete description of the nonlinear acoustic properties of a material demands knowledge of all the independent third-

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order elastic constants (TOEC). The previous studies[12,13] were focused on measurement of the hydrostatic pressure derivatives of the elastic stiffness tensor components, which specify in part the elastic effects to third order in strain. However, for the cubic alloy $Fe_{72}Pt_{28}$ the measurements of the effects of hydrostatic pressure on the velocity of an ultrasonic mode provided data for only three independent combinations of the TOEC. Additional measurements of effects of uniaxial stress on ultrasonic mode velocity are needed to obtain a complete set of all six individual TOEC, to quantify the cubic terms in the strain free energy and hence complete information concerning the vibrational anharmonicity of the acoustic modes in the long-wavelength limit. To accomplish this task of providing a comprehensive description of the nonlinear elastic properties and vibrational anharmonicity of the long-wavelength acoustic modes in $Fe_{72}Pt_{28}$ Invar alloy, an experimental study of the elastic behavior under axial compression has now been carried out in the particularly interesting temperature range from 230 to 370 K in which this alloy contracts as the temperature is increased.

II. EXPERIMENTAL TECHNIQUES

Due to the difficulty of making reproducible alloys, the disordered $Fe_{72}Pt_{28}$ crystal, grown by the Bridgman-Stockbarger process, used for the study is necessarily the same as that on which measurements of the effects of hydrostatic pressure on ultrasonic pulse transit times were made.[12,13] Single crystals of about 6.5 mm diameter and 20 mm in length were grown, the crystal quality being examined by taking Laue back-reflection photographs along the boule. It has the same structure as the compound Fe_3Pt. Microprobe analysis scans around the crystal showed its composition to be $Fe_{72}Pt_{28}$ within ±1 at. %. The density was 11 939±4 kg m^{-3}. It becomes ferromagnetic at a Curie temperature T_C of 367 K.[10] To provide a sample suitable for the uniaxial stress experiments, the crystal was cut into a rectangular parallelepiped, having dimensions of about $0.7\times0.6\times0.4$ cm, with three pairs of orthogonal faces polished flat and parallel to optical precision. Parallelism of the faces was examined by using an optical interference method and found to be within one wavelength of sodium light. Quartz transducers, driven at their fundamental frequency of 10 MHz (X cut for longitudinal, Y cut for shear waves) were used to insert and receive ultrasonic signals. The configurations of the modes studied are given in Table I. Considerable effort was needed to solve the acoustic bonding problems involved in making the uniaxial stress experiments as a function of temperature. It was found that Nonaq stopcock grease and Dow Resin 276-V9 made satisfactory specimen-transducer bonds for modes 4 and 5 (see Table I) over the required temperature range. Q.D. colloidal silver, set by baking at about 80 °C for 24 h, was found to be suitable as a bonding material for insertion and detection of the shear mode 6, from room temperature up to 370 K. Uniaxial stress was applied in a screw press through a precalibrated proving ring. Measurements from room temperature down to 230 K were carried out in a liquid-nitrogen cryostat and at higher temperatures up to 370 K in a thermostatically controlled bath. It was essential to stabilize the temperature to within ±0.1 K over a time period of several minutes during which the measurements were made. Changes induced in ultrasonic wave velocity by application of a uniaxial stress were measured to the required sensitivity of 1 part in 10^7 using an automated gated pulse superposition technique.[15] To circumvent the requirement for determination of changes induced in sample dimensions, the "natural velocity W" technique[16] was employed. The effects of the uniaxial stress applied (up to about 2×10^7 Pa) on ultrasonic wave velocity are small; although the systematic errors in absolute magnitude of the TOEC are quite large, the error in the relative changes with temperature is much smaller.

TABLE I. The experimental configurations under hydrostatic (H) and uniaxial pressure and the relationships used for calculation of the six TOEC in the cubic Invar alloy $Fe_{72}Pt_{28}$. **N** and **U** are the propagation and polarization directions, respectively. $C_L=\frac{1}{2}(C_{11}^S+C_{12}^S+2C_{44})$, $C'=\frac{1}{2}(C_{11}^S-C_{12}^S)$, $a=c_{12}^T/[3B(C_{11}^T-C_{12}^T)]$, $b=(C_{11}^T+C_{12}^T)/[3B(C_{11}^T-C_{12}^T)]$, $c=1/(4C_{44})$, $B=(C_{11}^T+2C_{12}^T)/3$, and $d=\frac{1}{2}(1-b-2c)$.

Mode no.	N	U	Stress direction	$w=(\rho_0V^2)_{P=0}$	F_u	$\{d(\rho_0W^2)/dP\}_{P=0}$
1	[100]	[100]	H	C_{11}	–	$-1-\frac{2w}{3B}-\frac{(C_{111}+2C_{112})}{3B}$
2	[110]	[001]	H	C_{44}	–	$-1-\frac{2w}{3B}-\frac{(C_{144}+2C_{166})}{3B}$
3	[110]	[1$\bar{1}$0]	H	C'	–	$-1-\frac{2w}{3B}-\frac{(\frac{1}{2}C_{111}-\frac{1}{2}C_{123})}{3B}$
4	[110]	[110]	[001]	C_L	a	$2wF_u+\frac{1}{2}aC_{111}+\frac{1}{2}C_{112}(3a-b)+2aC_{166}-bC_{144}-\frac{1}{2}bC_{123}$
5	[001]	[001]	[110]	C_{11}	a	$2wF_u+aC_{111}+(a-b)C_{112}$
6	[001]	[110]	[110]	C_{44}	d	$2wF_u+\frac{1}{2}(a-b)C_{144}+\frac{1}{2}C_{166}(3a-b)-2cC_{456}$

III. EXPERIMENTAL CONFIGURATIONS FOR DETERMINATION OF THE TOEC OF A CUBIC CRYSTAL

The TOEC, which are sixth-rank tensor components C_{uvprqs} defining the cubic terms in the strain free-energy expansion, can be obtained from the measured stress derivatives $(\rho_0 W^2)'_{P=0}$ evaluated at zero stress using[17]

$$-(\rho_0 W^2)'_{P=0}=(\mathbf{N}\cdot\mathbf{M})^2+2wF_{UC}+G_{UC} \ , \qquad (1)$$

with

$$w=(\rho_0 W^2)_0=(\rho V^2)_0=C^S_{pqrs}N_pN_qU_rU_s \ , \qquad (2)$$

$$F_{UC}=S^T_{abrs}M_aM_bU_rU_s \ , \qquad (3)$$

$$G_{UC}=S^T_{abuv}C_{uvprqs}M_aM_bN_pN_qU_rU_s \ . \qquad (4)$$

Here W is the natural velocity, V is the measured velocity, $\mathbf{N}$ and $\mathbf{U}$ are unit vectors along the wave propagation and polarization directions, respectively; $\mathbf{M}$ is a unit vector along the applied stress direction; C^S_{IJ} and S^T_{IJ} are second-order isentropic stiffness and isothermal compliance tensor components, respectively. For a cubic crystal belonging to the Laue group CI, there are six independent third-order elastic stiffness tensor components C_{IJK}.

Measurements have been made of the effects of uniaxial stress applied to the $Fe_{72}Pt_{28}$ crystal on the ultrasonic velocities in the mode configurations 4, 5, and 6 given in Table I. The data obtained as a function of temperature for the dependence upon a stress applied in a [110] direction on the velocity of a longitudinal mode propagated along an [001] axis (mode configuration 5) are presented in Fig. 1; similar data have been obtained in the other mode configurations. It can be seen that the effects of uniaxial stress on the [001] longitudinal mode velocity are large and strongly dependent upon temperature even to the extent of changing sign. The experimental results have been used to obtain, using a reiterative least-mean-squares fitting procedure, the uniaxial pressure derivatives $\{(1/W)dW/dP\}_{P=0}$, given in Table II, as the gradients of the measured pressure dependence of the relative change $\Delta W/W_0$ in the natural velocities. These results for $\{(1/W)dW/dP\}_{P=0}$ have been transformed to $\{d(\rho_0 W^2)/dP\}_{P=0}$ using

$$\{d(\rho_0 W^2)/dP\}_{P=0}=2\rho_0 W_0^2\{(1/W)dW/dP\}_{P=0} \ . \qquad (5)$$

Then the values of $\{d(\rho_0 W^2)/dP\}_{P=0}$ obtained for all six mode configurations, including the data obtained previously under hydrostatic pressure,[12,13] have been used to determine the TOEC using the relationships given in Table I.[16] An iterative procedure of the type introduced by Dandekar[18] was used to improve the accuracy of determination of the elastic stiffness tensor components and their hydrostatic pressure derivatives as a function of temperature. The major sources of error in decreasing order of magnitude were in the measurement of pressure,

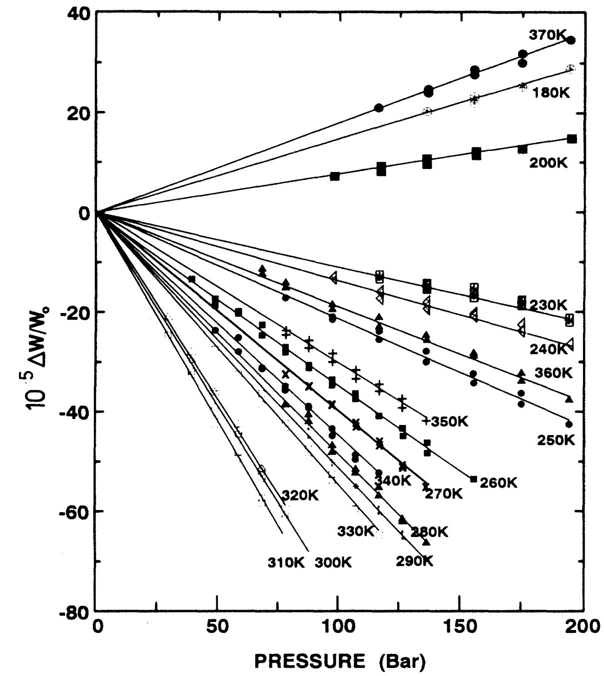

FIG. 1. Relative change $\Delta W/W_0$, induced by uniaxial stress applied in a [110] direction, in the natural wave velocity W of a longitudinal ultrasonic wave propagated along the [001] axis of $Fe_{72}Pt_{28}$ (mode 5) at selected temperatures.

alloy composition, sample dimensions, and alignment. The experimental errors in the TOEC are $C_{111}=\pm 0.1\times 10^3$ GPa, $C_{112}=\pm 0.1\times 10^3$ GPa, $C_{123}=\pm 0.2\times 10^3$ GPa, $C_{144}=\pm 0.8\times 10^3$ GPa, $C_{166}=\pm 0.7\times 10^3$ GPa, and $C_{456}=\pm 0.5\times 10^3$ GPa.

Use of the ultrasonic technique while applying a constant stress produces mixed moduli ($C^{S,T}_{IJK}$) (this has been without superscripts S and T throughout this paper),

TABLE II. Experimental data for the pressure gradient $\{(1/W)dW/dP\}_{P=0}$ (in units of 10^{-11} Pa^{-1}) of natural velocity W of ultrasonic modes propagated in $Fe_{72}Pt_{28}$ under uniaxial pressure at selected temperatures. The modes are labeled as in Table I. The errors are mode $4=\pm 0.002\times 10^{-11}$ Pa^{-1}, mode $5=\pm 0.002\times 10^{-11}$ Pa^{-1}, and mode $6=\pm 0.005\times 10^{-11}$ Pa^{-1}.

T (K)	Mode 4	Mode 5	Mode 6
230	−0.197	−1.097	
240	−0.305	−1.305	
250	−1.118	−2.118	
260	−1.291	−3.291	
270	−2.137	−4.137	
280	−2.924	−4.924	
290	−3.567	−5.569	
300	−3.868	−7.684	0.913
310	−4.618	−8.684	0.721
320	−4.212	−7.503	0.503
330	−3.632	−5.666	1.042
340	−3.311	−4.413	1.313
350	−2.992	−3.277	1.611
360	−2.407	−2.007	1.761

making it necessary to know the corrections required to determine adiabatic third-order elastic constants C^S_{IJK}. Following the techniques described by Shull,[19] it can be shown that the relationship giving the difference between the measured $C^{S,T}_{111}$ and the adiabatic quantity C^S_{111} is

$$(C^S_{111}-C^{S,T}_{111})=-\left\{\frac{B^S}{B^T}-1\right\}\left[\frac{(\partial C_{11}/\partial T)_P}{3\alpha}-\left[\frac{C_{111}+2C_{112}}{3}\right]\right] . \tag{6}$$

The coefficient α of linear thermal expansion has its largest magnitude at 340 K, where it has a value of -2.9×10^{-5} K^{-1},[8] and so at this temperature the largest difference between the measured $C^{S,T}_{111}$ and the adiabatic tensor component C^S_{111} occurs. The thermal Grüneisen parameter γ^{th} is 0.8 (Ref. 13), and therefore $B^S/B^T=(1+3\alpha\gamma^{th}T)$ is equal to 1.02. The data[13] for the temperature dependence of C^S_{11} give a value of -1.3×10^8 Pa K^{-1} for $(\partial C_{11}/\partial T)_P$ at 340 K. Hence the difference $(C^S_{111}-C^{S,T}_{111})$ is only 3.0×10^{10} Pa—substantially less than the experimental error. The magnitudes of this correction $(C^S_{IJK}-C^{S,T}_{IJK})$ are the same for the other TOEC. Therefore the data for the TOEC given in Fig. 2 can be taken as being the purely adiabatic constants C^S_{IJK} when they are required for computational purposes.

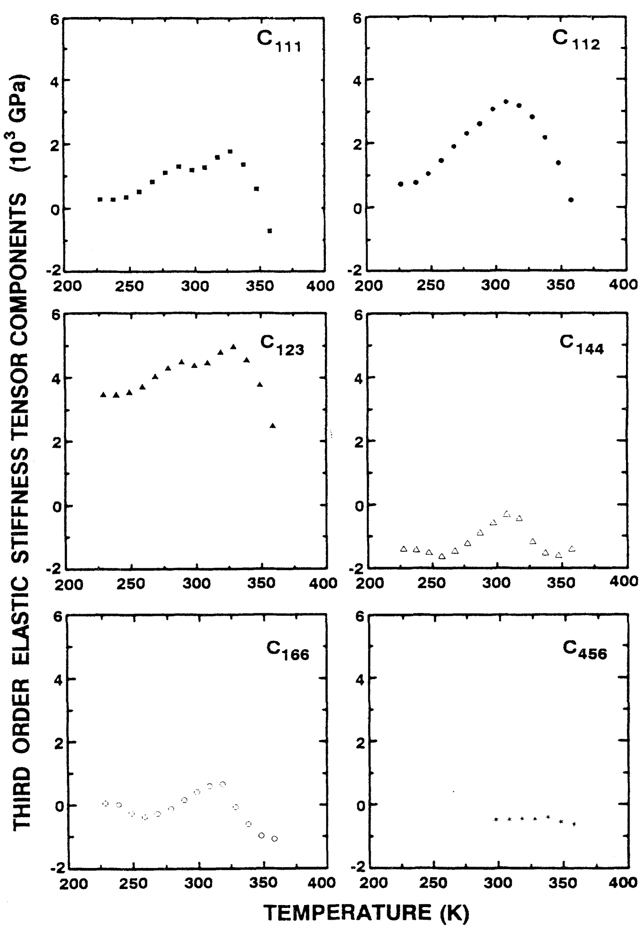

FIG. 2. The third-order elastic stiffness tensor components of $Fe_{72}Pt_{28}$ as a function of temperature.

IV. THE TOEC OF $Fe_{72}Pt_{28}$ INVAR ALLOY

Complete sets of the TOEC of $Fe_{72}Pt_{28}$ from 230–360 K are presented in Fig. 2. These TOEC quantify the lowest order anharmonic terms, which, at high temperatures especially, strongly influence properties, such as thermal expansion, which depend upon atomic thermal motion. In the absence of acoustic-mode softening, the second-order elastic stiffness tensor components and the lattice vibrational frequencies increase under pressure, raising the strain free energy. Then the hydrostatic pressure derivatives $(\partial C_{IJ}/\partial P)_{T,P=0}$ have positive and the TOEC have negative values (the compressive stress is defined as negative). However, for $Fe_{72}Pt_{28}$, C_{111}, C_{112}, and C_{123} are large and positive, while C_{166} and C_{456} are more normal in being small and negative. C_{144} oscillates between positive or negative values. Below the Curie temperature T_C the hydrostatic pressure derivative, $(\partial C_{11}/\partial P)_{T,P=0}$, which corresponds to an $\langle 001\rangle$ longitudinal wave, is a large negative quantity with a deep minimum centered at about 320 K.[12] This derivative is directly related to $(C_{111}+2C_{112})$ (Table I), so that C_{111} and C_{112} are positive and have maxima at 330 and 310 K, respectively. This accords with the previous finding that longitudinal-acoustic-mode softening is at its strongest at about 320 K, about 50 K below T_C.

In the paramagnetic phase there is no longitudinal-acoustic-mode softening. The combination $(C_{111}+2C_{112})$ is negative. The thermal expansion is positive. When $Fe_{72}Pt_{28}$ is cooled, $(C_{111}+2C_{112})$ becomes positive at 359 K about 8 K below T_C, behavior reflected by C_{111} and C_{112} (Fig. 2). The shear mode anharmonicities are more normal;[12] both $(\partial C_{44}/\partial P)_{T,P=0}$, except for a small negative excursion between about 300 and 320 K, and $(\partial C'/\partial P)_{T,P=0}$ are small and positive in the ferromagnetic phase. Hence, C_{144} is negative throughout. Limited shear mode softening about 50 K below T_C is reflected in the positive excursion of C_{166} (Fig. 2). C_{456} is small, negative, and almost independent of temperature.

The negative thermal expansion of $Fe_{72}Pt_{28}$ between about 260 K and T_C (Ref. 8) is consistent with the TOEC temperature dependences (Fig. 2). Thermal expansion relates to volume change and is associated only with the identical irreducible representation in Lagrangian strain space

$$\eta^0_0=\eta_{11}+\eta_{22}+\eta_{33} . \tag{7}$$

For a cubic crystal the symmetry nonbreaking terms in the strain free energy ϕ_{snb}, involving η_0^0 are[20,21]

$$\phi_{snb}=\tfrac{1}{6}(C_{11}+2C_{12})(\eta_0^0)^2+\tfrac{1}{54}(C_{111}+6C_{112}+2C_{123})(\eta_0^0)^3+\tfrac{1}{648}(C_{1111}+8C_{1112}+6C_{1122}+12C_{1123})(\eta_0^0)^4+\ldots . \quad (8)$$

Terms higher than the quadratic one contribute to the thermal expansion. Since each TOEC in the cubic invariant is large and positive and passes through a maximum, the net contribution to the thermal expansion from the long-wavelength acoustic phonons is negative and shows a deep minimum at about 320 K.

The phonon contribution to the free energy of a ferromagnetic metal, as well as that from electrons, depends on magnetization. For Fe_3Pt, theoretical calculations[14] of the magnetoelastic interaction suggest that the longitudinal phonon Grüneisen parameter could be negative. The uniaxial and hydrostatic pressure dependences of longitudinal wave velocities establish this experimentally, quantifying the mode parameters. Longitudinal-acoustic-mode softening plays a dominant role in the nonlinear acoustic and Invar properties of $Fe_{72}Pt_{28}$. Thermal expansion incorporates contributions from phonons of wave vectors **k**, which span the entire Brillouin zone in each branch p of the dispersion curves. Therefore, the thermal Grüneisen parameter γ^{th} is a weighted average $\sum_i C_i\gamma_i/\sum_i C_i$ of the individual mode (i) Grüneisen parameters γ_i. In the paramagnetic state the acoustic mode $\gamma(p,\mathbf{N})$ are all positive and so the material expands as the temperature is increased. Below T_C the longitudinal long-wavelength acoustic-mode Grüneisen parameters have negative values, the principle source[12] of the negative thermal expansion. The long-wavelength, small wave vector **k** acoustic phonons of lower energy play an increasingly important role in thermal expansion as temperature is reduced because their relative population is increased. The thermal expansion, and in turn γ^{th}, results from the mutual cancellation of Grüneisen parameters, some negative, others positive. The contributions to γ^{th} from the longitudinal-acoustic modes, which have large negative Grüneisen gammas, override those from the transverse modes, which have positive but numerically smaller $\gamma(p,\mathbf{N})$. Further confirmation[12] that the negative thermal expansion results from the soft longitudinal mode contributions comes from consideration of the temperature range about 260 and 376 K over which the effect occurs with a minimum at about 350 K.[8] The acoustic-mode Grüneisen parameter $\gamma_L[100]$ remains negative down to 220 K but it has a comparatively small value at the lower temperatures so that γ^{el}, which sums over both longitudinal and shear modes, becomes positive again. The contributions from the longitudinal-acoustic modes cause the thermal expansion to be negative over a restricted temperature range. These effects are due to the onset of a HS-LS transition. 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 modes with positive Grüneisen parameters, so that the thermal expansion resumes the normal positive sign, when the Fe atoms are in the HS state.

Total-energy band calculations[5–7] for ferromagnetic Fe alloys have established that the energy-volume curve has a low-spin (LS) solution centered at low volume and a high-spin (HS) solution at high volume. The energy difference $\Delta E(=E_{LS}-E_{HS})$ between the minima of the LS and HS branches decreases with increasing temperature and changes sign. For Invar alloys the HS solution defines the ground state at low temperatures and the LS solution defines the ground state at high temperatures. Recently a pressure-induced magnetic phase transition from the ferromagnetic high moment state to the low moment state has been observed in a study of the effects of pressure on the ^{57}Fe Mössbauer effect on the Invar $Fe_{72}Pt_{28}$,[22] confirming experimentally that the source of the Invar behavior is the volume dependence of the Fe moment and the HS-LS transition. The theory[4–7] explains qualitatively the essential experimental features of Invar behavior including the elastic effects. The thermal expansion pause (or the contraction) is due to increasing thermal population of the low volume LS state. At low temperatures the bulk modulus is determined by the HS state and should show a moderate decrease with increasing temperature. Above the crossover temperature, the bulk modulus increases to a larger value corresponding to the low volume, less compressible LS state. Further increase in temperature should lead to a gradual decrease in the bulk modulus. These predictions are in accord with the bulk modulus measurements for $Fe_{72}Pt_{28}$ Invar alloys.[23]

Application of hydrostatic or uniaxial pressure can be expected to enhance magnetovolume instabilities by changing ΔE and the relative populations of the HS and LS states, inducing large effects in the nonlinear acoustic properties. This is shown by the large, anomalously positive values of those TOEC which are volume dependent, especially C_{111} and C_{112} (Fig. 2). At low temperatures $Fe_{72}Pt_{28}$ is in the high volume HS state and accordingly has a small bulk modulus. At temperatures in the vicinity of the crossover temperature, application of hydrostatic pressure drives the material towards the lower volume LS state. Hence, $Fe_{72}Pt_{28}$ becomes more compressible as pressure is increased: This results in a negative $(\partial B/\partial P)_{P=0}$ related to the TOEC by

$$(\partial B/\partial P)=-(C_{111}+6C_{112}+2C_{123})/9B . \quad (9)$$

The strain potential-energy terms out to third order in the identical irreducible representation η_0^0 are[24]

$$\phi(\eta_0)=\tfrac{1}{2}B\eta_0^2-\tfrac{1}{6}B(\partial B/\partial P)\eta_0^3 . \quad (10)$$

Increasing temperature facilitates the ease with which the HS state can be transformed to the LS state. Therefore $(\partial B/\partial P)_{P=0}$ becomes more negative, as $(C_{111}+6C_{112}+2C_{123})$ becomes more positive [Eq. (9)]. As the temperature is increased further, the population of the LS state increases at the expense of the HS state. Above the crossover temperature but below T_C an Invar can be expected to be a composite of the HS and LS states.[5–7] The LS state has lower volume and is therefore less compressible than the HS state; in the limit of a pure LS state the material should have a large bulk modulus with a positive $(\partial B/\partial P)_{P=0}$. Hence as a consequence of the HS to LS transition there is a pronounced negative minimum in $(\partial B/\partial P)_{P=0}$ as a function of temperature and corresponding maxima in the volume dependent TOEC C_{111}, C_{112}, and C_{123} (Fig. 2).

The Invar behavior, the magnetoelastic and nonlinear acoustic properties of $Fe_{72}Pt_{28}$ can now be unified. A recent analysis[25] of the magnetoelastic behavior in terms of Landau theory has shown that the abrupt change in the bulk modulus observed[9] experimentally to the ferromagnetic transition can be interpreted quantitatively: Magnetism governs the softening of $Fe_{72}Pt_{28}$ as it is lowered through T_C. In addition, good agreement found with the measured[11,12] change in the hydrostatic pressure derivative $(\partial B/\partial P)_{P=0}$ when $Fe_{72}Pt_{28}$ transforms from the paramagnetic to the ferromagnetic state explains the remarkable property of this Invar alloy of becoming more compressible as pressure is increased. This verification that the anomalous elastic and nonlinear acoustic properties have a magnetic origin completes the synthesis. The magnetoelastic effects, based in the HS-LS transition, which produce magnetovolume instability, lead to softening of the long-wavelength acoustic modes and the consequent negative thermal expansion.

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*On leave from Department of Physics, Universiti Pertanian Malaysia, 43400 Serdang, Selangor, Malaysia.

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