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Study of the invar effect through ultrasonic measurements of the elastic properties of $Fe_{64}Ni_{36}$ under pressure

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Abstract

The elastic properties of a polycrystalline sample of invar $Fe_{64}Ni_{36}$ have been investigated at ambient temperature by ultrasonic experiments up to 7 GPa. The pressure dependence of the bulk modulus is extracted without using any model and discussed in terms of invar anomaly models.

Keywords: Invar; Speed of sound; Ultrasonic; High pressure

1. Introduction

Invar story has began in 1897, when Charles Edouard Guillaume [1] has discovered that iron–nickel alloy, with 35% of Ni, show a very small (almost zero) thermal expansion over a wide range around the room temperature. Since then, many other Fe-based ($Fe_3Pt, Fe_3C, \ldots$) alloys with this same unusual property have been synthesized and invar alloys are nowadays extensively used at the industrial scale as temperature-insensitive devices. It is well established that the invar effect is related to magnetism since it is only observed in the ferromagnetism phase. However, the microscopic processes responsible for the invar effect still remain unclear and the invar compounds are still the subject of numerous theoretical and experimental studies [2].

One of the most popular and accepted models is due to Weiss [3]. He has proposed, in 1963, that the iron can occupy two different states: a high-spin (HS) state and a low-spin (LS) state, the latter having a smaller volume and a slightly higher energy than the HS state. This interpretation, so-called the "2 γ-state model", explains the invar effect by a first order transition from the HS to the LS state when the temperature is raised. The gradual population of the LS state, at the expense of the HS one, compensates the usual thermal expansion up to a given volume, where all the electrons are in the LS state. Applying pressure to invar alloys gives rise to the same transition, resulting in a small (or even negative) pressure dependence of the bulk modulus. Experimental results [4,5] and band structure calculations [6,7] support this interpretation. In spite of the ability of this model to account for experimental data, some inconsistencies on Fe–Ni compounds have motivated a new interpretation. On the basis of ab initio calculation, van Schilfgaarde et al. [8] analysed the invar behaviour as a continuous variation of the iron spin alignment as the volume is decreased, accompanied by a slow reduction of the intensity of the iron magnetic moment. This is the main difference between the two models: in the non-collinear one, the physical properties of invar are expected to evolve continuously under pressure, in contrast with the 2 γ-state model which predicts discontinuities at a given pressure (corresponding to the end of the LS population). Interestingly, the occurrence (or the absence) of a discontinuity in the pressure dependence of the bulk modulus B can be a clear test of validity between the two models. Using X-ray diffraction technique, Dubrovinsky et al. [9] measured the volume pressure dependence of Fe–Ni alloys. Through the application of an *ad hoc* equation of state

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(EoS), they deduced a continuous variation of B under pressure, in very good agreement with the non-collinear model. On the other hand, to extract the $B(P)$ information without any model, that may induce artefact in the EoS, we have carried out ultrasonic experiments under high pressure.

2. Experimental set-up

Two different high pressure set-ups have been adapted to ultrasonic experiments. The first one is a classical piston-cylinder apparatus, with pentane as pressure medium transmitting. The pressure, limited to 1 GPa, is hydrostatically applied on the sample and it is determined from the variation of a manganin gauge. The sample, whose dimensions are about 10 mm, is embedded in a holder placed in the cell (Fig. 1). The $LiNbO_3$ transducer is mounted on one of the two flat parallel faces of a cylindrical sample and provides direct echoes through consecutives reflections (Fig. 2). The second set-up is dedicated to higher pressure measurements of sound velocities (Fig. 3). We used the Paris–Edinburgh press (detailed description in [10]), an opposed-anvil press allowing going up to 8 GPa. Simultaneously with ultrasonic measurements, we performed X-ray diffraction experiment on a NaCl powder located around and below the cylindrical sample. Thanks to the well known NaCl EoS [11], we then extract accurately the pressure. Both crystal and NaCl are putted in a boron epoxy gasket, which is designed to transmit to the sample a pressure as hydrostatic as possible. One can be noted that our set-up is designed

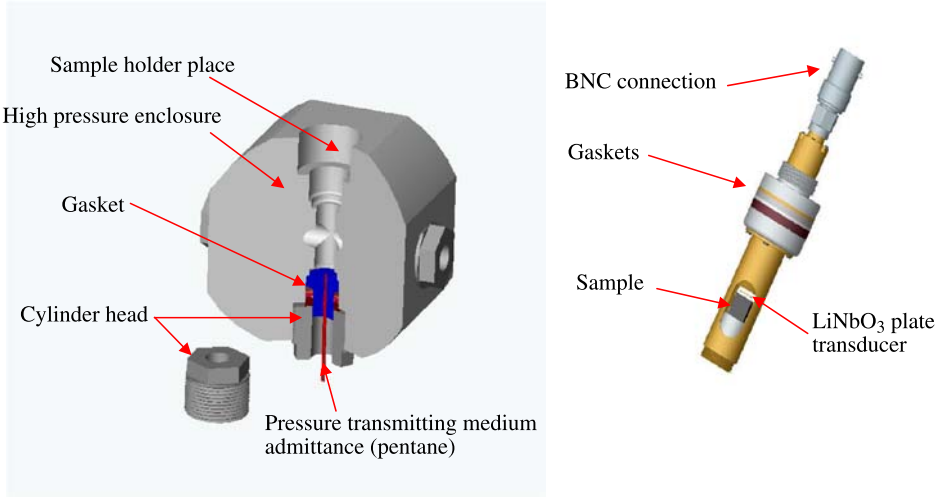

Fig. 1. Low pressure ultrasonic measurements set-up (vessel on the left and sample holder on the right).

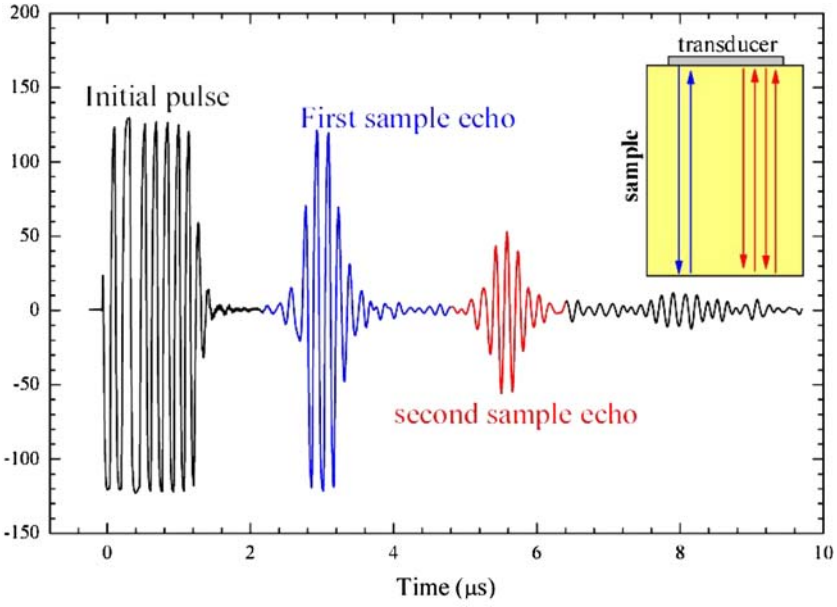

Fig. 2. Typical spectrum recorded in the low pressure press.

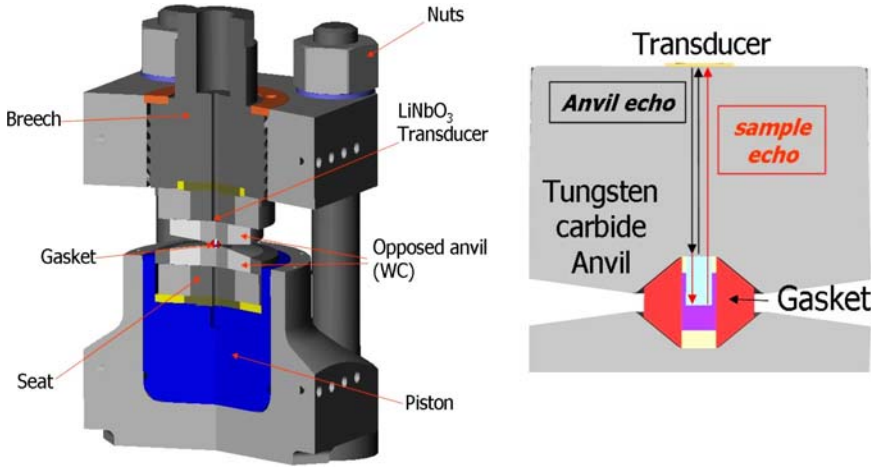

Fig. 3. High pressure ultrasonic measurements set-up (Paris–Edinburgh press and cross section of the anvil).

such as the transducer (placed on the top on the upper anvil) is only submitted to the atmospheric pressure. The initial pulse goes through this anvil and is partially reflected at the anvil/sample interface, while the other part of the ultrasonic energy is transmitted inside the sample. The corresponding pulse is then totally reflected at the bottom of the sample because of the large acoustic mismatch between the crystal and the NaCl (see Fig. 4).

The travel time is calculated with the pulse echo overlap method, using a signal cross correlation section between two consecutive echoes corresponding to the sample. Thus, with the measurement of the travel time (t) and the knowledge of the sample length (d), one can simply obtained the sound velocity (v) by $v = 2d/t$. To get the bulk modulus, we first have to deduce the elastic constants from the square of the sound velocities and the sample density (ρ). If the equation of state of the sample is not known, we have to make the typical hypothesis that B has linear pressure dependence between two successive measurements (with $\Delta P \ll B$). The thermodynamic definition $B = -V(\partial P/\partial V)_S$ can then be rewritten as $B = -V(\Delta P/\Delta V)_S$, where V is the volume. Finally, with the knowledge of the ambient condition values of V and B, all thermoelastic quantities can be determined using an iterative calculation with only pressure travel time dependence as input data [12].

3. Bulk modulus under pressure: data and discussion

Experiments have been carrying out with polycrystalline samples coming from the same source ($Fe_{64}Ni_{36}$ rod, provided by Goodfellow), homogenized at 880 °C for one week. The structure, density and elastic properties of this sample have been first determined at ambient conditions. Results are summarized in Table 1 and show excellent agreement with single crystal data of same composition [13]. Fig. 5 shows the longitudinal and transversal travel

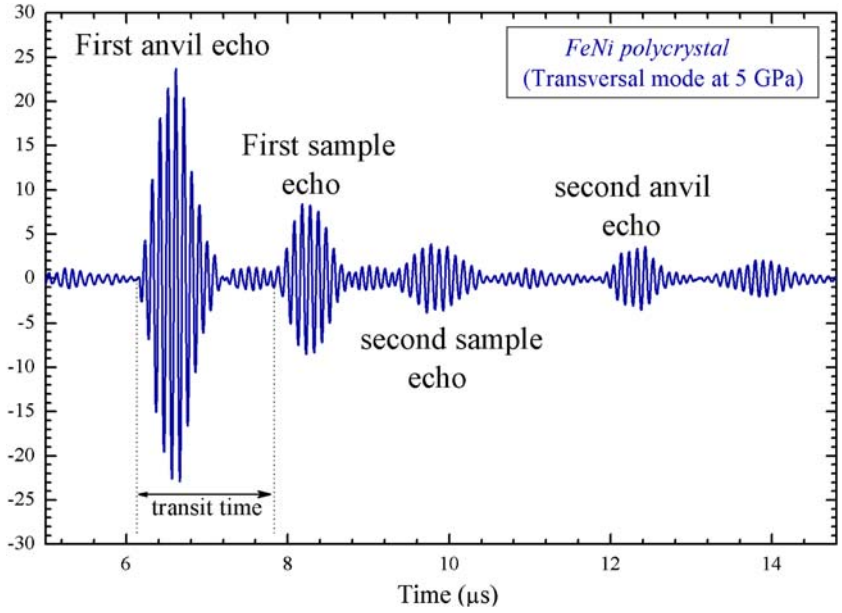

Fig. 4. Typical spectrum recorded in the Paris–Edinburgh press.

Table 1
Comparison of elastic properties at ambient conditions between our $Fe_{64}Ni_{36}$ polycrystalline sample and the single crystal (same composition, average values calculated with the Hashin–Shtrikman bounds model [16]): density (ρ_0), longitudinal and transversal sound velocities (v_l and v_t), bulk and shear moduli (B_0 and G_0)

Crystal	ρ_0	v_l	v_t	B_0	G_0
Poly-	8.066 (3)	4856 (7)	2610 (3)	117.0 (4)	55.3 (2)
Single- [13]	8.119	4816	2629	111.4	56.1

times obtained up to 7 GPa, with the two different ultrasonic high pressure set-up. In the Paris–Edinburgh press, the contact between the anvil and the sample is not good enough below 2 GPa to measure reliable travel times. As explained above, the measurement of the travel times allows the determination of the bulk modulus $B = \rho(v_l^2 - 4/3v_t^2) = C_l - 4/3C_t$. Its pressure evolution (Fig. 6) shows a linear dependence with a discontinuity in the slope at 3.1 GPa, the pressure derivate of B (dB/dP) going abruptly from 1.42 to 3.60. The unusual low value in the low pressure range is in good agreement with previous study [14] and can only be explained with the help of the 2 γ-state model. Up to 3.1 GPa, the classical effect of pressurization (increase of the

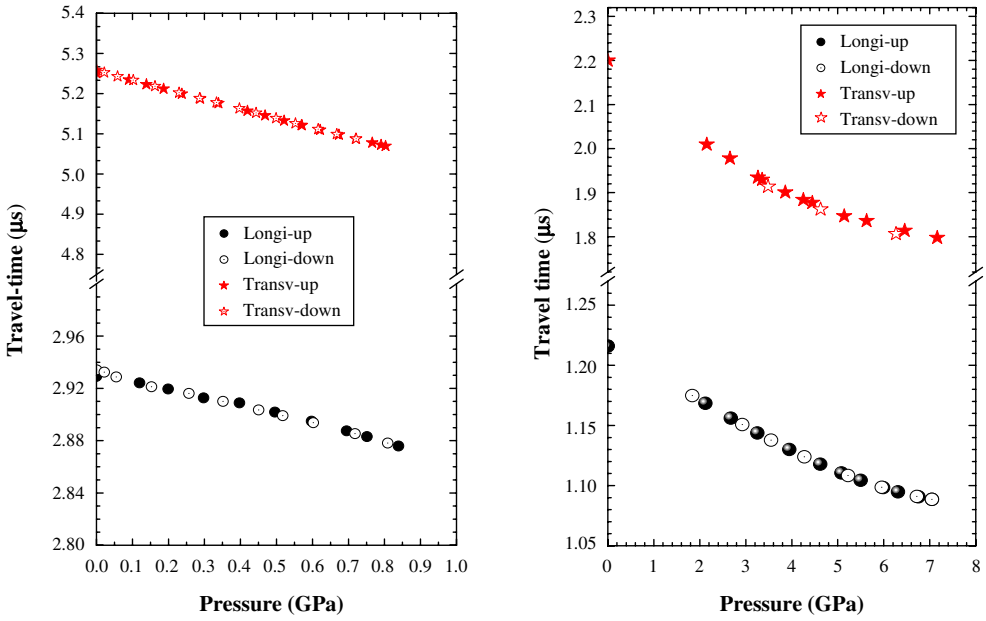

Fig. 5. Ultrasonic travel times under pressure in $Fe_{64}Ni_{36}$ (left: hydrostatic low pressure data, right: quasi-hydrostatic high pressure data).

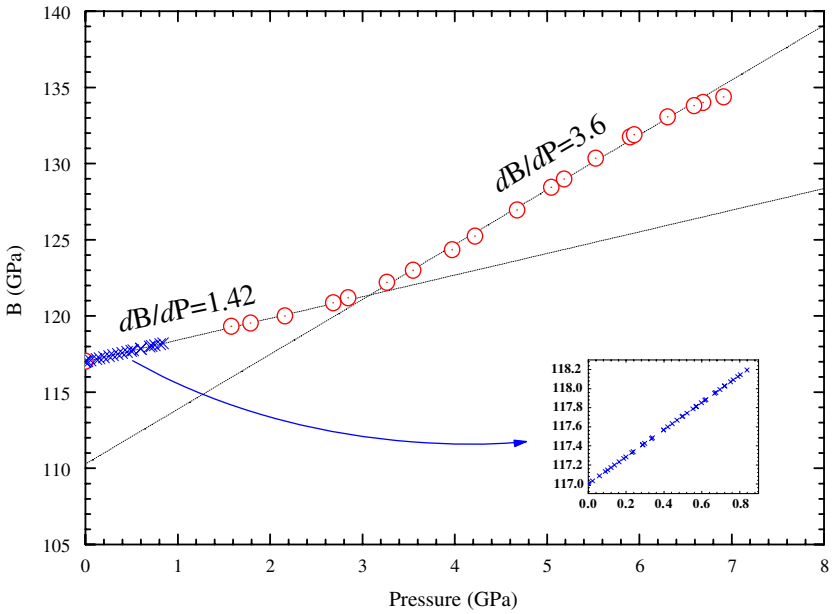

Fig. 6. Bulk modulus of polycrystalline $Fe_{64}Ni_{36}$ versus pressure. The low-range pressure (blue cross) is shown in the insight. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

bulk modulus) is in competition with the gradual population of the low-spin state (lowering the total sample volume), giving rise to a low value of dB/dP. When the low-spin to high-spin transition rate is saturated, no more magnetoelastic effect occurs. The invar alloy thus behaves as usual metal (with a classical value of dB/dP around 4). While the non-collinear model may also explain the low value of dB/dP, it fails to reproduce the linear dependence of the incompressibility as well as the existence of a pressure transition.

4. Conclusion

Ultrasonic high pressure measurements have been carrying out on a polycrystalline of $Fe_{64}Ni_{36}$ at ambient temperature. The bulk modulus B is accurately determined at each pressure, without using any fitting model. The observation of a linear behaviour versus pressure, with an abrupt change in the slope at 3.1 GPa, is in contraction with the non-collinear model. On the other hand, our ultrasonic results are well interpreted using the 2 γ-state model, in agreement with previous studies using different techniques as X-ray magnetic circular dichroïsm [5] or X-ray emission spectroscopy [15].

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