Abrupt discontinuity of the bulk modulus pressure-dependence in Fe 64 Ni 36

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Abrupt discontinuity of the bulk modulus pressure-dependence in $Fe_{64}Ni_{36}$

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Abstract

X-ray diffraction and ultrasonic measurements have been carried out simultaneously up to 7 GPa at ambient temperature on a polycrystalline sample of $Fe_{64}Ni_{36}$ Invar alloy. The bulk modulus is found to increase linearly with pressure with an unusual low value (1.4) of dB/dP up to about 3.1(2) GPa followed by a regular slope (3.6) at higher pressure. The observation of these two distinct regimes is in qualitative agreement with previous results on the variation of the iron magnetic moment, and can be interpreted using the 2 γ-state model in terms of gradual population of low spin-small volume state at the expense of the high spin-large volume state under pressure.

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Charles Edouard Guillaume was awarded the 1920 Physics Nobel Prize for the discovery of iron-nickel ferromagnetic alloys exhibiting for 35% of Ni remarkable magneto-volumic behaviors, such as a low and almost invariant thermal expansion in a broad range of temperature below the Curie temperature, the so-called Invar effect[1, 2]. Since then, similar properties have been reported for many other alloys such as crystalline Fe-Pt[3] or amorphous Fe-base alloys[4]. The Invar effect is intimately related to the large magnetic contribution to the total energy $U = U_n - 2J < S >^2$ where U_n is the non-magnetic energy part, and J and $< S >$ the effective exchange integral and the thermal average of the effective spins respectively. The two last terms are volume dependent which causes many other extraordinary behaviors beside the thermal expansion anomaly such as a simultaneous softening of the shear and bulk moduli with increasing temperature or a remarkably small (even negative) pressure dependence of the bulk modulus[5, 6]. However, while these compounds are extensively used at the industrial scale as temperature-insensitive devices, a detailed microscopic explanation of the Invar effect and its relationship to magneto-elasticity still remain puzzling for scientists.

Weiss proposed the first complete theory to account for both magnetic and elastic properties experimentally observed in Invar alloys[7]. This interpretation, called 2 γ-state model, is based on the hypothesis of two distinct spin states below the Curie temperature : a high spin (HS) configuration associated with a large volume and a low spin one (LS) with a small volume. Since the energy difference between these two allowed states is small, the Invar effect is assumed to be thermally induced by a gradual increase of the LS state population at the expense of the HS state up to a given volume (corresponding to a given pressure or temperature) where the HS-to-LS transition is saturated. This transition compensates the usual thermal expansion related to the anharmonicity of the lattice vibrations, giving a satisfactory explanation for the thermal expansion anomaly. More recently, on the basis of *ab-initio* calculations, van Schilfgaarde[8] proposed a new microscopic model of the zero-expansion anomaly, conceptually different from the 2 γ-state one since the Invar effect is expected to occur through a continuous variation of the spin directions from a parallel alignment to a disordered non-collinear state when the volume is reduced. One of the most notable difference of this model with the Weiss interpretation is the absence of transition pressure/temperature or of any discontinuity in the physical properties with pressure.

Experimentally, most of the studies focused on the magnetic properties of Invar alloys

under pressure or temperature gave results in agreement with the 2 γ-state model (with very few exceptions[9] which have motivated the van Schilfgaarde calculations). Odin *et al*[10] observed in $Fe_{72}Pt_{28}$ the HS-to-LS transition at 4 GPa through x-ray magnetic circular dichroism measurements at the L_{III} edge of platinum, conclusion corroborated by the high pressure ^{57}Fe Mössbauer measurements carried out by Abd-Elmeguid and co-workers[3]. More recently, Rueff *et al*[11] measured the x-ray emission spectra under high pressure in $Fe_{64}Ni_{36}$, and concluded to the occurrence of a HS-to-LS transition at a pressure of about 5 GPa (with a width of 3 GPa). On the other hand, recent "state of the art" measurements of the iron-nickel Invar equation of state up to 20 GPa were used to deduce the pressure dependence of the bulk modulus. The observation of a continuous variation of B *vs* P has been interpreted as a success of the non-collinear model[12].

The contradiction between the interpretation of experimental magnetic and structural results leaves the explanation of Invar behavior unclear and further insights are undoubtedly needed. Contrary to x-ray diffraction where the bulk modulus is obtained through modelization of the equation of state, the ultrasonic measurements of the sound velocity directly probe the elastic properties of the sample under consideration, without any modelization step. It is the reason why, in this Letter, we present high pressure ultrasonic measurements on the most common iron-nickel Invar alloy ($Fe_{64}Ni_{36}$) using a very recent technical development[13] allowing the measurement of sound wave velocities up to 7 GPa, almost one order of magnitude higher than what was usually performed up to now.

The high pressure ultrasonic experiments were carried out using the Paris-Edinburgh press[14], an opposed-anvil system allowing a compression of a mm-sized sample in the 10 GPa range. The complete set-up and the reliability/reproducibility of this technique are described in detail elsewhere[13]. Briefly, the sample, shaped as a cylinder with parallel end surfaces, is surrounded by a boron nitride (h-BN) cylinder, which is used as a solid pressure-transmitting medium. Compressed NaCl powder is located below and around the cylindrical sample. Simultaneously to the ultrasonic measurements, the NaCl lattice parameter was measured by energy dispersive x-ray diffraction carried out at the DW11 beamline of the L.U.R.E synchrotron (Orsay, France), and the *in-situ* pressure obtained with an accuracy of 3% using the Decker equation of state[15]. Finally, the sample and its environment are placed into a boron epoxy gasket.

Longitudinal and transverse waves are generated with frequency of about 15 MHz by

lithium niobate plates, fixed on the upper surface of the Paris-Edinburgh anvil. After propagating through the anvil, an initial pulse is partially reflected at the anvil-sample interface, resulting in a first echo (labelled B in figure 1), while the other part is transmitted inside the sample. The large acoustic mismatch between the sample and NaCl leads to the total reflection of the signal at the far end of the sample, giving rise to the sample echo (S) following B. The time difference needed to superpose the B and S echoes corresponds to the two-way travel time (t) of the pulse through the sample.

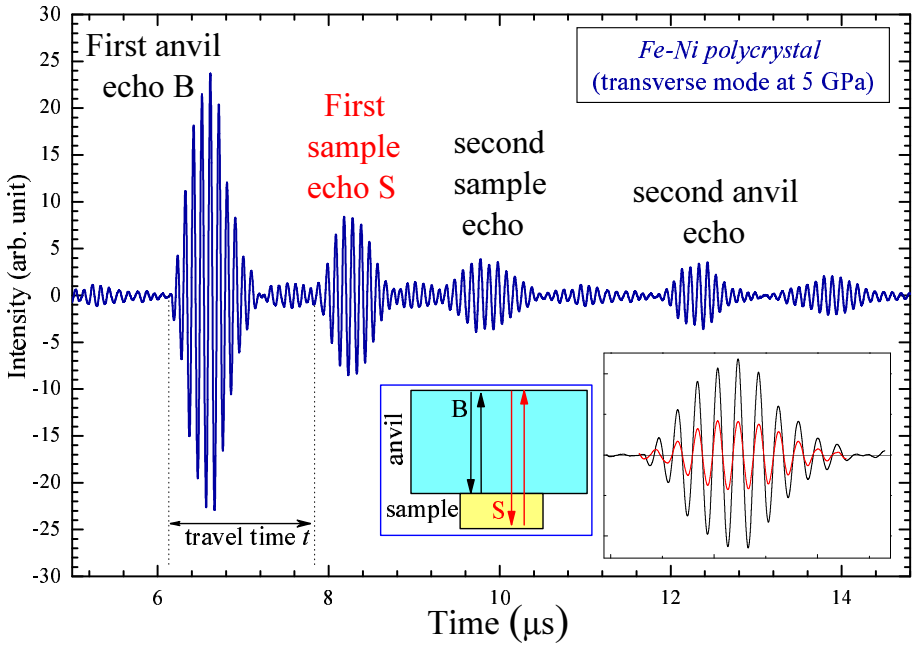

FIG. 1: Ultrasonic spectrum of $Fe_{64}Ni_{36}$ at 5 GPa. The first echo is the first reflection at the anvil/sample interface (B) and the second echo (S) the first reflection from the far end of the sample. The classical pulse echo superposition method (inset) using a signal cross correlation section between the B and S echoes is used to determine the travel time t.

The sound velocity v is thus deduced from the travel time t through $v = 2d/t$, where d is the sample length. The bulk modulus B of the polycrystalline sample is then deduced from the longitudinal and transverse sound velocities (respectively v_L and v_T) and the sample density ρ through $B = \rho(v_L^2 - 4/3v_T^2)$. Using a method conceptually similar to what has been proposed and demonstrated by Cook[16], the classical hypothesis of a linear volume dependence between two *consecutive* measurements at different pressure (with $\Delta P \ll B$) allows to rewrite the bulk modulus $B = -V(\partial P/\partial V)_S$ as $B = -V(\triangle P/\triangle V)_S$. Thus, with the knowledge of *t(P)* and the ambient conditions values of the volume V and the bulk

TABLE I: Comparison between the ambient values of density ρ_0 (g.cm^{-3}), bulk and shear moduli B_0 and G_0 (GPa), longitudinal and transverse sound velocities v_l and v_t (m.s^{-1}) of the $Fe_{64}Ni_{36}$ polycrystal and the single-crystal with same composition. The average elastic properties of the single-crystal have been extracted from the elastic constants values using the Hashin-Shtrikman bounds model[18]. (Number in parentheses corresponds to uncertainty in the last significant digits).

sample	ρ_0	v_l	v_t	B_0	G_0
poly-crystal	8.066(3)	4856(7)	2610(3)	117.0(4)	55.3(2)
single-crystal[5]	8.119	4816	2629	111.4	56.1

modulus B, a simple iterative calculation enables to obtain step by step all thermoelastic quantities as function of pressure.

The complete set of experiments have been carried out on cylindrical samples, all extracted from the same high purity polycrystalline sample[17] of face-centered cubic $Fe_{64}Ni_{36}$. The elastic properties have been first determined at ambient conditions with the ultrasonic method. The results summarized in table I are in excellent agreement with the single-crystal corresponding data previously published[5]. Moreover, using the zero-pressure x-ray diffraction data, the value of the poly-crystal lattice parameter a_0=3.5935(8) Å is obtained, also in very good agreement with previous studies[12].

The high pressure dependence of the ultrasonic travel time in $Fe_{64}Ni_{36}$ has been determined between 1.5 and 7 GPa. In the [0-1.5 GPa] range, the sample-anvil contact in the Paris-Edinburgh press is not good enough to obtain reliable travel time measurements. Thus ultrasonic experiments at low pressure using a piston-cylinder apparatus[19] have also been carried out on the same compound to obtain complementary results between 0 and 1 GPa. Using the iterative computation based on the Cook method, we obtained the value of the bulk modulus as a function of pressure (Fig. 2).

We observe a linear pressure dependence of the bulk modulus with a clear slope discontinuity at 3.1(2) GPa. In the low pressure range, the pressure derivative of the bulk modulus $B' = dB/dP$ is 1.42(3). This remarkably low value (in most solids B' ranges between 3 and 5) is in good agreement with previous ultrasonic measurements[5, 6] performed on Fe-Ni and Fe-Pt alloys up to 0.15 GPa, and can be explained within the high and low spin model. With increasing pressure, the population of the initial HS state of the sample[11]

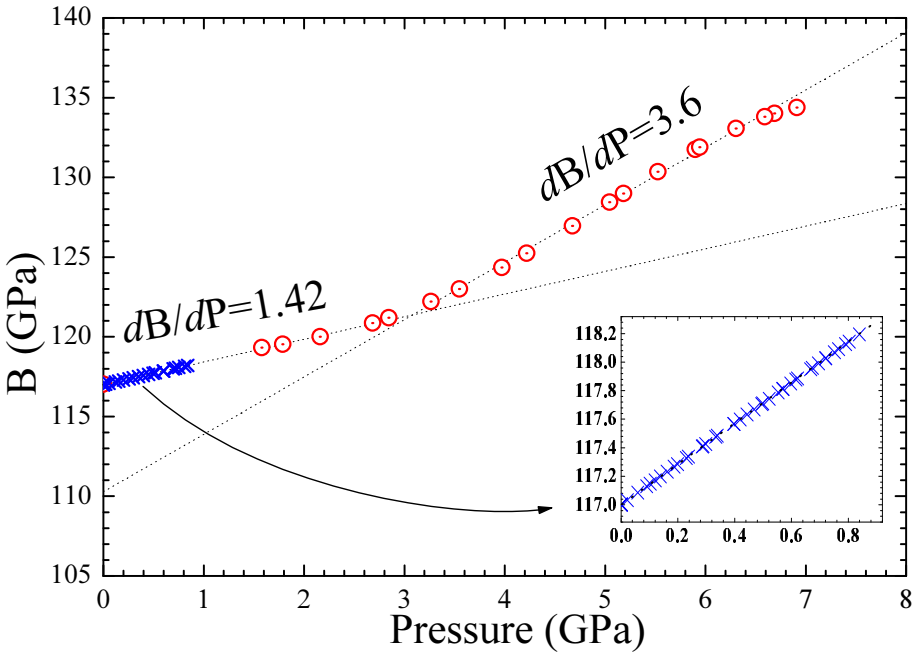

FIG. 2: Pressure dependence of bulk moduli in poly-crystalline $Fe_{64}Ni_{36}$. Between 0 and 1.0 GPa, experiments using the piston-cylinder apparatus (cross) supplement the high pressure Paris-Edinburgh measurements (open circles). The uncertainties in pressure and bulk modulus are within the symbol size.

continuously decreases at the benefit of the LS state. The lower volume of the low spin state does contribute to the non-magnetic compressibility of the iron-nickel alloy, giving rise to that peculiar value of B' pivotal to the Invar effect. At 3.1 GPa, the change of slope in the pressure dependence of B can be interpreted as a change of magnetic state from a mixed HS/LS to a pure LS configuration. At higher pressure, the magnetic state of the alloy is expected to remain purely LS (the HS level being empty), cancealling the Invar effect. This interpretation is further supported by the value of B', equal to 3.6 between 3 and 7 GPa, *i.e.* a value comparable to what is typically measured in solids where no magnetic transition occurs.

While the non-collinear model does succeed in explaining the unusual low value of B' at low pressure, it fails to reproduce the linear pressure dependence of B, as well as the existence of a transition pressure. These calculations predict a gradual increase of disorder in the spin alignment as the volume is reduced (pressure increases). This continuous variation of the ground-state spin structure is then responsible of a non-linear pressure dependence of the

bulk modulus, qualitatively incompatible with our measurements. On the other hand, from the x-ray diffraction experiments on iron-nickel alloys with three different compositions[12] (including $Fe_{64}Ni_{36}$), the bulk modulus is shown to exhibit a pressure behavior in complete agreement with the non-collinear model, *i.e* a low value of *B'* at low pressure and a non-linear pressure variation of B between 1 and 20 GPa. To explain the discrepancy with our results (and thus with our interpretation), we performed x-ray diffraction experiments on the $Fe_{64}Ni_{36}$ polycrystal simultaneously with the ultrasonic measurements. Our experiments confirm that in these alloys the pressure dependence of the bulk modulus cannot be derived from any classical equation of state like the Murnaghan one since *B'* is not expected to be constant. Thus, using the same procedure as that described in Ref. [12], we fitted our P-V curve with a 11th order polynomial function in order to determine the pressure dependence of B (Fig. 3). We obtained a behavior of *B(P)* in good agreement with Dubrovinsky *et al*[12] with a *continuous* variation of B, slightly decreasing from 0 to about 1.5 GPa followed by a gradual increase. On the other hand, a change of the polynomial order from 11 to 4 has a clear effect on the *B(P)* results, whereas the corresponding lattice parameter $a(P)$ fits both seem to be as good. This observation shows the inadequacy of the x-ray diffraction technique to measure *B(P)* in the peculiar case of the Invar compounds. Whereas non-physically based functions, like a i^{th} order polynomial, have to be used to reproduce the experimental equation of state of $Fe_{64}Ni_{36}$, the bulk modulus value at each pressure is directly determined with the ultrasonic method. The only hypothesis is a linear volume *vs* pressure variation between two consecutive pressure points (which is obviously correct taking into account that the pressure steps did not exceed 0.4 GPa during our experiments, much less than the B values). In other words, the determination of B at a given pressure using the ultrasonic method is completely independent from the B value at another pressure, which is not the case using the x-ray diffraction technique. Last but not least, the magnetic transition effect on the volume of $Fe_{64}Ni_{36}$ is known to be weak. The relative variation of the lattice parameter is about 2% up to 7 GPa. This value must be compared with the travel time $\Delta t/t_0$ variation, which is $\sim$10% for the longitudinal mode and $\sim$20% for the transverse one in the same pressure range. This clearly shows that the ultrasonic method is much more pressure sensitive than x-ray diffraction, and thus well adapted to the Invar problematic.

In summary, ultrasonic high pressure measurements below the Curie temperature on the Invar alloy $Fe_{64}Ni_{36}$ have provided experimental evidence for linear pressure dependence of

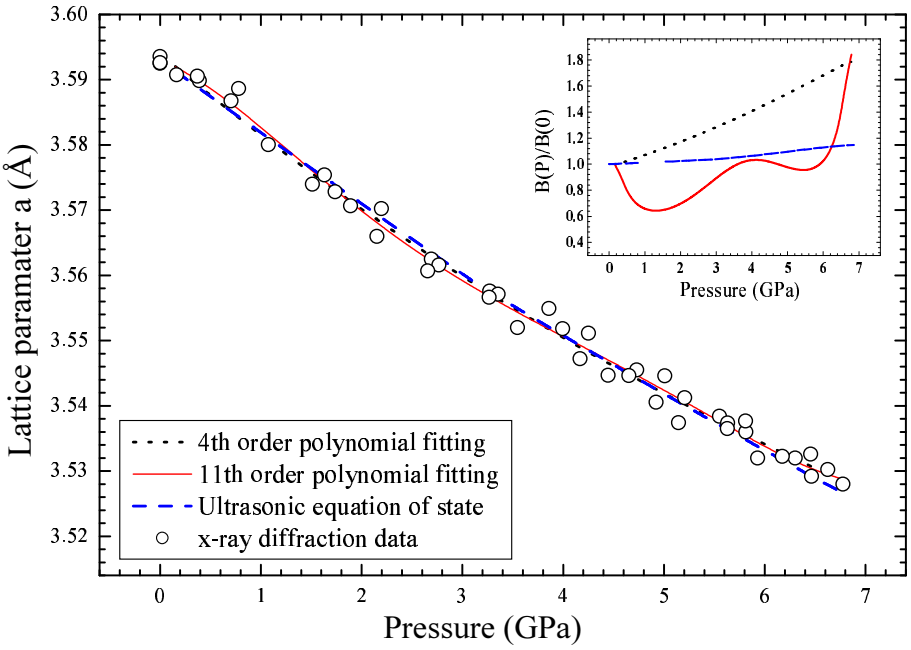

FIG. 3: Pressure dependence of polycrystalline $Fe_{64}Ni_{36}$ lattice parameter (circles) with 11th and 4th order polynomial fittings (solid and dot lines respectively). Dashed line : equation of state using the ultrasonic *B'(P)* data and 3.5935(8) *Å*. Inset : comparison between ultrasonic results and bulk modulus derived from the polynomial fitting curves using the thermodynamical definition of *B*.

the bulk modulus, with an abrupt discontinuity of *B'* at 3.1(2) GPa. Our results follow the behavior pattern proposed by Weiss, but can not be interpreted in terms of the non-collinear model. An explanation of the inability of the x-ray diffraction technique to measure accurately and independently the pressure dependence of the bulk modulus in the case of Invar compounds is given. In qualitative agreement with previous x-ray magnetic circular dichroism, Mössbauer and x-ray emission high pressure results, the present work allows to unify the magnetic and structural properties within the 2 γ-state model.

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[1] C.E. Guillaume, C.R. Acad. Sci. Paris **125**, 235 (1897).

[2] E.F. Wassermann, Europhys. News **22**, 150 (1991); E. F. Wassermann, in Ferromagnetic Materials, edited by K. H. Buschow and E. P. Wohlfarth **5** (North Holland, Amsterdam), 238 (1990).

[3] M.M. Abd-Elmeguid, and H. Micklitz, Phys. Rev. B **40**, 7395 (1989).

[4] K. Fukamichi, M. Kikuchi, S. Arikawa, and T. Masumoto, Solid State Commun. **2**3, 955 (1977).

[5] P. Renaud, Ph.D thesis, Universite de Lausanne, Switzerland (1988).

[6] Ll. Mañosa, G.A. Saunders, H. Rahdi, U. Kawald, J. Pelzl, and H. Bach, Phys. Rev. B **45**, 2224 (1992).

[7] R.J. Weiss, Proc. Phys. Soc. **82**, 281 (1963).

[8] M. van Schilfgaarde, I. A. Abrikosov, and B. Johansson, Nature (London) **400**, 46 (1999).

[9] H. Akai and P.H. Dederichs, Phys. Rev. B **47**, 8739 (1993).

[10] S. Odin, F. Baudelet, Ch. Giorgetti, E. Dartyge, J. P. Itié, A. Polian, J.C. Chervin, S. Pizzini, A. Fontaine, and J.P. Kappler, Eur. Phys. Lett. **47**, 378 (1999).

[11] J. P. Rueff, A. Shukla, A. Kaprolat, M. Krisch, M. Lorenzen, F. Sette, and R. Verbeni, Phys. Rev. B **63**, 132409 (2001).

[12] L. Dubrovinsky, N. Dubrovinskaia, I.A. Abrikosov, M. Vennström, F. Westman, S. Carlson, M. van Schilfgaarde, and B. Johansson, Phys. Rev. Lett. **86**, 4851 (2001).

[13] M. Gauthier, D. Lheureux, F. Decremps, M. Fischer, J.-P. Itié, G. Syfosse and A. Polian, Rev. Sci. Instrum. **74**, 3712 (2003).

[14] JJ. M. Besson, R. J. Nelmes, G. Hamel, J. S. Loveday, G. Weill, and S. Hull, Physica B **180&181**, 907 (1992).

[15] L. Decker, J. Appl. Phys. **36**, 157 (1965).

[16] R.K. Cook, J. Acoust. Soc. Am. **29**, 445 (1957).

[17] The initial rod of $Fe_{64}Ni_{36}$ (provided by Goodfellow, Ref. FE027905/3) has been homogenized at 880 K for one week.

[18] Z. Hashin and S. Shtrikman, J. Mech. Phys. Solids **10**, 343 (1962).

[19] In the ultrasonic set-up for highly accurate measurements under hydrostatic pressure up to 1.0 GPa, the pressure is generated in a piston-cylinder setup through the use of a low pressure compressor, and is measured through the variation of the manganin wire gauge resistivity with an accuracy better than 0.01 GPa. The sample is completely immersed in the pressure transmitting medium (pentane-isopentane mixture) with an holder which also maintains the transducer mounted on the sample (dimensions of about 10 mm).