Pressure-Induced Invar Effect in Fe-Ni Alloys

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We have measured the pressure-volume (P-V) relations for cubic iron-nickel alloys for three different compositions: $Fe_{0.64}Ni_{0.36}$, $Fe_{0.55}Ni_{0.45}$, and $Fe_{0.20}Ni_{0.80}$. It is observed that for a certain pressure range the bulk modulus does not change or can even decrease to some minimum value, after which it begins to increase under still higher pressure. In our experiment, we observe for the first time a new effect, namely, that the Fe-Ni alloys with high Ni concentrations, which show positive thermal expansion at ambient pressure, become Invar system upon compression over a certain pressure range.

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Properties of magnetic materials are a subject of a great scientific and practical interest. An enormous amount of experimental and theoretical investigations have been carried out to get a deeper understanding of the nature of magnetism in solids [1]. One of the most well-known and still not fully understood phenomena related to magnetism is the so-called Invar effect. In 1897 Guillaume [2] discovered the original Invar property of the face-centered cubic (fcc) iron-nickel alloys containing about 35 at. % Ni, which exhibits an anomalously low (almost zero) and constant thermal expansion over a wide region around room temperature. Subsequently, he found the temperature-independent elastic behavior of Fe-Ni-Cr alloys that is now known as the "Elinvar" effect.

The Invar effect has been found at ambient pressure in various alloys and even in amorphous materials. A comprehensive review of the experimental information and theoretical approaches to the Invar problem can be found in Ref. [3]. In particular, it was demonstrated that not only the thermal expansion, but also other physical properties, such as molar volume, elastic modulus, heat capacity, and magnetization, also show anomalous behavior. Recently, by means of ultrasonic measurements at pressures up to 0.2 GPa, it was shown [4] that for some Invar alloys in the ferromagnetic state, $Fe_{0.72}Pt_{0.28}$, for example, the bulk modulus decreases with pressure, and it was proposed that longitudinal-acoustic-mode softening due to magnetoelastic interaction could be the origin for Invar behavior of these alloys. Theoretical *ab initio* calculations [5] of the volume dependence of magnetic and thermodynamic properties for a random face-centered cubic iron-nickel alloy with optimized noncollinear spin alignments have shown that, even at zero temperature, the magnetic structure is characterized by a continuous transition from the ferromagnetic state at high volumes to a disordered noncollinear configuration at low volumes. There is an additional, comparable contribution to the net magnetization from the changes in the amplitudes of the local magnetic moments. The theory [5] clearly demonstrates that the noncollinearity gives rise to an anomalous volume dependence of the binding energy curve, and also predicts that the Invar effect generally should be associated with a small or even negative pressure derivative of the bulk modulus. Thus, materials would show the extraordinary feature of becoming easier to squeeze when pressure is applied to them. In this Letter, we verify this theoretical prediction by measurements of P-V relations for cubic iron-nickel alloys for three different compositions: $Fe_{0.64}Ni_{0.36}$, $Fe_{0.55}Ni_{0.45}$, and $Fe_{0.20}Ni_{0.80}$.

The samples were prepared by arc melting appropriate amounts of nickel and iron rods of high purity (99.999% Alfa Inc.) in an arc furnace in a pure argon atmosphere. Ingots were homogenized in vacuum at 1050 K for ten days. Diffraction patterns of synthetic materials contain reflections of only a face-centered cubic phase with lattice parameters 3.5957(1), 3.5904(1), and 3.5512(1) Å for the compositions $Fe_{0.64}Ni_{0.36}$, $Fe_{0.55}Ni_{0.45}$, and $Fe_{0.20}Ni_{0.80}$, correspondingly, in good agreement with previous studies [6] (numbers in parentheses are standard deviations in the last significant digits). We conducted *in situ* x-ray high-pressure experiments in the Uppsala Lab in Sweden and at ESRF (on beam lines ID30 and BM02). In the Uppsala Lab, we obtained powder x-ray diffraction data with a Siemens x-ray system consisting of a Smart CCD Area Detector and a direct-drive rotating anode as an x-ray generator (18 kW). MoK_α radiation (tube voltage 50 kV, tube current 24 mA, cathode gun 0.1×1 mm) was focused with a capillary x-ray optical system to ∅40 μm FWHM. At ESRF, powder diffraction data were collected with a fine incident x-ray beam of approximately rectangular

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shape ($8 \times 9\ \mu\text{m}^2$) of 0.3738 Å wavelength at the MAR345 imaging plate. In all measurements, NaCl [7] was used as a pressure medium and pressure standard. Experiments were performed in a membrane driven diamond anvil cell, which allowed fine changes of pressure (with a step of 0.2–0.3 GPa). Using beryllium seats for diamonds and x-ray area detectors, it was possible to collect complete Debye rings to 0.7 Å. See our earlier papers [8–10] for more details.

Full-profile Rietveld refinements of the resulting patterns were carried out using the GSAS [11] package (Fig. 1). A wide d-spacing range in association with an angle-dispersive area detector technique allowed us to determine lattice parameters of both NaCl pressure standard and iron-nickel alloy samples with accuracy better than 0.0004 Å at pressures up to 20 GPa. As a result, the uncertainty in the pressure determination associated with errors in the molar volume of NaCl is less than 0.03 GPa, while the uncertainty of the NaCl pressure scale itself is 3% at 25 GPa [7]. It is important that we have used the same pressure scale and the same experimental setup for all alloys, so that the observed effects are related to the material studied, and not to the experimental procedure.

In Fig. 2, we show the measured P-V curves for the studied alloys. There are pronounced "bumps" between 9 and 14 GPa for $\text{Fe}_{0.20}\text{Ni}_{0.80}$, between 5 and 9 GPa for $\text{Fe}_{0.55}\text{Ni}_{0.45}$, and a similar but less clear feature between ambient pressure and 3 GPa for $\text{Fe}_{0.64}\text{Ni}_{0.36}$. Figure 2(c) also shows the P-V relations for Pt, which demonstrate smooth variations of volume with pressure and confirm that peculiarities of compression curves of Fe-Ni alloys are related to their properties at high pressure and not to the experimental technique.

Such a complex shape of the P-V curves as for the studied Fe-Ni alloys cannot be described by any known equation of state (e.g., Birch-Murnaghan, Mie-Grüneisen, etc. [12]). Therefore, we used a polynomial fit $P = \sum_{i=0}^{n} a_i V^i$ (Fig. 2) in order to describe the P-V relations for these alloys. Polynomials of the 11th order were sufficient to describe the data with the experimental precision (0.03 GPa in pressure and 0.05% in relative volume at 20 GPa). The isothermal bulk moduli $K_{291} = -V(dP/dV)$ were determined by differentiation of the polynomials. This procedure was tested for Pt [Fig. 2(c)]. At ambient pressure and temperature, we obtained $K_{291} = 281(2)$ GPa, in good agreement with ultrasonic data [13] ($K_{291} = 283$ GPa). The bulk moduli for $\text{Fe}_{0.20}\text{Ni}_{0.80}$, $\text{Fe}_{0.55}\text{Ni}_{0.45}$, and $\text{Fe}_{0.64}\text{Ni}_{0.36}$ at ambient pressure and room temperature were found to be 145(2), 136(2), and 130(3) GPa, respectively. The last two values are in good agreement with ultrasonic measurements [4,14] ($K_{291} = 132\text{-}134$ GPa for $\text{Fe}_{0.64}\text{Ni}_{0.36}$, and $K_{291} = 129\text{-}136$ GPa for $\text{Fe}_{0.55}\text{Ni}_{0.45}$). Comparison with the bulk modulus of pure α-Fe [13] ($K_{293} = 167$ GPa) and Ni [13] ($K_{293} = 184$ GPa) confirms an earlier observed [4] phenomenon that the bulk moduli of the Invar Fe-Ni alloys are significantly lower than those of the pure elements forming the Invar.

We have observed that, with increasing pressure in $\text{Fe}_{0.64}\text{Ni}_{0.36}$, the bulk modulus does not change or even decreases, showing a minimum at ~1.8 GPa. After this, it gradually increases with increasing pressure (Fig. 3).

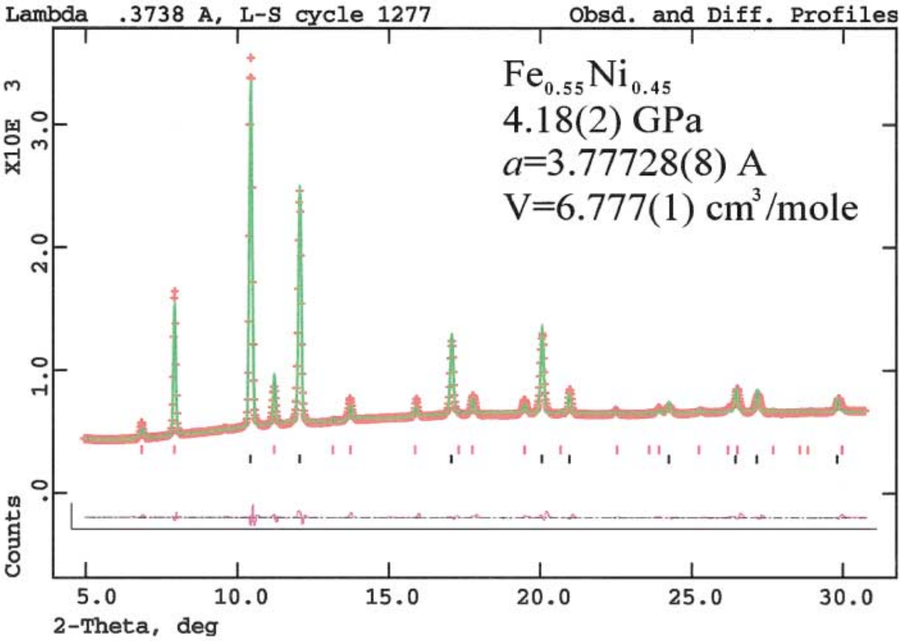

FIG. 1 (color). Typical example of analyzed integrated patterns of the spectrum collected at 4.18(2) GPa and ambient temperature for the $\text{Fe}_{0.55}\text{Ni}_{0.45}$ alloy. GSAS program package [11] was used. The lower ticks mark positions of the $\text{Fe}_{0.55}\text{Ni}_{0.45}$ alloy and the upper one marks the NaCl calibrant.

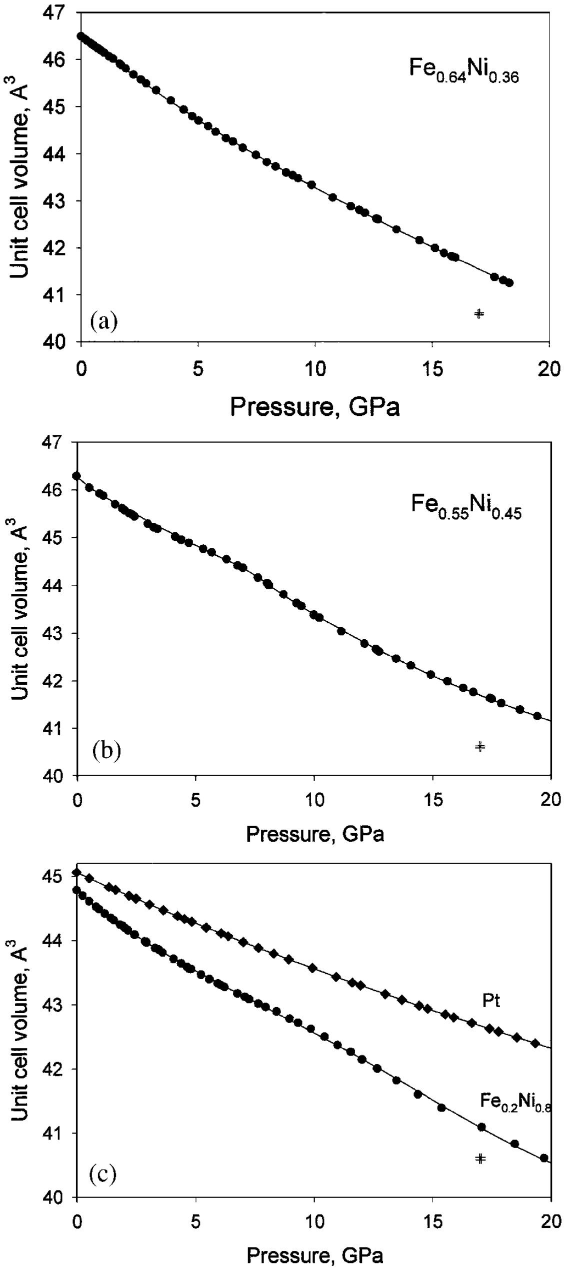

FIG. 2. P-V curves of (a) Fe$_{0.64}$Ni$_{0.36}$, (b) Fe$_{0.55}$Ni$_{0.45}$, and (c) Fe$_{0.20}$Ni$_{0.80}$ alloys. There are pronounced "bumps" between 9 and 14 GPa for Fe$_{0.20}$Ni$_{0.80}$, between 5 and 9 GPa for Fe$_{0.55}$Ni$_{0.45}$, and a similar but less clear feature between ambient pressure and 3 GPa for Fe$_{0.64}$Ni$_{0.36}$. (c) shows also P-V relations for Pt, which demonstrate smooth variations of volume with pressure and confirm that peculiarities of compression curves of Fe-Ni alloys are related to their properties at high pressure and not to the experimental technique. Continuous lines show results of the polynomial fitting. Error bars show uncertainties in pressure and volume.

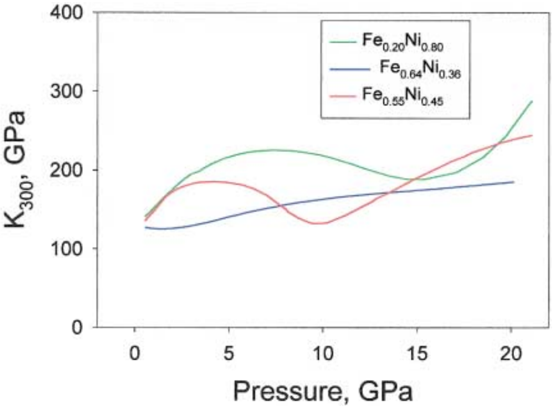

FIG. 3 (color). Bulk moduli of Fe-Ni alloys as a function of pressure.

This behavior of K is in complete agreement with theoretical calculations [5]. The effect is actually even more pronounced for Fe$_{0.55}$Ni$_{0.45}$ and for Fe$_{0.20}$Ni$_{0.80}$ alloys (Fig. 3). However, for those alloys it occurs at higher pressures. In other words, over a certain pressure range iron-nickel alloys become more compressible with pressure and, accordingly, the pressure derivative of the bulk modulus $K' = dK_T/dP$ is negative. As has been suggested in Ref. [5], this peculiar behavior of the bulk moduli indicates that the anharmonicity of the phonons in the Invar alloys may be suppressed due to the system's ability to relax its magnetic structure, and this leads to the observed low thermal expansion. In particular, in the Fe$_{0.64}$Ni$_{0.36}$ alloy the anomalously low thermal expansion ($\sim 0.8 \times 10^{-5}$ K^{-1}) at ambient pressure and temperature (the typical Invar effect) does correlate with the very small value of K' (Fig. 3). For Fe$_{0.55}$Ni$_{0.45}$, the thermal expansion at ambient pressure is 2.2×10^{-5} K^{-1} and for Fe$_{0.20}$Ni$_{0.80}$ it is even higher, 4.1×10^{-5} K^{-1} (see Ref. [14] and references therein). However, according to Fig. 3 at pressures $\sim$7.5 GPa for Fe$_{0.55}$Ni$_{0.45}$ and $\sim$12 GPa for Fe$_{0.20}$Ni$_{0.80}$, one can expect a significant decrease of the thermal expansion. To check this hypothesis we conducted isobaric heating of Fe$_{0.55}$Ni$_{0.45}$ at 0.41(3), 7.7(1), and 28.3(3) GPa, and Fe$_{0.20}$Ni$_{0.80}$ at 12.6(1) GPa using an external electrical heating method described elsewhere [9,10]. During the heating, the pressure was maintained constant within the experimental error. Figure 4 shows that at 7.7(1) GPa and at temperatures between 291 and 500 K, Fe$_{0.55}$Ni$_{0.45}$ practically does not expand ($\alpha = 0.2(3) \times 10^{-5}$ K^{-1}), while no anomalies in the thermal expansion of this alloy were observed at 0.41(3) and 28.3(3) GPa. Similarly, for Fe$_{0.20}$Ni$_{0.80}$ at 12.6(1) GPa, we found a zero thermal expansion at temperatures up to 460 K. In other words, at high pressure both Fe$_{0.55}$Ni$_{0.45}$ ($\sim$7.5 GPa) and Fe$_{0.20}$Ni$_{0.80}$ ($\sim$12 GPa) alloys exhibit anomalously low thermal expansion over a certain pressure interval. Thus, we observe a pressure-induced Invar effect.

Our experimental results can be fully understood in the framework of a model suggested by van Schilfgaarde, Abrikosov, and Johansson [5]. According to this theoretical study, the anomalous behavior of the binding

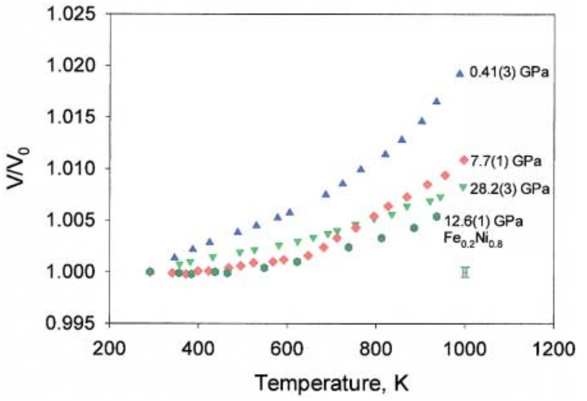

FIG. 4 (color). Variation of relative volume of the $Fe_{0.55}Ni_{0.45}$ alloy at 0.41(3), 7.7(1), and 28.2(3) GPa, and $Fe_{0.20}Ni_{0.80}$ alloy at 12.6(1) GPa. During the heating, the pressure maintained constant within the experimental error. At 7.7(1) GPa and at temperatures between 291 and 500 K, $Fe_{0.55}Ni_{0.45}$ practically does not expand [$\alpha = 0.2(3) \times 10^{-5}\ \mathrm{K}^{-1}$], while no anomalies in thermal expansion of this alloy were observed at 0.41(3) and 28.3(3) GPa. At 12.6(1) GPa, the $Fe_{0.20}Ni_{0.80}$ alloy also shows practically zero thermal expansion. Error bars show uncertainties in temperature and volume.

energy curve in Fe-Ni alloys and the Invar effect itself are associated with the transition from the high-spin ferromagnetic state at high volumes [3,15] to the increasingly noncollinear configurations at low volumes. For $Fe_{0.64}Ni_{0.36}$, this transition occurs around equilibrium volume, i.e., at ambient pressure. With increasing Ni concentration, the high-spin state becomes increasingly more stable [16,17], and one needs to apply pressure to induce noncollinear magnetic moments. Thus, according to theory, one can expect the existence of a pressure-induced Invar effect in the Fe-Ni alloys. Our experiments fully confirm these expectations.

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