High-pressure structural study of Fe$_{64}$Ni$_{36}$ and Fe$_{72}$Pt$_{28}$ Invar alloys at low-temperature

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Structural properties at 30 K of Fe$_{64}$Ni$_{36}$ and Fe$_{72}$Pt$_{28}$ Invar alloys have been investigated through x-ray diffraction experiments up to 20 GPa. The Invar magnetovolumic characteristic property clearly affects the equation of state of both Fe-Ni and Fe-Pt samples between 2 and around 6 GPa. A fit function based on the 2-$\gamma$ model is used to analyze our $(p,V,T)$ data and is shown to be suitable to interpret them.

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I. INTRODUCTION

A stimulating topic in solid state physics is the understanding of the unusual behavior of various metal transition alloys, known as the Invar effect. Discovered in 1897 by Guillaume on Fe$_{65}$Ni$_{35}$, this anomaly consists in the absence of thermal expansion between a few Kelvin and the Curie temperature. Magnetovolumic instabilities are responsible for a negative contribution which compensates the usual expansion due to the lattice vibrations. Invar alloys are supposed to present unusual behavior under pressure. For example, a very small (even negative) pressure derivative of the bulk modulus ($B'$) (Refs. 2 and 3) has been observed. However, the microscopic processes are still not clearly identified and are thus the subject of controversial discussions.4

Various Fe-based alloys belong to the Invar family. Among them, Fe$_{64}$Ni$_{36}$ and Fe$_{72}$Pt$_{28}$ are usually considered as “typical” Invar, in spite of their physical differences. In the case of Fe-Ni alloys, deviation of the concentration dependence of the lattice constant from the Vegard law5 and of the magnetic moment from the Slater Pauling curve6 are observed. In Fe-Pt samples, no such deviations occur.7 Furthermore iron-nickel alloys, where both atoms are responsible for the magnetism, show properties that can be analyzed in the itinerant ferromagnetism framework. On the contrary, the magnetism of iron-platinum alloys is known to be better interpreted by the localized model.8

Currently, mainly two models are usually invoked in the analysis of the Invar properties. The older one, called the 2-$\gamma$ state model, originates from Weiss9 and a more recent proposal by van Schilfgaarde et al.10 based on the noncollinear model. The first description is based on the existence of two distinct magnetic states for the iron: a high spin (HS) large volume state and a low spin (LS) small volume state, the latter having a slightly higher energy. The Invar effect is expected to occur through a transition from the HS to the LS state as the temperature is raised. The gradual population of the LS state at the expense of the HS state compensates the thermal expansion up to a given temperature, where all the electrons have been promoted in the LS state. Applying pressure to Invar gives rise to a decrease of the energy difference $\Delta E = E_{HS} - E_{LS}$ between the two states as shown in Fig. 1. According to this scheme, the behavior of Invar compounds should be modified at a transition pressure $p_T$ corresponding to $\Delta E = 0$. Around this critical pressure, the coexistence of both the HS and LS phases could be observed through thermal energy activation. This transition to the smaller volume state gives a microscopic explanation of the low “effective” $B'$ value,3 one of the Invar alloys characteristics. Later theoretical works have supported this picture based on the existence of two distinct states.11-13 Indeed, modern band structure calculations showed that the HS to LS transition corresponds to an electronic transfer from the majority antibonding orbital ($t_2$) to the minority nonbonding orbital ($e_g$), lying close to the Fermi level. According to this model, as it has already been observed in experimental studies,14-16 first order discontinuities are expected to occur in pressure or temperature dependence of Invar physical properties.

Some inconsistencies between experimental data and prediction from the previous model on Fe-Ni compounds have conducted van Schilfgaarde et al.10 to propose a new microscopic explanation of the Invar anomaly. Using ab initio simulation, they have proposed to interpret the Invar properties through a continuous variation of the iron spin alignment and a decrease of the amplitude of the magnetic moment as the volume is decreased. This picture of a noncollinear ground state succeed in reproducing the gradual decrease of the magnetic moment as a function of the composition. Low value of the bulk modulus (compared to usual transition metal) and negative value of its pressure derivative are also predicted, in good agreement with experimental studies.2 Within this approach, no first order discontinuity in pressure or temperature evolution should be measured.

As shown in Ref. 17, x-ray diffraction at room temperature is not an appropriate technique to discuss the validity of one model with respect to the other. Actually at room temperature electrons can be either in high spin or low spin state, in the 2-$\gamma$ state point of view. To force all the electrons to be in the HS state, samples must be at such a low-temperature that the thermal energy is not large enough to populate the LS state at ambient pressure [configuration corresponding to Fig. 1(a)]. As a consequence, at $T = 0$ K the 2-$\gamma$ state model predicts a first order transition in the volume evolution when pressure is increased, corresponding to the $V_{HS} - V_{LS}$ volume collapse at the transition pressure. On the other hand, a continuous evolution is expected by the “noncollinear” interpretation. Therefore the existence of a kink in the $V(p)$ curve or not is a test of the ability of the Weiss model to account for experimental data. A previous study18 has been performed at low-temperature on Fe$_{70}$Pt$_{30}$. However the low number of
data points did not provide any new insights into the previous problematic.

In this paper, we report pressure dependence of the volume cell of disordered Fe\textsubscript{64}Ni\textsubscript{36} and ordered Fe\textsubscript{72}Pt\textsubscript{28} compounds at 30 K and propose an analysis based on the 2-\gamma state model. The question was also to find out whether or not the different magnetic characteristics of the two Invar require different models for results interpretation.

II. EXPERIMENTAL PROCEDURE

The samples were disks of 30 \( \mu m \) in diameter and 10 \( \mu m \) thick, extracted from a polycrystalline rod. They have been annealed for one day in an argon atmosphere at 800 °C to remove residual stress. The densities have been measured \([\rho_{\text{Fe}_{64}\text{Ni}_{36}} = 8.078(5) \text{ g/cm}^3 \text{ and } \rho_{\text{Fe}_{72}\text{Pt}_{28}} = 11.973(5) \text{ g/cm}^3]\) and found close to those of single crystal values.\textsuperscript{19,20} More-over these samples have been characterized and investigated in previous studies.\textsuperscript{15,17} Diffraction spectra (Fig. 2) give also an indication about the good quality of our samples. A membrane diamond anvil cell (MDAC) with a large x-ray conical aperture\textsuperscript{21} has been used as high pressure generator. Samples were placed in a 100 \( \mu m \) diameter hole of a stainless-steel gasket. Using a cryogenic loading, the sample chamber was filled with argon as pressure medium. A ruby ball\textsuperscript{22} was loaded close to the sample in order to measure the temperature and the pressure. The cell was placed into a cryostat equipped with Mylar windows. The pressure was determined by the ruby fluorescence method,\textsuperscript{23} with the exception of the Fe\textsubscript{64}Ni\textsubscript{36} run above 9 GPa where the equation of state of argon must be used.\textsuperscript{24–26} The temperature was determined thanks to the relative intensity of the ruby luminescence peaks.\textsuperscript{27} High pressure powder diffraction was performed at ESRF (beamline ID 09) using the monochromatic...
(λ=0.4130 Å) angular dispersive method. Reflections were collected with an image plate detector (MAR 345). During acquisition, the MDAC was tilted through ±3° in order to improve the powder statistic.

III. RESULTS AND ANALYSIS

Spectra collected on both samples at different pressures are shown in Fig. 2. For the disordered Fe64Ni36 sample, the (hkl) Bragg reflections (111), (200), (220), (311) of the fcc phase were always observed and give rise to an accurate determination (10−3) of the cell parameter as function of pressure. On the other hand, the Fe72Pt28 sample was observed to be partially ordered since simple cubic Bragg reflections were observed on the whole pressure range. In Fig. 2 simulated spectra are also represented and show good superposition with experimental spectra. During all experiments, the width of the diffraction peaks has been measured and found to remain constant, indicating that the samples were not subject to significant uniaxial strain. The width of Fe64Ni36 diffraction peaks are found to be larger than the Fe72Pt28 ones in agreement with the respective disorder of samples. Moreover, neither disappearance nor appearance of diffraction peak occurred, demonstrating that both sample remained in their initial space group in the whole pressure range.

The ambient pressure lattice parameter at 30 K was 3.6027(1) Å for Fe64Ni36 and Fe72Pt28, respectively. In Fig. 3, normalized volume variations with pressure at 30 K for Fe72Pt28 and Fe64Ni36 samples are shown. One can observe a clear magnetovolumic effect of the V(p) curve, especially for the Fe-Pt alloy. To analyze our data within the framework of the 2-γ state picture, the following processing has been used.

As discussed in the introduction, this model leads to defining three regions. In the first and last ones [pure HS, Fig. 1(a) and pure LS, Fig. 1(c), configuration, respectively] no magnetovolumic effect occurs and the alloys are expected to behave as simple metal. We thus used the Murnaghan equation of state [Eq. (1)] to fit their volume pressure dependence in these two ranges,

\[ V_{HS,LS}(p) = V_{HS,LS}^0 \left( 1 + B_{HS,LS}' \frac{p}{B_{HS,LS}^0} \right)^{-1/B_{HS,LS}'}, \]  

(1)

where \( V_{HS,LS}^0 \) and \( B_{HS,LS}^0 \) are ambient pressure cell volume and bulk modulus, respectively, in pure HS or LS state and \( B_{HS,LS}' \) are pressure derivatives of \( B_{HS,LS}^0 \). In these fits, since the pressure range is limited, bulk modulus derivatives were fixed to 4, in accordance with ultrasonics measurements\(^{11} \) and with usual value observed in metals. In the intermediate region [Fig. 1(b)], the energy difference between the two spin states is lower than 30 K so that the LS state can be thermally populated at the expense of the HS one. Within the 2-γ state interpretation, the unit cell volume can be written as a weighted sum as follows:

\[ V(p) = n(p)V_{HS}(p) + [1 - n(p)]V_{LS}(p), \]  

(2)

where \( V_{HS} \) (\( V_{LS} \)) is the volume corresponding to the high (low) spin state and \( n \) represents the HS state density. The

\[ n(E) = \frac{1}{1 + \exp\left( \frac{E - E_0}{k_B T} \right)}, \]  

(3)

where \( \Delta E \) is the energy difference between the HS and LS states. Assuming that the pressure dependencies of both the \( t_2 \) and \( e_g \) levels are linear, it follows:

\[ \Delta E = \Delta E_0 - \frac{\partial \Delta E}{\partial p} p, \]  

(4)

where \( \Delta E_0 \) is the energy difference between the two states at ambient pressure. Using Eqs. (3) and (4) the pressure dependence of the HS state population \( n(p) \) can be represented through the simple form:

\[ n(p) = \frac{1}{1 + \exp\left( \frac{p - p_T}{\Delta p} \right)} \]  

(5)

with

![Fig. 3. (Color online) Pressure dependence of normalized volume: (a) Fe72Pt28 and (b) Fe64Ni36. Focus of the 0–10 GPa is shown in the inset. The lines result from the “Weiss-like equation of state” fitting procedure.](image.png)
\[ p_T = \Delta E_0 \frac{\partial p}{\partial \Delta E} \quad \text{and} \quad \Delta p = k_B T \frac{\partial p}{\partial \Delta E}, \] (6)

where \( p_T \) could be associated to the HS to LS transition pressure and \( \Delta p \) to the pressure range during which both spin states coexist. Finally Eqs. (1), (2), and (5) define a Weiss-like equation of state (WEOS) that can be used to fit the volume pressure dependence of solids which exhibit magnetovolumic contribution. Using the WEOS fitting procedure, our experimental data are successfully reproduced on the whole pressure range (continuous lines on Fig. 3). Values obtained from this fit are summarized in Table I.

### IV. DISCUSSION

In order to compare the high pressure behavior of the cell volume with respect to the temperature, we report in Fig. 4 the experimental data at ambient temperature and at 30 K in the low pressure range (up to 10 GPa, i.e., where the magnetovolumic effect occurs). For the Fe-Pt compound, the different shape of the two curves clearly points out the temperature dependence of the magnetic configuration. The temperature effect on the \( V(p) \) curve of Fe\(_{72}\)Pt\(_{28}\) is tiny but a magnetovolumic effect can still be observed, more pronounced at low-temperature than at 291 K.

#### A. Fe\(_{72}\)Pt\(_{28}\)

Using the fit function described above, we obtained \( B_{0,\text{HS}} = 165 \pm 4 \) GPa for the high spin state and \( B_{0,\text{LS}} = 181 \pm 3 \) GPa for the low spin state, in good agreement with previous studies.\(^{2,15}\) The transition pressure (5.7 GPa) is found to be slightly higher than at room temperature (found to be 4 GPa by Odin et al.\(^{15}\)). Applying the same analysis to ambient temperature results is less straightforward since in that case the ambient pressure electronic configuration is a mixture of both the HS and LS states. However, fitting process of the Odin et al. data gives a lower limit of \( \Delta p \) to be 0.70 GPa. In agreement with the Weiss model and with Eq. (6) (in which \( \Delta p \) is proportional to \( T \) ) the pressure range during which the HS to LS transition occurs is found to be smaller at 30 K than at ambient temperature.

Thus, the good ability of the Weiss-like equation of state to reproduce our experimental data demonstrates that the initial phenomenological Weiss description in three different domains of the magnetovolumic effect is well suitable to account for the behavior of Fe\(_{72}\)Pt\(_{28}\) under pressure and temperature.

#### B. Fe\(_{64}\)Ni\(_{36}\)

The anomaly in the pressure dependence of the Fe\(_{72}\)Pt\(_{28}\) volume is less pronounced for Fe\(_{64}\)Ni\(_{36}\). However, according to the high accuracy of our data, the low pressure domain shows a “bump” (at least a change of the curvature sign, see Fig. 5) that does not arise from any experimental artefact. We thus use the same analysis procedure as described in the previous part.

As for the Fe-Pt sample, the fit function [line in Fig. 3(b)] succeed in reproducing the experimental data in the whole pressure range. The pure LS bulk modulus values are similar to what has been found from ultrasonic measurements performed on the same sample\(^{17}\) and with previous studies.\(^{2,28}\) One can also notice that the HS to LS pressure transition is.

### Table I. Results obtained using the “Weiss-like EOS” for each sample.

<table>
<thead>
<tr>
<th></th>
<th>( B_{0,\text{HS}} )</th>
<th>( B_{0,\text{LS}} )</th>
<th>( V_{0,\text{LS}} / V_{0,\text{HS}} )</th>
<th>( p_T )</th>
<th>( \Delta p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(<em>{72})Pt(</em>{28})</td>
<td>165±4 GPa</td>
<td>181±3 GPa</td>
<td>0.981</td>
<td>5.7±0.1 GPa</td>
<td>0.35±0.04 GPa</td>
</tr>
<tr>
<td>Fe(<em>{64})Ni(</em>{36})</td>
<td>109±10 GPa</td>
<td>132±2 GPa</td>
<td>0.986</td>
<td>3.5±0.6 GPa</td>
<td>0.96±0.15 GPa</td>
</tr>
</tbody>
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FIG. 4. Pressure dependence of normalized volume at ambient temperature (open circles) and at 30 K (crosses) for (a) Fe\(_{72}\)Pt\(_{28}\) (Ref. 15) and (b) Fe\(_{64}\)Ni\(_{36}\) (Ref. 28).
found to lie between 2.5 and 4.5 GPa in very good agreement with room temperature data.\textsuperscript{16,17}

The good agreement between present values and those found in literature support our 2-\textgamma state based analysis, even for Fe-Ni alloys. The smooth kink in the V\textsubscript{p}/H20849 curve compared to the Fe-Pt case shows that other fit functions are conceivable. However no classical equation of state based on physical assumptions can be found in the literature to fit our data with an acceptable accuracy.

C. Fe\textsubscript{64}Ni\textsubscript{36} vs Fe\textsubscript{72}Pt\textsubscript{28}

The volume of the low spin state compared to the high spin one is found to be smaller for the Fe\textsubscript{72}Pt\textsubscript{28} sample than for Fe\textsubscript{64}Ni\textsubscript{36}. The volume difference between the two states is thus higher for Fe-Pt than for Fe-Ni, as previously predicted through band structure calculations.\textsuperscript{11,12} We also notice that (i) the transition pressure is higher for the Fe\textsubscript{72}Pt\textsubscript{28} alloy and (ii) the difference between pressure transition at low temperature and value at room temperature is larger in the case of Fe-Pt. These last two points are in good agreement with Mössbauer experiments on Fe\textsubscript{65}Ni\textsubscript{35−x}Pt\textsubscript{x} alloys performed by Kong \emph{et al.}\textsuperscript{29} Using a Weiss-like model they concluded that the energy difference between the two states increases with the Pt concentration x. The narrower pressure range of the transition for Fe-Pt than for Fe-Ni goes in the same way.

Using Eq. (2), the HS state density n can be deduced from the data through

\[ n(p) = \frac{V(p) - V\textsubscript{L5}(p)}{V\textsubscript{HS}(p) - V\textsubscript{L5}(p)}, \]

where V(p) is the experimental measurement, V\textsubscript{HS} is obtained through the Murnaghan fit of V(p) in the low pressure range (i.e., pure HS) and V\textsubscript{L5} through the fit of the high pressure domain (i.e., pure LS). Results for each sample are reported in Fig. 6 where the distribution function [Eq. (5)] is also represented. The decrease corresponds to the gradual population of the LS state and the different shape of those curves must be related to the different magnetic properties of the alloys.

V. CONCLUSION

The aim of this work was to test the ability of the 2-\textgamma state model to interpret the low temperature structural behavior of prototypical Invar alloys. In this purpose, data from x-ray diffraction experiments at high pressure and at 30 K on Fe\textsubscript{64}Ni\textsubscript{36} and Fe\textsubscript{72}Pt\textsubscript{28} polycrystals have been reported and analyzed using a “Weiss-like equation of state.” This fit function is shown to be appropriate to reproduce the anomalous V(p) curve for both compounds. Moreover, values of the bulk modulus, transition pressure and low spin volume compared to the high spin one are in good agreement with previous studies. For the Fe-Ni sample the conclusion is less straightforward since the itinerant character of its magnetic properties implies that the Weiss interpretation cannot be to-
tally suitable. Therefore, it could be of interest to test whether or not the noncollinear model reproduces our Fe-Ni experimental data. Another perspective is to perform x-ray diffraction at lower temperature (4 K) in order to vanish the thermal energy and find out if the kink in the volume evolution with pressure becomes more significant. A different way to obtain a smaller thermal energy compared to the energy level difference should be to investigate other Fe-Ni samples with higher Ni concentration. In these alloys, the Invar effect is known to occur at higher pressure, indicating a higher energy difference between the two states.

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3 We would like to emphasize that in the case of magnetovolumic effects superimposed with a "normal" pressure effect, the standard notion of \( B' \), has no clear meaning. One can define and measure an effective bulk modulus and its pressure derivative that take into account both effects (Ref. 17) in the pressure range where magnetovolumic effects exist, and the standard quantities at higher pressure.
24 Above 9 GPa, the width of the ruby luminescence peaks increased, the ruby ball being probably constrained against the gasket. During the cooling of the MDAC, argon has solidified as a single crystal in such a way that its accurate cell volume measurement was allowed under pressure. In a first step, we have fitted the \( V(p) \) of argon in the low-pressure range (up to 9 GPa) with a Vinet equation of state (EOS). We obtained \( B_0 = 2.53 \) GPa and \( B' = 7.45 \), in good agreement with literature data (Ref. 25 and 26). In a second step, we have used the Vinet EOS with previous \((B_0, B')\) couple to extract the \textit{in-situ} pressure value from the cell volume measurement of argon. To resume, the luminescence shift of the ruby has been used to determine the pressure up to 9 GPa with a high accuracy (0.1 GPa). Above this pressure, the ruby ball being constrained, EOS of argon was used to extract the pressure with a lower accuracy (0.5 GPa).