# Pressure-induced magnetic phase transitions in Fe-based Invar alloys

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Pressure variations of the magnetic state in $Fe_{65}Ni_{27}Mn_8$ and disordered $Fe_{72.8}Pt_{27.2}$ Invar alloys have been investigated by ac susceptibility measurements under high pressure up to 7.5 GPa. In both alloys, the ferromagnetic state vanished and high-pressure magnetic states came to appear with increasing pressure. In addition, we observed the pressure-induced phase transition from the high-pressure magnetic phase to nonmagnetic state in disordered $Fe_{72.8}Pt_{27.2}$. These results are corresponding to the previous theoretical studies.

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## I. INTRODUCTION

Invar alloys, such as Fe-Ni, Fe-Pt, and Fe-Ni-Mn, have some characteristic magnetic and elastic properties, the so-called Invar effect.[1,2] It is well known that Invar alloys show the low thermal expansion below $T_C$, and this phenomenon has close connection to magnetism. However, magnetic properties of Fe-Ni- and Fe-Ni-based Invar alloys are different from those of Fe-Pt Invar alloys. In particular, it is very interesting that Fe-Ni Invar alloys, which show weak itinerant ferromagnetism in contrast to disordered Fe-Pt Invar alloys, which show strong ferromagnetism. In spite of a large number of studies on the Invar effect, common properties of all Fe-based Invar alloys have been discovered to be very few; thus, we have not reached a complete understanding of the mechanism of the Invar effect.

Recent theoretical studies pointed out that Invar alloys had some high-pressure magnetic phases. In addition, they reported that the high-pressure magnetic phases would have a close connection to the origin of the Invar effect.[3–9]

Some band calculations for Fe-Ni and Fe-Pt Invar alloys predicted the pressure- or temperature-induced phase transition from ferromagnetic high-spin ground state (HS) to a low-spin–low-volume excited state (LS).[3–7] From these calculation results, they explained that the Invar effect took place with the HS-LS transition with increasing temperature or pressure.[2–7] This explanation reminds us of the $2\gamma$ model by Weiss,[10] which explained that the Invar effects were caused by the hybrid of two states that each had different volumes.

On the other hand, some recent band calculations predicted a noncollinear magnetic order state was the most stable in the intermediate volume range between ferromagnetic HS and LS.[8,9] A theoretical study for ordered $Fe_3Pt$ pointed out a spin-spiral magnetic phase (SP) took the lowest energy in the intermediate volume range between HS and LS.[8] The magnetic moment of the SP took the value between 0 and that of the HS. In addition, another theoretical study,[9] for $Fe_{65}Ni_{35}$ reported the ground state of $Fe_{65}Ni_{35}$ was noncollinear spin alignments,[9] and the magnetic structure showed a continuous transition to a more disordered noncollinear configuration with increasing pressure. This calculation predicted that the anomalous volume dependence of the binding energy that accompanied the anomalous volume dependence of the magnetic structure, caused an anomaly in a Grüneisen constant ($\gamma$). They reported the anomaly of $\gamma$ was the origin of the low thermal expansion of the Invar alloy, and the existence of the anomalous volume dependence of the binding energy was proved by the observation of the negative pressure dependence of a bulk modulus ($B$).

The experimental investigations of the magnetic state of Invar alloy under high pressure are usual methods to prove the above-mentioned theoretical studies. Abd-Elmeguid *et al.*[11] and Abd-Elmeguid and Micklitz[12] performed some Mössbauer spectroscopy (MS) measurements for $Fe_{68.5}Ni_{31.5}$, ordered and disordered $Fe_{72}Pt_{28}$ Invar alloys under high pressure. In the case of $Fe_{68.5}Ni_{31.5}$,[11] the effective hyperfine field ($B_{eff}$) and the Curie temperature ($T_C$) decreased rapidly with increasing pressure. However, above 5.8 GPa, the rates of the decrease of both the $B_{eff}$ and the $T_C$ became slow. From these results, they concluded a pressure-induced magnetic phase transition took place at 5.8 GPa. In the ordered $Fe_{72}Pt_{28}$,[12] the $T_C$ decreased down to 100 K at 6 GPa, and then became constant up to 10 GPa with increasing pressure. From these results, they concluded a pressure-induced magnetic phase transition took place at 6 GPa. On the other hand, in the case of disordered $Fe_{72}Pt_{28}$,[12] $T_C$ decreased down to 40 K at the pressure up to 4.2 GPa and then became constant with increasing pressure. From these results, they concluded a pressure-induced magnetic phase transition took place at 4.2 GPa.

Rueff *et al.*[13] performed x-ray-emission spectroscopy (XES) measurements for $Fe_{64}Ni_{36}$ Invar alloy under high pressure up to 20 GPa at 300 K. They reported that the localized magnetic moment in $Fe_{64}Ni_{36}$ decreased with two characteristic steps with increasing pressure. From this result, they concluded that a high-pressure magnetic state with small magnetic moment existed in the intermediate volume range between the ferromagnetic state and the nonmagnetic state.

We performed ac susceptibility measurements for $Fe_{68.1}Ni_{31.9}$,[14] disordered $Fe_{70}Pt_{30}$ (Ref. 15) and ordered $Fe_{72.2}Pt_{27.8}$ (Ref. 16) Invar alloys under pressures up to

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7.7 GPa. The ac-susceptibility measurement is a usual method to investigate the pressure variation of a macroscopic magnetic order. In the case of $Fe_{68.1}Ni_{31.9}$,[14] a reentrant spin-glass-like high-pressure magnetic state appeared above 3.5 GPa in a low-temperature region, and then the ferromagnetic state collapsed with increasing pressure up to 7.7 GPa. On the other hand, in the case of disordered $Fe_{70}Pt_{30}$,[15] a high-pressure magnetic state appeared above 6.0 GPa in a low-temperature range, and the ferromagnetic state remained at 7.5 GPa. In the case of ordered $Fe_{72.2}Pt_{27.8}$,[16] a high-pressure magnetic state appeared above 3.5 GPa in a low-temperature range, and then the ferromagnetic state vanished with increasing pressure up to 7.0 GPa. However, the high-pressure magnetic state remained, then the transition temperature of the high-pressure magnetic state increased with increasing pressure up to 7.5 GPa. Considering from the temperature dependence of the real part $(\chi')$ and the imaginary part $(\chi'')$ of the ac susceptibility, each of the high-pressure magnetic states in $Fe_{68.1}Ni_{31.9}$, disordered $Fe_{70}Pt_{30}$, and ordered $Fe_{72.2}Pt_{27.8}$ are different one another.

In the previous ac-susceptibility measurements under high pressure for $Fe_{68.1}Ni_{31.9}$ Invar alloy,[14] we observed a high-pressure magnetic state that resembled in the reentrant spin-glass phase that observed in the Fe-Ni-Mn Invar alloy at ambient pressure.[17,18] However, we could not observe the pressure variation of the high-pressure state above the pressure range in which the ferromagnetic state vanished. Therefore, there are two reasons that we cannot observe high-pressure magnetic state in Fe-Ni Invar alloy above the pressure range in which the ferromagnetic state vanished. One reason is the limit of the generative pressure of our high-pressure apparatus, which is 7.7 GPa. Another is the martensite transition of Fe-Ni alloy system. The composition of Fe-Ni Invar alloy shifts more Fe side than $Fe_{68.1}Ni_{31.9}$ in order to reduce $T_C$, in which case a martensite transition takes place around room temperature. Also we could not observe the magnetic state of disordered Fe-Pt Invar alloy above the pressure range in which the ferromagnetic state vanished.

In this time, we have performed ac-susceptibility measurements under high pressure for $Fe_{65}Ni_{27}Mn_8$ and disordered $Fe_{72.2}Pt_{27.8}$ Invar alloy in order for the pressure variation of the high-pressure magnetic state above the pressure range in which the ferromagnetic state vanishes. Fe-Ni-Mn Invar alloy is the Fe-based invar alloy, which consists of the only 3*d* transition metals. Then, $Fe_{65}Ni_{27}Mn_8$ and disordered $Fe_{72.2}Pt_{27.8}$ has lower curie temperature than $Fe_{68.1}Ni_{31.9}$, disordered $Fe_{70}Pt_{30}$, respectively. Thus, it can be expected that the ferromagnetism vanished at a lower pressure than 7.7 GPa.

## II. SAMPLE PROCEDURE AND EXPERIMENTS

The samples of $Fe_{65}Ni_{27}Mn_8$ and disordered $Fe_{72.2}Pt_{27.8}$ were prepared by arc melting of 99.99% pure Fe and 99.9% pure the other elements, and then homogenized at 1273 K for a week in an evaluated silica tube. We powdered these samples suitable for the ac-susceptibility measurements under high pressure and then annealed them at 1273 K for 3 h and quenched them into water. The $T_C$ of $Fe_{65}Ni_{27}Mn_8$ and disordered $Fe_{72.2}Pt_{27.8}$ at ambient pressure were determined to be 250 and 332 K, respectively, by ac-susceptibility measurements. In the present experiment, $T_C$ was defined as the temperature where an $\chi'$-$T$ curve took the maximum slope. We determined chemical compositions of both alloys by the $T_C$ because the $T_C$ had the large composition dependence in the Invar composition range. We confirmed the crystal structures of these samples were disordered fcc phases by x-ray diffraction.

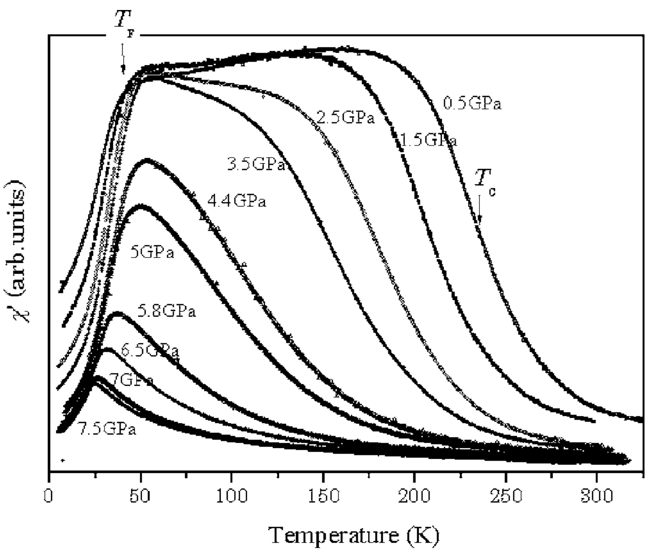


FIG. 1. Observed $\chi'$-$T$ curves for $Fe_{65}Ni_{27}Mn_8$ at various pressures.

The ac-susceptibility measurements under high pressure were performed in the same way as previous studies.[14,15] To generate the pressure, we used a cubic anvil-type high-pressure apparatus. The ac-susceptibility signals are detected by primary and secondary coils of the inner diameter 0.7 mm that was made of Cu wire. We stuffed the coils with powder sample and then inserted the coils and samples into a Teflon™ capsule with liquid pressure medium (Florinate). Then the Teflon capsule put in the center of a cube which was made of pyrophillite with the edge length of 6.0 mm, that was compressed by six WC-Co anvils with the front edge length of 4.0 mm.

We performed the pressure determination by the calibrated curve of the relation between press load and actual pressure established before experiments about the pressure dependence of the transition temperature of the superconductivity of Pb. The error of the pressure is $<0.3$ GPa. The Si diode thermometer that was placed on the surface of the anvil to measure the temperature. The frequency and the maximum intensity of the ac field were 1000 Hz and 0.5 Oe, respectively.

## III. RESULTS AND DISCUSSIONS

Observed $\chi'$-$T$ curves in $Fe_{65}Ni_{27}Mn_8$ under various pressures are shown in Fig. 1. In this figure, at 0.5 GPa, it is seen that the sample has two magnetic phase transitions as re-

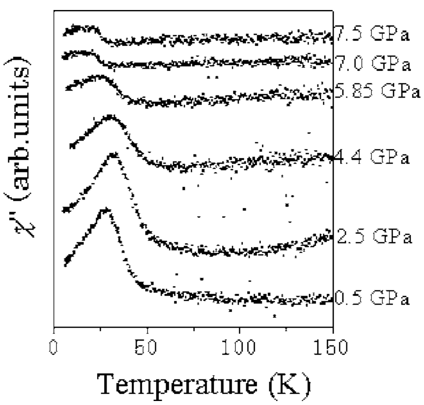


FIG. 2. Observed $\chi''$-$T$ curves for $Fe_{65}Ni_{27}Mn_8$ at various pressures.

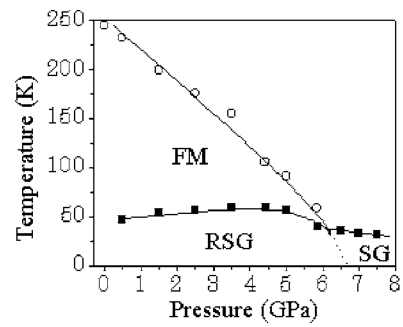


FIG. 3. Pressure-temperature phase diagram of $Fe_{65}Ni_{27}Mn_8$. The circles show $T_C$, and the squares show $T_F$. The curves in this figure are guides to eyes. FM, RSG, and SG are the mean ferromagnetic state, reentrant spin-glass state, and the spin-glass state, respectively.

ported in the previous papers,[17,18] one at the high-temperature side is the $T_C$, and another one at the low-temperature side is the reentrant-type spin-glass transition temperature ($T_F$). We defined the $T_C$ as the temperature where the $\chi'$-$T$ curve took the maximum slope and the $T_F$ as the temperature where the $\chi'$ begin to decrease drastically with decreasing temperature. The $T_C$ decreases rapidly with increasing pressure. On the other hand, the $T_F$ increases in the pressure range below 4.4 GPa. Above 2.5 GPa, the $\chi'$ takes a maximum at the $T_F$, which means the ferromagnetism gradually becomes unstable with increasing pressure, and then, at 4.4 GPa, the $\chi'$-$T$ curves show the spin-glass-like shape. These changes show the ferromagnetic interaction weakens faster than the other interactions that form the spin-glass-like state. Above the pressure range in which ferromagnetic state vanishes, $T_F$ decreases with further increasing pressure. From this result, it is considered the interactions that form the spin-glass state also weaken with increasing pressure.

Figure 2 shows the temperature dependence of $\chi''$ in $Fe_{65}Ni_{27}Mn_8$ at the various pressures below 150 K. We can see a cusp at a temperatures slightly below $T_F$. These behaviors of $\chi''$ show the delay of a relaxation time with a transition at the $T_F$. That is a typical behavior of the $\chi''$-$T$ curve of the spin-glass state.

Figure 3 shows the pressure-temperature phase diagram of the $Fe_{65}Ni_{27}Mn_8$ Invar alloy determined from the present experiments. The phase diagram is similar to that of the Fe-Ni Invar alloy in the previous studies.[11,13]

Figure 4 shows the $\chi'$-$T$ curves in the disordered $Fe_{72.8}Pt_{27.2}$ Invar alloy at various pressures. At 1.2 GPa, the $\chi'$-$T$ curve is the typical shape of a ferromagnet. However, at 2.3 GPa, we can find an anomalous behavior that $\chi'$ begins to decrease below 58 K. This anomalous behavior shows an appearance of a new magnetic state. We defined the $T_P$ where $\chi'$ began to decrease with decreasing temperature. The anomalous reduction of $\chi'$ with decreasing temperature became clearer, and $T_P$ shifts to the higher temperature side with increasing pressure. The ferromagnetic state weakens with increasing pressure, at 5.4 GPa; we cannot see any ferromagnetic behavior of $\chi'$, and only a cusp corresponding to the $T_P$ exists.

At 6.5 GPa, we could not observe any signal. From these results, it is concluded that the magnetic state in this sample changes continuously with increasing pressure from the ferromagnetic state to the high-pressure magnetic state and then to the nonmagnetic state. These changes correspond to the result of the band calculation.[8]

Figure 5 shows the $\chi''$-$T$ curves in disordered $Fe_{72.8}Pt_{27.2}$ Invar alloy at various pressures. The behaviors of the $\chi''$-$T$ curves correspond to the $\chi'$-$T$ curves. From these facts, the new high-pressure magnetic state in $Fe_{72.8}Pt_{27.2}$ is different from the spin-glass-like high-pressure magnetic state observed in $Fe_{65}Ni_{27}Mn_8$ and $Fe_{68.1}Ni_{31.9}$.[14]

Figure 6 shows the pressure-temperature phase diagram of the disordered $Fe_{72.8}Pt_{27.2}$ Invar alloy determined from the present experiments. The pressure at which the ferromagnetic state vanishes almost corresponds to the magnetic phase transition pressure reported by Abd-Elmeguid and Micklitz[12] The high-pressure magnetic state in disordered $Fe_{72.8}Pt_{27.2}$ is unstable above the pressure at which the

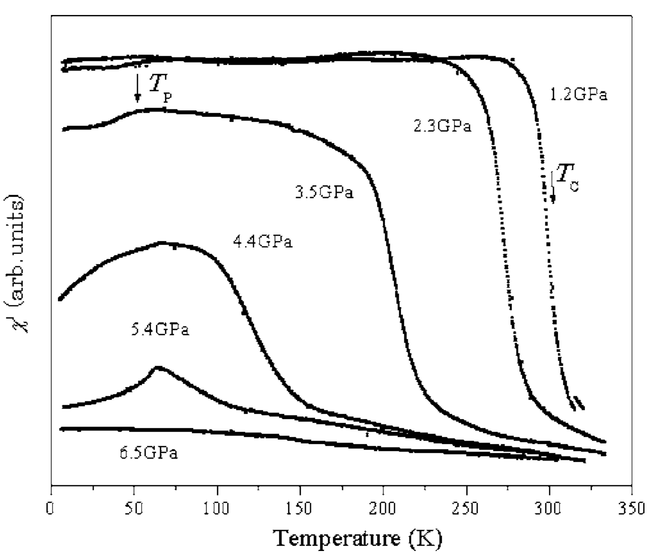


FIG. 4. Observed $\chi'$-$T$ curves for disordered $Fe_{72.8}Pt_{27.2}$ at various pressures.

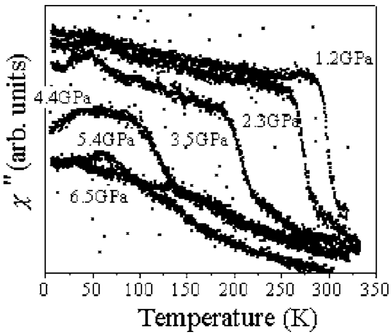


FIG. 5. Observed $\chi''$-$T$ curves for disordered $Fe_{72.8}Pt_{27.2}$ at various pressures.

ferromagnetic state vanishes, in spite of the fact that in ordered $Fe_{72.8}Pt_{27.2}$ it is stable with increasing pressure.[16] Furthermore, the shape of the $\chi'$-$T$ curves of the high-pressure magnetic state in the disordered $Fe_{72.8}Pt_{27.2}$ Invar alloy is different from those in ordered $Fe_{72.8}Pt_{27.2}$ Invar alloy. Considering from these results, the high-pressure magnetic state of the disordered $Fe_{72.8}Pt_{27.2}$ Invar alloy is different from the one of the ordered $Fe_{72.8}Pt_{27.2}$ Invar alloy. Therefore, we conclude that the interactions among the nearest-neighbor atoms have great influence on the nature of the high-pressure magnetic state in the Fe-Pt Invar alloy.

In Fig. 7, we show the pressure dependence of $T_C{}^2$ in various Invar alloys.[14,16] In the Stoner model,[22] the pressure dependence of the $T_C$ in a weak itinerant ferromagnetism shows the following:

$$T_C \approx (P - P_C)^{1/2},$$

where $P_C$ is at the critical pressure that the ferromagnetic state vanishes.

On the other hand, in the spin-fluctuation theory established by Moriya and Kawabata,[23] the $T_C$ shows the following:

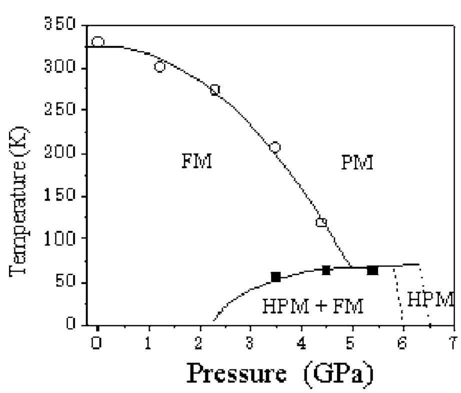


FIG. 6. Pressure-temperature phase diagram of disordered and ordered $Fe_{72.8}Pt_{27.2}$. The circles show $T_C$, and the squares show $T_F$. The curves in this figure are guide to eyes. FM and HPM are the mean ferromagnetic state and high-pressure magnetic state, respectively.

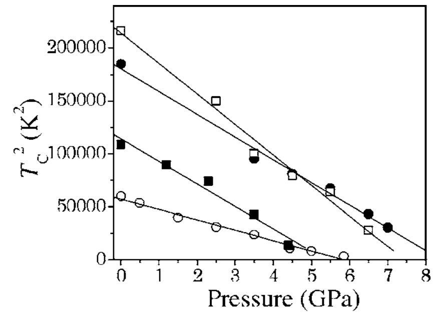


FIG. 7. The pressure dependence of $T_C{}^2$ in various Invar alloys; ●: $Fe_{68.1}Ni_{31.9}$, ○: $Fe_{65}Ni_{27}Mn_8$, ■: disordered $Fe_{72.8}Pt_{27.2}$, and □: ordered $Fe_{72.8}Pt_{27.2}$.

$$T_C \approx (P - P_C)^{3/4}$$

The experimental results show almost linear dependence of $T_C{}^2$ with $P$ in $Fe_{68.1}Ni_{31.9}$, $Fe_{65}Ni_{27}Mn_8$, and ordered, disordered $Fe_{72.8}Pt_{27.2}$. Thus, it is difficult to explain that the Invar effect is the nature of the weak itinerant ferromagnetism with the large spin fluctuation.

In the previous our x-ray-diffraction experiments under high pressure for ordered $Fe_{72.8}Pt_{27.2}$ and disordered $Fe_{70}Pt_{30}$, we observed negative thermal expansion under high pressure and negative pressure dependence of $B$.[19,20] In addition, Dubrovinskaia *et al.* also reported the negative pressure dependence of $B$ in the Fe-Ni invar alloy.[21] These results and the results of our ac-susceptibility measurements are good, corresponding to the theoretical model of the Invar effect suggested by van Shilfgaarde *et al.*[9]

On the other hand, our results differ from the $2\gamma$ model. If the Invar effect is generated by the transition from the ferromagnetic ground state to the low-volume state, we should have to observe large positive thermal expansion, the so-called anti-Invar effect, above the pressure range that the high-pressure magnetic state appears. However, in ordered $Fe_{72.8}Pt_{27.2}$, we did not observed positive thermal expansion in the pressure range above 3.5 GPa. These results suggest that the simple volume change of the phase transition from ferromagnetic state to the low-volume state with increasing temperature or pressure is not the origin of the Invar effect.

## IV. CONCLUSION

The pressure-induced continuous magnetic phase transitions exist in Fe-based Invar alloys as we investigated; however, the high-pressure magnetic phases of each alloy are different. Considering these results, the pressure-induced continuous magnetic phase transition is one of the common properties of both Fe-Pt Invar alloys and Fe-Ni-based Invar alloys. In addition, our results correspond to some theoretical calculations[8,9] and maintain the mechanism model of the Invar effect by van Schilfgaarde *et al.*[9]

From the previous studies at ambient pressure, it was discovered that a common property in Fe-based Invar alloys was the existence of a gap between short time-scale observation by neutron scattering and long time-scale observation by magnetization measurements.[24] From these results, it is said that “hidden excitation,” which cannot be observed by the short time-scale observation, exists in the Invar alloy.

We believe the existence of the pressure-induced continuous magnetic phase transition and the hidden excitation is the key to the general understanding of Invar effects. We think it is very important to make clear the identity of the hidden excitation and transition process from ferromagnetic ground states to high-pressure phase by experimental studies.

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