Pressure–volume–temperature relationship of Fe$_{72}$Pt$_{28}$ alloy under high pressure and temperature

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Abstract. The pressure–volume relationship of Fe$_{72}$Pt$_{28}$ alloy was investigated at 300, 500, 700, 900, 1100, and 1300 K by performing energy-dispersive X-ray diffraction measurements using a white X-ray beam produced from synchrotron radiation at the High Energy Accelerator Organization, Japan. The pressure–volume relationship measurements were performed only along the decreasing the pressure path. Below 700 K and 3.5 GPa, the compressibility of Fe$_{72}$Pt$_{28}$ alloy increased with the pressure. Above 900 K, the pressure–volume relationship was almost linear. Further the temperature-volume relationship at high pressures was linear. An abrupt decrease in the volume or a thermal expansion coefficient anomaly, which was observed in the case of Fe$_{69}$Ni$_{31}$ alloy in previous experiments, was not observed in the case of Fe$_{72}$Pt$_{28}$ alloy.

1. Introduction
Magnetic state, above the disappearance of macroscopic magnetic order above Curie temperature ($T_C$) is an interesting subject in the physics of magnetism. In particularly, the influence of the disordered magnetic moment and/or short range magnetic order (SRO) above $T_C$ on the thermal expansion coefficient and pressure-volume ($P$-$V$) relationship is very interesting. Some theoretical studies have shown that Fe-based FCC alloys such as Fe-Ni and Fe-Pt alloys tend to exhibit compensations of some magnetic interactions, high spin state (HS) and low spin state (LS) at a finite temperature [1-5]. Therefore these alloys provide a fascinating basis for the investigation of the relationship between the disordered magnetic state and volume above $T_C$.

Our group has discovered a discontinuous decrease in the volume with an increase in the pressure and a pressure induced anti-Invar to Invar transition above 1100 K in FCC Fe$_{60}$Ni$_{31}$ alloy ($T_C = 340$ K) [6]. It is considered that the anomalous behavior above $T_C$ is caused by the anomalous shrinkage of the disordered magnetic moment. The origin of the shrinkage of the disordered magnetic moment is considered to be an effect of pressure on the local magnetic moments and band structure or transition from the HS to HS + LS state. Moreover, recent research on Pd$_3$Fe alloy has also revealed pressure induced Invar effect appears under high pressure and temperature [7].
Fe\textsubscript{72}Pt\textsubscript{28} alloy with an FCC structure shows very large Invar effect. Moreover, the bulk modulus of this alloy shows a remarkable decrease at \(T_C\). On the other hand, some differences have been reported in the magnetic behavior between Fe-Pt and Fe-Ni Invar alloys in previous studies [8]. Magnetization measurements have revealed that the magnetic moment of Fe\textsubscript{72}Pt\textsubscript{28} alloy is so larger than that of Fe-Ni Invar alloy. In addition, its magnetic moment is stable, in other words, longitudinal and transverse spin fluctuations are small. Several theoretical calculations have shown that the energy barrier between the HS and LS states is higher in Fe\textsubscript{72}Pt\textsubscript{28} Invar alloy than that of Fe-Ni in Invar alloys [2, 3]. A characteristic \(P-V\) relationship has been observed in Fe\textsubscript{72}Pt\textsubscript{28} below \(T_C\) and it can be explained in term of the macroscopic magnetic order and spontaneous magnetostriction [9-10].

In present study, we have investigated the \(P-V\) relationship of Fe\textsubscript{72}Pt\textsubscript{28} alloy at high temperatures of 300, 500, 700, 900, 1100, and 1300 K, and then, we have investigated the volume–temperature (\(V-T\)) relationship at several pressures. Further we have discussed and compared our results with those of a previous study on Fe\textsubscript{69}Ni\textsubscript{31} alloy.

2. Experimental method

Measurement paths of \(P-V-T\) relationship in Fe\textsubscript{72}Pt\textsubscript{28} alloy are shown in Figure 1. The pressure–volume relationship measurements were performed only along the decreasing the pressure path by means of energy-dispersive X-ray diffraction measurements using a white X-ray beam produced from synchrotron radiation. Experiments were performed at the beam line NE-5C at the Photon Factory Advanced Ring, High Energy Research Organization, Japan. High pressure was generated using cubic-anvil-type high-pressure apparatus, so-called Max 80, installed at NE-5C. Tungsten carbide anvils with front face of \(4 \times 4\) mm\(^2\) were used. The incident beam size was reduced to \(0.1 \times 0.2\) mm\(^2\) using double slits and the diffracted X-ray beam was passed through a collimator with a diameter 0.1 mm. Diffracted pattern was detected using a Ge solid state detector. The diffraction angle was fixed at 6\(^\circ\). A graphite capsule was used as a heater, and the temperature was measured by using a tungsten-rhenium thermocouple (TC), as shown in Figure 2. The heating current was supplied to the heater through a molybdenum wire. The sample and the pressure marker were filled in separate capsules made from boron nitride (BN) to prevent any unexpected reaction and maintain the symmetry against TC. Powders of Au and MgO were used as the pressure markers [11, 12]. Both these markers indicated similar pressure values. A boron-epoxy cube with edge lengths of \(6 \times 6\) mm was used as a pressure transmitting material.

![Figure 1](image1.png)

**Figure 1.** Measurement path of present experiment.

![Figure 2](image2.png)

**Figure 2.** Schematic diagram of high pressure cell.
3. Results and discussion

One of the observed X-ray diffraction pattern of Fe$_{72}$Pt$_{28}$ alloy is shown in Figure 3. 5 main peaks of Fe$_{72}$Pt$_{28}$ alloy and some characteristic X-rays and an absorption edge of Pt can be observed in this pattern.

![Figure 3](image)

**Figure 3.** XRD diffraction patterns of Fe$_{72}$Pt$_{28}$. * indicates characteristic X-rays and an arrow indicate the absorption edge of Pt. The measurement was performed at 1300 K and 7.5 GPa.

$P$–$V$ curves of Fe$_{72}$Pt$_{28}$ alloy measured at various temperatures are shown in Figure 4. A Boltzmann function and a polynomial equation were used to obtain a fit of the data, because the conventional equations of state (EOS) did not provide good fit. The $P$–$V$ curve measured at 300 K became steeper with an increase in the pressure. It did not fit the conventional EOS. This $P$–$V$ curve corresponded to that measured in a previous experiment performed under increasing pressure. It was considered that this curve was formed by the destruction of ferromagnetic order with the increase in the pressure, because the bulk modulus of Fe$_{72}$Pt$_{28}$ alloy decreases drastically at $T_C$ ($T_C = 380$ K at ambient pressure) [8]. The anomalous $P$–$V$ curves were generated as the result of the decrease in bulk modulus accompanying the decrease in $T_C$ with the increase in the pressure. Further, below 3.5 GPa, the curves measured at 500 and 700 K showed this tendency clearly, i.e., the effect of destruction of ferromagnetic order influenced the $P$–$V$ curves in the high-temperature range.

![Figure 4](image)

**Figure 4.** Pressure-Volume curves of Fe$_{72}$Pt$_{28}$ alloy at various temperatures.

![Figure 5](image)

**Figure 5.** Volume-Temperature curves of Fe$_{72}$Pt$_{28}$ alloy at various pressures.
The $P$–$V$ curves measured at high temperatures did not show a remarkable anomaly. A discontinuous decrease in volume, which was observed in Fe$_{69}$Ni$_{31}$ alloy, was not observed in Fe$_{72}$Pt$_{28}$ alloy [13]. Figure 5 shows the $V$–$T$ relationship of Fe$_{72}$Pt$_{28}$ alloy at various pressures, which were estimated from the fitted curves of $P$–$V$ data obtained at various temperatures. These $V$–$T$ relationships were linear. Further, the anomalies observed in Fe$_{69}$Ni$_{31}$ alloy, such as anti-Invar to the Invar effect transition observed at high temperature and high pressure, were not observed in Fe$_{72}$Pt$_{28}$ alloy [13]. In general, the anti-Invar type behavior under high pressure is caused by longitudinal moment fluctuations and variations in the short-range magnetic interaction above $T_C$.

We consider that this difference of $P$–$V$–$T$ relationship can be attributed to the shrinkage or disappearance of disordered magnetic moments. The following two differences are considered that the origin of the difference of $P$–$V$–$T$ relationship between Fe$_{72}$Pt$_{28}$ alloy and Fe$_{69}$Ni$_{31}$ alloy.

1. The magnetic interaction and intensity of disordered magnetic moment in Fe$_{69}$Ni$_{31}$ is more unstable than those in Fe$_{72}$Pt$_{28}$ alloy. Therefore, the magnetic contribution of each alloy to volume is different.

2. According to theoretical calculations, the energy barrier between the HS and the LS of Fe$_{72}$Pt$_{28}$ alloy is higher than that of Fe-Ni alloys [1, 3]. Thus there is possibility that the transition from HS to HS + LS state occur under different conditions.

4. Conclusion

The $P$–$V$–$T$ relationship of Fe$_{72}$Pt$_{28}$ alloy has been investigated by performing energy-dispersive X-ray diffraction measurements along decreasing pressure and temperature path. The $P$–$V$ curves becomes steeper with an increase in the pressure, not only at 300 K, but also 500 and 700 K. Considering from these results indicate the $P$–$V$ curve anomaly is caused by disappearance of macroscopic magnetic order below $T_C$ influences $P$–$V$ curve at 500 and 700 K. $P$–$V$ curves measured at high temperature do not exhibit remarkable anomalous behaviour, and $V$–$T$ relationship was linear. These results are different from those of Fe$_{69}$Ni$_{31}$ alloy obtained in a previous study [6].

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