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Pressure variation of the magnetic state in Co–Fe–Cr stainless Invar alloy

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Abstract

Magnetic properties of a $Co_{52.5}Fe_{38}Cr_{9.5}$ Invar alloy have been investigated under high-pressure by ac susceptibility measurements. With increasing pressure, ferromagnetic ground state disappeared and new high-pressure magnetic states came to appear. Further increasing pressure up to 4.6 GPa, the high-pressure magnetic states vanished and no magnetic signal observed in the investigation range 5–300 K. These pressure variations of magnetic phases are similar to Fe based Invar alloy. So far considering from the series of our experimental results, it is concluded that the moment-volume instability in Invar alloys are associated with a several magnetically ordered phases that exist in low volume side of ground state. These facts support some theoretical model for the origin of Invar effect.

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Keywords: Invar alloy; High-pressure; ac susceptibility; Magnetic phase transition

1. Introduction

The relation between the Invar effect and a high-pressure magnetic state has been discussed by several theoretical and experimental studies.

According to several recent experimental studies under high-pressure, a high-pressure magnetic phase exists in Fe based alloys and compounds that show a low thermal expansion and large magneto-volume insanities, such as Fe–Ni Invar alloy [1–3], Fe–Pt Invar alloy [4–8], Fe–Ni–Mn Invar alloy [8], Y_2Fe_{17} [9,10].

On the other hand, according to a theoretical study by Weiss, he assumed the existences of a high-volume high-moment state (HM) and a low-volume low-moment state (LM), and explained Invar effect was caused by the variation of the proportion of HM to LM with increasing temperature or pressure [11]. Since then, some theoretical studies, for example Refs. [12–17], pointed out that a high spin state (HS) and a low spin state (LS) were corresponding to HM and LM of Weiss's model. They explained a HS–LS transition accompanied by the transferring of an electron from t_{2g} orbital in majority band to e_g orbital in minority band was the origin of Invar effect. In addition, Uhl et al. [18] and Schilfgaarde et al. [19] pointed out that a non-collinear magnetic order was the most stable state in the volume range between HS and LS. Schilfgaarde et al. [19] explained the anomalous volume dependence of a binding energy was caused by the anomalous volume variation of the magnetic order from a ferromagnetic to the non-collinear magnetically ordered state with decreasing volume. The anomalous volume dependence of the binding energy generated negative pressure derivative of a bulk modulus, as a result an anomalously small Grüneisen constant was generated. Hence low thermal expansion evidenced in Invar alloy.

In any case, theoretical aspects have predicted that pressure-induced magnetic phase transition would take place in Invar alloy.

Our group has investigated the pressure variation of the magnetic properties of Fe based FCC Invar alloys by ac susceptibility measurements under high-pressure [3,6–8]. We observed a pressure-induced magnetic phase transition in all the investigated Invar alloys, such as $Fe_{68.1}Ni_{31.9}$ [3], $Fe_{65}Ni_{27}Mn_8$ [8], ordered $Fe_{72.8}Pt_{27.2}$ [7], and disordered $Fe_{70}Pt_{30}$ [6], $Fe_{72.8}Pt_{27.2}$ [8]. However these high-pressure magnetic phases and pressure variations are slightly different from each alloy. In addition, we observed the pressure induced magnetic phase transition

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from the high-pressure magnetic state to the non-magnetic state in disordered $Fe_{72.8}Pt_{27.2}$ [8]. The results of the series of our experiment can be seen good corresponding to the theoretical calculations mentioned above.

However, above mentioned experimental and theoretical studies are only concerning with Fe based Invar alloys, with FCC crystal structure. Hence, there has not been discussed Co rich Invar alloy, such as Co–Fe–Cr Invar alloy. Ternary Co rich alloys of Co–Fe–Cr show the Invar effect in fcc stability range, very close to the boundaries of HCP and BCC, with composition roughly $Co_xFe_{(100-y-x)}Cr_y$ and $52 \leq x \leq 54$, $9 \leq y \leq 10$ at% [20]. These alloys so called "stainless Invar alloy", are important for technical applications. If the origin of the Invar effect was connected to the existence of LM, we would observe pressure induced magnetic phase transition to a high-pressure magnetic state in Co–Fe–Cr Invar alloys. Thus we have performed ac susceptibility measurements under high-pressure for a $Co_{52.5}Fe_{38}Cr_{9.5}$ stainless Invar alloy to demonstrate whether the existence of LM in a common property of the Invar alloys that consist of 3d transition metal.

2. Experiment

We performed sample preparation by arc melting of 99.99% pure Fe and 99.9% pure Co and Cr. After arc melting, the sample was enclosed in an evaluated silica tube, and then annealed for a week at 1273 K. Then, the sample was powdered suitable for experiments, and annealed for 5 h in evaluated silica tube at 1273 K to remove residual stress.

The FCC crystal structure was confirmed by an X-ray diffraction measurement as shown in Fig. 1, and the lattice parameter of 3.574 obtained from the [2 2 2] diffraction line. This lattice constant is almost as same as Fe–Ni, Fe–Ni–Mn Invar alloys.

The Curie temperature (T_C) was measured 325 K by an ac susceptibility measurement shown in Fig. 2. In this paper, we defined T_C as maximum slope of a X'–T curve. This result is almost corresponding to previous report [20].

We performed ac susceptibility measurements under high-pressures up to 4.6 GPa, in the temperature range 5–310 K, by using a cubic anvil type high-pressure apparatus [21]. The pressures were determined from the pressure–press load calibrated curve obtained from the previous experiments for the pressure dependence of the superconductivity transition temperature of Pb, and the resistance of Bi at room temperature. This cubic anvil press can be controlled press load during both heating and cooling cycles.

The preparation processes of the pressure cell are given in Fig. 3. The powdered sample was stuffed into coils with inner diameter 0.65 mm. The coils were made of Cu wire. The sample and the coils were enclosed in a Teflon capsule with

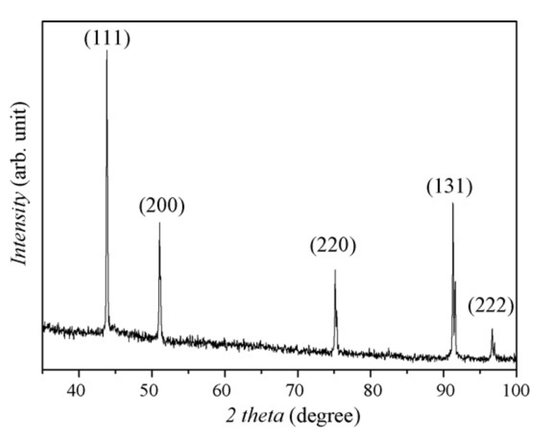

Fig. 1. : X-ray diffraction lines for $Co_{52.5}Fe_{38}Cr_{9.5}$ at ambient pressure.

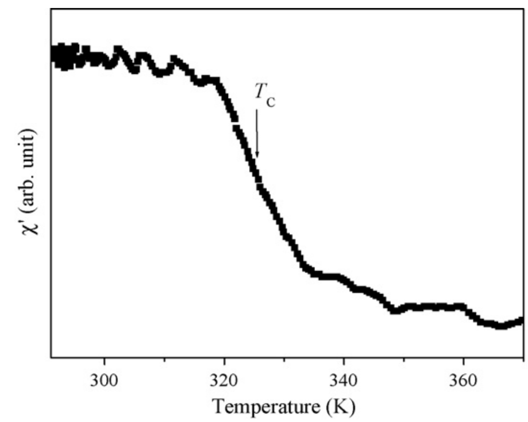

Fig. 2. Observed X'–T curves for $Co_{52.5}Fe_{38}Cr_{9.5}$ at ambient pressure.

Florinate as liquid pressure medium, and then put in the center of a pyrophillite cubic with an edge length of 6.0 mm. The cubic anvils made of WC–Co with a front face 4.0 mm × 4.0 mm, compressed the pyrophillite cubic. We used a 2-phase lock-in amplifier to generate stabilized an ac field, and to detect a real part (X') and an imaginary part (X'') of the ac susceptibility. The frequency and the intensity of the ac field were 1000 Hz and 0.3 Oe, respectively. Temperatures were measured by a Si diode thermometer placed on the side face of an anvil.

3. Results and discussion

We performed ac susceptibility measurements under high-pressures, in both a cooling and heating cycle, but we did not observe any temperature hysterezis. Observed the X'–T curves during heating cycles for $Co_{52.5}Fe_{38}Cr_{9.5}$ at various pressures are given in Fig. 4.

At 1.5 GPa, the X'–T curve above 150 K shows almost typical ferromagnetic shape. However below 150 K, the X' decreases gradually with decreasing temperature. This fact means that the ferromagnetic state is already unstable.

At 2.4 GPa, the X'–T curve obviously shows a coexistence of the ferromagnetic state and another magnetic state. This state corresponds to the new high-pressure magnetic order which is commonly seen in other typical Fe-based Invar alloys. From the paramagnetic state at high temperature, with decreasing temperature, the X' increases more gradually and shows a weak shoulder at 150 K, and then increases to take a maximum at 40 K. Blow 40 K, the X' decreases rapidly with decreasing temperature. From these variations, the magnetic order in $Co_{52.5}Fe_{38}Cr_{9.5}$ at 2.4 GPa can be classified three kinds. The one is the ferromagnetic state above 150 K, the second one is an intermediate, ferromagnetic large moment state between 40 and 150 K, and the last one is a low moment, low temperature state below 40 K. These pressure variations of the X'–T curves are similar to that of previous studied Invar alloys, in particular very similar to disordered Fe–Pt Invar alloys [6,8]. We defined the peak temperature of X' as T_F.

At 3.0 GPa, the ferromagnetic state disappears, and the low-moment state that shows the cusp, only remains. These pressure variations of X'–T curves are again similar to other Invar alloys [3,6–8]. The pressure that ferromagnetic state disappears (P_C), namely the pressure that the X'–T curve becomes to show only a cusp, is smaller than in other Invar alloys [3,7,8]. In addition,