

Temperature dependent local structures in an Invar alloy

Shinya HOSOKAWA,^{1,*} Jens Rüdiger STELLHORN,¹ Tomohiro MATSUSHITA,²
Naohisa HAPPO,³ Koji KIMURA,⁴ Kouichi HAYASHI,⁴ and Kunio YUBUTA⁵

¹ Department of Physics, Kumamoto University, Kumamoto 860-8555, Japan

² Japan Synchrotron Radiation Research Institute (JASRI), Sayo 679-5198, Japan

³ Graduate School of Information Sciences, Hiroshima City University, Hiroshima 731-3194, Japan

⁴ Department of Physical Science and Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan

⁵ Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Fe and Ni $K\alpha$ x-ray fluorescence holography (XFH) measurements were carried out on a single crystal of the traditional Fe₆₅Ni₃₅ Invar alloy at 100 and 300 K to investigate the temperature dependence of the three-dimensional local structures around the Fe and Ni atoms, respectively. Local structural information was obtained by detailed analyses using a L_1 -regularized linear regression for the experimental data. At 100 K, the local atomic arrangements around both the elements show *fcc* structures. At 300 K, however, only the image around Fe shows a *bcc*-like neighboring arrangement. From these XFH data, we propose a model that with increasing temperature, an Fe atom with the low-spin state enters at the central position of the *fcc* lattice and is stabilized. And then, large angular positional fluctuations are induced for the atoms at the face-centered positions around the central Fe atom only.

1 Introduction

In 1897, Guillaume [1] discovered an Invar alloy of Fe₆₅Ni₃₅, which has anomalously small thermal expansion over a wide temperature range. It has been recognized that the Invar effect originates from the magnetism, i.e., there is two types of electronic states in Fe, typically high-spin (HS) and low-spin (LS) states [2]. In this two-state model, the equilibrium potential energy is lower in the HS state than in the LS one, while the atomic radius is larger in the former. This results in the compensation between the usual thermal expansion and the increase of number density of the smaller atomic size of LS state with increasing temperature.

X-ray fluorescence holography (XFH) [3] is a newly developed technique that enables one to draw three-dimensional (3D) atomic images around a specific element emitting fluorescent x-rays. Owing to the interference between the direct incident x-rays and those scattered by the surrounding atoms, the fluorescent x-ray intensity from the emitter slightly modulates with the incident x-ray angles by about some 0.1% (called a hologram), from which 3D images can be obtained without any special models.

We have measured Fe and Ni $K\alpha$ XFH on the single crystal Fe₆₅Ni₃₅ Invar alloy at 100 and 300 K to study the temperature dependence of the local structures around the Fe and Ni atoms independently [4].

2 Experiment

A single crystal of the Fe₆₅Ni₃₅ Invar alloy was grown in the Cooperative Research and Development Center for Advanced Materials, Institute for Materials Research, Tohoku University, using an optical floating zone method. The crystallinity of the sample was examined by taking a Laue photograph, and the concentration and homogeneity

over the sample were confirmed within the experimental errors by an electron-probe micro-analysis.

Fe (6.403 keV) and Ni (7.477 keV) $K\alpha$ XFH measurements were carried out on the Fe₆₅Ni₃₅ single crystal at 100 and 300 K using a cryostream apparatus at BL6C in PF-KEK and at BL39XU and BL12B2 of the SPring-8. The sample was placed on a two-axes table of a goniometer. The measurements were performed in inverse mode by changing two axes, the incident angle of $0^\circ \leq \theta \leq 75^\circ$ in steps of 1° and the azimuthal angle of $0^\circ \leq \phi \leq 360^\circ$ in steps of about 0.35° , of the sample. The fluorescent x-rays were collected using an avalanche photodiode detector, capable of more than one million cps, via a toroidal graphite crystal energy analyzer. Details of the experimental setup are given elsewhere [3].

Holographic oscillation data (hologram) were obtained by subtracting the background from the fluorescent x-ray intensities and normalizing them to the incident x-ray intensities measured with an ion chamber. Usual extensions of the holographic data to the 4π sphere were made using the crystal symmetry and the measured x-ray standing wave (XSW) lines. The holograms were recorded at eight incident x-ray energies of 7.5–11.0 (8.5–12.0) keV for the Fe (Ni) $K\alpha$ XFH in steps of 0.5 keV.

From the obtained holograms, 3D atomic configuration images were reconstructed using a L_1 -regularized linear regression, which is an inverse problem analysis based on a sparse modeling approach to the experimental holographic data. Details of this analytical method are given elsewhere [5], and successfully adopted in recent papers [6,7].

3 Results and Discussion

Figure 1 shows examples of the (a) Fe and (b) Ni $K\alpha$ holograms of Fe₆₅Ni₃₅ single crystal measured at the

incident x-ray energies of 8.5 keV, which are drawn under an orthographic projection. The radial and angular directions indicate θ and ϕ , respectively, and the magnitudes are given as the color bars beside the holograms. A fourfold rotational symmetry including XSW signals was observed in the holographic patterns, indicating a good quality of the sample crystal. The holograms at 100 K look similar to those at 300 K except that the magnitude of the oscillations are slightly larger in 100 K than in 300 K.

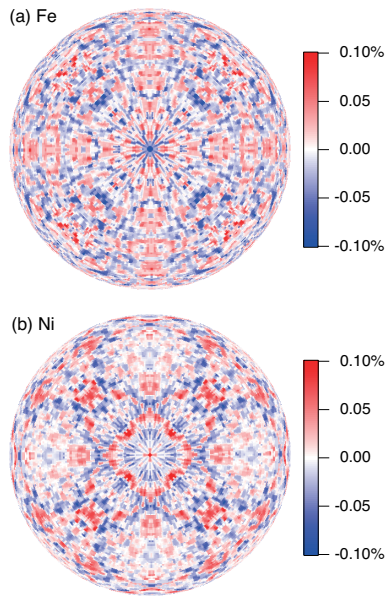


Fig. 1: Examples of the (a) Fe and (b) Ni $K\alpha$ holograms of $\text{Fe}_{65}\text{Ni}_{35}$ single crystal measured at 300 K at the incident x-ray energies of 8.5 keV. Taken from Ref. [4].

From these holograms, we can point out two importances on the local structures of $\text{Fe}_{65}\text{Ni}_{35}$ Invar alloy crystal. The first is that the magnitudes of the holographic oscillations of both the Fe and Ni $K\alpha$ are about 0.1%, much weaker than those of the usual crystal samples of some 0.1%. The second is that the spectral features around the Fe and Ni atoms are quite different from each other, although based on the XRD data, $\text{Fe}_{65}\text{Ni}_{35}$ is believed to have the same *fcc* structures around the Fe and Ni atoms.

Figure 2 shows 3D atomic images around the (a) Fe and (b) Ni atoms measured at 100 K. The dashed lines indicate the cubic unit cells, where the lattice constant, a , is 0.3569 nm [8], and the central Fe/Ni atoms are located at the left-bottom corners. Every images in Fig. 2 are drawn as the 12% contour of the maximum of the Ni images at 100 K. As seen in the figure, *fcc* lattices are clearly observed around both the Fe and Ni central atoms. The atomic arrangements around the Fe and Ni atoms are very similar to each other.

Figures 2(c) and (d) show the same 3D atomic images measured at 300 K around Fe and Ni, respectively. The atomic images around the Fe atoms in (c) are very different from those at 100 K in (a). The *fcc* images of the

nearest-neighboring atoms disappear as indicated by upward arrows, although the second-neighboring atoms are clearly observed as a spread disk shape. Of special interest is that there appears a relatively strong atomic image at exactly the body-centered position as indicated by the downward arrow.

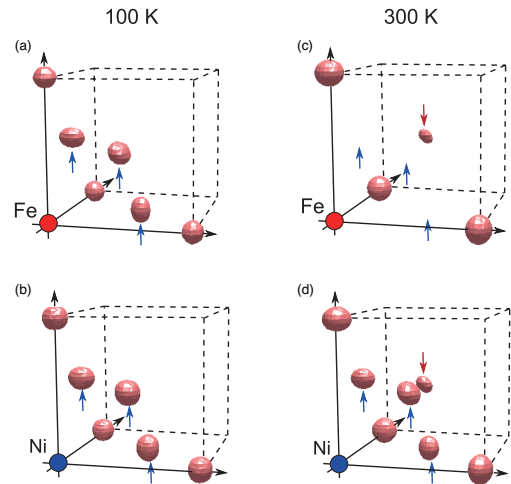


Fig. 2: 3D atomic images around the (a) Fe and (b) Ni atoms at 100 K and (c)(d) those at 300 K. Taken from Ref. [4].

Since the *bcc* structure is much sparse in space compared with *fcc*, we cannot believe that a *fcc-bcc* transformation happens with increasing temperature. Such a simple structural change should produce a much larger thermal expansion unlike the Invar effect.

The atomic image around the Ni atoms in (d) looks mostly similar to that at 100 K in (b) indicating the *fcc* structure. However, an additional image with a similar size of that around the Fe atom is observed at the *bcc* position of the cubic lattice as indicated by downward arrow. This image is disk-like, where the positional fluctuation in the angular direction is slightly larger than that in the radial direction.

From the present XFH results, we propose a new structural model for the Invar effect of the $\text{Fe}_{65}\text{Ni}_{35}$ alloy. At 100 K, the structure of this alloy is a *fcc* structure as shown in Fig. 3(a). With increasing temperature, the fraction of the Fe LS atoms becomes larger and correspondingly free volume increases owing to the small diameter of the LS Fe compared with the HS Fe. The largest vacancy in the *fcc* lattice is located at the body-centered position of the cubic, and a LS Fe atom preferring the *bcc* structure can enter there and form a quasi-simple cubic lattice as shown in Fig. 3(b).

Since the interatomic length of the quasi-simple cubic is only 0.1792 nm, which is much smaller than the *fcc* value of 0.2534 nm [8], the additional Fe atom must displace the neighboring atoms at the face-centered positions even though the cubic center atom is a LS atom with the smaller atomic size. Thus, the body-centered atom with the LS state may make the positions of the face-centered

atoms unstabilized in the direction perpendicular to the cubic faces as shown in Fig. 3(c), because the central Fe atom prefers to form a *bcc* lattice around it. As a result, the XFH image around Fe at 300 K looks *bcc*-like as shown in Fig. 2(c), but the stabilized body-centered atoms and unstabilized face-centered atoms co-exist.

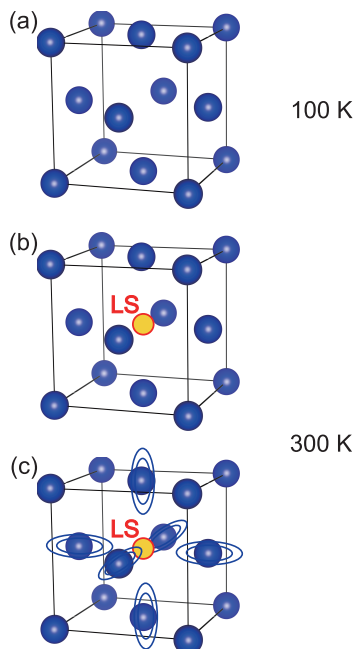


Fig. 3: A structural model for the Invar effect at (a) 100 K, and 300 K (b) without and (c) with the positional fluctuations. Taken from Ref. [4].

On the other hand, the *fcc* lattice around the central Ni atom highly preserved even entering an atom in the body-centered position as shown in Fig. 2(d). This result may originate from an intrinsic nature of Ni atom that prefers a *fcc* structure at room temperature. As a result, the XFH image around Ni at 300 K looks primitive cubic like in Fig. 2(b), where the stabilized body-centered atoms and face-centered atoms coexist.

Owing to this additional LS Fe atom, the density of this Invar alloy increases, and compensate for the normal density decrease with increasing temperature. The HS-LS spin transition does not solely happen with increasing temperature, but is accompanied by the structural change from *fcc* to quasi-primitive cubic structures.

In summary, Fe and Ni $K\alpha$ XFH measurements were carried out on a single crystal of the traditional $\text{Fe}_{65}\text{Ni}_{35}$ Invar alloy at 100 and 300 K to investigate the temperature dependence of the 3D local structures around the Fe and Ni atoms, respectively. Local structural information was obtained by detailed analyses using a L_1 -regularized linear regression for the experimental data. At 100 K, the local atomic arrangements around both the elements show *fcc* structures. At 300 K, however, only the image around Fe shows a *bcc*-like neighboring arrangement. From these XFH data, we propose a model that with increasing temperature, an Fe atom with the LS state enters at the central position of the *fcc* lattice and is

stabilized. And then, large angular positional fluctuations are induced for the atoms at the face-centered positions around the central Fe atom only.

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* shhosokawa@kumamoto-u.ac.jp