Magnetic EXAFS study of Fe-Ni invar alloy under high pressure using nano-polycrystalline diamond anvilss

Ken Matsumoto¹, Hiroshi Maruyama¹, Naoki Ishimatsu¹, Naomi Kawamura², Masaichiro Mizumaki², Tetsuo Irifune³, and Hitoshi Sumiya⁴

¹Graduate School of Science, Hiroshima University, 1-3-1, Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8526, Japan.
²Japan Synchrotron Radiation Research Institute, SPring-8, 1-1-1 Kouto, Sayo, Hyogo 679-5198, Japan.
³Geodynamics Research Center, Ehime University, 2-5 Bunkyo, Matsuyama, Ehime 790-8577, Japan.
⁴Electronics and Materials R&D Laboratories, Sumitomo Electric Industries, 1-1-1 Koyakita, Itami, Hyogo 664-0016, Japan.

Abstract. The magnetic EXAFS technique was applied to study the local magnetic structure in Fe-Ni Invar alloy under high pressures. Nano-polycrystalline diamond was used to apply pressure in a diamond anvil cell. As a result, we succeeded in recording a glitch-free spectrum with a high accuracy by preventing Bragg diffraction from the diamonds. As the pressure was increased, the ferromagnetic correlation was strongly reduced, which was more remarkable for Fe atoms than for Ni atoms. The canting effect of the magnetic moment may be crucial for a rapid decrease in the ferromagnetic correlation. This local magnetic structure in the Invar alloy is consistent with a model based on the non-collinear spin structure.

1. Introduction

Extended X-ray absorption fine structure (EXAFS) is a well-established technique used to provide information about the structural and electronic properties of various materials. This technique has also been applied to study the local structure under extreme conditions. However, it is impossible to directly probe local magnetic structure in magnetic materials by means of EXAFS. The physical origin of magnetic EXAFS, defined as X-ray magnetic circular dichroism in the EXAFS region, has been considered to be the exchange contribution to the backscattering amplitude caused by neighboring magnetic atoms [1]. Thus, magnetic EXAFS is a powerful technique for examining the ferromagnetic correlation in the local environment.

In order to study pressure-induced magnetic phase transition, we apply magnetic EXAFS to a high pressure experiment using a diamond-anvil cell (DAC). Although DAC has been widely used as a device for generating high pressures, Bragg reflections from the single-crystal diamond are in general strong and superimpose a spikelike profile on the spectrum. Therefore, the magnetic EXAFS spectrum is subject to distortions in the oscillatory profile and to reduction in the data accuracy. To prevent the influence of Bragg diffraction, we introduced nano-polycrystalline diamond (NPD) anvils [2, 3]. Since NPD is harder and more mechanically isotropic than the single-crystal diamonds, it is suitable for applying higher pressure by DAC.
In this paper, magnetic EXAFS at high pressures is presented for fcc Fe$_{65}$Ni$_{35}$ Invar alloy, in which the DAC with NPD anvils was employed for the first time. Fe and Ni metals were also measured at ambient pressure as reference materials in bcc and fcc structures. Fe-Ni Invar alloy has been regarded as a prototypical material that exhibits anomalously low thermal expansion [4]. Because the magnetic EXAFS is element-specific and electronic-shell selective, it is appropriate for comparing Fe and Ni atoms in the local environment.

2. Experiment

X-ray absorption and dichroic spectra were recorded at the Fe and Ni K-edges using the helicity-modulation method on beamline 39XU at SPring-8 [5], which was equipped with a diamond 111 double-crystal monochromator, Kirkpatrick-Baez focusing mirrors [6], and a diamond λ/4-plate to produce a circularly polarized beam. A magnetic field of 0.6 T was sufficient to magnetically saturate the sample. The generated pressure was estimated by the ruby fluorescence method. Two kinds of diamond anvil, single-crystal and nano-polycrystalline diamonds are compared in the photograph in figure 1. Although the NPD exhibits a dark yellow due to nitrogen impurities and lattice defects [7], it has a high transparency for X-rays. Figure 2 shows the raw EXAFS spectra of Fe metal recorded using the DAC with single-crystal diamond and NPD. The latter gives a much better spectrum without any spikelike noise. We succeeded in recording a glitch-free spectrum with a high accuracy over a wide range of photon energy (6 - 10 keV). The experiment was carried out at room temperature.

Figure 1. Photograph of diamond anvils.

Figure 2. EXAFS spectra obtained with single-crystal diamond anvil and NPD anvil.

Figure 3. EXAFS spectra at the Fe K-edge (left panel) and Ni K-edge (right panel) in Fe-Ni invar alloy, Fe and Ni foils.

Figure 4. Pressure variation of RDF for Fe and Ni absorbing atoms.
3. Results and Discussion

Figure 3 shows the pressure variation of the normalized EXAFS spectrum in Fe<sub>65</sub>Ni<sub>35</sub> alloy at the Fe and Ni K-edges in comparison with those of pure Fe and pure Ni metals. Difference in the spectral profile between Fe and Ni metals is ascribed to the difference in crystal structure, fcc and bcc. It is clearly seen that the EXAFS oscillation in the Fe-Ni alloy closely resembles that of fcc Ni metal. As the pressure increases, the spectral shape and oscillatory intensity show no drastic changes at either edge, but the oscillation period becomes slightly longer because of the contraction of lattice spacing. These trends indicate that the Fe<sub>65</sub>Ni<sub>35</sub> alloy maintains the fcc structure even at 6 GPa and does not undergo any structural transition, and the local environment is notably similar around Fe and Ni absorbing atoms.

For the EXAFS analysis, we used the following conventional procedure [8]: background removal, base-lining of oscillation, determination of absorption edge energy, normalization of spectral intensity by edge jump, and then Fourier transform to obtain the radial distribution function (RDF). As shown in figure 4, the RDF has an intense peak at an interatomic distance of about 2.2 Å, which corresponds to the nearest neighbor (NN) interatomic pair around Fe and Ni atoms; the subsidiary peaks correspond to 2nd, 3rd, and 4th NNs. The RDF profile is well reproduced by the theoretical simulation using FEFF code [8]. It should be noted that the chemical structure of the alloy is quite stable in the local environment even at high pressures.

Figure 5 shows the magnetic EXAFS spectrum at the Fe and Ni K-edges, compared with those of Fe and Ni metals. As the pressure is increased up to 6 GPa, the magnetic dichroic amplitude is significantly reduced, and the magnetic EXAFS oscillation is also drastically suppressed by the applied pressure. However, the magnetic EXAFS pattern is very similar for both the edges, which indicates that the Fe and Ni atoms are in similar magnetic states in the local environment. On the other hand, the magnetic EXAFS shows a different pattern between Fe and Ni metals.

The pressure variation of the magnetic RDF is shown in figure 6, together with those of Fe and Ni metals. The magnetic RDF has an intense peak at about 2.2 Å, which corresponds to the ferromagnetic NN spin pairs around the Fe and Ni atoms. The subsidiary peaks are associated with the 2nd (3.2 Å), 3rd (3.8 Å) and 4th (4.5 Å) NN pairs, which are also ferromagnetically coupled with the absorbing atom [9]. For bcc Fe metal, the two prominent peaks are located at about 2.2 Å and 4.5 Å, as a result of the bcc structure. The latter peak is enhanced by the focusing effect of multiple scattering paths, in addition to contribution of the single scattering path [10]. For fcc Ni metal and Fe-Ni alloy, the main peak is located at about 2.2 Å, and the intensity is significantly reduced as the pressure is increased up to 6 GPa.

Figure 5. Magnetic EXAFS spectra at the Fe K-edge (left panel) and Ni K-edge (right panel) in Fe-Ni invar alloy, Fe and Ni foils.

Figure 6. Pressure variation of magnetic RDF for Fe and Ni absorbing atoms.
Magnetic RDF intensity is a measure of strength in ferromagnetic correlation. From the pressure variation in figure 6, a drastic reduction is observed in the NN peak intensity for both the Fe and Ni K-edges. This trend contrasts with that of the RDF for the chemical structure (cf. figure 4). This fact demonstrates that the ferromagnetic correlation is strongly reduced by the applied pressure. This feature is common to both Fe and Ni absorbing atoms. However, Fe and Ni atoms show different tolerance for the pressure; that is, the ferromagnetic correlation around the Fe atom is subject to a larger reduction than that around the Ni atoms. There is a considerable decline in the ferromagnetic correlation for the Fe NN pairs. It is possibly caused by a reduction in the magnitude of magnetic polarization or by an increase in canting angle of magnetic moments. It should be emphasized that the canting effect of the magnetic moment is crucial for a rapid decrease in the ferromagnetic correlation for the Fe NN pairs. This local magnetic structure in the Invar alloy is consistent with the theoretical prediction based on the non-collinear spin structure [11].

4. Conclusion
The magnetic EXAFS study of Fe-Ni Invar alloy under high pressure has been made using a DAC with NPD anvils for the first time. We demonstrate that the NPD is very effective at avoiding Bragg diffraction from the diamond anvils. It was revealed that the ferromagnetic correlation is drastically suppressed by the applied pressure, and that the suppression is more remarkable for Fe atoms than for Ni atoms. This trend probably involves the canting effect of the magnetic moment, so that non-collinear spin configuration increasing at high pressures should be taken into account from the viewpoint of local magnetic structure [12]. Magnetic EXAFS is an effective probe for investigating local magnetic structure under extreme conditions.

Acknowledgement
This study was performed at SPring-8 with the approval of PRC-JASRI (Nos. 2009A1302 and 2009B1495).

References
[1] Schütz G, Knülle M and Ebert H 1993 Phys. Scr. T49A 302
[2] Irifune T, Kurio A, Sakamoto S, Inoue T and Sumiya H 2003 Nature 421 599–600
[3] Sumiya H, Irifune T, Kurio A, Sakamoto S and Inoue T 2004 Mater. Sci. 39 445–50
[4] Guillaume C E 1897 C. R. Acad. Sci. 125 235
[5] Kawamura N, Ishimatsu N and Maruyama H 2009 J. Synchrotron Radiat. 16 730–6
[6] Yumoto H, Hirata K, Nisawa A, Ueno G, Sato M, Son J-Y, Koganezawa T, Machida M, Muro T, Hirosawa I, Suzuki M, Kawamura N, Mizumaki M, Ohashi H, Yamamoto M, Watanabe Y and Goto S 2009 Proc. SPIE 7448 74480Z
[7] Sumiya H, Harano K, Kagi H and Irifune T 2009 (in press) Jpn. J. Appl. Phys. Optical characteristics of nano-polycrystalline diamond synthesized by direct conversion from graphite
[8] Ravel B and Newville M 2005 J. Synchrotron Radiat. 12 537–41
[9] Popescu V, Güssmann M, Fähnle M and Schütz G 2009 Phys. Rev. B 79 014440
[10] Kurde J, Ponpandian N, Luo J, Weis C and Baberschke K 2007 Phys. Rev. B 76 224418
[11] Schilfgaarde M V, Abrikosov I A and Johansson B 1999 Nature 400 46–9
[12] Matsumoto K, Maruyama H, Ishimatsu N, Kawamura N, Mizumaki M, Irifune T and Sumiya H 2011 J. Phys. Soc. Jpn. 80 023709