

Elongation and compression of Fe-Fe atomic pairs in Fe-Ni invar alloys: Microscopic observations of the magnetovolume effect in ferromagnetic Fe-Ni fcc-based alloys

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The atomic scale origin of the invar effect and the large magnetovolume effect in Fe-Ni alloys is revisited by investigating the Ni-content dependence of bulk modulus B_0 of Fe-Fe, Fe-Ni, and Ni-Ni atomic pairs using reverse Monte Carlo modeling with a dataset of extended x-ray absorption fine structure and powder x-ray diffraction under high pressure. To this end, the results of the Fe₆₅Ni₃₅ invar alloy were compared with those of Ni-rich ferromagnetic Fe₅₅Ni₄₅ and Fe₂₀Ni₈₀ alloys. The elongation of Fe-Fe pairs compared to the bond lengths of Fe-Ni and Ni-Ni pairs is commonly observed in the ferromagnetic states of all Fe-Ni alloys. The B_0 value of each atomic pair is comparable to the value of bulk B_0 when the ferromagnetic phase is stable under high pressure, while the rapid shrinkage of the elongating Fe-Fe pairs results in a smaller value of B_0 at the destabilized ferromagnetic region. Therefore, the magnetovolume effect in Fe-Ni alloys is interpreted as a result of the elongating Fe-Fe pairs and their population in the alloy. The elongation and subsequent shrinkage of Fe-Fe pairs at the destabilization of the ferromagnetic order plays a crucial role for initiating the invar effect.

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I. INTRODUCTION

Iron-nickel alloys with a disordered face-centered-cubic (fcc) structure are characterized by a ferromagnetic order with an expanded lattice due to the anomalously large magnetovolume effect. According to the fundamental Stoner-Edward-Wohlfarth (SEW) theory [1–3], the magnitude of the magnetovolume effect (ω_s) is proportional to the squared product of the spontaneous magnetization. ω_s shows the maximum at a narrow composition range of ~ 35 Ni at. %, as summarized in Fig. 1(a) [4]. The maximum ω_s at Fe₆₅Ni₃₅ gives rise to large volume contraction with increasing temperature and reducing magnetization, which compensates the conventional thermal expansion and consequently results in zero-thermal expansion known as the invar effect [5,6]. The small thermal expansion coefficient ($\alpha \sim 1.19 \times 10^{-6}/\text{K}$) of the Fe₆₅Ni₃₅ invar alloy appears within a wide temperature range up to the Curie temperature ($T_C \sim 505$ K), whereas

Fe-Ni alloys with larger Ni content rapidly recover the thermal expansion of normal metal with a typical value of α of $\sim 10^{-5}/\text{K}$ [4] and higher T_C [Fig. 1(b)]. Why does the invar effect appear in a narrow Ni content around 35 at. % of the Fe-Ni alloys?

Disordered alloys comprise different types of metal elements occupying the lattice randomly with small displacements from the periodic ideal positions; however, the displacement seems not completely random but a characteristic order depending on the constituent element exists. Interestingly, recent *ab initio* calculations [7,8] demonstrated that the noncollinear spin alignment of Fe moments develops significantly with decreasing volume of the lattice, whereas the noncollinear structure of Ni moments grows moderately, which explains properly the elastic softening behaviors in not only the invar alloy but also Ni-rich Fe-Ni alloys. The element-dependent response of magnetic structure encouraged us to experimentally determine the local structure around Fe and Ni atoms separately under pressure. Therefore, we examined the distance of the nearest-neighboring Fe-Fe, Fe-Ni, and Ni-Ni atomic pairs in the ferromagnetic invar alloy using extended x-ray absorption fine structure (EXAFS), x-ray diffraction (XRD), and reverse Monte Carlo (RMC) modeling, which revealed that the average atomic distance of Fe-Fe pairs is longer than those of the other two atomic pairs [9,10]. Although similar elongation has been investigated by other researchers [11,12], we reported that the elongation of Fe-Fe pairs decreases accompanied with the pressure-induced transition to the paramagnetic phase. Therefore, the

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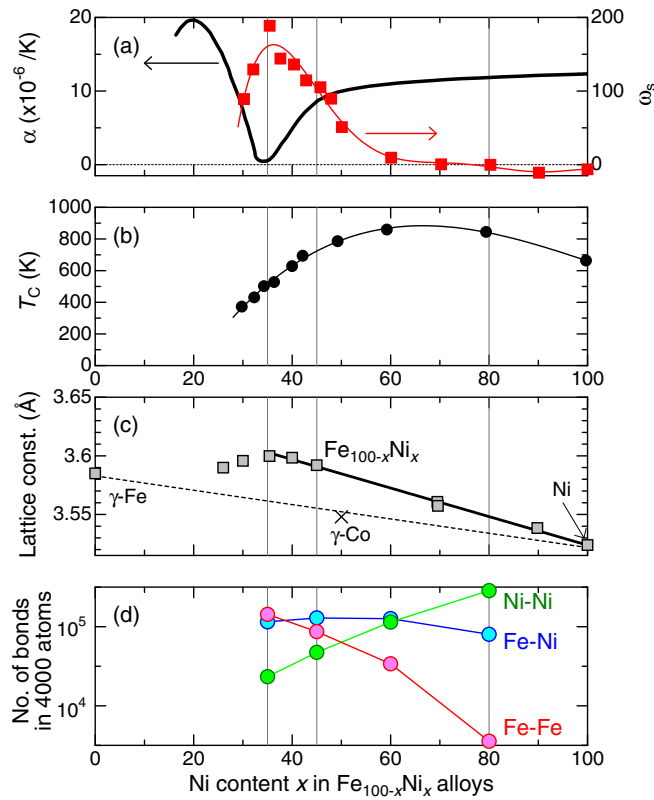


FIG. 1. Physical properties of Fe-Ni alloys as a function of the Ni content. Grayish vertical lines indicate the Ni contents of the samples used in this study. (a) Linear expansion constant α and magnitudes of magnetovolume effect ω_s [4]. (b) Curie temperatures at ambient pressure [13]. (c) Lattice constants at ambient pressure compared to the lattice constants of antiferromagnetic γ (fcc)-Fe and ferromagnetic γ -Co [14]. (d) Number of the nearest-neighboring atomic bonds in the 4000 atomic cluster of Fe-Ni alloys.

magnetovolume effect can be clarified based on the elongation of Fe-Fe atomic pairs from an atomic viewpoint.

A systematic atomic-scale study that focuses on composition dependence is an interesting approach for highlighting the anomalous elastic properties in an invar alloy. The pioneering macroscopic investigation conducted by Hayase *et al.* demonstrated that the magnitude of ω_s decreases with increasing Ni content and becomes zero or negative above the content of 60 at. % [see Fig. 1(a)] [4]. As summarized in Fig. 1(c), the comparison of lattice constants between fcc-based Fe-Ni alloys and other 3d transition metals is a good scale to illustrate the magnetovolume effect working in the Fe-Ni alloys. The plot indicates that the lattice constants of Fe-Ni alloys are larger than the interpolated line for the lattice constants of antiferromagnetic γ (fcc)-Fe, ferromagnetic γ -Co, and pure Ni metal. Further, the larger lattice constants support an interpretation that volume expansion attributed to the magnetovolume effect exists in Fe-Ni alloys for stabilizing their ferromagnetic states, and the magnitude reaches a maximum in the narrow range at the Ni composition of the invar alloy.

We revealed that the elongation of Fe-Fe bonds remains in the ferromagnetic phase of a non-invar $\text{Fe}_{55}\text{Ni}_{45}$ alloy [10] by using RMC modeling with the data of EXAFS and XRD;

however, the atomic structure in a more Ni-rich alloy is of great interest for verifying the relationship between the elongation of Fe-Fe pairs and the magnetovolume effect.

In this paper, the atomic scale origin of the invar effect and the large magnetovolume effect in the Fe-Ni alloy is revisited by investigating the Ni-content dependence of elongation and the bulk modulus B_0 of each atomic pair. To this end, we newly determined the structure of a Ni-rich Fe-Ni alloy, $\text{Fe}_{20}\text{Ni}_{80}$, via RMC analysis using a dataset of EXAFS and XRD under quasihydrostatic high pressures, and we compared the results with those of the $\text{Fe}_{65}\text{Ni}_{35}$ invar alloy and ferromagnetic $\text{Fe}_{55}\text{Ni}_{45}$. The stability of the ferromagnetic phase under high pressure was examined using x-ray magnetic circular dichroism (XMCD). As shown in Fig. 1(a), the $\text{Fe}_{20}\text{Ni}_{80}$ alloy completely recovers normal thermal expansion with $\alpha \sim 1.2 \times 10^{-5}/\text{K}$ and possesses an almost zero magnetovolume effect, confirming that $\text{Fe}_{20}\text{Ni}_{80}$ is a good alloy to investigate the relationship between the magnetovolume effect and elongation of Fe-Fe pairs from an atomic point of view. Although it is difficult to examine the elongation for this alloy through experiments because of a factor of 2 order number of Fe-Fe pairs less than the number of pairs in invar and $\text{Fe}_{55}\text{Ni}_{45}$ alloys [see Fig. 1(d)], we successfully revealed that the elongation of the Fe-Fe bond exists even in the Ni-rich $\text{Fe}_{20}\text{Ni}_{80}$ alloy.

II. EXPERIMENTAL PROCEDURES

Fe-Ni powder samples were made from polycrystalline ingots by a diamond file and pelletized for the EXAFS and XRD measurements. The ingots were synthesized by the arc-melting method. Annealing of the ingots was performed at 900 °C for one week for homogenization. The prepared pellets were annealed at 400 °C to remove distortion introduced during the pelletization. For the $\text{Fe}_{20}\text{Ni}_{80}$ alloy, the pressure dependence of XRD and EXAFS/XMCD was measured on beamlines 10XU and 39XU at SPring-8 [15] using a fresh (uncompressed) pellet, respectively. Helium fluid pressurized to 200 MPa was loaded into the diamond anvil cell (DAC) as a pressure-transmitting medium for realizing quasihydrostatic pressure conditions. For $\text{Fe}_{65}\text{Ni}_{35}$ and $\text{Fe}_{55}\text{Ni}_{45}$ alloys, both XRD and EXAFS/XMCD measurements were performed on beamline 39XU. A Fluorinert 70 + 77 solution was used as the pressure-transmitting medium. The applied pressure on the sample was monitored by the conventional ruby fluorescence method. Nanoprecrystalline diamond (NPD) anvils were utilized for the EXAFS measurement to prevent Bragg diffraction from the anvil crystals [16–18]. In this study, a small edge jump of the absorption profile of $\text{Fe}_{20}\text{Ni}_{80}$ at the Fe K -edge enlarged the distortion caused by the 331 Bragg diffraction of NPD, resulting in a small hump at 7575 eV ($k \sim 11 \text{ \AA}^{-1}$) superimposed on the EXAFS oscillation, as shown in Fig. 2 [17]. The hump was carefully eliminated by proper background removal based on the arctangent function. All measurements were performed at room temperature.

It is difficult to distinguish the neighboring Fe and Ni atoms using conventional EXAFS analyses because of the small differences in EXAFS parameters such as backscattering amplitudes and phase factors of Fe and Ni atoms [19,20]. Thus, conventional EXAFS curve fitting could not separate the like

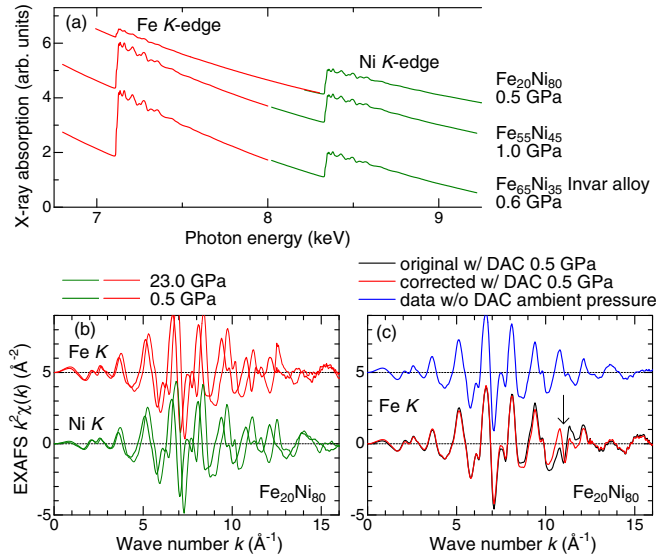


FIG. 2. (a) Raw x-ray absorption profiles of Fe-Ni alloys under high pressures. Each profile is shifted upward for clarity. (b) Pressure dependence of EXAFS oscillation $k^2\chi(k)$ of Fe₂₀Ni₈₀ at Fe and Ni *K*-edges. (c) Demonstration of the removal of Bragg reflection from the NPD anvils by background subtraction based on the arctangent function for Fe₂₀Ni₈₀. The downward arrow indicates the position of Bragg reflection at $k \sim 11 \text{\AA}^{-1}$.

(Fe-Fe or Ni-Ni) and unlike (Fe-Ni or Ni-Fe) atomic pairs in the same shell [11,21,22]. In contrast, RMC modeling constructs an atomic cluster and determines the best model of the cluster that reproduces the experimental EXAFS profiles at both Fe and Ni edges through trial and error. As demonstrated in our previous works, the determined cluster enables us to estimate the length of each atomic pair separately [9,10]. We used the RMCProfile software for the RMC algorithm [23–27] and constructed a cubic cluster comprising 4000 Fe/Ni atoms ($10 \times 10 \times 10$ fcc unit cells).

XMCD spectra were measured by modifying the transmission setup for EXAFS measurements on beamline 39XU. We obtained XMCD spectra by the helicity-modulation method [15]. Left and right circularly polarized x-rays were generated by a diamond phase retarder. A magnetic field of 0.6 T was applied parallel to the incident x-ray by using electromagnets.

III. RESULTS AND DISCUSSION

A. XMCD spectra of Fe-Ni alloys

Figure 3 shows the pressure dependence of XMCD spectra of the Fe-Ni alloys. Compared with the spectra of the Fe₆₅Ni₃₅ invar alloy and the Fe₅₅Ni₄₅ alloy, positive peaks near the absorption edge of the Fe₂₀Ni₈₀ alloy are absent because of the higher occupancy of 3*d* electrons provided from the 80 at. % of Ni [9,28,29]. These figures demonstrate the Ni-content-dependent stability of the ferromagnetic state in the Fe-Ni alloys. The XMCD spectra of Fe₂₀Ni₈₀ remain almost unchanged at pressures up to 23 GPa. The pressure-independent behavior of the Fe₂₀Ni₈₀ alloy is in contrast to the large pressure dependence of the XMCD spectra for the Fe₆₅Ni₃₅ invar alloy and the Fe₅₅Ni₄₅ alloy,

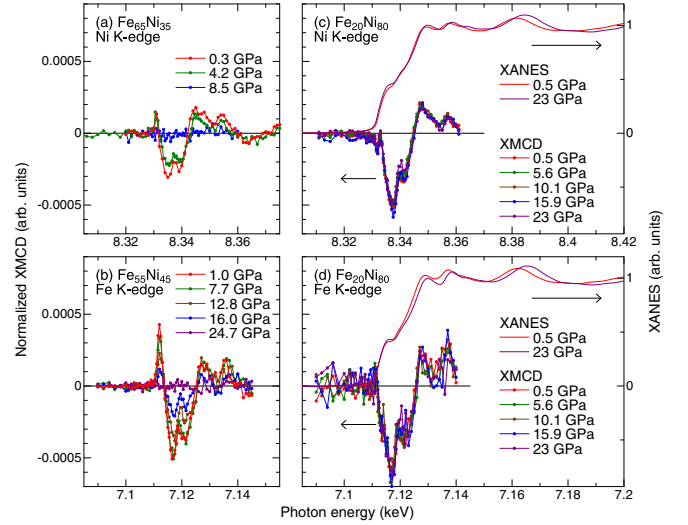


FIG. 3. Pressure dependence of XMCD spectra of the (a) Fe₆₅Ni₃₅, (b) Fe₅₅Ni₄₅, and (c) and (d) Fe₂₀Ni₈₀ alloys.

where the pressure-induced disappearance of XMCD caused by the transition from ferromagnetic to paramagnetic phases occurs at $P_c = 7$ and 18.7 GPa, respectively [9,10,30]. P_c of the Fe₂₀Ni₈₀ alloy is expected to appear at pressures higher than 23 GPa.

B. RMC fits of Fe-Ni alloys

The RMC fits of the EXAFS spectra and XRD patterns at selected pressures are summarized in Fig. 4 for the Fe₆₅Ni₃₅ and Fe₅₅Ni₄₅ alloys and Fig. 5 for the Fe₂₀Ni₈₀ alloy. These figures also illustrate examples of the determined atomic cluster. The k ranges used for the Fourier transformation were chosen as wide as possible with taking into account the signal-to-noise ratio. The determined k ranges are summarized in Table I. The RMC fits show good agreement between the experimental and calculated profiles of the absolute values of the Fourier-transformed profiles ($|FT[k^2\chi(k)]|$) at the Fe and Ni edges of all samples. For the Fe₂₀Ni₈₀ alloy, Fourier-transformed profiles at the Fe *K*-edge are broadened compared with the profile at the Ni *K*-edge because of the narrow range of the k space for the Fourier transform and the small atomic content of 20 at. % of Fe. The height of each peak increases with increasing pressure because of the suppression of the Debye-Waller factor, which is fairly reproduced by the RMC calculations of all data within an R range up to 6.0 $\text{\AA}$. Prominent peaks at $R \sim 2.2 \text{\AA}$ correspond to the first shells of the local structure, where a total of 12 atoms of Fe and Ni participate as the first-nearest-neighboring (1NN) bonds around the x-ray-absorbing atom. The $|FT[k^2\chi(k)]|$ profiles up to $R = 6.0 \text{\AA}$ provide information on the atomic arrangements of the 1NN–5th-NN (5NN) atoms in the fcc lattice.

Figure 5(c) shows the experimental and fitted XRD patterns for Fe₂₀Ni₈₀ alloys. Five Bragg peaks up to the 222 reflection of the fcc structure are used for the RMC calculations. Sharp Bragg peaks are successfully generated by the RMC calculations at the same 2θ positions of the experimental profiles, which ensures a long-range periodicity of the fcc symmetry in the atomic cluster as shown in Fig. 5(d).

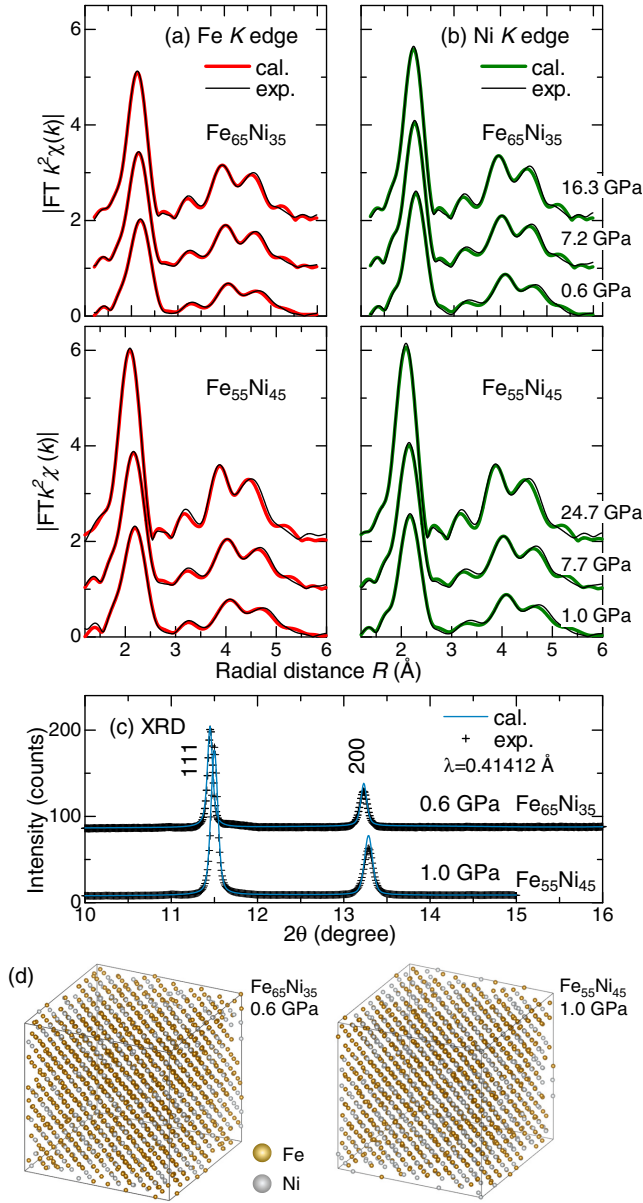


FIG. 4. Comparison of the experimental profiles with RMC fits for the Fe₆₅Ni₃₅ and Fe₅₅Ni₄₅ alloys. Absolute values of Fourier-transformed profiles ($|FT[k^2\chi(k)]|$) at (a) the Fe *K*-edge and (b) the Ni *K*-edge. (c) XRD patterns under selected pressures. (d) Atomic clusters obtained by the RMC method. The clusters are viewed from the [121] direction.

For the Fe₆₅Ni₃₅ and Fe₅₅Ni₄₅ alloys, only two Bragg reflections (111 and 200) are used for the RMC fits because of the limited area of the camera used for the XRD measurement. As shown in Fig. 4(d), Bragg peaks generated by the RMC calculations also ensure a long-range periodicity of the fcc symmetry in the atomic cluster.

C. Partial pair distribution functions $g_{ij}(R)$

Partial pair distribution functions $g_{ij}(R)$ are calculated from the fitted atomic clusters, where i and j correspond to the elements in the pair of Fe/Ni atoms. Figure 6 shows $g_{ij}(R)$ functions around the 1NN atomic pairs for the Fe-Ni alloys

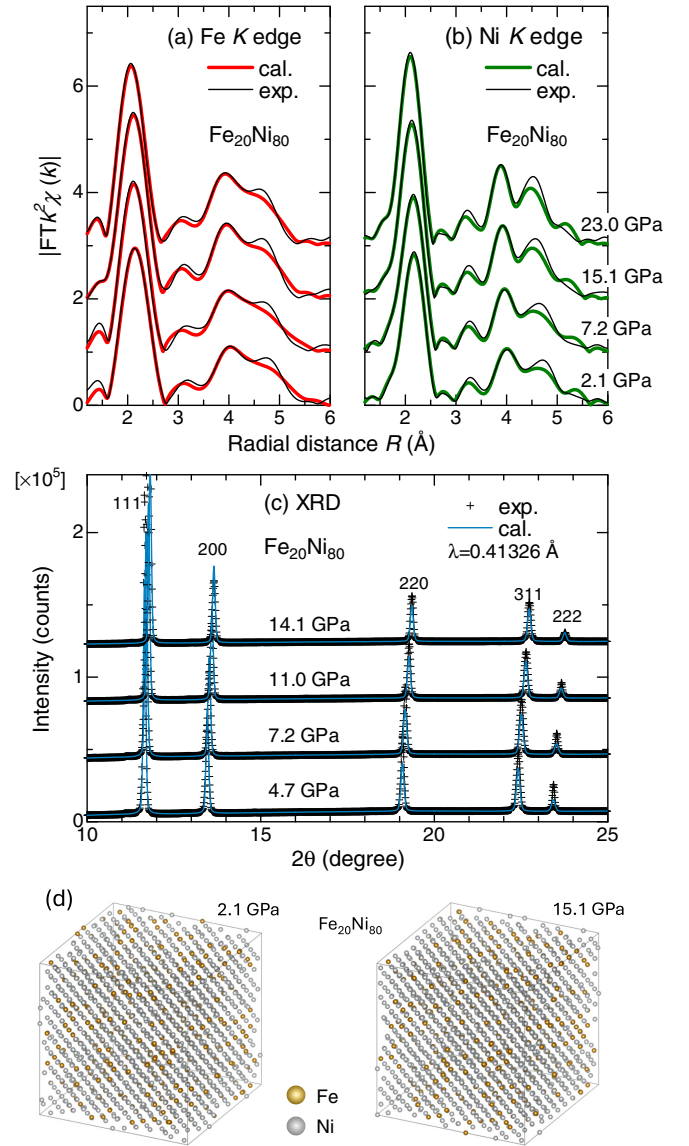


FIG. 5. Comparison of the experimental profiles with RMC fits for the Fe₂₀Ni₈₀ alloy. Absolute values of Fourier-transformed profiles ($|FT[k^2\chi(k)]|$) at the (a) Fe *K*-edge and (b) the Ni *K*-edge. (c) XRD patterns under selected pressures. (d) Atomic clusters of the Fe₂₀Ni₈₀ alloy obtained by the RMC method. The clusters are viewed from the [121] direction.

at selected pressures together with examples of the $g_{ij}(R)$ functions in a wide R range up to 6 Å. The peak profiles appear sharp due to the suppressed Debye-Waller factors with increasing pressure, which is attributed to the lattice compression that raises the stiffness of the atomic interaction. For

TABLE I. k ranges used for the Fourier transformation of the $k^2\chi(k)$ profile.

Abs. edge	Fe ₆₅ Ni ₃₅	Fe ₅₅ Ni ₄₅	Fe ₂₀ Ni ₈₀
Fe <i>K</i>	3.0–13.3 Å ⁻¹	3.0–13.3 Å ⁻¹	3.0–11.0 Å ⁻¹
Ni <i>K</i>	3.0–13.3 Å ⁻¹	3.0–13.3 Å ⁻¹	3.0–13.0 Å ⁻¹

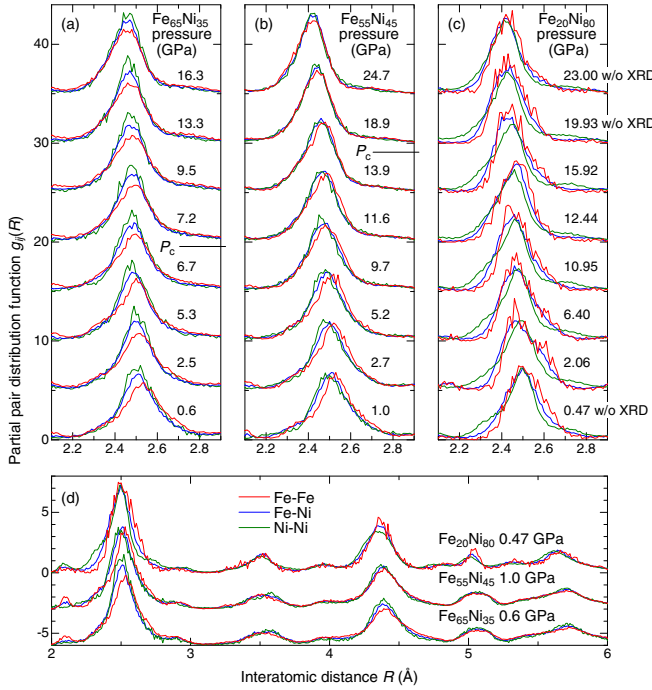


FIG. 6. Partial pair distribution functions $g_{ij}(R)$, where $i, j = \text{Fe}$ or Ni , for the (a) Fe₆₅Ni₃₅, (b) Fe₅₅Ni₄₅, and (c) Fe₂₀Ni₈₀ alloys around the nearest-neighboring atomic pairs at selected pressures. (d) $g_{ij}(R)$ profiles of the Fe-Ni alloys in a wide R range.

the Fe₂₀Ni₈₀ alloy, Ni-Ni and Fe-Ni show a prominent peak profile with moderate slopes at the shorter length side, and Fe-Fe pairs exhibit noisy profiles with steep and moderate slopes at the shorter and longer length sides, respectively. The noise is attributed to the lower number of Fe-Fe pairs compared to the numbers of Fe-Ni and Ni-Ni pairs. A closer observation reveals that the $g_{ij}(R)$ profiles around the 1NN Fe-Fe atomic pairs are located at a longer R range with respect to the positions of Fe-Ni and Ni-Ni pairs. This shift is commonly observed in the pressure regions of the ferromagnetic phases of the three Fe-Ni alloys. This shift becomes smaller and disappears when the alloys enter the paramagnetic phase at pressures above P_c .

To quantify these phenomena, the average lengths of the 1NN atomic pairs were evaluated from $g_{ij}(R)$ functions using two methods: Gaussian curve fitting and gravity of center around the peak of the 1NN atomic pairs. The obtained pressure dependence is displayed in Figs. 7(a)–7(c). Gaussian fitting was performed within a range of $2.2 \text{ Å} \leq R \leq 2.8 \text{ Å}$, which covers the entire profile of the 1NN peaks in the asymmetric real space function. The gravity of center $\langle R_{ij} \rangle$ corresponds to the average length within the range corresponding to 12 coordinates estimated by

$$\langle R_{ij} \rangle = \frac{\int_{R_1}^{R_2} R \times 4\pi R^2 g_{ij}(R) \rho_j dR}{\int_{R_1}^{R_2} 4\pi R^2 g_{ij}(R) \rho_j dR}, \quad (1)$$

where R_1 and R_2 define the lower and upper limits of integration, respectively, and ρ_j represents the number of j atoms in a unit volume. An advantage of the expected value is

minimizing the ambiguities from the asymmetric real space function. For comparison with the Gaussian fit, we used a wider integration range from $R_1 = 0.0 \text{ Å}$ to $R_2 \approx 3.05 \text{ Å}$ that covers all 12 Fe/Ni atoms in the first shell of the fcc lattice.

D. Elongation and shrinkage of Fe-Fe pairs in the Fe-Ni alloys

For the Gaussian fits, the elongation of $R_{\text{Fe-Fe}}$ with respect to $R_{\text{Fe-Ni}}$ and $R_{\text{Ni-Ni}}$ is clearly recognized in the characteristic pressure range of each Fe-Ni alloy [Figs. 7(a)–7(c)]. The elongation for Fe₂₀Ni₈₀ is observed in the entire pressure range measured, although the pressure dependence of $R_{\text{Fe-Fe}}$ contains noise due to the lower amount of Fe atoms. The magnitude of the elongation for $R_{\text{Fe-Fe}}$ is estimated to be $0.013(5) \text{ Å}$, which is slightly smaller than the elongation in the ferromagnetic states of the invar alloy and the Fe₅₅Ni₄₅ alloy ($\approx 0.02 \text{ Å}$) [9,10]. When estimating with the gravity center, the elongation of the Fe-Fe bond remains within the entire pressure range up to 23 GPa, although the elongation is a factor of one-half or one-third smaller than the result of the Gaussian fits. The suppressed elongation of $\langle R_{\text{Fe-Fe}} \rangle$ is observed for all three samples, and it is attributed to the wide integration range covering small humps and the asymmetric profiles of the peak.

The elongation of Fe-Fe pairs appears only at the ferromagnetic phase of each alloy, while the elongation is suppressed and eliminated with the decrease in ferromagnetic order and paramagnetic phase above P_c , respectively. P_c can be determined by the pressure dependence of the integrated XMCD for three Fe-Ni alloys as shown in Figs. 7(d)–7(f). The integrated XMCD at the K -edge corresponds to the $4p$ -orbital moment [31,32]. The $4p$ -orbital moment is induced by the net magnetization originating from the $3d$ moment, and therefore, the integrated XMCD is considered a probe of the ferromagnetic order of the Fe $3d$ moment. Fe₆₅Ni₃₅ invar and Fe₅₅Ni₄₅ alloys undergo a phase transition from the ferromagnetic to the paramagnetic phase at $P_c = 7$ and 18.7 GPa , respectively, whereas the XMCD of Fe₂₀Ni₈₀ remains unchanged up to 23 GPa . XMCD measurements of pure Ni revealed that Ni metal remains ferromagnetic at 200 GPa , and the critical pressure is theoretically estimated to be $P_c \geq 400 \text{ GPa}$ [32]. Therefore, 80 at. % of the Ni content stabilizes the ferromagnetic state of the Fe₂₀Ni₈₀ alloy under high pressure. The shrinkage of Fe-Fe pairs near the P_c of the Fe₂₀Ni₈₀ alloy probably appears at a very high pressure below 400 GPa .

According to previous reports [7,33], the invar effect occurs at pressures of softening behavior and is accompanied by the destabilization of the ferromagnetic phase originating from the noncollinear spin structure of Fe atoms. In the invar alloy, the destabilized ferromagnetic structure causes the rapid shrinkage of Fe-Fe pairs because of the pressure-induced loss of the magnetovolume effect as shown in Fig. 7(a). To quantify the softening behavior, the bulk modulus B_0 is evaluated by the fit of the second-order Birch-Murnaghan equation of state (B-M EOS [34]) to the compression curves of the gravity center $\langle R_{ij} \rangle$. Further, we evaluated B_0 values as a macroscopic average using the compression curves measured by XRD [Figs. 7(g)–7(i)]. As for the Fe₅₅Ni₄₅

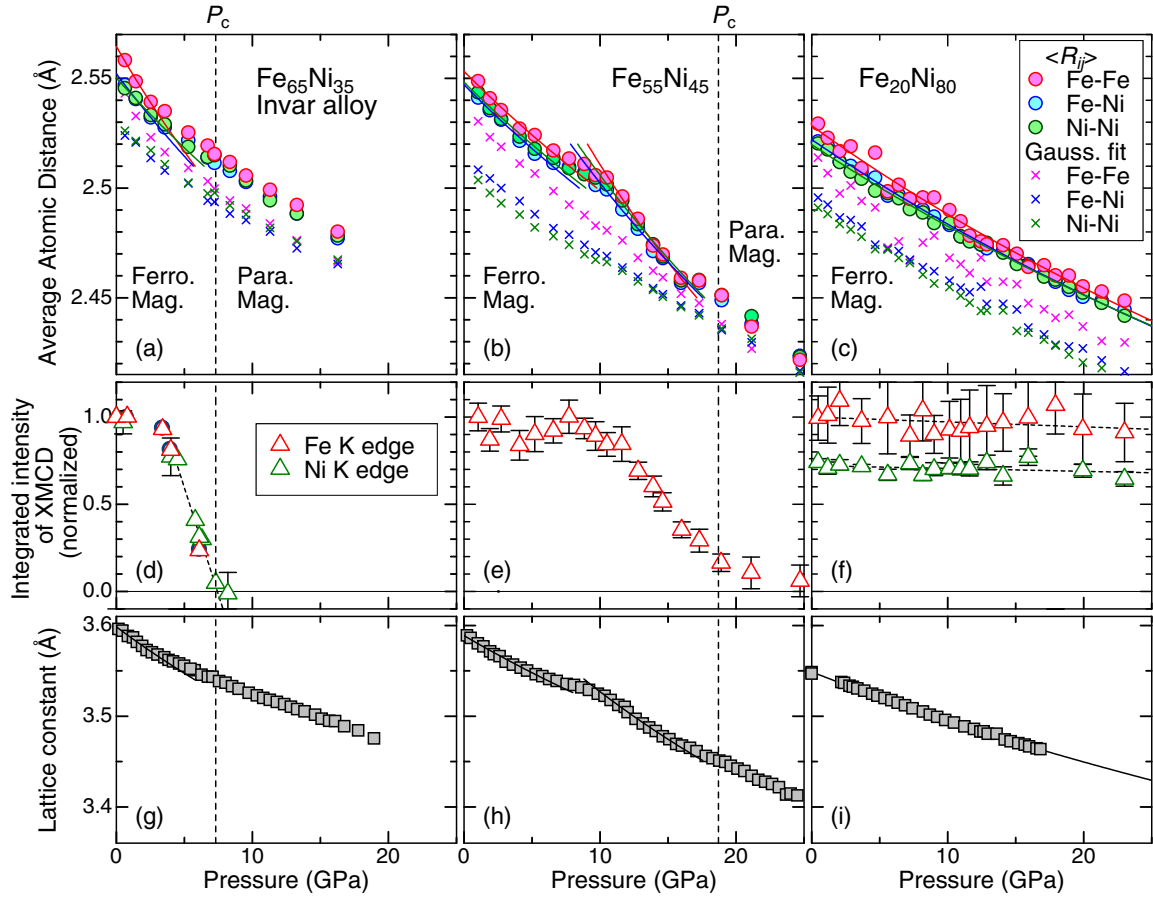


FIG. 7. Comparison of the structural and magnetic parameters between $\text{Fe}_{20}\text{Ni}_{80}$ alloy, $\text{Fe}_{55}\text{Ni}_{45}$ alloy, and $\text{Fe}_{65}\text{Ni}_{35}$ invar alloy as a function of pressure: (a)–(c) Average lengths of R_{ij} evaluated by Gaussian fits (crosses) and gravity center (circles). The solid lines represent the equation of state curve based on the Birch-Murnungaham equation of state. (d)–(f) Integrated intensity of XMCD. (g)–(i) Compression curves determined by XRD. The vertical dashed lines represent pressures of P_c , where the magnetic transition to the paramagnetic phase occurs.

alloy, softening behavior of the lattice constants is observed above 10 GPa as the knee shape of the compression curve, which is accompanied with the rapid suppression of XMCD. The B_0 value of this pressure region is also evaluated [see Fig. 7(b)]. The determined B_0 values of each atomic pair, macroscopic averages, and their bond lengths are presented in Fig. 8.

The Fe-Fe pair of the invar alloy has a value of $B_0 = 78.9(7)$ GPa smaller than those of Fe-Ni and Ni-Ni pairs and the B_0 evaluated by XRD. This indicates that the softening behavior is attributed to the weak force constant working between Fe atoms. On the other hand, the difference in B_0 between Fe-Fe, Fe-Ni, and Ni-Ni bonds is small for $\text{Fe}_{55}\text{Ni}_{45}$ and $\text{Fe}_{20}\text{Ni}_{80}$ alloys even though the elongation of the Fe-Fe bond exists. The B_0 values of the three bonds are comparable to the bulk values of B_0 evaluated by XRD. Interestingly, for $\text{Fe}_{55}\text{Ni}_{45}$, the softening of the Fe-Fe bond and the smaller B_0 value of this bond occur in the subsequent pressure region of the suppression of XMCD above 10 GPa, as displayed by the data in the dashed rectangle of Fig. 8(a), which suppresses the elongation of Fe-Fe bonds toward the paramagnetic phase above P_c . Because the pressure-induced invar effect occurs with the softening behavior [33], the same mechanism induced by the shrinkage of the Fe-Fe bond can be assumed as

the atomic-scale interpretation of not only the conventional invar alloy but also the alloy of the pressure-induced invar effect. Very recently, the instability of the ferromagnetic phase for the $\text{Fe}_{55}\text{Ni}_{45}$ alloy has been confirmed at a pressure around 10 GPa by nuclear resonant scattering using the neon pressure medium [35]. They also confirmed the pressure-induced invar effect by XRD in the same pressure range. This report supports our scenario that the instability of the ferromagnetic phase initiates the softening behavior of the Fe-Fe bond and the invar effect.

Figure 8 shows that B_0 becomes monotonically larger with increasing Ni content. The elongation of Fe-Fe pairs occurs to stabilize the ferromagnetic order between Fe moments in the fcc lattice by reducing the overlap between the electronic wave functions of $3d$ orbitals [37,38]. Therefore, the elongation of Fe-Fe atomic pairs is maintained even in a Ni-rich $\text{Fe}_{20}\text{Ni}_{80}$ alloy, while the B_0 values of Fe-Fe pairs increase with a decreasing population of the Fe-Fe bond. The small number of elongating Fe-Fe pairs in the $\text{Fe}_{20}\text{Ni}_{80}$ alloy indicates that the Fe atom is mostly surrounded by Ni atoms as the neighboring atom, weakening the contribution from Fe-Fe pairs and alternatively enhancing the contribution from Fe-Ni bonds. Consequently, the $\text{Fe}_{20}\text{Ni}_{80}$ alloy has a mostly zero ω_s and a large B_0 comparable to that of pure Ni ($B_0 \sim 186$ GPa).

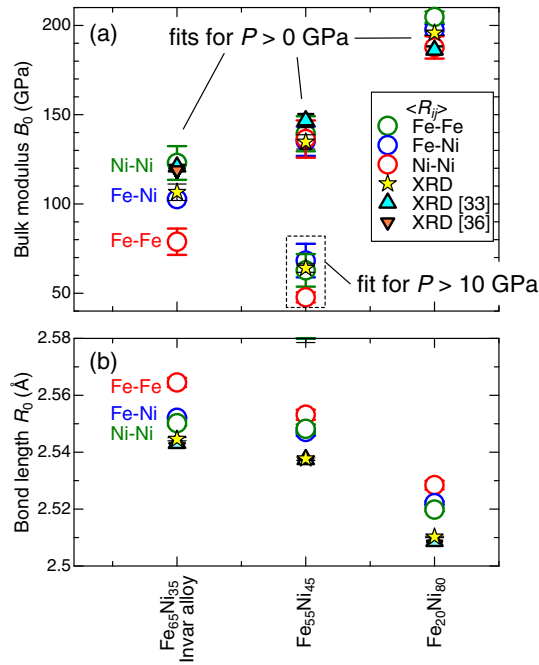


FIG. 8. Comparison of (a) bulk modulus B_0 and (b) extrapolated bond length at ambient pressure, $R_0 = V_0^{1/3}$, between the three Fe-Ni alloys. These values were evaluated from the B-M EOS fit to the compression curve of $\langle R_{ij} \rangle$ for Fe-Fe, Fe-Ni, and Ni-Ni pairs. The B-M EOS fit was performed in the range of the pressure independent of XMCD near ambient pressure. The data in the dashed rectangle indicate results of the additional fit in the pressure region above 10 GPa of Fe₅₅Ni₄₅, where the suppression of XMCD and the softening behavior appear. B_0 and R_0 values evaluated from previous works [33,36] are plotted as references.

IV. CONCLUSIONS

Our study revealed that the elongation of the Fe-Fe bond exists in the ferromagnetic Fe-Ni alloy with the fcc symmetry. Interestingly, the elongation remains even in a

Ni-rich Fe₂₀Ni₈₀ alloy, where the number of Fe-Fe bonds is more than 2 orders less than that of the Fe₆₅Ni₃₅ invar alloy. Therefore, the atomic scale origin of the magnetovolume effect in the Fe-Ni alloys can be explained by the elongating Fe-Fe bonds and their population in the alloy. From an atomic point of view, the elongation of Fe-Fe pairs and their rapid shrinkage induced by the destabilization of ferromagnetic order plays a crucial role in initiating the invar effect and the accompanied softening behavior. The balance between the number of elongating Fe-Fe pairs and the Curie temperature as a function of Ni content determines the appearance of the invar effect under ambient and high pressures. Finally, we should note that the problem of how the significant shrinkage of Fe-Fe pairs induces the macroscopic volume shrinkage is still an open question. To solve this problem, the analysis of distortion and volume in the local structure around Fe/Ni atom is indispensable.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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