Local thermal expansion of Co-containing invar alloys

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Thermal expansion of Co-containing invar alloys of GX1Ni29-Co17 Fe₅₄Co₁₇Ni₂₉ and stainless invar Fe₃₉Co₅₀Cr₉Ni₂ was investigated from the viewpoint of local structure by analyzing temperature-dependent extended x-ray absorption fine-structure (EXAFS) spectra combined with the computational simulations based on the path-integral effective classical potential (PIECP) method. For detailed comparative discussion, FeNi invar alloys of 36invar, 42invar, and 45invar were also examined. It is found by EXAFS that in stainless invar, Co exhibits a noticeable invar effect, while the invar effect on Co in GX1Ni29-Co17 is negligibly small. The PIECP simulations provide qualitative agreement with this finding, exemplifying that the Co magnetization is more effectively suppressed in stainless invar with a temperature rise, because of a smaller lattice constant and shorter corresponding interatomic distances. The present study clearly demonstrates the importance of the local structural point of view to understand the detailed low thermal expansion mechanism, in which microscopic local thermal expansion.

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I. INTRODUCTION

It is well known that FeNi alloys show a so-called invar effect [1-5], which exhibits almost zero thermal expansion over a wide temperature range and have been applied to precision equipment such as telescopes, microscopes, and nanodevices. Recently, as a practical usefulness close to our daily lives, the FeNi invar alloy has been applied to core cables of electric high-voltage power lines to avoid sagging due to heat on high current conduction. Here, we will regard the invar effect as anomalously low thermal expansion originating from temperature-dependent variation of the spin electronic structure of transition metal atoms [5] to distinguish from transversal vibration-induced thermal contraction that is often observed in tetrahedrally coordinated systems as Si, CdTe, water, and so forth [6-8]. In the FeNi invar case, Fe exhibits suppression of magnetic moments with a temperature rise, leading to thermal contraction of the Fe atomic radius, which compensates for normal thermal expansion due to anharmonic thermal vibration [9].

It is quite interesting and important to see such anomalous thermal expansion from the local structure point of view. Even in simple fcc crystals such as FeNi invar, it is known that the interatomic distances of Fe-Fe, Fe-Ni, and Ni-Ni pairs are slightly but meaningfully different from each other and correspondingly that the thermal expansions are also dissimilar [9–14]. In Fe₆₄Ni₃₆ invar, Fe exhibits the invar effect almost exclusively, which is quite reasonable because the Fe spin state varies depending on temperature. From the local structure point of view, high-spin (HS) Fe with a larger atomic radius is more stable at low temperature and is gradually transformed to the low-spin (LS) state with a smaller atomic radius as temperature increases, while the Ni electronic structure exhibits little change. In such a local structure point of view, the extended x-ray absorption fine-structure (EXAFS) spectroscopy technique should be the most suitable experimental method since the technique separately provides local structure information on each x-ray absorbing atom.

Recently, Fujii et al. [15,16] successfully developed a novel Co-containing invar alloy, Fe₃₉Co₅₀Cr₉Ni₂, which is called stainless invar in this paper, and has already been practically utilized as a securing bracket for an infrared cryogenic space telescope. Since Fe usually plays a major role in the invar effect of Fe-containing alloys, it is quite interesting to investigate how Co contributes to the (partial) invar effect in this alloy that contains a greater concentration of Co than Fe. In the present study, we have thus investigated the local thermal expansion of Co-containing invar alloys of this stainless invar alloy and also GX1Ni29-Co17 (Fe₅₃Co₁₇Ni₂₉X₁, where X is the contamination as Mn, etc., often called Kovar, the registered trademark of Westinghouse Electric Corp.) for comparison. We have measured and analyzed temperaturedependent EXAFS spectra concerning the corresponding metal K edges, together with computational simulations using the path-integral effective classical potential (PIECP) theory [17–22]. GX1Ni29-Co17 is a famous partial invar alloy that shows low thermal expansion to match that of Pyrex borosilicate hard glass above room temperature and is widely utilized as a metal-glass sealing material like viewing ports in high vacuum chambers. In this work, to recognize local thermal expansion systematically, the EXAFS spectra were also measured and analyzed for FeNi invar alloys of Fe₆₄Ni₃₆ [9], Fe₅₈Ni₄₂, and Fe₅₅Ni₄₅. Moreover, the previously reported

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EXAFS results [11] concerning stainless steel 304 (SUS304 or AISI304, $Cr_{18.09}Fe_{71.98}Ni_{9.07}X_{0.86}$) and the Ni spanC elinvar alloy ($Cr_{5.49}Fe_{49.66}Ni_{42.38}Ti_{2.47}$) are taken into consideration.

It is found by EXAFS that in GX1Ni29-Co17, Co exhibits sufficiently large (normal) thermal expansion, while stainless invar gives much lower (anomalous) thermal expansion, implying that the invar effect on Co is more noticeable in stainless invar. The PIECP simulations provide qualitative agreement with this finding, indicating that in stainless invar, the Co magnetization is more effectively suppressed with a temperature rise, because of a slightly smaller lattice constant and thus shorter interatomic distances in stainless invar. The present study clearly demonstrates the importance of the local structure point of view to get a deeper insight into the detailed low thermal expansion nature in the invar alloys, in which microscopic local thermal expansion often differs from macroscopic lattice thermal expansion.

II. EXAFS MEASUREMENTS AND ANALYSIS

The stainless invar alloy foils of 10 μ m thickness were prepared at Shinhokoku Material Corporation [15,16]. The elemental compositions were determined by the x-ray fluorescence spectra, yielding Fe_{38.8}Co_{50.1}Cr_{9.2}Ni_{1.9} (denoted as sample 1 hereafter) and Fe_{37.8}Co_{51.3}Cr_{9.0}Ni_{1.9} (sample 2). Both samples were confirmed to consist of a single fcc phase by the powder x-ray diffraction measurements. Other alloy foils examined in the present work were commercially available GX1Ni29-Co17 (Kovar Fe₅₃Co₁₇Ni₂₉X₁, 10 μ m, Nilaco Corporation), 36invar (Fe_{64.6}Ni_{35.4}, 8 μ m, GoodFellow Japan), 42invar (Fe₅₈Ni₄₂, 10 μ m, Nilaco Corporation), and 45invar (Fe₅₅Ni₄₅, 45permalloy, 10 μ m, Nilaco Corpoation). The lattice thermal expansions of GX1Ni29-Co17, stainless invar, and 42invar were also measured by the dilatometer at Shinhokoku Material Corporation.

Cr, Fe, Co, and Ni K-edge EXAFS spectra were recorded at Beamline 9C [23] of Photon Factory (top-up operation, the electron storage ring energy of 2.5 GeV and the ring current of \sim 450 mA) of the High Energy Accelerator Research Organization (KEK-PF) with the transmission mode using a Si(111) double crystal monochromator. To avoid contamination of third-order harmonic x rays, the double crystal monochromator was slightly detuned by the piezoelectric device to provide 70% intensity of the fully optimized x-ray beams. Ionization chambers filled with pure N2, 17 and 31 cm in length, were used to measure the incident and transmitted x-ray intensities, respectively. The samples were cooled down using a He gas-circulating refrigerator and the measurement temperature range was 30-300 K. Typical EXAFS spectra are depicted in Figs. S1 and S2 of the Supplemental Material [24]. Because of the sequential presence of 3d transition metals in GX1Ni29-Co17 and stainless invar alloys, available wave number (energy) ranges in the EXAFS analysis were limited only up to the absorption edges of the subsequent metals. The Cr K-edge EXAFS was also disturbed by the presence of Mn contamination in the stainless invar.

The EXAFS oscillation functions $k^3\chi(k)$ (*k* the photoelectron wave number) were obtained based on the standard procedures as the preedge baseline and the post-edge background subtractions and the subsequent normalization with atomic absorption coefficients. The $k^3\chi(k)$ functions were subsequently Fourier transformed, Fourier filtered for the peaks of interest, and were finally curve fitted in *k* space. In the present study, the first– to fourth–nearest neighbor (NN) shells were quantitatively analyzed, although only the first–NN shells will be mainly discussed below. The EXAFS functions $k^3\chi(k)$ and their Fourier transforms are depicted in Figs. S3–S14, and the *k* and *R* spaces employed in the analysis are summarized in Table S1 [24].

The single-shell EXAFS formula employed is given as [25]

$$\chi(k) = \frac{S_0^2 NF(k)}{kR^2} \exp\left[-2C_2 k^2 + \frac{2}{3}C_4 k^4\right] \\ \times \sin\left[2kR + \phi(k) - \frac{4}{3}C_3 k^3\right],$$

where *N* is the coordination number, S_0^2 the intrinsic reduction factor due to the many-electron effect, *F*(*k*) the backscattering amplitude including the inelastic scattering loss factor, and $\phi(k)$ the total phase shift between the x-ray absorbing and photoelectron scattering atoms. *C*₂ is the Debye-Waller factor as $C_2 = \langle (r - R)^2 \rangle$, and *C*₃ and *C*₄ are the third- and fourth-order cumulants, respectively, describing vibrational anharmonicity and/or non-Gaussian radial distribution; *C*₃ = $\langle (r - R)^3 \rangle$ and $C_4 = \langle (r - R)^4 \rangle - 3C_2^2$.

For the curve-fitting analysis to obtain the structural parameters, theoretical standards were at first calculated using FEFF8.4 [26]. Here, we assumed randomly distributed clusters with a perfect fcc lattice constant of 3.578 Å (the number of the fcc unit cells of 4^3), where the composition ratios were assumed to be Fe₆₄Ni₃₆ (36invar), Fe₅₈Ni₄₂ (42invar), Fe₅₅Ni₄₅ (45invar), Fe₅₄Co₁₇Ni₂₉ (GX1Ni29-Co17), and Cr₉Fe₃₈Co₅₁Ni₂ (stainless invar). Ten random alloy clusters were evaluated and the average EXAFS spectra were obtained as consequent theoretical standards. Although static lattice strains are expected in these alloys, the FEFF simulations were conducted with the assumption that all the atoms are distributed at ideal fcc lattice positions. The curve-fitting analysis of the experimental EXAFS spectra at the lowest temperature was performed using the FEFF standards obtained above. Here, the one-shell analysis for the first-NN shell was conducted. In the Cr K-edge EXAFS of the stainless invar alloy, for instance, there exist Cr-Cr, Cr-Fe, Cr-Co, and Cr-Ni x-ray-absorber and photoelectron scatterer atom pairs in the first-NN shells. In the one-shell analysis, only the average quantities between these different pairs were obtained. The parameters fitted were S_0^2 , R, ΔE_0 (edge energy shift), and C_2 with fixed parameters of N = 12, $C_3 = 0$, and $C_4 = 0$. Note here that the metal K-edge EXAFS spectra were analyzed separately without restriction of equivalence, for instance, for the Cr-Co and Co-Cr interatomic distances between Cr and Co K edges.

Temperature dependence of the EXAFS spectra was subsequently analyzed by the empirical analysis method, where the lowest-temperature data (30 K) were used as empirical standards. Here, S_0^2 , N, ΔE_0 , and C_4 were assumed to be identical to those of the lowest temperature, while R, C_2 , and C_3 were fitting variables. The analysis of the higher–NN (second, third, and fourth) shells was similarly performed. Here, the three shells were simultaneously analyzed. In the analysis of higher-NN shells in fcc metals, especially the fourth-NN shell, the multiple-scattering effect should be considered. In the present analysis, the fourth-NN contributions including the multiple-scattering paths were summed up and treated as an average single-shell contribution, and the curve-fitting analysis in which the fourth-NN shell was regarded as a one-shell contribution was performed. For the second- and third-NN shells, the multiple-scattering effect was neglected, because the FEFF simulations yielded sufficiently small multiple-scattering effect using appropriate Debye-Waller factors. In the lowest-temperature data analysis, the FEFF standards were employed to fit S_0^2 , R, ΔE_0 , and C_2 , while in the temperature dependence analysis, the empirical standard method was used to fit R and C_2 . Note here that higher-order cumulants in the second-, third-, and fourth-NN shells are known to be neglected with high accuracy because of the absence of the chemical bonds that induce anharmonicity [27] as in the central limit theorem that random distribution without correlation approaches Gaussian distribution.

In the one-shell EXAFS analysis for the first–NN shell, only the average interatomic distance is directly obtained. For instance, in the FeNi invar case where a completely random alloy is assumed, the obtained Fe K-edge EXAFS distance R_{Fe} is given as the average such that

$$R_{\rm Fe} = c_{\rm Fe}R_{\rm Fe-Fe} + c_{\rm Ni}R_{\rm Fe-Ni},$$

where c_i (i = Fe and Ni) is the composition ratio and R_{ij} is the interatomic distance between atoms i and j. Assuming here that the interatomic distance is expressed as a sum of the atomic radii, namely,

$$R_{\text{Fe-Fe}} = 2r_{\text{Fe}}, \quad R_{\text{Fe-Ni}} = r_{\text{Fe}} + r_{\text{Ni}}, \quad \text{and} \quad R_{\text{Ni-Ni}} = 2r_{\text{Ni}},$$

where r_i (*i* = Fe and Ni) is the atomic radius of atom *i*. Using the assumption, which is called the constant atomic radius model hereafter, all the interatomic distances can separately be estimated by solving simple simultaneous linear equations if all the corresponding edge EXAFS spectra can successfully be analyzed.

III. PIECP SIMULATIONS

To investigate the temperature-dependent structural properties of GX1Ni29-Co17 and stainless invar theoretically, PIECP [17–20] Monte Carlo (MC) simulations were conducted under a constant number of particles, pressure, and temperature (*NPT*) condition. Detailed PIECP formalism for the application to EXAFS is described in the literature [9,14,21,22]. The normal vibrational analysis should be carried out prior to the MC simulation because the quantum and classical mean square relative displacements parallel and perpendicular to the bond direction of each NN atom pair [17–20] are necessary in order to evaluate the effective classical potentials that modify the classical potentials so that the quantum mechanical fluctuation can approximately but appropriately be taken into account.

The interatomic potentials of Cr, Fe, Co, and Ni are given, based on the empirical modified embedded-atom method [28–31]. The numerical parameters [31] employed in this

work are tabulated in Table S2 [24]. The energy differences between the HS and LS states in Fe and Co are numerically given as functions of the natural logarithm of the sum of the *d*-electron density by the surrounding atoms, where the *d*-electron density is calculated using the Clementi-Roetti double- ζ wave function [32], these functions being given as separated text files [24]. The compositions of the GX1Ni29-Co17 and stainless invar alloys were assumed to be Fe₁₃₉Co₄₃Ni₇₄ and Cr₂₅Fe₁₀₁Co₁₂₅Ni₅, respectively, where the total number of atoms was 256 (4^3 fcc cubic unit cells), and the distributions of atoms were chosen randomly. In a similar manner to the FEFF evaluations, ten types of the superlattices were simulated and the results were averaged to provide consequent physical quantities. In each superlattice, up to the second-NN force constants were taken into consideration, and the 768×768 Hermitian dynamical matrices were diagonalized over the first Brillouin zone $(21^3 = 9261 k$ points) to evaluate the eigenfrequencies and eigenvectors for all the vibrational modes. All the inequivalent mean square relative displacements along and normal to the bond direction up to the fourth-NN shells were calculated in the temperature range of 1-400 K. A typical phonon dispersion is depicted in Fig. S15 [24], where high-frequency phonons are distributed almost continuously because of a large superlattice unit cell including allowed structural relaxation within the supercell.

To verify that the superlattice size is sufficiently large, similar PIECP MC simulations for the 108-atom systems were conducted, and the results were found to be essentially equivalent to those for the 256-atom system. After the normal vibrational analysis of the superlattice, the PIECP MC simulations were performed based on the conventional Metropolis method, where 200 000 MC steps were calculated with 256 times trials of the atom movement and one trial of the lattice constant variation in each MC step. In the calculations of thermodynamical quantities, the results before the system reaches sufficient equilibrium (\sim 20 000 MC steps) were excluded. The temperatures considered in the present simulations were in the range of 1–400 K (21 temperatures).

IV. RESULTS

A. Stainless steel 304

Before discussing the present EXAFS results, let us see the previously reported results concerning SUS304 (stainless steel, AISI304), which shows essentially no invar effect or no ferromagnetism [11]. Figure 1 shows the first–NN interatomic distances assuming the constant atomic radius model as mentioned above, together with the macroscopic lattice constant [33]. Although the interatomic distances of atomic pairs are slightly different from each other, indicating small strains from an ideal fcc lattice, the thermal expansion behaviors of all the atomic pairs are very well coincident with the lattice thermal expansion. The thermal expansion coefficients α at 200 K obtained by EXAFS [11] are tabulated in Table I, together with the results of all the alloys examined in this study. All the α values are located around 10×10^{-6} (K⁻¹) or a little larger and are comparable with the expansions of pure metals at 200 K. The estimated Debye temperatures



FIG. 1. The interatomic distances of Cr-Cr (green), Cr-Fe (magenta), Cr-Ni (light blue), Fe-Fe (red), Fe-Ni (orange), and Ni-Ni (blue) atom pairs of SUS304 $Cr_{18.09}Fe_{71.98}Ni_{9.07}X_{0.86}$ estimated from the experimental EXAFS analysis [11], together with macroscopic thermal expansion of the lattice constant [33]. The constant atomic radius model was assumed to yield each interatomic distance separartely (see text for details).

 Θ_D from the temperature dependence of C_2 in SUS304 are also summarized in Table S3 [24], together with those of all the alloys examined in this study. These thermal expansion coefficients and Debye temperatures will be good references for the following discussion.

B. FeNi invar

The interatomic distances of the first–NN Fe-Fe, Fe-Ni, and Ni-Ni shells for 36invar, 42invar, and 45invar are shown in Fig. 2, where the constant atomic radius model men-

tioned above is adopted. The EXAFS analysis results of the average distances, C_2 and C_3 , for the first–NN shells of 36invar, 42invar, and 45invar are also shown, respectively, in Figs. S16–S18 and S19–S21 [24]. In Fig. 2, thermal expansion is confirmed to increase gradually with an increase in the Ni concentration, and positive thermal expansion is clearly seen in the Ni-Ni distance even at 36invar.

There is almost no difference in the temperature dependence of C_2 between Fe and Ni in Figs. S19–S21 [24], resulting in the Debye temperatures Θ_D being almost equal for Fe and Ni (numerical results are given in Table S3 [24]). C_3 does not change significantly for Fe and Ni, either, indicating that asymmetric radial distribution and vibrational anharmonicity are clearly present even around Fe with zero or negative thermal expansion. It should also be noted that although the average fcc structure (all the first-NN distances should be equivalent for an ideal fcc structure), the local structure (e.g., differences in absolute values of interatomic distances) and thermal expansion are slightly but meaningfully different for each element. The thermal expansion results are summarized in Table I. Thermal expansion of the Fe-Fe interatomic distance at 200 K is -2.5×10^{-6} K⁻¹ for 36invar, $+1.0 \times 10^{-6}$ K⁻¹ for 42invar, and $+2.7 \times 10^{-6}$ K⁻¹ for 45invar, quantitatively exemplifying the weakening of the invar effect with this sequence. On the other hand, the thermal expansion of the Fe-Ni interatomic distance at 200 K is $1.9 \times 10^{-6} \text{ K}^{-1}$, $4.6 \times 10^{-6} \text{ K}^{-1}$, and $5.3 \times 10^{-6} \text{ K}^{-1}$ for 36invar, 42invar, and 45invar, respectively, and that of the Ni-Ni interatomic distance at 200 K is 6.3×10^{-6} K⁻¹, 8.3×10^{-6} K⁻¹, and 7.9×10^{-6} K⁻¹, respectively, which are slightly smaller than those of the fcc pure Ni metal (9.5 \times 10^{-6} K⁻¹ for the first-NN shell and 11.3×10^{-6} K⁻¹ for the lattice). These results clearly show positive thermal expansion in the local structure around Ni even in 36invar alloys.

TABLE I. Thermal expansion coefficients for the first–NN interatomic distances at 200 K (10^{-6} K⁻¹), estimated by the EXAFS analysis, together with those by the PIECP simulations. For the lattice thermal expansion, stainless invar, GX1Ni29-Co17, and 42invar were measured by the dilatometer in the present work, and those of elinvar, SUS304, hcp Co, and fcc Ni are given in the literature [33].

Sample	Lattice	Fe-Fe	Fe-Co	Fe-Ni	Fe-Cr	Co-Co	Co-Ni	Co-Cr	Ni-Ni	Ni-Cr	Cr-Cı
Stainless invar sample 1	-1.62	-11.2	-2.4		-0.9	6.4		7.9			9.5
Stainless invar sample 2	0.74	-10.3	-2.4		4.1	5.7		12.1			18.6
Stainless invar average	-0.44	-10.7	-2.4		1.6	6.0		10.0			14.0
Stainless invar PIECP ^a	1.82	4.17	5.74	7.84	6.20	6.12	5.71	3.77		8.04	13.08
Stainless invar PIECP ^b	2.57	4.73	6.38	8.24	6.54	6.70	6.16	5.97		7.98	13.02
Stainless invar PIECP ^c	5.04	9.34	8.58	9.80	7.69	9.05	8.38	7.28		9.99	10.05
GX1Ni29-Co17	3.89	2.2	9.8	11.3		17.5	18.9		20.4		
GX1Ni29-Co17 PIECP ^a	1.13	3.10	6.09	5.88		7.77	5.16		5.71		
GX1Ni29-Co17 PIECP ^c	6.36	10.8	11.0	10.1		13.0	9.63		10.7		
36invar Fe ₆₄ Ni ₃₆	0.6	-2.5		1.9					6.3		
42invar Fe ₅₈ Ni ₄₂	5.62	1.0		4.6					8.3		
45invar Fe ₅₅ Ni ₄₅		2.7		5.3					7.9		
Elinvar	6.7	4.0		6.7	7.4				9.4	10.1	10.9
SUS304	13.0	10.0		11.3	10.8				12.7	12.2	11.6
hcp Co	11.5					13.6					
fcc Ni	11.3								9.5		

^aPIECP results with variable spin states in both Fe and Co.

^bPIECP results with variable spin states in Fe only.

°PIECP results without variation of the spin states.



FIG. 2. The first–NN interatomic distances of Fe-Fe (red), Fe-Ni (blue), and Ni-Ni (green) atom pairs of FeNi invar alloys 36invar, 42invar, and 45invar estimated from the experimental EXAFS analysis assuming the constant atomic radius model, together with the lattice thermal expansion (black). In 45invar, no lattice thermal expansion is available, and the average third–NN distance is plotted, instead.

C. Ni spanC elinvar

The Ni spanC elinvar alloy, Cr_{5,49}Fe_{49.66}Ni_{42.38}Ti_{2.47}, for which the EXAFS measurement and analysis have already been published [11], is known as an alloy with almost no temperature variation of elastic constants as Young's modulus and isothermal compressibility, and exhibits the partial invar effect. The temperature variation of the interatomic distances for the first–NN shells and the lattice constant are shown in Fig. 3, and the thermal expansion coefficients are summarized in Table I. Thermal expansion of Fe at 200 K is positive but



FIG. 3. The first–NN interatomic distances of Cr-Cr (green), Cr-Fe (magenta), Cr-Ni (light blue), Fe-Fe (red), Fe-Ni (orange), and Ni-Ni (blue) atom pairs of Ni span C elinvar alloy Cr_{5.49}Fe_{49.66}Ni_{42.38}Ti_{2.47} estimated from the experimental EXAFS analysis assuming the constant atomic radius model, together with the lattice thermal expansion (black).

small $[\alpha_{\text{Fe-Fe}} = 4.0 \times 10^{-6} \text{ (K}^{-1})]$, implying the presence of the partial invar effect, while thermal expansion of Cr and Ni is comparable to or slightly smaller than thermal expansion of normal metals. As in the FeNi invar case, the invar effect can thus be attributed to Fe only. It can be remarked that Cr or Ni does not show the invar effect. From temperature variations of C_2 , we also obtained the Debye temperatures as given in Table S3 [24]. As in the case of SUS304, the Debye temperature of Cr is lower than those of Fe and Ni.

D. GX1Ni29-Co17

The GX1Ni29-Co17 alloy (Kovar), which exhibits thermal expansion almost equivalent to that of borosilicate hard glass above room temperature and is often used as a window port in high vacuum chambers, also exhibits the partial invar effect. Figure 4 shows temperature dependence of the first– NN interatomic distances in GX1Ni29-Co17, estimated from the EXAFS results with the constant atomic radius model. The thermal expansion around Fe is positive but is much smaller than those of Co and Ni, clearly showing the partial invar effect on Fe. Thermal expansion of Co is slightly smaller than that of Ni, but not by much, so we can expect that Co or Ni does not seem to show the partial invar effect.

For GX1Ni29-Co17, Figs. S22 and S23 [24] show the firstand third–NN average distances, C_2 and C_3 , directly obtained by the EXAFS analysis. The Debye temperatures are given in Table S3 [24], all of which are quite similar to each other. C_3 seems slightly smaller for Fe than for Co and Ni, in contrast to the FeNi invar where the C_3 values for Fe and Ni are similar. C_3 of Fe, however, has a positive value and tends to increase with temperature, indicating the meaningful appearance of the asymmetric radial distribution and anharmonicity despite the partial invar effect, as in FeNi invar and elinvar.

The thermal expansion coefficients at 200 K are also summarized in Table I. As shown in Fig. 4 and Table I, the thermal



FIG. 4. The first–NN interatomic distances of Fe-Fe (red), Fe-Co (magenta), Fe-Ni (light blue), Co-Co (blue), Co-Ni (orange), and Ni-Ni (green) atom pairs of GX1Ni29-Co17 $Fe_{53}Co_{17}Ni_{29}X_1$, estimated from the experimental EXAFS analysis assuming the atomic radius model, together with the lattice thermal expansion (black).

expansion of Fe-Fe is positive but very small $[\alpha_{\text{Fe-Fe}} = 2.2 \times 10^{-6} \text{ (K}^{-1})]$, and the partial invar effect is quantitatively confirmed. On the contrary, thermal expansion of Co and Ni is rather large. It is noted that the thermal expansion coefficients around Co and Ni are larger than those of hcp Co and fcc Ni. We can conclude that there can be observed no partial invar effect for Co as well as Ni in GX1Ni29-Co17.

E. Stainless invar

The first–NN interatomic distances of the stainless invar are shown in Fig. 5, obtained by the EXAFS results with the constant atomic radius model, and the resultant thermal expansion coefficients are again summarized in Table I. In Fig. 5, the quantities are the averaged ones between samples 1 and 2, and Figs. S26 and S27 [24] give the separated results



FIG. 5. The first–NN interatomic distances of Cr-Cr (green), Cr-Fe (light blue), Cr-Co (orange), Fe-Fe (red), and Co-Co (blue) atom pairs of the stainless invar (average of samples 1 and 2) estimated from the experimental EXAFS analysis assuming the constant atomic radius model, together with the lattice thermal expansion (black).



FIG. 6. Temperature dependence of the HS state compositions of Fe and Co in GX1Ni29-Co17 and stainless invar, evaluated by the PIECP simulations.

of samples 1 and 2, respectively. The EXAFS analysis results of the average first– and third–NN distances, C_2 and C_3 , are shown in Figs. S24 and S25 [24]. The results show negative thermal expansion in Fe and positive thermal expansion in Cr and Co. The Debye temperatures are also given in Table S3 [24]. Like elinvar and SUS304, the Debye temperature of Cr is slightly lower than those of Fe and Ni. The present stainless invar alloy exhibits negative thermal expansion around Fe, and in this respect the behavior is quite different from that of GX1Ni29-Co17. The Cr-Cr interatomic distance exhibits large thermal expansion comparable to that of fcc metals, which may be similar to those of Co and Ni in GX1Ni29-Co17 and of Cr and Ni in elinvar.

The small positive thermal expansion of Co-Co might be a similar behavior to that of Ni-Ni in 36invar. Since the invar effect is not expected to occur in Ni of 36invar (at least the electronic state of Ni does not change with temperature), the invar effect of Co would be only auxiliary. The difference in the Co behaviors between GX1Ni29-Co17 and stainless invar is, however, apparently significant, and we will further discuss the Co behaviors by combining the PIECP results.

V. DISCUSSION

To understand the low thermal expansion nature in GX1Ni29-Co17 and stainless invar in more detail, we have performed the PIECP simulations of GX1Ni29-Co17 and stainless invar. Figure 6 gives the temperature dependence of the HS-state composition ratios of Fe and Co. With a temperature rise, the HS state is gradually transformed to the LS state, leading to the (partial) invar effect. It is clearly found that in GX1Ni29-Co17, all the Fe and Co atoms are in the LS state at low temperature less than ~100 K, while in stainless invar, more than 30% Fe atoms are in the LS state at absolute temperature because of the Cr coordination in the first–NN shell that favors antiferromagnetic coupling with Fe and Co. More importantly, it is found that at higher temperature the HS Co composition ratio is smaller in stainless invar than in GX1Ni29-Co17.



FIG. 7. Thermal expansion coefficients α (10⁻⁶ K⁻¹) at 200 K for the first–NN interatomic distances obtained by EXAFS and the lattice constant a_0 versus corresponding distances of (a) FeNi invar and (b) GX1Ni29-Co17 and stainless invar.

Detailed simulation results are given in Figs. S28-S30 [24]. Although the computational results may not quantitatively be in good agreement with the EXAFS experimental results, some qualitative findings that could explain the experimental observations can be seen. Thermal expansion around Co is found to be smaller in stainless invar; at 200 K, $\alpha_{\text{Co-Fe}} = 5.73 \times 10^{-6} \text{ (K}^{-1}) \text{ and } \alpha_{\text{Co-Co}} = 6.12 \times 10^{-6} \text{ (K}^{-1})$ in stainless invar are smaller than $\alpha_{\text{Co-Fe}} = 6.09 \times 10^{-6} (\text{K}^{-1})$ and $\alpha_{Co-Co} = 7.77 \times 10^{-6}$ (K⁻¹) in GX1Ni29-Co17, which agree with the experimental trend qualitatively. The difference in Co thermal expansion obtained in the PIECP simulations can be attributed to the difference in the HS ratios between GX1Ni29-Co17 and stainless invar, as shown in Fig. 6. Gradual suppression of the HS ratio with a temperature rise yields the invar effect more significantly, and the reason for this difference in the HS state suppression is ascribed to the difference in the lattice constant and the corresponding interatomic distances. Since the lattice constant is smaller in stainless invar $[a_0^{\text{PIECP}} = 3.5712 \text{ (Å)} \text{ and } a_0^{\text{expt.}} = 3.5618 \text{ (Å)}]$ than in GX1Ni29-Co17 $[a_0^{\text{PIECP}} = 3.5997 \text{ (Å)}$ and $a_0^{\text{expt.}} = 3.5820$ (Å)] possibly due to the presence of Cr that favors antiferromagnetic coupling in the former, the transformation from the HS to LS states could more easily take place.

Let us once again see the EXAFS findings based on this consequence. Figure 7 gives the thermal expansion coefficients α at 200 K obtained by the present EXAFS and

dilatometric measurements, together with the literature data [33], as a function of the distance. In the (partial) invar alloys, shorter Fe-Fe and possibly Fe-Co and Co-Co distances will lead to smaller thermal expansion because of a significant contribution to the (partial) invar effect at a shorter distance. In FeNi nvar in Fig. 7(a), 36invar may provide the most suitable Fe-Fe distance to exhibit zero or negative thermal expansion. In Fig. 7(b), it is clearly found that the lattice constant is smaller in stainless invar, indicating a more significant invar effect in stainless invar. All the Fe-Fe, Fe-Co, and Co-Co interatomic distances are shorter in stainless invar, being consistent with a smaller thermal expansion and thus a larger invar effect. We can therefore conclude that the stainless invar alloy shows a much more noticeable invar effect than GX1Ni29-Co17 and that in stainless invar the Co contribution to the invar effect is quite significant because of shorter Co-Co and Co-Fe distances than in GX1Ni29-Co17.

It may be better at the end of this paper to briefly mention the difference in the invar effect between Ni in FeNi invar and Co in stainless invar. In FeNi invar, thermal expansion of Ni is somewhat smaller than elemental fcc Ni; $\alpha_{\text{Ni-Ni}} = 6.3 \times 10^{-6}$ (K^{-1}) in Fe₆₄Ni₃₆, 8.3 × 10⁻⁶ (K^{-1}) in Fe₅₈Ni₄₂, 7.9 × 10⁻⁶ (K^{-1}) in Fe₅₅Ni₄₅, and 9.5×10^{-6} (K^{-1}) in elemental fcc Ni. The Ni atoms, however, may not transform the spin electronic state depending on temperature. It is considered that in 36FeNi invar, Ni is a minor element and not only the Ni-Fe but also the Ni-Ni interatomic distances should be affected by the main element Fe. When thermal expansion of Fe is suppressed by the invar effect, thermal expansion of the lattice constant is correspondingly suppressed to minimize the total lattice energy, leading to a smaller thermal expansion also in the Ni-Ni interatomic distance. This may not be regarded as a direct invar effect on Ni, and should be different from the Co role in the present stainless invar alloy. The differences in Ni-Ni thermal expansion among the FeNi invar alloys and Ni metal are much smaller than the difference in Co-Co thermal expansion between GX1Ni29-Co17 and stainless invar.

VI. SUMMARY

We have performed temperature-dependent EXAFS measurements of Co-containing invar alloys of GX1Ni29-Co17 Fe₅₄Co₁₇Ni₂₉ and stainless invar Fe₃₉Co₅₀Cr₉Ni₂ alloys, combined by the PIECP computational simulations, to get a deeper insight into the low thermal expansion mechanism from the viewpoint of the local structure. For more detailed systematic discussion, we also investigated FeNi invar alloys of 36invar, 42invar, and 45invar, and moreover reconsidered previously reported results on SUS304 and elinvar. It is found by EXAFS that in GX1Ni29-Co17, Co exhibits sufficiently large normal thermal expansion, while stainless invar gives much lower thermal expansion, implying that the Co contribution to the invar effect is much more significant in stainless invar. The PIECP simulations provide at least qualitative agreement with this trend, indicating that the Co magnetization is more effectively suppressed with a temperature rise in stainless invar, because of a smaller lattice constant and shorter first-NN interatomic distances around Co in stainless invar. The present study clearly demonstrates the importance of the local structure point of view to understand the detailed mechanism of low thermal expansion alloys, in which microscopic local thermal expansion noticeably differs from macroscopic lattice thermal expansion.

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