Quantum Effect and Anharmonicity in an Invar Alloy Studied by EXAFS Spectroscopy

We have investigated the vibrational anharmonicity and quantum effects in the Invar alloy Fe$_{64.6}$Ni$_{35.4}$ which shows anomalously small thermal expansion. We have performed Fe and Ni *K*-edge EXAFS spectroscopic measurements and computational simulations based on the path-integral effective-classical-potential theory. The first nearest-neighbor (NN) shells around Fe showed almost no thermal expansion, while those around Ni exhibited significant but smaller expansion than that of fcc Ni. At low temperature (<100 K), the vibrational quantum effect was found to play an essential role. This was confirmed by comparing the quantum mechanical simulations to the classical ones: the latter exhibited large (normal) thermal expansion at low temperature. It was also revealed that thermal expansion of the Ni-Ni and Ni-Fe pairs was noticeably suppressed, even though the Ni electronic state may not vary with temperature.

Anomalously small thermal expansion over a wide temperature range in an iron-nickel alloy with a nickel concentration of around 35% was discovered by Guillaume [1] in 1897. The effect is well known as the Invar effect and has been used in various kinds of industrial products. The effect is known to originate from magnetism, and many papers have still been published on the origins of the Invar effect, implying a lack of full understanding of the effect. The basic concept of the Invar effect is that there exist at least 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 equilibrium atomic radius is larger in the former. This results in the compensation of thermal expansion due to increasing density of the LS state at higher temperature. In the present work [3], we conducted an experimental study on the local thermal expansion and anharmonic behavior around Fe and Ni by measuring Fe and Ni *K*-edge EXAFS of the Invar alloy. EXAFS is a very powerful tool for the characterization of local thermodynamic properties and has been extensively applied to various kinds of thermodynamic systems. We also performed Monte-Carlo (MC) simulations of thermal expansion and vibrational anharmonicity obtained by the path-integral effective-classical-potential (PIECP) theory within the simple two-state (HS+LS) model.

The Fe and Ni *K*-edge EXAFS spectra of an Invar foil (8 μm thick) were recorded at Beamline 9C in transmission mode over the temperature range of 12.5–300 K. The EXAFS oscillation functions $k^3x(k)$ were analyzed by the *k*-space curve-fitting method for the Fourier-filtered $k^3x(k)$. Note that the neighboring atoms of surrounding Fe or Ni were not distinguished because there is only a small difference in the backscattering amplitudes between Fe and Ni, and therefore the resultant values obtained experimentally are the average one for each X-ray absorbing atom. The average bond distance R, the mean square relative displacements $C_2 = \langle(r-R)^2\rangle$, and the mean cubic relative displacements $C_3 = \langle(r-R)^3\rangle$ were obtained. C_2 and C_3 correspond to the thermal and static variance of the bond distance and the asymmetry of the pair distribution function, respectively. PIECP MC simulations within the low coupling approximation were performed under constant number of particles, pressure, and temperature (*NPT*) conditions. Details of the computational method are given in the literature [3].

Figure 1 shows the experimental and simulated bond distances around Fe (a) and Ni (b) and the lattice constants (c). Almost no thermal expansion is seen in the local structure around Fe, while it is clearly observed around Ni. The magnitude of thermal expansion around Ni is, however, significantly smaller than that of fcc Ni, indicating the suppression of thermal expansion around Ni as well as Fe. As we expected from the two-state model, the almost complete lack of thermal expansion around Fe can be ascribed to the direct effect of the increasing population of the LS state in Fe with increasing temperature. On the other hand, the behavior around Ni may be attributed to the indirect effect in the two-state model. Although Ni is likely to expand normally with increasing temperature, this is also suppressed by the almost fixed lattice constant. In Fig. 1, the agreement between the PIECP and experiments is good: almost no thermal expansion around Fe and significant thermal expansion around Ni. On the contrary, the classical method is found to give fatal discrepancies at low temperature below ~100 K; the bond and lattice distances significantly increase with increasing temperature. These findings imply the importance of the vibrational quantum effect, which is recognized as a zero-point vibration.

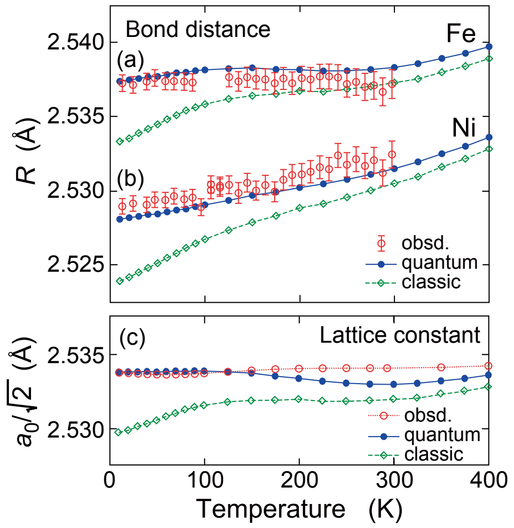

Figure 1
(a, b) Experimentally obtained 1st NN bond distance around Fe (a) and Ni (b) (red open circles with an error bar), together with the simulated results by the PIECP (blue circles and solid line, quantum) and the classical MC (green diamonds and dashed line, classic) methods. (c) Lattice constant scaled for the 1st NN distance ($a_0/\sqrt{2}$) given by the X-ray diffraction data in the literature (red circles and dotted line) and the PIECP and classical MC simulations.

To get further insights into local thermal expansion, the bond distance of each component (Fe-Fe, Ni-Ni and Ni-Fe) pair is shown in Fig. 2. In this plot, the PIECP MC results by using only the HS Fe state are also depicted to determine the hypothetical normal thermal expansion in this system. As expected, the Fe-Fe pair shows the largest discrepancies between the two-state (HS+LS) and the HS-only models. This is caused by the increasing population of the Fe LS state with higher temperature, yielding compensation of the thermal expansion with the one originating from anharmonic vibration. The most important finding in Fig. 2 is that even Ni-Ni and Ni-Fe pairs exhibit significant suppression of thermal expansion compared to the results by the HS-only model. This is consistent with the above experimental finding that thermal expansion around Ni is noticeably suppressed compared to that of fcc Ni. Although Ni does not change its electronic configuration depending on temperature and tends to expand because of anharmonic vibration, the Ni-Ni or Ni-Fe bond expansion is significantly suppressed due to the anomalously small expansion of the lattice. Interestingly, the suppression of thermal expansion seems to be more significant in the Ni-Fe bond than in the Ni-Ni bond. This can be explained by the fact that the Fe atom surrounded by many Ni atoms tends to maintain the HS state. Furthermore, the Ni-Ni bond is noticeably softer than the Ni-Fe bond and is more likely to match the lattice parameter. These effects yield smaller thermal expansion in the Ni-Ni bond than the Ni-Fe one.

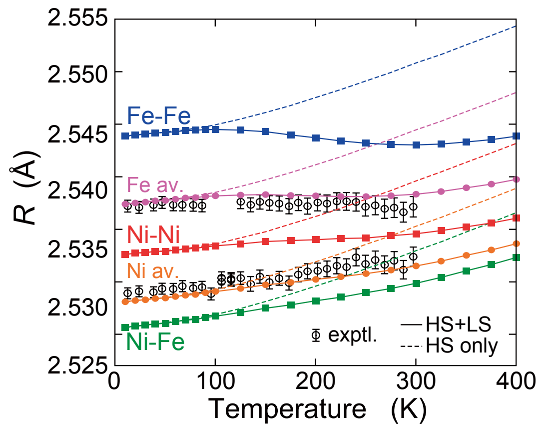

Figure 2
Simulated bond distances of Fe-Fe (blue squares and solid line), Ni-Ni (red squares and solid line), and Ni-Fe (green squares and solid line) pairs, together with the average ones around Fe (pink circles and solid line) and Ni (orange circles and solid line). The experimental data for the average one around Fe and Ni are again shown. The dashed lines are the PIECP results by using only the HS state in Fe.

Clear and significant third-order anharmonicity C_3 in the Invar alloy was confirmed not only by experiments but also by simulations in spite of almost no thermal expansion. The simulated values for the LS and HS states exhibit essentially the same C_3 values, implying no suppression of C_3 due to the contribution of the LS state, as observed in the thermal expansion. Since the asymmetric radial distribution for the 1st NN shell almost exclusively originates from the anharmonic interatomic potential, the present result implies that the third-order anharmonicity clearly exists even in the case of no thermal expansion.

REFERENCES

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