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 Fe₉₀Ni₁₀ 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 Guil- laume [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 magneto-magnetic interaction. The Fe and Ni atoms are known to have large magnetic moments and to be ferromagnets. However, the magnetic moments of adjacent atoms can be aligned to reduce the total magnetic energy. In this case, the atoms are called anisotropic. The magnitude of thermal expansion around Fe is, however, significantly smaller than that of fcc Ni, indicating the suppression of thermal expansion around Fe as well as Ni. 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 \(\approx 100\) 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.

To get further insights into local thermal expansion, the bond distance of each component (Fe-Fe, Ni-Ni and Ni-Fe) 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 show 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.

REFERENCES

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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, classical) methods: (c) Lattice constant scaled for the 1st NN distance \((\AA)^{-1}\) given by the X-ray diffraction data in the literature (red circles and dotted line) and the PIECP and classical MC simulations.

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 one 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.