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Anharmonicity and Quantum Effects in Thermal Expansion of Invar Alloy

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Introduction

Anomalously small thermal expansion over a wide temperature range in an FeNi alloy with a Ni concentration of around 35% was discovered by Guillaume in 1897 [1]. Extensive efforts have been devoted to the understanding of this effect. In this work, we have investigated the local thermal expansion and the anharmonic behavior around Fe and Ni by measuring Fe and Ni K-edge EXAFS spectra of the Invar alloy. We have also carried out the Monte-Carlo (MC) computational simulations of thermal expansion and vibrational anharmonicity obtained by the path-integral effective-classical-potential (PIECP) theory.

Experimental & Simulations

The Fe and Ni K-edge EXAFS spectra of $Fe_{65}Ni_{35}$ foil were recorded at BL 9C with the transmission mode. The measurement temperature range was 12.5-300 K.

The PIECP simulations were performed according to the previous work [2]. For the Fe atomic potential, a two-state model of the high-spin (HS) and low-spin (LS) states was employed. For comparison, the classical MC and the PIECP simulations were also performed in order to verify the quantum effect and the anomalous behaviors in the Invar effect. Computational details will be given elsewhere.

Results and Discussion

Figure 1 shows the experimental and simulated bond distances and the lattice constants. We observed almost no thermal expansion for the first nearest neighbor (NN) shell around Fe and meaningful but small thermal expansion for that around Ni. Note that the first NN bond distance in Figs. 1(a) and 1(b) means the average value of surrounding Fe and Ni atoms since the Fe and Ni atoms are indistinguishable in EXAFS analysis. The agreements between the PIECP simulations and experiments are excellent. On the contrary, the classical MC method is found to give fatal discrepancies at low temperature below ~100 K; the bond and lattice distances significantly increase with the temperature rise. These findings imply the essential importance of the quantum effect, which is recognized as a zero-point vibration.

The bond distance of each component (Fe-Fe, Ni-Ni and Ni-Fe) pair was evaluated in the simulations. For this purpose, the PIECP simulations between the two-state (HS+LS states) and HS-only state were compared. The

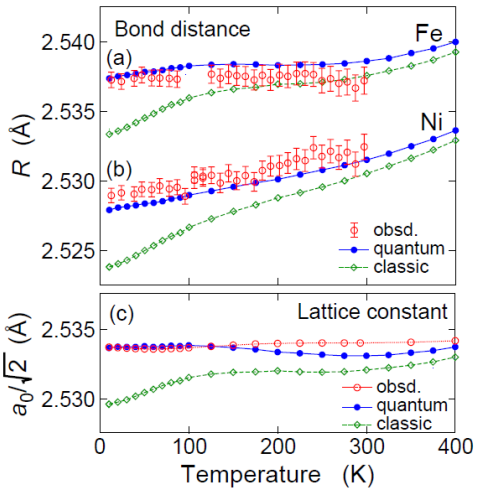

Fig. 1. (a,b) The first NN bond distance around Fe (a) and Ni (b) given by experimental EXAFS (red open circle with an error bar) and by the PIECP (blue circle and solid line, quantum) and the classical MC (green diamond and dashed line, classic) simulations. (c) Equilibrium first NN distance ($a_0/\sqrt{2}$) given by the x-ray diffraction experiment and by the PIECP and classical MC simulations.

Fe-Fe pair shows the largest discrepancies, as expected. The most important finding is that even Ni-Ni and Ni-Fe pairs exhibits significant suppression of thermal expansion compared to the results by the HS-only model. This agrees well with the experimental finding that thermal expansion around Ni is noticeably suppressed compared to that of fcc Ni.

Clear anharmonicity in the Invar alloy is confirmed by the experimental EXAFS analysis and also the PIECP simulations. Since the asymmetric radial distribution for the first NN shell almost exclusively originates from the anharmonic interatomic potential, the present result implies that the anharmonicity clearly exists even in the case of no thermal expansion. Although in a simple two-body model the anharmonicity of the interatomic potential directly corresponds to thermal expansion, the Invar alloy is not the case.

References

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