

Metallic bonds and thermal vibration in brass

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1 Introduction

The CuZn alloy called brass is one of the most familiar alloys. Cu and Zn exhibit significantly different thermodynamical properties in elemental metals such as the boiling point, the melting point, the adhesive energy, the bulk modulus, and the interatomic distance. In the present study, local structural and thermal vibrational properties of the brass alloy were investigated by analysing temperature dependent Cu and Zn K-edge EXAFS (extended x-ray absorption fine structure) spectra and conducting the theoretical PIECP (path integral effective classical potential) simulations. For details of the present study, see the already published reference [1].

2 Experiment

The Cu and Zn K-edge EXAFS spectra of a commercially available brass foil Cu_{64.7}Zn_{35.3} with 10 μm thickness were recorded at BL9C with the transmission mode for the temperature range of 20-300 K.

3 Results and Discussion

Figure 1 shows the mean square relative displacements C_2 for the first-NN (nearest neighbor) shells obtained by the experimental EXAFS analysis and the theoretical PIECP simulation. It is found that the absolute C_2 values are noticeably larger in the EXAFS results than in the PIECP simulation, indicating much larger static disorder in the real alloy sample. More importantly, the EXAFS results show slightly smaller temperature dependence around Zn than around Cu, this yielding the Debye

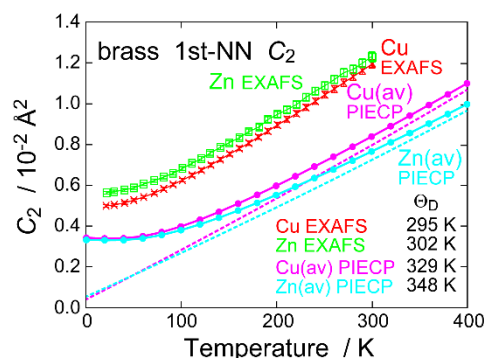


Fig. 1 Mean square relative displacements C_2 for the first-NN pairs obtained by the one-shell EXAFS analysis (with error bars; Cu: red; Zn: green) and the PIECP simulations (average Cu: magenta; average Zn: light blue; solid line: quantum; dashed line: classical), respectively. The corresponding Debye temperatures are also given in the figure.

temperatures of $\Theta_D(\text{Cu}) = 295$ K and $\Theta_D(\text{Zn}) = 302$ K. The PIECP results agree with the EXAFS ones at least qualitatively [$\Theta_D(\text{Cu}) = 329$ K and $\Theta_D(\text{Zn}) = 348$ K]. This finding is rather surprising since it seems to be essentially contradictory to the simple prediction based on the potential stiffness (Cu should be much stiffer than Zn).

Figure 2 shows temperature dependence of the interatomic distance R [Fig. 2(a)], the third- and fourth-order cumulants, C_3 [Fig. 2(b)] and C_4 [Fig. 2(c)], for the first-NN shells. In Fig. 2(b), although the PIECP simulation slightly underestimates the C_3 values, the agreement in C_3 between the EXAFS and PIECP results is

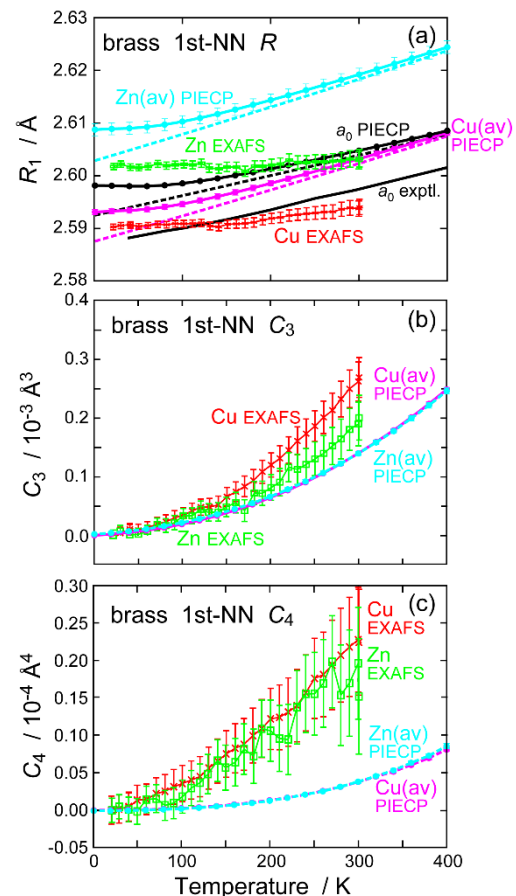


Fig. 2 Temperature dependence of (a) the interatomic distance R , (b) third- and (c) fourth-order cumulants, C_3 and C_4 , for the first-NN pairs obtained by the EXAFS analysis (with error bars; Cu: red; Zn: green) and the PIECP simulations (average Cu: magenta; average Zn: light blue). The lattice constant ($a_0/\sqrt{2}$) are also plotted in (a), where the experimental thermal expansion coefficient was referred to from the literature.

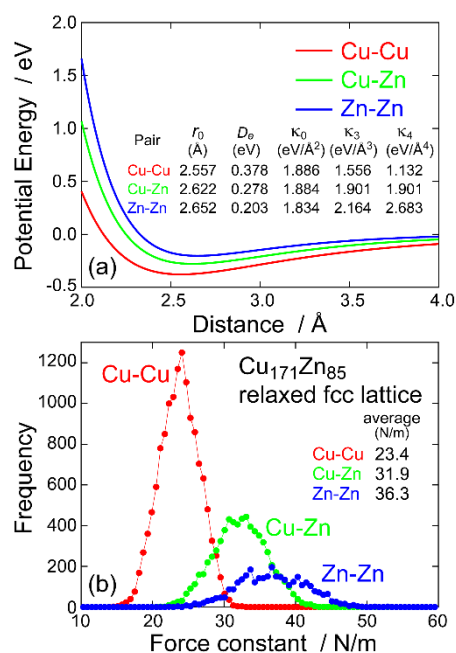


Fig. 3 (a) Two-body interatomic potentials of Cu–Cu, Cu–Zn, and Zn–Zn pairs estimated the EAM (embedded atom method). Numerical potential indicators are given in the figure. (b) Frequency distribution of the first-NN Cu–Cu, Cu–Zn, and Zn–Zn force constants in ten types Cu₁₇₁Zn₈₅ superlattices. The average force constant values for the Cu–Cu, Cu–Zn, and Zn–Zn pairs are given in the figure.

fairly good. The EXAFS $C_3(\text{Zn})$ seems to be a little smaller than $C_3(\text{Cu})$, and temperature dependence of PIECP $C_3(\text{Zn})$ also looks slightly smaller than the PIECP $C_3(\text{Cu})$, implying consistency between the EXAFS and PIECP results at least qualitatively.

Figure 3(a) shows the two-body interatomic potential for each atom pair, employed in the present PIECP simulations. As expected, the Zn–Zn potential is actually the shallowest, while the Cu–Cu potential is the deepest. On the contrary, Fig. 3(b) shows the frequency distribution of the first-NN force constants in the present Cu₁₇₁Zn₈₅

superlattices, and it is clearly found that the Zn–Zn atom pair gives a larger force constant than the Cu–Cu pair. The reason for a larger force constant in Zn–Zn atom pair is probably ascribed to a steeper repulsive potential at a shorter distance side in the Zn–Zn pair. When the system is really diatomic, the Zn–Zn distance is hardly contracted due to the steep repulsive potential and is easily elongated, resulting in large anharmonic vibrational amplitude in the diatomic Zn₂ molecule. On the contrary, in a closed packed solid like *fcc*, the Zn–Zn distance is hardly elongated due to the existence of other atoms at the opposite side, leading to confinement of the Zn atom. This is coincident to the interatomic distance determined by the EXAFS analysis. It is expected that the first-NN interatomic distance around Zn would be significantly larger than that around Cu, while the EXAFS analysis reveals that the first-NN interatomic distances are not very different from each other [only ~0.01 Å difference between Cu and Zn. See Fig. 2(a)]. This indicates that the Zn atoms in brass are likely to be confined in a space that is a little too small for Zn and are hardly movable.

In summary, local thermal vibration in brass was investigated by the temperature dependent Cu and Zn K-edge EXAFS measurements and the theoretical PIECP simulation. It is unexpectedly found that the thermal vibrational amplitude around Zn is meaningfully smaller than that around Cu and that the first-NN interatomic distances are nearly equivalent between Zn and Cu. Although brass is one of the most familiar alloys, the fundamental thermal properties are still not easily predicted. The experimental EXAFS and theoretical PIECP techniques have successfully settle the problem in the present work and will remain useful techniques for future works.

References

- [1] T. Yokoyama, *Phys. Chem. Chem. Phys.* **25**, 3413 (2023); DOI: 10.1039/D2CP05035H.

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