Anharmonic effective pair potentials of group VIII and Ib fcc metals

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The temperature dependence of EXAFS Debye-Waller factors and anharmonic effective pair potentials of group VIII and Ib fcc metals were investigated by a cumulant expansion method. The EXAFS spectra near K- or L_3-edges were measured at the temperatures from 30 to 800 K using synchrotron radiation from the Photon Factory, Tsukuba. The effective pair potentials, $a\cdot u^2/2!+ b\cdot u^3/3!$ denote that the group Ib has obviously larger anharmonisity than the group VIII metals. The discrepancy between the Morse potential approximation and determined effective pair potential is discussed.

KEYWORDS: Debye-Waller factors, anharmonicity, effective pair potential, fcc metal, Morse potential

1. Introduction

The analysis of EXAFS Debye-Waller factor provides an anharmonic effective pair potential (Kamishima et al. 1997) and can give detailed information about the thermal vibration of atoms (Sevillano et al. 1979). The analysis of temperature-dependent EXAFS Debye-Waller factor allows us to evaluate the anharmonicity of effective pair potentials (Yoshiasa et al., 1998 and Yoshiasa & Maeda, 1999).

Yokoyama et al. (1989) investigated the interatomic potentials for fcc metals (Cu, Pd, Ag and Au) by an EXAFS cumulant method and the reliability of the Morse potential as a candidate to describe an interatomic potential for fcc metals. They indicated that the Morse potential is not suitable for fcc metals because the dissociation energies obtained from it were not in good agreement with the data in the literature.

Au is used as a pressure calibrant for in-situ anvil cell experiments. In order to determine the precise equation of state of Au under high pressure and high temperature, it is important to understand the thermal expansion behavior. For this purpose, it is necessary to investigate anharmonicity in thermal vibrations and determine the anharmonic effective pair potential.

In this study, we investigate the anharmonic interatomic potentials of Ni, Pd, Pt (group VIII metals) and Cu, Ag, Au (group Ib metals) by the cumulant expansion method to compare each other in fcc metal group. We also found systematically the difference in anharmonicity between the group VIII metals and group Ib metals and the usefulness of the Morse potential for fcc metals was discussed.

2. Experimental and analysis

Experiments were carried out at the XAFS station of BL10B of Photon Factory in the National Laboratory for High energy Physics (KEK-PF), Tsukuba, Japan. The samples were Ni (99.5%), Cu (99.9%), Pt (99.95%) and Au (99.95%) foils. The thickness for Ni, Cu, Pt and Au was 4, 5, 4 and 5 μm, respectively. X-ray absorption spectra near K or L_3-edges of each metal were measured at temperatures from 30 to 800 K. The Incident X-ray beams was monochromatized by a Si (311) channel-cut monochromator. The intensities of the incident and transmitted x-rays were measured by ionization chambers. We used a water-cooled electric furnace with Kapton windows to heat samples and a cryostat with Kapton windows to cool samples.

The EXAFS interference function, $\chi(k)$, was extracted from the measured absorption spectra following standard procedure (Maeda, 1987), where k denotes the wave number of photoelectrons : $k=[2m(E-E_0)/\hbar^2]^{1/2}$. The $\chi(k)$ was normalized using MacMaster coefficients according to the EXAFS work shop report (Lytle et al. 1989). In quantitative analyses we carried out the Fourier-filtering technique and a nonlinear-least squares fitting method by comparing the observed $\chi_{\exp}(k)$ and calculated $\chi_{calc}(k)$. We used EXAFS formula in the single scattering theory with the cumulant expansion up to the fourth order term (Ishii, 1992):

$$\chi(k)=\sum_B (N_B/kR^2{}_{AB})\left|f_B(k;\pi)\right|\exp(-2R_{AB}/(k/\eta)\exp(-2\sigma 2k^2+(2/3)\sigma 4k^4))$$
$$\times\sin(2kR_{AB}-(2k/R_{AB})(1+2R_{AB}/(k/\eta))\sigma 2-(4/3)\sigma 3k^3+\psi_{AB}(k)),$$

where N_B is the coordination number of scattering atoms B at distance R_{AB} from the absorbing atom A, $|f_B(k;\pi)|$ the backscattering amplitude of photoelectrons and $\psi_{AB}(k)$ the phase shift function. Values of the function $|f_B(k;\pi)|$ and $\psi_{AB}(k)$ were calculated using the FEFF3 program (Rehr et al. 1991). σ n denotes the nth cumulant. The mean free path λ of the photoelectron is assumed to depend on the wave number, $\lambda=k/\eta$, where η is a constant. Details of the analysis were given in reference (Yoshiasa et al. 1997)

Single-shell fitting was carried out for the first nearest bond distances of each fcc metal, where the number of neighbouring atoms was fixed at the crystallographic value as $N_B=12$. We assumed that η and ΔE_0 have negligible temperature dependence. Here ΔE_0 is the difference between the theoretical and experimental threshold energies. The values of η and ΔE_0 are determined so as to give the best fit to the spectrum at the lowest temperatures. Because the fourth-order term was negligible, the refinement was performed to the structure parameters R_{AB}, $\sigma 2$ and $\sigma 3$ in each shell by use of the fixed η and ΔE_0 values. The reliability of fit parameters,

$$R=\sum_s\left|k_s{}^3\chi(k_s)_{\exp}-k_s{}^3\chi(k_s)_{calc}\right|/\left|k_s{}^3\chi(k_s)_{\exp}\right|,$$

between the experimental and calculated EXAFS functions were around 0.003.

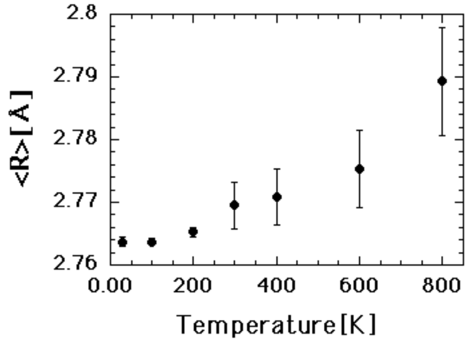

Figure 1. Temperature dependence of the first nearest-neighbour distances in Pt

3. Results and discussion

Figure 1 shows the temperature dependence of the first nearest-neighbour distances of Pt, for an example. The thermal expansion tendency in Fig. 1 is in good agreement with that derived from the recommended thermal expansion coefficient (Touloukian et al. 1975). Figures 2 and 3 show the temperature dependence of $\sigma 2$ and $\sigma 3$, respectively. The values for Ag and Pd are obtained from Yokoyama et al. (1989). The values of $\sigma 2$ and $\sigma 3$ for the group Ib metals are larger than those for the group VIII metals (Cu > Ni, Ag>Pd, Au>Pt, respectively). Cu in the group Ib metals and Pt in the group VIII metals has the smallest value, respectively. (Ag>Au>Cu for group Ib and Ni>Pd>Pt for group VIII). By the values of $\sigma 2$ and $\sigma 3$, one may distinguish group VIII from group Ib.

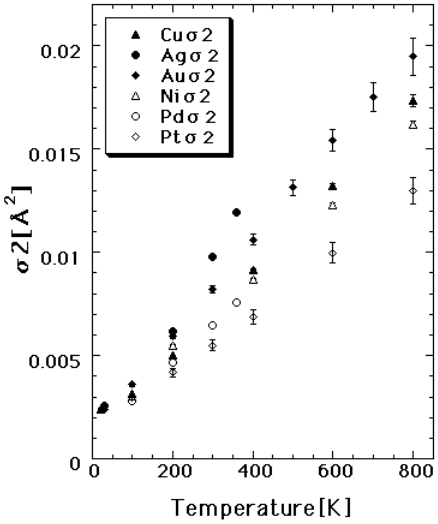

Figure 2. Temperature dependence of $\sigma 2$ in the group VIII and Ib metals

The Debye-Waller type factor $\sigma 2$ includes the effects of static and dynamic disorders. The static disorder is the configuration disorder, while the dynamic disorder arises from the thermal vibration of atoms. In addition, there is a correlation in calculation between $\sigma 2$ and the mean free path λ of the photoelectron. The contribution of the thermal vibration, $\sigma_{\text{thermal,}}$ can be estimated under the assumption of classical statistical dynamics by the temperature dependence of $\sigma 2$ (Yoshiasa et al., 1999a, 1999b). A steep slope in the figure represents a weak bonding. The gradient for the experimental $\sigma 2$ is equal to k_B/a, if we evaluate the anharmonic potential $V(u)=a\cdot u^2/2!+b\cdot u^3/3!$, where k_B is the Boltzman constant, a and b are the potential coefficients and u is the deviation of the bond distance from the location of the potential minimum. b is calculated from the values of $\sigma 2$ and $\sigma 3$ (Ishii, 1994). The potential parameters calculated in this study are summarized in Table 1. The order of the parameter a is Ni<Pd<Pt for group VIII and Cu<Au<Ag for group Ib. This order is essentially the same as that of melting point. The absolute values of potential parameter b for group VIII metals and group Ib metals are about –6.0 and –8.0 eV/Å^3, respectively. The values of b indicate that the group Ib has obviously larger anharmonicity than the group VIII metals. The calculated potentials are shown in Fig. 4.

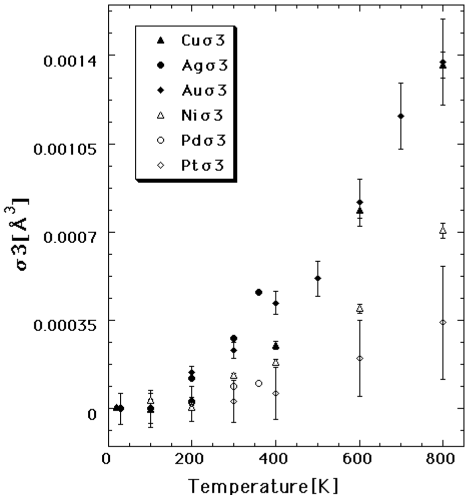

Figure 3. Temperature dependence of $\sigma 3$ in the group VIII Ib metals

We tried to compare obtained effective pair potentials with popular anharmonic potential models. The simple Morse potential (Morse, 1929) is described with several theoretical assumption by $V(u)=D[\exp\{-2\alpha u\}-2\exp\{-\alpha u\}]$, where D is dissociation energy and $1/\alpha$ corresponds to the width of the potential. The values of D are from American Institute of Physics Handbook (Gray et al. 1972), α is determined by means of a least square fitting (see Table 2). Some doubts arose about reliability of these D values, because D values from different literatures were not consistent with one another. Then we also try to adopt the D values fixed at 2.0 eV for all samples. The values of $\alpha_{2.0}$ from fixed $D_{2.0}$ show the same tendency with α. The calculated $\alpha_{2.0}$ values show the same tendency with potential parameter a. The fitted potentials with $D_{2.0}$ and with D did not have significant discrepancies (Fig. 4).

The Morse potential shows good approximation on the left side from the potential minimum (the repulsive side) but not on the right side (the antibonding side). Morse potential model would over estimate the anharmonicity. The Morse potentials for the group VIII metals have large discrepancy, because the group VIII metals have more harmonic potentials than the group Ib metals. The simple Morse potential model is applicable to these fcc metals as a first approximation, which it would be remarked that it shows larger anharmonicity in thermal vibration than it really is.

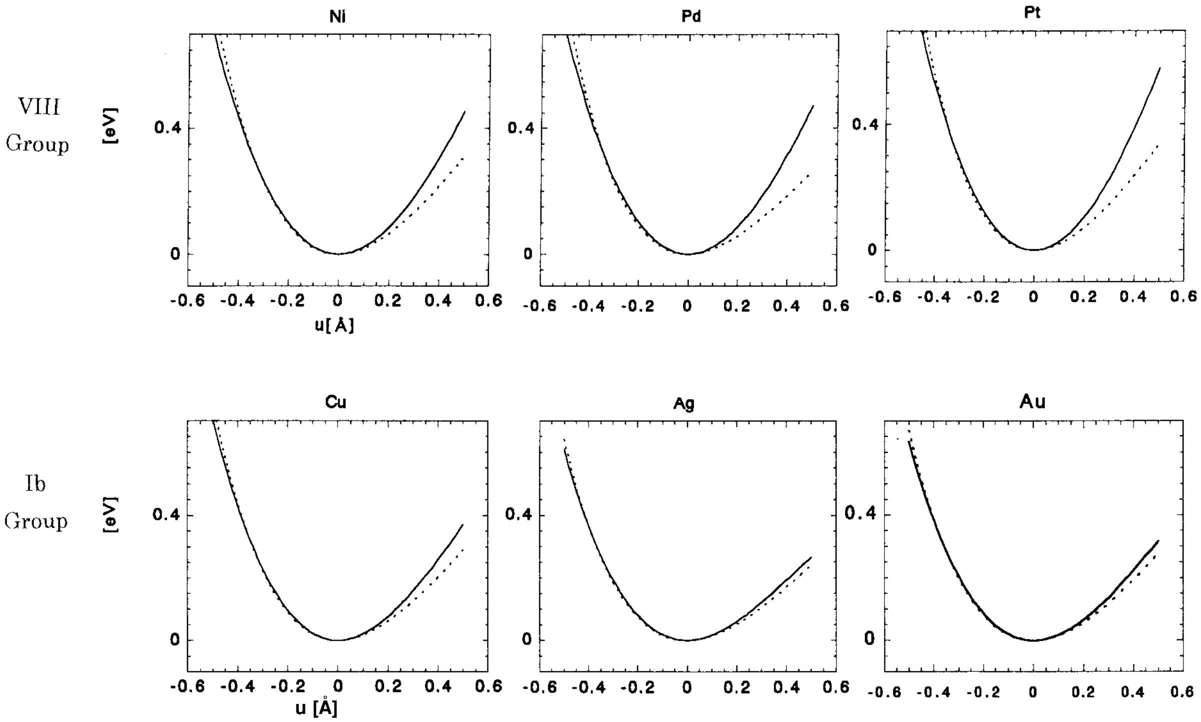

Figure 4. The anharmonic effective pair potentials (solid line) and the calculated Morse potentials (dashed line) for the group VIII and Ib metals

Table 1. Potential parameters and melting point for the group VIII and Ib metals

Group Ib	*a* (eV/Å^2)	*b* (eV/Å^3)	Melting Point [K]	Group VIII	*a* (eV/Å^2)	*b* (eV/Å^3)	Melting Point [K]
Ni	4.6	-5.9	1692	Cu	4.3	-8.1	1320
Pd	4.7	-5.6	1792	Ag	3.5	-8.3	1197.5
Pt	5.7	-6.4	2011	Au	3.8	-7.6	1300

Table 2. Detailed parameters of Morse potenrial of the fcc metals.

Group VIII	D* (eV)	α (Å^{-1})	$D_{2.0}$ (eV)	$\alpha_{2.0}$ (Å^{-1})	Group Ib	D* (eV)	α (Å^{-1})	$D_{2.0}$ (eV)	$\alpha_{2.0}$ (Å^{-1})
Ni	2.3	0.915	2	0.97	Cu	1.97	0.966	2	0.96
Pd	1.43	1.11	2	0.97	Ag	1.63	0.972	2	0.89
Pt	-	-	2	1.05	Au	2.2	0.877	2	0.91

*From American Institute of Physics Handbook (1972).

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