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Anharmonic Effective Pair Potentials of KBr and CsBr Determined by EXAFS

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Abstract. The anharmonic effective pair potentials $V(u) = \alpha u^2/2 + \beta u^3/3! + \gamma u^4/4!$ in KBr and CsBr have been investigated at room temperature by the EXAFS technique. In the parameter fitting, we have directly carried out the numerical integration of EXAFS function and evaluated the anharmonic effective pair potential. The Grüneisen parameters γ_G were calculated from the obtained values of α and β as 1.65 for KBr and 1.37 for CsBr, respectively. Contribution of the van der Waals term to the total energy has been determined by comparing with the calculated curve obtained by the empirical estimation, and rises from 1.8 % for KBr to 3.0 % for CsBr.

1. INTRODUCTION

The NaCl-type KBr and CsCl-type CsBr are stable under ambient conditions. Each ion in KBr and CsBr has six and eight equidistant nearest neighbours, respectively. KBr transforms to CsCl-type structure under pressure of 1.74 GPa at room temperature. Alkaline halides are a favorable compounds to estimate the interatomic pair potential curve on reasonable assumptions. Typical sets of data such as the Grüneisen parameter γ_G can be obtained and systematic tendency can be noticed.

The usefulness of EXAFS as a probe of vibration dynamics were discussed by many authors [1]. EXAFS results have been utilized as a reliability test for the interatomic potentials in MD simulations. The analysis of temperature-dependent EXAFS spectra with the cumulant expansion method can yield detailed information on the effects of anharmonicity and provide the effective pair potential [2].

In this study, we directly estimate the EXAFS function by numerical integration in order to determine the precise anharmonic effective pair potential for Br-K and Br-Cs bonds without mediating the cumulant terms.

2. EXPERIMENTAL AND ANALYSIS

KBr and CsBr crystals of purity 99.99 % were ground using an agate mortar. The appropriate amounts of fine powder samples were pressed with powder of boron nitride into pellets of 10.0 mm in diameter. The Br K-edge EXAFS were measured in transmission mode at 23 K and room temperature with synchrotron radiation from the Photon Factory in the National Laboratory for High Energy Physics, Tsukuba.

The EXAFS interference function, $\chi(k)$, was extracted from the measured absorption spectra using the standard procedure [3], 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 workshop report [4]. The largest peak in the radial structure functions $\phi_{AB}(R)$, obtained by the Fourier transform of $k^2\chi(k)$ for the corresponding edges, was considered nearly to be the nearest-neighbour distance.

We consider the vibration of cation and anion, interacting via an anharmonic pair potential $V(u)$: $V(u) = \alpha u^2/2 + \beta u^3/3! + \gamma u^4/4! \dots$ (1), where u is the deviation of the bond length from the location R_0 of the potential minimum. In order to determine the anharmonic effective pair potentials, we used an average of EXAFS formula, based on the single-scattering theory and expressed by a distribution function $\rho(u)$ [5,6]:

$$\chi(k) = \text{Im} \left[\sum_n \frac{-1}{k} f_n(k; \pi) \exp(i2\delta_n) \int_{-\infty}^{\infty} \frac{\rho(u)}{(R_0 + u)^2} \exp\left(-\frac{2(R_0 + u)}{\lambda(k)}\right) \exp(i2k(R_0 + u)) du \right] \quad \dots(2).$$

The Debye temperature Θ_D for KBr and CsBr have been reported to be 152 and 119 K, respectively [7]. Then we assumed the classical Boltzmann distribution at room temperature: $\rho(u) = \exp(-V(u)/k_B T) / \int_{-\infty}^{\infty} \exp(-V(u)/k_B T) du \dots$ (3), where k_B is the Boltzmann constant. The EXAFS functions $\chi(k)$ is rewritten from above Eqs. (1), (2) and (3), and we carried out a non-linear least-squares parameter fitting by comparing the observed and calculated $\chi(k)$:

$$\chi(k) = \frac{N_s}{k} |f_n(k; \pi)| \frac{\int_{-\infty}^{\infty} \frac{1}{(R_0 + u)^2} \exp\left(-\frac{1}{k_B T} \left(\frac{\alpha}{2} u^2 + \frac{\beta}{3!} u^3 + \frac{\gamma}{4!} u^4\right)\right) \exp\left(-\frac{2(R_0 + u)}{\eta/k}\right) \sin(2k(R_0 + u) + \delta_{\text{total}}) du}{\int_{-\infty}^{\infty} \exp\left(-\frac{1}{k_B T} \left(\frac{\alpha}{2} u^2 + \frac{\beta}{3!} u^3 + \frac{\gamma}{4!} u^4\right)\right) du} \quad \dots(4)$$

where the back-scattering amplitude of photoelectrons, $|f_n(k; \pi)|$, and the phase shift function, $\delta_{\text{total}}(k)$, were taken from the

theoretical table [8]. The number of neighboring atoms was fixed at the crystallographic value as $N_b=6$ and 8. The mean free path λ of the photoelectron is assumed to depend on the wave number k : $\lambda(k)=k/\eta$ where η is constant. The parameters are R_0 , α , β , γ , η and ΔE_0 . Here ΔE_0 is the difference between the theoretical and experimental threshold energies. On the parameter fitting, according to the EXAFS workshop report [4], the calculated EXAFS function was also filtered by the same way as done for the observed function in order to eliminate the truncation effects through the Fourier transform of the data. The equal deformation of observed and calculated EXAFS functions improves the accuracy of the parameter fitting. Local structural parameters are given in Table 1, where the mean interatomic distance $\langle R \rangle$ is defined by $\langle R \rangle = R_0 + \langle u \rangle$: $\langle u \rangle = \int u \exp(-V(u)/k_B T) du / \int \exp(-V(u)/k_B T) du$. For comparison, we also carried out the parameter fitting with an analytical EXAFS formula expressed by a cumulant expansion up to fourth-order terms [9] (Table 2.). Details of the analyses with cumulant expansion method were given in reference [10].

Table 1. Local structural parameters for the anharmonic potential model.

	KBr	CsBr
R_0 (Å)	3.26(1)	3.69(1)
$\langle R \rangle$ (Å)	3.29(1)	3.73(1)
α ($\times 10^{-12}$ erg/Å ²)	1.45(2)	1.35(2)
β ($\times 10^{-12}$ erg/Å ³)	-4.4(3)	-3.0(6)
γ ($\times 10^{-12}$ erg/Å ⁴)	3.3(8)	0.0(8)
η (Å ⁻²)	0.68(8)	0.84(8)
ΔE_0 (eV)	-0.5(1.2)	-2.4(1.5)
R-factor (%)	5.7	4.1
Grüneisen parameter γ_G	1.65	1.37

Table 2. The structure parameters of KBr and CsBr obtained from cumulant expansion model. The quantities $\sigma(n)$ are the n th cumulant.

	KBr	CsBr
R_{23K} (Å)	3.277(5)	3.688(6)
R_{RT} (Å)	3.31(3)	3.73(4)
$\sigma(2)$ ($\times 10^{-2}$ Å ²)	3.2(4)	3.0(7)
$\sigma(3)$ ($\times 10^{-3}$ Å ³)	1.5(7)	1.9(9)
$\sigma(4)$ ($\times 10^{-4}$ Å ⁴)	4.1(2.6)	2.3(7)
η (Å ⁻²)	0.40(5)	0.79(5)
ΔE_0 (eV)	0.7(6)	0.8(6)
R-factor (%)	7.3	4.2

Fig. 1. Effective pair potentials (solid line) and calculated curves by empirical estimation with (dashed and dotted line) and without (dotted line) the van der Waals term.

3. RESULTS AND DISCUSSION

The values of $\langle R \rangle$ and R_{RT} for both compounds agree well with the 3.301(1) Å of Br-K and 3.720(1) Å of Br-Cs distances determined by our X-ray diffractometer. Thermal linear expansions, $(R_0 - \langle R \rangle)/\langle R \rangle$ or $(R_{23} - R_{RT})/R_{RT}$, agree with the data in literature; the thermal linear expansions [11], $\Delta L/L_0$, between 25 and 293 K are -0.820 % for KBr and -1.065 % for CsBr. The Grüneisen parameters γ_G were also calculated from the obtained values of α and β : $\gamma_G = -R_0\beta/6\alpha$ (Table 1). The derived Grüneisen parameters are compared with the values in the literature [12] though the value of 1.37 for CsBr is smaller than 2.0 by other method. The derived values of α , β and γ for KBr from the cumulant expansion model are 1.3×10^{-12} erg/Å², -2.0×10^{-12} erg/Å³ and 5×10^{-12} erg/Å⁴ and those for CsBr 1.3×10^{-12} erg/Å², -3.1×10^{-12} erg/Å³ and 6×10^{-12} erg/Å⁴, respectively.

The determined effective pair potentials for both compounds are compared with the calculated curve obtained by the empirical estimation [13] with the van der Waals term (Fig. 1). Excellent agreement is achieved when the contribution of the van der Waals term to the total energy is 1.8 % for KBr and 3.0 % for CsBr. In alkaline halides the van der Waals energy is normally a few percent of the total energy and rises from 1.5 % for NaCl to 5 % for CsI. We conclude that the reliable anharmonic pair potentials can be determined by the numerical integration of EXAFS function. We can use determined effective pair potentials to estimate the van der Waals energy in the complicated materials.

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