Anharmonic effective potential, thermodynamic parameters, and EXAFS of hcp crystals

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Abstract. Anharmonic effective potential, effective local force constant, thermal expansion coefficient, three leading cumulants, and EXAFS (Extended X-ray Absorption Fine Structure) of hcp crystals have been studied. Analytical expressions for these quantities have been derived. Numerical calculations have been carried out for Zn and Cd. They show a good agreement with experiment results measured at HASYLAB (DESY, Germany) and unnegligible anharmonic effects in the considered quantities.

1. Introduction

EXAFS and its parameters are often measured at low temperatures and well analysed by the harmonic procedure [1] because the anharmonic contributions to atomic thermal vibrations can be neglected. But EXAFS may provide apparently different information on structure and on other parameters of the substances at different high temperatures [2-11,14,15] due to anharmonicity.

This work is devoted to development of a new method for calculation and analysis of the high order anharmonic effective potential, local force constant, three leading cumulants, thermal expansion coefficient, and EXAFS of hcp crystals. Derivation of analytical expressions for these quantities is based on quantum statistical theory with the anharmonic correlated Einstein model [9] and Morse potential is used to characterize interaction between each pair of atoms. Numerical results for Zn and Cd are found to be in good agreement with experiment [16] and show unnegligible anharmonic effects in the considered quantities.

2. Formalism

According to cumulant expansion approach the EXAFS oscillation function is given by [11]

$$\chi(k) = F(k)\frac{e^{-2R/\lambda(k)}}{kR^2} \, \text{Im}\left\{e^{i\Phi(k)} \exp\left[2ikR + \sum_n \frac{(2ik)^n}{n!}\sigma^{(n)}\right]\right\}, \tag{1}$$

where $F(k)$ is the real atomic backscattering amplitude, Φ is the net phase shift, k and λ are the wave number and the mean free path of the photoelectron, respectively, $R = \langle r \rangle$ with r as the

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instantaneous bond length between absorbing and backscattering atoms and $\sigma^{(n)}$ (n = 1, 2, 3, ...) are the cumulants [2].

The total mean square relative displacement (MSRD) or 2nd cumulant $\sigma^2(T)$ at a given temperature T is given as the sum of harmonic $\sigma^2(T)$ and anharmonic $\sigma_A^2(T)$ contributions [11]

$$\sigma_{tot}^2(T) = \sigma^2(T) + \sigma_A^2(T), \quad \sigma_A^2 = \beta(T)\left[\sigma^2(T) - \sigma_0^2\right], \quad \beta(T) = 2\gamma_G \frac{\Delta V}{V}, \tag{2}$$

where γ_G is Grüneisen parameter, $\Delta V/V$ is the relative volume change due to thermal expansion, σ_o^2 is zero-point contribution to $\sigma^2(T)$.

The anharmonic effective potential can be expressed as a function of the displacement $x = r - r_0$ along the $\hat{R}^0$ direction, r and r_0 being the instantaneous and equilibrium bondlengths between absorbing and backscattering atoms, respectively

$$V_{eff}(x) \approx \frac{1}{2} k_0 x^2 + k_3 x^3 \tag{3}$$

where k_0 is effective local force constant, and k_3 is cubic parameter giving the asymmetry due to anharmonicity. (Here and in the following, the constant contributions are neglected).

For calculation of thermodynamic parameters we use the further definition $y = x - a$, $a = \langle r - r_0 \rangle$ [9, 18], to write Eq. (3) as

$$V_{eff}(y) \cong (k_0 + 3k_3 a)ay + \frac{1}{2}k_{eff}y^2 + k_3 y^3, \tag{4}$$

where k_{eff} is an effective local force constant, in principle different from k_0.

Making use of quantum statistical methods [13], the physical quantity is determined by an averaging procedure using canonical partition function Z and statistical density matrix ρ

$$\langle y^m \rangle = \frac{1}{Z} Tr(\rho\, y^m), \quad m = 1, 2, 3, \ldots \tag{5}$$

Atomic vibrations are quantized in terms of phonon, and anharmonicity is the result of phonon-phonon interaction, that is why we express y in terms of annihilation and creation operators, $\hat{a}$ and $\hat{a}^+$, respectively

$$y \equiv a_0(\hat{a} + \hat{a}^+), \quad a_0^2 = \frac{\hbar\omega_E}{2k_{eff}}, \tag{6}$$

and use the harmonic oscillator state $|n\rangle$ as the eigenstate with the eigenvalue $E_n = n\hbar\omega_E$, ignoring the zero-point energy for convenience, here ω_E is correlated Einstein frequency.

A Morse potential is assumed to describe the interatomic interaction, and expanded to the third order around its minimum

$$V(x) = D(e^{-2\alpha x} - 2e^{-\alpha x}) \cong D(-1 + \alpha^2 x^2 - \alpha^3 x^3 + \cdots), \tag{7}$$

where α describes the width of the potential and D is the dissociation energy.

In the case of relative vibrations of absorber and backscatterer atoms, including the effect of correlation and taking into account only the nearest neighbor interactions, the effective pair potential is given by

$$V_{eff}(x) = V(x) + \sum_{i=a,b}\sum_{j\neq a,b} V\left(\frac{1}{2}x\hat{\mathbf{R}}^0.\hat{\mathbf{R}}_{ij}\right) = V(x) + 2V\left(-\frac{x}{2}\right) + 8V\left(-\frac{x}{4}\right) + 8V\left(\frac{x}{4}\right), \qquad (8)$$

where the first term on the right concerns only absorber and backscatterer atoms, the remaining sums extend over the remaining neighbors, and the second equality is for monoatomic hcp crystals.

In accordance with Eq. (4), using Morse potential Eq. (7), and $k_0 = 5D\alpha^2$ the effective potential Eq. (8) is expressed as

$$V_{eff}(y) \cong 5D\alpha^2\left(1 - \frac{9}{20}\alpha a\right)ay + \frac{5}{2}D\alpha^2\left(1 - \frac{9}{10}\alpha a\right)y^2 - \frac{3}{4}D\alpha^3 y^3, \qquad (9)$$

where the local force constant is given by

$$k_{eff} = 5D\alpha^2\left(1 - \frac{9}{10}\alpha a\right) = \mu\omega_E^2, \quad \theta_E = \frac{\hbar\omega_E}{k_B}, \qquad (10)$$

where θ_E, μ are the correlated Einstein temperature and reduced mass, respectively.

For further calculation we write the effective interatomic potential as the sum of the harmonic contribution and a perturbation δV due to the weak anharmonicity

$$V_{eff}(y) = \frac{1}{2}k_{eff}y^2 + \delta V(y), \quad \delta V \cong D\alpha^2\left(5a - \frac{3}{4}\alpha y^2\right)y. \qquad (11)$$

Using the above results for correlated atomic vibrations and the procedure depicted by Eqs. (5, 6), as well as, the first-order thermodynamic perturbation theory with considering the anharmonic component in the potential Eq. (9), we derived the cumulants.

The 2nd cumulant or mean square relative displacement (MSRD) is expressed as

$$\sigma^2(T) = \sigma_0^2\frac{1+z}{1-z}, \quad \sigma_0^2 = \frac{\hbar\omega_E}{10D\alpha^2}, \quad z = e^{-\theta_E/T}. \qquad (12)$$

First and third cumulants are

$$\sigma^{(1)}(T) = \sigma_0^{(1)}\frac{1+z}{1-z} = \frac{9\alpha}{20}\sigma^2, \quad \sigma_0^{(1)} = \frac{9\alpha}{20}\sigma_0^2, \qquad (13)$$

$$\sigma^{(3)}(T) = \sigma_0^{(3)}\frac{1+10z+z^2}{(1-z)^2} = \frac{3\alpha}{10}\left[3\left(\sigma^2\right)^2 - 2\left(\sigma_0^2\right)^2\right], \quad \sigma_0^{(3)} = \frac{3\alpha}{10}\left(\sigma_0^2\right)^2, \qquad (14)$$

and Eq. (13) the thermal expansion coefficient is resulted as

$$\alpha_T = \alpha_T^0\frac{z|\ln(z)|^2}{(1-z)^2} = \frac{9D\alpha^3}{4Rk_BT^2}\left[\left(\sigma^2\right)^2 - \left(\sigma_0^2\right)^2\right], \quad \alpha_T^0 = \frac{9k_B}{100D\alpha R}, \qquad (15)$$

where R is the bond length, $\sigma_0^{(1)}$, $\sigma_0^2, \sigma_0^{(3)}$ are zero-point contributions to $\sigma^{(1)}, \sigma^2, \sigma^{(3)}$ and α_T^0 is the constant value of α_T at high-temperature.

To calculate the total MSRD including anharmonic contribution Eq. (2) an anharmonic factor has been derived

$$\beta(T) = \frac{9\alpha^2}{8}\sigma^2\left[1 + \frac{3\alpha}{4R}\sigma^2\left(1 + \frac{3\alpha}{4R}\sigma^2\right)\right]. \qquad (16)$$

The anharmonic contribution to the EXAFS phase at a given temperature is the difference between the total phase and the one of the harmonic EXAFS, and it is given by

$$\Phi_4(T,k) = 2k\left[\sigma^{(1)}(T) - 2\sigma_A^2(T)\left(\frac{1}{R} + \frac{1}{\lambda(k)}\right) - \frac{2}{3}\sigma^{(3)}(T)k^2\right].$$ (17)

We obtained from Eq. (1), taking into account the above results, the temperature dependent K-edge EXAFS function including anharmonic effects as

$$\chi(k,T) = \sum_j \frac{S_0^2 N_j}{kR_j^2} F_j(k)e^{-\left(2k^2\left[\sigma_H^2(T) + \sigma_A^2(T)\right] + 2R_j/\lambda(k)\right)} \sin\left(2kR_j + \Phi_j(k) + \Phi_4'(k,T)\right),$$ (18)

where S_0^2 is the square of the many body overlap term, N_j is the atomic number of each shell, the remaining parameters were defined above, the mean free path λ is defined by the imaginary part of the complex photoelectron momentum $p = k + i/\lambda$, and the sum is over all atomic shells.

3. Numerical results and comparison to experiment

Now we apply the above derived expressions to numerical calculations compared to experiment for Zn and Cd measured at HASYLAB (DESY, Germany) [16]. Morse potential parameters of Zn and Cd have been calculated by generalizing the procedure for cubic crystals [12] to the one for hcp crystals. They are compared to the EXAFS experimental data [16]. Effective local force constants, correlated Einstein frequencies and temperatures have been calculated using these Morse parameters. The results are written in Table 1. They are used for calculation of anharmonic EXAFS and its parameters. The calculated anharmonic effective potentials for Zn and Cd are compared to experiment and to their harmonic components (Figure 1a). The calculated anharmonic factors for Zn and Cd are shown in Figure 1b). They agree with the extracted experimental results [16].

Table 1. Calculated and experimental values of D, α, r_0, and k_{eff}, ω_E, θ_E for Zn, Cd

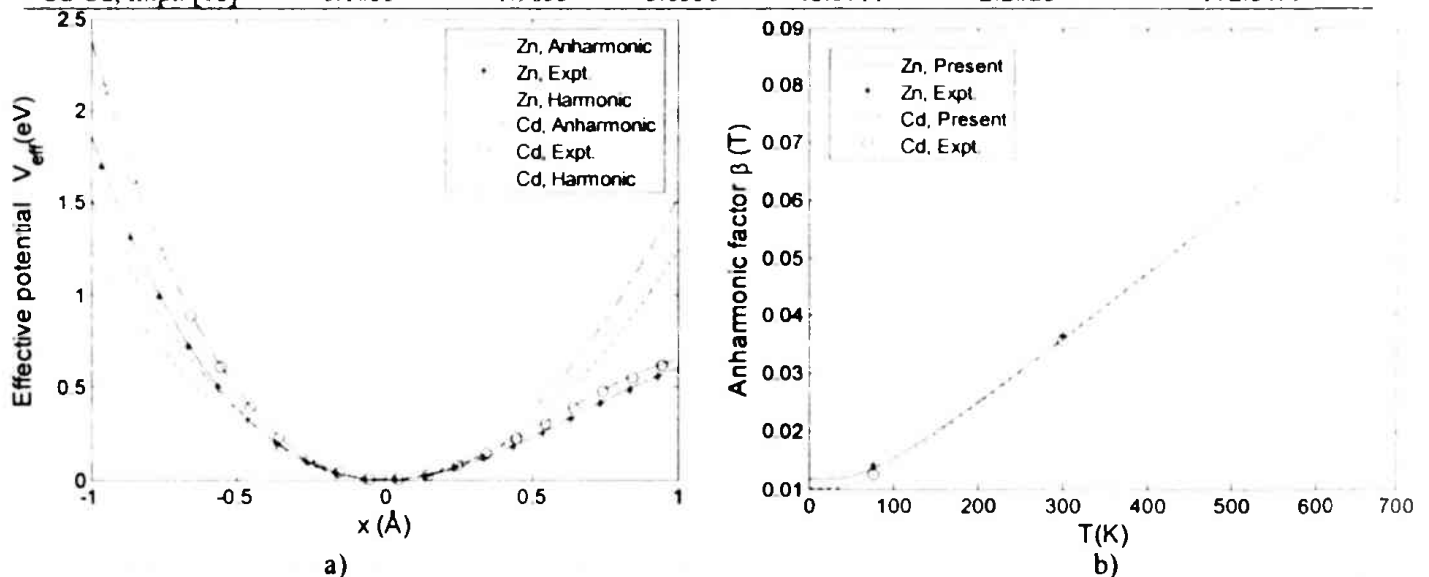| Bond	D(eV)	α (Å^{-1})	r_0 (Å)	k_{eff} (N/m)	ω_E (×10^{13} Hz)	θ_E (K)
Zn-Zn, Calc.	0.1698	1.7054	2.7931	39.5616	2.6917	205.6101
Zn-Zn, Expt. [16]	0.1685	1.7000	2.7650	39.0105	2.6729	204.1730
Cd-Cd, Calc.	0.1675	1.9069	3.0419	48.7927	2.2798	174.1425
Cd-Cd, Expt. [16]	0.1653	1.9053	3.0550	48.0711	2.2628	172.8499

Fig. 1. Calculated anharmonic effective potentials and their harmonic components (a), and anharmonic factors (b) for Zn, Cd. They are compared to experiment [16].

Figure 2 illustrates the temperature dependence of our calculated 1st cumulant (a) describing the net thermal expansion and 2nd cumulant (b) describing Debye-Waller factor for Zn and Cd compared to experiment at 77 K and 300 K [16].
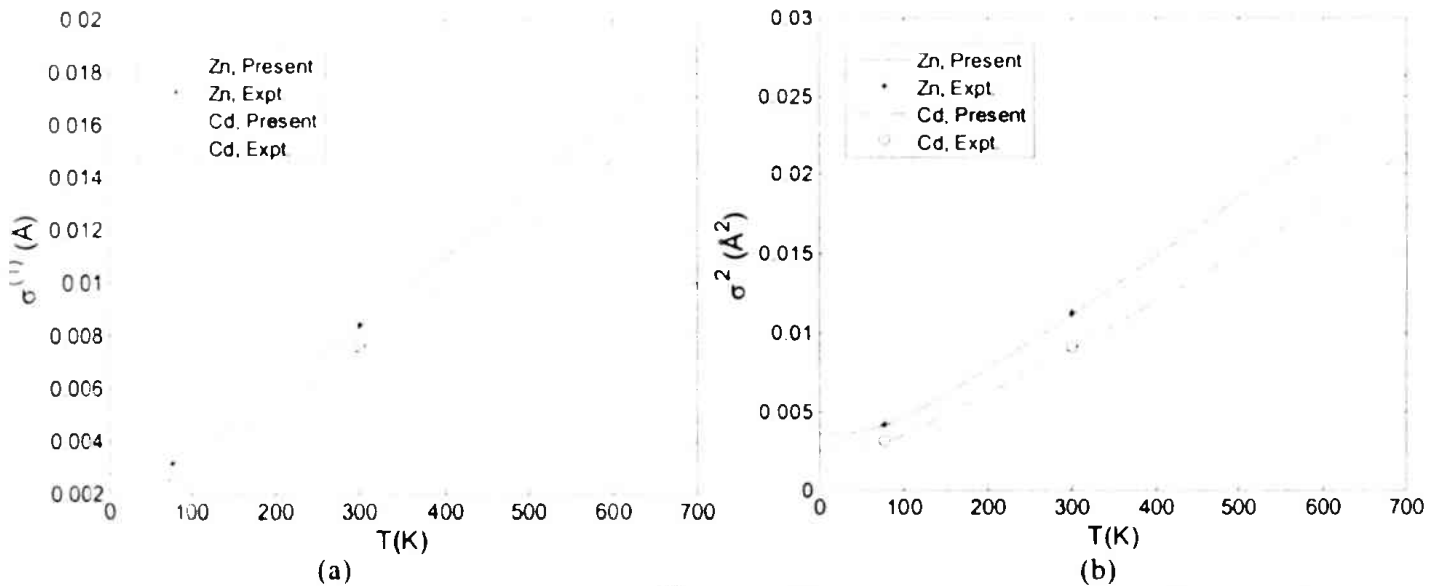

Fig. 2. Calculated temperature dependence of 1st (a) and 2nd (b) cumulants for Zn and Cd compared to experiment at 77 K and 300 K [16].

Figure 3 demonstrates the temperature dependence of our calculated 3rd cumulant and thermal expansion coefficient for Zn and Cd. They agree with the measured values at 77 K and 300 K [16]. All three calculated cumulants of Zn and Cd satisfy their fundamental properties. They contain zero-point contribution at low temperature as quantum effects. At high-temperatures the 1st and 2nd cumulants are linearly proportional to the temperature T, but the 3rd cumulant to T^3. Our calculated temperature dependence of thermal expansion coefficients for Zn and Cd agree with experimental values at 77 K and 300 K. Moreover, they satisfy Grueneisen theorem, where at low temperatures they behave as T^3 and at high-temperatures they approach the constant values as the form of specific feat.
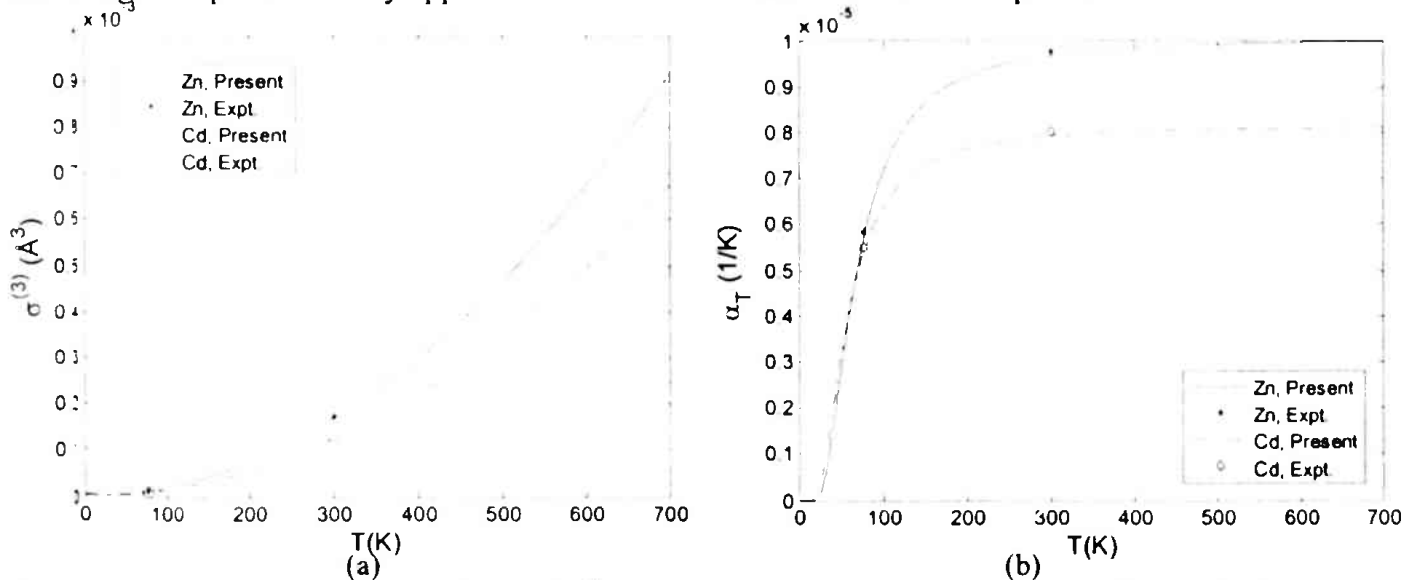

Fig. 3. Calculated temperature dependence of 3rd cumulants (a) and thermal expansion coefficients for Zn and Cd compared to experiment at 77 K and 300 K [16].

Figure 4 shows the EXAFS spectra χk^3 calculated by our theory at 77 K, 300 K and 500 K (a) and their Fourier transform magnitude at 300 K (b) compared to experiment [16]. The EXAFS are attenuated and shifted shifted to the right as the temperature increases. Our calculated Fourier transform magnitude agrees with experiment [16] and is shifted to the left compared to the harmonic FEFF code results [1]. This is indicative of the necessity of including anharmonic contributions in the EXAFS data analysis.

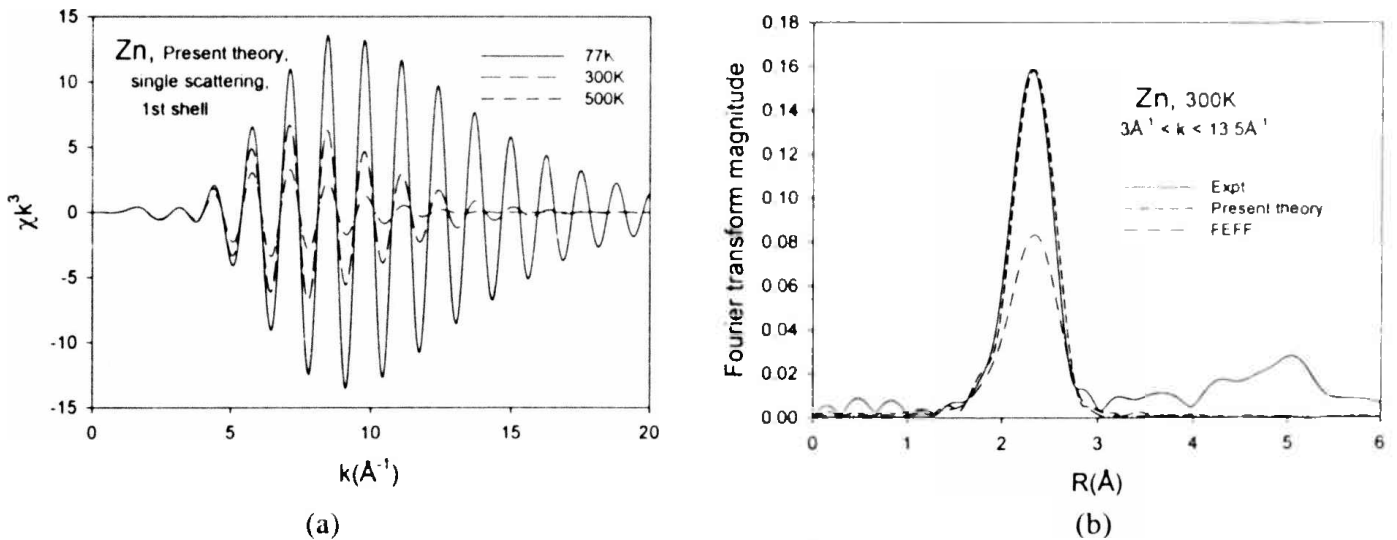(a)   (b)

Fig. 4. Calculated anharmonic EXAFS at 77 K, 300 K, 500 K (a) and Fourier transform magnitude at 300 K compared to experiment [16] and to FEFF result [1] for Zn.

4. Conclusions

In this work a new method for calculation and analysis of anharmonic effective potential, effective local force constant, three leading cumulants, and EXAFS for hcp crystals has been explored. This anharmonic theory contains the harmonic model at low temperatures and the classical limit at high temperatures as special cases.

Derived analytical expressions for the considered quantities satisfy all their fundamental properties and provide a good agreement between the calculated and experimental results. This emphasizes the necessity of including anharmonic contributions in the EXAFS data analysis.

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