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Anharmonic Correlated Debye Model high-order Expanded Debye-Waller Factors of BCC Crystals: Application to Metallic Wolfram

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Abstract: Anharmonic correlated Debye model is derived for Debye-Waller factors of bcc (body-centered cubic) crystals presented in terms of cumulant expansion up to the fourth order. The many-body effects are taken into account in the present one-dimensional model based on the anharmonic effective potential that includes interactions of absorber and backscatterer atoms with their first shell near neighbors, where Morse potential is assumed to describe the single-pair atomic interaction. Analytical expressions for dispersion relation, correlated Debye frequency and temperature and four first temperature-dependent XAFS (X-ray absorption fine structure) cumulants of bcc crystals have been derived using the many-body perturbation approach. Numerical results for W are found to be in good agreement with experiment.

Keywords: Debye-Waller factor, effective potential, correlated Debye model, bcc crystals.

1. Introduction

X-ray Absorption Fine Structure (XAFS) has developed into a powerful technique for providing information on local atomic structure and thermal effects of the substances [1-14]. The formalism for including anharmonic effects in XAFS is often based on the cumulant expansion approach [1] from which the expression for anharmonic XAFS is given by [2]

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

where Φ is net phase shift, λ is mean free path, k is wave number of photoelectron, $R = \langle r \rangle$ with r being the instantaneous bond length between absorber and backscatterer atoms, and $\sigma^{(n)}$ (n = 1, 2, 3, 4, …) are the cumulants describing the high-order expanded Debye-Waller factors (DWFs).

Hence, cumulants (the moments in anharmonic expansion of DWFs) are very important for the accurate structural determinations (e.g., the coordination numbers and the atomic distances) from

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XAFS experiment, where the even cumulants contribute to the amplitude, the odd one to the phase of XAFS and for small anharmonicities, it is sufficient to keep the third and fourth cumulant terms [3]. Many efforts have been made to develop procedure for the calculation and analysis of XAFS cumulants using the classical [4,5] and quantum [6-12] theories. Unfortunately, there is still no theoretical result for bcc crystals while their experimental results are available [13].

The purpose of this work is to derive an anharmonic correlated Debye model (ACDM) for studying the high-order expanded DWFs for the local vibrational amplitudes in XAFS of bcc crystals. Our contributions to this work presented in Sect. 2 are the derivations of firstly, the anharmonic effective potential for bcc crystals expanded up to the fourth order based on the first shell near neighbor contribution approach (FNNCA) instead of the single-bond (SB) [6] and single-pair (SP) [7] potentials, and secondly, the analytical expressions of four first temperature-dependent XAFS cumulant for bcc crystals using the many-body perturbation approach (MBPA) [14], the derived dispersion relation and the obtained anharmonic effective potential parameters, where Morse potential is assumed to describe the single-pair atomic interaction. Numerical results for W are compared to experiment [13] which show good agreement.

2. Anharmonic correlated Debye model for bcc crystals

2.1. Anharmonic interatomic effective potential of bcc crystals

The anharmonic interatomic *effective potential* expanded up to the fourth order in the present theory for bcc crystals can be expressed as

$$V_{eff}(x) \approx \frac{1}{2}k_{eff}x^2 + k_{3eff}x^3 + k_{4eff}x^4, \;\; x = r - r_0, \tag{2}$$

where k_{eff} is the effective local force constant, r and r_0 are the instantaneous and equilibrium distances between absorber and backscatterer atoms, k_{3eff} and k_{4eff} are the anharmonic parameters giving an asymmetry of the anharmonic effective potential.

For bcc crystals, each atom is bonded to its 8 first shell near neighbors so that in the present FNNCA the oscillation of a single bond pair of atoms (e.g., absorber and backscatterer) is influenced by their first shell near neighbors. Therefore, the anharmonic interatomic effective potential in the present ACDM defined based on an assumption in the center-of-mass frame of single bond pair of absorber and backscatterer atoms, has the form

$$V_{eff}(x) = V(x) + 2V\left(-\frac{x}{2}\right) + 6V\left(\frac{x}{6}\right) + 6V\left(-\frac{x}{6}\right), \tag{3}$$

which is the sum over not only the term V(x) describing the pair-interaction between absorber and backscatterer atoms but also the other terms describing the projections of their pair-interactions with 14 first shell near neighbors of bcc crystals along the bond direction excluding the absorber and backscatterer themselves whose contributions are already described by V(x).

Applying Morse potential expanded up to the fourth order as

$$V(x) = D\left(e^{-2\alpha x} - 2e^{-\alpha x}\right) \approx D\left(-1 + \alpha^2x^2 - \alpha^3x^3 + \frac{7}{12}\alpha^4x^4\right) \tag{4}$$

to Eq. (3) and comparing the result to Eq. (2), we obtain the values of $k_{eff}, k_{3eff}, k_{4eff}$ for bcc crystals in terms of Morse potential parameters

$$k_{eff} = \frac{11}{3} D\alpha^2, \quad k_{3eff} = -\frac{3}{4} D\alpha^3, \quad k_{4eff} = \frac{1715}{2592} D\alpha^4, \tag{5}$$

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

Hence, the anharmonic effective potential for bcc crystals of Eq. (3) has resulted as

$$V_{eff}(x) \approx \frac{11}{6} D\alpha^2 x^2 - \frac{3}{4} D\alpha^3 x^3 + \frac{1715}{2592} D\alpha^4 x^4, \tag{6}$$

which is different from the SB and SP potentials denoted by SPP containing only V(x) describing the pair-interaction between absorber and backscatterer atoms in the form

$$V_{SP}(x) = V(x) \approx D\alpha^2 x^2 - D\alpha^3 x^3 + \frac{7}{12} D\alpha^4 x^4. \tag{7}$$

Note that the above mentioned lattice contributions based on the FSNNCA, to the oscillation between absorber and backscatterer atoms described by the projections of their pair-interactions with 14 first shell near neighbors along the bond direction, make it possible to take into account the many-body effects in the present one-dimensional model for bcc crystals.

2.2. XAFS cumulants of bcc crystals

In order to include the anharmonic effects, Hamiltonian of the system is written in the summation of the harmonic and anharmonic components, H_0 and H_a, respectively

$$H = H_0 + H_a, \quad H_a = H_c + H_q, \tag{8}$$

which are used for deriving analytical expressions of the cumulants where H_0 containing the local force constant k_{eff} is used for derivation of second cumulant, the cubic term H_c containing k_{3eff} is used for derivation of the first and third cumulants, and H_a consisting of H_c and the quartic term H_q containing k_{4eff} is used for derivation of the fourth cumulant of bcc crystals.

Derivation of the present ACDM for bcc crystals using the MBPA [14] is based on the dualism of an elementary particle in quantum theory, i.e., its corpuscular and wave property. Then, we can describe the system in Debye model involving all different frequencies up to the Debye frequency as a system consisting of many bodies, i.e., of many phonons, each of which corresponds to a wave having frequency ω(q) and wave number q varied in the first BZ.

For this purpose, the displacement u_n's in the parameter x in terms of the displacement of nth atom u_n of the one dimensional chain described by

$$x_n = u_{n+1} - u_n \tag{9}$$

is related to the phonon displacement operators A_q [15] in the form

$$u_n = \sqrt{\frac{\hbar}{2NM}} \sum_q \frac{e^{iqan}}{\sqrt{\omega(q)}} A_q, \quad A_q = A_{-q}^{+}, \quad [A_q, A_{q'}] = 0 \tag{10}$$

to be given by

$$x_n = \sum_q e^{iqan} f(q) A_q , \quad f(q) = \sqrt{\frac{\hbar}{2NM\omega(q)}} \left(e^{iqa} - 1\right) , \tag{11}$$

where N is atomic number, M is the mass of composite atoms and *a* is lattice constant.

The frequency ω(*q*) contained in Eq. (11) and then in all cumulant expressions derived for the vibration between absorber and backscatterer atoms in XAFS process describes the dispersion relation. Using the local force constant of the first equation of Eqs. (5), it has resulted as

$$\omega(q) = 2\alpha \sqrt{\frac{11D}{3M}} \left| \sin\left(\frac{qa}{2}\right) \right| , \quad |q| \le \frac{\pi}{a} . \tag{12}$$

At the bounds of the first Brillouin zone (BZ of the linear chain, $q = \pm\pi / a$, the frequency has maximum so that from Eq. (12) we obtain the correlated Debye frequency ω_D and temperature θ_D for bcc crystals in the form

$$\omega_D = 2\alpha \sqrt{\frac{11D}{3M}} , \qquad \theta_D = \frac{\hbar\omega_D}{k_B} , \tag{13}$$

where k_B is Boltzmann constant.

Using the above results in the MBPA [14], we have derived the analytical expressions for XAFS DWFs presented in terms of cumulant expansion up to the fourth order for bcc crystals.

The first cumulant describing the net thermal expansion or disorder in XAFS theory has resulted as

$$\begin{gathered} \sigma^{(1)}(T) = \langle x \rangle = \sigma_0^{(1)} \int_0^{\pi/a} \omega(q) \frac{1+Z(q)}{1-Z(q)} dq = \frac{\sigma_0^{(1)}}{\sigma_0^2} \sigma^2 , \\ \sigma_0^{(1)} = \frac{81a\hbar}{484\pi D\alpha} , \; Z(q) = \exp\left(\beta\hbar\omega(q)\right), \; \beta = 1/k_B T. \end{gathered} \tag{14}$$

Here, σ^2 is second cumulant describing the mean square relative displacement (MSRD) and has the following form

$$\sigma^2(T) = \left\langle x^2 \right\rangle = \sigma_0^2 \int_0^{\pi/a} \omega(q) \frac{1+z(q)}{1-z(q)} dq , \; \sigma_0^2 = \frac{3\hbar a}{22\pi D\alpha^2} . \tag{15}$$

The third cumulant is the mean cubic relative displacement (MCRD) describing the asymmetry of the pair distribution function in XAFS theory and has resulted as

$$\begin{aligned} \sigma^{(3)}(T) &\cong \left\langle x^3 \right\rangle - 3\left\langle x^2 \right\rangle \langle x \rangle = \sigma_0^{(3)} \int_0^{\pi/a} dq_1 \int_{-\pi/d}^{\pi/a - q_1} dq_2 \frac{\omega(q_1)\omega(q_2)\omega(q_1+q_2)}{\omega(q_1)+\omega(q_2)+\omega(q_1+q_2)} \\ &\times \left\{ 1 + 6 \frac{\omega(q_1)+\omega(q_2)}{\omega(q_1)+\omega(q_2)-\omega(q_1+q_2)} \frac{e^{\beta\hbar[\omega(q_1)+\omega(q_2)]} - e^{\beta\hbar\omega(q_1+q_2)}}{\left(e^{\beta\hbar\omega(q_1)} - 1\right)\left(e^{\beta\hbar\omega(q_2)} - 1\right)\left(e^{\beta\hbar\omega(q_1+q_2)} - 1\right)} \right\}, \\ \sigma_0^{(3)} &= \frac{114 \times 10^{-4} \hbar^2 a^2}{\pi^2 D^2 \alpha^3} . \end{aligned} \tag{16}$$

The fourth cumulant describes the anharmonic contribution to XAFS amplitude. It has been derived and given by

$$\sigma^{(4)}(T) \cong \left\langle x^4 \right\rangle - 3\left\langle x^2 \right\rangle^2 = \sigma_0^{(4)} \int_0^{\pi/a} dq_1 \int_0^{\pi/a-q_1} dq_2 \int_{-\pi/a}^{\pi/a-(q_1+q_2)} dq_3 \frac{\omega(q_1)\omega(q_2)\omega(q_3)\omega(q_4)}{\omega(q_1)+\omega(q_2)+\omega(q_3)+\omega(q_4)}$$
$$\times \left\{ 1 + 8\frac{Z(q_1)Z(q_2)Z(q_3)-Z(q_4)}{(Z(q_1)-1)(Z(q_2)-1)(Z(q_3)-1)(Z(q_4)-1)} \frac{\omega(q_1)+\omega(q_2)+\omega(q_3)}{\omega(q_1)+\omega(q_2)+\omega(q_3)-\omega(q_4)} \right. \tag{17}$$
$$\left. + 6\frac{Z(q_1)Z(q_2)-Z(q_3)Z(q_4)}{(Z(q_1)-1)(Z(q_2)-1)(Z(q_3)-1)(Z(q_4)-1)} \frac{\omega(q_3)+\omega(q_4)}{\omega(q_1)+\omega(q_2)-\omega(q_3)-\omega(q_4)} \right\},$$
$$\sigma_0^{(4)} = \frac{165\times 10^{-4}\hbar^3 a^3}{2\pi^3 D^3 \alpha^4}, \quad q_4 = -(q_1+q_2+q_3).$$

Note that in the above expressions for the cumulants of bcc crystals, $\sigma_0^{(1)}, \sigma_0^2, \sigma_0^{(3)}, \sigma_0^{(4)}$ are zero-point energy contributions to the first, second, third and fourth cumulant, respectively, and they have been obtained for the case of large phonon number, when the summation over q is replaced by the corresponding integral in the first BZ.

3. Numerical results and discussions

Now the expressions derived in the previous section are applied to numerical calculations for W using its Morse potential parameters [16] D = 0.979 eV, α = 1.441 Å^{-1}.

Note that the correlated Debye frequency and temperature (Tab. 1), anharmonic effective potential (Fig. 1a), dispersion relation (Fig. 1b) and XAFS cumulants (Figs. 2 – 3) of W calculated using the present theory agree well with the experimental values [13] and are quite different from those calculated using the SPP (Tab. 1, Fig. 1 - 2). Based on Eq. (1) they contribute to getting the accurate information on W, a bcc crystal, from XAFS experiment.

Table 1. Debye frequency ω_D and temperature θ_D of W calculated using the present theory compared to the experimental values (Expt.) [13] and to those calculated using the SPP

	ω_D (10^{13}Hz)			θ_D (K)		
Crystal	Present	Expt. [13]	SPP	Present	Expt. [13]	SPP
W	3.8864	3.9634	2.8703	296.87	302.6±17	219.25

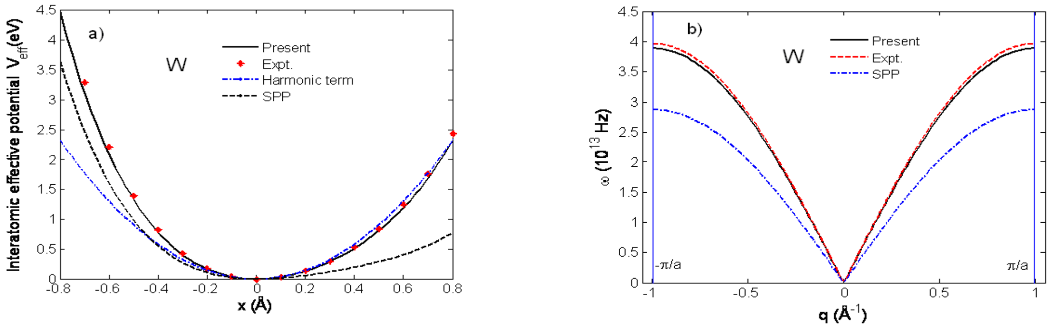

Figure 1. a) Anharmonic effective potential and b) dispersion relation of W calculated using the present theory compared to experiment [13] and to those calculated using SPP parameters.

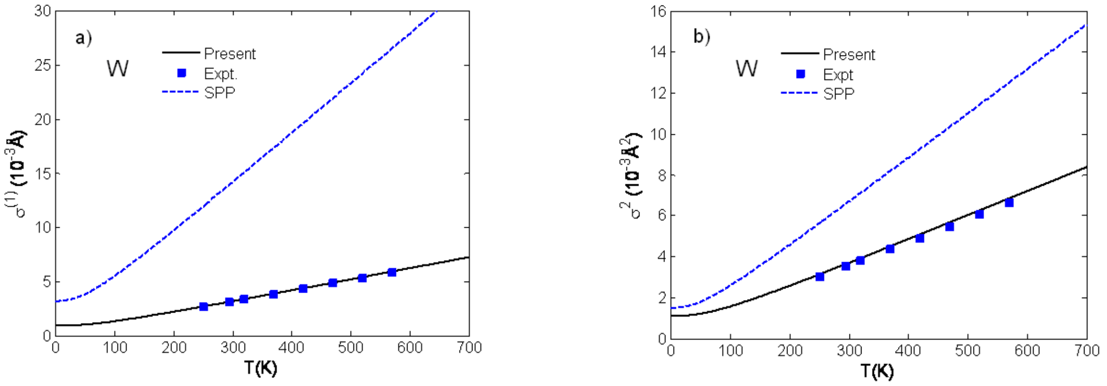

Figure 2. Temperature dependence of a) first cumulant $\sigma^{(1)}(T)$ and b) second cumulant $\sigma^2(T)$ of W calculated using the present thery compared to the experimental values [13] and to those calculated using the SPP parameters.

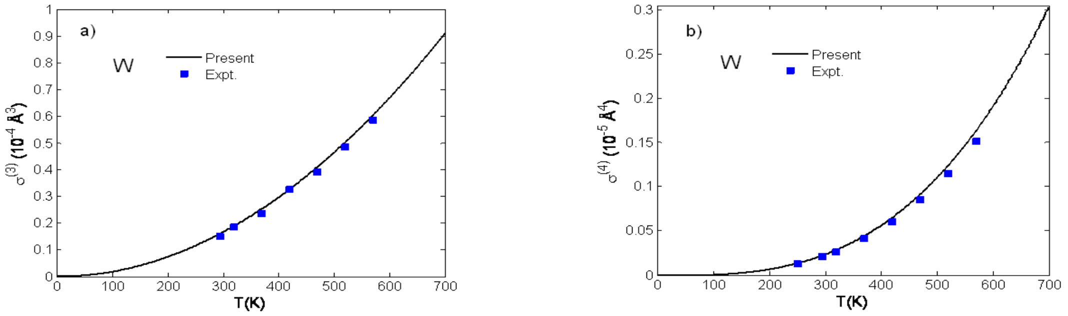

Figure 3. Temperature dependence of a) third cumulant $\sigma^{(3)}(T)$ and b) fourth cumulant $\sigma^{(4)}(T)$ of W calculated using the present theory compared to the experimental values [13].

4. Conclusions

An ACDM has been derived for studying the anharmonic effective potential, DWF expanded up to the fourth order and anharmonic effects in XAFS of bcc crystals. This leads to getting the accurate information on their structural and other parameters taken from XAFS experiment.

The significant discrepancies of the results calculated using the SPP parameters with experiment can be attributed to neglecting the many-body effects in the SPP so that they are able to be treated by the present theory using the anharmonic effective potential.

The advantage and efficiency of the present theory in XAFS data analysis are illustrated by the good agreement of the numerical results for XAFS cumulants of W with experiment. This makes it possible to reproduce the experimental XAFS data of bcc crystals using the present theory.

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