Anharmonic Correlated Debye Model Debye-Waller Factors of Metallic Copper Compared to Experiment and to Other Theories

Nguyen Van Hung[1,*], Nguyen Bao Trung[1], Nguyen Cong Toan[1], Ha Dang Khoa[2]

Faculty of Physics, VNU University of Science, 334 Nguyen Trai, Hanoi, Vietnam

[2]*School of Engineering Physics, Hanoi University of Science and Technology, 1 Dai Co Viet, Hanoi, Vietnam*

Abstract: Debye-Waller factors (DWFs) of metallic Cu (fcc crystal) in X-ray absorption fine structure (XAFS) presented in terms of cumulant expansion have been studied based on the anharmonic correlated Debye model (ACDM). This ACDM is derived from the many-body perturbation approach and the anharmonic effective potential that includes the first shell near neighbor contributions to the vibration between absorber and backscatterer atoms. Analytical expressions of three first XAFS cumulants of Cu have been derived involving more information of phonon-phonon interactions taken from integration over the first Brillouin zone. Morse potential is assumed to describe the single-pair atomic interaction. Numerical results for Cu using the present ACDM show their good agreement with experiment and with those of other theories, as well as their advantages compared to those calculated using the single-pair potential.

Keywords: Debye-Waller factor, XAFS cumulants, effective potential, correlated Debye model, metallic Cu.

1. Introduction

X-ray absorption fine structure (XAFS) has developed into a powerful probe of atomic structure and thermal effects of substances. XAFS expression contains Debye-Waller factor (DWF) presented in terms of cumulant expansion, where the first cumulant describes the net thermal expansion, the second one describes the mean square relative displacement (MSRD), the third cumulant describes the anharmonic contribution to XAFS phase [1]. The accurate cumulants are crucial to quantitative treatment of anharmonic XAFS. Consequently, the lack of the precise cumulants has been one of the biggest limitations to accurate structural determinations (e.g., the coordination numbers and the atomic

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distances) and other parameters from XAFS experiment [2]. Therefore, investigation of XAFS cumulants is of great interest.

The purpose of this work is to study XAFS DWFs presented in terms of cumulant expansion up to the third order describing the thermodynamic properties of Cu (fcc crystal) based on the anharmonic correlated Debye model (ACDM). The ACDM is derived from the many-body perturbation approach (MBPA) [3] and the anharmonic interatomic effective potential that includes the first shell near neighbor contributions to the vibration between absorber and backscatterer atoms. In Section 2, the analytical expressions for the dispersion relation, correlated Debye frequency and temperature and three first XAFS cumulants of fcc crystals have been derived which contain more information taken from integration over the phonon wave numbers varied in the first Brillouin zone (BZ). Morse potential is assumed to describe the single-pair atomic interaction included in the derived anharmonic interatomic effective potential. Numerical results for Cu (Section 3) using the present ACDM show their good agreement with those calculated using the anharmonic correlated Einstein model (ACEM) [4], the Path-integral Monte-Carlo (PIMC) [5] and with experiment [5-8], as well as their advantages compared to those calculated from the single-pair potential (SPP) [9, 10].

2. Theory

2.1. XAFS cumulants

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

$$H = H_0 + H_c \ . \tag{1}$$

Here H_0 and H_c contain the local force constant k_{eff} and cubic parameter k_{3eff} of the anharminic effective potential of fcc crystals, respectively. This effective potential is defined based on the *first shell near neighbor contribution approach* (FSNNCA) as

$$V_{eff}\left(x\right) \approx \frac{1}{2}k_{eff}x^2 + k_{3eff}x^3 = V\left(x\right) + 2V\left(-\frac{x}{2}\right) + 8V\left(-\frac{x}{4}\right) + 8V\left(\frac{x}{4}\right), \ \ x = r - r_0 \ , \tag{2}$$

which is the sum over not only the term V(x) describing the pair-interaction between absorber and backscatterer atoms but also the other ones describing the projections of their pair-interactions with 18 first shell near neighbors of fcc crystals along the bond direction excluding the absorber and the backscatterer themselves whose contributions are already described by V(x), as well as 4 others located in the surface perpendicular to the bond direction providing zero contribution.

The values of k_{eff}, k_{3eff} are determined by applying the Morse potential expanded to the third order around its minimum

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

where α describes the width of the potential and D is the dissociation energy, to each term of the second equation of Eqs. (2) and comparing the results to the first equation. They are quite different from those of the SPP [8, 9] which include only the first term V(x) on the right of Eqs. (2).

Derivation of the present ACDM for fcc crystals is performed using the MBPA [3] 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 the present ACDM involving all different frequencies up to the Debye frequency as a system consisting of many bodies or many phonons, each of which corresponds to a wave having frequency $\omega(q)$ and wave number q varied in the first BZ. Moreover, based on the FSNNCA only backscattering from the first shell of absorber and backscatterer atoms is taken into consideration. This reduces and simplifies the derivations of the analytical expressions of the considered XAFS cumulants.

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

$$x_n = u_{n+1} - u_n,$$
(4)

is related to the phonon displacement operators A_q [11] in the form

$$u_n = \sqrt{\frac{\hbar}{2NM}} \sum_q \frac{e^{iqan}}{\sqrt{\omega(q)}} A_q, \quad A_q = A_{-q}^+, \quad \left[A_q, A_{q'} \right] = 0,$$
(5)

to be given by

$$x_n = \sum_q e^{iqan} f(q) A_q, \quad f(q) = \sqrt{\frac{\hbar}{2NM\omega(q)}} \left(e^{iqa} - 1 \right),$$
(6)

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

The frequency $\omega(q)$ contained in Eq. (6) and then in all cumulant expressions derived for the oscillation between absorber and backscatterer atoms in XAFS process under the interactions of these atoms with their first shell near neighbors, describes the dispersion relation. Using the obtained local force constant for fcc crystals, it has resulted as

$$\omega(q) = 2\alpha \sqrt{\frac{5D}{M}} \left| sin\left(\frac{qa}{2} \right) \right|, \quad |q| \le \frac{\pi}{a}.$$
(7)

At the bounds of the first BZ of the linear chain, $q = \pm \pi / a$, the frequency has a maximum so that from Eq. (7) we obtain the correlated Debye frequency ω_D and temperature θ_D for fcc crystals in the form

$$\omega_D = 2\alpha \sqrt{\frac{5D}{M}}, \quad \theta_D = \frac{\hbar \omega_D}{k_B},$$
(8)

where k_B is Boltzmann constant.

Based on the above results the cubic anharmonic effective parameter can be expressed as

$$H_c = k_{3eff} x^3 = \sum_{q_1,q_2,q_3} V(q_1,q_2,q_3) A_{q_1} A_{q_2} A_{q_3},$$
(9)

or in the following form using Eq. (5) for the displacement of nth atom

$$H_c = k_{3eff} \sum_n \left(u_{n+1} - u_n \right)^3 = k_{3eff} \sum_{q_1,q_2,q_3} \left(\sum_n e^{i(q_1+q_2+q_3)an} \right) f(q_1) f(q_2) f(q_3) A_{q_1} A_{q_2} A_{q_3}.$$
(10)

Comparing Eq. (10) to Eq. (9) and indicating

$$\Delta(q) = \frac{1}{N} \sum_n e^{iqna}, \quad \Delta(0) = \sum_n e^{i0na} = N,$$
(11)

with N as the atomic number, we obtain

$$V(q_1, q_2, q_3) = k_{3eff} \Delta(q_1 + q_2 + q_3) f(q_1) f(q_2) f(q_3). \tag{12}$$

Using Eq. (5) and Eq. (11), this Eq. (12) changes into

$$V(q_1, q_2, q_3) = k_{3eff} \left(\frac{\hbar}{2NM} \right)^{3/2} \left(\sum_n e^{i(q_1+q_2+q_3)an} \right) \frac{\left(e^{iq_1 a} - 1\right)\left(e^{iq_2 a} - 1\right)\left(e^{iq_3 a} - 1\right)}{\sqrt{\omega(q_1)\omega(q_2)\omega(q_3)}} . \tag{13}$$

In the MBPA [3] the value $\langle x \rangle$ is calculated using the expression

$$\langle x \rangle = \frac{\sum_q f(q) \langle A_q S(\beta) \rangle_0}{\langle S(\beta) \rangle_0}, \tag{14}$$

$$S(\beta) = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \int_0^\beta d\tau_1 \ldots \int_0^\beta d\tau_n T[H_a(\tau_1)\ldots H_a(\tau_n)], \quad H_a(t) = e^{tH_0} H_a e^{-tH_0}, \tag{15}$$

which takes backscattering only from the first shell.

Substituting into Eq. (14) the relations [3]

$$\langle A_q S(\beta) \rangle_0 = -\int d\tau \langle T[A_q \hat{H}_1(\tau)] \rangle, \quad \langle A_q \rangle_0 = 0, \tag{16}$$

we obtain

$$\langle x \rangle = -\sum_q f(q) \sum_{q_1, q_2, q_3} V(q_1, q_2, q_3) \int_0^\beta d\tau \langle T[\hat{A}_q(0)\hat{A}_{q_1}(\tau)\hat{A}_{q_2}(\tau)\hat{A}_{q_3}(\tau)] \rangle_0. \tag{17}$$

Using Wick theorem for T-product in the integral, the harmonic phonon Green function [3]

$$G^0_{q,q'}(\tau) = \langle T[\hat{A}_q(\tau)\hat{A}_{q'}(0)] \rangle_0, \quad G^0_{q,q'}(\tau) = -\delta_{q,-q'} \left\{ \langle n_q + 1 \rangle e^{-\hbar\omega(q)\tau} + \langle n_q \rangle e^{\hbar\omega(q)\tau} \right\}, \tag{18}$$

the symmetric properties of V(q₁,q₂,q₃) [11], properties of function $\delta_{q,-q'}$, the phonon density

$$\langle n_q \rangle = \frac{1}{Z(q)-1}, \quad Z(q) = exp(\beta\hbar\omega(q)), \quad \beta = 1/k_B T, \tag{19}$$

as well as $\omega(q)$ from Eq. (7), f(q) from Eq. (6), $\Delta(0)$ from Eq. (11) and the phonon momentum conservation in the first BZ we change Eq. (17) into the one in terms of Morse parameters for fcc crystals

$$\langle x \rangle = \frac{3\hbar\alpha}{8NM} \sum_q \frac{\left(e^{iqa} - 1\right)\left(e^{-iqa} - 1\right)}{\omega(q)} \frac{1+Z(q)}{1-Z(q)} = \frac{3\hbar}{4N\sqrt{5MD}} \sum_q sin\frac{qa}{2} \frac{1+Z(q)}{1-Z(q)}. \tag{20}$$

Using this expression, the first cumulant describing the net thermal expansion or lattice disorder in XAFS theory has resulted as

$$\sigma^{(1)}(T) = \langle x \rangle = \sigma_0^{(1)} \int_0^{\pi/a} \omega(q) \frac{1+Z(q)}{1-Z(q)} dq = \frac{\sigma_0^{(1)}}{\sigma_0^2} \sigma^2, \tag{21}$$

$$\sigma_0^{(1)} = \frac{3a\hbar}{40\pi D\alpha}, \quad Z(q) = exp(\beta\hbar\omega(q)), \quad \beta = 1/k_B T.$$

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

$$\sigma^2(T) = \langle x^2 \rangle = \left\langle \sum_n (u_{n+1} - u_n)^2 \right\rangle = \sigma_0^2 \int_0^{\pi/a} \omega(q) \frac{1+z(q)}{1-z(q)} dq, \quad \sigma_0^2 = \frac{\hbar a}{10\pi D\alpha^2}, \tag{22}$$

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

$$\sigma^{(3)}(T) \cong \langle x^3 \rangle - 3\langle x^2 \rangle \langle x \rangle = \sigma_0^{(3)} \int_0^{\pi/a} dq_1 \int_{-\pi/d}^{\pi/a-q_1} dq_2 \frac{\omega(q_1)\omega(q_2)\omega(q_1+q_2)}{\omega(q_1)+\omega(q_2)+\omega(q_1+q_2)}$$

$$\times \left\{ 1 + 6 \frac{\omega(q_1)+\omega(q_2)}{\omega(q_1)+\omega(q_2)-\omega(q_1+q_2)} \frac{e^{\beta\hbar[\omega(q_1)+\omega(q_2)]} - e^{\beta\hbar\omega(q_1+q_2)}}{\left(e^{\beta\hbar\omega(q_1)}-1\right)\left(e^{\beta\hbar\omega(q_2)}-1\right)\left(e^{\beta\hbar\omega(q_1+q_2)}-1\right)} \right\}, \tag{23}$$

$$\sigma_0^{(3)} = \frac{\hbar^2 a^2}{400\pi^2 D^2 \alpha^3}.$$

Note that in the above expressions for the cumulants of fcc crystals in the present ACDM, $\sigma_0^{(1)}, \sigma_0^2, \sigma_0^{(3)}$ are zero-point energy contributions to the first, second and third cumulant, respectively, and these cumulant expressions have been obtained for the case of large phonon numbers, when the summation over q is replaced by the corresponding integral in the first BZ. Moreover, we have used the phonon momentum conservation in the first BZ [11] to describe the value of q_3 by q_1 and q_2 for the first and third cumulants. This leads to reducing the integrations for these cumulants given by Eqs. (21) and (23), respectively.

2.2. High- and low-temperature limits

It is useful to consider the high-temperature (HT) limit, where the classical approach [12, 13] is applicable, and the low-temperature (LT) limit, where the quantum theory must be used [4]. In the HT limit we use the approximation

$$Z(q) \approx 1 + \beta\hbar\omega(q) \tag{24}$$

to simplify the expressions for the cumulants. In the LT limit $Z(q) \gg 1$, so that all temperature-dependent terms approach zero, and in the LT limit, the cumulants approach constant values, e. g., their zero-point contributions. These results are written in Table 1.

Table 1. The expressions of cumulants in LT and HT limits.

Cumulant	LT limit	HT limit
$\sigma^{(1)}$	$\dfrac{6\hbar}{4\pi\sqrt{5MD}}(1+z)$	$\dfrac{3k_B T}{20D\alpha}$
σ^2	$\dfrac{2\hbar}{\pi\alpha\sqrt{5MD}}(1+z)$	$\dfrac{k_B T}{5D\alpha^2}$
$\sigma^{(3)}$	$\dfrac{3\hbar^2}{200N^2 D^2\alpha^3} \sum_{q_1,q_2,q_3} \dfrac{\omega(q_1)\omega(q_2)\omega(q_3)}{\omega(q_1)+\omega(q_2)+\omega(q_3)}(1+Z_3)$	$\dfrac{6(k_B T)^2}{100D^2\alpha^3}$
$\sigma^{(1)}\sigma^2 / \sigma^{(3)}$		$1/2$

where

$$z = \frac{1}{a} \int_0^{\pi/a} \frac{sin\frac{qa}{2}}{Z(q)} dq \,,\, Z_3 = \frac{6\left[\omega(q_1)+\omega(q_2)\right]}{\left[\omega(q_1)+\omega(q_2)\right]^2 - \omega^2(q_3)} \frac{Z(q_3)-Z(q_1)Z(q_2)}{Z(q_1)Z(q_2)Z(q_3)} . \tag{25}$$

Note from Table 1 that at high-temperatures the first and second cumulants are proportional to the temperature T, the third cumulant to T^2 as the standard characters for these quantities as it was mentioned for the other crystal structures [4, 9]. At low-temperatures, they approach their zero-point energy contributions which also involve the contributions of q-values from the first BZ. Moreover, at high-temperature the cumulant ratio $\sigma^{(1)}\sigma^2/\sigma^{(3)}$ approaches the classical value of 1/2 [12, 13].

3. Comparison of numerical results to experiment and to other theories

Now the expressions derived in the previous section are applied to numerical calculations for Cu using its Morse parameters [14] D = 0.337 eV, α = 1.358 Å^{-1}. The values of local force constant k_S, correlated Debye frequency ω_{DS} and temperature θ_{DS} calculated using the present theory (S = *eff*) written in Table 1 are found to be in good agreement with experiment [6] and in significant difference from those calculated using the SPP.

Table 2. The values of $k_S, \omega_{DS}, \theta_{DS}$ of Cu calculated using the present theory (S = *eff*) compared to experiment (S = Expt.) [6] and to those calculated using the SPP.

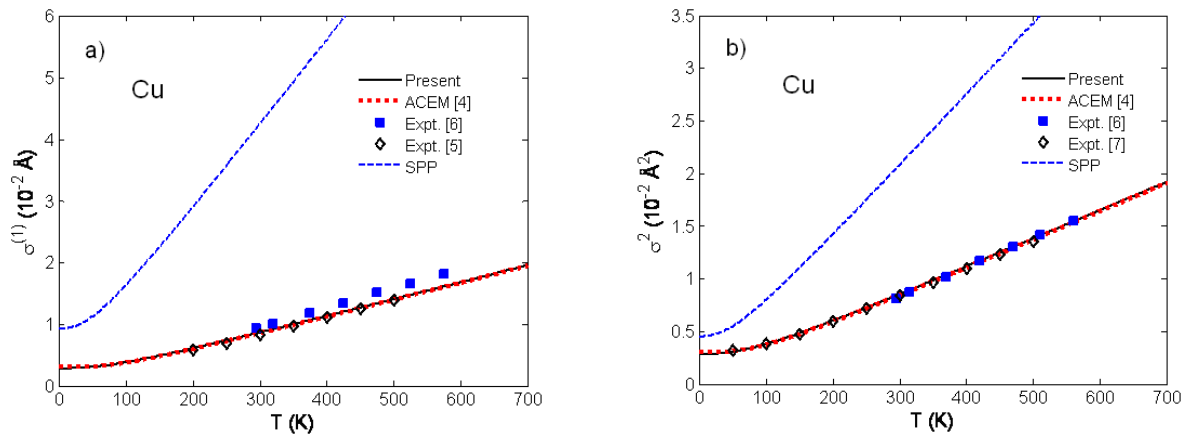| S	$k_S\,(N/m)$	$\omega_{DS}\left(\times 10^{13}Hz\right)$	$\theta_{DS}\,(K)$
eff (Present)	50.7181	4.3717	333.9399
Expt. [6]	50.3450	4.3556	332.7094
SPP	20.2872	2.7649	211.2021

Figure 1. Temperature dependence of a) first cumulant $\sigma^{(1)}(T)$ and b) second cumulant $\sigma^2(T)$ of Cu calculated using the present theory compared to those calculated using the ACEM [4] and SPP and to the experimental values: Expt. [6, 5] for $\sigma^{(1)}(T)$, and Expt. [6, 7] for $\sigma^2(T)$.
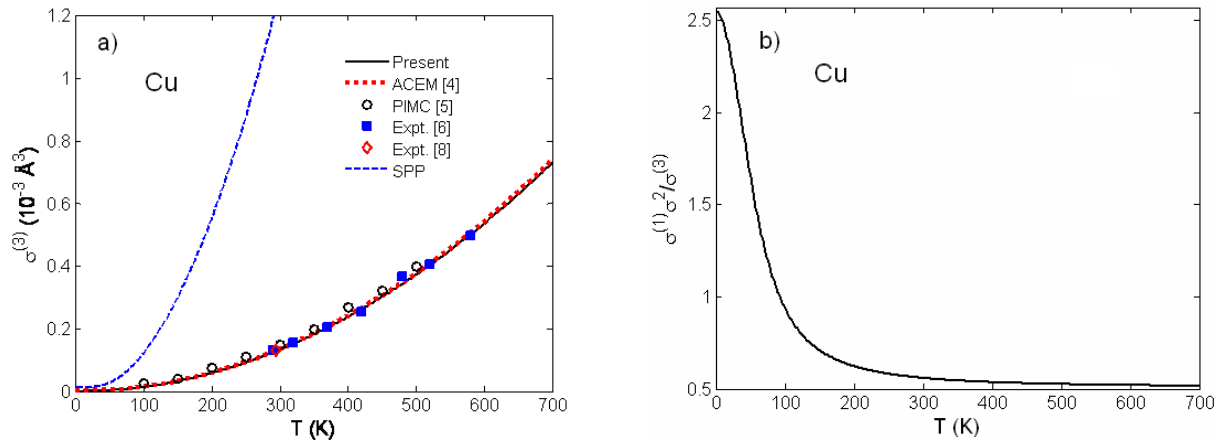
Figure 2. Temperature dependence of a) third cumulant $\sigma^{(3)}(T)$ and b) cumulant ratio $\sigma^{(1)}\sigma^2/\sigma^{(3)}$ of Cu calculated using the present theory compared to those calculated using the ACEM [4], the PIMC [5], the SPP, and to the experimental values Expt. [6, 8] for $\sigma^{(3)}(T)$.

Consequently, temperature dependence of three first XAFS cumulants of Cu (fcc crystal) calculated using the present ACDM is found to be in good agreement with experiment [5-8] and with those calculated using the ACEM [4] and the PIMC [5], but in difference with those calculated using the SPP. The significant discrepancies of the results of SPP with experiment can be attributed to neglecting the many-body effects. The above obtained temperature-dependent cumulants describe the thermodynamic properties of the considered materials such as the net thermal expansion or lattice disorder described by the first cumulant, the MSRD described by the second cumulant and the MCRD or the asymmetry of pair atomic distribution described by the third cumulant. All they contribute to providing the accurate information of the considered materials from XAFS experiment.

4. Conclusions

In this work, XAFS Debye-Waller factors presented in terms of cumulant expansion up to the third order describing the thermodynamic properties of Cu have been studied based on the ACDM which is derived for studying XAFS cumulants of fcc crystals.

Derived analytical expressions of the anharmonic effective potential, dispersion relation, correlated Debye frequency and temperature, as well as three first XAFS cumulants satisfy all their fundamental properties and provide good results which overcome the significant discrepancies with experiment of those calculated from the SPP.

The good agreement of numerical results for Cu with experiment and with those calculated using the ACEM and the PIMC illustrates the advantages and efficiency of the present theory and of using the anharmonic effective potential in XAFS data analysis.

Acknowledgements

References

[1] E. D. Crozier, J. J. Rehr, and R. Ingalls, in X-ray Absorption, edited by D. C. Koningsberger and R. Prins (Wiley, New York, 1988). Chap. 9.

[2] Fernando D. Vila, J. J. Rehr, H. H. Rossner, and H. J. Krappe, "Theoretical x-ray absorption Debye-Waller factors", Phys. Rev. B 76 (2007) 014301.

[3] G. D. Mahan, Many-Particle Physics (Plenum, New York, 1990) 2nd ed

[4] N. V. Hung and J. J. Rehr, "Anharmonic correlated Einstein model Debye-Waller factors", Phys. Rev. B 56 (1997) 43.

[5] S. a Beccara, G. Dalba, P. Fornasini, R. Grisenti, F. Pederiva, and A. Sanson, "Local thermal expansion in copper: EXAFS measuearments and Path-integral Monte-Carlo calculations", Phys. Rev. B 68 (2003) 140301(R).

[6] V. Pirog, T. I. Nedoseikina, A. I. Zarubin, and A. T. Shuvaev, "Anharmonic pair potentials in face centered cubic metals" J. Phys.: Condens. Matter 14 (2002) 1825.

[7] P. Fornasini, S. a Beccara, G. Dalba, R. Grisenti, A. Sanson, and M. Vaccari, "Extended x-ray absorption fine structure measurements of copper: Local dynamics, anharmonicity, and thermal expansion", Phys. Rev. B 70 (2004) 174301.

[8] T. Yokoyama, T. Sasukawa, and T. Ohta, "Anharmonic interatomic potentials of metals and metal bromides determined by EXAFS", Jpn. J. Appl. Phys. 28 (1989) 1905.

[9] A. I. Frenkel and J. J. Rehr, "Thermal expansion and x-ray absorption fine structure cumulants", Phys. Rev. B 48 (1993) 585.

[10] T. Miyanaga and T. Fujikawa, "Quantum Statistical Approach to Debye-Waller Factor in EXAFS, EELS and ARXPS. Application of Debye and Einstein Approximation", J. Phys. Soc. Jpn. 63 (1994) 3683.

[11] A. A. Maradudin, Dynamical Properties of Solids, ed. by G. K. Horton and A. A. Maradudin (North Holland, Amsterdam, 1974) Vol. 1, p. 1.

[12] E. A. Stern, P. Livins, and Zhe Zhang, "Thermal vibration and melting from a local perspective", Phys. Rev. B 43 (1991) 8850.

[13] N. V. Hung, T. S. Tien, N. B. Duc, D. Q. Vuong, "High-order expanded XAFS Debye-Waller factors of hcp crystals based on classical Anharmonic correlated Einstein model", Mod. Phys. Lett. B 28 (2014) 1450174.

[14] L. A. Girifalco and W. G. Weizer, "Application of the Morse Potential Function to Cubic Metals", Phys. Rev. 114 (1959) 687.