Physics

ANHARMONIC EFFECTIVE POTENTIAL, LOCAL FORCE CONSTANT AND CORRELATION EFFECTS IN XAFS OF BCC CRYSTALS

Nguyen Van Hung* **and Nguyen Bao Trung**

Department of Physics, Hanoi University of Science, 334 Nguyen Trai, Hanoi

*E-mail: hungnv@vnu.edu.vn

Le Hai Hung

Institute of Engineering Physics,

Hanoi University of Technology, 1 Dai Co Viet, Hanoi

Abstract. Analytical expressions for the anharmonic effective potential, local force constant, Displacement-displacement Correlation Function (DCF) C_R and Debye-Waller factor described by the Mean Square Relative Displacement (MSRD) σ^2 and by the Mean Square Displacement (MSD) u^2 of bcc crystals in the X-ray Absorption Fine Structure (XAFS) have been derived. The effective interatomic potential of the system has been considered by taking into account the influences of nearest atomic neighbors, and it contains the Morse potential characterizing the interaction of each pair of atoms. Numerical results for u^2, σ^2 and C_R of Fe and W are found to be in good agreement with experiment. The ratios C_R/u^2 and C_R/σ^2 approach constant values at high temperatures showing the same properties obtained by the Debye model.

1. INTRODUCTION

In XAFS process the emitted photoelectron is transferred and scattered in the vibrating atomic environment before interfering with the out going photoelectron. At any temperature the positions $\mathbf{R}_j$ of the atoms are smeared by thermal vibrations. Therefore, in all treatments of XAFS the effect of this vibrational smearing has been included in the XAFS function [1]

$$\chi = \chi_0 \left\langle e^{2ik\Delta_j} \right\rangle ; \quad \Delta_j = \hat{\mathbf{R}}_j^0 \cdot (\mathbf{u}_j - \mathbf{u}_0) , \ \ \hat{\mathbf{R}} = \mathbf{R}/\left|\mathbf{R}\right| , \tag{1}$$

where $\mathbf{u}_j$ and $\mathbf{u}_0$ are the jth atom and the central-atom displacement, respectively.

This Eq. (1) contains a thermally averaging $\left\langle e^{i2k\Delta_j} \right\rangle$ of the photoelectron function leading to the Debye-Waller factor $DWF = e^{-2k^2\sigma_j^2}$ where k is the wave number. Since this factor is meant to account for the thermal vibrations of the atoms about their equilibrium sites $\mathbf{R}_j^0$, someone assume that the quantity σ_j^2 is identical with the MSD [1]. But the oscillatory motion of nearby atoms is relative so that including correlation effect is necessary [2-6]. In this case σ_j^2 is the MSRD containing the MSD and DCF. Anharmonic interatomic potential has been studied intensively in XAFS but mostly by experiment [3, 6]. The correlation effects of fcc crystal have been studied [9] using the anharmonic correlated Einstein model [4].

The purpose of this work is to develop a new procedure for calculation and analysis of the anharmonic effective potential and local force constant, the DCF (C_R) for the atomic vibration of bcc crystals in XAFS based on quantum statistical theory with the anharmonic correlated Einstein model [4]. Expression for the MSD (u^2) has been derived. Using it and the MSRD (σ^2) we derive C_R. The anharmonic effective interaction potential of the system has been considered by taking into account the influences of the nearest atomic neighbors. It contains Morse potential characterizing the interaction of each pair of atoms. Numerical calculations have been carried out for bcc crystals Fe and W. The calculated results for u^2, σ^2, C_R, C_R/u^2, C_R/σ^2 of these crystals are compared to their experimental values deducted from the measured Morse potential parameters [7].

2. FORMALISM

For perfect crystals with using Eq. (1) the MSRD is given by

$$\sigma_j^2 = \left\langle \Delta_j^2 \right\rangle = 2u_j^2 - C_R. \tag{2}$$

Here the MSD function has been defined as

$$u_j^2 = \left\langle \left(\mathbf{u}_0 \cdot \hat{\mathbf{R}}_j^0 \right)^2 \right\rangle = \left\langle \left(\mathbf{u}_j \cdot \hat{\mathbf{R}}_j^0 \right)^2 \right\rangle \tag{3}$$

so that the DCF is given by

$$C_R = 2 \left\langle \left(\mathbf{u}_0 \cdot \hat{\mathbf{R}}_j^0 \right) \left(\mathbf{u}_j \cdot \hat{\mathbf{R}}_j^0 \right) \right\rangle = 2u_j^2 - \sigma_j^2. \tag{4}$$

It is clear that all atoms vibrate under influence of the neighboring environment. Taking into account the influences of the nearest atomic neighbors based on the anharmonic correlated Einstein model [4] the anharmonic effective interatomic potential for a singly vibrating atom is given by (ignoring the overall constant)

$$U_{eff}^o (x) = \sum_{j=1}^{8} U \left(x\hat{\mathbf{R}}_{01} \cdot \hat{\mathbf{R}}_{0j} \right) = \frac{1}{2} k_{eff}^o x^2 + k_3^o x^3 \quad , \tag{5}$$

or by using the definitions $y = x - a$, $x = r - r_0$, $a = \langle r - r_0 \rangle$ with r and r_0 as the instantaneous and equilibrium bond length of the absorber and backscatterer, respectively, we obtain the effective local force constant for singly vibrating atom in the form

$$U_{eff}^o (y) \cong \frac{1}{2} k_{eff}^o y^2 + k_3^o y^3, \quad k_{eff}^o = 2D\alpha^2 \left(\frac{8}{3} - 2\alpha\, a \right) = M_0 \omega_E^{02}, \quad k_3^o = -2D\alpha^3, \quad (6)$$

where M_0 is the central atomic mass; D and α are parameters of the Morse potential expanded to the third order about its minimum

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

Using Eqs. (5)–(7) we obtained the Einstein frequency ω_E^0 and temperature θ_E^0

$$\omega_E^0 = \left[2D\alpha^2 \left(\frac{8}{3} - 2\alpha\, a \right) / M_0 \right]^{1/2}, \;\; \theta_E^0 = \hbar\omega_E^0 / k_B, \tag{8}$$

where k_B is Boltzmann constant.

The atomic vibration is quantized as phonon, that is why we express y in terms of annihilation and creation operators, $\hat{a}$ and $\hat{a}^+$, i. e.,

$$y \equiv a_0 \left(\hat{a} + \hat{a}^+ \right) , \quad a_0^2 = \frac{\hbar\omega_E^0}{2k_{eff}^o}, \tag{9}$$

and use the harmonic oscillator state $|n\rangle$ as the eigenstate with the eigenvalue $E_n = n\hbar\omega_E^0$, ignoring the zero-point energy for convenience.

Using the quantum statistical method, where we have used the statistical density matrix Z and the unperturbed canonical partition function ρ_0

$$Z = Tr\rho_0 = \sum_n \exp\left(-n\beta\,\hbar\omega_E^0 \right) = \sum_{n=0}^{\infty} z_0^n = \frac{1}{1 - z_0}, \quad \beta = 1/k_B T, \quad z_0 = e^{-\theta_E^0/T}, \tag{10}$$

we determine the MSD function

$$\begin{aligned}
u^2 = \langle y^2 \rangle &\approx \tfrac{1}{Z} Tr\left(\rho_0 y^2 \right) = \tfrac{1}{Z} \sum_n \exp\left(-n\beta\,\hbar\omega_E^0 \right) \langle n| \, y^2 \, |n\rangle \\
&= 2a_0^2 \left(1 - z_0 \right) \sum_n \left(1 + n \right) z_0^n \ = \frac{\hbar\omega_E^0}{2k_{eff}^o} \frac{1+z_0}{1-z_0} = \frac{3\hbar\omega_E^0}{32D\alpha^2} \frac{1+z_0}{1-z_0} \\
&= u_0^2 \frac{1+z_0}{1-z_0}, \qquad u_0^2 = \frac{3\hbar\omega_E^0}{32D\alpha^2} \ .
\end{aligned} \tag{11}$$

In the crystal each atom vibrates in the relation to the others so that the correlation must be included. Based on quantum statistical theory with the correlated Einstein model [4] the anharmonic correlated vibrating interatomic effective potential and the correlated effective local force constant have been derived and they are given by

$$U_{eff}\left(y \right) \cong \frac{1}{2} k_{eff} y^2 + k_3 y^3 + \cdots , \quad k_{eff} = D\alpha^2 \left(\frac{11}{3} - \frac{15}{2}\alpha\, a \right) = \mu\omega_E^2, \ k_3 = -\frac{5}{4} D\alpha^3 , \tag{12}$$

so that the derived MSRD function for bcc crystals is resulted as

$$\sigma^2\left(T \right) = \frac{\hbar\omega_E}{2k_{eff}} \frac{1+z}{1-z} \ = \ \sigma_o^2 \frac{1+z}{1-z} \ , \quad \sigma_o^2 = \frac{3\hbar\omega_E}{22D\alpha^2} \ ; \ z = e^{-\theta_E/T}; \tag{13}$$

$$\omega_E = \sqrt{\frac{k_{eff}}{\mu}} = \left[\frac{D\alpha^2}{\mu} \left(\frac{11}{3} - \frac{15}{2}\alpha\, a \right) \right]^{\frac{1}{2}} ; \quad \mu = \frac{M_a M_s}{M_a + M_s}; \quad \theta_E = \frac{\hbar\omega_E}{k_B}, \tag{14}$$

where M_a and M_S are the masses of absorbing and backscattering atoms; and in Eqs. (11, 13) u_0^2, σ_0^2 are the zero point contributions to u^2 and to σ^2; ω_E, θ_E are the correlated Einstein frequency and temperature, respectively.

From the above results we obtained the DCF C_R, the ratios C_R/u^2 and C_R/σ^2

$$C_R = \frac{2u_0^2 \left(1 + z_0 \right)\left(1 - z \right) - \sigma_0^2 \left(1 - z_0 \right)\left(1 + z \right)}{\left(1 - z_0 \right)\left(1 - z \right)} \quad , \tag{15}$$

$$\frac{C_R}{u^2} = 2 - \frac{\sigma_0^2 \left(1 + z \right)\left(1 - z_0 \right)}{u_0^2 \left(1 - z \right)\left(1 + z_0 \right)}, \tag{16}$$

$$\frac{C_R}{\sigma^2} = \frac{2u_o^2 \left(1 + z \right)\left(1 - z_o \right) - \sigma_o^2 \left(1 - z_o \right)\left(1 + z \right)}{\sigma_o^2 \left(1 - z_o \right)\left(1 + z \right)}. \tag{17}$$

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

In the HT limit we use the approximation

$$z(z_0) \approx 1 - \hbar\omega_E \left(\omega_E^0\right)/k_B \tag{18}$$

to simplify the expressions of the thermodynamic parameters. In the LT limit $z(z_0) \Rightarrow 0$, so that we can neglect $z^2 \left(z_0^2\right)$ and higher power terms. The results for these limits are written in Table 1.

Table 1. *Expressions of u^2, σ^2, C_R, C_R/u^2, C_R/σ^2 in the LT and HT limits*

| Function	$T \to 0$	$T \to \infty$
u^2	$u_0^2 (1 + 2z_0)$	$3k_B T/16D\alpha^2$
σ^2	$\sigma_0^2 (1 + 2z)$	$3k_B T/11D\alpha^2$
C_R	$2u_0^2 (1 + 2z_0) - \sigma_0^2 (1 + 2z)$	$9k_B T/88D\alpha^2$
C_R/u^2	$2 - \sigma_0^2 (1 + 2z)/u_0^2 (1 + 2z_0)$	0.54
C_R/σ^2	$2u_o^2 (1 + 2z_o)/\sigma_o^2 (1 + 2z) - 1$	0.37

3. NUMERICAL RESULTS AND COMPARISON TO EXPERIMENT

Now we apply the expressions derived in the previous section to numerical calculations for bcc crystals Fe and W. The Morse potential parameters D and α of these crystals have been calculated by using our procedure presented in [8]. The calculated values of Morse potential parameters D, α, r_0, the effective local spring or force constants, the Einstein frequency and temperature k_{eff}^0, ω_E^0, θ_E^0 for singly vibrating atom and those of k_{eff}, ω_E, θ_E for correlated vibration are presented in Table 2. They show a good agreement of our calculated values with experiment [7]. The effective force constant, the Einstein frequency and temperature change significantly when the correlation is included. The calculated Morse potentials for Fe and W are illustrated in Figure 1 showing a good agreement with experiment [7]. Figure 2 demonstrates the anharmonic correlated effective potentials for Fe and W compared to experiment [7]. The anharmonic correlated effective potential, the anharmonic singly atomic vibration effective potential and their harmonic term are compared in Figure 3 showing their significant differences. Figure 4 presents the temperature dependence of the Debye-Waller factors described by MSRD $\sigma^2(T)$ and MSD $u^2(T)$. They agree well with experiment [7], contain zero-point contributions at low temperature as a quantum effect and are linearly proportional to temperature at high temperatures thus satisfying all their standard properties[10]. They also show that the displacement becomes greater ($\sigma^2 > u^2$) especially at high temperatures when the correlation is included. The temperature dependence of our calculated correlation function (DCF) C_R of Fe and W is illustrated in Figure 5 and their ratios with the MSD function u^2 and with the MSRD σ^2 in Figure 6. All they agree well with experiment [7]. The DCF is linearly proportional to the temperature at high-temperatures and contain zero-point

contributions at low-temperatures, the ratios C_R/u^2 and C_R/σ^2 increase fastly at low temperatures and approach constant values at high temperatures showing the same properties of these functions obtained by the Debye model [2, 11]. Hence, they show significant correlation effects contributing to the Debye-Waller factor in XAFS. Figure 5 and 6 show the importance of correlation effects described by C_R in the atomic vibration influencing on XAFS of bcc crystals.
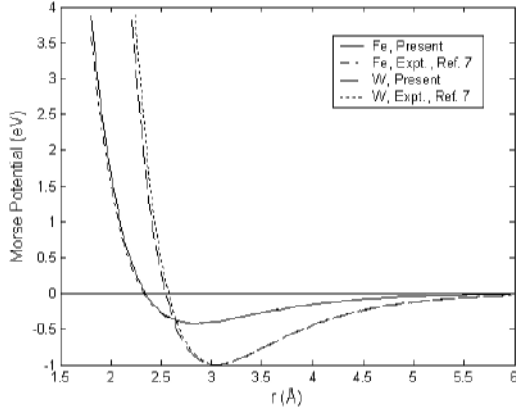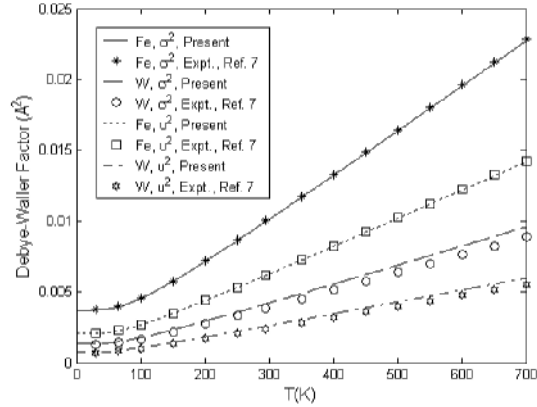

Fig. 1. Calculated Morse potential of Fe and W compared to experiment [7].
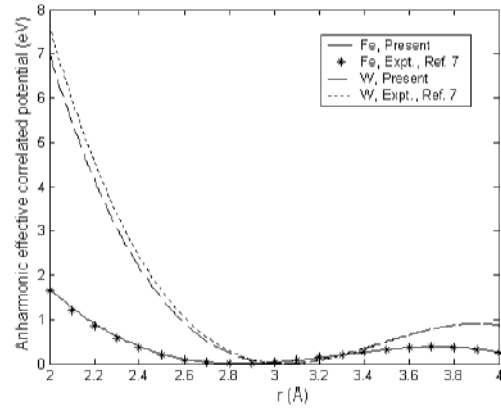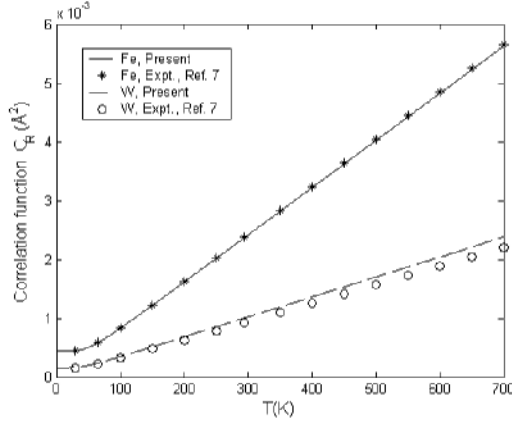

Fig. 2. Calculated anharmonic correlated effective potential for Fe and W compared to experiment [7].
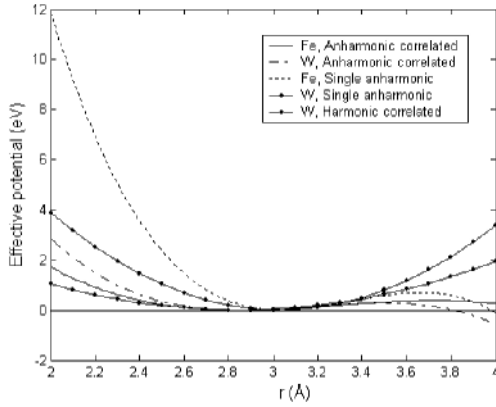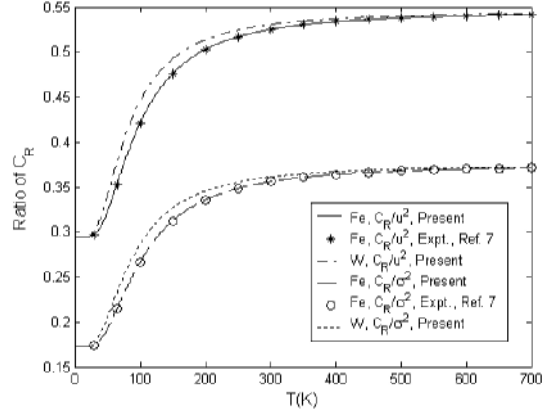

Fig. 3. Comparison between calculated effective potentials for Fe and W.

Fig. 4. Calculated σ^2, u^2 for Fe and W compared to experiment [7].

Fig. 5. Temperature dependence of the calculated DCF C_R of Fe and W compared to experiment [7].

Fig. 6. Temperature dependence of the calculated ratios C_R/u^2 and C_R/σ^2 for Fe and W compared to experiment [7].

Table 2. *Calculated values of D, α, r_o, k^o_{eff}, k_{eff}, ω^o_E, ω_E, θ^o_E, θ_E for Fe and W compared to experiment [7].*

Crystal	$D(eV)$	α	r_o	k^o_{eff} $(eV.\mathring{A}^{-2})$	k_{eff} $(eV.\mathring{A}^{-2})$	ω^o_E $(10^{13}Hz)$	ω_E $(10^{13}Hz)$	θ^o_E(K)	θ_E(K)
Fe, present	0.417	1.382	2.845	4.266	2.933	2.707	3.174	206.76	242.5
Fe, exp. [7]	0.420	1.380	2.831	4.266	2.933	2.707	3.174	206.76	242.5
W, present	0.992	1.412	3.035	10.548	7.252	2.346	2.751	175.77	210.1
W, exp. [7]	0.990	1.440	3.052	10.948	7.527	2.390	2.803	182.57	214.1

4. CONCLUSIONS

In this work a new procedure for studying anharmonic interatomic effective potential, effective local force constant and correlation effects in the atomic vibration of bcc crystals in XAFS has been developed.

Derived analytical expressions for C_R, u^2, σ^2 are linearly proportional to the temperature at high-temperatures and contain zero-point contributions at low temperatures. The displacement becomes greater when the correlation is included, especially at high temperatures. The ratios C_R/u^2 and C_R/σ^2 approach the constant values at high-temperatures showing the same properties obtained by the Debye model.

This model avoids full lattice dynamical calculations yet provides a good agreement with experiment thus denoting the simplicity and efficiency of the derived procedure for study of anharmonic effective potential, local force constant, Debye-Waller factor and correlation effects in XAFS theory.

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