

## PRESSURE DEPENDENCE OF EXAFS DEBYE-WALLER FACTORS IN CRYSTALS

VU VAN HUNG

*Hanoi National University of Education*

HO KHAC HIEU

*National University of Civil Engineering*

NGUYEN VAN HUNG

*Hanoi University of Science*

**Abstract.** *In present article the pressure dependence of Debye-Waller factors in crystals has been investigated by using statistical moment method and anharmonic correlated Einstein model. These two methods provide similar results which indicate that the Debye-Waller factors of crystals decreases slightly under high pressure. Our numerical results for several crystals are compared to other theoretical and experimental values and showed a good agreement.*

### I. INTRODUCTION

EXAFS (Extended X-ray Absorption Fine Structure) spectroscopy has become a powerful technique for determining local structures of noncrystalline as well as crystalline materials. It is of great interest in EXAFS procedure to characterize the local atomic environment of substances under the temperature  $T$  and pressure  $P$  dependence.

EXAFS data are analyzed by means of the cumulant expansion technique. In this formulation, an EXAFS oscillation function  $\chi(k)$  is given by [1]

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

where  $k$  and  $\lambda$  are the wave number and mean free path of emitted photoelectrons,  $F(k)$  is the real atomic backscattering amplitude,  $\phi(k)$  is the net phase shift, and  $\sigma^{(n)}$  ( $n = 1, 2, 3, \dots$ ) are the cumulants which can be extracted from experimental EXAFS data.

This EXAFS oscillation function Eq.(1) contains the second cumulant which is equal to the mean square relative displacement (MSRD) or Debye-Waller factor (DWF)  $\sigma^2$  accounting for the effects of the thermal vibrations of atoms.

The temperature dependence of DWF in crystals (metals, quantum crystals, ...) has been studied by many authors [1,5]. However, the researches on pressure dependence of DWF in crystals are still limited.

The purpose of this paper is to investigate the pressure dependence of DWF in crystals by using the anharmonic correlated Einstein model (ACEM) [5] and the statistical moment method (SMM) [6–9]. Numerical calculations have been carried out for metal Cu

(fcc), quantum crystal Kr (fcc) and semiconductor Si (dia). The calculated results are found to be in good agreement with the other theories [2–4] and experimental values [3, 4].

## II. FORMALISM

### II.1. Statistical Moment Method

We will derive the pressure versus volume relation of crystals limiting only quadratic terms in the atomic displacements. The pressure versus volume relation of lattice is given by [8, 9]

$$Pv = -a \left[ \frac{1}{3} \frac{\partial U_0}{\partial a} + \theta x \coth x \frac{1}{2k} \frac{\partial k}{\partial a} \right], \quad x = \frac{\hbar\omega}{2\theta}, \theta = k_B T, \quad (2)$$

where  $P$  denotes the hydrostatic pressure and  $v$  is the atomic volume  $v = \frac{V}{N}$  of a crystal having volume  $V$  and  $N$  atoms. Using Eq.(2) one can find the nearest neighbor distance  $a$  at pressure  $P$  and temperature  $T$ . However, for numerical calculations it is convenient to determine firstly the nearest neighbor distance  $a(P, 0)$  at pressure  $P$  and at absolute zero temperature  $T = 0K$ . For  $T = 0K$ , Eq.(2) is reduced to

$$Pv = -a \left[ \frac{1}{3} \frac{\partial U_0}{\partial a} + \frac{\hbar\omega_0}{4k} \frac{\partial k}{\partial a} \right]. \quad (3)$$

For simplicity, we take the effective pair interaction energy in crystal systems as the power law, similar to the Lennard-Jones potential

$$\phi(r) = \frac{D}{m-n} \left[ n \left( \frac{r_0}{r} \right)^m - m \left( \frac{r_0}{r} \right)^n \right], \quad (4)$$

where  $D$  and  $r_0$  are determined by fitting the experimental data (e.g., cohesive energy and elastic modulus). The potential parameters of some crystals are shown in Table 1 [10, 11].

Using the effective pair potential of Eq.(4), it is straightforward to get the interaction energy  $U_0$ , the quantity  $k$ , and the parameter  $\gamma$  in the crystal as

$$\begin{aligned} U_0 &= \frac{D}{n-m} \left[ mA_n \left( \frac{r_0}{a} \right)^n - nA_m \left( \frac{r_0}{a} \right)^m \right], \\ k &= \frac{1}{2} \sum_i \left( \frac{\partial^2 \phi}{\partial u_{i\beta}^2} \right) \\ &= \frac{Dnm}{2a^2(n-m)} \left[ (n+2) A_{n+4}^{a_{ix}^2} - A_{n+2} \right] \left( \frac{r_0}{a} \right)^n \\ &\quad - \frac{Dnm}{2a^2(n-m)} \left[ (m+2) A_{m+4}^{a_{ix}^2} - A_{m+2} \right] \left( \frac{r_0}{a} \right)^m \\ &= m_0 \omega_0^2, \end{aligned} \quad (5)$$

$$\gamma = \frac{Dnm}{12a^4(n-m)} \left[ \begin{array}{l} (n+2)(n+4)(n+6) \left( A_{n+8}^{a^4_{ix}} + 6A_{n+8}^{a^2_{ix}a^2_{iy}} \right) \\ -18(n+2)(n+4)A_{n+6}^{a^2_{ix}} + 9(n+2)A_{n+4} \end{array} \right] \left( \frac{r_0}{a} \right)^n$$

$$- \frac{Dnm}{12a^4(n-m)} \left[ \begin{array}{l} (m+2)(m+4)(m+6) \left( A_{m+8}^{a^4_{ix}} + 6A_{m+8}^{a^2_{ix}a^2_{iy}} \right) \\ -18(m+2)(m+4)A_{m+6}^{a^2_{ix}} + 9(m+2)A_{m+4} \end{array} \right] \left( \frac{r_0}{a} \right)^m, \quad (6)$$

where  $m_0$  is the mass of particle,  $\omega_0$  is the frequency of lattice vibration,  $A_n, A_m, A_n^{a^2_{ix}}, A_m^{a^2_{ix}}$  are the structural sums for the given crystal.

From Eqs. (3, 4, 5, 6) we obtain equation of state of crystals at zero temperature as

$$Pv = \frac{Dnm}{6(n-m)} \left[ n \left( \frac{r_0}{r} \right)^m - m \left( \frac{r_0}{r} \right)^n \right] + \frac{1}{a} \frac{\hbar}{4\sqrt{m_0}} \sqrt{\frac{Dnm}{2(n-m)}} \times \frac{\left\{ (n+2) \left[ (n+2)A_{n+4}^{a^2_{ix}} - A_{n+2} \right] \left( \frac{r_0}{a} \right)^n - (m+2) \left[ (m+2)A_{m+4}^{a^2_{ix}} - A_{m+2} \right] \left( \frac{r_0}{a} \right)^m \right\}}{\sqrt{\left[ (n+2)A_{n+4}^{a^2_{ix}} - A_{n+2} \right] \left( \frac{r_0}{a} \right)^n - \left[ (m+2)A_{m+4}^{a^2_{ix}} - A_{m+2} \right] \left( \frac{r_0}{a} \right)^m}} \quad (7)$$

Using Maple or Matlab program and the values of parameters  $D$  and  $r_0$  determined by the experimental data [10, 11] (Table 1), we found the values of the nearest neighbor distance  $a(P, 0)$  at  $T = 0K$  and pressure  $P$ . Using the obtained results of nearest neighbor distance  $a(P, T)$ , we found the values of parameters  $k(P, 0)$ ,  $\gamma(P, 0)$  at pressure  $P$  and  $T = 0K$ .

The thermally induced lattice expansion  $y_0(P, T)$  at pressure  $P$  and temperature  $T$  is given in the below formula using the force balance criterion of the fourth order moment approximation as [6, 9]

$$y_0(P, T) = \sqrt{\frac{2\gamma(P, 0)\theta^2}{3k^3(P, 0)}} A(P, 0), \quad (8)$$

where

$$A(P, T) = a_1 + \frac{\gamma(P, 0)^2 \theta^2}{k(P, 0)^4} a_2 + \frac{\gamma^3(P, 0) \theta^3}{k(P, 0)^6} a_3 + \frac{\gamma(P, 0)^4 \theta^4}{k(P, 0)^8} a_4, \quad (9)$$

$$a_1 = 1 + \frac{x \coth(x)}{2}, a_2 = \frac{13}{3} + \frac{47}{6}x \coth(x) + \frac{23}{6}x^2 \coth^2(x) + \frac{1}{2}x^3 \coth^3(x),$$

$$a_3 = - \left[ \frac{25}{3} + \frac{121}{6}x \coth(x) + \frac{50}{3}x^2 \coth^2(x) + \frac{16}{3}x^3 \coth^3(x) + \frac{1}{2}x^4 \coth^4(x) \right],$$

$$a_4 = \frac{43}{3} + \frac{93}{2}x \coth(x) + \frac{169}{3}x^2 \coth^2(x) + \frac{83}{3}x^3 \coth^3(x) + \frac{22}{3}x^4 \coth^4(x) + \frac{1}{2}x^5 \coth^5(x),$$

$$x = \frac{\hbar\omega(P, 0)}{2\theta}; \omega(P, 0) = \sqrt{\frac{k(P, 0)}{m_0}}; \theta = k_B T.$$

Then, one can find the nearest neighbor distance  $a(P, T)$  at pressure  $P$  and temperature  $T$  as

$$a(P, T) = a(P, 0) + y_0(P, T). \quad (10)$$

The parallel mean square relative displacement (MSRD) to a good approximation corresponds to the second cumulant:

$$\sigma^2 = \left\langle \left[ \vec{R} \cdot (\vec{u}_i - \vec{u}_0) \right]^2 \right\rangle = \langle u_i^2 \rangle + \langle u_0^2 \rangle - 2 \langle u_i u_0 \rangle. \quad (11)$$

The first two terms on the right-hand side are the uncorrelated mean square displacement (MSD), while the third term is the parallel displacement correlation function (DCF).

Using the expression of the second order moment [9], we obtain the MSD

$$\langle u_i^2 \rangle = \langle u_i \rangle^2 + \theta A_1 + \frac{\theta}{k} (x \coth x - 1), \quad (12)$$

where

$$A_1 = \frac{1}{k} \left[ 1 + \frac{2\gamma^2}{k^4} \left( 1 + \frac{x \coth x}{2} \right) (x \coth x + 1) \right], \quad (13)$$

$$\langle u_i u_0 \rangle \approx \langle u_i \rangle \langle u_0 \rangle, \quad \langle u_i^2 \rangle \approx \langle u_0^2 \rangle.$$

From Eqs. (5, 6, 8, 10) we derive the second cumulant of crystals at pressure  $P$  and temperature  $T$  as

$$\sigma^2(P, T) \approx \frac{4\gamma(P, 0)^2 \theta^3}{k(P, 0)^5} \left( 1 + \frac{x \coth x}{2} \right) (x \coth x + 1) + \frac{2\theta}{k(P, 0)} x \coth x \quad (14)$$

## II.2. Anharmonic Correlated Einstein Model

The anharmonic correlated Einstein model [5] is now widely used in EXAFS data analysis [1]. In the present approach we apply this theory to the calculation of the cumulants where the effective interaction potential is given by

$$\phi_{eff}(x) \approx \frac{1}{2} k_{eff} x^2 + k_3 x^3 + \dots = \phi(x) + \sum_{j \neq i} \phi \left( \frac{\mu}{M_i} \cdot \hat{R}_{12} \hat{R}_{ij} \right) \quad (15)$$

where  $x$  is the deviation of instantaneous bond length between two atoms from equilibrium,  $k_{eff}$  is the effective spring constant, and  $k_3$  is the cubic anharmonicity parameter and  $\hat{R}$  is the bond unit vector. The correlated Einstein model may be defined as an oscillation of a pair of atoms with masses  $M_1$  and  $M_2$  (e.g., absorber and backscatterer) in a given system. Their oscillation is influenced by their neighbors given by the last term in the left-hand side of Eq.(12), where the sum  $i$  is over absorber ( $i = 1$ ) and backscattering atom ( $i = 2$ ), and the sum  $j$  is over all their nearest neighbors, excluding the absorber and backscatterer themselves whose contributions are described by the term  $\phi(x)$ .

For the calculation of thermodynamic parameters, we use the further definition  $x = r - r_0$ ,  $a = \langle r - r_0 \rangle$  and  $y = x - a$  [1, 5] as the deviation from the equilibrium value

of  $x$  at temperature  $T$  to rewrite Eq. (15) in the  $y$ -dependence as

$$\varphi_{eff}(y) = \frac{1}{2}k_{eff}y^2 + \delta\varphi_{eff}(y), \quad (16)$$

where  $\delta\varphi_{eff}(y)$  is the anharmonic contribution of the effective pair potential.

By using quantum statistical method we derived the 2<sup>nd</sup> cumulant or DWF of crystals as

$$\sigma^2 = \sigma_0^2 \frac{1+z}{1-z}, \quad \sigma_0^2 = \frac{\hbar\omega_E}{2k_{eff}}, \quad (17)$$

where  $\sigma_0^2$  is zero-point contribution to  $\sigma^2$ ,  $k_B$  is the Boltzmann constant and

$$\omega_E = \sqrt{\frac{k_{eff}}{\mu}}, \quad \mu = \frac{M_1 M_2}{M_1 + M_2}, \quad z = \exp(\theta_E/T), \quad \theta_E = \frac{\hbar\omega_E}{k_B}.$$

To build the pressure dependence of DWF expressions of crystals we start with the definition of the Gruneisen parameter  $\gamma_G$

$$\gamma_G = -\frac{\partial \ln \omega_E}{\partial \ln V}. \quad (18)$$

This parameter  $\gamma_G$  depends on volume which, in turn, depends on pressure. With a slight modification of a formula found in Refs. [12, 13], the simplest parametrization of the volume dependence for crystals can be written as

$$\frac{\gamma_G(V(P))}{V(P)} = \frac{\gamma_G(V_0)}{V_0} = const, \quad (19)$$

where the subscript 0 indicates zero pressure. Integration of Eq. (18) and using Eq. (19) we obtained the Einstein frequency at pressure  $P$  and temperature  $T$  as

$$\omega_E(V(P)) = \omega_E(V_0) \exp \left\{ \gamma_G(V_0) \left[ 1 - \frac{V(P)}{V_0} \right] \right\}, \quad \frac{V(P)}{V_0} = \frac{a^3(P, T)}{a^3(0, 0)}. \quad (20)$$

This fraction can be calculated by using any appropriate isothermal equation of state. For simplicity, we used the data of  $a(P, T)$  derived from SMM to calculate this fraction.

Using the above results, we obtain the pressure dependence of the effective spring constant expression as

$$k_{eff}(V(P)) = \mu\omega_E^2(V(P)). \quad (21)$$

Eqs. (20, 21) are then inserted into those of the ACEM which express the EXAFS DWF in crystals as a function of pressure

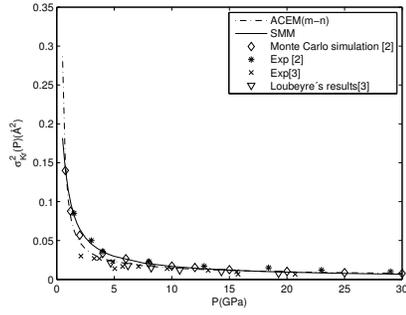
$$\sigma^2(P, T) = \frac{\hbar\omega_E(V(P))}{2k_{eff}(V(P))} \frac{1 + \exp[-\beta\hbar\omega_E(V(P))]}{1 - \exp[-\beta\hbar\omega_E(V(P))]}; \quad \beta = 1/k_B T. \quad (22)$$

### III. DISCUSSION OF NUMERICAL RESULTS

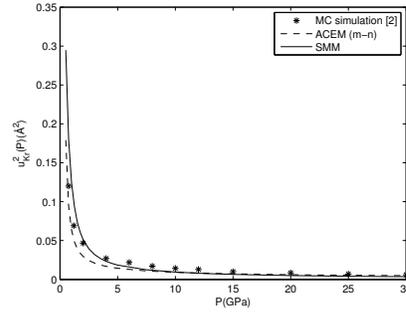
Now we apply the expressions derived in previous section to numerical calculations for metal crystal (Cu), quantum crystal (Kr) and semiconductor crystal (Si). The m-n potential parameters of Cu, Kr, and Si have been listed in Table 1 and the Morse potential parameters of Cu are  $D = 0.3429eV$ ,  $\alpha = 1.3588\text{\AA}^{-1}$  [14]. They will be used for further calculations.

**Table 1:** Lennard-Jones potential parameters  $D$  and  $r_0$  for Cu, Kr and Si.

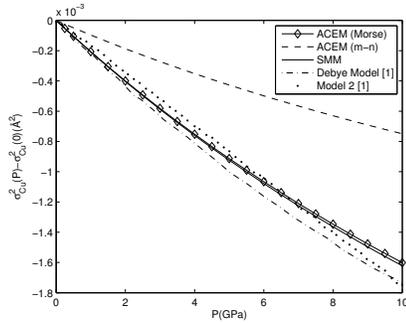
Crystal	m	n	$r_0$ ( $\text{\AA}$ )	$D/k_B$ (K)
Cu	5.5	9.0	2.5487	4125.7
Kr	6.63	16.42	3.993	237.16
Si	6.0	12.0	2.2950	3269.1



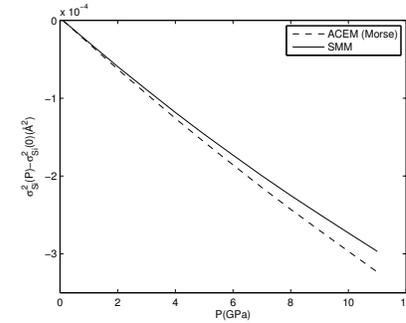
**Fig. 1.** The pressure dependence of DWF of Kr



**Fig. 2.** The pressure dependence of MSD of Kr



**Fig. 3.** The pressure dependence of DWF of Cu



**Fig. 4.** The pressure dependence of DWF of Si

Fig. 1 shows the pressure dependence of our calculated second cumulant or DWF of Kr crystal compared to those calculated by Monte-Carlo simulation [2] and Loubeyre [3] as well as to the experimental values [3,4]. The pressure dependence of our calculated MSD of Kr crystal is presented in Fig. 2 in comparison to Monte-Carlo simulation result [3]. It is shown that our calculated MSD and MSD are found to be in good agreement with

the experimental values [3,4] and with the other theoretical results [3,4]. Fig. 3 presents the pressure dependence of the second cumulant or DWF of Cu crystal, calculated using the SMM and ACEM with Lennard-Jones and Morse interaction potentials, respectively. The calculated results of both methods are found to be in good agreement with those of Debye model [2] and the model for calculation of the moments of the nearest neighbor distance distribution from an expansion to third order of the potential energy [2]. Fig. 3 shows that the SMM values are considerably higher those calculated using the ACEM with the Lennard-Jones potential. It indicates that the Morse potential is the best choice for Cu crystal when using ACEM to investigate the thermodynamic properties of Cu. Fig. 4 shows the pressure dependence of the DWF of Si crystal calculated using SMM with Lennard-Jones potential.

#### IV. CONCLUSIONS

In this work a formalism for the statistical moment method and the anharmonic correlated Einstein model using Lennard-Jones and Morse potentials to investigate the pressure dependence of EXAFS Debye-Waller factors has been developed. Our new development is the derivation of analytical expressions of the pressure dependence of EXAFS second cumulant or Debye-Waller factors in crystals and carrying out numerical calculations for Cu, Kr, Si.

The good agreement of our calculated results using these two methods as well as their agreement with experimental and other theories values shows the advantage and efficiency of these theoretical for the calculation and analysis of the pressure dependent cumulants and other parameters of anharmonic EXAFS of crystals.

#### ACKNOWLEDGEMENTS

This work is supported by the research projects No. 103.01.09.09 and No. 103.01.26.09 of NAFOSTED.

#### REFERENCES

- [1] N. V. Hung, N. B. Duc, and R. R. Frahm, *J. Phys. Soc. Jpn.* **72** (2003) 1254.
- [2] J. Freund, R. Ingalls, and E. D. Crozier, *Phys. Rev. B* **39** (1989) 12537.
- [3] A. Di Cicco, A. Filipponi, J. P. Itie and A. Polian, *Phys. Rev. B* **54** (1996) 9086.
- [4] A. Polian, J. P. Itie, E. Daartyge, A. Fontaine, G. Tourillon, *Phys. Rev. B* **39** (1989) 3369.
- [5] N. V. Hung and J. J. Rehr, *Phys. Rev. B* **56** (1997) 43.
- [6] V. V. Hung and K. Masuda-Jindo, *J. Phys. Soc. Jpn.* **69** (2000) 2067-2075.
- [7] V. V. Hung, K. Masuda-Jindo, P. T. M. Hanh, and N. T. Hai, *J. Phys.* **98** (2008) 032001.
- [8] R. B. Capaz, G. C. de AraDujo, B. Koiller, J. P. von der Weid, *J. Appl. Phys.* **74** (1993) 5531.
- [9] N. Tang and V. V. Hung, *Physica Status Solidi B* **149** (1988) 511.
- [10] K. Masuda-Jindo, V. V. Hung, and P. D. Tam, *Phys. Rev. B* **67** (2003) 094301.
- [11] Erkoç S., *Phys. Reports*, **278** (2) (1997) 81-88.
- [12] J. Ramakrishnan, R. Boehler, G. H. Higgins, and G. C. Kennedy, *J. Geophys. Res.* **83** (1978) 3535.
- [13] U. Walzer, W. Ullmann, and V. L. Pan'kov, *Phys. Earth Planet. Inter.* **18** (1979) 1.
- [14] L. A. Girifalco, V. G. Weizer, *Phys. Rev.* **114** (1959) 687.

*Received 30 September 2009.*