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DEBYE-WALLER FACTOR AND CORRELATION EFFECTS IN XAFS OF CUBIC CRYSTALS

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Abstract. *Analytical expressions for the 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 cubic (fcc, 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 calculations have been carried out for u^2, σ^2, and C_R functions of Cu (fcc) and W (bcc). The ratio C_R/u^2 is about 40% for fcc and 54% for bcc at high temperatures. They are found to be in good agreement with experiment and with those calculated by the Debye model.*

I. INTRODUCTION

It is of great interest in XAFS procedure to characterize the local atomic environment of the substances, i.e., we would in principle like to determine the position, type, and number of the central atoms and their neighbors in a cluster and to determine such interesting properties as the relative vibrational amplitudes and spring constants of these atoms. 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]

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

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

This XAFS function (1) contains the thermaly averaging value $\langle e^{i2k\Delta_j}\rangle$ leading to the Debye-Waller factor $DWF = e^{-2k^2\sigma_j^2}$. Since this factor is meant to account for the thermal vibrations of the atoms about their equilibrium sites $\mathbf{R}_j^0$, one usually assumes that the quantity σ_j^2 is identical with the MSD [1]. But the oscillatory motion of nearby atoms is relative. Hence, including the correlation effect in the atomic vibration is necessary [2-9]. In this case σ_j^2 is the MSRD containing the MSD and DCF.

The pupose of this work is to study the correllation effects in atomic vibrations of cubic crystals in XAFS, i.e., to develop a new procedure for calculation of the DCF (C_R) for atomic vibration in the cubic crystals (fcc, bcc) in XAFS. Expression for the MSD (u^2) has been derived. Using it and the MSRD (σ^2) we derive C_R. The effective interaction potential of the system has been considered by taking into account the influences of the nearest atomic neighbors based on the anharmonic correlated Einstein model [3]. This potential contains the Morse potential characterizing the interaction of each pair of atoms. Numerical calculations have been carried out for Cu (fcc) and W (bcc). The calculated u^2, σ^2, C_R functions and the ratio $C_R/u^2, C_R/\sigma^2$ of these crystals are found to be in good agreement with those calculated by the Debye model [2] and with experiment [6, 7, 9].

II. FORMALISM

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

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

Here we defined the MSD function as

$$u_j^2 = \langle(\mathrm{u}_0.\hat{\mathrm{R}}_j^0)^2\rangle = \langle(\mathrm{u}_j.\hat{\mathrm{R}}_j^0)^2\rangle \tag{3}$$

and the DCF

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

It is clear that all atoms vibrate under influence of the neighboring environment. Taking into account the influences of the nearest atomic neighbors the Einstein effective interatomic potential for single vibrating atom is given by (ignoring the overall constant)

$$U^o_{eff}(x) = \sum_{j=1}^{N} U(x\hat{\mathrm{R}}_{01}.\hat{\mathrm{R}}_{0j});\, N = \begin{cases} 12, & for\ fcc, \\ 8, & for\ bcc, \end{cases} \tag{5}$$

$$U^o_{eff}(y) = \frac{1}{2}k^o_{eff}y^2,\, k^o_{eff} = D\alpha^2(S_0 - 4\alpha a) = M_0\omega_E^{02}, \tag{6}$$

where M_0 is the central atomic mass; D and α are the parameters of the Morse potential

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

and the other parameters have been defined as follows

$$y = x - a,\, x = r - r_0,\, a = < r - r_0 >,\, S_0 = \begin{cases} 8, & \text{for fcc} \\ 16/3, & \text{for bcc} \end{cases} \tag{8}$$

with r and r_0 as the instantaneous and equilibrium bond length of absorber and backscatterer.

Using Eqs. (5 - 8) we obtained the Einstein frequency ω_E^0 and temperature θ_E^0

$$\omega_E^0 = [D\alpha^2(S_0 - 4\alpha a)/M_0]^{1/2},\, \theta_E^0 = \hbar\omega_E^0/k_B, \tag{9}$$

where k_B is Boltzmann constant.

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

$$y \equiv a_0 = (\hat{a} + \hat{a}^+),\, a_0^2 = \frac{\hbar\omega_E^0}{2k^o_{eff}}, \tag{10}$$

and use the harmonic oscilator state $|n\rangle$ as the eigenstate with the eigenvalue $E_n = n\hbar\omega$ 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

$$Z = Tr\rho_0 = \sum_n \exp(-n\beta\hbar\omega_E^0) = \sum_{n=0}^{\infty} z_0^n = \frac{1}{1-z_0}, \beta = 1/k_BT, z_0 = e^{-\theta_E^0/T}, \tag{11}$$

we determined the MSD function

$$\begin{aligned} u^2 = \langle y^2 \rangle &\approx \frac{1}{Z}\sum_n \exp(-n\beta\hbar\omega_E^0)\langle n|y^2|n\rangle \\ &= 2a_0^2(1-z_0)\sum_n (1+n)z_0^n = \frac{\hbar\omega_E^0}{2k_{eff}}\frac{1+z_0}{1-z_0} = \frac{\hbar\omega_E^0}{2S_0D\alpha^2}\frac{1+z_0}{1-z_0} \\ &= u_0^2\frac{1+z_0}{1-z_0}, \quad u_0^2 = \frac{\hbar\omega_E^0}{2S_0D\alpha^2}. \end{aligned} \tag{12}$$

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 [3] the MSRD function for fcc and bcc crystals has been calculated and is given by

$$\sigma^2(T) = \sigma_0^2\frac{1+z}{1-z}, \quad \sigma_0^2 = \frac{\hbar\omega_E}{2SD\alpha^2}; \ z = e^{-\theta_E/T}; \ S = \begin{cases} 5, & \text{for fcc} \\ 11/3, & \text{for bcc} \end{cases}, \tag{13}$$

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

where M_a and M_s are the masses of absorbing and backscattering atoms; and in Eqs. (12), (13) , u_0^2, σ_0^2 are the zero point contributions to u^2 and σ^2; ω_E, θ_E are the correlated Einstein frequency and temperature, respectively; S, S_0 are the structural parameters [8].

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

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

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

$$\frac{C_R}{\sigma^2} = \frac{2u_0^2(1+z)(1-z_0) - \sigma_0^2(1-z_0)(1+z)}{\sigma_0^2(1-z_0)(1+z)}, \tag{17}$$

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.

In the HT limit we use the approximation

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

to simplify the expressions of the thermodynamic parameters. In the LT limit $z(z_0) \Rightarrow 0$, so that we can neglect $z^2(z_0^2)$ and higher power terms. The results of 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	$T << 0_E$	$T >> 0_E$
u^2	$u_0^2(1+2z_0)$	$k_BT/S_0D\alpha^2$
σ^2	$\sigma_0^2(1+2z)$	$k_BT/SD\alpha^2$
C_R	$2u_0^2(1+2z_0)-\sigma_0^2(1+2z)$	$(2S-S_0)k_BT/SS_0D\alpha^2$
$\frac{C_R}{u^2}$	$2-\frac{\sigma_0^2(1+2z)}{u_0^2(1+2z_0)}$	$2-\frac{S_0}{S}=\begin{cases}0.04, & \text{fcc}\\ 0.54 & \text{bcc}\end{cases}$
$\frac{C_R}{\sigma^2}$	$2\frac{u_0^2(1+2z_0)}{\sigma_0^2(1+2z)}-1$	$\frac{2S-S_0}{S_0}=\begin{cases}0.25, & \text{fcc}\\ 0.37 & \text{bcc}\end{cases}$

III. NUMERICAL RESULTS

Now we apply the expressions derived in the previous section to numerical calculations for Cu (fcc) and W (bcc). The Morse potential parameters D and α of these crystals have been calculated by using the procedure presented in [11]. The calculated values of D, α, r_0, k^0_{eff}, k_{eff}, ω^0_E, ω_E, θ^0_E, θ_E are presented in Table 2. They show a good agreement of our calculated values with experiment [6, 7] and with those calculated by another procedure [12]. The effective spring constants, the Einstein frequencies and temperatures change significantly when the correlation is included. The calculated Morse potentials compared to experiment [6] for Cu and [7] for W are illustrated in Fig. 1 showing a good agreement with experiment. Fig. 2 shows temperature dependence of the calculated MSRD σ^2 of Cu and W compared to their MSD u^2. The MSRD are greater than the MSD, especially at high temperature. The temperature dependence of our calculated correlation function (DCF) C_R of Cu and W is illustrated in Fig. 3 and their ratio with the MSD function u^2 in Fig. 4. All they agree well with experiment [6, 7]. The MSRD, MSD and DCF are linearly proportional to the temperature at high-temperatures and contain zero-point contributions at low-temperatures showing the same properties of these functions obtained by the Debye model [2] and satisfying all standard properties of these quantities [10]. Hence, they show the significance of the correlation effects contributing to the Debye-Waller factor in XAFS. Fig. 4 shows the significance of the correlation effects described by C_R in the atomic vibration influencing on XAFS. At high temperatures it is about 40

Table 2. *Calculated values of* D, α, r_0, k^0_{eff}, ω^0_E, ω_E *for Cu (fcc) and W (bcc) compared to experiment [6, 7] and to those of the other precedure [12]*

Crystal	D (eV)	α (Å^{-1})	r_0 (Å)	k^0_{eff} (N/m)	k_{eff} (N/m)	ω^0_E (10^{13} Hz)	ω_E (10^{13} Hz)	θ^0_E (K)	θ_E (K)
Cu, present	0.337	0.358	2.868	79.66	49.789	2.739	3.063	209.25	233.95
Cu, exp. [6]	0.330	1.380	2.862		50.345		3.082		235.26
Cu, [12]	0.343	1.359	2.866	81.20	50.748	2.766	3.092	211.26	236.20
W, present	0.992	1.411	3.035	168.8	116.03	2.344	2.748	179.01	209.98
W, exp. [7]	0.990	1.440	3.052		120.60		2.803		214.08
W, [12]	0.991	1.412	3.032	168.8	116.07	2.345	2.749	179.11	210.02

for fcc and 54% for bcc crystals that is the same conclusion resulted by the Debye model. Table 1 shows that the ratio C_R/σ^2 is 25% for fcc and 37% for bcc at high temperatures.

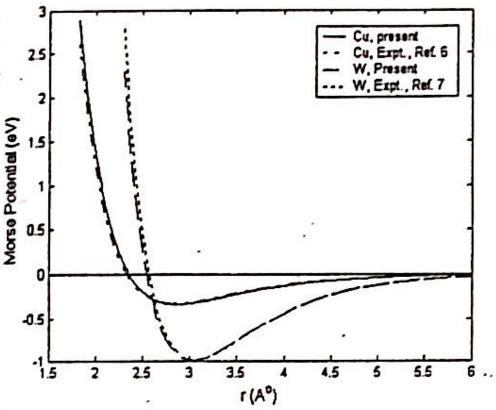

Fig. 1. Calculated Morse potential of Cu and W compared to experiment [6,7]

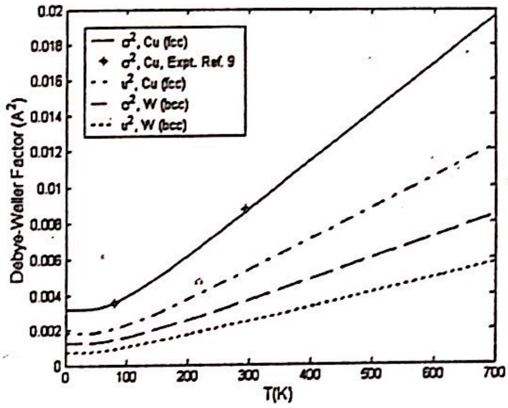

Fig. 2. Temperature dependence of the calculated σ^2, u^2 for Cu and W compared to experiment [9]

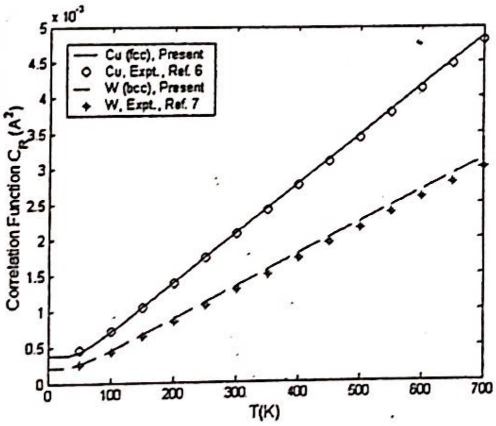

Fig. 3. Temperature dependence of the calculated DCF C_R of Cu and W compared to experiment [6,7]

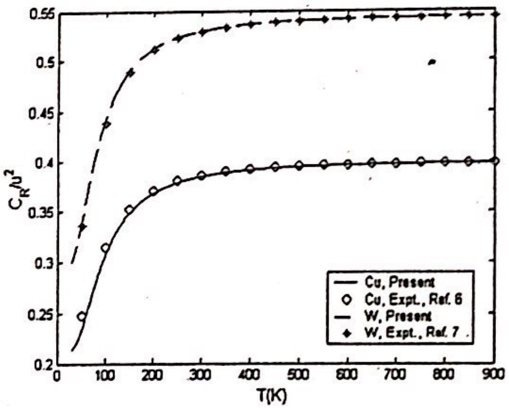

Fig. 4. Temperature dependence of the calculated ratio C_R/u^2 for Cu and W compared to experiment [6,7]

IV. CONCLUSSIONS

In this work a new procedure for studying Debye-Waller factor and correlation effects in the atomic vibration of cubic (fcc, bcc) crytals in XAFS has been developed.

Derived functions C_R, u^2, σ^2 are linearly proportional to temperature at high-temperatures and contain zero-point contributions at low temperatures. The ratio C_R/u^2 accounts for 40% for fcc and 53% for bcc crystals, the ratio C_R/σ^2 is 25% for fcc and 37% for bcc at high-temperatures showing the significance of correlation effects in the atomic vibration of crystals.

Good agreement of our calculated functions with experiment and with those obtained by the Debye model denotes a new procedure for study of Debye–Waller and of the atomic correlated vibration in XAFS theory.

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REFERENCES

[1] C. A. Ashley and S. Doniach, *Phys. Rev. B* **10** (1975) 3027.
[2] G. Beni and P. M. Platzman, *Phys. Rev. B* **14** (1976) 1514.
[3] N. V. Hung and J. J. Rehr, *Phys. Rev. B* **56** (1997) 43.
[4] N. V. Hung, N. B. Duc, and R. R. Frahm, *J. Phys. Soc. Jpn.*, **72** (2003) 1254.
[5] M. Daniel, D. M. Pease, N. V. Hung, and J. I. Budnick, *Phys. Rev. B* **69** (2004) 134414.
[6] I. V. Pirog and T. I. Nedoseikina, *Physica B* **334** (2003) 123.
[7] I. V. Pirog, T. I. Nedoseikina, I. A. Zarubin, and A. T. Shuvaev, *J. Phys.: Condens. Matter*, **14** (2002) 1825.
[8] N. V. Hung, N. B. Duc, and D. Q. Vuong, *Comm. in Phys.* **11** (2001) 1.
[9] T. Yokoyama, T. Satsukawa, and T. Ohta, *Jpn. J. Appl. Phys.*, **28** (1989) 1905.
[10] J. M. Ziman, *Principle of the Theory of Solids*, 2nd ed. by Cambrige University Press, 1972.
[11] N. V. Hung, *Comm. in Phys.* **14** (2004) 7.
[12] L. A. Girifalco and V. G. Weizer, *Phys. Rev.*, **114** (1959) 687.