# CORRELATION EFFECTS IN ATOMIC THERMAL VIBRATION OF FCC CRYSTALS

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Abstract: Analytical expression for the Displacement-displacement Correlation Function (DCF) $C_R$ has been derived based on the derived Mean Square Relative Displacement (MSRD) $\sigma^2$ and the Mean Square Displacement (MSD) $u^2$ for fcc crystals. The effective interaction 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 $u^2, \sigma^2$ and $C_R$ functions of Cu and Ni. The ratio $C_R/u^2$ is 40% and $C_R/\sigma^2$ 25% at high temperatures. They are found to be in good agreement with experiment and with those calculated by the Debye model.

## 1. Introduction

In the X-ray Absorption Fine Structure (XAFS) procedure it is of great interest to characterize the local atomic environment of the substances as completely as possible, 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. The photoelectron emitted from the absorber in the XAFS process is transferred and scattered in this atomic vibrating environment. Therefore, in all treatments of XAFS the effect of this vibrational smearing has been included in the XAFS function [1]

$$\chi(k) \sim \sum_j F_j(k) e^{-2R_j/\lambda(k)} \mathrm{Im}\left\{ e^{i\Phi_j(k)} \left\langle e^{i2kR_j} \right\rangle \right\}, \qquad (1)$$

where $F(k)$ is the real atomic backscattering amplitude, $\Phi$ is the net phase shift, $k, \lambda$ are the wave number and the mean free path of the photoelectron, respectively. This function contains the averaging value $\left\langle e^{i2kR_j} \right\rangle$ 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 $\sigma_j^2$ is identical with the MSD [2]. But the oscillatory motion of nearby atoms is relative and including the correlation effect is necessary [1, 3-9]. In this case $\sigma_j^2$ is the MSRD containing the MSD and DCF.

The purpose of this work is to study the correlation effects in atomic vibrations of fcc crystals in XAFS, i.e., to develop a new procedure for calculation of the DCF ($C_R$) for atomic vibration in the fcc crystals. Expression for the MSD ($u^2$) has been derived. Using it and the MSRD ($\sigma^2$) 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 [4]. This potential contains the Morse potential characterizing the interaction of each pair of atoms. Numerical calculations have been carried out for Cu and Ni. The calculated $u^2, \sigma^2, C_R$ functions and the ratio $C_R/u^2$, $C_R/\sigma^2$ of these crystals are analysed. They are found to be in good agreement with those calculated by the Debye model [3] and with experiment [7-9].

## 2. Formalism

For the purpose of this investigation it is better to rewrite the XAFS function Eq. (1) in the form [2]

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

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

To valuate Eq. (2) we make use of the well-known relation [11]

$$\left\langle e^{2ik\Delta_j} \right\rangle = e^{-2k^2\left\langle \Delta_j^2 \right\rangle} = e^{-2k^2\sigma_j^2} \tag{3}$$

and obtain

$$\chi = \chi_0 e^{-2k^2\sigma^2}, \tag{4}$$

so that the thermal vibration effect in XAFS is defined by $\sigma^2$.

For perfect crystals with using Eq. (2) the MSRD is given by

$$\sigma_j^2 = \left\langle \Delta_j^2 \right\rangle = 2u_j^2 - C_R. \tag{5}$$

Here we defined the MSD function as

$$u_j^2 = \left\langle \left(\mathbf{u}_0 \cdot \hat{\mathbf{R}}_j^0\right)^2 \right\rangle = \left\langle \left(\mathbf{u}_j \cdot \hat{\mathbf{R}}_j^0\right)^2 \right\rangle \tag{6}$$

and the DCF

$$C_R = 2\left\langle \left(\mathbf{u}_0 \cdot \hat{\mathbf{R}}_j^0\right)\left(\mathbf{u}_j \cdot \hat{\mathbf{R}}_j^0\right) \right\rangle = 2u_j^2 - \sigma_j^2. \tag{7}$$

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 interaction potential for single vibrating atom is given by (ignoring the overall constant)

$$U^o_{eff}(x)=\sum_{j=1}^{N}U\left(x\hat{\mathbf{R}}_{01}\cdot\hat{\mathbf{R}}_{0j}\right);\qquad N=12\,, \tag{8}$$

$$U^o_{eff}(y)=\frac{1}{2}k^o_{eff}y^2\,,\ k^o_{eff}=4D\alpha^2(2-\alpha\, a)=M_0\omega_0^2\,, \tag{9}$$

where $M_0$ is the central atomic mass; $D$ and $\alpha$ are the parameters of the Morse potential

$$U(x)=D\left(e^{-2\alpha x}-2e^{-\alpha x}\right)\cong D\left(-1+\alpha^2x^2-\alpha^3x^3+\cdots\right), \tag{10}$$

and the other parameters have been defined as follows

$$y=x-a\,,\ x=r-r_0\,,\ a=\langle r-r_0\rangle\,, \tag{11}$$

with $r$ and $r_0$ as the instantaneous and equilibrium bond length between absorber and backscatterer, respectively.

Using Eqs. (8-11) we obtained the Einstein frequency $\omega^0_E$ and temperature $\theta^0_E$

$$\omega^0_E=2\left[D\alpha^2(2-\alpha\, a)/M_0\right]^{1/2},\ \theta^0_E=\hbar\omega^0_E/k_B\,, \tag{12}$$

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.,

$$y\equiv a_0\left(\hat{a}+\hat{a}^+\right),\ a_0^2=\frac{\hbar\omega^0_E}{2k^o_{eff}}\,, \tag{13}$$

and use the harmonic oscilator state $|n\rangle$ as the eigenstate with the eigenvalue $E_n=n\hbar\omega^0_E$, 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 $\rho_0$

$$Z=Tr\rho_0=\sum_n\exp\left(-n\beta\hbar\omega^0_E\right)=\sum_{n=0}^{\infty}z_0^n=\frac{1}{1-z_0},\ \beta=1/k_BT\,,\ z_0=e^{-\theta^0_E/T}\,, \tag{14}$$

we determined the MSD function

$$\begin{aligned}u^2=\langle y^2\rangle&\approx\frac{1}{Z}Tr\left(\rho_0y^2\right)=\frac{1}{Z}\sum_n\exp\left(-n\beta\hbar\omega^0_E\right)\langle n|y^2|n\rangle=\\&=2a_0^2(1-z_0)\sum_n(1+n)z_0^n=\frac{\hbar\omega^0_E}{2k_{eff}}\frac{1+z_0}{1-z_0}=\frac{\hbar\omega^0_E}{16D\alpha^2}\frac{1+z_0}{1-z_0}=\\&=u_0^2\frac{1+z_0}{1-z_0},\qquad u_0^2=\frac{\hbar\omega^0_E}{16D\alpha^2}\ .\end{aligned} \tag{15}$$

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 MSRD function for fcc crystals has been calculated and is given by

$$\sigma^2(T) = \sigma_o^2 \frac{1+z}{1-z}, \quad \sigma_o^2 = \frac{\hbar\omega_E}{10D\alpha^2}; \quad z = e^{-\theta_E/T}; \quad \theta_E = \frac{\hbar\omega_E}{k_B}, \tag{16}$$

$$\omega_E = \sqrt{\frac{k_{eff}}{\mu}} = \left[\frac{5D\alpha^2}{\mu}\left(1 - \frac{3}{2}\alpha a\right)\right]^{1/2}; \qquad \mu = \frac{M_a M_s}{M_a + M_s}, \tag{17}$$

where $M_a$ and $M_S$ are the masses of absorbing and backscattering atoms; and in Eqs. (15, 16) $u_0^2$ , $\sigma_0^2$ are the zero point contributions to $u^2$ and $\sigma^2$; $\omega_E$ , $\theta_E$ are the correlated Einstein frequency and temperature, respectively.

From the above results we obtained the DCF $C_R$, the ratio $C_R/u^2$ and $C_R/\sigma^2$

$$C_R = \frac{2u_0^2(1+z_0)(1-z) - \sigma_0^2(1-z_0)(1+z)}{(1-z_0)(1-z)}, \tag{18}$$

$$\frac{C_R}{u^2} = 2 - \frac{\sigma_0^2(1+z)(1-z_0)}{u_0^2(1-z)(1+z_0)}, \tag{19}$$

$$\frac{C_R}{\sigma^2} = \frac{2u_o^2(1+z)(1-z_o) - \sigma_o^2(1-z_o)(1+z)}{\sigma_o^2(1-z_o)(1+z)}. \tag{20}$$

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

$$z(z_0) \approx 1 - \hbar\omega_E\left(\omega_E^0\right)/k_B T \tag{21}$$

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. These results are written in Table 1.

Note that from this table the functions $u^2, C_R, \sigma^2$ are linearly proportional to the temperature at high-temperatures and contain the zero-point contributions at low-temperatures, satisfying all standard properties of these quantities [12, 13]; the ratio $C_R/u^2$ approaches a constant value of 40%. These results agree with those calculated by the Debye model [3].

**Table 1:** Expressions of $u^2, \sigma^2, C_R, C_R/u^2, C_R/\sigma^2$ in the LT and HT limits .

| Function | $T \to 0$ | $T \to \infty$ |
|---|---|---|
| $u^2$ | $u_0^2(1+2z_0)$ | $k_BT/8D\alpha^2$ |
| $\sigma^2$ | $\sigma_0^2(1+2z)$ | $k_BT/5D\alpha^2$ |
| $C_R$ | $2u_0^2(1+2z_0)-\sigma_0^2(1+2z)$ | $k_BT/20D\alpha^2$ |
| $\frac{C_R}{u^2}$ | $2-\frac{\sigma_0^2(1+2z)}{u_0^2(1+2z_0)}$ | 0.40 |
| $\frac{C_R}{\sigma^2}$ | $2\frac{u_0^2(1+2z_o)}{\sigma_0^2(1+2z)}-1$ | 0.25 |

## 3. Numerical results

Now we apply the expressions derived in the previous section to numerical calculations for Cu and Ni. The Morse potential parameters $D$ and $\alpha$ of these crystals have been calculated by using the procedure presented in [10]. The calculated values of $D$, $\alpha$, $r_o$, $k_{eff}^o$, $k_{eff}$, $\omega_E^o$, $\omega_E$, $\theta_E^o$, $\theta_E$ are presented in Table 2. They show a good agreement of our calculated values with experiment [7-9] and with those calculated by another procedure [14].

Table 2: Calculated values of $D$, $\alpha$, $r_o$, $k_{eff}^o$, $k_{eff}$, $\omega_E^o$, $\omega_E$, $\theta_E^o$, $\theta_E$ for Cu and Ni compared to experiment [7-9] and to those of other procedure [14].

| *Crystal* | *D(eV)* | $\alpha$ *(Å$^{-1}$)* | $r_o$*(Å)* | $k_{eff}^o$ *(N/m)* | $k_{eff}$ *(N/m)* | $\omega_E^o$ $(10^{13}Hz)$ | $\omega_E$ $(10^{13}Hz)$ | $\theta_E^o$ *(K)* | $\theta_E$ *(K)* |
|---|---|---|---|---|---|---|---|---|---|
| *Cu, present* | 0.337 | 1.358 | 2.868 | 79.659 | 49.787 | 2.739 | 3.063 | 209.25 | 233.95 |
| *Cu, exp.[7]* | 0.330 | 1.380 | 2.862 | | 50.345 | | 3.082 | | 235.26<br>232[9] |
| *Cu, [14]* | 0.343 | 1.359 | 2.866 | 81.196 | 50.748 | 2.766 | 3.092 | 211.26 | 236.20 |
| *Ni, present* | 0.426 | 1.382 | 2.803 | 104.29 | 65.179 | 3.261 | 3.646 | 249.12 | 278.53 |
| *Ni, exp.[7]* | 0.410 | 1.390 | 2.804 | | 63.460 | | 3.600 | | 274.83 |
| *Ni, [14]* | 0.421 | 1.420 | 2.780 | 108.81 | 68.005 | 3.331 | 3.725 | 254.46 | 284.50 |

The effective spring constants, the Einstein frequencies and temperatures change significantly when the correlation is included. The calculated Morse potentials for Cu and Ni are illustrated in Figure 1 showing a good agreement with experiment [7]. Figure 2 shows the temperature

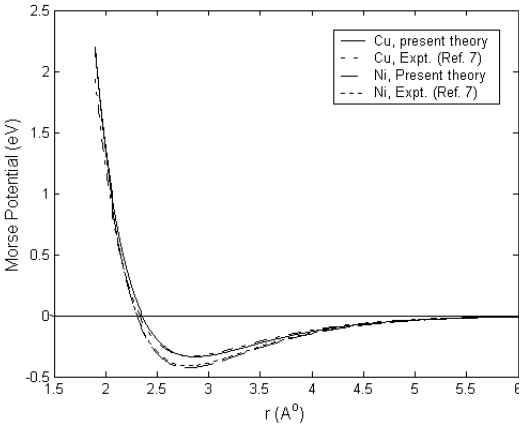


*Figure 1:* Calculated Morse potential of Cu and Ni compared to experiment [7].

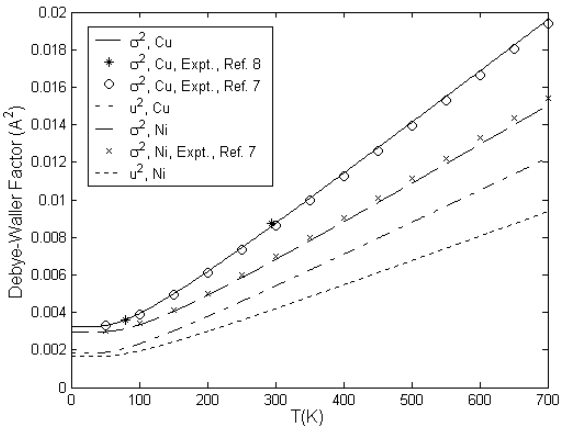


*Figure 2:* Temperature dependence of the calculated $\sigma^2$, $u^2$ for Cu and Ni compared to experiment [7,8].

dependence of the calculated MSRD $\sigma^2$ of Cu and Ni compared to their MSD $u^2$ and to experiment. 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 Ni is illustrated in Figure 3 and their ratio with function $u^2$ and

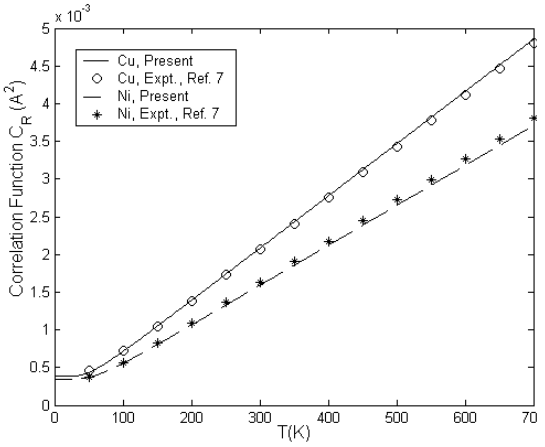


*Figure 3:* Temperature dependence of the calculated DCF $C_R$ of Cu and Ni compared to experiment [7].

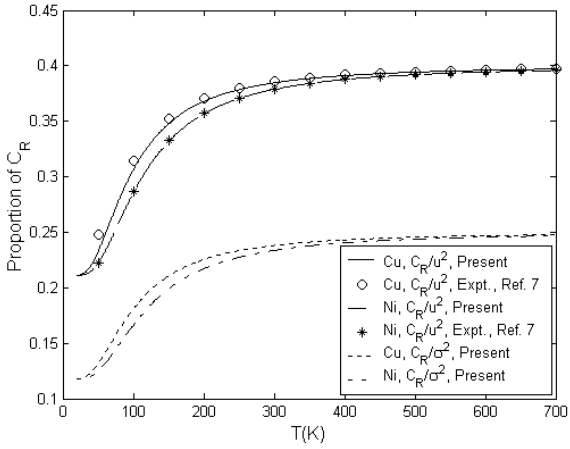


*Figure 4:* Temperature dependence of the calculated ratio $C_R/u^2$, $C_R/\sigma^2$ for Cu and Ni compared to experiment [7].

$\sigma^2$ in Figure 4. All they agree well with experiment [7, 8]. 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 [3] and satisfying all standard properties of these quantities [12, 13]. Hence, they show the significance of the correlation effects contributing to the Debye-Waller factor in XAFS. Figure 4 shows significance of the correlation effects described by $C_R$ in the atomic vibration influencing on XAFS. At high temperatures it is about 40% for $C_R/u^2$ and 25% for $C_R/\sigma^2$.

## 4. Conclussions

In this work a new procedure for study of correlation effects of the atomic vibration of fcc crytals in XAFS has been developed. Analytical expressions for the effective spring constants, correlated Einstein frequency and temperature, for DCF ($C_R$), MSD ($u^2$) and their ratio $C_R/u^2$, $C_R/\sigma^2$ have been derived for absorbing and backscattering atoms in XAFS with the influence of their nearest neighbors.

Derived expressions of the mentioned thermodynamic functions show their fundamental properties in temperature dependence. The functions $C_R, u^2, \sigma^2$ 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% coinsiding with the result obtained by the Debye method and the ratio $C_R/\sigma^2$ 25% at high-temperatures, thus showing the significance of correlation effects in the atomic vibration in fcc crystals.

Properties of our derived functions agree with experiment and with those obtained by the Debye model thus denoting a new procedure for study of Debye-Waller and of the atomic correlated vibration in XAFS theory.

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