

THERMODYNAMIC AND CORRELATION EFFECTS IN ATOMIC VIBRATION OF BCC CRYSTALS CONTAINING DOPANT ATOM

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Abstract: A new procedure for calculation and analysis of thermodynamic and correlation effects of bcc crystals under influence of dopant atom in the X-ray Absorption Fine Structure (XAFS) has been developed. Analytical expression for the Displacement-displacement Correlation Function (DCF) C_R has been derived based on the derived Mean Square Relative Displacement (MSRD) σ^2 and Mean Square Displacement (MSD) u^2 of bcc crystals containing dopant atom. Numerical calculations have been carried out for Fe doped by W and by Cr atom. They are found to be in good agreement with experiment.

1. Introduction

Thermodynamic effects of atomic vibration have been oft studied by the XAFS procedure because the emitted photoelectron is transferred and scattered in the vibrating atomic environment before interfering with the out going photoelectron. Therefore, it is necessary to take a thermal averaging $\langle e^{i2kR_j} \rangle$ 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 MSD and DCF. The doping effects have been investigated to compare the XAFS results to the Mossbauer studies [6] and to consider their influence on the XAFS cumulants of fcc [9] and bcc [10] crystals.

The purpose of this work is to develop a new procedure for calculation and analysis of the DCF (C_R), the MSD (u^2) for atomic vibration in bcc crystals under influence of dopant atom. Expressions for these quantities have been derived. The effective interaction potential of the system has been considered by taking into account the influences of 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 Fe doped by W and by Cr. The calculated u^2 , σ^2 , C_R and ratios C_R/u^2 , C_R/σ^2 , which are oft studied in XAFS technique [2], of these crystals have been analyzed. They are found to be in good agreement with their experimental values deduced from the measured Morse potential parameters [7].

2. Formalism

In this investigation for XAFS process we consider the dopant (D) atom as absorber and the host (H) atom as scatterer so that we write the XAFS function in the form

$$\chi = \chi_0 \langle e^{2ik\Delta} \rangle ; \quad \Delta = \hat{\mathbf{R}} \cdot (\mathbf{u}_S - \mathbf{u}_A) , \quad \hat{\mathbf{R}} = \mathbf{R}/|\mathbf{R}|, \quad (1)$$

where \mathbf{u}_s and \mathbf{u}_A are the scatterer or host atom and central-atom displacement, respectively.

To evaluate Eq. (1) we make use of the well-known relation [11]

$$\langle e^{2ik\Delta} \rangle = e^{-2k^2 \langle \Delta^2 \rangle} = e^{-2k^2 \sigma^2} \quad (2)$$

to obtain Eq. (1) in the form

$$\chi = \chi_0 e^{-2k^2 \sigma^2}, \quad (3)$$

so that the thermal vibration effect in XAFS is defined by σ^2 .

For crystals containing doping atom by using Eq. (1) the MSR is given by

$$\sigma^2 = \langle \Delta_j^2 \rangle = u_A^2 + u_S^2 - C_R. \quad (4)$$

Here we defined the MSD function for dopant (D) as absorber (A) u_A^2 and for the host (H) atom as scatterer u_S^2 having a dopant as nearest neighbor as

$$u_A^2 = \langle (\mathbf{u}_A \cdot \hat{\mathbf{R}})^2 \rangle, \quad u_S^2 = \langle (\mathbf{u}_S \cdot \hat{\mathbf{R}})^2 \rangle, \quad (5)$$

so that the DCF is given by

$$C_R = 2 \langle (\mathbf{u}_A \cdot \hat{\mathbf{R}})(\mathbf{u}_S \cdot \hat{\mathbf{R}}) \rangle = u_A^2 + u_S^2 - \sigma^2 \quad (6)$$

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

- for absorber (A):

$$U_{eff}^A(x) = \sum_{j=1}^8 U_{HD}(x\hat{\mathbf{R}}_{01} \cdot \hat{\mathbf{R}}_{0j}) = \frac{1}{2} k_{eff}^A x^2 + k_3^A x^3 + \dots, \quad x = r - r_0, \quad (7)$$

- for scatterer (S):

$$U_{eff}^S(x) = U_{HD}(x) + \sum_{j=1}^7 U_H(x\hat{\mathbf{R}}_{01} \cdot \hat{\mathbf{R}}_{0j}) = \frac{1}{2} k_{eff}^S x^2 + k_3^S x^3 + \dots, \quad (8)$$

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

By using the definitions $y = x - a$, $a = \langle r - r_0 \rangle$, we obtain Eqs. (7, 8) in the form

$$U_{eff}^A(y) \cong \frac{1}{2} k_{eff}^A y^2 + k_3^A y^3, \quad U_{eff}^S(y) \cong \frac{1}{2} k_{eff}^S y^2 + k_3^S y^3. \quad (9)$$

Applying the Morse potentials expanded to the third order about its minimum

$$U_{HD}(x) = D_{HD} \left(e^{-2\alpha_{HD}x} - 2e^{-\alpha_{HD}x} \right) \cong D \left(-1 + \alpha_{HD}^2 x^2 - \alpha_{HD}^3 x^3 + \dots \right), \quad (10)$$

$$U_H(x) = D_H \left(e^{-2\alpha_H x} - 2e^{-\alpha_H x} \right) \cong D \left(-1 + \alpha_H^2 x^2 - \alpha_H^3 x^3 + \dots \right), \quad (11)$$

$$D_{HD} = \frac{D_D + D_H}{2}, \quad \alpha_{HD} = \left(\frac{D_D \alpha_D^2 + D_H \alpha_H^2}{D_D + D_H} \right)^{1/2}, \quad (12)$$

for Eqs. (7, 8) we obtain the effective local force constants k_{eff} and the cubic anharmonic parameters k_3 for the absorber (A) and for the backscatterer (S)

$$k_{eff}^A \cong \frac{16}{3} D_{HD} \alpha_{HD}^2 = M_D \omega_D^2, \quad k_3^A = -2 D_{HD} \alpha_{HD}^3, \quad (13)$$

$$k_{eff}^S \cong 2 \left(D_{HD} \alpha_{HD}^2 + \frac{5}{3} D_H \alpha_H^2 \right) = M_S \omega_S^2, \quad k_3^S = - \left(D_{HD} \alpha_{HD}^3 + D_H \alpha_H^3 \right). \quad (14)$$

Using Eqs. (13, 14) we calculate the Einstein frequencies and temperatures for absorber and backscatterer

$$\omega_A = \sqrt{\frac{16}{3M_A} D_{HD} \alpha_{HD}^2}, \quad \theta_A = \hbar \omega_A / k_B, \quad (15)$$

$$\omega_S = \sqrt{2 \left(D_{HD} \alpha_{HD}^2 + \frac{5}{3} D_H \alpha_H^2 \right) / M_S}, \quad \theta_S = \hbar \omega_S / k_B, \quad (16)$$

where k_B is Boltzmann constant, M_A and M_S are the masses of absorber and backscatterer.

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.,

$$y \cong a_0 (\hat{a} + \hat{a}^+), \quad a_0^2 = \frac{\hbar \omega_{A,S}}{2k_{eff}^{A,S}}, \quad (17)$$

and use the harmonic oscillator state $|n\rangle$ as the eigenstate with the eigenvalue $E_n = n\hbar \omega_{A,S}$, ignoring the zero-point energy for convenience.

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

$$Z = Tr \rho_0 = \sum_n \exp(-n\beta \hbar \omega_{A,S}) = \sum_{n=0}^{\infty} z_{A,S}^n = \frac{1}{1 - z_{A,S}}, \quad \beta = 1/k_B T, \quad z_{A,S} = e^{-\theta_{A,S}/T}, \quad (18)$$

to determine the MSD function

$$\begin{aligned} u_{A,S}^2 &= \langle y^2 \rangle \approx \frac{1}{Z} \text{Tr}(\rho_0 y^2) = \frac{1}{Z} \sum_n \exp(-n\beta \hbar \omega_{A,S}) \langle n | y^2 | n \rangle = \\ &= 2a_0^2 (1 - z_{A,S}) \sum_n (1+n) z_{A,S}^n = \frac{\hbar \omega_{A,S}}{2k_{\text{eff}}^{A,S}} \frac{1+z_{A,S}}{1-z_{A,S}}. \end{aligned} \quad (19)$$

From Eqs. (13, 14, 19) we obtain the MSD for bcc crystals containing dopant atom for absorber and backscatterer

$$u_A^2 = u_A^0 \frac{1+z_A}{1-z_A}, \quad u_A^0 = \frac{3\hbar\omega_A}{32D_{HD}\alpha_{HD}^2}, \quad z_A = e^{-\theta_A/T}, \quad (20)$$

$$u_S^2 = u_S^0 \frac{1+z_S}{1-z_S}, \quad u_S^0 = \frac{3\hbar\omega_S}{4\left(D_{HD}\alpha_{HD}^2 + \frac{5}{3}D_H\alpha_H^2\right)}, \quad z_S = e^{-\theta_S/T}. \quad (21)$$

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 MSD function for bcc crystals including dopant atom has been calculated using the procedure presented in [10] and they are given by

$$\sigma^2 = \sigma_o^2 \frac{(1+z)}{(1-z)}, \quad \sigma_o^2 = \frac{\hbar\omega_E}{4\left[D_{HD}\alpha_{HD}^2\left(1+\frac{5\kappa_H^2}{3}\right) + \frac{5}{12}D_H\alpha_H^2\right]}, \quad (22)$$

$$\omega_E \approx \left\{ \frac{2}{\mu} \left[D_{HD}\alpha_{HD}^2 \left(1 + \frac{5\kappa_H^2}{3} \right) + \frac{5}{12} D_H\alpha_H^2 \right] \right\}^{1/2}, \quad (23)$$

$$\theta_E \approx \frac{\hbar}{k_B} \left\{ \frac{2}{\mu} \left[D_{HD}\alpha_{HD}^2 \left(1 + \frac{5\kappa_H^2}{3} \right) + \frac{5}{12} D_H\alpha_H^2 \right] \right\}^{1/2}, \quad (24)$$

$$\mu = \frac{M_D \cdot M_H}{M_D + M_H}, \quad \kappa_H = \frac{M_H}{M_D + M_H}, \quad z = e^{-\theta_E/T}, \quad (25)$$

where 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_A^2 and C_R/σ^2

$$C_R = u_A^0 \frac{(1+z_A)}{(1-z_A)} + u_S^0 \frac{(1+z_S)}{(1-z_S)} - \sigma_o^2 \frac{(1+z)}{(1-z)}, \quad (26)$$

$$\frac{C_R}{u_A^2} = 1 + u_S^0 \frac{u_S^0}{u_A^0} \frac{(1+z_S)(1-z_A)}{(1-z_S)(1+z_A)} - \frac{\sigma_o^2}{u_A^0} \frac{(1+z)(1-z_A)}{(1-z)(1+z_A)}, \quad (27)$$

$$\frac{C_R}{\sigma^2} = \frac{u_A^0 (1+z_A)(1-z)}{\sigma_0^2 (1-z_A)(1+z)} + \frac{u_S^0 (1+z_S)(1-z)}{\sigma_0^2 (1-z_S)(1+z)} - 1. \quad (28)$$

If the dopant atom is taken from the host crystal, i., e.,

$$D_{HD} = D_H = D; \quad \alpha_{HD} = \alpha_H = \alpha, \quad (29)$$

the above obtained results will change into those for the pure bcc crystals [12]

$$k_A = k_S = k_{eff} = \frac{16}{3} D\alpha^2; \quad k_{3A} = k_{3S} = k_3 = -2D\alpha^3, \quad (30)$$

$$u_A^2 = u_S^2 = u^2 = \frac{\hbar\omega}{2k_{eff}} \frac{1+z}{1-z} = \frac{3\hbar\omega}{32D\alpha^2} \frac{1+z}{1-z}. \quad (31)$$

3. Numerical results and comparison to experiment

Now we apply the expressions derived in the previous section to numerical calculations for Fe doped by W and by Cr. The Morse potentials for Fe doped by W and by Cr have been calculated using the Morse potential parameters D and α of these crystals computed by using our procedure presented in [8]. They are shown in Figure 1 in a good agreement with experiment [7]. The temperature dependent values of u_A^2 , u_S^2 , σ^2 , C_R have been calculated and the results are presented in Table 1. Figure 2 illustrates the temperature dependence of our

Table 1: Calculated values of u_A^2 , u_S^2 , σ_{calc}^2 , C_R^{calc} for Fe doped by W compared to experimental values of σ_{exp}^2 , C_R^{exp} [7] at different temperatures.

T(K)	$u_A^2 (10^{-2}\text{\AA}^2)$	$u_S^2 (10^{-2}\text{\AA}^2)$	$\sigma_{calc}^2 (10^{-2}\text{\AA}^2)$	$\sigma_{exp}^2 (10^{-2}\text{\AA}^2)$	$C_R^{calc} (10^{-2}\text{\AA}^2)$	$C_R^{exp} (10^{-2}\text{\AA}^2)$
30	0.09	0.19	0.26	0.25	0.02	0.02
50	0.10	0.19	0.26	0.26	0.02	0.02
70	0.11	0.20	0.28	0.28	0.03	0.03
100	0.14	0.22	0.32	0.32	0.04	0.04
150	0.19	0.28	0.41	0.40	0.06	0.06
200	0.24	0.35	0.51	0.50	0.08	0.08
250	0.30	0.42	0.62	0.61	0.10	0.10
300	0.36	0.50	0.73	0.72	0.12	0.12
350	0.41	0.57	0.84	0.83	0.14	0.14
400	0.47	0.65	0.96	0.94	0.17	0.17
450	0.53	0.73	1.07	1.05	0.19	0.19
500	0.59	0.81	1.12	1.08	0.21	0.21
550	0.64	0.88	1.30	1.27	0.23	0.23
600	0.70	0.96	1.41	1.38	0.25	0.25

calculated MSD $\sigma^2(T)$, MSD $u_A^2(T)$ and $u_S^2(T)$ showing $\sigma^2 > u_S^2 > u_A^2$ especially at high temperatures. The temperature dependence of our calculated DCF $C_R(T)$ for Fe doped by W and by Cr is presented in Figure 3. The functions MSD, MSD and DCF contain zero-point contribution at low temperature and are linearly proportional to the temperature at high temperatures. The temperature dependence of the ratios C_R/u_A^2 and C_R/σ^2 for Fe doped by W are shown in Figure 4. They have the same form as for the pure bcc crystals [12] satisfying the same properties obtained by the Debye model [2]. They increase fastly at low temperatures and approach a constant values at high temperatures (about 36% for C_R/u_A^2 and 18% for C_R/σ^2) taking from our calculated correlated Einstein temperature $\theta_E = 217 K$. These results denote the significant rate of the correlation effect in atomic vibration. Our calculated quantities shown in Table 1 and in Figures 2 - 4 are found to be in good agreement with the experiment [7]

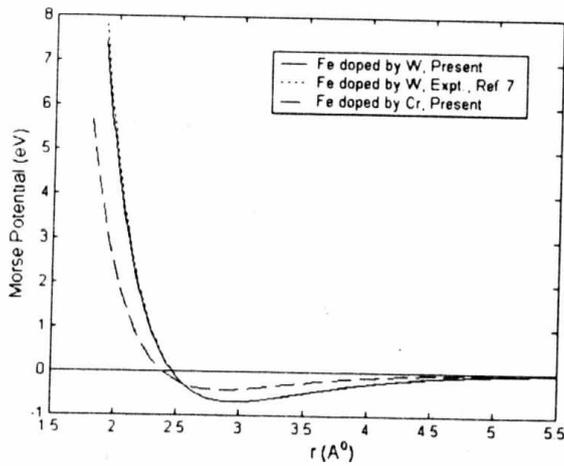


Figure 1: Calculated Morse potentials for Fe doped by W and Cr compared to experiment [7]

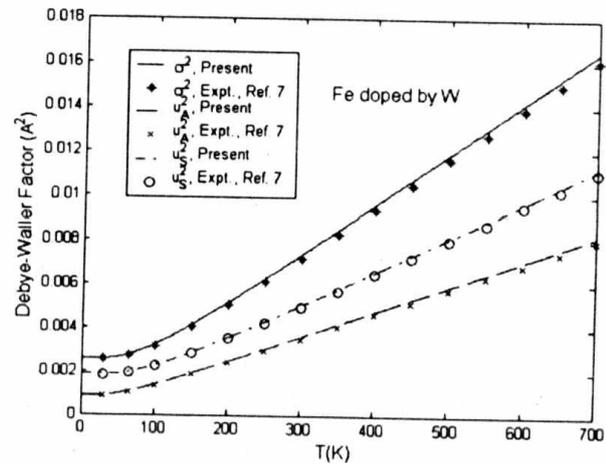


Figure 2: Calculated MSD and MSD for Fe doped by W compared to experiment [7].

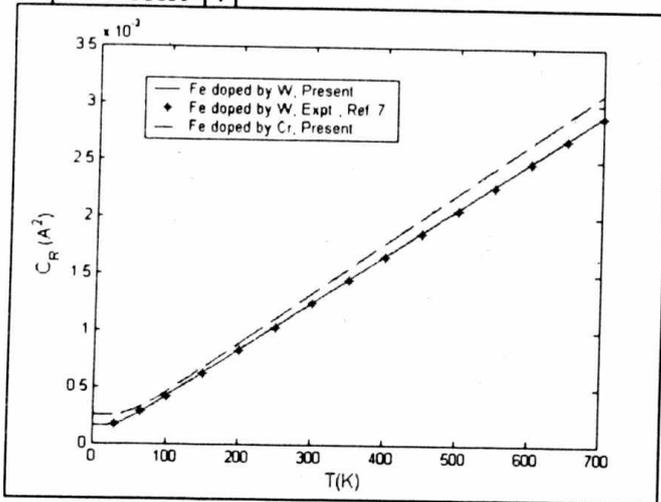


Figure 3: Calculated DCF for Fe doped by W and by Cr compared to experiment [7].

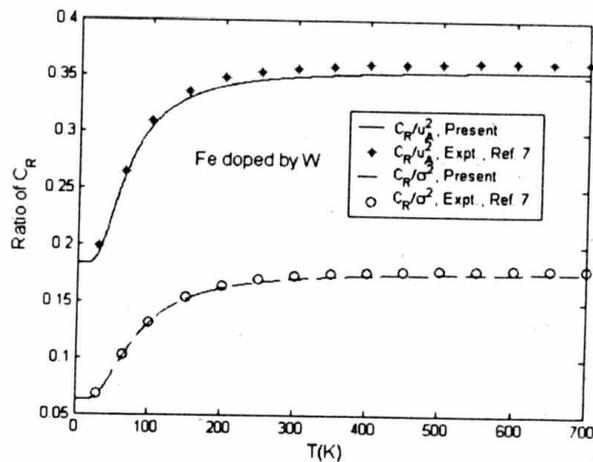


Figure 4: Calculated C_R/u_A^2 and C_R/σ^2 for Fe doped by W compared to experiment [7].

4. Conclusions

In this work a new procedure for study of the thermodynamic and correlation effects in the atomic vibration of bcc crystals under influence of a dopant atom in XAFS has been developed. Analytical expressions for the effective local force constants, the DCF (C_R), the MSD for the dopant as absorber (u_A^2) and for the scatterer as host atom (u_S^2) containing a dopant atom as nearest neighbor and the ratios C_R/u_A^2 , C_R/σ^2 have been derived based on the anharmonic correlated Einstein model.

Obtained expressions of the mentioned thermodynamic functions show their fundamental properties in temperature dependence. The functions C_R , u_A^2 , u_S^2 , σ^2 are linearly proportional to temperature at high-temperatures and contain zero-point contributions at low temperatures. The ratio C_R/u_A^2 accounts for about 36% and the ratio C_R/σ^2 about 18% at high-temperatures.

Our developed theory for the doping bcc crystals contain the one for the pure materials as a special case when the dopant is taken away. The result $\sigma^2 > u_S^2 > u_A^2$ shows the role of location of the dopant (as the central or as the neighboring atom) and the correlation effect in studying atomic vibration.

The agreement of our calculated values with experiment shows the efficiency of the present procedure in studying thermodynamic parameters and correlation effects of bcc crystals under influence of dopant atom.

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