

# INTERATOMIC POTENTIAL AND CUMULANTS OF BCC CRYSTALS UNDER INFLUENCE OF ANHARMONIC AND IMPURITY EFFECTS IN EXAFS THEORY

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**Abstract:** A new procedure for calculation and evaluation of interatomic potentials and EXAFS cumulants of bcc crystals influenced by anharmonic and impurity effects has been developed. Analytical expressions for the anharmonic interatomic effective potential, effective local force constants, correlated Einstein frequency and temperature, first, second and third cumulant have been derived. Anharmonic correlated Einstein model has been generalized to derivation of the considered expressions. Numerical results for Fe, W, W-Fe are found to be in good agreement with experiment.

## 1. Introduction

Extended X-ray absorption fine structure (EXAFS) provide information on structure and thermodynamic effects of substances [1]. Anharmonic EXAFS involves anharmonic contribution to the above information discovered by theory and experiment [1, 2, 6, 7], and it contains the cumulants  $\sigma^{(n)}$  ( $n = 1, 2, 3, \dots$ ) [6]. An experimental investigation of local force constants of transition metal dopants in a Nickel host with comparison to Mossbauer studies has been carried out [7] in which the measured results are analyzed by using the anharmonic correlated Einstein model [4].

The purpose of this work is to develop a method for calculation and evaluation of the anharmonic interatomic potential, effective local force constants, correlated Einstein frequency and temperature, first cumulant or net thermal expansion, second cumulant which is equal to the mean square relative displacement (MSRD) or Debye Waller factor (DWF), third cumulant of bcc crystals containing a dopant or impurity (I) atom as absorber in the EXAFS process. Its nearest neighbors are the host (H) atoms. Anharmonic correlated Einstein model [4] has been generalized to derivation of the analytical expressions. Numerical calculations have been carried out for Fe, W, and Fe doped by W atom (W-Fe). The calculated results are found to be in good agreement with experiment [2].

## 2. Formalism

Generalizing the anharmonic correlated Einstein model [4] to a system containing impurity the anharmonic interatomic effective potential of the system consisting of an impurity (I) atom as absorber and of the other host (H) atoms as scatterers in XAFS process as well as using the definition [4]  $y = x - a$  with  $a = \langle x \rangle$ ,  $\langle y \rangle = 0$ , and  $x$  as the deviation of

instantaneous bond length  $r$  from its equilibrium value  $r_0$ , is written in the sum of the harmonic contribution and the anharmonic one  $V_a$

$$V_{\text{eff}}(y) = \frac{1}{2} k_{\text{eff}} y^2 + V_a(y). \quad (1)$$

Taking into account the atomic distribution of bcc crystal we derived the effective local force constant  $k_{\text{eff}}$  and  $V_a$

$$k_{\text{eff}} = 2 \left[ D_{\text{IH}} \alpha_{\text{IH}}^2 \left( 1 + \frac{5m_{\text{H}}^2}{3} \right) + \frac{5}{12} D_{\text{H}} \alpha_{\text{H}}^2 \right] \approx \mu \omega_{\text{E}}^2. \quad (2)$$

$$V_a(y) = 2 \left[ D_{\text{IH}} \alpha_{\text{IH}}^2 \left( 1 + \frac{5m_{\text{H}}^2}{3} \right) + \frac{5}{12} D_{\text{H}} \alpha_{\text{H}}^2 \right] a y - \left[ (1 + m_{\text{H}}^3) D_{\text{IH}} \alpha_{\text{IH}}^3 + \frac{1}{8} D_{\text{IH}} \alpha_{\text{IH}}^3 \right] y^3, \quad (3)$$

the correlated Einstein frequency  $\omega_{\text{E}}$  and temperature  $\theta_{\text{E}}$

$$\omega_{\text{E}} \approx \left\{ \frac{2}{\mu} \left[ D_{\text{IH}} \alpha_{\text{IH}}^2 \left( 1 + \frac{5m_{\text{H}}^2}{3} \right) + \frac{5}{12} D_{\text{H}} \alpha_{\text{H}}^2 \right] \right\}^{1/2}, \quad (4)$$

$$\theta_{\text{E}} \approx \frac{\hbar}{k_{\text{B}}} \left\{ \frac{2}{\mu} \left[ D_{\text{IH}} \alpha_{\text{IH}}^2 \left( 1 + \frac{5m_{\text{H}}^2}{3} \right) + \frac{5}{12} D_{\text{H}} \alpha_{\text{H}}^2 \right] \right\}^{1/2}, \quad (5)$$

where

$$m_{\text{H}} = \frac{M_{\text{H}}}{M_{\text{I}} + M_{\text{H}}}, \quad m_{\text{I}} = \frac{M_{\text{I}}}{M_{\text{I}} + M_{\text{H}}}, \quad (6)$$

$$D_{\text{IH}} = \frac{D_{\text{I}} + D_{\text{H}}}{2}, \quad \alpha_{\text{IH}}^2 = \frac{D_{\text{I}} \alpha_{\text{I}}^2 + D_{\text{H}} \alpha_{\text{H}}^2}{D_{\text{I}} + D_{\text{H}}}, \quad \alpha_{\text{IH}}^3 = \frac{D_{\text{I}} \alpha_{\text{I}}^3 + D_{\text{H}} \alpha_{\text{H}}^3}{D_{\text{I}} + D_{\text{H}}}. \quad (7)$$

The considered thermodynamic parameters have been derived by an averaging procedure in statistics [4] in which we expressed  $y$  in terms of annihilation and creation operators and use harmonic oscillator state  $|n\rangle$  with eigenvalue  $E_n = n\hbar\omega_{\text{E}}$  and  $n$  as phonon number for the perturbation calculation. We derived the expressions for the first, second, and third cumulant

$$\sigma^{(1)} = a(T) = \sigma_0^{(1)} \frac{1+z}{1-z}, \quad \sigma_0^{(1)} = \frac{3 D_{\text{IH}} \alpha_{\text{IH}}^3 (1 + m_{\text{H}}^3) + \frac{1}{8} D_{\text{H}} \alpha_{\text{H}}^3}{8 \left[ D_{\text{IH}} \alpha_{\text{IH}}^2 \left( 1 + \frac{5m_{\text{H}}^2}{3} \right) + \frac{5}{12} D_{\text{H}} \alpha_{\text{H}}^2 \right]} \hbar \omega_{\text{E}}, \quad (8)$$

$$\sigma^2 = \sigma_0^2 \frac{(1+z)}{(1-z)}, \quad \sigma_0^2 = \frac{\hbar \omega_{\text{E}}}{4 \left[ D_{\text{IH}} \alpha_{\text{IH}}^2 \left( 1 + \frac{5m_{\text{H}}^2}{3} \right) + \frac{5}{12} D_{\text{H}} \alpha_{\text{H}}^2 \right]}, \quad z = e^{-\hbar \omega_{\text{E}} / T}, \quad (9)$$

$$\sigma^{(3)} = \sigma_0^{(3)} \frac{(1+10z+z^2)}{(1-z)^2}, \quad \sigma_0^{(3)} = \frac{(\hbar \omega_{\text{E}})^2}{16} \frac{D_{\text{IH}} \alpha_{\text{IH}}^3 (1 + m_{\text{H}}^3) + \frac{1}{8} D_{\text{H}} \alpha_{\text{H}}^3}{\left[ D_{\text{IH}} \alpha_{\text{IH}}^2 \left( 1 + \frac{5m_{\text{H}}^2}{3} \right) + \frac{5}{12} D_{\text{H}} \alpha_{\text{H}}^2 \right]^3}. \quad (10)$$

Note that the total Debye-Waller factor is the sum of the harmonic contribution and the anharmonic one  $\sigma_a^2$

$$\sigma_{\text{tot}}^2(T) = \sigma^2(T) + \sigma_a^2(T), \quad \sigma_a^2(T) = 5(T) \left[ \sigma^2(T) - \sigma_0^2 \right], \quad (11)$$

$$5(T) = \frac{9k_B T}{8D_{\text{IH}}} \frac{z}{1+z} \left[ 1 + \frac{3k_B T}{8rD_{\text{IH}}\alpha_{\text{IH}}} \left( 1 + \frac{3k_B T}{8rD_{\text{IH}}\alpha_{\text{IH}}} \right) \right]. \quad (12)$$

For the case when the impurity atom is taken from the host material, i. e.,

$$D_{\text{IH}} = D_{\text{H}} = D, \quad \alpha_{\text{IH}} = \alpha_{\text{H}} = \alpha, \quad m_1 = m_2 = 1/2.$$

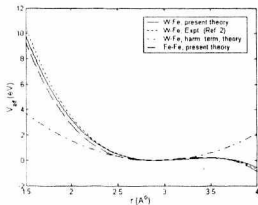
the above expressions will change into those derived for the bcc pure materials [5].

### 3. Numerical results and comparison to experiment

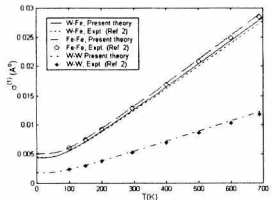
Now we show the results of numerical calculations for Fe, W and Fe doped by W atom as absorber in the EXAFS process. They are found to be in good agreement with experiment [2].

**Table I:** Calculated values of Morse potential parameters  $D$ ,  $\alpha$ ,  $r_0$ ; correlated Einstein frequency  $\omega_E$  and temperature  $\theta_E$ , effective spring constant  $k_{\text{eff}}$  for Fe-Fe, W-W, W-Fe, compared to experiment [2].

| Bond                  | $D(\text{eV})$ | $\alpha(\text{\AA}^{-1})$ | $r_0(\text{\AA})$ | $k_{\text{eff}}(\text{N/m})$ | $\omega_E(\times 10^{13} \text{ Hz})$ | $\theta_E(\text{K})$ |
|-----------------------|----------------|---------------------------|-------------------|------------------------------|---------------------------------------|----------------------|
| <b>FE-FE, PRESENT</b> | 0.4174         | 1.3885                    | 2.8450            | 47.2748                      | 3.1836                                | 243.1829             |
| <i>Fe-Fe, exp.[2]</i> | 0.4200         | 1.4000                    | 2.8560            | 48.3605                      | 3.2199                                | 245.9595             |
| <i>W-W, present</i>   | 0.9920         | 1.3850                    | 3.0350            | 111.7884                     | 2.6982                                | 206.1087             |
| <i>W-W, exp.[2]</i>   | 0.9900         | 1.4400                    | 3.0420            | 120.5995                     | 2.8026                                | 214.0784             |
| <b>W-FE, PRESENT</b>  | 0.7047         | 1.3895                    | 2.9400            | 58.2869                      | 2.8541                                | 218.0174             |
| <i>W-Fe, exp.[2]</i>  | 0.7050         | 1.4285                    | 2.949             | 61.2403                      | 2.9256                                | 223.4724             |

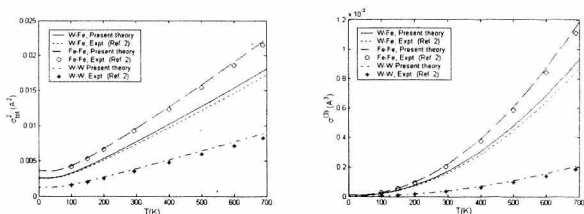


a)



b)

**Fig.1.** Calculated effective potential (a) and 1<sup>st</sup> cumulant (b) for Fe, W and W-Fe, compared to experiment [2].



**Fig.2.** Calculated DWF (a) and 3<sup>rd</sup> cumulant (b) for Fe, W and W-Fe, compared to experiment [2].

## References

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