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# Effective Anharmonic Einstein Potential for the Thermodynamic Parameters, Three First Cumulants and Anharmonic Perturbation Factor of Iron Doped Molybdenium Crystals

Nguyen Ba Duc, Nguyen Thi Lan Anh

Physic Faculty, Tan Trao University, Tuyen Quang, Vietnam

**Email address**

hieutruongdhtt@gmail.com (N. B. Duc), lananhnguyen1609@gmail.com (N. T. L. Anh)

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**Abstract**

Using the effective anharmonic Einstein potential is a new procedure for calculation and analysis of X-ray absorption fine structure (XAFS) cumulants of mixed body center cubic (bcc) crystals and has been derived based on quantum statistical theory. This study has formulated the expressions that describe asymmetric component for dopant bcc crystals that include the first cumulant or net thermal expansion, the second cumulant or mean square relative displacement (MSRD), the third cumulant, thermodynamic parameters and anharmonic perturbation factors. These contain the anharmonic effects contributions of body center cubic crystals that have been doped with Einstein frequency, Einstein temperature, and thermal expansion coefficient constant. Numerical results for pure Iron (Fe) and pure Molybdenium (Mo), and Fe doped by Mo (FeMo) are found to be good agreement with experiment.

**1. Introduction**

X-ray Absorption Fine Structure (XAFS) spectra is a powerful structural analysis technique, in which the XAFS functions provide information on atomic number of each shell, and their Fourier magnitudes provide information on radius of atomic shell [4]. The use of XAFS theory for studying thermodynamic properties of lattice crystals of a substance is necessary and has been executed [2]. The thermodynamic parameters for pure cubic crystals, and for mixed face centered cubic (fcc) crystals are provided by correlated - anharmonic Einstein model in XAFS theory [3, 6, 8]. However, the thermodynamic parameters, cumulants and anharmonic perturbation factor for doped body centered cubic (bcc) crystals are not mentioned.

This study uses the anharmonic effective Einstein potential [5] to formulate effective force constant, thermodynamic parameters, anharmonic perturbation factor and the cumulants expressions of dopant bcc crystals. These include the first cumulant or net thermal expansion, the second cumulant or mean square relative displacement, the third cumulant, and Einstein frequency and temperature which are contained in the XAFS. In this paper, the bcc crystals which contain a dopant atom called as absorbing atom in the XAFS process, its nearest neighbors are host atoms as backscattering atoms. Numerical calculation for Iron (Fe) doped by Molybdenium (Mo) crystal has been carried out to

show the thermo dynamical effects of bcc crystal under the influence of the doping atom. The calculated results are in good agreement with experimental values.

## 2. Fomalism

The expression of anharmonic XAFS spectra is often described by [2]:

$$\chi(k) = \frac{S_0^2 N}{kR^2} F(k) \exp\left(-\frac{2R}{\lambda(k)}\right) \text{Im}\left(e^{i\Phi(k)} \exp\left(2ikr_0 + \sum_n \frac{(2ik)^n}{n!} \sigma^{(n)}(T)\right)\right), \quad (1)$$

where  $S_0^2$  is the intrinsic loss factor due to many electron effects,  $N$  is atomic number of as well,  $F(k)$  is atomic backscattering amplitude,  $\Phi(k)$  is total phase shift of photoelectron,  $k$  and  $\lambda$  are wave number and mean free path of the photoelectron, respectively, and  $\sigma^{(n)}$  ( $n=1, 2, 3, \dots$ ) are the cumulants to describe asymmetric components. They all appear due to the thermal average of the function  $e^{-2ikr}$ , in which the asymmetric terms are expanded in a Taylor series around value  $R = \langle r \rangle$  with  $r$  is instantaneous bond length between absorbing and backscattering atoms at  $T$  temperature.

According to the anharmonic correlated Einstein model [4], effective interaction between absorbing and backscattering atoms with contributions of atomic neighbors is characterized by an effective potential:

$$U(x) \approx \frac{1}{2} k_{\text{eff}} x^2 + k_3 x^3 + \dots, \quad (2)$$

with net deviation  $x = r - r_0$ , and  $r$  is spontaneous bond length between absorbing and backscattering atoms,  $r_0$  is its equilibrium value, in Eq.(2),  $k_{\text{eff}}$  is effective spring constant because it includes total contribution of neighboring atoms,  $k_3$  is cubic anharmonicity parameter which gives an asymmetry in the pair distribution function. Because oscillations of a pair single bond between of absorbing and backscattering atoms with masses  $M_1, M_2$  are affected by neighboring atoms, when taking into account these effects via an anharmonic correlated Einstein model, effective Einstein potential to be formed:

$$U_E(\chi) = \frac{1}{2} k_{\text{eff}} x^2 + k_3 x^3 + \dots + \sum_{i=1}^2 \sum_{j \neq i} U\left(\frac{\mu}{M_i} \hat{R}_{12} \cdot \hat{R}_{ij}\right); \quad (3)$$

$$\mu = M_1 M_2 / (M_1 + M_2)$$

In Eq.(3),  $\hat{R}$  is the unit bond length vector,  $\mu$  is reduced mass of atomic mass  $M_1$  and  $M_2$ , the sum according to  $i, j$  is the contribution of cluster nearest atoms. The atomic vibration is calculated based on quantum statistical procedure with approximate quasi-harmonic vibration, in which the Hamiltonian of the system is written as harmonic term with respect to the equilibrium at a given temperature plus an anharmonic perturbation.

$$H = \frac{P^2}{2\mu} + U_E(\chi) = H_0 + U_E(a) + \delta U_E(y); \quad (4)$$

$$H_0 = \frac{P^2}{2\mu} + \frac{1}{2} k_{\text{eff}} y^2$$

$$y = x - a, a(T) = \langle x \rangle, \langle y \rangle = 0$$

with  $a$  is the net thermal expansion,  $y$  is the deviation from the equilibrium value of  $x$  at temperature  $T$ . Next, the use of potential interaction between each pair of atoms in the single bond can be expressed by anharmonic Morse potential for cubic crystals. Expanding to third order around its minimum, we have:

$$U_E(x) = D(e^{-2\alpha x} - 2e^{-\alpha x}) \approx D(-1 + \alpha^2 x^2 - \alpha^3 x^3 + \dots) \quad (5)$$

where  $D$  is the dissociation energy by  $U(r_0) = -D$ , and  $\alpha$  is expansion thermal parameter. In the case of dopant crystals, we have expression of the Morse potential formed:

$$U_E(x) = D_{12}(-1 + \alpha_{12}^2 x^2 - \alpha_{12}^3 x^3 + \dots) \quad (6)$$

Morse potential parameters in Eq.(6) have been obtained by averaging those of the pure crystals and they are given by:

$$\alpha_{12}^2 = \frac{D_1 \alpha_1^2 + D_2 \alpha_2^2}{D_1 + D_2}, \quad \alpha_{12}^3 = \frac{D_1 \alpha_1^3 + D_2 \alpha_2^3}{D_1 + D_2}, \quad (7)$$

$$D_{12} = \frac{D_1 + D_2}{2}$$

From expressions (3), (6) we have effective interaction Einstein potential as:

$$U_E(\chi) = U_E(a) + \frac{1}{2} k_{\text{eff}} y^2 + \delta U_E(y), \quad (8)$$

Substituting Eq. (6) with  $x = y + a$  into (3) and using Eq. (8) to calculate the second term in Eq. (2) with reduced mass of metals doped:

$$\mu_{12} = \frac{\mu_1 \mu_2}{\mu_1 + \mu_2}; \quad (9)$$

From the sum of  $i$  is over absorbing and backscattering atoms, and the sum of  $j$  which is over all their near

neighbors, and calculation of  $(\hat{R}_{12} \cdot \hat{R}_{ij})$  with lattice bcc crystals, we obtain thermodynamic parameters like effective spring constant  $k_{\text{eff}}$  and anharmonic parameter  $k_3$ :

$$k_3 = -\frac{5D_{12}\alpha_{12}^3}{4}; k_{\text{eff}} = 5D_{12}\alpha_{12}^2 \approx \mu_{12}\omega_E^2; \quad (10)$$

To derive the analytical formulas of cumulants of the bcc crystals, we use perturbation theory [1]. The atomic vibration is quantized as phonon, with consideration of the phonon-phonon interaction for taking into account the anharmonicity, we obtain the cumulants:

$$\sigma^{(1)} = a = \frac{3\hbar\omega_E}{40D_{12}\alpha_{12}} \frac{(1+z)}{(1-z)} \quad (11)$$

$$\sigma^{(2)} = \langle y^2 \rangle = \frac{\hbar\omega_E}{10D_{12}\alpha_{12}^2} \frac{(1+z)}{(1-z)} \quad (12)$$

$$\sigma^{(3)} = \frac{\hbar^2\omega_E^2}{200D_{12}^2\alpha_{12}^3} \frac{(1+10z+z^2)}{(1-z)^2} \quad (13)$$

where  $z \equiv e^{-\beta\hbar\omega_E} = e^{-\theta_E/T}$  is the temperature variable and determined by the  $\theta_E = \frac{\hbar\omega_E}{k_B}$  is Einstein temperature,  $k_B$  is Boltzmann's constant.

And anharmonic perturbation factor  $\partial U_E(y)$  has determined form:

$$\delta U_E(y) = 5D_{12}\alpha_{12}^2 \left( a(a-x) - \frac{\alpha_{12}(a-x)^3}{4} \right) \quad (14)$$

Factor  $\partial U_E(y)$  dependence T temperature and net deviation x.

### 3. Comparison

We applied the expressions which are derived in the previous section to numerical calculation for mixed crystal is Iron-Molybdenium (FeMo). According to Morse potential parameters for pure Fe, Mo crystal have been known [3, 6], we calculated parameters  $D_{12}$  and  $\alpha_{12}$  for dopant crystals above, shown on Table 1.

**Table 1.** Morse potential parameters values for crystals

Crystals	$D_{12}$ (eV)	$\alpha_{12}$ ( $\text{\AA}^{-1}$ )
Fe-Fe	4.821	1.3885
Mo-Mo	6.822	1.4232
Fe-Mo	5.782	1.4029

Based on  $D_{12}$ ,  $\alpha_{12}$  thermodynamic parameters from Table 1 into Eqs.(9, 10) with Boltzmann's constant  $k_B = 8.617 \times 10^{-5} \text{ eV}\text{\AA}^{-1}$ , Plank's constant  $\hbar = 6.5822 \times 10^{-16} \text{ eV}\cdot\text{s}$ ,

we calculated values of other thermodynamic parameters like effective force constant  $k_{\text{eff}}$ , reduced mass  $\mu_{12}$ , correlated Einstein frequency  $\omega_E$  and Einstein temperature  $\theta_E$  for Fe crystal doped by Mo crystal according to Table 2.

**Table 2.** Thermodynamic parameters values  $k_{\text{eff}}$ ,  $\mu$ ,  $\omega_E$ ,  $\theta_E$

Crystals	$k_{\text{eff}}$ (N/m)	$\mu$ ( $\text{eV}/\text{\AA}^2 \cdot \text{s}^{-2}$ )	$\omega_E$ ( $10^{13}$ Hz)	$\theta_E$ (K)
Fe-Fe	47.275	$0.2919 \cdot 10^{-26}$	3.184	243
Mo-Mo	107.289	$0.5004 \cdot 10^{-26}$	3.659	280
Fe-Mo	57.273	$0.3962 \cdot 10^{-26}$	1.762	134

Substituting values of thermodynamic parameters from Table 2 into Eqs. (11, 12, 13, 14), we received the expressions of cumulants and anharmonic perturbation factor to describe temperature variable  $z = e^{-\theta_E/T}$ . Next, replacing Einstein temperature value  $\theta_E$ (K) into expression of z temperature variable, we have the expressions to only illustrate T dependence temperature of cumulants and thermal expansion coefficient constant, dependence temperature and net deviation of anharmonic perturbation factor.

Figure 1 and Figure 3 illustrate the temperature dependence of the first cumulant  $\sigma^{(1)}(T)$  or net thermal expansion and third cumulant  $\sigma^{(3)}(T)$  of Fe doped by Mo crystal and FeMo pure crystals. Theoretical results of  $\sigma^{(1)}(T)$  agreed well with the experimental values at 77K, 295K and 700K temperatures for Fe pure crystals [3, 7] and at 300K, 683K temperatures for Mo pure crystal and dopant FeMo crystal. Theoretical results of  $\sigma^{(3)}(T)$  are also in good agreement with the experimental values at 295K temperature for Fe pure crystal and Fe doped by Mo crystal, and at 300K temperature for Mo pure crystal [6, 7]. Figure 2 illustrates the temperature dependence of our calculated anharmonic contribution the second cumulant  $\sigma^{(2)}(T)$ . Moreover the mean square relative displacement (MSRD) of FeMo mixed crystal and Fe, Mo pure crystals and compared to the measured values at 77K, 295K and 700K temperatures for FeMo [5], and at 10K, 295K and 683K temperatures for Fe and Mo [5, 7] theoretical results also agree well with the experiment. Noted that the experimental values from XAFS spectra measured at HASYLAB and BUGH Wuppertal (DESY, Germany) [5]. In the graphs we know that, at low temperatures, the cumulants  $\sigma^{(1)}$ ,  $\sigma^{(2)}$ ,  $\sigma^{(3)}$  included zero-point energy contributions, and this is quantum effects. At high temperatures, the cumulants  $\sigma^{(1)}$ ,  $\sigma^{(2)}$  are linear proportional to the T temperature, and the third cumulant  $\sigma^{(3)}$  is proportional to the square temperature  $T^2$ . They all agreed with results of classical theory and experiment. Figure 4 illustrates the temperature dependence of thermal expansion coefficient constant  $\alpha_T$  of Fe, Mo and FeMo in our calculated. They also have the form of specific heat which reflects the fundamental of solid state theory, that the thermal expansion is the result

of anharmonic effects and is also proportional to specific heat, and  $\alpha_T$  factor approach constant values at high temperatures and it is approximate zero at low temperature that agree with classical theory. Figure 5 illustrates dependence temperature T and net deviation x of the anharmonic perturbation factor of dopand crystal FeMo and style of graph approximation with the classical theory and other theories[2].

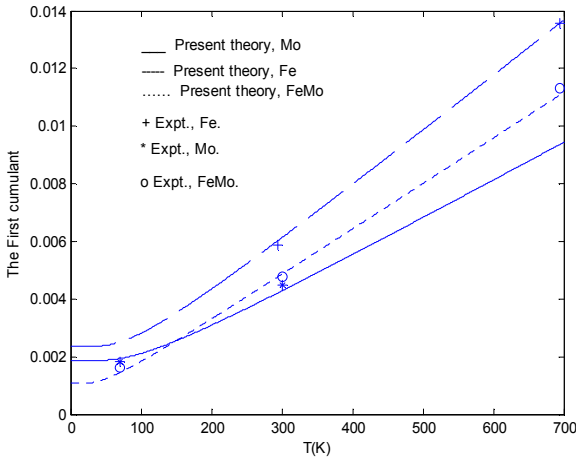


Figure 1. Dependence the temperature of the first cumulant  $\sigma^{(1)}(T)$

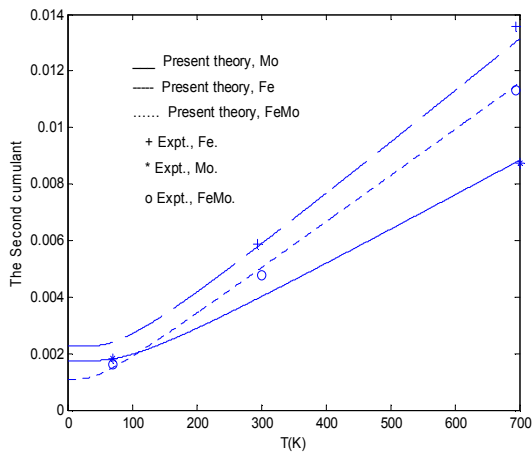


Figure 2. Dependence the temperature of the second cumulant  $\sigma^{(2)}$

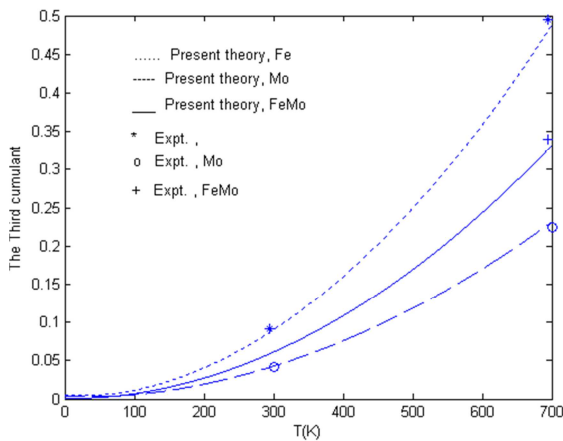


Figure 3. Dependence the temperature of the third cumulant  $\sigma^{(3)}(T)$

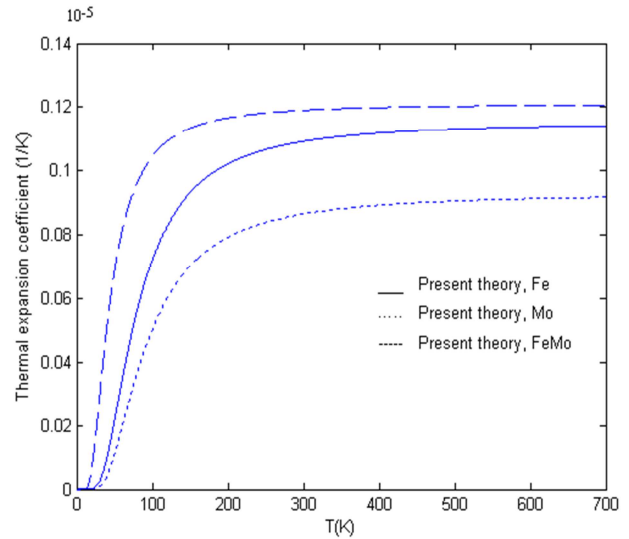


Figure 4. Dependence temperature T of the thermal expansion coefficient constant  $\alpha_T$

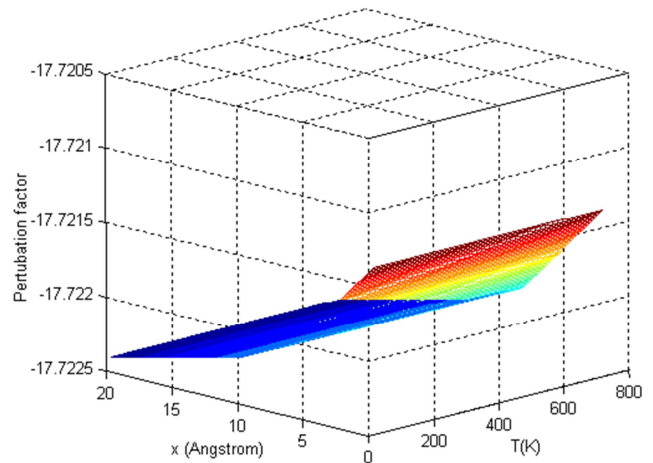


Figure 5. Dependence temperature and net expansion x of anharmonic perturbation factor

#### 4. Conclusion

A new analytical theory for calculation and evaluation of the thermodynamic properties of bcc dopant crystals have been developed based on the quantum statistical theory with the effective anharmonic Einstein potential developed for the doping bcc crystals. The expressions for the thermodynamic parameters, effective force constant, correlated Einstein frequency and temperature, the first, second and third cumulants, thermal expansion coefficient, anharmonic perturbation factor in an harmonic XAFS spectra of bcc crystals including dopant crystals all agree with all standard properties of these quantities. The quantity calculation for the doping crystals has the same form as for the pure crystals themselves.

The well agreement between the results of calculated theory and the experimental values demonstrates possibility is expected to be used the present developed theory in XAFS data analysis.

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