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# Using the Anharmonic Correlated Einstein Model for Calculation the Thermodynamic Parameters and Cumulants of Dopant Face Cubic Center Crystals

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**Abstract**

A new procedure for calculation and analysis of X-ray absorption fine structure (XAFS) cumulants of mixed fcc crystals has been derived based on quantum statistical theory with generalized an harmonic correlated Einstein model. This work has been formulated from the expressions of describing asymmetric component (the first cumulant or net thermal expansion, the second cumulant or mean square relative displacement (MSRD), the third cumulate) and thermodynamic parameters including the anharmonic effects on contributions of mixed face cubic center (fcc) crystals as and Einstein frequency and temperature. Numerical results for Cu doped by Ni are found to be good agreement with experiment.

**1. Introduction**

Research on thermodynamic properties of lattice crystals of a substance is necessary, and it has been studied in certain degree [3]. However, today X-ray Absorption Fine Structure (XAFS) becomes a powerful structural analysis technique in which the XAFS functions provide information with atomic number of each shell, and their Fourier magnitudes provide information on radius of atomic shell [4]. The thermodynamic parameters for cubic pure crystals are provided by correlated - an harmonic Einstein model in XAFS theory [6,7]. However, doped face center cubic (fcc) crystals has not been seriously taken on research.

The purpose of this work is using the anharmonic correlated Einstein model to formulate effective force constant, the cumulant expressions and thermodynamic parameters of dopant fcc crystals. These include: the first cumulate or net thermal expansion, the second cumulant or mean square relative displacement (MSRD) characterizing Debye Waller factor, and the third cumulant and Einstein frequency and temperature which are contained in the XAFS. In this work, the fcc crystals contain a dopant atom as absorbing atom in the XAFS process, and its nearest neighbors are host atoms as backscattering atoms. Numerical calculation for cooper (Cu) crystal doped by nikel (Ni) crystal has been carried out to show the thermo dynamical effects of fcc crystal under influence of the doping atom. The calculated results are in good agreement with experiment values.

## 2. Formalism

The expression of anharmonic XAFS spectra often is described by [4]:

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

where  $F(k)$  is atomic backscattering amplitude,  $\Phi(k)$  is total phase shift of photoelectron,  $k$  is wave number,  $\lambda$  is mean free path of the photoelectron, and  $\sigma^{(n)}$  ( $n = 1, 2, 3, \dots$ ) are the cumulants which 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  $R \approx \langle r \rangle$  with  $r$  is instantaneous bond length between absorbing and backscattering atoms at  $T$  temperature.

According to an harmonic correlated Einstein model [7] the interaction between absorber and backscatterer with affected by neighboring atoms is via an effective - anharmonic Einstein potential:

$$U_E(\chi) = \frac{1}{2} k_{\text{eff}} x^2 + k_3 x^3 + \dots + \sum_{i=1,2} \sum_{j \neq i} U \left( \frac{\mu}{M_i} \times \hat{R}_{i2} \cdot \hat{R}_{ij} \right) \quad (2)$$

This potential includes anharmonicity parameter  $k_3$  that describes an asymmetry or skew in the pair distribution function and the contributions of a small atom cluster, surrounding the absorbing (is do paint atom) and backscattering atoms (is host atom), and therefore, spring constant becomes an effective one  $k_{\text{eff}}$ . The contributions of such cluster are described in Eq. (2) by the sum  $i$  which is over absorber ( $i = 1$ ) and backscatterer ( $i = 2$ ), and the sum  $j$  which is over all their near neighbors, excludes the absorber and backscatterer themselves because they contribute in the  $U(x)$ .  $\hat{R}$  is the unit bond length vector,  $\mu$  is reduced mass of absorbing  $M_1$  and backscattering  $M_2$  atoms, respectively,  $x = r - r_0$  is deviation of the instantaneous bond length of two atoms from their equilibrium distance or the location of the interaction potential minimum [9].

The atomic vibration is calculated based on quantum statistical procedure with approximate quasi - hamonic vibration, in which the Hamiltonian of the system is written as harmonic term with respect to the equilibrium at a given temperature plus an harmonic perturbation. Taking account from that we have:

$$H = \frac{P^2}{2\mu} + U_E(\chi) = H_0 + U_E(a) + \delta U_E(y); H_0 = \frac{P^2}{2\mu} + \frac{1}{2} k_{\text{eff}} y^2, \quad (3)$$

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

with  $a$  is the net thermal expansion, and  $y$  is the deviation from the equilibrium value of  $x$  at  $T$  temperature. The using

interaction potential 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 Morse expression for the fcc pure csystals:

$$U_E(\chi) = D(e^{-2\alpha x} - 2e^{-\alpha x}) \approx D(-1 + \alpha^2 x^2 - \alpha^3 x^3 + \dots) \quad (4)$$

In case dopant crystals, expression of the Morse potential has form:

$$U_E(\chi) = D_{12}(-1 + \alpha_{12}^2 x^2 - \alpha_{12}^3 x^3 + \dots) \quad (5)$$

In Eqs.(4, 5)  $\alpha$  is expansion thermal parameter,  $D$  is the dissociation energy by  $U(r_0) = -D$ . This Morse potential parameters in Eq.(5) have been obtained by averaging those of the pure crystals and they are given by:

$$\alpha_{12}^2 = \frac{D_1 \alpha_1^2 + D_2 \alpha_2^2}{D_1 + D_2}, \alpha_{12}^3 = \frac{D_1 \alpha_1^3 + D_2 \alpha_2^3}{D_1 + D_2}, D_{12} = \frac{D_1 + D_2}{2} \quad (6)$$

From expressions (2), (4) we have potential effective interaction Einstein generalize as:

$$U_E(\chi) = U_E(a) + \frac{1}{2} k_{\text{eff}} y^2 + \delta U_E(y), \quad (7)$$

Substituting Eq. (5) with  $x = y + a$  into (2) and using Eq. (7) to calculate the second term in Eq. (2) with  $\mu = M/2$  ( $M_1 = M_2 = M$ ), sum of  $i$  is over absorbing and backscattering atoms, and the sum of  $j$  is over all their near neighbors, and from calculation of  $(\hat{R}_{i2} \cdot \hat{R}_{ij})$  with lattice fcc crystals, we obtain thermodynamic parameters like  $k_{\text{eff}}$ ,  $k_3$  and  $\delta U_E(y)$ :

$$k_3 = -\frac{5D_{12}\alpha_{12}^3}{4}; k_{\text{eff}} = 5D_{12}\alpha_{12}^2 \approx \mu_{12}\omega_E^2; \quad \delta U_E(y) = 5D_{12}\alpha_{12}^2 \left( ay - \frac{\alpha_{12}y^3}{4} \right) \quad (8)$$

To derive the analytical formulas for cumulants for the crystals of cubic structure, we use perturbation theory [1,5]. The atomic vibration is quantized as phonon and anharmonicity is the result of phonon interaction. Accordingly, we express  $y$  in terms of annihilation and creation operators  $\hat{a}^+$ ,  $\hat{a}$ , respectively:

$$y = \sigma^0 \left( \hat{a} + \hat{a}^+ \right); \quad \sigma^0 = \sqrt{\hbar / 2m\omega_E}; \quad \hat{a}^+ \hat{a} = n,$$

and use the harmonic oscillator states  $|n\rangle$  as eigenstates with eigenvalues  $E_n = n\hbar\omega_E$ , ignoring the zero-point energy for convenience. The  $\hat{a}^+$ ,  $\hat{a}$  operators satisfies the following properties  $[\hat{a}, \hat{a}^+] = \hat{a}\hat{a}^+ - \hat{a}^+\hat{a} = 1$ ;  $\hat{a}^+|n\rangle = \sqrt{n+1}|n+1\rangle$ ;  $\hat{a}|n\rangle = \sqrt{n}|n-1\rangle$ . The cumulants are calculated by the average value  $\langle y^m \rangle = \frac{1}{Z} \text{Tr}(\rho y^m)$ ,  $m = 1, 2, 3, \dots$ ,  $\rho = \exp(-\beta H)$ ,  $\beta = (k_B T)^{-1}$ , where  $Z$  is the canonical partition function,  $\rho$  with  $\beta$  is the statistical density matrix,  $k_B$  is Boltzmann's constant. The corresponding unperturbed quantities are  $Z_0 = \text{Tr}(\rho_0)$ , and  $\rho_0 = \exp(-\beta H_0)$ . To leading order in perturbation  $\delta U_E$ ,  $\rho = \rho_0 + \delta\rho$  with  $\partial\rho$  is given by:

$$\partial\rho = -H\rho\partial\beta; \partial\rho_0 = -H_0\rho_0\partial\beta$$

we obtained:

$$\delta\rho = -\int_0^\beta e^{-\beta H_0} \delta\tilde{U}_E(\beta') d\beta'; \delta\tilde{U}_E(\beta) = e^{\beta H_0} \delta U_E e^{-\beta H_0}.$$

If we put unperturbed quantities equal to zero, we have:

$$Z_0 = \text{Tr}\rho_0 = \sum_n \exp(-n\beta\hbar\omega_E) = \sum_{n=0}^{\infty} z^n = \frac{1}{1-z},$$

where  $z \equiv e^{-\beta\hbar\omega_E} = e^{-\theta_E/T}$  is the temperature variable and determined by the  $\theta_E = \hbar\omega_E / k_B$  is Einstein temperature. For taking into account the anharmonicity we obtain the cumulants:

$$\sigma^{(1)} = a = \frac{3\hbar\omega_E}{40D_{12}\alpha_{12}} \frac{(1+z)}{(1-z)} \quad (9)$$

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

$$\sigma^{(3)} = \frac{\hbar^2\omega_E^2}{200D_{12}^2\alpha_{12}^3} \frac{(1+10z+z^2)}{(1-z)^2} \quad (11)$$

where  $z \equiv e^{-\beta\hbar\omega_E} = e^{-\theta_E/T}$  is the temperature variable and determined by the  $\theta_E = \hbar\omega_E / k_B$  is Einstein temperature.

### 3. Numerical Results and Comparison with Experimental

We applied the expressions derived in the previous section to numerical calculation for mixed crystal is Cooper-Nikel (CuNi). According to Morse potential parameters for pure Cu, Ni crystals have been known [7] we calculated parameters  $D_{12}$  and  $\alpha_{12}$  for dopaintcrystals above follow Table 1.

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

Crystals	D(eV)	$\alpha(\text{\AA}^{-1})$
Cu-Cu	0,3429	1,3588
Ni-Ni	0,4205	1,4149
Cu-Ni	0,3817	1,3900

Substituting  $D_{12}$ ,  $\alpha_{12}$  thermodynamic parameters from Table 1 into Eq.(8) 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  $\mu$ , correlated Einstein frequency  $\omega_E$  and Einstein temperature  $\theta_E$  for Cu crystal doped by Ni crystal according to Table 2.

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

Tinh thể	$k_{\text{eff}}(\text{eV}\text{\AA}^{-2})$	$\mu(\text{eV}/\text{\AA}^2 \cdot \text{s}^{-2})$	$\omega_E(10^{13} \text{ Hz})$	$\theta_E(\text{K})$
Cu-Cu	3,165546	$0,331262 \cdot 10^{-26}$	3,09275	235,950
Ni-Ni	4,209083	$0,305981 \cdot 10^{-26}$	3,61024	275,773
Cu-Ni	3,687413	$0,318622 \cdot 10^{-26}$	3,40191	259,859

Substituting values of thermodynamic parameters from Table 2 into Eqs. (8, 9, 10) we received expressions of cumulants to describe temperature variable  $z = e^{-\theta_E/T}$ . Next, substituting Einstein temperature value  $\theta_E(\text{K})$  into expression of  $z$  temperature variable, we have expressions to only illustrate T dependence temperature of cumulants.

$$\sigma^{(1)} = 3.165326 \times 10^{-3} \times \frac{1 + e^{-\frac{259,86}{T}}}{1 - e^{-\frac{259,86}{T}}} \quad (\text{A}) \quad (12)$$

$$\sigma^{(2)} = 3,036284 \times 10^{-3} \times \frac{1 + e^{-\frac{259,86}{T}}}{1 - e^{-\frac{259,86}{T}}} \quad (\text{A}^2) \quad (13)$$

$$\sigma^{(3)} = 0,00641 \times 10^{-3} \frac{1 + 10e^{-\frac{259,86}{T}} + \left( e^{-\frac{259,86}{T}} \right)^2}{\left( 1 - e^{-\frac{259,86}{T}} \right)^2} \quad (\text{A}^3) \quad (14)$$

To graph the temperature dependence of cumulants from to Eqs.(12, 13, 14) for Cu, Ni pure crystals and Cu doped by Ni crystal we have formed graphs follow Figures (1, 2, 3). Figure 1 and Figure 3 shows the temperature dependence of the calculated from first cumulant  $\sigma^{(1)}(T)$  or net thermal expansion and third cumulant  $\sigma^{(3)}(T)$  of Cu doped by Ni crystal and Cu, Ni pure crystals. They contribute to the phase shifts of the XAFS due to anhamonicity. Theoretical results for  $\sigma^{(1)}(T)$  agree well with the experimental values at 77K, 295K and 700K temperatures for Cu pure crystals[8, 9] and

at 300K, 683K temperatures for Ni pure crystal and mixed CuNi crystal. Theoretical results for  $\sigma^{(3)}(T)$  are associated of good agreement with the experimental values at 295K temperature for Cu pure crystal and Cu doped by Ni crystal, and at 300K temperature for Ni pure crystal [8, 9, 10]. Figure 2 illustrates the temperature dependence of our calculated anharmonic contribution the second cumulant  $\sigma^{(2)}(T)$  or the mean square relative displacement (MSRD) of CuNi mixed crystal and Cu, Ni pure crystals and compared to the measured values at 77K, 295K and 700K temperatures for CuNi [9] and at 10K, 295K and 683K temperatures for Cu and Ni [8, 9, 10], theoretical results also agrees well with experimental. Note that the experimental values from XAFS spectra have been measured at HASYLAB and BUGH Wuppertal (DESY, Germany)[7]. In the graphs we are known that at low temperatures the cumulants  $\sigma^{(1)}, \sigma^{(2)}, \sigma^{(3)}$  included zero-point energy contributions, these are 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 agree with results of classical theory and experiment.

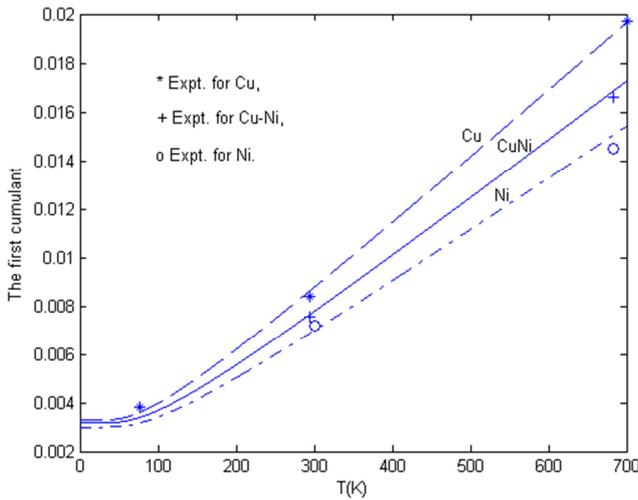


Fig. 1. The temperature dependence of the  $\sigma^{(1)}(T)$

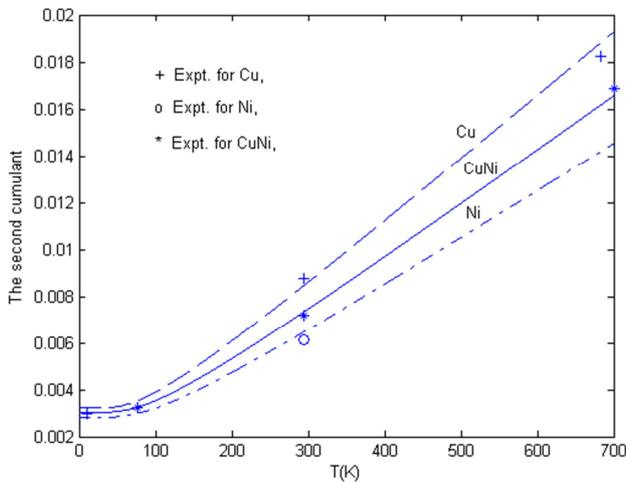


Fig. 2. The temperature dependence of the  $\sigma^{(2)}(T)$

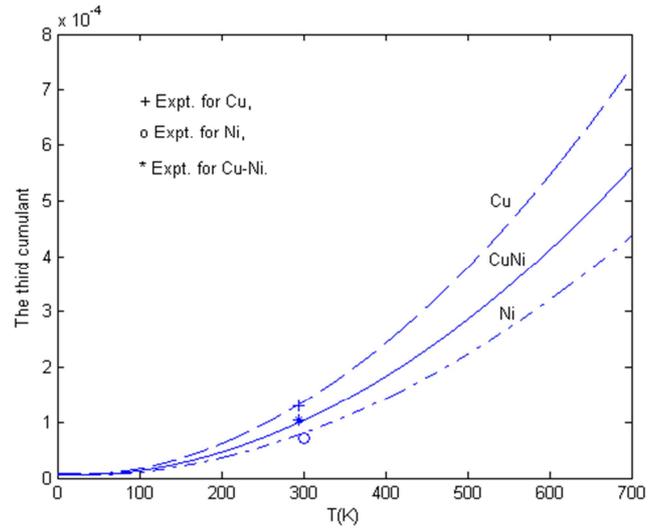


Fig. 3. The temperature dependence of the  $\sigma^{(3)}(T)$

#### 4. Conclusion

A new analytical theory for calculation and evaluation of the thermodynamic properties of fcc dopant crystals has been developed based on the quantum statistical theory with the anharmonic correlated Einstein model of the doping fcc crystals. The expressions for the thermodynamic parameters, effective force constant, correlated Einstein frequency and temperature are in correspondence with the first, second and third cumulants in anharmonic XAFS spectra of fcc crystals that include dopant crystals, agree with all standard properties of these quantities. The calculation quantities for the doping crystals has the same form as for the pure crystals themselves.

The agreement between the results of calculated theory and the experimental values demonstrates possibility that may be adopted for the present theory in XAFS data analysis.

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