CALCULATION OF XAFS CUMULANTS FOR FCC CRYSTALS CONTAINING IMPURITY ATOM

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Abstract: A new procedure for calculation and evaluation of XAFS cumulants of fcc crystals containing impurity atom has been developed based on the quantum statistical theory with correlated Einstein model. Analytical expressions for the effective local force constants, correlated Einstein frequency and temperature, first cumulant or net thermal expansion, second cumulant or Debye Waller factor and third cumulant of fcc crystals containing impurity atom have been derived. Morse potential parameters of pure crystals and those with impurity included in the derived expressions have been calculated. Numerical results for Cu, Ni, Ni-Cu are found to be in good agreement with experiment.

. Introduction

The crystals with fcc structure occupies about 25 % of elements in the periodical Mendeleev system. That is why the calculation of physical parameters of hese crystals is very important. To study thermodynamic properties of a substance t is necessary to investigate its effective local force constants, correlated Einstein requency and temperature, net thermal expansion, mean square relative lisplacement (MSRD) or Debye Waller factor and third cumulant [1-13] which are ontained in the X-ray absorption fine structure (XAFS) [9]. Moreover, the impurity or dopant atom can infuence on the physical parameters taken from the XAFS pectra [10] and on the efficiency of using these substances. Thermodynamic properties of alkali metals under influence of impurity has been studied [11].

The purpose of this work is to develop a method for calculation and evaluation of the effective local force constants, correlated Einstein frequency and emperature, first cumulant or net thermal expansion, second cumulant which is qual to MSRD or Debye Waller factor and third cumulant of fcc crystals containing l dopant or impurity (I) atom as absorber in the XAFS process. Its nearest neighbors are the host (H) atoms. The derivation is based on the quantum statistical theory with the correlated Einstein model [7] which is considered at present as "the best theoretical framework with which the experimentalist can elate force constants to temperature dependent XAFS" [10]. For completing the ab nitio calculation procedure the parameters of Morse potential of pure crystals and hose with impurity have been also calculated. Numerical calculations for Cu, Ni, and Cu doped by Ni atom have been carried out in comparison to those of the pure naterials to show thermodynamical effects of fcc crystal under influence of the mpurity atom. The calculated results are found to be in good agreement with xperiment for Morse potential and for the other thermodynamic parameters [13].

2. Formalism

The expression for the MSRD in XAFS theory is derived based on the anharmonic correlated Einstein model [7] according to which the effective interaction Einstein potential of the system consisting of an impurity (I) atom as absorber and the other host (H) atoms is given by

$$V_{eff}(x) \cong \frac{1}{2}k_{eff}x^2 + k_3x^3 + \cdots = V_{IH}(x) + \sum_{j \neq i} V_{IH}\left(\frac{\mu}{M_i}x\hat{R}_{12}.\hat{R}_{ij}\right), \quad \mu = \frac{M_I M_H}{M_I + M_H}. \tag{1}$$

Here x is deviation between the instantaneous bond length r and its equilibrium value r_0, k_{eff} is effective local force constant, and k_3 the cubic parameter giving an asymmetry in the pair distribution function, $\hat{R}$ is bond unit vector. The correlated Einstein model may be defined as a oscillation of a pair of atoms with masses M_I and M_H (e.g., of impurity atom as absorber and of host atom as backscatterer) in a given system. Their oscillation is influenced by their neighbors given by the last term in the left-hand side of Eq. (1), where the sum i is over absorber ($i = 1$) and backscatterer ($i = 2$), and the sum j is over all their nearest neighbors, excluding the absorber and backscatterer themselves. The latter contributions are described by the term $V_{IH}(x)$.

For weak anharmonicity in the XAFS process the Morse potential is given by the expansion

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

for the pure material and

$$V_{IH}(x) = D_{IH}\left(-1 + \alpha_{IH}^2 x^2 - \alpha_{IH}^3 x^3 + \cdots\right) \tag{3}$$

for the case with impurity, where Morse potential parameters have been obtained by averaging those of the pure materials and are given by

$$D_{IH} = \frac{D_I + D_H}{2}, \quad \alpha_{IH}^2 = \frac{D_I \alpha_I^2 + D_H \alpha_H^2}{D_I + D_H}, \quad \alpha_{IH}^3 = \frac{D_I \alpha_I^3 + D_H \alpha_H^3}{D_I + D_H}. \tag{4}$$

Using the definition [2, 7] $y = x - a$ as the deviation from the equilibrium value of x the Eq. (1) is rewritten in the sum of the harmonic contribution and the anharmonic contribution δV as a purturbation

$$V_{eff}(y) = \frac{1}{2}k_{eff}y^2 + \delta V. \tag{5}$$

Taking into account the atomic distribution of fcc crystal and using the above equations we obtain the effective local force constant

$$k_{eff} = 2\left[D_{IH}\alpha_{IH}^2[1 + 3(\mu_1^2 + \mu_2^2)] + \frac{1}{2}D_H\alpha_H^2\right] = \mu\omega_E^2, \tag{6}$$

the cubic anharmonic parameter

$$k_3 = D_{IH}\alpha_{IH}^3(1+\mu_1^3+\mu_2^3), \tag{7}$$

the anharmonic contribution to the effective potential of the system

$$\delta V(y) = 2\left[D_{IH}\alpha_{IH}^2\left(1+3(\mu_1^2+\mu_2^2)\right)+\frac{1}{2}D_H\alpha_H^2\right]ay - D_{IH}\alpha_{IH}^3(1+\mu_1^3+\mu_2^3).y^3, \tag{8}$$

the correlated Einstein frequency

$$\omega_E = \left\{\frac{2}{\mu}\left[D_{IH}\alpha_{IH}^2[1+3(\mu_1^2+\mu_2^2)]+\frac{1}{2}D_H\alpha_H^2\right]\right\}^{1/2}, \tag{9}$$

and the correlated Einstein temperature

$$\theta_E = \frac{\hbar}{k_B}\left\{\frac{2}{\mu}\left[D_{IH}\alpha_{IH}^2[1+3(\mu_1^2+\mu_2^2)]+\frac{1}{2}D_H\alpha_H^2\right]\right\}^{1/2}, \tag{10}$$

where

$$\mu_1 = \frac{M_I}{M_I+M_H}, \quad \mu_2 = \frac{M_H}{M_I+M_H}, \quad \mu_2 = \frac{M_H}{M_I+M_H}. \tag{11}$$

The cumulants have been derived by averaging procedure, using the statistical density matrix ρ and the canonical partition function Z in the form

$$< y^m > = \frac{1}{Z}Tr(\rho y^m), \quad m = 1,2,3,\cdots \quad , \tag{12}$$

$$Z = Tr\rho, \quad \rho = \rho_o + \delta\rho, \quad Z \approx Z_o = Tr\rho_o \quad , \tag{13}$$

$$\rho_o = e^{-\beta H_o}, \quad H_o = \frac{P^2}{2\mu}+\frac{1}{2}k_{eff}y^2, \quad \beta = 1/k_BT, \tag{14}$$

where k_B is Boltzmann constant and $\delta\rho$ is neglected due to small anharmonicity in XAFS [2].

Using the above results we calculate the second cumulant or Debye-Waller factor

$$\sigma^2 \approx \frac{1}{Z_o}Tr\left(\rho y^2\right) = \frac{1}{Z_o}\sum_n e^{-n\hbar\omega_E}\langle n|y^2|n\rangle = \frac{\hbar\omega_E(1+z)}{2k_{eff}(1-z)}, \quad z = e^{-\theta_E/T}, \tag{15}$$

where we express y in terms of anihilation and creation operators, $\hat{a}$ and $\hat{a}^+$, i. e.,

$$y = \kappa\left(\hat{a}+\hat{a}^+\right); \quad \kappa^2 = \frac{\hbar}{2\mu\omega_E} \tag{16}$$

and use harmonic oscillator state $|n\rangle$ with eigenvalue $E_n = n\hbar\omega_E$ (ignoring the zero point energy for convenience).

Therefore, the expression for second cumulant (MSRD) or Debye-Waller factor is resulted as

$$\sigma^2 = \sigma_o^2\frac{(1+z)}{(1-z)}, \quad \sigma_o^2 = \frac{\hbar\omega_E}{4\left[D_{IH}\alpha_{IH}^2[1+3(\mu_1^2+\mu_2^2)]+\frac{1}{2}D_H\alpha_H^2\right]}. \tag{17}$$

Now we calculate the odd cumulants

$$\sigma^{(m)} = \langle y^m \rangle = \frac{1}{Z_0} \sum_{n,n'} \frac{e^{-\beta E_n} - e^{-\beta E_{n'}}}{E_n - E_{n'}} \langle n|\delta V|n'\rangle\langle n'|y^m|n\rangle. \tag{18}$$

Using the calculated matrix elements and mathematical formulas for different transformations we obtain the expressions for the first cumulant ($m=1$)

$$\sigma^{(1)} = a(T) = \sigma_o^{(1)} \frac{(1+z)}{(1-z)}; \quad \sigma_o^{(1)} = \frac{3D_{IH}\alpha_{IH}^3(1+\mu_1^3+\mu_2^3)\kappa^2}{2\left[D_{IH}\alpha_{IH}^2(1+3\mu_1^2+\mu_2^2)+\frac{1}{2}D_H\alpha_H^2\right]}, \tag{19}$$

and for the third cumulant ($m=3$)

$$\sigma^{(3)} = \sigma_o^{(3)} \frac{(1+10z+z^2)}{(1-z)^2}; \quad \sigma_o^{(3)} = \frac{(\hbar\omega_E)^2}{16} \frac{D_{IH}\alpha_{IH}^3(1+\mu_1^3+\mu_2^3)}{\left[D_{IH}\alpha_{IH}^2(1+3\mu_1^2+\mu_2^2)+\frac{1}{2}D_H\alpha_H^2\right]^3}. \tag{20}$$

In the above expressions $\sigma_o^{(1)}$, σ_o^2, $\sigma_o^{(3)}$ are zero-point contributions to the first, second and third cumulants, respectively. They characterize quantum effects occurred by using quantum theory in our calculation and influence on the obtained results. The above derived cumulants are contained in the XAFS including anharmonic contributions [9].

3. Numerical results and comparison to experiment

Now we apply the derived expressions to numerical calculations for Cu, Ni and Cu doped by Ni atom as absorber in the XAFS process. Their Morse potential parameters have been calculated using the procedure presented in [16]. The calculated values of Morse potential parameters; correlated Einstein frequency and temperature; effective local force constant for the pure Cu, Ni and those doped by Ni atom are written in Table I. They are found to be in good agreement with experiment [13].

Table I: Calculated values of Morse potential parameters D, α; correlated Einstein frequency ω_E and temperature θ_E; effective local force constant k_{eff} for Ni-Ni, Cu-Cu, Ni-Cu in comparison to experiment [13].

Bond	$D(eV)$	$\alpha(\text{Å}^{-1})$	$r_o(\text{Å})$	$k_{eff}(N/m)$	$\omega_E(\times10^{13}\,Hz)$	$\theta_E(K)$
Ni-Ni, present	0.4263	1.3819	2.8033	65.2158	3.6473	278.6038
Ni-Ni, exp.[13]	0.4100	1.3900	2.9035	63.4596	3.5979	274.8271
Cu-Cu, present	0.3367	1.3549	2.8701	49.5156	3.0544	233.3151
Cu-Cu, exp.[13]	0.3300	1.3800	2.9802	50.3450	3.0799	235.2661
Ni-Cu, present	0.3817	1.3928	2.9537	60.1340	3.4348	262.3749
Ni-Cu, exp.[13]	0.3700	1.3855	2.9337	57.8621	3.3693	257.3708

Figure 1 illustrates our calculated Morse potentials of Cu, Ni and of Cu dopped by Ni atom which agrees well with the experimental result [13].
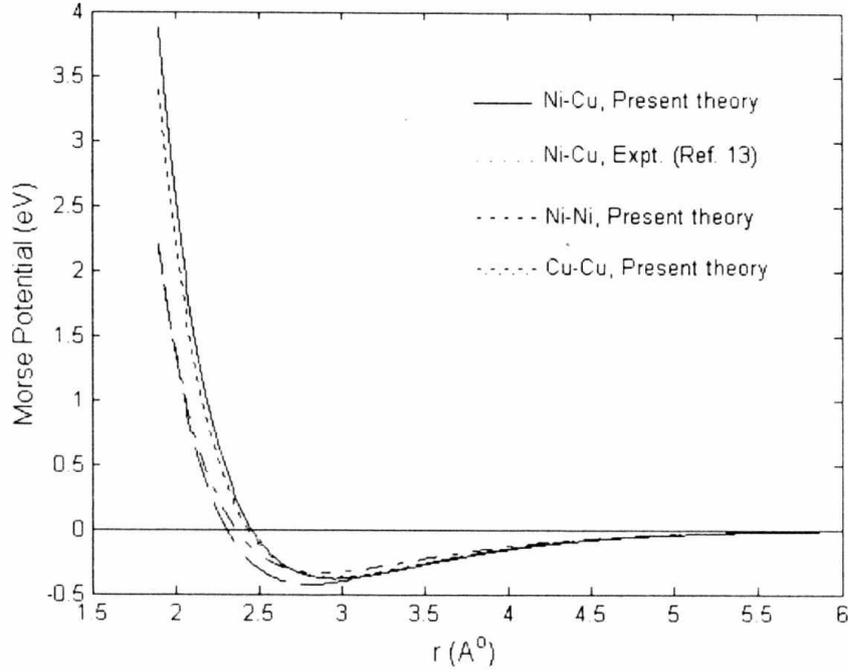

Figure 1: Morse potentials of Cu, Ni and Cu doped by Ni atom compared to experiment [13].
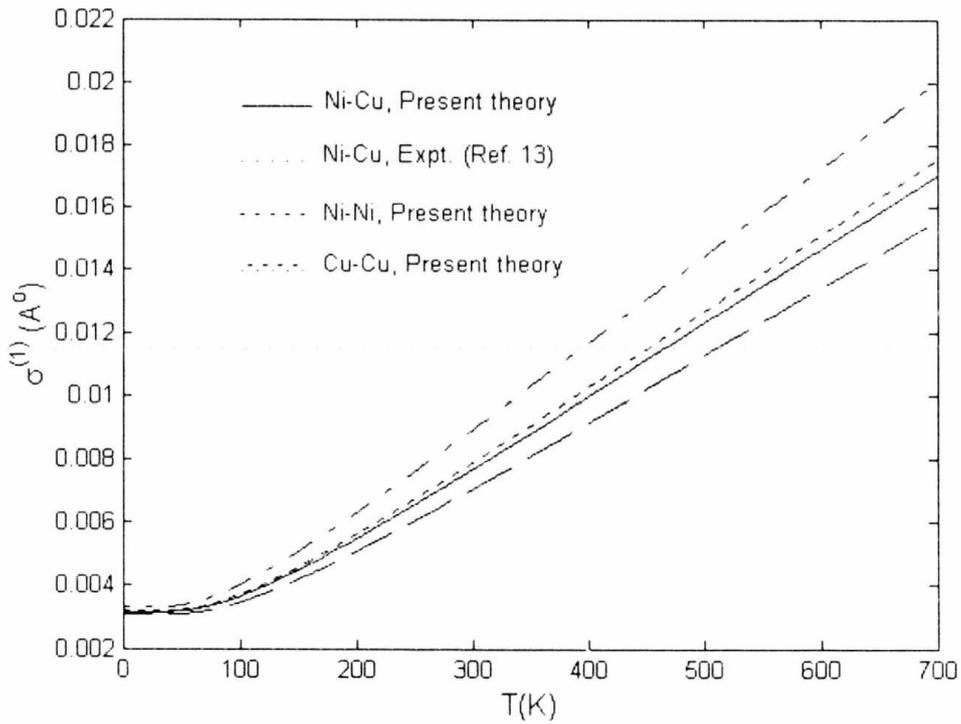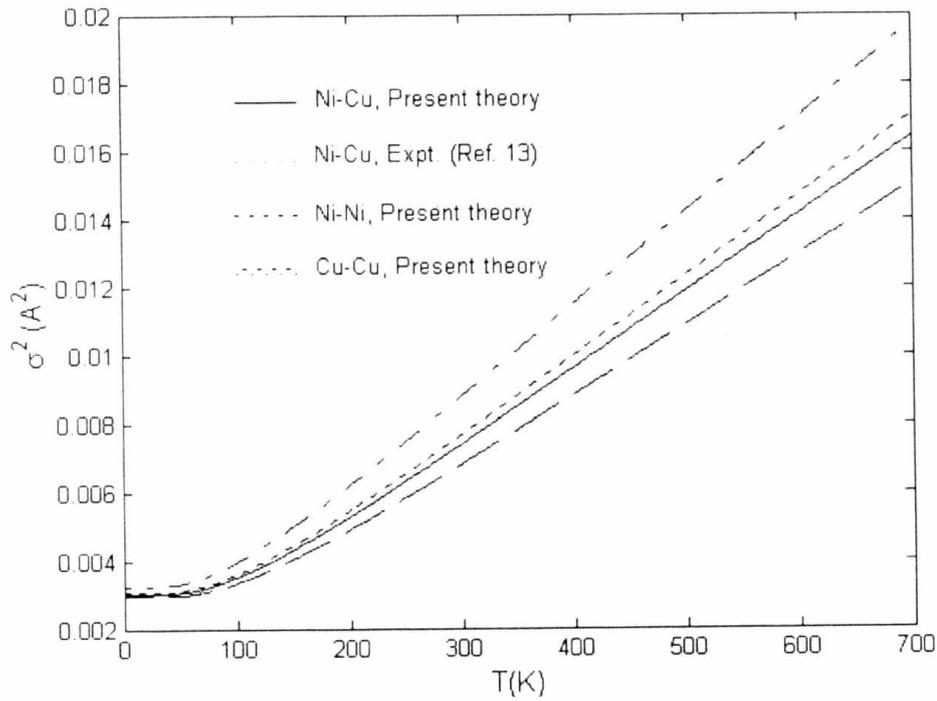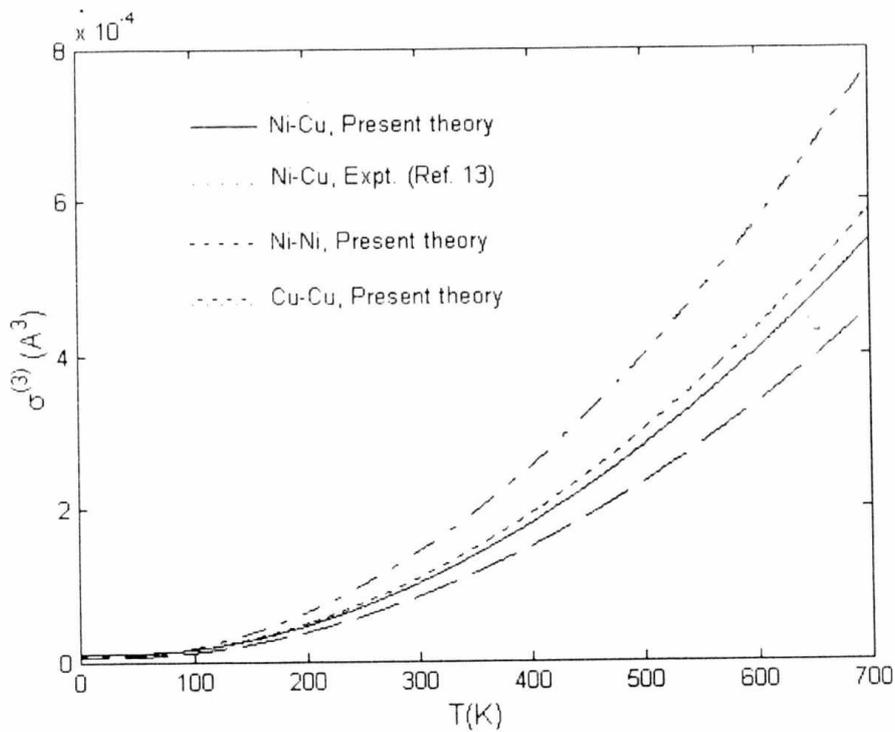

Figure 2: Temperature dependence of our calculated first cumulant $\sigma^{(1)}(T)$ of Cu (dash-dot), Ni (dash) and of Cu doped by Ni atom (solid) compared to experiment (dot) [13].

Figure 3: Temperature dependence of our calculated second cumulant $\sigma^2(T)$ of Cu (dash-dot), Ni (dash) and of Cu doped by Ni atom (solid) compared to experiment (dot) [13].

Figure 4: Temperature dependence of our calculated third cumulant $\sigma^{(3)}(T)$ of Cu (dash-dot), Ni (dash) and of Cu doped by Ni atom (solid) compared to experiment (dot) [13].

The temperature dependence of our calculated first cumulant or net thermal expansion $\sigma^{(1)}(T)$ (Figure 2), second cumulant or Debye-Waller factor $\sigma^2(T)$ (Figure 3) and third cumulant $\sigma^{(3)}(T)$ (Figure 4) shows significant changes of these values when Cu is dopped by Ni atom and a reasonable agreement between the calculated by the present theory and experimental values. Figures 2, 3, 4 show that the cumulants of Cu become weaker due to the dopant by Ni atom. These impu`rity effects are very important and they have to be taken into account in the evaluation of thermodynamic properties of the substances. The calculated first, second and third cumulant containing impurity atom also satisfy all important properties discovered in theory [7, 17] and experiment [1]. They contain zero-point contribution at low temperature and approach the classical theory results at high temperature, i., e., the proportionality to the high temperature is linear for the first and second cumulant and quadratical for the third cumulant.

4. Conclusions

A new analytical method for calculation and evaluation of thermodynamic properties of the fcc crystals containing impurity atom has been developed based on the quantum statistical theory with correlated Einstein model.

Our development is the derivation of the analytical expressions for the local effective force constants, correlated Einstein frequency and temperature, the first, second and third XAFS cumulant of fcc crystals containing impurity atom. They are significantly different from those of the pure materials, but satisfy all standard properties of these quantities. These differences denote the impurity effects which discovered in experiment and they have to be taken into account in the evaluation of thermodynamic properties of the substances.

Morse potential parameters have been also analytically calculated thus completing the ab initio calculation procedure of the considered values.

The good agreement between the calculated and the experimental results demonstrates the efficiency and possibility of using the present developed procedure in XAFS data analysis.

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