

Anharmonic effective potential and XAFS cumulants for hcp crystals containing dopant atom

Nguyen Van Hung*, Le Thi Thuy Hau, Tong Sy Tien

*Department of Physics, College of Science, VNU
334 Nguyen Trai, Hanoi, Vietnam*

Received 17 June 2007

Abstract. A new procedure for calculation and analysis of XAFS (X-ray Absorption Fine Structure) cumulants of hcp crystals containing dopant atom has been derived based on quantum statistical theory with generalized anharmonic correlated Einstein model. Analytical expressions for 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 hcp crystals containing dopant atom have been derived. Morse potential parameters of pure crystals and those with dopant included in the derived expressions have been calculated. Numerical results for Zn doped by Cd are found to be in good agreement with experiment.

1. Introduction

To study thermodynamic properties of a substance it is necessary to investigate its effective local force constants, correlated Einstein frequency and temperature, net thermal expansion, mean square relative displacement (MSRD) or Debye Waller factor and third cumulant [1-14] which are contained in the XAFS [12]. Local force constants of transition metal dopants in a nickel host in XAFS has been investigated but only for comparison to Mossbauer studies [10].

The purpose of this work is to develop a method for calculation and evaluation of the effective local force constants, correlated Einstein frequency and temperature, first cumulant or net thermal expansion, second cumulant or MSRD characterizing Debye Waller factor and third cumulant of hcp crystals containing a dopant (D) atom as absorber in the XAFS process. Its nearest neighbors are the host (H) atoms. The derivation is based on the generalization of the anharmonic correlated Einstein model [7] which is considered at present as "the best theoretical framework with which the experimentalist can relate force constants to temperature dependent XAFS" [10] to the case for crystal containing dopant atom. For completing the ab initio calculation procedure the parameters of Morse potential of pure crystals and those with dopant have been also calculated. Numerical calculations for Zn doped by Cd atom have been carried out to show the thermodynamical effects of hcp crystal under influence of the doping atom. The calculated results are found to be in good agreement with experiment for Morse potential and for the other thermodynamic parameters [13].

* Corresponding author. Tel: 84-4-8587425
E-mail: hungnv@vnu.edu.vn

2. Formalism

The expression for the MSD in XAFS theory is derived based on the anharmonic correlated Einstein model [7] generalized to the case with a dopant atom according to which the effective interaction Einstein potential of the system consisting of an dopant (D) atom as absorber and the other host (H) atoms as scatterers is given by

$$V_{eff}(x) \cong \frac{1}{2}k_{eff}x^2 + k_3x^3 + \dots = V_{HD}(x) + \sum_{j \neq i} V_{HD} \left(\frac{\mu}{M_i} x \hat{\mathbf{R}}_{i2} \cdot \hat{\mathbf{R}}_j \right) \\ = V_{HD}(x) + V_{HD}(-\kappa x) + 4V_{HD} \left(\kappa \frac{x}{2} \right) \tag{1}$$

$$+ 4V_{HD} \left(-\kappa \frac{x}{2} \right) + 4V_{HH} \left(\frac{1}{2} \cdot \frac{x}{2} \right) + 4V_{HH} \left(-\frac{1}{2} \cdot \frac{x}{2} \right) + V_{HH} \left(-\frac{1}{2} x \right). \\ \mu = \frac{M_D M_H}{M_D + M_H}, \quad \kappa = \frac{M_H}{M_D + M_H}. \tag{2}$$

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, $\hat{\mathbf{R}}$ is bond unit vector. The correlated Einstein model is here generalized as a oscillation of a pair of atoms with masses M_D and M_H (e.g., of dopant atom as absorber and of host atom as backscatterer) in a given system. Their oscillation is influenced by their neighbors given by the 2nd term in the right side of the second 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 $V_{HD}(x)$. The third equality is for hcp crystals containing dopant atom.

For weak anharmonicity in XAFS the Morse potential is used expanded to the 3rd order

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

for the pure material and

$$V_{HD}(x) = D_{HD}(-1 + \alpha_{HD}^2 x^2 - \alpha_{HD}^3 x^3 + \dots) \tag{4}$$

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

$$D_{HD} = \frac{D_D + D_H}{2}, \quad \alpha_{HD}^2 = \frac{D_D \alpha_D^2 + D_H \alpha_H^2}{D_D + D_H}, \quad \alpha_{HD}^3 = \frac{D_D \alpha_D^3 + D_H \alpha_H^3}{D_D + D_H}. \tag{5}$$

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 perturbation

$$V_{eff}(y) = \frac{1}{2}k_{eff}y^2 + \delta V. \tag{6}$$

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

$$k_{eff} = 2 \left[(1 + 3\kappa^2) D_{HD} \alpha_{HD}^2 + \frac{3}{4} D_H \alpha_H^2 \right] = \mu \omega_E^2, \tag{7}$$

the cubic anharmonic parameter

$$k_3 = - \left[(1 - \kappa^3) D_{HD} \alpha_{HD}^3 - \frac{1}{8} D_H \alpha_H^2 \right], \tag{8}$$

the anharmonic contribution to the effective potential of the system

$$\delta V(y) = 2 \left[(1 + 3\kappa^2) D_{HD} \alpha_{HD}^2 + \frac{3}{4} D_H \alpha_H^2 \right] ay - \left[(1 - \kappa^3) D_{HD} \alpha_{HD}^3 - \frac{1}{8} D_H \alpha_H^3 \right] y^3, \tag{9}$$

the correlated Einstein frequency and temperature

$$\omega_E = \sqrt{k_{eff} / \mu}, \quad \theta_E = \hbar \omega_E / k_B \tag{10}$$

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

$$\langle y^m \rangle = \frac{1}{Z} Tr(\rho y^m), \quad m = 1, 2, 3, \dots, \tag{11}$$

$$Z = Tr \rho, \quad \rho = \rho_0 + \delta \rho, \quad Z \approx Z_0 = Tr \rho_0, \tag{12}$$

$$\rho_0 = e^{-\beta H_0}, \quad H_0 = \frac{p^2}{2\mu} + \frac{1}{2} k_{eff} y^2, \quad \beta = 1 / k_B T, \tag{13}$$

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

$$\sigma^2 \approx \frac{1}{Z_0} Tr(\rho y^2) = \frac{1}{Z_0} \sum_n e^{-n\hbar\omega_E} \langle n | y^2 | n \rangle = \frac{\hbar \omega_E}{2k_{eff}} \frac{1+z}{1-z}, \quad z = e^{-\theta_E/T}, \tag{14}$$

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

$$y = a_0 (\hat{a} + \hat{a}^+); \quad a_0^2 = \frac{\hbar}{2\mu\omega_E} \tag{15}$$

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

$$\sigma^2 = \sigma_0^2 \frac{(1+z)}{(1-z)}, \quad \sigma_0^2 = \frac{\hbar \omega_E}{4 \left[(1 + 3\kappa^2) D_{HD} \alpha_{HD}^2 + \frac{3}{4} D_H \alpha_H^2 \right]}. \tag{16}$$

Now we calculate the odd cumulants

$$\sigma^{(m)} = \langle y^m \rangle = \frac{1}{Z_0} \sum_{n,n'} \frac{e^{-\beta E_n} - e^{-\beta E_{n'}}}{E_n - E_{n'}} \langle n | \delta V | n' \rangle \langle n' | y^m | n \rangle. \tag{17}$$

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

$$\sigma^{(1)} = a(T) = - \frac{3k_3}{k_{eff}} \sigma^2 = \sigma_0^{(1)} \frac{1+z}{1-z}, \quad \sigma_0^{(1)} = \frac{3 \left[(1 - \kappa^3) D_{HD} \alpha_{HD}^3 - \frac{1}{8} D_H \alpha_H^2 \right] \hbar \omega_E}{8 \left[(1 + 3\kappa^2) D_{HD} \alpha_{HD}^2 + \frac{3}{4} D_H \alpha_H^2 \right]^2}, \tag{18}$$

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

$$\sigma^{(3)} = \sigma_o^{(3)} \frac{(1 + 10z + z^2)}{(1 - z)^2}; \quad \sigma_o^{(3)} = \frac{(\hbar\omega_E)^2}{16} \frac{\left[(1 - \kappa^3) D_{HD} \alpha_{HD}^3 - \frac{1}{8} D_H \alpha_H^2 \right]}{\left[(1 + 3\kappa^2) D_{HD} \alpha_{HD}^2 + \frac{3}{4} D_H \alpha_H^2 \right]^3}. \quad (19)$$

From Eq. (18) we obtain the thermal expansion coefficient

$$\alpha_T = \frac{1}{r} \frac{da}{dT} = \alpha_T^0 \frac{z |\ln(z)|^2}{(1 - z)^2}, \quad \alpha_T^0 = \frac{3k_B \left[(1 - \kappa^3) D_{HD} \alpha_{HD}^3 - \frac{1}{8} D_H \alpha_H^2 \right]}{4r \left[(1 + 3\kappa^2) D_{HD} \alpha_{HD}^2 + \frac{3}{4} D_H \alpha_H^2 \right]^2}. \quad (20)$$

In the above expressions $\sigma_o^{(1)}$, $\sigma_o^{(2)}$, $\sigma_o^{(3)}$ 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, α_T^0 is constant value which α_T approaches at high temperatures. The above derived values are contained in the XAFS including anharmonic contributions [7, 12]. If the doping atom is taken out from the host material all the above expressions will be changed into those of the pure hcp crystals [14].

3. Numerical results and comparison to experiment

Now we apply the above derived expressions to numerical calculations for Zn doped by Cd atom as absorber in the XAFS process. Their Morse potential parameters have been calculated using the procedure presented in [15, 16]. The Calculated values of Morse potential parameters; correlated Einstein frequency and temperature; effective local force constant for the pure Zn, Cd and those for Zn doped by Cd atom are written in Table I. They agree well with experiment [13].

Table 1. Calculated Morse potential parameters D , α ; Einstein frequency ω_E and temperature θ_E ; effective local force constant k_{eff} for Zn-Zn, Cd-Cd, Zn-Cd compared to experiment [13].

Bond	$D(eV)$	$\alpha (\text{\AA}^{-1})$	$r_o (\text{\AA})$	$k_{eff} (N/m)$	$\omega_E (\times 10^{13} \text{ Hz})$	$\theta_E (K)$
Zn-Zn, present	0.1698	1.7054	2.7931	39.5616	2.6917	205.6101
Zn-Zn, exp.[13]	0.1685	1.7000	2.7650	39.0105	2.6729	204.1730
Cd-Cd, present	0.1675	1.9069	3.0419	48.7927	2.2798	174.1425
Cd-Cd, exp.[13]	0.1653	1.9053	3.0550	48.0711	2.2628	172.8499
Zn-Cd, present	0.1687	1.8084	2.9175	36.7083	2.3057	176.1268
Zn-Cd, exp.[13]	0.1669	1.8046	2.9100	36.1851	2.2893	174.8673

Figure 1 illustrates our calculated Morse potential (a) and anharmonic effective potential (b) for Zn doped by Cd atom. The Morse potential for this case has the same form as for the pure material, the anharmonic effective potential becomes asymmetric due to the third order of the potential. All they agree well with experiment [13].

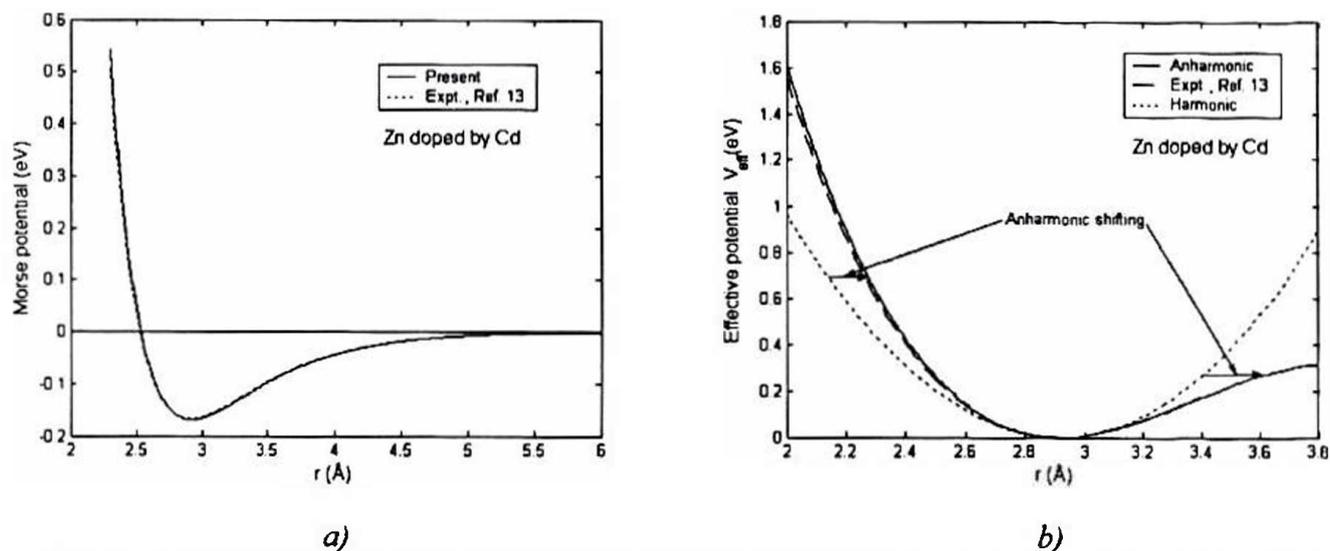


Figure 1. Calculated Morse potential (a) and anharmonic effective potential (b) for Zn doped by Cd atom compared to experiment [13].

Figure 2 demonstrates the calculated first cumulant or net thermal expansion $\sigma^{(1)}(T)$ (a), and second cumulant or Debye-Waller factor $\sigma^2(T)$ (b). The third cumulant $\sigma^{(3)}(T)$ and cumulant relation $\sigma^{(1)}\sigma^2/\sigma^{(3)}$, which is oft studied in XAFS, are illustrated in Figure 3 showing a good agreement with experiment [13] at 77K and 300K. In this doping material the relation $\sigma^{(1)}\sigma^2/\sigma^{(3)}$ decreases fastly from the value 1.5 at 0K and then approaches a constant value $\frac{1}{2}$ at high temperatures as for the hcp pure crystals [14] and for the other crystal structures such as fcc [7]. Hence, this cumulant relation is an important standard characteristic in XAFS technique not only for the pure crystals but also for the doping materials. Moreover, our calculated cumulants satisfy all their fundamental properties [17], i. e., they contain zero-point contributions due to quantum effects at low temperatures, the 1st and 2nd cumulants are linearly proportional to the temperature and the 3rd one to the square of temperature at high temperatures. They agree well with experiment at 77K and 300K [13].

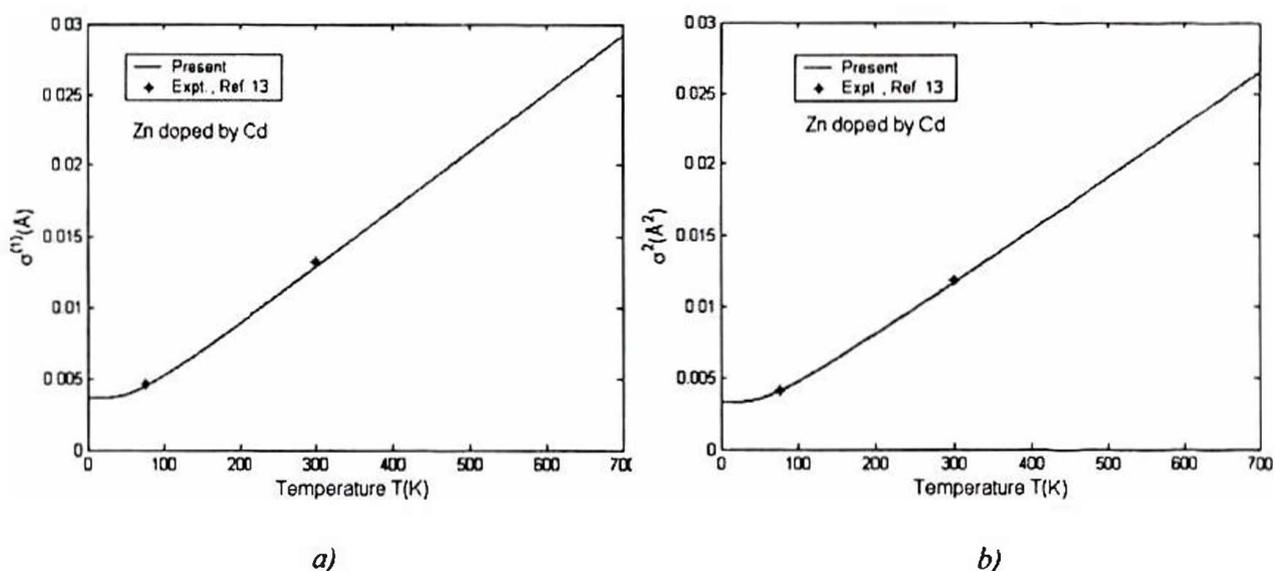


Figure 2. Temperature dependence of our calculated 1st $\sigma^{(1)}(T)$ (a) and 2nd (b) $\sigma^2(T)$ cumulant for Zn doped by Cd compared to experiment at 77K and 300K [13].

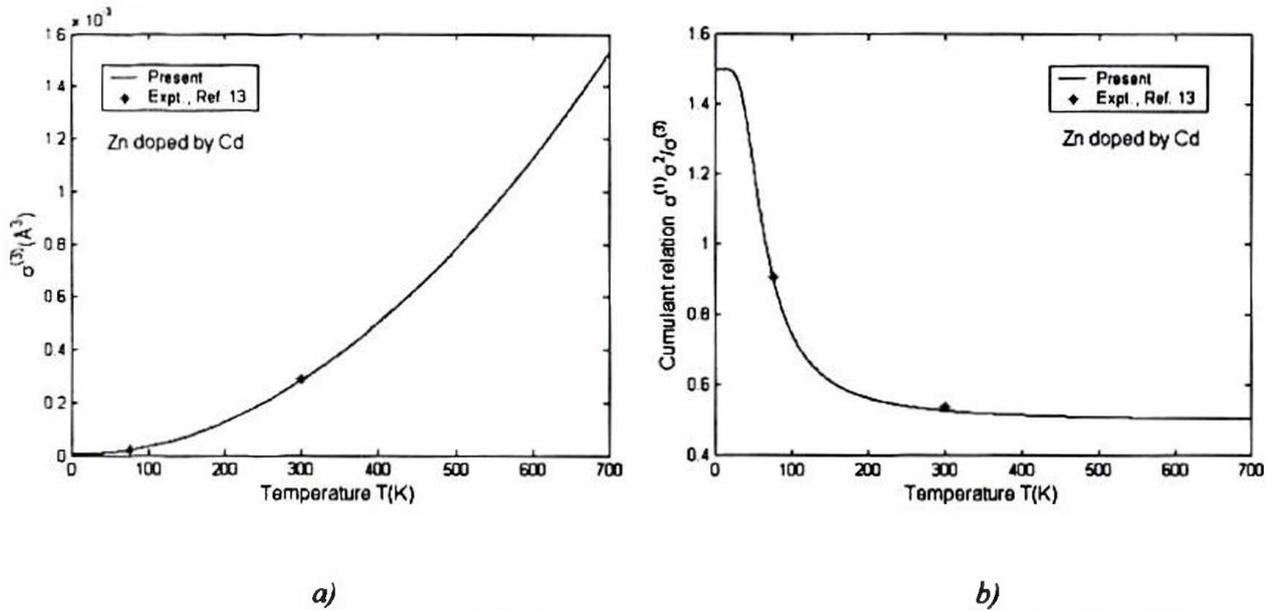


Figure 3. Calculated second cumulant $\sigma^{(2)}(T)$ (a) and cumulant relation (b) for Zn doped by Cd compared to experiment at 77K and 300K [13].

4. Conclusions

A new analytical method for calculation and evaluation of the thermodynamic properties of hcp crystals containing dopant atom has been developed based on the quantum statistical theory with the anharmonic correlated Einstein model generalized for the doping hcp crystal.

The derived expressions for the local effective force constants, anharmonic effective potential, correlated Einstein frequency and temperature, the first, second and third XAFS cumulant of hcp crystals containing dopant atom satisfy all standard properties of these quantities. The cumulant relation $\sigma^{(1)}\sigma^2 / \sigma^{(3)}$, which is oft studied in XAFS technique, for doping materials also has the same properties as for the pure crystals with different structures.

The calculated Morse potential for the doping material has the same form as for the pure one, the anharmonic effective potential becomes asymmetric due to the anharmonicity.

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.

Acknowledgments. This work is supported in part by the basic science research national program provided by the Ministry of Science and Technology No. 40.58.06.

References

- [1] E.A. Stern, P. Livins, Z. Zhang, *Phys. Rev. B* 43 (1991) 8550.
- [2] A.I. Frankel, J.J. Rehr, *Phys. Rev. B* 48 (1993) 585.
- [3] T. Miyanaga, T. Fujikawa, *J. Phys. Soc. Jpn.* 63 (1994) 1036 and 3683.
- [4] N.V. Hung, R. Frahm, *Physica B* 208-209 (1995) 91.
- [5] N.V. Hung, R. Frahm, H. Kamitsubo, *J. Phys. Soc. Jpn.* 65 (1996) 3571.
- [6] N.V. Hung, *J. de Physique IV* (1997) C2 : 279.
- [7] N.V. Hung, J.J. Rehr, *Phys. Rev. B* 56 (1997) 43.

- [8] N.V. Hung, *Commun. Phys.* 8 (1998) 46-54.
- [9] N.V. Hung, N.B. Duc, R. Frahm, *J. Phys. Soc. Jpn.* 72 (2003) 1254.
- [10] M. Daniel, D.M. Pease, N.V. Hung, J.I. Budnick, *Phys. Rev. B* 69 (2004) 134414.
- [11] N.V. Hung, Paolo Fornasini, *J. Phys. Soc. Jpn.* 76 (2007) 084601.
- [12] See *X-ray absorption*, edited by D.C. Koningsberger and R. Prins (Wiley, New York, 1988).
- [13] R.R. Frahm, N.V. Hung (to be published).
- [14] N.V. Hung et al. (to be published).
- [15] L.A. Girifalco, V.G. Weizer, *Phys. Rev.* 114 (1959) 687.
- [16] N.V. Hung, D.X. Viet, *VNU Journal of Science* 19 N₀2 (2003) 19.
- [17] J.M. Ziman, *Principles of the Theory of Solids*, 2nd ed. by Cambridge University Press, 1972.