VNU. JOURNAL OF SCIENCE, Mathematics - Physics, T.XXII, $N_0$3, 2006

STUDY OF EXAFS CUMULANTS OF FCC CRYSTALS CONTAINING N DOPANT ATOMS

Nguyen Van Hung, Tran Trung Dung, Nguyen Cong Toan

Department of Physics, College of Science, VNU

ABSTRACT. A new procedure for description and calculation of the EXAFS (Extended X-ray Absorption Fine Structure) cumulants for fcc crystals containing an abitrary number n of dopant atoms have been developed. Analytical expressions for the 1st, 2nd and 3rd cumulants have been derived. They depend on the number of dopant atoms and approach those derived by anharmonic correlated Einstein model, if all dopant atoms are taken out or replacing all the host atoms. Numerical results for Cu doped by Ni atoms based on the Morse potential show significant dependence of thermodynamic parameters of the substance on the number of dopant atoms and a reasonable agreement with experiment .

1. Introduction

Cumulant expansion approach has been developed [1, 2] to include anharmonic effects in the EXAFS procedure. These anharmonic effects are contained in the first cumulant or net thermal expansion, the second cumulant or Debye-Waller factors, the third cumulant, and the thermal expansion expansion coefficient, which are investigated intensively in the EXAFS experiment and theory [1-14]. It is also very important to study thermodynamic properties of materials containing dopant atoms [10, 14, 16]. Some investigations for crystals containing one dopant atom have been performed [10, 14, 16]. But normally more than one atom can be doped into a crystal. This case can lead to developing procedures for studying thermodynamic properties of alloys with nano structure which are often semiconductors containing some components with different atomic sourses. The effective interatomic potential and local force constant for fcc crystals containing *n* dopant atomts have been studied [16].

The purpose of this work is following our previous one [16] to develop a new procedure for description and calculation of the EXAFS cumulants and other thermodynamic parameters of fcc crystals containing some (*n*) dopant atoms, where one dopant atom [10, 14, 16] is only a special case of this theory. Our development is derivation of the analytical expressions for the correlated Einstein frequencies and temperature, for the 1st, 2nd and 3rd cumulants, where the host atom is denoted by the letter *H* and the dopant atom by the letter *D*. All these expressions are different if the number of dopant atoms changes. The results in the case if all the dopant atoms are taken out or if all the host atoms are replaced by the dopant atoms are reduced to those derived by using the anharmonic correlated Einstein model [8] for the pure materials. Numerical calculations have been carried out for

Cu doped by one or more Ni dopant atoms, and the results are compared to those of the pure materials and some to experiment deducted from the measured Morse potential parameters [15].

2. Formalism

2.1. Anharmonic effective potential, local force constant and derivation of correlated Einstein frequency and temperature

Following [16] the anharmonic correlated interatomic effective potential of a fcc crystal doped by n atoms from another source is given by

$$V_E(x) \approx \frac{1}{2} k_{eff} x^2 + k_{3eff} x^3 + \cdots \tag{1}$$

as a function of the displacement $x = r - r_0$ for r and r_0 being the instantaneous and equilibrium distances between absorber and backscatterer atoms.

Using the definitions [8] $y = x - a$, $a = \langle x \rangle$ Eq. (1) is changed into

$$V_{eff}(y) = \frac{1}{2} k_{eff} y^2 + V_{anh}(y), \quad V_{anh}(y) = \delta V(y) = k_{eff} a y + K_{3eff} y^3, \tag{2}$$

containing an effective local force constant k_{eff}

$$k_{eff} = \frac{2(A.k_H + B.k_{HD} + C.k_D)}{(1+m)^2} = \mu\left(\omega_E^{HD}\right)^2, \quad \mu = \frac{M_H M_D}{M_H + M_D} \tag{3}$$

and anharmonic effective factor k_{3eff}

$$k_{3eff} = \frac{2(A_3.k_{3H} + B_3.k_{3HD} + C_3.k_{3D})}{(1+m)^3}, \tag{4}$$

involving contributions of immediate atomic neighbors, where

$$\begin{cases} A = m^2(1 + 4\delta_{0n} - \gamma_n + \frac{\beta_n}{8}), \; C = 3\gamma_n + \delta_{13n} - \frac{\delta_{10n}}{2} + \frac{1}{8}[(1-\delta_{0n})(n-1) + \gamma_n(9-n) \\ B = \frac{1}{2}[1 - 5\delta_{0n} + \delta_{10n} - \delta_{13n} + (1+m)^2(1-\gamma_n)] + \frac{1}{8}[(9-n)(1-\delta_{0n}-\gamma_n) + m^2(4 - 4\delta_{13n} - \beta_n - 4\delta_{0n})] \end{cases} \tag{5}$$

$$\begin{cases} A_3 = m^3(1 + 4\delta_{0n} - \gamma_n + \frac{\beta_n}{8}), \; C_3 = C, \\ B_3 = \frac{1}{2}[1 - \delta_{0n} + \delta_{10n} - \delta_{13n} + (1+m)^2(1-\gamma_n-\delta_{0n})] + \frac{1}{8}[(9-n)(1-\delta_{0n}-\gamma_n) \\ \quad + m^3(4 - 4\delta_{13n} - \beta_n - 4\delta_{0n})] \end{cases} \tag{6}$$

$$\gamma_n = \delta_{10n} + \delta_{11n} + \delta_{12n} + \delta_{13n}, \; \beta_n = 4\delta_{1n} + 3\delta_{2n} + 2\delta_{3n} + \delta_{4n}, \; m = \frac{M_D + \delta_{0n}(M_H - M_D)}{M_H + \gamma_n(M_D - M_H)}. \tag{7}$$

Using the anharmonic effective local force constant Eq. (3) the correlated Einstein frequency ω_E^{HD} and temperature θ_E^{HD} are given by

$$\omega_E^{HD} = \sqrt{\frac{2(A.k_H + B.k_{HD} + C.k_D)}{(1+m)^2}}, \quad \theta_E^{HD} = \frac{\hbar\omega_E^{HD}}{k_B}, \tag{8}$$

where k_B is the Boltzmann constant.

Morse potential parameters for the case with doping are obtained by an averaging calculation from those for the host (H) and the doping (D) crystals expanded to the third order around it equilibrium

$$V(x) = D_{H(D)}(e^{-2\alpha_{H(D)}x} - 2e^{-\alpha_{H(D)}x}) \approx D_{H(D)}(-1 + \alpha_{H(D)}^2 x^2 - \alpha_{H(D)}^3 x^3 + \cdots). \tag{9}$$

Denoting the equilibrium bondlength of the host atom by r_{0H}, of the doping atom by r_{0D} and between the host and the doping atom by r_{0HD} and solving the equation system of averaging procedure, the Morse potential parameter D_{HD} characterizing dissociation energy, the Morse potential parameter α_{HD} characterizing the width of the potential, and the equilibrium bondlength between H and D atoms r_{0HD} are resulted as

$$D_{HD} = \frac{1}{2}\frac{\left[D_H\alpha_H^2 + D_D\alpha_D^2 + \dfrac{3(r_{0D} - r_{0H})\alpha_H^2\alpha_D^2 D_H D_D(\alpha_D - \alpha_H)}{D_H\alpha_H^2 + D_D\alpha_D^2}\right]^3}{(D_H\alpha_H^3 + D_D\alpha_D^3)^2}, \tag{10}$$

$$\alpha_{HD} = \frac{D_H\alpha_H^3 + D_D\alpha_D^3}{D_H\alpha_H^2 + D_D\alpha_D^2 + \dfrac{3(r_{0D} - r_{0H})\alpha_H^2\alpha_D^2 D_H D_D(\alpha_D - \alpha_H)}{D_H\alpha_H^2 + D_D\alpha_D^2}}, \tag{11}$$

$$r_{0HD} = \frac{D_H r_{0H}\alpha_H^2 + D_D r_{0D}\alpha_D^2}{D_H\alpha_H^2 + D_D\alpha_D^2}. \tag{12}$$

They will be used for calculation of thermodynamic parameters of crystals in the doping case.

2.2. Derivation of analytical expressions for EXAFS cumulants

Making use of quantum statistical methods [19] the physical quantity is determined by an averaging procedure using canonical partition function Z and statistical density matrix ρ, e. g.,

$$\langle y^m \rangle = \frac{1}{Z} Tr(\rho y^m), \; m = 1,2,3,... \tag{13}$$

Atomic vibrations are quantized in terms of phonon, and anharmonicity is the result of phonon-phonon interaction, that is why we express y in terms of phonon annihilation and creation operators, $\hat{a}$ and $\hat{a}^+$, respectively

$$y \equiv \sigma_0\left(\hat{a}+\hat{a}^+\right),\ \sigma_0^2=\frac{\hbar\omega_E^{HD}}{2k_{eff}}\ , \tag{14}$$

satisfying relations

$$[\hat{a},\hat{a}^+]=1\ ,\ \ \hat{a}^+\,|\,n>=\sqrt{n+1}\,|\,n+1>\ ,\ \ \hat{a}\,|\,n>=\sqrt{n}\,|\,n-1>\ , \tag{15}$$

and use the harmonic oscillator state $|n\rangle$ as the eigenstate with the eigenvalue $E_n=n\hbar\omega_E^{HD}$, ignoring the zero-point energy for convenience.

Using the above results for correlated atomic vibration and the first-order thermodynamic perturbation theory [19] considering the anharmonic term in the potential Eq. (2) as a perturbation δV due to the weak anharmonicity in EXAFS. Based on the procedure described by Eqs. (13-15) we derived the cumulants

$$0=<y>=\frac{1}{Z}Tr(\rho y)\approx\frac{1}{Z_0}Tr(\delta\rho y)\ , \tag{16}$$

$$\sigma^{(2)}=<y^2>=\frac{1}{Z}Tr(\rho y^2)\approx\frac{1}{Z_0}Tr(\rho_0 y^2)\ , \tag{17}$$

$$\sigma^{(3)}=<y^3>=\frac{1}{Z}Tr(\rho y^3)\approx\frac{1}{Z_0}Tr(\delta\rho y^3)\ , \tag{18}$$

$$\rho=\rho_0+\delta\rho\ ,\ \ Z=Z_0+\delta Z\ , \tag{19}$$

where ρ_0, Z_0 are unperturbed quantities and $\delta\rho, \delta Z$ the perturbations of the statistical density matrix and the canonical partition function, respectively.

The second cumuland or Mean Square Relative Displacement (MSRD) describing Debye-Waller factor (DWF) has been derived

$$\sigma^2=<y^2>\approx\frac{1}{Z_0}Tr(\rho_0 y^2)=\sum_n z^n<n\,|\,y^2\,|\,n>,\ z=e^{-\theta_E^{HD}/T}\ . \tag{20}$$

Substituting the calculated matrix element, i. e.,

$$<n\,|\,y^2\,|\,n>=(2n+1){\sigma_0}^2 \tag{21}$$

into Eq. (20) we obtained

$$\sigma^2=\frac{1}{Z_0}\sigma_0^2\sum_n(2n+1)z^n=\frac{1}{Z_0}\sigma_0^2\left\{\frac{1}{1-z}+\frac{2z}{(1-z)^2}\right\}=\frac{\hbar}{2\sqrt{\mu\,k_{eff}}}\frac{1+z}{1-z}=\sigma_0^2\frac{1+z}{1-z}\ ,\quad \sigma_0^2=\frac{\hbar\omega_E^{HD}}{2k_{eff}}\ . \tag{22}$$

The odd moments $<y>$ and $<y^3>$ have been calculated using the general expression

$$<y^m>=\frac{1}{Z_0}Tr(\delta\rho y^m)=\frac{1}{Z_0}\sum_{nn'}\frac{e^{-\beta\varepsilon_n}-e^{-\beta\varepsilon_n{'}}}{\varepsilon_n-\varepsilon_n{'}}<n\,|\,\delta U_E\,|\,n'><n'|\,y^m\,|\,n>,\ \ \beta=1/k_BT\ . \tag{23}$$

Since $<y>$ contains $<n'|y|n>$ which is different from zero only for $n'=n\pm 1$ that is why from Eq. (22) we obtain

$$<y>=\frac{1}{Z_0}\sum_n \left\{ \begin{array}{l} \dfrac{e^{-\beta\varepsilon_n}-e^{-\beta\varepsilon_{n+1}}}{-\hbar\omega} <n|\delta V|n+1><n+1|y|n> \\ +\dfrac{e^{-\beta\varepsilon_n}-e^{-\beta\varepsilon_{n-1}}}{\hbar\omega} <n|\delta V|n-1><n-1|y|n> \end{array} \right\}. \qquad (24)$$

Calculating the matrix elements

$$<n|y|n+1>=\sigma_0(n+1)^{1/2}, \quad <n|y^3|n+1>=3\sigma_0{}^3(n+1)^{3/2} \qquad (25)$$

and satisfying the condition Eq. (16) we obtained the 1st cumulant

$$\sigma^{(1)}=a=-\frac{3k_{3eff}}{k_{eff}}\frac{\hbar}{2\sqrt{\mu k_{eff}}}\frac{1+z}{1-z}=\sigma_0^{(1)}\frac{1+z}{1-z}=-\frac{3k_{3eff}}{k_{eff}}\sigma^2,\ \sigma_0^{(1)}=-\frac{3k_{3eff}}{k_{eff}}\sigma_0^2 . \qquad (26)$$

Since $<y^3>$ contains $<n|\delta V|n'><n'|y^3|n>$ which is different from zero only for $n'=n\pm 1$, $n'=n\pm 3$ so that from Eq. (22) we obtained

$$\sigma^{(3)}=<y^3>=\frac{1}{Z_0}\left\{ \begin{array}{l} \displaystyle\sum_n \frac{e^{-\beta\varepsilon_n}-e^{-\beta\varepsilon_{n+1}}}{-\hbar\omega} <n|\delta V|n+1><n+1|y^3|n> \\ \displaystyle +\sum_n \frac{e^{-\beta\varepsilon_n}-e^{-\beta\varepsilon_{n-1}}}{\hbar\omega} <n|\delta V|n-1><n-1|y^3|n> \\ \displaystyle +\sum_n \frac{e^{-\beta\varepsilon_n}-e^{-\beta\varepsilon_{n+3}}}{-3\hbar\omega} <n|\delta V|n+3><n+3|y^3|n> \\ \displaystyle +\sum_n \frac{e^{-\beta\varepsilon_n}-e^{-\beta\varepsilon_{n-3}}}{3\hbar\omega} <n|\delta V|n-3><n-3|y^3|n> \end{array} \right\}. \qquad (27)$$

We calculated the matrix element

$$<n|y^3|n+3>=(\sigma_0)^3[(n+1)(n+2)(n+3)]^{1/2} \qquad (28)$$

Substituting Eqs. (25, 28) into Eq. (27) we obtained the 3rd cumulant as

$$\sigma^{(3)}=\frac{\hbar^2 k_{3eff}}{k_{eff}^2\mu}\left[1-\frac{3}{2}\left(\frac{1+z}{1-z}\right)^2\right]=\sigma_0^{(3)}\frac{1+10z+z^2}{(1-z)^2},\ \sigma_0^{(3)}=-\frac{k_{3eff}\left(\hbar\omega_E^{HD}\right)^2}{2k_{eff}^3}=-\frac{k_{3eff}\hbar\omega_E^{HD}}{k_{eff}^2}\sigma_0^2 .$$

$$(29)$$

Note that in the above expressions $\sigma_0^{(1)}, \sigma_0^2, \sigma_0^{(3)}$ are zero-point contributions to the 1st, 2nd, and 3rd cumulants, respectively, and when the doping atoms are taken from the host material all the above expressions will be reduced to those of the pure material [8, 20].

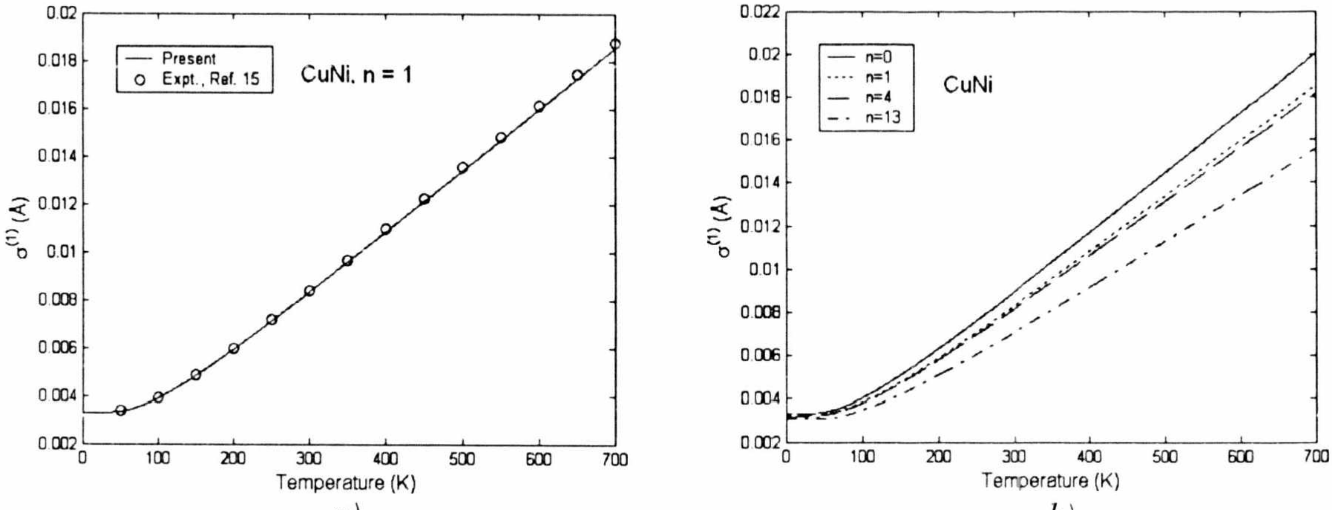
3. Numerical results and comparison to experiment

Table 1: Calculated values of k_{eff} and k_{3eff} of Cu doped by n = 0, 1, 4, 8, 10, 13 atoms of Ni compared to experiment [15].

n	0	1	4	8	10	13
$k_{eff}(eV/Å^2)$, present	3.0905	3.4451	3.5188	3.5834	3.9221	4.0704
$k_{eff}(eV/Å^2)$, Expt.[15]	3.1423	3.4415	3.5030	3.5567	3.8379	3.9608
$k_{3eff}(eV/Å^3)$, present	-1.0468	-1.2018	-1.2289	-1.2531	-1.3524	-1.4062
$k_{3eff}(eV/Å^3)$, Expt.[15]	-1.0841	-1.2143	-1.2362	-1.2560	-1.3325	-1.3764

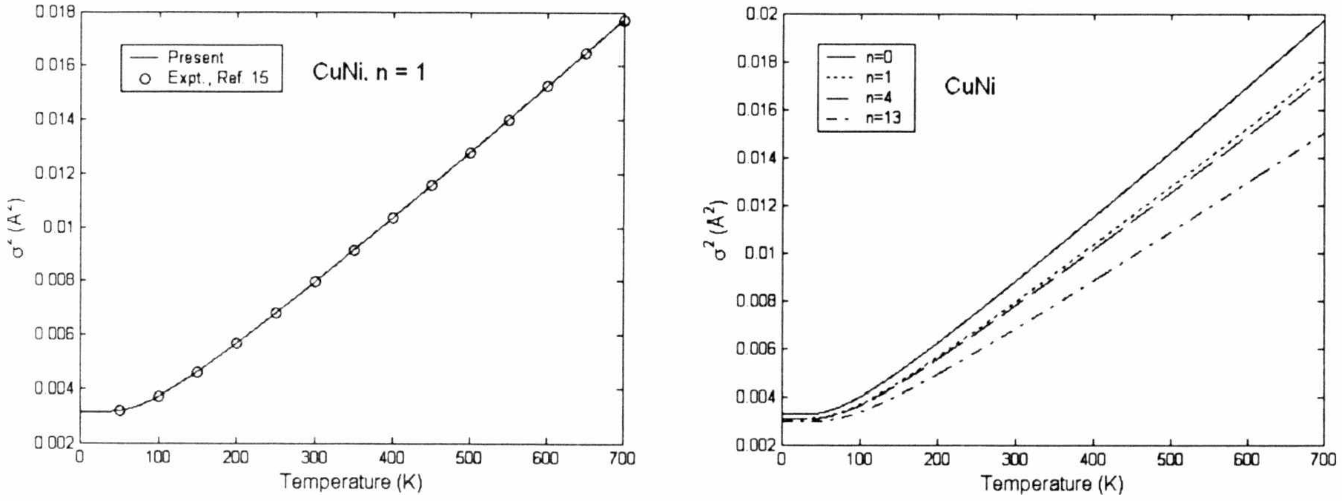
Now we apply expressions derived in the previous section to numerical calculation for Cu doped by n atoms of Ni. Morse potential parameters for Cu and Ni have been calculated by procedured presented in [17, 18]. They are used for calculation of Morse parameters for Cu doped by Ni. The results are presented in Table 1 compared to experiment extracted from the measured Morse potential parameters. The case n = 0 corresponds to the pure Cu and the case n = 13 to the pure Ni because all Cu atoms are replaced by the Ni atoms. All they are found to be in good agreement with experiment extracted from measured Morse parameters [15].

Figure 1 shows temperature dependence of the 1st cumulant or net thermal expansion $\sigma^{(1)}(T)$ of Cu doped by one Ni atom compared to experiment extracted from the measured Morse potential parameters [15] (*a*) and by n =0, 1, 4, 13 Ni atoms (*b*). Figure 2 illustrates the temperature dependence of the calculated 2nd cumulant $\sigma^2(T)$ or DWF of Cu doped by n = 1 Ni atom compared to experiment extracted from the measured Morse potential parameters [15] (*a*) and by n = 0, 1, 4, 13 atoms of Ni (*b*). Figure 3 shows the temperature dependence of the calculated 3rd cumulant of Cu doped by one Ni atom compared to experiment extracted from measured Morse potential parameters [15] (*a*) and by n = 0, 1, 4, 13 Ni atoms (*b*). All the above Figures contain zero-point contributions and satisfy all their fundamental properties, e. g., at high-temperatures the 1st and 2nd cumulants are linearly proportional to the temperature and the 3rd cumulant to the square of temperature. They provide a reasonable agreement with experiment for the case n = 1 doping atom.



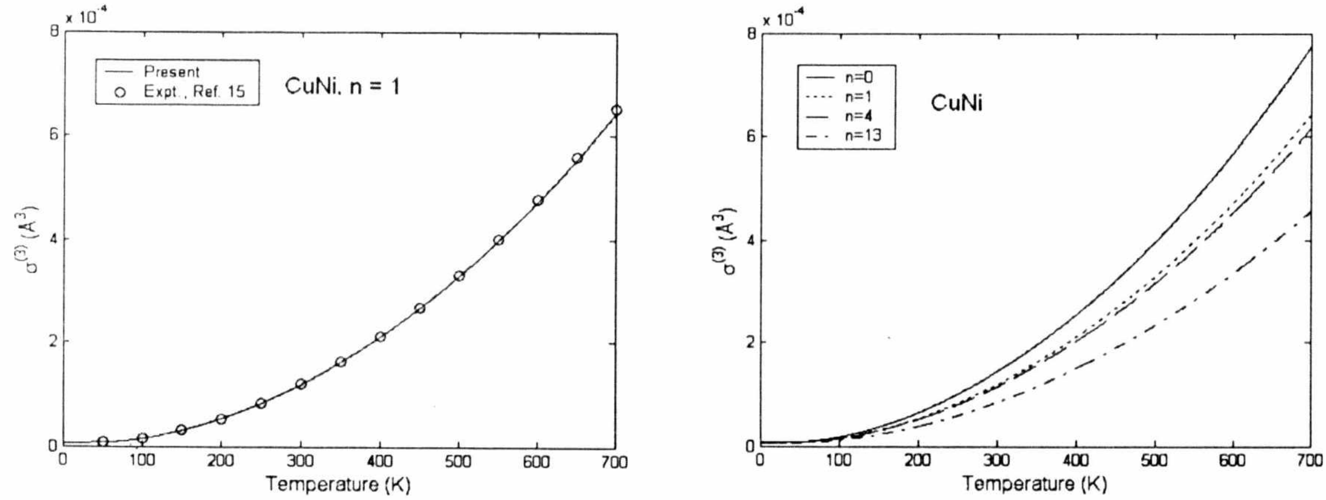
a) *b)*

Figure 1: Calculated 1st cumulant $\sigma^{(1)}(T)$ of Cu doped by n=1 Ni atom compared to experiment [15] (a) and by n =0, 1, 4, 13 Ni atoms (b).



a) b)

Figure 2: calculated 2nd cumulant $\sigma^2(T)$ or DWF of Cu doped by n = 1 Ni atom compared to experiment [15] (a) and by n =0, 1, 4, 13 Ni atoms (b).



a) b)

Figure 3: Calculated 3rd cumulant of Cu doped by n=1 Ni atom compared to experiment [15] (a) and by n =0, 1, 4, 13 Ni atoms (b).

4. Conclussions

This work has developed a new procedure for description and calculation of the correlated Einstein frequency and temperature, the 1st, 2nd, and 3rd cumulants for a fcc crystal doped by an arbitrary number n of atoms from another material.

Derived expressions of the considered quantities approach those derived by using the anharmonic correlated Einstein model for the pure materials which can be considered as a special case of present procedure. They satisfy all their fundamental properties and provide a reasonable agreement with experiment extracted from measured Morse potential parameters.

This method considered for small cluster can be generalized for the whole crystal so that from the present procedure one can develop a method for description and calculation of the thermodynamic parameters of an alloy consisting of different percentage of constituent elements.

Acknowledgements. The authors thank Prof. D. M. Pease (University of Connecticut) for useful discussions and comments. This work is supported inpart by the Bisic Science Research Project No. 4 058 06 and the special research project of VNU Hanoi No. QG.05.04.

References

1. E. D. Crozier, J. J. Rehr, and R. Ingalls, in *X-ray absorption,* edited by D. C. Koningsberger and R. Prins (Wiley, New York, 1988).
2. G. Bunker, *Nucl.&Instrum. Methods* **207** (1983) 437.
3. J. M. Tranquada and R. Ingalls, *Phys. Rev.* B **28** (1983) 3520.
4. E. A. Stern, P. Livins, and Zhe Zhang, *Phys. Rev.* B **43** (1991) 8850.
5. N. V. Hung, R. Frahm, *Physica* B **208** & **209** (1995) 91.
6. N. V. Hung, R. Frahm, and H. Kamitsubo, *J. Phys. Soc. Jpn.* **65** (1996) 3571.
7. N. V. Hung, *J. de Physique* **IV** (1997) C2 : 279.
8. N. V. Hung and J. J. Rehr, *Phys. Rev.* B **56** (1997) 43.
9. N. V. Hung, N. B. Duc, and R. R. Frahm, *J. Phys. Soc. Jpn.* **72** (2003) 1254.
10. N. V. Hung, *VNU-Jour. Science,* Vol. **18**, No. 3 (2002) 17.
11. A. V. Poiarkova and J. J. Rehr, *Phys. Rev.* B **59** (1999) 948.
12. J. J. Rehr, R. C. Albers, *Rewiews of Modern Physics*, Vol. **72** (2000) 621-653 .
13. P. Fornasini, F. Monti and A. Sanson, *J. Synchrotron Radiation* **8** (2001) 1214.
14. M. Daniel, D. M. Pease, N. V. Hung, J. I. Budnick, to be published in *Phys. Rev.* B **69** (2003) 134414.
15. I. V. Pirog, T. I. Nedoseikina, I. A. Zarubin, and A. T. Shuvaev, *J. Phys.: Condens. Matter* **14** (2002) 1825.
16. N. V. Hung, T. T. Dung, N. C. Toan, *VNU-Jour. Science*, Vol. **20**, No. 2 (2004) 9.
17. L. A. Girifalco and V. G. Weizer, *Phys. Rev.* **114** (1959) 687.
18. N. V. Hung and D. X. Viet, *VNU-Jour. Science* Vol. **19**, No. 2 (2003) 19-24.
19. R. F. Feynman, *Statistical Mechanics* (Benjamin, Reading, MA, 1972).
20. A. I Frenkel and J. J. Rehr, *Phys. Rev.* B **48** (1993) 585.