No.07_March 2018|Số 07– Tháng 3 năm 2018|p.102-107

TẠP CHÍ KHOA HỌC ĐẠI HỌC TÂN TRÀO
ISSN: 2354 - 1431
http://tckh.daihoctantrao.edu.vn/

High – order anharmonic effective potentials and EXAFS cumulants of Nickel crystal by quantum perturbation theory

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Article info

Recieved:
15/01/2018
Accepted:
10/3/2018

Keywords :
EXAFS cumulants;
quantum perturbation theory;Nickel crystals.

Abstract

High-order anharmonic effective potentials and four EXAFS cumulants have been studied taking into account the influence of the nearest neighbors of absorbing and backscattering atoms by the anharmonic correlated Einstein model. *Analytical expressions of these quantities have calculated based on the quantum-statistical perturbation theory* derived from a Morse interaction potential expanded in the fourth order which influences from the *2nd*to the *4th*cumulants. Numerical results for Ni are found to be in good agreement with experiment and the classical theory.

1. Introduction

Extended X-ray Absorption Fine Structure (EXAFS) has been developed into apowerful technique for providing information on the local atomic structure and thermodynamic parameters of the substances [5, 6]. At any temperature the position of the atoms and interatomic distances are changed by thermal vibrations. For a two-atomic molecule, the EXAFS cumulants can be expressed as a function of the force constant of the one-dimensional interaction bare potential [1, 4]. For many-atomic systems, like crystals, the EXAFS cumulants are often connected to the force constants of a one-dimensional effective pair potential using the same relation as for a two-atomic molecule. However, the connection between EXAFS cumulants and physical properties of many-atomic systems is still a matter of debate, in particular with reference to the meaning of the effective potential [5, 9]. The anharmonic effective potential expanded to the *3rd* order and three EXAFS cumulants have been calculated [6, 9]. Experimental EXAFS results have been analyzed by the cumulant expansion approach [4] up to the *4th*order, where the parameters of the interatomic potential of the system are still unknown [10].

The purpose of this work is following [10] to develop an analytical method for calculation of the high-order anharmonic effective potentials, local force constants, and the first four cumulants of a monoatomic Nickel crystalsystem. Analytical expressions for parameters of high-order anharmonic effective potential and local force constant of the system have been derived based on the structure of a small cluster of immediate neighboring atoms surrounding absorber and backscatterer, and the Morse potential characterizing the interaction between a pair of atoms. Analytical expressions of the first four EXAFS cumulants have been derived based on quantum statistical method [1, 6, 8].

2. Formalism

2.1. EXAFS and cumulants

The thermal average of the EXAFS oscillation function for a single shell is described by

$$\chi(k) = A(k)\,\mathrm{Im}\left[e^{i\phi(k)}\left\langle e^{2ikr}\right\rangle\right], \qquad (1)$$

where r is the bond length between X-ray absorbing and backscattering atoms, k is the photoelectron wave number, $\phi(k)$ is the total phase shift, $A(k)$ is the real amplitude factor, and $\langle\ \rangle$ denotes the thermal average.

In order to evaluate $\left\langle e^{2ikr}\right\rangle$ we use the cumulant-expansion approach [4] to obtain

$$\left\langle e^{2ikr}\right\rangle = \exp\left[2ikr_0 + \sum_n \frac{(2ik)^n}{n!}\sigma^{(n)}\right], \quad (2)$$

where r_0 is the distance at the potential minimum and $\sigma^{(n)}$ are the cumulants.

A usual EXAF analysis deals with the cumulants up to the third or the fourth order, which are related to the moments of the distribution function such as [4, 10]

$$R = \langle r\rangle = r_0 + \sigma^{(1)}; (3)$$

$$\sigma^{(2)} = \left\langle (r-R)^2\right\rangle; (4)$$

$$\sigma^{(3)} = \left\langle (r-R)^3\right\rangle; (5)$$

$$\sigma^{(4)} = \left\langle (r-R)^4\right\rangle - 3\left(\sigma^{(2)}\right)^2; \quad (6)$$

By analyzing experimental EXAFS spectra of well-established procedures, one obtains structural parameters such as $R, \sigma^{(1)}, \sigma^{(2)}, \sigma^{(3)}, \sigma^{(4)}$ and N as the atomic number of a shell, where the second cumulant $\sigma^{(2)}$ is equal to the Debye-Waller factor (DWF) σ^2.

2.2. High-order anharmonic effective potential

To determine thermodynamic parameters of a system it is necessary to specify and force constant. Let us consider a monoatomic system with anharmonic interatomic potential V(r) described by

$$V_{eff}(x) \approx \frac{1}{2}k_{eff}x^2 - k_3x^3 + k_4x^4, \quad x = r - r_0,$$

(7)

where k_{eff} is effective local force constant, k_3 and k_4 are parameters given the asymmetry of potential due to including the anharmonicity, r and r_0 are instantaneous and equilibrium bond lengths, respectively.

A Morse potential is assumed to describe the interatomic interaction and expanded in the fourth order around its minimum as follows

$$V(x) = D\left(e^{-2\alpha x} - 2e^{-\alpha x}\right)$$
$$\cong -D + D\alpha^2x^2 - D\alpha^3x^3 + \frac{7}{12}D\alpha^4x^4,$$

(8)

where α describes the width.of the potential, and D is the dissociation energy.

In the case of relative vibrations of absorbing *(A)* and backscattering *(B)*atoms, including the effect of correlation and with taking into account only the nearest neighbor interactions [6], the effective pair potential is given by

$$V_{eff} = V(x) + \sum_{i=A,B}\sum_{j\neq A,B} V\left(\frac{\mu}{M_i}x\hat{R}_{AB}\hat{R}_{ij}\right), \ \mu = \frac{M_AM_B}{M_A+M_B}$$
$$= V(x) + 4V(0) + 2V\left(\frac{1}{2}x\right) + 8V\left(-\frac{1}{4}x\right) + 8V\left(\frac{1}{4}x\right),$$

(9)

where M_A and M_B are masses of absorbing *(A)* and backscattering *(B)*atoms, $\hat{R}$ is a unit vector, the sum i is over absorber *(i = A)* and backscatterer *(i = B),* the sum j is over all near neighbors. The first term on the right concerns only absorbing and backscattering atom, the remaining sums extend over the remaining immediate neighbors.

Nickel crystals have a face centered cubic (f.c.c) structure. Considering the f.c.c structure of the nearest neighbors of the absorbing and backscattering atoms and the Morse potential in Eq. (8), the anharmonic effective potential Eq. (9) is resulted as

$$V_{eff}(x) \cong \frac{5}{2}D\alpha^2x^2 - \frac{5}{4}D\alpha^3x^3 + \frac{133}{192}\alpha^4x^4,$$

(10)

Comparing Eq. (10) to Eq, (7) we determine the effective local force constant $k_{eff}$and the anharmonic parameters k_3 and k_4 as follows

$$k_{eff} = 5D\alpha^2, \quad k_3 = \frac{5}{4}D\alpha^3, \quad k_4 = \frac{133}{192}D\alpha^4,$$

(11)

2.3. Determination of EXAFS cumulants

Let us recall the formalism of thermal averages within quantum statistical perturbation theory [8]. A quantum-statistical Hamiltonian is assumed to be given by

$$H = H_0 + H', \qquad (12)$$

where

$$H_0 = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}\mu\omega_E^2 x^2, \ \omega_E = \sqrt{\frac{k_{eff}}{\mu}}, \ \mu = \frac{1}{2}m, \ (13)$$

is the nonperturbed Hamiltonian whose Schrodinger equation is solved exactly and gives eigenvalue $\varepsilon_n = n\hbar\omega_E$ and eigenfunction $\left|n\right\rangle$, *m* is atomic mass, and perturbation term is

$$H' = -\frac{5}{4}D\alpha^3 x^3 + \frac{133}{192}D\alpha^4 x^4, (14)$$

A thermal average of a certain physical quantity $\left\langle M \right\rangle$ is given exactly by using the density matrix as

$$\left\langle M \right\rangle = \frac{1}{Z} Tr M e^{-\beta(H_0+H')}, \ Z = Tr e^{-\beta(H_0+H')}, \ \beta = \frac{1}{k_B T}, \ (15)$$

where *z* is the partition function, k_B is Boltzmann constant.

On performing the integral using $\left|n\right\rangle$ and ε_n for the nonperturbed system, from Eq.(15) it is given by

$$\begin{aligned}\left\langle M \right\rangle \approx & (1-z)\sum_n z^n \left\langle n|M|n \right\rangle \\ & + (1-z)\sum_{n,n'} \frac{z^n - z^{n'}}{\varepsilon_n - \varepsilon_{n'}} \left\langle n|M|n' \right\rangle \left\langle n'|H'|n \right\rangle \\ & + (1-z)^2 \beta \sum_n z^n \left\langle n|M|n \right\rangle \cdot \sum_n z^n \left\langle n|H'|n \right\rangle \qquad (16)\end{aligned}$$

The partition function of the nonperturbed system *Z₀*has the form as

$$Z_0 = Tr e^{-\beta H_0} = \sum_n \left\langle n \right| e^{-\beta H_0} \left| n \right\rangle = \sum_n z^n = \frac{1}{1-z} (17)$$

where the temperature parameter *z* and Einstein temperature θ_E are expressed as

$$z = e^{-n\hbar\omega_E} = e^{-\frac{\theta_E}{T}}, \ \theta_E = \frac{\hbar\omega_E}{k_B T}, \qquad (18)$$

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

$$x = \sigma_0(\hat{a}^+ + \hat{a}), \quad \hat{n} = \hat{a}^+\hat{a}, \ \sigma_0 = \sqrt{\frac{\hbar\omega_E}{2k_{eff}}}, (19)$$

which have the following properties

$$[\hat{a}^+, \hat{a}] = 1, \ \hat{a}^+\left|n\right\rangle = \sqrt{n+1}\left|n+1\right\rangle, \ \hat{a}\left|n\right\rangle = \sqrt{n}\left|n-1\right\rangle, (20)$$

Using the above results for correlated atomic vibrations and the procedure depicted by Eqs. (16), (19), (20), as well as the first-order thermodynamic perturbation theory, we calculated the cumulants.

For the even cumulants σ^2 and $\sigma^{(4)}$, all the terms in Eq. (16) should be evaluated while the odd cumulant $\sigma^{(1)}$ and $\sigma^{(3)}$ requires only the second term in Eq. (16). The consequent expressions are resulted as

$$\sigma^{(1)} = \left\langle x \right\rangle \cong \frac{3k_3\sigma_0^2}{k_{eff}}\left(\frac{1+z}{1-z}\right) = \frac{3\hbar\omega_E}{40D\alpha}\left(\frac{1+z}{1-z}\right) \qquad (21)$$

$$\begin{aligned}\sigma^2 &= \left\langle \left(x - \left\langle x \right\rangle\right)^2 \right\rangle = \left\langle x^2 \right\rangle - \left\langle x \right\rangle^2 \cong \left\langle x^2 \right\rangle \\ &= \sigma_0^2\left(\frac{1+z}{1-z}\right) - \frac{6k_4\sigma_0^4}{k_{eff}}\left(\frac{1+z}{1-z}\right)^2 - \frac{24k_4\sigma_0^6}{k_B T}\cdot\frac{z(z+1)}{(1-z)^3} \\ &= \frac{\hbar\omega_E}{10D\alpha^2}\left(\frac{1+z}{1-z}\right) - \frac{133\hbar^2\omega_E^2}{16000D^2\alpha^2}\left(\frac{1+z}{1-z}\right)^2 \qquad (22) \\ &\quad - \frac{133\hbar^3\omega_E^3}{8000D^2\alpha^2 k_B T}\cdot\frac{z(1+z)}{(1-z)^3}\end{aligned}$$

$$\begin{aligned}\sigma^{(3)} &= \left\langle \left(x - \left\langle x \right\rangle\right)^3 \right\rangle = \left\langle x^3 \right\rangle - 3\left\langle x^2 \right\rangle\left\langle x \right\rangle + 2\left\langle x \right\rangle^3 \\ &\cong \left\langle x^3 \right\rangle - 3\left\langle x^2 \right\rangle\left\langle x \right\rangle \\ &= \frac{2k_3\sigma_0^4}{k_{eff}}\frac{1+10z+z^2}{(1-z)^2} + \frac{54k_3k_4\sigma_0^6}{k^2_{eff}}\left(\frac{1+z}{1-z}\right)^3 \\ &\quad + \frac{216k_3k_4\sigma_0^8}{k_{eff}k_B T}\cdot\frac{z(1+z)^2}{(1-z)^4} \\ &= \frac{(\hbar\omega_E)^2}{200D^2\alpha^3}\cdot\frac{1+10z+z^2}{(1-z)^2} + \frac{1197(\hbar\omega_E)^3}{640000D^3\alpha^3}\left(\frac{1+z}{1-z}\right)^3 \\ &\quad + \frac{1197(\hbar\omega_E)^4}{320000D^3\alpha^3 k_B T}\cdot\frac{z(1+z)^2}{(1-z)^4} \qquad (23)\end{aligned}$$

$$\begin{aligned}\sigma^{(4)} &= \left\langle x^4 \right\rangle + 12\left\langle x^2 \right\rangle\left\langle x \right\rangle^2 - 3\left\langle x^2 \right\rangle^2 - 4\left\langle x^3 \right\rangle\left\langle x \right\rangle - 6\left\langle x \right\rangle^4 \\ &\cong \left\langle x^4 \right\rangle + 12\left\langle x^2 \right\rangle\left\langle x \right\rangle^2 - 3\left\langle x^2 \right\rangle^2 - 4\left\langle x^3 \right\rangle\left\langle x \right\rangle \\ &\cong \frac{3{k_3}^2\sigma_0^6}{\left(k_{eff}\right)^2}\frac{(z+1)(5+104z+5z^2)}{(1-z)^3} + \frac{360{k_3}^2\sigma_0^8}{k_{eff}k_B T}\frac{z^2}{(1-z)^4} \\ &\quad - \frac{6k_4\sigma_0^6}{k_{eff}}\frac{(z+1)(1+8z+z^2)}{(1-z)^3} - \frac{144k_4\sigma_0^8}{k_B T}\frac{z^2}{(1-z)^4}\end{aligned}$$

$$= \frac{(\hbar\omega_E)^3}{160000D^3\alpha^4}\cdot\frac{(z+1)(17+2056z+17z^2)}{(1-z)^3} + \frac{51(\hbar\omega_E)^4}{40000D^3\alpha^4 k_B T}\frac{z^2}{(1-z)^4} \quad (24)$$

Note that comparing to the results of the anharmonic,correlated Einstein model [6], our *1st* cumulant have the same values as Eq. (21). But the *2nd* and *3rd* cumulantsare different from theterms on the right hand site of Eqs. (22) and (23) due to taking k_4, it will vanish when k_4 is neglected, the *4th* cumulant is defined by Eq. (24) appears due to not only, but also k_3 in our potential in Eq. (10).

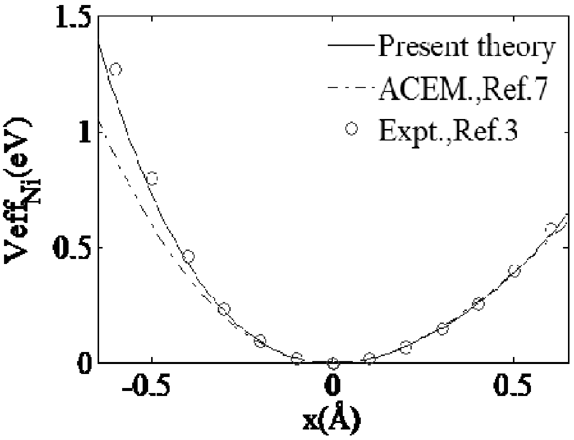
3. Results and discussion

Now we apply the expressions derived in the previous section to numerical calculations for Nickel crystal.

Table 1. Calculated values D, α, k_{eff}, ω_E, θ_E for Ni compared to experiment.

Quantity	D (eV)	α (eVÅ^{-3})	k_{eff} (N/m)	ω_E (× 10^{13}Hz)	θ_E (K)
Calc.	*0.4205*	*1.4199*	*67.792*	*3.722*	*284.31*
Expt. [3]	*0.4100*	*1.3900*	*62.485*	*3.600*	*274.83*

Its Morse potential parameters have been calculated [5] and they are used for our calculation of the force constant k_{eff}, Einstein frequency ω_E and temperature θ_E. The results are given in Table 1 and are compared to experimental values [3].



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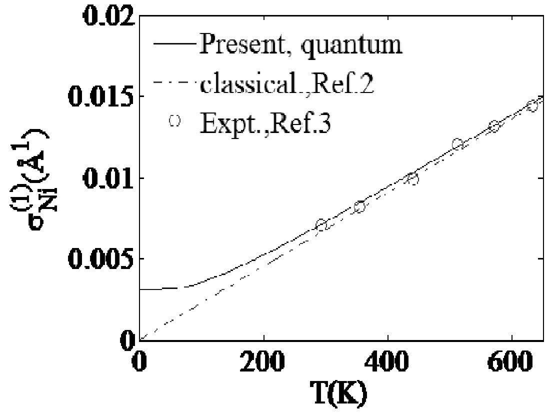
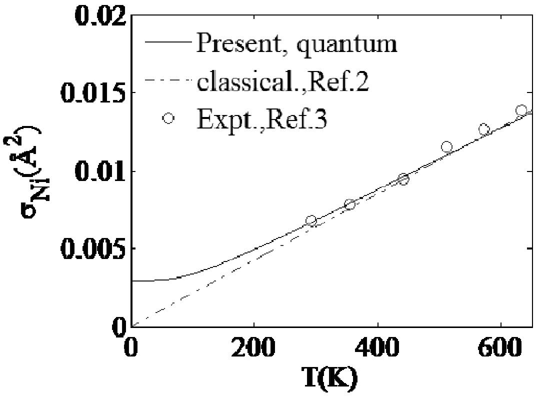
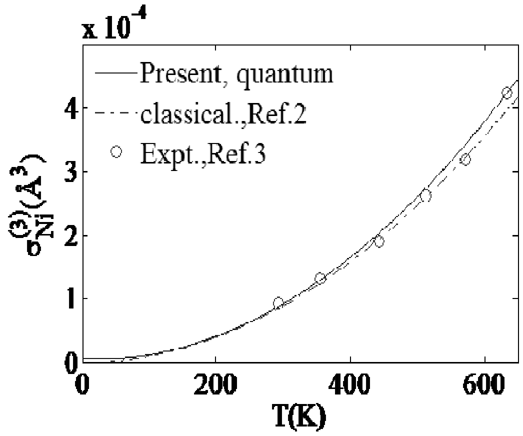


b)

Figure 1:a) Calculated anharmonic effective potential in comparison to calculated by the ACEM procedure [7] and the experimental results [3], b) Temperature dependence of calculated 1st cumulant of the first shell of Ni compared to the classical procedure [2] and the experimental results [3].



a)



b)

Figure 2: Temperature dependence of calculating 2nd and 3rd cumulants of the first shell of Ni compared to the classical procedure [2] and the experimental results [3].

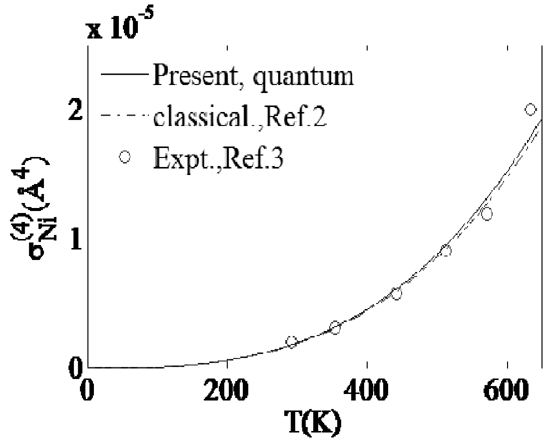


Figure 3:Temperature dependence of calculated 4^{th} cumulant of the first shell of Ni compared to classical procedure [2] and to experimental results [3].

potential parameters [5]. Figure. 2 represents the calculated *2^{nd}* or DWF and *3^{rd}* cumulants of Ni. The above calculated results for the cumulant agree well to classical procedure [2] and to experimental results [3]. Figure. 3. Shows the calculated *4^{th}* cumulant for Ni compared to classical procedure [2] and to experimental results [3]. This quantity is very small even at 650K. A small difference of this procedure resulted from the one of the anharmonic correlated Einstein model at high temperatures appears due to including the *4^{th}*order in expansion of potentials Eqs.(8) and (10)

The temperature dependences of all cumulants calculated by the present theory satisfies all their fundamental properties in temperature dependence, i. e., they contain zero-point contribution at low temperature, the the *1^{st}* and *2^{nd}* cumulants are linearly proportional to the temperature *T*, the *3^{nd}* cumulant to *T^2* and the *4^{th}*cumulant to *T^3* at high temperature as for the other crystals [2, 6, 10].

4. Conclusions

In this work a new analytical method for calculation and analysis of the high-order anharmonic effective potentials and EXAFS cumulants for the Nickel crystal as functions of the Morse interaction potential parameters has been derived quantum statistically by perturbation theory. The obtained quantities satisfy all their fundamental properties in temperature dependence.

The advantage of this procedure in comparison to the anharmonic correlated Einstein model is that this makes it possible to derive high-order anharmonic effective potential which slightly influences from the *2^{nd}* to the *4^{th}* cumulants.

The good agreement of our calculated values with experiment denotes the efficiency and reliability of the present procedure as well as by applying the effective potential method in the EXAFS data analysis.

Acknowledgements

[7] and the influence of

The author thanks Prof. Dr. Nguyen Van Hung and Assoc. Prof. Dr Nguyen Ba Duc for useful comments.

classical procedure deducted from the

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Thế hiệu dụng phi điều hòa bậc cao và các cumulant trong EXAFS của tinh thể Niken sử dụng lý thuyết nhiễu loạn lượng tử

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Thông tin bài viết

Ngày nhận bài:
15/01/2018
Ngày duyệt đăng:
10/3/2018

Từ khóa:
cumulant phổEXAFS; lý thuyết nhiễu loạn lượng tử; tinh thể Niken.

Tóm tắt

Thế hiệu dụng phi điều hòa bậc cao và bốn cumulant của phổ EXAFS đã được nghiên cứu khi có tính đến ảnh hưởng của các nguyên tử hấp thụ và tán xạ gần nhất trong mô hình Einstein tương quan phi điều hòa. Các biểu thức giải tích của các đại lượng này đã được tính toán dựa trên lý thuyết nhiễu loạn lượng tử xuất phát từ thế tương tác Morse được mở rộng đến bậc 4 có ảnh hưởng đến các cumulant từ bậc 2 đến bậc 4. Kết quả tính số cho Ni cho kết quả trùng hợp tốt với thực nghiệm và lý thuyết cổ điển.