CALCULATION OF THERMAL-VIBRATION PARAMETERS IN XAFS THEORY

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bstract: *This work presents a new quantum-thermodynamic procedure for calculation of ermal-vibration parameters in X-ray Absorption Fine Structure (XAFS) theory such as ring constant, Einstein frequency and Einstein temperature using anharmonic-correlated nstein model. These parameters have been used for calculation of 1st cumulant, 2nd culant or Debye- Waller factors, 3rd cumulant and thermal expansion coefficient. Numerl results for cumulants of Cu agree very well with experimental values, and the agreement better than the other methods at present time. A computer program have been coded for lculation of these parameters and linked with the computer program FEFF of the Unirsity of Washington as a subroutine for evaluation of XAFS spectra at any temperature ich provide correct structural information of substances.*

Introduction

It is known that the XAFS spectra, proding structural information, is desribed by e oscillation function [1]

$$\chi(k) = A(k)[\epsilon^{i\phi(k)}\langle\epsilon^{2ikr}\rangle], \tag{1}$$

ere $A(k)$ is real amplitude, r is instantaneous bond length between absorbing and ckscattering toms, $\phi(k)$ is the total phase shift, and the thermal evarage is often realized cumulant expansion approach [1]

$$\langle\epsilon^{2ikr}\rangle = \exp[2ikr_0 + \sum_n \frac{(2ik)^n}{n!}\sigma^{(n)}]. \tag{2}$$

Here r_0 is the distance at the equilibrium or potential minimum and $\sigma^{(n)}$ are the culants. The most important quality in the thermal effect is atomic vibration determined the potential.

$$V_E(x) = \frac{1}{2}k_{eff}x^2 + k_3x^3 + \cdots, \quad x = r - r_0. \tag{3}$$

In this work based on the anharmonic-correlated Einstein model [2] we present new quantum thermodynamic procedure to calculate effective spring constant k_{eff} bik factor c_3, describing anharmonic effect, as well as Einstein frequency and Einstein temperature. Numerical calculation is realized for several fcc crystals. Comparison experiment is done for Cu and the agreement is very good. These thermal vibr parameters are applied to calculation of cumulants in the XAFS theory.

II. Theory

The correlated model is used in this work because it was discovered that the c lation part of atomic-position displacement occupied about 40% of mean-square disp ment at high temperatures by Einstein model [3] as by Debye model [4].

In the anharmonic-correlated Einstein model the interaction between absorbing backscattering atoms is characterized by an effective potential

$$V_E = V(x) + \sum_{i \neq j} V\left(\frac{\mu}{M_i} x \hat{R}_{12}.\hat{R}_{ij}\right),$$

where $\mu = M_1 M_2/(M_1 + M_2)$ with mass of absorber M_1 and mass of backscattere , $\hat{R}$ is bond unit vector; the sum i is over absorber ($i = 1$) and backscatterer (i = and the sum j is over all their near neighbors, excluding the absorber and backscat themselves. The latter contributions are described by the first term in the left side o equation. The interactions between the two atoms alone are described in this work Morse potential, expanded in the form

$$V(x) = D(\epsilon^{-2\alpha x} - 2\epsilon^{-\alpha x}) \cong D(-1 + \alpha^2 x^2 - \alpha^3 x^3 + \cdots),$$

where D is dissociation energy and $1/\alpha$ corresponds to the width of potential. sufficient to consider weak anharmonicity (i. e, first order perturbation theory) so only the cubik term in this equation must be kept. Using eqs.(3-5) the effective s constant and cubik term are derived

$$k_{eff} = 5D\alpha^2\left(1 - \frac{3}{2}\alpha a\right); k_3 = -\frac{5}{4}D\alpha^3; \quad a = \langle x \rangle.$$

The other parameters obtained from spring constant are Einstein frequency

$$\omega_E^2 = \frac{k_{eff}}{\mu} = \frac{5}{\mu} D\alpha^2\left(1 - \frac{3}{2}\alpha a\right),$$

and Einstein temperature

$$\theta_E = \frac{\hbar}{k_B}\sqrt{\frac{k_{eff}}{\mu}} = \frac{\hbar}{k_B}\left[\frac{5}{\mu} D\alpha^2\left(1 - \frac{3}{2}\alpha a\right)\right]^{1/2},$$

where k_B is Boltzman's constant. Present calculations were based on the quasi-harr approximation in which the Hamiltonian of the system is written as a harmonic h respect to the equilibrium position at a given temperature, plus an anharmonic turbation

$$H = \frac{P^2}{2\mu} + V_E(x) = \frac{P^2}{2\mu} + \frac{1}{2}k_{eff}y^2 + V_E(a) + \delta V_E(y), \tag{9}$$

$$\delta V_E(y) \cong 5D\alpha^2 \left(ay - \frac{1}{4}\alpha y^3 \right); \quad y = x - a. \tag{10}$$

We now use first-order thermodynamic perturbation [5] to derive the formulas for cumulants using the expression

$$\sigma^{(n)} = \langle y^n \rangle = \frac{1}{z} Tr\rho y^n; \quad n = 1, 2, 3, 4, ...; \quad Z = Tr\rho; \quad \rho = \epsilon^{-\beta H}. \tag{11}$$

From all the above considerations we obtain the first $\sigma^{(1)}$, second σ^2, and third $\sigma^{(3)}$ nulant as well as thermal expansion coefficient α_T in the following forms

$$\sigma^{(1)} = a = \frac{3\hbar\omega_E}{40D\alpha} \frac{1+z}{1-z}, \tag{12}$$

$$\sigma^{(2)} = \frac{\hbar\omega_E}{10D\alpha^2} \frac{1+z}{1-z}, \tag{13}$$

$$\sigma^{(3)} = \frac{(\hbar\omega_E)^2}{200D^2\alpha^3} \frac{1+10z+z^2}{(1-z)^2}, \tag{14}$$

$$\alpha_T = \frac{3k_B}{20D\alpha r} \frac{z(\ln z)^2}{(1-z)^2} \tag{15}$$

re the temperature parameter $z = e^{-\theta_E/T}$ with Einstein temperature θ_E is included very of the eqs.(12-15), and the source of θ_E is spring constant. So we can see the ation behaviors of the cumulant formulation.

. Numerical Results and discussion

The formulas for thermal-vibration parameters presented in previous section have n applied to coding a computer program which is linked with the code FEFF of the versity of Washington and used for numerical calculation of several fcc crystals. The ilts are presented in Table I. The Morse potential parameters α and D were obtained ig experimental values for the energy of sublimation, the compressibility and the lattice stant [6]. They can be used for calculation of the first, second, third cumulant and mal expansion coefficient in the XAFS technique [7]. In Table II we present the results Debye-Waller factors σ^2 and third cumulant $\sigma^{(3)}$ of Cu. They agree very well with erimental values and the agreement is better than the other methods.

Metal	α (Å^{-1})	D(eV)	k_{eff} (N/m)	ω_E (. 10^{13}Hz)	θ_E (I
Pb	1.1836	0.2348	26.3507	1.2341	9
Ag	1.3690	0.3323	49.8910	2.3533	18
Ni	1.4199	0.4205	67.9150	3.7217	28
Cu	1.3588	0.3429	50.7478	3.0922	23
Al	1.1646	0.2703	29.3686	3.6101	2
Ca	0.8054	0.1623	8.4328	1.5872	1
Sr	0.7377	0.1513	6.5971	0.9495	7

Table I: *The values of* k_{eff}, ω_E *and* θ_E *calculated by present procedure*

	σ^2 (.10^{-2} Å^2)				$\sigma^{(3)}$ (.10^{-3} Å^3)		
T(K)	present	Expt.[8]	Expt.[9]	Other[10]	Present	Expt.[9]	Other[
77	0.333	0.325			0.010		
295	0.803	0.774	0.876	0.520	0.131	0.130	
300	0.817				0.136		0.12
683	1.858	1.823					

Table II: *Comparison of the values* σ^2 *and* $\sigma^{(3)}$ *of Cu calculated by present proced*
with experimental and by other methods calculated respective results.

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TÍNH CÁC THAM SỐ DAO ĐỘNG NHIỆT TRONG LÍ THUYẾT XAFS

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Bài này trình bầy một phưng pháp nhiệt động lượng từ mới để tính các tham số o động nhiệt trong lý thuyết về cấu trúc tinh tế của hấp thụ tia X (XAFS) như hệ số n hồi, tần số dao động Einstein, nhiệt độ Einstein và hệ số dãn nở nhiệt trên cơ sở mô ıh Einstein tương quan phi điều hòa. Các đại lượng này đã được tính số cho một số h thể dạng fcc. Các tham số dao động nhiệt được sử dụng để tính các cumulant bậc ıt, bậc hai hay hệ số Debye-Waller, cumulant bậc ba và hệ số dãn nở nhiệt. Các kết ả tính số cho các cumulant của Cu trùng tốt với thực nghiệm và trùng tốt hơn các ương pháp hiện hành. Một chương trình máy tính đã được xây dựng để tính các tham trên và liên kết với bộ chương trình FEFF của Đại học Washington để đánh gía các ố XAFS ở mọi nhiệt độ và từ đó nhận các thông tin chính xác về cấu trúc của vật thể.