

GENERALIZED XAFS CUMULANT THEORY AND A NEW PROCEDURE FOR STRUCTURAL DETERMINATION

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Abstract: *A new generalized XAFS cumulant theory has been developed based on the anharmonic thermal vibration between absorbing and backscattering atoms in a small atomic cluster. By taking into account the contributions of their immediate neighbors to this vibration the atomic distribution or structure is considered and a new structural parameter has been derived which has the value 3 for fcc and 5/3 for bcc crystals. Numerical calculations for several fcc and bcc crystals have been carried out. The good agreement between theoretical and experimental values denotes the advantages of present new procedure for determination of thermodynamic properties and structure of the crystals.*

I. Introduction

X-ray Absorption Fine Structure (XAFS) becomes a powerful structural analysis technique in which the XAFS functions provide information on atomic number of each shell, and their Fourier transform magnitudes provide information on radius of atomic shell [1]. But as the temperature increases the uncertainties can appear in the information on the shell radius [2,3] and on the atomic number of the shell [4]. Moreover, still no exact method for determination of atomic distribution has been formulated. To interpret the uncertainties in the information on shell radius and to fit the XAFS spectra the cumulant expansion approach [1] has been developed according to which the XAFS functions contain the cumulants. Therefore, to calculate high-temperature XAFS spectra the cumulant calculation procedure is necessary. In the efforts for cumulant calculation the anharmonic correlated Einstein model [5] has corrected some limitations of the anharmonic single particle potential [6], of the anharmonic single bond potential [7], and of the full lattice dynamical calculation [8], but it was applied only for fcc [5] or for bcc crystals [9].

This work is our development of a generalized model to overcome both the above mentioned uncertainties in the shell radius and in the atomic number of the shell. Our derivation is based on quantum statistical theory for the anharmonic vibration between absorbing and backscattering atoms in a small cluster. The obtained expressions of cumulants are valid for low and high temperatures as well as for different structures which are determined by a new structural parameter. By extracting this parameter from the measured cumulants one can define the structure of the crystal. Numerical calculations have been carried out for several fcc and bcc crystals showing a good agreement between our theoretical results and the experimental values.

II. Theory

In this model we consider anharmonic vibration between absorbing and backscattering atoms with contributions of their immediate neighbors so that their interaction is characterized by an effective anharmonic potential:

$$U_{eff}(x) \cong \frac{1}{2}k_{eff}x^2 + k_3x^3 + \dots, \quad x = r - r_0, \quad (1)$$

where r is spontaneous bond length between absorbing and backscattering atoms, r_0 is its equilibrium value, k_{eff} is effective spring constant, and k_3 is cubic anharmonicity parameter which gives an asymmetry in the pair distribution function.

In present formalism our derivation is based on quantum statistical theory with quasi-harmonic approximation, according to which the Hamiltonian of the system contains a harmonic term with respect to the equilibrium at a given temperature and an anharmonic perturbation [5]. Using the definition [7] $y = x - a$ as the deviation from the equilibrium value of x at temperature T and $a(T) = \langle r - r_0 \rangle$ as the net thermal expansion we express Eq. (1) in the form:

$$U_{eff} = \frac{1}{2}k_{eff}y^2 + \delta U(y). \quad (2)$$

The atoms in cluster are distributed according to the structure like fcc, bcc, hcp, ... of the substance. Considering the contributions of the immediate neighbors in this cluster to the vibration between absorber and backscatterer as well as the calculated value $k_3 = -5D\alpha^3/4$ we derived the effective spring constant:

$$k_{eff} = D\alpha^2 \left(S + 2 - \frac{15}{2}a\alpha \right), \quad (3)$$

and the anharmonic perturbation:

$$\delta U(y) = D\alpha^2 \left((S + 2)ay - \frac{5}{4}\alpha y^3 \right), \quad (4)$$

where D is the dissociation energy, and $1/\alpha$ corresponds to the width of the potential. They are parameters of the Morse pair potential:

$$u(x) = D(e^{-2\alpha x} - 2e^{-\alpha x}) \approx D(-1 + \alpha^2 x^2 - \alpha^3 x^3 + \dots). \quad (5)$$

In this generalization a new parameter is derived and given by:

$$S = \sum_{j=2}^N (\hat{\mathbf{R}}_{01} \cdot \hat{\mathbf{R}}_{0j})^2, \quad \hat{\mathbf{R}} = \mathbf{R}/|\mathbf{R}|, \quad (6)$$

where $\hat{\mathbf{R}}_{01}$ is unit vector directed from absorber to backscatterer, and the sum j is over all N immediate neighbors of the absorber excluding the backscatterer. Determining S

one can obtain the structure of the substance. Therefore, S is defined as a new structural parameter.

In this approach we consider the local vibration, that is why, it is appropriate to use a Einstein model [5,7]. From the above quantities we derived the correlated Einstein frequency:

$$\omega_E = \alpha \left[\frac{D}{\mu} \left(S + 2 - \frac{15}{2} a\alpha \right) \right]^{1/2}, \quad \mu = \frac{M_A M_S}{M_A + M_S}, \quad (7)$$

and the correlated Einstein temperature:

$$\theta_E = \frac{\hbar\alpha}{k_B} \left[\frac{D}{\mu} \left(S + 2 - \frac{15}{2} a\alpha \right) \right]^{1/2}, \quad (8)$$

where M_A is mass of absorber, M_S is mass of backscatterer, and k_B is Boltzmann's constant.

The cumulants are derived by averaging the value of y [5,7,10]. Atomic vibration is quantized as phonon and anharmonicity is the result of phonon interaction. Therefore, to evaluate the matrix elements we express y in terms of creation and annihilation operators, \hat{a} and \hat{a}^+ , i. e.,

$$y = \sigma_0(\hat{a} + \hat{a}^+); \quad \sigma_0 = \sqrt{\hbar/2\mu\omega_E}. \quad (9)$$

Using oscillator state $|n\rangle$ as eigenstate with eigenvalue $E_n = n\hbar\omega_E$ (ignoring the zero-point energy for convenience) and the method of density matrix [10] we derived the second cumulant or Debye-Waller factor:

$$\sigma^2 = \frac{1}{Z_0} \sum_n e^{-n\hbar\omega_E/k_B T} \langle n|Y^2|n\rangle, \quad Z_0 = \frac{1}{1 - e^{-\theta_E/T}},$$

which by using y from Eq. (9) to calculate the matrix elements is changed into:

$$\sigma^2 = \frac{\hbar\omega_E}{2D\alpha^2(S+2)} \frac{1+z}{1-z}, \quad z = e^{-\theta_E/T}. \quad (10)$$

Evaluating the traces in the density matrix method, the remaining odd moments are given by:

$$\langle y^m \rangle = \frac{1}{Z_0} \sum_{n,n'} \frac{e^{-E_n/k_B T} - e^{-E_{n'}/k_B T}}{E_n - E_{n'}} \langle n|\delta U(y)|n'\rangle \langle n'|y^m|n\rangle. \quad (11)$$

Using δU from Eq. (4) and y from Eq. (9) to calculate the matrix elements in Eq. (11) with taking into account the selection rule, and by setting $\langle y \rangle = \langle x - a \rangle = 0$, we derived the first cumulant or net thermal expansion:

$$\sigma^{(1)} = a = \frac{15\hbar\omega_E}{8D\alpha(S+2)^2} \frac{1+z}{1-z}, \quad (12)$$

and the third cumulant:

$$\sigma^{(3)} = \frac{5(\hbar\omega_E)^2}{8(S+2)^3 D^2 \alpha^3} \frac{1+10z+z^2}{(1-z)^2}, \quad (13)$$

The net thermal expansion describes an asymmetry of the atomic interaction potential due to anharmonicity. Using its expression (12) we derived the thermal expansion coefficient:

$$\alpha_T = \frac{15k_B\theta_E^2}{4(S+2)^2 D\alpha r} \frac{z}{[T(1-z)]^2}. \quad (14)$$

In order to define the behaviors of the above obtained thermodynamic quantities in temperature dependence we derived them in the low temperature ($T \rightarrow 0$) and high temperature ($T \rightarrow \infty$) limits. The results are presented in Table I.

Table I. The values of $\sigma^{(1)}, \sigma^2, \sigma^{(3)}, \alpha_T$ at low-temperature ($T \rightarrow 0$) and high-temperature ($T \rightarrow \infty$) limits.

Value	$T \rightarrow 0$	$T \rightarrow \infty$
$\sigma^{(1)}$	$15\hbar\omega_E(1+2z)/[8(S+2)^2 D\alpha]$	$15k_B T/[4(S+2)^2 D\alpha]$
σ^2	$\hbar\omega_E(1+2z)/[2(S+2)D\alpha^2]$	$k_B T/[(S+2)D\alpha]$
$\sigma^{(3)}$	$5(\hbar\omega_E)^2(1+12z)/[8(S+2)^3 D^2\alpha^3]$	$15(k_B T)^2/[2(S+2)^3 D^2\alpha^3]$
α_T	$15k_B z(\ln z)^2(1+2z)/[4(S+2)^2 D\alpha]$	$15k_B/[4(S+2)^2 D\alpha]$

Note that our new structural parameter (6) is contained in the expressions of correlated Einstein frequency, correlated Einstein temperature, first, second, and third cumulants, as well as in the expression of thermal expansion coefficient at all temperatures. Therefore, we can measure one of these quantities and extract the structural parameter S from the measured values to define the structure of the crystal.

III. Numerical results and discussions

Now we apply the above theory to numerical calculations for some fcc and bcc crystals and the results are compared with experimental data. The parameters D and α were obtained using experimental values for the energy of sublimation, the compressibility, and the lattice constant [11]. Based on structure of the crystals we calculated the structural parameter S according to Eq. (6). It has the value $S = 3$ for fcc and $S = 5/3 \approx 1.67$ for bcc. In Table II we present the value of structural parameter S extracted from experimental values of correlated Einstein temperature θ_E of Cu [12], of Debye-Waller factor σ^2 of Al [14], of third cumulant $\sigma^{(3)}$ of Cu [13], and of thermal expansion coefficient α_T of W [15]. For evaluation of the accuracy of our new structural parameter S we also present the value:

$$\Delta S = |S(\text{calc.}) - S(\text{expt.})|/S(\text{calc.}). \quad (15)$$

Table II. The values of our calculated structural parameter S for fcc, bcc and those extracted from measured quantities Q like $\theta_E, \sigma^2, \sigma^{(3)}, \alpha_T$, as well as ΔS .

Sample	fcc	bcc	$Cu(\theta_E)$	$Al(\sigma^2)$	$Cu(\sigma^{(3)})$	$W(\alpha_T)$
T(K)	any	any	Any	600	295	2000
Q			237K[12]	0.0287Å ² [14]	0.00013Å ³ [13]	6.4x10 ⁻⁵ K ⁻¹ [15]
S	3	1.67	3.036	0.287	3.018	1.632
ΔS			0.012	0.025	0.006	0.020

In The table II the quantities Q are the measured values of Einstein temperature of $Cu(Cu(\theta_E))$, of Debye-Waller factor of $Al(Al(\sigma^2))$, of third cumulant of $Cu(Cu(\sigma^{(3)}))$, and of thermal expansion coefficient of $W(W(\alpha_T))$. The results show a high accuracy of our new procedure for structural determination. Namely, the difference of our theoretical structural parameter S for fcc with those extracted from the measured Einstein temperature θ_E of Cu [12] is only 1.2% and with those extracted from the measured Debye-Waller factor σ^2 of Al at 600K [14] only 2.5% or with those extracted from the measured third cumulant $\sigma^{(3)}$ of Cu at 295K [13] only 0.6%. The difference of our theoretical structural parameter S for bcc with those extracted from the measured thermal expansion coefficient of W at 2000K [15] is only 2%.

Figure 1 shows the temperature dependence of our calculated first cumulant or net thermal expansion of Ag in comparison with experimental values [13]. Figure 2 illustrates the temperature dependence of our calculated second cumulant or Debye-Waller factor of Al compared with the experimental results [14] as well as of Cu in comparison with the measured data [16]. Figure 3 demonstrates the temperature dependence of our calculated third cumulant of Cu in comparison with an experimental value [13]. All these Figures show that the first, second and third cumulants contain zero-point contributions as quantum effects, and our calculated results agree well with those measured in the experiment. Figure 4 illustrates the temperature dependence of our calculated thermal expansion coefficient of bcc crystal W in comparison with the experimental values [15]. Our results agree with those measured in the experiment [15] and reflect the fundamental theory of thermal expansion [10], i.e., the thermal expansion coefficient has the form of specific heat, which approaches the constant value at high temperature as the Dulong-Petit rule and approaches the zero at low temperatures according to the T^3 rule.

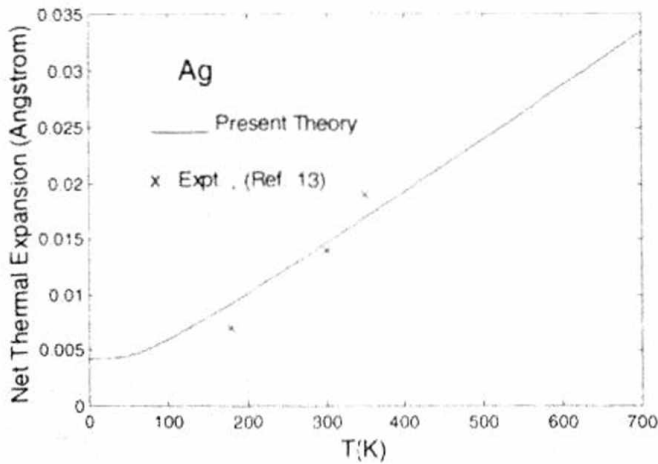


Fig. 1. Temperature dependence of our calculated net thermal expansion of Ag in comparison with experimental values [13].

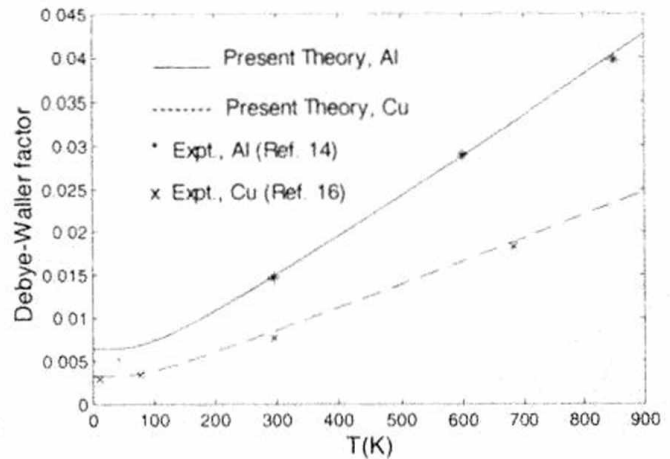


Fig. 2. Temperature dependence of our calculated Debye-Waller factor σ^2 (\AA^2) of Al and Cu in comparison with their experimental values [14,16].

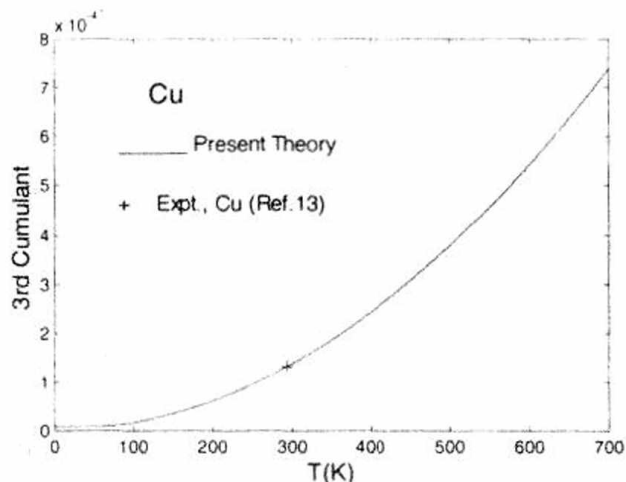


Fig. 3. Temperature dependence of our calculated third cumulant of Cu $\sigma^{(3)}$ (\AA^3) in comparison with experimental value [13].

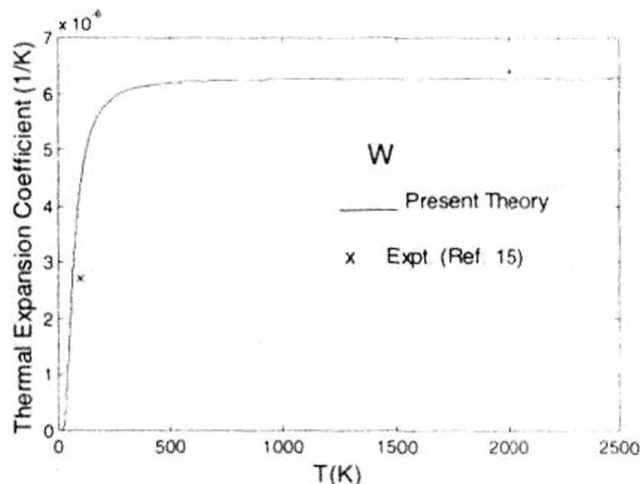


Fig. 4. Temperature dependence of our calculated thermal expansion coefficient α_T (K⁻¹) of W in comparison with experimental values [15].

IV. Conclusions

In this work a generalized theory on XAFS cumulants has been developed based on the quantum statistical theory and the anharmonic vibration between absorbing and backscattering atoms in a small cluster. The obtained expressions are valid for low and high temperatures and for different structures separated by a new structural parameter.

Our new structural parameter S is contained in the expressions of all thermodynamic quantities and cumulants, that is why one can extract this parameter from the measured values like correlated Einstein frequency, correlated Einstein temperature, thermal expansion quantities and cumulants to define the structure of the crystals. For example, the substance has the fcc structure, if $S = 3$, or bcc structure if $S = 5/3 \approx 1,67, \dots$ This theory is a further improvement of our model described in [17]. Discovery of the atomic number and radius of atomic shell from the XAFS spectra leads to opening the structural analysis XAFS technique, therefore, our discovery of the above new structural parameter may give some contribution to this direction.

Our derived expressions of cumulants contain zero-point contributions at low temperature as the quantum effects (see Figures) and approach the classical behaviours, i. e., $\sigma^{(1)}, \sigma^2 \sim T$, and $\sigma^{(3)} \sim T^2$ (see Table I and Figures) at high temperatures.

Our derived thermal expansion coefficient has the form of specific heat, thus reflecting the fundamental theory, i. e., it approaches the constant value as Dulong-Petit rule at high temperature and approaches the zero as the T^3 rule at low temperatures (see Table I and Figure 4).

The good agreement between our theoretical results and the experimental values denotes the advantages of present procedure in the determination of thermodynamic quantities and structure of the substances.

Acknowledgement. The author thanks Prof. M. Sarikaya (University of Washington) for providing the data of Debye-Waller factor of Al. This work was also supported in part by the fundamental research project No. 410 801 and by the project QT 00-06.

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TAP CHÍ KHOA HỌC ĐHQGHN, Toán - Lý, T.XVIII, Số 2 - 2002

LÝ THUYẾT TỔNG QUÁT VỀ XAFS CUMULANT VÀ MỘT PHƯƠNG PHÁP MỚI VỀ XÁC ĐỊNH CẤU TRÚC

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Bài này xây dựng một lý thuyết tổng quát mới về XAFS cumulant dựa trên dao động phi điều hoà giữa nguyên tử hấp thụ và nguyên tử tán xạ trong một nhóm nguyên tử. Qua xét các đóng góp của các nguyên tử lân cận vào dao động trên, sự phân bố của các nguyên tử đã được tính đến và một tham số cấu trúc mới đã được xây dựng. Nó có giá trị bằng 3 đối với cấu trúc fcc và 5/3 đối với bcc. Các tính số được thực hiện đối với một số tinh thể fcc và bcc. Các kết quả thu được trùng tốt với các số liệu thực nghiệm. Điều đó khẳng định các ưu điểm của phương pháp trên trong tính các tham số nhiệt động và xác định cấu trúc bằng kỹ thuật XAFS (Cấu trúc tinh thể của hấp thụ tia X).