5

Tính TS

COMMUNICATIONS IN PHYSICS

Published by
NATIONAL CENTRE FOR NATURAL
SCIENCE AND TECHNOLOGY OF VIETNAM

Volume 11, Number 1

March 2001

Contents

Page

1. **Nguyen Van Hung, Nguyen Ba Duc, and Dinh Quoc Vuong** - Theory of thermal expansion and cumulants in XAFS technique. 1-9
2. **Nguyen Huyen Tung** - Asymptotics of the density of states in disordered bulk semiconductors. 10-15
3. **Dao Nguyen Hoai Nam, R. Mathieu, P. Nordblabd, Nguyen Van Khiem, and Nguyen Xuan Phuc** - Magnetic properties of the $Y_{0.7}Ca_{0.3}MnO_3$ compound. 16-29
4. **Nguyen Tuan Khai, and Le Hong Khiem** - Energy loss and range of heavy ions in some typical stopping materials. 30-36
5. **Nguyen Van Khanh, Nguyen Van Vuong, Man Minh Tan** - The self-demagnetization factor of bonded magnets. 37-44
6. **Tran Thanh Minh, Nguyen Van Do** - Study on the separation of decay schemes of two Ba-129 states. 45- 50
7. **Pham Thu Nga, Le Ngoc Chung** - Optical properties of Eu^{3+} in the new efficient laser material of strontium fluorovanadate. 51- 57

Letters to the Editor

8. **Hoang Dac Luc, Co Tuong Hanh, Le Tien Quan** - Assessment of waste water pollution by heavy metals using nuclear analytical techniques. 58- 61
9. **D. C. Hiep, L. V. Hong, N. M. Ha, P. V. Phuc, D. N. H. Nam, N. X. Phuc, T. T. Phuong, T. L. Hung, and N. M. Hong** - 39 K superconducting alloy of MgB_2 62- 64

COMMUNICATIONS IN PHYSICS

Address of Editorial Office:

70 Tran Hung Dao Str,

Hanoi - Vietnam

Tel: 8.252825

E-Mail: Phi-com@isi.ac.vn

Communications in Physics, Vol. 11, No. 1 (2001), pp. 1-9

THEORY OF THERMAL EXPANSION AND CUMULANTS IN XAFS TECHNIQUE

NGUYEN VAN HUNG, NGUYEN BA DUC,
AND DINH QUOC VUONG

Faculty of Physics, University of Science, VNU-Hanoi.

Abstract. *A new theory of thermal expansion and cumulants in XAFS has been formulated, developing further the anharmonic-correlated Einstein model. The expressions were derived for spring constant, Einstein temperature, Einstein frequency, first cumulant or net thermal expansion describing an asymmetry of interaction potential, second cumulant or Debye-Waller factor, third cumulant, and thermal expansion coefficient. The cubic parameter of interaction potential is included in all expressions describing anharmonic effects. Derivation is based on quantum statistical procedure and the results describe thermodynamic properties of crystals for any structure and any temperature. Some new structural parameters have been developed describing atomic distribution in XAFS technique.*

I. INTRODUCTION

It is known that X-ray Absorption Fine Structure ($XAFS$) provides information on atomic number and radius of atomic shell of substances and hence becomes a powerful structural analysis technique. But two things are still required to solve: firstly, several uncertainties in the information on the atomic shell radius occur due to thermodynamic effects, especially at high temperatures, where the anharmonic contributions must be included [1, 2]; secondly, still no exact method for determination of atomic distribution or structure has been formulated. To solve the first problem the cumulant expansion approach [3] has been developed. According to this approach the $XAFS$ function for a single shell is described with in the frame work of a single-scattering and plane-wave approximation by

$$\chi(k) = A(k)\, Im\left[e^{i\Phi(k)}\left\langle e^{2ikr}\right\rangle\right] = A(k)\, Im\left\{e^{i\Phi(k)} exp\left[2ikr_0 + \sum_{0} \frac{(2ik)^n}{n!}\sigma^{(n)}\right]\right\}, \qquad (1)$$

where k, A, Φ are the wave number, amplitude, and total phase shift of photoelectron, respectively, r is the instantaneous distance between absorbing and backscattering atoms, and r_0 is its value at the equilibrium or minimum position of the interaction potential, the brackets $<>$ denote a thermal average, and $\sigma^{(n)}$ are the cumulants. This approach has been used mainly in fitting the $XAFS$ spectra to extract physical parameters from experimental data. The anharmonic single-particle potential theory [6], single-bond spring constant [5], full-lattice dynamical procedure [11], and anharmonic-correlated Einstein model [4] have been developed to approximate cumulants in $XAFS$ spectroscopy. The comparison of these methods will be discussed in the Section 5 of present paper.

Contributing to solving the first problem in this work we develop further the anharmonic - correlated Einstein model, deriving general expressions for thermal expansion and $XAFS$ cumulants which are valid for any structure and any temperature. Then the results for fcc and bcc structure published before [8, 9] as well as for simple cubic (s.c.) obtained in this work are only the special cases of present theory.

To solve the second problem from our developed theory some parameters will be derived as the new structural parameters describing atomic distribution in structural analysis by $XAFS$. Attention will be focused on cubic crystals and the advantages of present procedure in comparison with other methods will be discussed in details.

II. DERIVATION OF THERMODYNAMIC PARAMETERS

Thermodynamic properties of substances are known as the results of their thermal atomic vibration. At low temperatures this vibration is harmonic, but anharmonic contributions must be included at high temperatures [1-4]. Present derivation is based on quantum statistical procedure with quasi-harmonic approximation, according to which the Hamiltonian of the system is written as a harmonic term with respect to the equilibrium at a given temperature, plus an anharmonic perturbation

$$H = \frac{p^2}{2\mu} + U_E(x) \equiv H_0 + U_E(a) + \delta U_E(y)\,; \; H_0 = \frac{p^2}{2\mu} + \frac{1}{2}k_{eff}y^2, \tag{2}$$

where

$$x = r - r_0;\; y = x - a;\; a = \langle x \rangle\,;\; \mu = \frac{M_0 M}{M_0 + M};\; \langle y \rangle = 0. \tag{3}$$

Here μ is reduced mass of absorber with mass M_0 and backscatterer with mass M, r and r_0 have the same meaning as for Eq.(1). We define y to be the deviation from the equilibrium value of x at temperature T and determine the net thermal expansion $a(T) =< r - r_0 >$ which characterizes an asymmetry in the interaction potential (Fig.1). This asymmetry occurs due to anharmonic effects.

According to anharmonic-correlated Einstein model [4] the interaction between absorber and backscatterer is via an effective-anharmonic Einstein potential

$$U_E(x) = \frac{1}{2}k_{eff}x^2 + k_3x^3 + \ldots + \sum_{j \neq i} U\left(\frac{\mu}{M_i}x\, \hat{R}_{01}\hat{R}_{ij}\right). \tag{4}$$

This potential includes anharmonicity parameter k_3 describing an asymmetry or skew in the pair distribution function and the contributions of a small atom cluster, surrounding the absorbing and backscattering atoms, and therefore, spring constant becomes an effective one k_{eff}. The contributions of such cluster is described in Eq.(4) by the sum i which is over absorber ($i = 0$) and backscatterer ($r = 1$), and the sum j which is over all their near neighbors, excluding the absorber and backscatterer themselves. The latter contributions are described by the term $U(x)$, and $\widehat{R}$ in Eq.(4) is the unit bond length vector.

From Eqs.(2-4) the interacting effective Einstein potential is given by

$$U_E(y) \equiv U_E(a) + \frac{1}{2}k_{eff}y^2 + \delta U_E(y) \tag{5}$$

The interaction between atoms of each pair in the single bond can be via an imperical potential like Lennard-Jones, or Morse, or Mardelung potential. In this work we use an anharmonic Morse potential which is appropriate for cubic crystals.

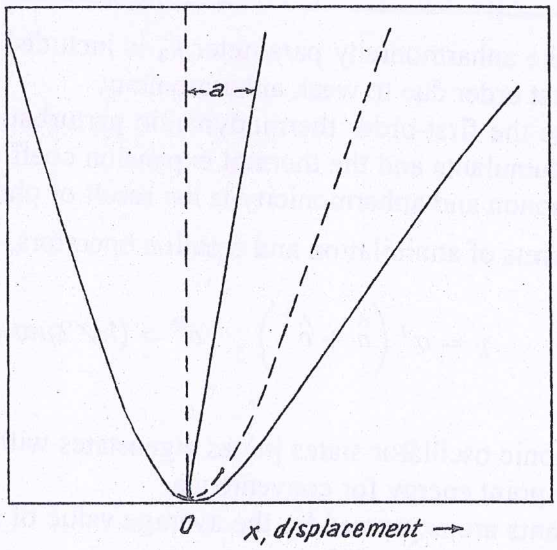

Fig. 1. Potential energy U and net thermal expasion $a = \langle x \rangle$ decribing an asymmetry of interaction potential. Dashed line describes symmetry potential

Expanded to third order about its minimum this model becomes

$$U(x) = D\left(e^{-2ax} - 2e^{-ax}\right) \approx D\left(-1 + \alpha^2x^2 - \alpha^3x^3 + \ldots\right), \tag{6}$$

where D is dissociation energy, and corresponds to the width of potential. It is sufficient to consider weak anharmonicity, i.e., the first order perturbation theory, so that only the cubic term in this equation must be kept.

Substituting (6) into Eq.(4) and using Eq.(5) we derived the following expressions

$$k_{eff} = c_j\left(D\alpha^2 + c_2ak_3\right) = \mu\varpi_E^2;\ k_3 = -c_3D\alpha^3\ ; \tag{7}$$

$$\begin{aligned} \delta U_E(y) &= \left(c_1D\alpha^2a + 3k_3a^2\right)y + k_3y^3 \approx c_1D\alpha^3ay + k_3y^3 \\ &= D\alpha^2\left(c_1ay - c_3\alpha y^3\right). \end{aligned} \tag{8}$$

Here the factors c_1, c_2 and c_3 contain the sum of the projection of contributions of near neighbors to the pair potential between absorber and backscatterers, i.e., the scalar product in Eq.(4). Therefore, they characterize the distribution of neighboring atoms surrounding the absorber and backscatterer and are different for different structures. They were derived for cubic crystals and are presented in Table 1.

Table 1 : The values of atomic distribution parameters c_1, c_2, and c_3 derived for s.c., fcc, and bcc crystals

Structure	c_1	c_2	c_3
s.c	3	1	5/4
fcc	5	6/5	5/4
bcc	11/3	18/11	5/4

Moreover, the anharmonicity parameter k_3 is included in each of (7), (8), and we limited only its first order due to weak anharmonicity.

Now we use the first-order thermodynamic perturbation theory [7] to derive the formulas for the cumulants and the thermal expansion coefficient. The atomic vibration is quantized as phonon and anharmonicity is the result of phonon interaction. Therefore, we express y in terms of annihilation and creation operators, $\hat{a}$ and $\hat{a}^{+}$, i.e.,

$$y = \sigma^0 \left(\hat{a} + \hat{a}^{+} \right) ; \quad \sigma^0 = \left(\hbar / 2\mu\varpi_E \right)^{1/2} , \tag{9}$$

and use the harmonic oscillator states $|n\rangle$ as eigenstates with eigenvalues $E_n = n\hbar\varpi_E$, ignoring the zero-point energy for convenience.

The cumulants are expressed by the average value of y, that's why, to derive their formulas we use the expression [7]

$$\langle y^m \rangle = \frac{1}{Z} Tr\rho y^m \quad ; m = 1, 2, 3, ..., \tag{10}$$

where $\rho = e^{-\beta H}$ with $\beta = 1/k_B T$ is the statistical density matrix, $Z = Tr\rho$ is the canonical partition function, and k_B is Boltzmann's constant. The corresponding unperturbed quantities are $\rho_0 = e^{-\beta H_0}$ and $Z_0 = Tr\rho_0$. To leading order in the perturbation δU_E, $\rho = \rho_0 + \delta\rho$, where $\delta\rho$ is given by

$$\delta\rho = - \int_0^\beta e^{-\beta H_0} \delta \tilde{U}_E \left(\beta' \right) d\beta' ; \quad \delta \tilde{U}_E \left(\beta \right) = e^{\beta H_0} \delta U_E e^{-\beta H_0} . \tag{11}$$

With the above arguments we have

$$Z_0 = \sum_n e^{-n\beta\hbar\varpi_E} = \sum z^n = \sum_{n=0}^{\infty} \frac{1}{1-z}\,, \tag{12}$$

where the temperature variable $z = e^{-n\beta\hbar\varpi_E} = e^{-\theta_E/T}$ is determined by the Einstein temperature, derived from Eqs.(2-4)

$$\theta_E = \frac{\hbar}{k_B}\left[c_1\left(D\alpha^2 + c_2 a k_3\right)/\mu\right]^{\frac{1}{2}} = \frac{\hbar\alpha}{k_B}\left[c_1 D\left(1 - c_2 c_3 \alpha a\right)/\mu\right]^{\frac{1}{2}}. \tag{13}$$

For further derivation of expressions for the cumulants we calculated the matrix elements

$$\begin{aligned}
\langle n|y^2|n\rangle &= \left(\sigma^0\right)^2(2n+1)\,;\\
\langle n|y|n+1\rangle &= \sigma^0(n+1)^{\frac{1}{2}}\,;\\
\langle n|y^3|n+1\rangle &= 3\left(\sigma^0\right)^3(n+1)^{\frac{3}{2}}\\
\langle n|y^3|n+3\rangle &= \left(\sigma^0\right)^3(n+1)(n+2)(n+3)^{\frac{1}{2}}
\end{aligned} \tag{14}$$

and applied the following mathematical expressions

$$\begin{aligned}
\sum_n nz^n &= \frac{z}{(1-z)^2}\,;\ \sum_n z^n(n+1) = \frac{1}{(1-z)^2}\,;\ \sum_n z^n(n+1)^3 = \frac{1+4z+z^2}{(1-z)^4}\\
\sum_n z^n(n+1)^2 &= \frac{1+z}{(1-z)^3};\ \sum_n z^n(n+1)(n+2)(n+3) = \frac{6}{(1-z)^4}
\end{aligned} \tag{15}$$

We neglected all the terms containing a^s with $s \geq 2$ due to the weak anharmonicity.

From Eq.(10), first equation of (14) and first equation of (15) we obtain for the even cumulants

$$\sigma^2 = \langle y^2\rangle = \frac{1}{Z}Tr\rho y^2 = \frac{1}{Z_0}Tr\rho_0 y^2 = \frac{1}{Z_0}\sum_n e^{-n\beta\hbar\varpi_E}\langle n|y^2|n\rangle = \frac{\hbar\varpi_E}{2k_{eff}}\frac{1+z}{1-z} \tag{16}$$

By performing the intergral in Eq. (11) over β' and evaluating the traces, the remaining odd moments are given by

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

Using Eqs.(10), (17) we obtain for $m = 1$

$$\langle y\rangle = \frac{1}{Z}Tr\rho y \approx \frac{1}{Z_0}Tr\rho_0 y = \frac{2\left(\sigma^0\right)^2}{\hbar\varpi_E}\left[c_1 D\alpha^2 a + 3k\left(\sigma_0\right)^2\frac{1+z}{1-z}\right] \qquad (18)$$

By setting $< y >= 0$ we obtain from Eqs.(7), (16), (18) the first cumulant or net thermal expansion

$$\sigma^{(1)} = a = \frac{3k_3\hbar\varpi_E}{2c_1^2D^2\alpha^4}\frac{1+z}{1-z} = -\frac{3k_3}{c_1D\alpha^2}\sigma^{(2)} = \frac{3c_3\hbar\varpi_E}{2c_1^2D\alpha}\frac{1+z}{1-z} = \frac{3c_3\alpha}{c_1}\sigma^{(2)}, \qquad (19)$$

and hence, the second cumulant $\sigma^{(2)}$ which is equal Debye-Waller factor σ^2

$$\sigma^2 = \frac{\hbar\varpi_E}{2c_1D\alpha^2}\frac{1+z}{1-z} \qquad (20)$$

Since $\delta U_E\left(y\right)$ has the expression (8) to leading order in k_3 and $m = 1$ or 3, the matrix elements only couple n to $n \pm 1$, $n{\pm}3$. Also, making use of the hermiticity of $\delta U_E\left(y\right)$ and y^m, we can demonstrate the equivalence of the $n' = n \pm j$ terms in Eq.(17). Therefore, from Eqs.(7) and (17) we derived the third cumulant

$$\sigma^{(3)} = -\frac{k_3\left(\hbar\varpi_E\right)^2}{2c_1^3D^3\alpha^6}\frac{1+10z+z^2}{\left(1-z\right)^2} = \frac{3c_3\left(\hbar\varpi_E\right)^2}{2c_1^3D^2\alpha^3}\frac{1+10z+z^2}{\left(1-z\right)^2} \qquad (21)$$

Using Eqs.(7, 19) we derived the thermal expansion coefficient

$$\alpha_T = \frac{3k_3k_B}{c_1^2D^2\alpha^4r}\frac{z\left(lnz\right)^2}{\left(1-z\right)^2} = \frac{3c_3k_B}{c_1^2D\alpha r}\frac{z\left(lnz\right)^2}{\left(1-z\right)^2} \qquad (22)$$

From above results it is easy to get the following relations

$$\frac{\alpha_T r T\sigma^2}{\sigma^{(3)}} = \frac{3z\left(1+z\right)ln\left(1/z\right)}{\left(1-z\right)\left(1+10z+z^2\right)}; \qquad (23)$$

$$\frac{\sigma^{(1)}\sigma^2}{\sigma^{(3)}} = \frac{3\left(1+z\right)^2}{2\left(1+10z+z^2\right)} \qquad (24)$$

Note that $\sigma^{(1)}, \sigma^{(3)}$, α_T contain the anharmonicity parameter k_3, and occur only when this parameter is included, that is why $\sigma^{(1)}, \sigma^{(3)}$and α_T must be taken into account for consideration of anharmonic effects in $XAFS$ technique.

III. DESCRIPTION OF THERMODYNAMIC PARAMETERS BY DEBYE-WALLER FACTORS

One of our important efforts is to simplify the theoretical description, so that it can lead to reducing the numerical calculations and measurements. For this purpose we may describe the temperature variable in term of Debye-Waller factor σ^2

$$z = \frac{\sigma^2 - \sigma_0^2}{\sigma^2 + \sigma_0^2} \tag{25}$$

Using Eq. (25) we get all expressions derived in the previous section for thermodynamic parameters in the following forms

$$\sigma^{(1)} = \sigma_0^{(1)} \frac{1+z}{1-z} = \frac{3c_3\alpha}{c_1}\sigma^2 \, ; \; \sigma_0^{(1)} = \frac{3c_3\alpha}{c_1}\sigma_0^2 \, , \tag{26}$$

$$\sigma^2 = \sigma_0^2 \frac{1+z}{1-z} \, ; \; \sigma_0^2 = \frac{\hbar\omega_E}{2c_1 D\alpha^2} \, ; \tag{27}$$

$$\sigma^{(3)} = \sigma_0^{(3)} \frac{3\left(\sigma^2\right)^2 - 2\left(\sigma_0^2\right)^2}{\left(\sigma_0^2\right)^2} \, ; \; \sigma_0^{(3)} = \frac{2c_3\alpha}{c_1}\left(\sigma_0^2\right)^2 \, ; \tag{28}$$

$$\alpha_T = \alpha_T^0 \left(\frac{c_1 D\alpha^2\sigma^2}{k_B T}\right)^2 \left[1 - \left(\frac{\sigma_0^2}{\sigma^2}\right)^2\right]^2 ; \; \alpha_T^0 = \frac{3c_3 k_B}{c_1^2 D\alpha r} \, , \tag{29}$$

$$\frac{\alpha_T r T \sigma^2}{\sigma^{(3)}} = \frac{c_1 D\alpha^2\sigma^2}{2k_B T} \frac{1 - \left(\sigma_0^2/\sigma^2\right)^2}{1 - (2/3)\left(\sigma_0^2/\sigma^2\right)^2} \tag{30}$$

$$\frac{\sigma^{(1)}\sigma^2}{\sigma^{(3)}} = \frac{1}{2 - (4/3)\left(\sigma_0^2/\sigma^2\right)^2} \, , \tag{31}$$

where $\sigma_0^{(1)}$, σ_0^2 and $\sigma_0^{(3)}$ are zero-point contributions to $\sigma^{(1)}$, σ^2 and $\sigma^{(3)}$, respectively.

In the above description, besides the Morse potential parameters are given, to calculate the thermodynamic parameters $\sigma^{(1)}$, σ^2 , $\sigma^{(3)}$, α_T and the relations (31, 32) we have to calculate only the Debye-Waller factors σ^2. So far, calculating or, measuring σ^2 one can predict the other cumulants, thus reducing the calculations and measurements.

IV. HIGH-AND LOW TEMPERATURE LIMITS

The above derived formulas are valid for all temperatures, but it is useful to consider their high-temperature (HT) limit, where the classical approach is applicable, and low-temperature (LT) limit, where the quantum theory must be used.

In the HT limit we use the approximation $z \approx 1 - \hbar\omega_E/k_B T$ to simplify the expressions of thermodynamic parameters. In the LT limit $z \to 0$, so that we can neglect z^2 and higher powers. The results of these approximations are presented in Table 2.

All the above results reflect the proportionality to k_3 of $\sigma^{(1)}$, $\sigma^{(3)}$ and α_T, so that these values characterize the anharmonic effects. Note that $\sigma^{(1)}$, σ^2 , $\sigma^{(3)}$ contain zero-point contributions, α_T approaches the constant value α_T^0 at high temperatures but vanishes exponentially with θ_E/T at low temperatures.

Table 2 Expressions of $\sigma^{(1)}$, σ^2 , $\sigma^{(3)}$, α_T and their relations in low-temperature and high-temperature limits

Value	$T \to 0$	$T \to \infty$
$\sigma^{(1)}$	$\sigma_0^{(1)}(1+2z)$	$3c_3k_BT/c_1^2D\alpha$
σ^2	$\sigma_0^2(1+2z)$	$k_BT/c_1D\alpha^2$
$\sigma^{(3)}$	$\sigma_0^{(3)}(1+12z)$	$6c_3(k_BT)^2/c_1^3D^2\alpha^3$
α_T	$\alpha_T^0 z(\ln z)^2(1+2z)$	α_T^0
$\alpha_T rT\sigma^2/\sigma^{(3)}$	$3z\ln(1/z) \to 0$	$1/2$
$\sigma^{(1)}\sigma^2/\sigma^{(3)}$	$3(1+2z)^2/2(1+12z) \to 3/2$	$1/2$

V. DISCUSSION AND CONCLUSIONS

Developing further the anharmonic correlated Einstein model [4] we derived a general theory for calculation of thermal expansion and cumulants in $XAFS$ theory including anharmonic contributions. The expressions are valid for any temperature and different structures seperated by our new structural parameters . The results for fcc and bcc structure published before [8, 9], and for s.c. structure obtained in this work become special cases of present procedure when we put the magnitudes of c_1, c_2, c_3 from Table 1 into the above obtained expressions.

With the discovery that the $XAFS$ spectra provide the number of atoms and the radius of each shell, the $XAFS$ spectroscopy becomes a powerful structural analysis technique, but the problem remained to solve is the distribution of these atoms. The factors c_1, c_2 and c_3 introduced in present work contain the angle between the bond connecting absorber with each atom and the bond between absorber and backscatterer. That is why they can provide the atomic distribution and hence discovered as new structural parameters. Knowing structure of the crystals like cubic crystals, i. e., the magnitudes of c_1, c_2, c_3 from Table 1 we can calculate the cumulants and then the $XAFS$ spectra according to Eq.(1). But for structure unknown substances we can extract the atomic number and the radius of each shell from the measured $XAFS$ spectra, as well as, extract the factors c_1, c_2, c_3 according to our theory from the measured cumulants like Debye-Waller factor to get information about atomic distribution or structure.

Our developed expressions for thermal expansion and $XAFS$ cumulants contain the information on effective spring constant, correlated Einstein temperature, Einstein frequency, Morse potential parameters, and describe their temperature dependence involving the results of quantum theory and classical limit. These behaviours are as follows: at low temperature $\sigma^{(1)}$, σ^2 , $\sigma^{(3)}$, contain zero-point contribution as quantum effects; at high temperature $\sigma^{(1)}$, σ^2 are proportional to T, and $\sigma^{(3)}$ is proportional to T^2 as conclusions of classical approach [1]. The thermal expansion coefficient has the form similar to the specific heat, thus agreeing with the fundamental of solid state theory.

Our description of all thermodynamic parameters by Debye-Waller factor is very convenient, since determination of σ^2 allows one to predict the other cumulants, thus reducing the numerical calculations and measurements.

Anharmonic single-particle potential theory [6] does not give an accurate description of the situation because it ignores the correlated motion of the atoms, the single-bond spring constant [5] does not take sufficient contribution to atomic vibration. Both they are used actually for explanation and extraction of physiscal parameters from the experiment. Present theory avoids the disadvantages of the above procedures as well as the tensive calculations of the full lattice dynamical approximation [11]. Due to limitation of the paper volume the numerical results of cubic crystals according to present theory will be published elsewhere [12]. They show very good agreement with the experimental results and several advantages of present theory in comparison with the others.

Note that the relations $\alpha_T r T \sigma^2/\sigma^{(3)}$ and $\sigma^{(1)}\sigma^2/\sigma^{(3)}$ approach the classical expression of $1/2$ at high temperature (see Tab.2). This conclusion not only reflects the results of classical method but also agrees well with the experimental results [1, 10]. Therefore, both they are used as a criterion to identify the temperature above which the classical limit is applicable and below which quantum theory must be applied. This issue will be discussed in our another paper [12].

ACKNOWLEDGMENT

One of the authors (N. V. Hung) thanks Prof. J. J. Rehr and Prof. E. A. Stern (University of Washington) for useful discussions. This work is supported in part by the Fundamental Science Research Program No 410-801 provided by the MOSTE.

REFERENCES

1. E. A. Stern, P. Livins, and Zhe Zhang, *Phys. Rev.* B **43** (1991) 8850.
2. N. V. Hung, R. Frahm, and H. Kamitsubo, *J. Phys. Soc. Jpn.* **65** (1996) 3571.
3. E. D. Crozier, J. J. Rehr, and R. Ingalls, in *"X-ray Absorptions"*, edited by D.C.Koningsberger and X. Prins (Wiley. New York, 1983).
4. N. V. Hung and J .J. Rehr, *Phys. Rev.* B **56** (1997) 43.
5. A. I. Frenkel and J. J. Rehr, *Phys. Rev.* B **48** (1993) 585.
6. J. M. Tranquada and R. Ingalls, *Phys. Rev.* B **28** (1983) 3520.
7. R. P. Feynman, *Statistics Mechanics* (Benjamin, Reading, 1972).
8. N. V. Hung, *J. Communications in Phys.*, **8** (1998) 46.
9. N. V. Hung, Vu Kim Thai, and Nguyen Ba Duc, *J. Science of VNU*-Hanoi. **15**, No.6 (1999).
10. L. Wenzel, D. Arvanitis, H. Rabus, T. Lederer, K. Baberschke and G. Comelli, *Phys. Rev. Lett.* **64** (1990) 1765.
11. T. Miyanaga and T. Fujikawa, *J. Phys. Soc. Jpn.* **63** (1994) 1036 and 3683.
12. N. V. Hung and N. B. Duc, J. *Commun. in Phys.*,**10** (2000) 15.

Received 3 September 2000.