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USAGE OF THE ANHARMONIC CORRELATED EINSTEIN MODEL TO DEFINE THE EXPRESSIONS OF CUMULANTS AND THERMODYNAMIC PARAMETERS IN THE CUBIC CRYSTALS WITH NEW STRUCTURE FACTORS

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By using potential effective interaction in the anharmonic correlated Einstein model on the basis of quantum statistical theory with phonon interaction procedure, the expressions describing asymmetric component (cumulants) and thermodynamic parameters including the anharmonic effects contributions and by new structural parameters of cubic crystals has been formulated. This new parameters describing the distribution of atoms. The expansion of cumulants and thermodynamic parameters through new structural parameters has been performed.

Keywords: anharmonic XAFS, cumulants, thermodynamic parameters.

Fig. 1. Tab. 3. Ref.: 4 titles.

ИСПОЛЬЗОВАНИЕ АНГАРМОНИЧЕСКОЙ КОРРЕЛЯЦИОННОЙ МОДЕЛИ ЭЙНШТЕЙНА С ЦЕЛЬЮ ОПРЕДЕЛЕНИЯ ВЫРАЖЕНИЙ ДЛЯ КУМУЛЯНТОВ И ТЕРМОДИНАМИЧЕСКИХ ПАРАМЕТРОВ В КУБИЧЕСКИХ КРИСТАЛЛАХ С НОВЫМИ СТРУКТУРНЫМИ ФАКТОРАМИ

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Используя потенциально эффективное взаимодействие в ангармонической корреляционной модели Эйнштейна на основании квантовой статистической теории с фононным взаимодействием, были сформулированы выражения, описывающие асимметричные компоненты (кумулянты) и термодинамические параметры, включая вклад ангармонических эффектов и новых структурных параметров кубических кристаллов. Предлагаемые новые параметры описывают распределение атомов. В работе осуществлялось расширение кумулянтов и термодинамических параметров, используя новые структурные параметры.

Ключевые слова: ангармоническая тонкая структура рентгеновского поглощения, кумулянты, термодинамические параметры.

Ил. 1. Табл. 3. Библиогр.: 4 назв.

Introduction. In the harmonic approximation X-ray Absorption Fine Structure spectra (XAFS), the theoretical calculations are generally well appropriate with the experimental results at low temperatures, because the anharmonic contributions from atomic thermal vibrations can be neglected. However, at the different high temperatures, the XAFS spectra provide apparently diffirent structural information due to the anharmonic effects and these effects need to be evaluated. Furthermore, the XAFS spectra at low temperatures may not provide a correct picture of crystal structure, therefore, this study of the XAFS spectra including the anharmonic effects at high temperatures is to be needed. The expression of anharmonic XAFS spectra often is described by [1]

$$\chi(k) = F(k)\frac{\exp[-2R/\lambda(k)]}{kR^2}\,\mathrm{Im}\times$$

$$\times\left\{e^{i\Phi(k)}\exp\left[2ikR+\sum_n\frac{(2ik)^n}{n!}\sigma^{(n)}\right]\right\}, \qquad (1)$$

where $F(k)$ – is the real specific atomic backscattering amplitude; $\Phi(k)$ – is total phase shift of photoelectron; k – is wave number; λ – is mean free path of the photoelectron, and $\sigma^{(n)}$ (n = = 1, 2, 3, …) – are the cumulants to describe asymmetric components, they all appear due to the thermal average of the function e^{-2ikr}, in which the asymmetric terms are expanded in a Taylor series around value $R = \langle r \rangle$ with r is instantaneous bond length between absorbing and backscattering atoms at T temprature and then are rewritten in terms of cumulants.

At first, the cumulant expansion approach has been used mainly fitting the XAFS spectra to extract physical parameters from experimental values. Thereafter, some procedure were formulated for the purpose of analytic calculation of cumulants, and the anharmonic correlated Einstein model [2] which has been given results good agreement with experimental values. The important development in this procedure is that model has been calculated into the interaction between absorbing and backscattering atoms with neighboring atoms in a cluster of nearest atoms at high temperatures. The potential interaction between the atoms becomes asymmetric due to the anharmonic effects and the asymmetric components were written in terms of the cumulants. The first cumulant or net thermal expansion, the second cumulant or Debye-Waller factor, the third cumulant is description phase shift of anharmonic XAFS spectra. The purpose of this work is to formulate the cumulant expressions and write thermodynamic parameters as general form through the new structure parameters by using the anharmonic correlated Einstein model.

Formalism. Because the oscillations of a pair single bond between of absorbing and backscattering atoms with masses M_1, M_2, respectively, is affected by neighboring atoms, when taking into account these effects via an anharmonic correlated Einstein model, effective Einstein potential is formed as follow:

$$U_E(\chi) = U(x) + \ldots + \sum_{i=1,2} \sum_{j \neq i} U\left(\frac{\mu}{M_i} R_{12} R_{ij}\right), \quad (2)$$

where R – is the unit bond length vector, μ – is reduced mass of atomic mass M_1 and M_2; the sum according to i, j – is the contribution of cluster nearest atoms; $U(x)$ an effective potential:

$$U(x) \approx \frac{1}{2} k_{eff} x^2 + k_3 x^3 + \ldots, \quad x = r - r_0, \quad (3)$$

where r – is spontantaneous bond length between absorbing and bacskcattering atoms r_0 is its equilibrium value; k_{eff} – is effective spring constant because it includes total contribution of neighboring atoms; k_3 – is cubic anharmonicity parameter which gives an asymmetry in the pair distribution function.

The atomic vibration is calculated based on quantum statistical procedure with approximate quasi – harmonic vibration, in which the Hamiltonian of the system is written as harmonic term with respect to the equilibrium at a given temperature plus an anharmonic perturbation, with $y = x - a$, $a(T) = \langle x \rangle$, $\langle y \rangle = 0$, we have:

$$H = \frac{P^2}{2\mu} + U_E(\chi) = H_0 + U_E(a) + \delta U_E(y);$$

$$H_0 = \frac{P^2}{2\mu} + \frac{1}{2} k_{eff} y^2, \quad (4)$$

with a is the net thermal expansion, y – is the deviation from the equilibrium value of x at temperature T. Next, the use of potential interaction between each pair of atoms in the single bond can be expressed by anharmonic Morse potential for cubic crystals. Expanding to third oder around its minimum, we have:

$$U_E(x) = D(e^{-2\alpha x} - 2e^{-\alpha x}) \approx$$
$$\approx D\left(-1 + \alpha^2 x^2 - \alpha^3 x^3 + \ldots\right), \quad (5)$$

where α – is expansion thermal parameter; D – is the dissociation energy by $U(r_0) = -D$.

From expressions (4), (5) we have potential effective interaction Einstein generalize as:

$$U_E(\chi) = U_E(a) + \frac{1}{2} k_{eff} y^2 + \delta U_E(y), \quad x = y + a. \quad (6)$$

Substituting Eq. (5) into (3) and using Eq. (6) to calculate the second term in Eq. (3) with $\mu = M/2$ ($M_1 = M_2 = M$), sum of i is over absorber $(i=1)$ and backscatterer $(i=2)$, and the sum of j which is over all their near neighbors, excluding the absorber and backscatterer themselves, because they contribute in the $U(x)$, and calculation of $(R_{12} R_{ij})$ with lattice cubic crystals like s.c, fcc and bcc crystals, we obtain thermodynamic parameters like k_{eff}, k_3 and $\partial U_E(y)$ in Tab. 1.

Table 1

The expressions of thermodynamic parameters for cubic crystals

Factor	s.c crystal	fcc crystal	bcc crystal
k_3	$-5D\alpha^3/4$	$-5D\alpha^3/4$	$-5D\alpha^3/4$
k_{eff}	$3D\alpha^2(1-5\alpha a/4)$	$5D\alpha^2(1-3\alpha a/2)$	$11D\alpha^2(1-45\alpha a/22)/3$
$\delta U_E(y)$	$D\alpha^2\left(3ay-5\alpha y^3/4\right)$	$5D\alpha^2\left(ay-\alpha y^3/4\right)$	$D\alpha^2\left(11ay/3-5\alpha y^3/4\right)$

To compare the above expressions in Tab. 1, we see although different structures of cubic crystals and which have special common factors, we call these factors as new structure factors c_1, c_2, the parameters calculated statistically is in Tab. 2.

Table 2

New structural parameters of cubic crystals

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

The k_3 parameter is indentical with any structures, the expressions of k_{eff}, $\delta U_E(y)$ thermodynamic parameters for the structural cubic crystals generalize according to new structural parameters are the following forms:

$$k_{eff} = c_1\left(D\alpha^2 + c_2 a k_3\right) = \mu\omega_E^2;$$

$$\delta U_E(y) = D\alpha^2\left[c_1 a y - 5\alpha y^3/4\right]. \qquad (7)$$

To derive the analytical formulas for cumulants through new structural parameters for the crystals of cubic structure, we use perturbation theory [3]. The atomic vibration is quantized as phonon and anharmonicity is the result of phonon interaction. Accordingly, we express y in terms of annihilation and creation operators a^+, a, respectively:

$$y = \sigma^0\left(a + a^+\right);\quad \sigma^0 = \sqrt{\hbar/2m\omega_E};\quad a^+a = n, \qquad (8)$$

and use the harmonic oscillator states $|n>$ as eigenstates with eigenvalues $E_n = n\hbar\omega_E$, ignoring the zero-point energy for convenience. The a^+, a operators satisfying the following properties $\left[a,\ a^+\right] = aa^+ - a^+a = 1;\qquad a^+\left\langle n\right| = \sqrt{n+1}\left|n+1\right\rangle;$ $a\left\langle n\right| = \sqrt{n}\left|n-1\right\rangle$. The cumulants are calculated by the average value $\left\langle y^m\right\rangle = \frac{1}{Z}Tr\left(\rho y^m\right)$, $m = 1, 2, 3, \ldots;$ $\rho = \exp\left(-\beta H\right)$; $\beta = (k_B T)^{-1}$, where Z is the canontical partition function, ρ with β is the statistical density matrix, k_B is Boltzmann's constant. The corresponding unperturbed quantities are $Z_0 = Tr(\rho_0)$, and $\rho_0 = \exp\left(-\beta H_0\right)$. To leading order in perturbation δU_E, $\rho = \rho_0 + \delta\rho$ with $\partial\rho$ is given by:

$$\partial\rho = -H\rho\partial\beta;\quad \partial\rho_0 = -H_0\rho_0\partial\beta \qquad (9)$$

we obtained:

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

$$\delta\tilde{U}_E\left(\beta\right) = e^{\beta H_0}\delta U_E e^{-\beta H_0}.$$

If we put unperturbed quantities equal to zero, we have:

$$Z_0 = Tr\rho_0 = \sum_n \exp\left(-n\beta\hbar\omega_E\right) = \sum_{n=0}^{\infty} z^n = \frac{1}{1-z},$$

where $z \equiv e^{-\beta\hbar\omega_E} = e^{-\theta_E/T}$ is the temperature variable and determined by the $\theta_E = \hbar\omega_E/k_B$ is Einstein temperature. Now we are using above expressions to calculate analytics of the cumulants.

- *The cumulants even order:*

$$\left\langle y^m\right\rangle\Big|_{mchSn} \approx \frac{1}{Z}Tr\rho y^m \approx \frac{1}{Z_0}Tr\rho_0 y^m =$$

$$= \frac{1}{Z_0}\sum_n e^{-n\beta\hbar\omega_E}\left\langle n\right|y^m\left|n\right\rangle.$$

With $m = 2$ we have calculation expression of the second cumulant

$$\left\langle y^2\right\rangle = \sigma^{(2)} = \frac{1}{Z_0}\sum_n e^{-n\beta\hbar\omega_E}\left\langle n\right|y^2\left|n\right\rangle. \qquad (10)$$

Using matrix $\left\langle n\right|y^2\left|n\right\rangle = \left\langle n\right|a^+a + aa^+\left|n\right\rangle =$ $= \left(\sigma_0\right)^2\left(2n+1\right)$ and substituting into (10) and applying the mathematical transformations and according to (7) we have expression of second cumulant which is rewritten through c_1 structural parameter:

$$\sigma^{(2)} = \left\langle y^2\right\rangle = \frac{\hbar\omega_E}{2c_1 D\alpha^2}\frac{\left(1+z\right)}{\left(1-z\right)}. \qquad (11)$$

- *The cumulants odd order:*

$$\left\langle y^m\right\rangle\Big|_{mlo\hat{\imath}} \approx \frac{1}{Z}Tr\rho y^m \approx \frac{1}{Z_0}Tr\delta\rho y^m. \qquad (12)$$

With $m = 1, 3$ we have expression to calculate first cumulant and third cumulant. Transformation following matrix correlative with $\left\langle y\right\rangle$ and $\left\langle y^3\right\rangle$, we have:

$$\langle n|y|n+1\rangle = \sigma_0 \langle n|a+a^+|n+1\rangle =$$
$$= \sigma_0 \sqrt{n+1}\langle n|n\rangle = \sigma_0 (n+1)^{1/2}; \qquad (13)$$

$$\langle n|y^3|n+1\rangle = (\sigma_0)^3 \left(3n\sqrt{n+1}+3\sqrt{n+1}\right)\langle n|n\rangle =$$
$$= 3(\sigma_0)^3 (n+1)^{3/2}; \qquad (14)$$

$$\langle n|y^3|n+3\rangle = 3(\sigma_0)^3 \left[(n+1)(n+2)(n+3)\right]^{1/2}. \qquad (15)$$

- *The first cumulant (m = 1)*

$$\sigma^{(1)} = \langle y\rangle = \frac{1}{Z_0}\sum_{nn'} \frac{e^{-\beta n\hbar\omega_E} - e^{-\beta n'\hbar\omega_E}}{n\hbar\omega_E - n'\hbar\omega_E} \times$$
$$\times \langle n|D\left[\alpha^2 c_1 a y - \alpha^3 c_3 y^3\right]|n'\rangle\langle n'|y|n\rangle$$

with $n' = n+1$ and from Eq. (12), (13) and transform, we have:

$$\langle \mathrm{y}\rangle = -\frac{D\alpha^2}{\hbar\omega_E}(\sigma_0)^2\left[c_1 a - 3c_3\alpha(\sigma_0)^2\frac{(1+z)}{(1-z)}\right] =$$
$$= -\frac{D\alpha^2}{\hbar\omega_E}\frac{\hbar\omega_E}{2k_{eff}}\left[c_1 a - 3c_3\alpha(\sigma_0)^2\frac{(1+z)}{(1-z)}\right],$$

because $\langle y\rangle = 0$ and approximate $k_{eff} \approx c_1 D\alpha^2$, the transformation and reduction we obtained first cumulant

$$\sigma^{(1)} = a = \frac{15\hbar\omega_E}{8c_1^2 D\alpha}\frac{(1+z)}{(1-z)} = \frac{15\alpha}{4c_1}\sigma^{(2)}. \qquad (16)$$

- *The third cumulant (m = 3)*

$$\sigma^{(3)} = \langle y^3\rangle =$$
$$= \frac{1}{Z_0}\sum_{nn'}\frac{e^{-\beta E_n} - e^{-\beta E_{n'}}}{E_n - E_{n'}}\langle n|\delta U_E|n'\rangle\langle n'|y^3|n\rangle. \qquad (17)$$

From Eq. (7), (17), we have:

$$\langle y^3\rangle = \frac{D\alpha^2}{Z_0}\sum_{nn'}\frac{e^{-\beta n\hbar\omega_E} - e^{-\beta n'\hbar\omega_E}}{n\hbar\omega_E - n'\hbar\omega_E} \times$$
$$\times\left[\langle n|c_1 a y|n'\rangle - \langle n|\alpha c_3 y^3|n'\rangle\right]\langle n'|y^3|n\rangle. \qquad (18)$$

Using Eq. (14), (15), the calculation of Eq. (18) with $n' = n+1$, $n' = n+3$, respectively, and note that matrix only affect with y^3 and according to Eq. (7), (8), we determine third cumulant:

$$\sigma^{(3)} = \frac{15(\hbar\omega_E)^2}{8c_1^3 D^2\alpha^3}\frac{\left(1+10z+z^2\right)}{(1-z)^2} =$$
$$= \frac{15\hbar\omega_E}{4c_1^2 D\alpha}\frac{\left(1+10z+z^2\right)}{1-z^2}\sigma^{(2)}. \qquad (19)$$

The results of the numerical calculations according to present method for cumulants good agreement with experimental values for Cu crystal (Tab. 3). The Fig. 1 illustrates good agreement of the second and third cumulants in present theory with experiment values.

Table 3

The comparison of the results of $\sigma^{(2)}$ and $\sigma^{(3)}$ calculated by present theory with experimental data for Cu crystal at different temperatures

T (K)	$\sigma^{(2)}$ (A^2)		$\sigma^{(3)}$ (A^3)	
	Present	Expt.	Present	Expt.
10	0,00298	0,00292	–	–
77	0,00333	0,00325	0,000100	–
295	0,01858	0,01823	0,000131	0,000130
683	0,01858	0,01823	–	–

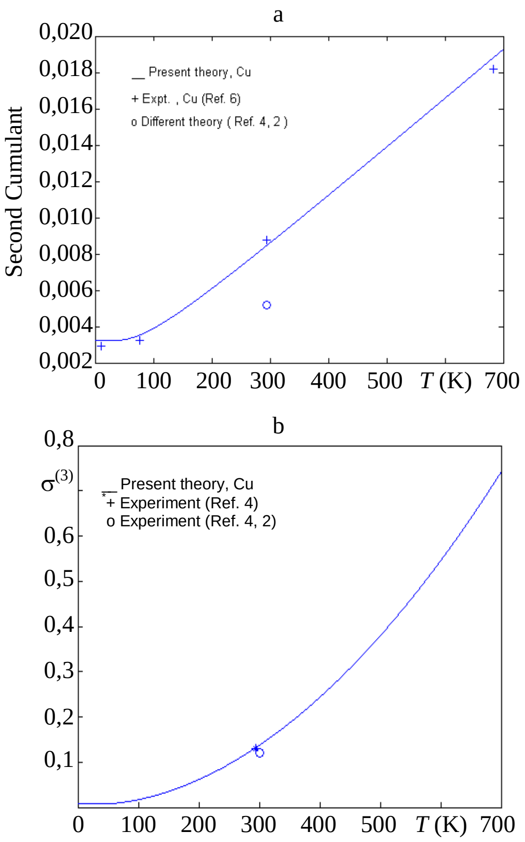

Fig. 1. The graphs illustrate temperature dependence of second (a) and third (b) cumulants by present theory and compared to experiment values

Discussion and conclusions. Developing further the anharmonic correlated Einstein model we obtained a general theory for calculation cumulants and thermodynamic parameters in XAFS theory including anharmonic contributions. The expressions are described through new structural parameters agree with structural contributions of cubic crystals like face center cubic (fcc), body center cubic (bcc), and results published before [4]. The expression in this work is general case of present procedure when we insert the magnitudes of c_1, c_2, from Tab. 2 into the calculation of the thermodynamic parameters and above obtained expressions of cumulants. The results of the numerical calculations according to present method for cumulants good agreement with experimental values for Cu crystal (Tab. 3) and illustrates by graphs in Fig. 1, note that the experimental values from XAFS spectra measured at HASYLAB (DESY, Germany).

With the discovery of the XAFS spectra, it provides the number of atoms and the radius of each shell, the XAFS spectroscopy becomes a powerful structural analysis technique, but the problem remained to be solved is the distribution of these atoms. The factors c_1, c_2, introduced in the presented work contains the angle between the bond connecting absorber with each atom and the bond between absorber and backscatterer, that is why they can describe the nearest atoms distributions surround absorber and backscatterer atoms. Knowing structure of the crystals and the magnitudes of c_1, c_2, from Tab. 2 we can calculate the cumulants and then XAFS spectra. But for structure unknown substances we can extract the atomic number from the measured XAFS spectra, as well as, extract the factors c_1, c_2, according to our theory from the measured cumulants like Debye-Waller factor to get information about atomic distribution or structure.

The thermodynamic parameters expressions described by second cumulant or Debye-Waller factor is very convenient, when second cumulant $\sigma^{(2)}$ is determined, it allows to predict the other cumulants according to Eq. (21), (24), consequently reducing the numerical calculations and experimental measurements.

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ФОРМАЛИЗАЦИЯ КРИТЕРИЯ МИНИМУМА ЭНЕРГОЗАТРАТ УСТАНОВКИ, ПРОИЗВОДЯЩЕЙ ДРОБЛЕНИЕ

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Построены аналитические выражения, описывающие зависимость между основными параметрами процесса дробления калийных руд. Учитывая общность формулы Кирпичева, были внесены некоторые коррективы для непосредственного применения данной гипотезы в расчете энергии, идущей на разрушение образца калийной руды, что позволяет брать во внимание не только общий, усредненный размер образцов, но и процентное содержание каждого конкретного образца заданных размеров. В результате исследования состава калийной руды заданного объема было установлено, что каждый компонент, входящий в состав образца, имеет свои предел прочности и модуль упругости. Кроме того, процентное содержание компонент, входящих в состав калийной руды (сильвинита, галита и нерастворимого осадка), различно.