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CALCULATION OF THERMODYNAMIC PARAMETERS OF BBC CRYSTALS IN XAFS THEORY

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Abstract. *In this work a new quantum statistical procedure for calculation of thermodynamic parameters of bcc crystals in X-ray Absorption Fine Structure (XAFS) theory, using anharmonic-correlated Einstein model, has been presented. The expressions were derived for spring constant, Einstein temperature, Einstein frequency, first cumulant or net-thermal expansion, second cumulant or Debye-Waller factor, third cumulant and thermal expansion coefficient. The anharmonic contributions have been included and the theory is valid for all temperatures. Numerical calculations were carried out for bcc crystals Mo and W. The results provide thermodynamic properties of these systems.*

I. INTRODUCTION

It is known that XAFS is the result of scattering of photoelectron by surrounding neighbors of absorbing atom. Therefore, to get correct structural information of substances from XAFS spectra it is very important to know their thermodynamic properties at any temperatures, especially with including anharmonic contributions [1-3]. The cumulant expansion approach [4,5] has been developed to interpret these effects in XAFS spectroscopy. Thermodynamic parameters of fcc crystals described by cumulants have been evaluated [6]. This work is the next step of [6] devoted to calculation of thermodynamic parameters of bcc crystals in XAFS theory, using anharmonic - correlated Einstein model [7]. Quantum statistical theory with phonon interaction procedure was used to derive the expressions for spring constant, Einstein temperature, Einstein frequency, first cumulant or net - thermal expansion, second cumulant or Debye - Waller factor, third cumulant and thermal expansion coefficient. They describe the temperature dependence of these values including the anharmonic effects. Numerical calculations have been carried out for bcc crystals Mo and W. The results provide thermodynamic properties of these systems.

II. THEORY

The derivation of expressions for thermodynamic parameters of bcc crystals in this work is based on quantum statistical theory 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

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

where

$$y = x - a; \quad x = r - r_0; \quad a = < x >; \quad \mu = \frac{M_0 M}{M_0 + M}; \quad < y > = 0. \qquad (2)$$

Here x is deviation of the instantaneous bond length r of two atoms from their equilibrium distance r_0 or the location of the interaction potential minimum; M_0 and M are the mass of absorbing and backscattering atom, respectively; the brackets <> denote a thermal average. According to anharmonic-correlated Einstein model the interaction between absorber and backscatterer is via an effective anharmonic Einstein potential

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

which includes anharmonicity parameter k_3 describing an asymmetry or skew in the pair distribution function, as well as, contributions of a small atom cluster surrounding the absorbing and backscattering atom, so the spring constant now becomes an effective one k_{eff}. The contributions of such cluster is taken into account by the sum i which is over absorber ($i = 0$) and backscatterer ($i = 1$) and by 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 $\hat{R}$ is the unit bond length vector.

From Eqs.(1-3) the interacting effective Einstein potential is given by

$$U_E(y) = U_E(a) + \frac{1}{2}k_{eff}y^2 + \delta U_E(y). \qquad (4)$$

In this work the interaction between each pair of atoms in the single bond is via an anharmonic Morse potential. Expanded to third order about its minimum this model becomes

$$U(x) = D(e^{-2\alpha x} - 2e^{-\alpha x}) \approx D(-1 + \alpha^2x^2 - \alpha^3x^3 + ...), \qquad (5)$$

where D is the dissociation energy, and $1/\alpha$ corresponds to the width of the potential. It is usually sufficient to consider weak anharmonicity (i.e., first - order perturbation theory) so that only the cubic term in this equation must be kept.

Substituting Eq.(5) into Eq.(3) with considering Eq.(4) and using the values $(\hat{R}_{01}.\hat{R}_{ij})$ from the table 1 for summation we obtain

$$k_{eff} = \frac{11}{3}D\alpha^2 + 6k_3a = D\alpha^2\left(\frac{11}{3} - \frac{15}{2}\alpha a\right) = \mu\omega_E^2; \; k_3 = -\frac{5}{4}D\alpha^3; \qquad (6)$$

$$\delta U_E(y) = \left(\frac{11}{3}D\alpha^2a + 3k_3a^2\right)y + k_3y^3 \approx D\alpha^2\left(\frac{11}{3}ay - \frac{5}{4}\alpha y^3\right). \qquad (7)$$

No	x	y	z	$(\hat{R}_{01}.\hat{R}_{ij})$
0	0	0	0	
1	$-a_0/2$	$-a_0/2$	$a_0/2$	1
2	$-a_0/2$	$a_0/2$	$a_0/2$	1/3
3	$a_0/2$	$-a_0/2$	$a_0/2$	1/3
4	$a_0/2$	$a_0/2$	$-a_0/2$	−1/3
5	$a_0/2$	$a_0/2$	$-a_0/2$	
6	$a_0/2$	$-a_0/2$	$-a_0/2$	−1/3
7	$-a_0/2$	$a_0/2$	$-a_0/2$	−1/3
8	$-a_0/2$	$-a_0/2$	$a_0/2$	1/3

Table 1. Coordinations of 8 neighbors of a bcc crystal with a_0 as lattice constant surrounding the backscatterer at (0,0,0) and the values of $(\hat{R}_{01}.\hat{R}_{ij})$.

Using these equations we got Einstein frequency ω_E and Einstein temperature θ_E

$$\omega_E = \left[\frac{D\alpha^2}{\mu}\left(\frac{11}{3} - \frac{15}{2}\alpha a\right)\right]^{1/2}; \quad \theta_E = \frac{\hbar}{k_B}\left[\frac{D\alpha^2}{\mu}\left(\frac{11}{3} - \frac{15}{2}\alpha a\right)\right]^{1/2}, \tag{8}$$

where k_B is Boltzmann's constant. The cubic anharmonicity parameter k_3 is included in all Eqs.(6-8). Now we use first- order thermodynamic perturbation theory [8,9] to derive the expressions for the cumulants and thermal expansion coefficient. The atom 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.,

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

and use the harmonic oscillator states $\mid n >$ as eigenstates with eigenvalues $E_n = n\hbar\omega_E$ (ignoring the zero point energy for convenience).

Using the derivation procedure as for the case of fcc crystals [6] we obtain the first cumulant or net-thermal expansion

$$\sigma^{(1)} = a = \frac{135}{968}\frac{\hbar\omega_E}{D\alpha}\frac{1+z}{1-z} = \frac{45}{44}\alpha\sigma^2, \tag{10}$$

the second cumulant or Debye-Waller factor (DWF):

$$\sigma^{(2)} = \frac{3}{22}\frac{\hbar\omega_E}{D\alpha^2}\frac{1+z}{1-z}, \tag{11}$$

the third cumulant:

$$\sigma^{(3)} = \frac{135}{10648}\frac{(\hbar\omega_E)^2}{D^2\alpha^3}\frac{1+10z+z^2}{(1-z)^2}, \tag{12}$$

and the thermal expansion coefficient:

$$\alpha_T = \frac{135}{484}\frac{k_B}{D\alpha r}\frac{z(lnz)^2}{(1-z)^2}, \tag{13}$$

as well as the relation:

$$\frac{\alpha_T r T \sigma^2}{\sigma^{(3)}} = \frac{3z(1+z)ln(1/z)}{(1-z)(1+10z+z^2)}. \tag{14}$$

In all the above formulas r is the radius of the first shell and the temperature variable $z = e^{-\theta_E/T}$ is determined by θ_E .The values of $\sigma^{(1)}, \sigma^2, \sigma^{(3)}, \alpha_T$, in Eqs.(10-13) are dependent on the temperature T.

We use the approaches:

$$lim_{T\to 0} z = 1 - \frac{\hbar\omega_E}{k_B T}; \quad lim_{T\to\infty} z = 0, \tag{15}$$

to get high-temperature limit, where the classical approximation is valid, and low temperature limit, where the quantum theory must be used. The above formulas (10-14) in these limits are presented in table 2

Values	T → 0	T → ∞
$\sigma^{(1)}$	$135\hbar\omega_E(1+2z)/968D\alpha$	$135k_BT/484D\alpha$
σ^2	$3\hbar\omega_E(1+2z)/22D\alpha^2$	$3k_BT/11D\alpha^2$
$\sigma^{(3)}$	$135(\hbar\omega_E)^2(1+12z)/10648D^2\alpha^3$	$405(k_BT)^2/2662D^2\alpha^3$
α_T	$135k_Bz(\ln z)^2(1+2z)/484D\alpha r$	$135k_B/484D\alpha r$
$\alpha_T rT\sigma^2/\sigma^{(3)}$	$3z\ln(1/z)$	$1/2$

Table 2. Expression of $\sigma^{(1)}, \sigma^2, \sigma^{(3)}, \alpha_T$ and their relation in low-temperature ($T \to 0$) and high-temperature ($T \to \infty$) limits.

Note that the results for bcc crystals presented above are different from those for fcc [6] not only in spring constant k_{eff}, cubic anharmonic parameter k_3, anharmonic perturbation potential δU_E, Einstein frequency ω_E and Einstein temperature θ_E presented in Eqs.(6-8), but also in the temperature variable z. All they lead to the difference in the thermodynamic parameters presented in Eqs.(10-14). Nevertheless, their form of temperature dependence is similar, so that we got the same form of the expression for the relation $\alpha_T r T\sigma^2/\sigma^{(3)}$ which approaches the classical value [2] of 1/2 at high temperatures as the conclusion by classical method and experiment [2,10].

III. NUMERICAL RESULTS AND DISCUSSION

Now we apply the formulas derived in the previous section to numerical calculation for bcc crystals Mo and W. The parameters D and α of the Morse potential were taken from Ref.11; they were obtained using experimental values for the energy of sublimation, the compressibility, and the lattice constant.

In table 3 we present the values of k_{eff} , ω_E, and θ_E calculated by present procedure for Mo and W.

Mo: Molybdenium – Z = 96 A z = 42 e, D = 6,82

Sample	Bond	k_{eff}(N/m)	ω_E ($\times 10^{13}$ Hz)	θ_E (K)
Mo	Mo-Mo	107.289	3.659	280
W	W-W	115.960	2.748	210

$D_W = 8,9$

~~$\theta_E = 420$ K~~

Fe – z = 26 e

(Iron $Z = 56$

$D = 4,82$ eV

Table 3. Calculated values of k_{eff}, ω_E and θ_E of Mo and W.

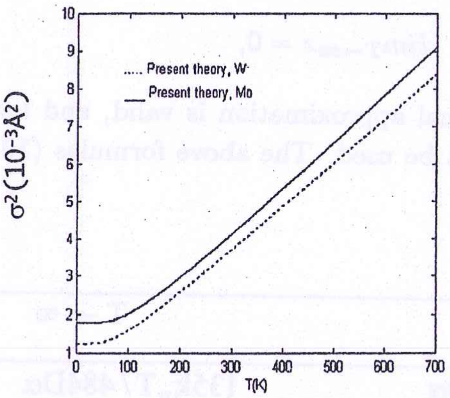

Figure 1. Temperature dependence of our calculated second cumulant σ^2 or Debye-Waller factor for Mo and W. They contain zero-point energy contributions at low temperatures and are linear proportional to T at high temperatures.

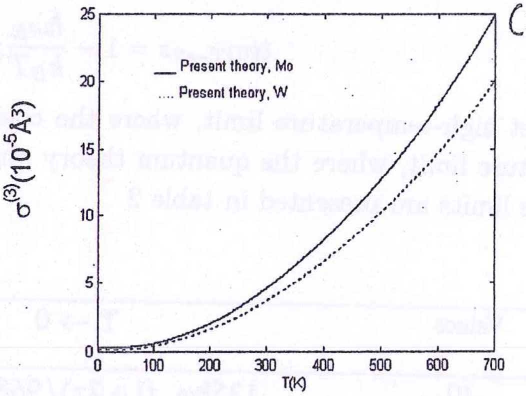

Figure 2. Temperature dependence of our calculated third cumulant $\sigma^{(3)}$ for Mo and W . They contain zero-point energy contributions at low temperatures and are proportional to T^2 at high temperatures

Figure 1 shows the temperature dependence of our calculated second cumulant σ^2 or DWF of Mo and W. They contain the zero point energy contribution and are linear promotional to the temperature T at high temperatures as the conclusion of classical theory and experiment [2,10]. Figure 2 illustrates the temperature dependence of our calculated third cumulant $\sigma^{(3)}$ of Mo and W. They contain zero point energy contributions and are proportional to T^2 at high temperatures as concluded by classical theory and experiment [2,10]. The third cumulant is the result of anharmonic effects, that is why it is very small and can be neglected at low temperatures. The temperature dependence of our calculated thermal expansion coefficient α_T of Mo and W is presented in Figure 3. They have the from of specific heat, thus reflecting the fundamental of solid state theory, that the thermal expansion is the result of anharmonic effects and is proportional to specific heat [9]. The relation $\alpha_T r T\sigma^2/\sigma^{(3)}$ determines the temperature, above which this relation approaches the classical expression of 1/2 (Figure 4), that means, the classical limit is valid [7]. In our case this temperature is about correlated Einstein temperature $\theta_E = 280K$ for Mo and $\theta_E = 210K$ for W. Below this temperature the relation is strong temperature dependent and quantum theory must be used.

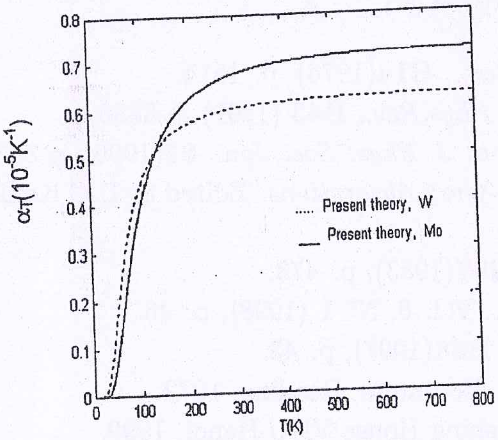

Figure 3. Temperature dependence of our calculated thermal expansion coefficient α_T for Mo and W. They have the form of specific heat and approach constant values at high temperatures.

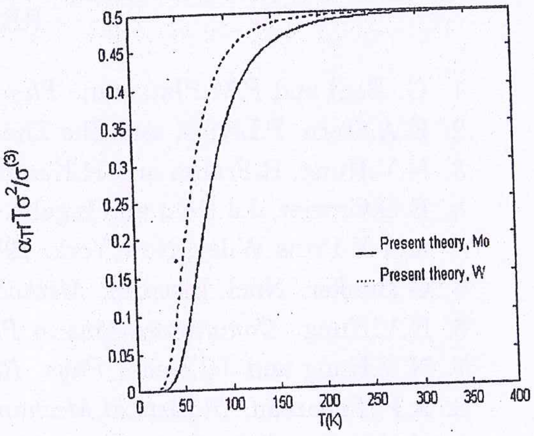

Figure 4. Temperature dependence of our calculated relation $\alpha_T r T\sigma^2/\sigma^{(3)}$ for Mo and W. They approach the classical value ½ at high temperatures.

IV. CONCLUSION

In this work a new quantum statistical procedure for calculation of thermodynamic parameters of bcc crystals in XAFS - theory using anharmonic-correlated Einstein model with Morse pair potential has been presented. The results are valid for all from low to high temperatures.

Effective spring constant and anharmonic perturbation potential contain the cubic anharmonicity parameter which influence on Einstein frequency and Einstein temperature leading to influence on the thermodynamic parameters such as cumulants and thermal expansion coefficient.

The above results express thermodynamic properties of bcc crystals. The first cumulant or net thermal expansion describing asymmetry of interacting potential, third cumulant, and thermal expansion coefficient are anharmonic effects, the second cumulant or DWF describes un clastic effect of photoelectron. They are different from those of fcc crystals [6] due to the difference in k_{eff} and δU_E, but they have the same qualities that $\sigma^{(1)}, \sigma^2, \sigma^{(3)}$ contain zero point energy contributions at low temperatures and at high temperatures $\sigma^2 \sim T, \sigma^{(3)} \sim T^2, \alpha_T r T\sigma^2/\sigma^{(3)} \to 1/2$ as the conclusion of classical theory and experiment [2,10], and α_T has the from of specific heat, thus reflecting the fundamental of solid state theory.

Numerical results presented in table 2, as well as, Figures 1-4 illustrate the derived formulas for the case of Mo and W. They can be used for evaluation of experimental results when the measured results are available.

With the help of the above thermodynamic parameters we can get correct structural information from XAFS of bcc crystals at any temperatures [2-6,10,12].

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TÍNH CÁC THAM SỐ NHIỆT ĐỘNG CỦA CÁC TINH THỂ CẤU TRÚC BCC TRONG LÝ THUYẾT XAFS

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Bài này trình bày một phương pháp thống kê lượng tử mới để tính các tham số nhiệt động của các tinh thể cấu trúc lập phương tâm khối (bcc) trong lýthuyết về cấu trúc tinh tế của hấp thụ tia X (XAFS) với sử dụng mô hình Einstein tương quan phi điều hòa. Công trình đã dẫn ra các biểu thức đối với hệ số đàn hồi, tần số Einstein, nhiệt độ Einstein, cumulant bậc 3 và hệ số dãn nở nhiệt. Các công thức chứa các đóng góp phi điều hòa và lý thuyết được thỏa mãn với mọi nhiệt độ. Các tính số đã được thực hiện *đối với* Mo và W. *Các kết quả thể hiện các tính chất nhiệt động của các hệ trên.*