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Study of Thermodynamic Properties of Cubic Systems in XAFS

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Thermodynamic properties of cubic systems in XAFS have been studied using anharmonic-correlated Einstein model. The expressions were derived for spring constant, Einstein frequency, correlated Einstein temperature, thermal expansion, and cumulants. Numerical calculations were carried out for Ag, Cu, and Fe. The results for Cu and correlated Einstein temperature of Ag agree well with experimental values, and they are compared with those, calculated by other theories, showing the advantage and simplicity of present procedure.

1. Introduction

For correction of uncertainties in structural information taken from Fourier transform magnitude of X-ray Absorption Fine Structure (XAFS) caused by thermodynamic effects [1-8] the XAFS function includes the cumulants $\sigma^{(n)}$ [2]. Using anharmonic-correlated Einstein model [8] in this work we derive the expressions for spring constant, Einstein frequency, correlated Einstein temperature, first cumulant or net thermal expansion describing an asymmetry of atomic interaction potential, second cumulant or Debye-Waller factor (DWF), third cumulant and thermal expansion coefficient of cubic systems. The derivation is based on quantum statistical procedure, and the theory is valid for all temperatures. Numerical calculations have been carried out for fcc crystals Ag, Cu, and bcc crystal Fe. The results agree well with experimental values [1,4,10,11] and compared with those calculated by other procedures [3,6,12].

2. Theoretical formulation

According to quasiharmonic approximation the Hamiltonian of the system is written as

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

$$x = r - r_0; \quad y = x - a; \quad a = \langle x \rangle; \quad \langle y \rangle = 0. \tag{2}$$

Here r is the bond length of two atoms; r_0 is its equilibrium value; μ is reduced mass of absorber and backscatterer; δU_E is anharmonic perturbation; and the brackets < > denote thermal average.

In anharmonic-correlated Einstein model the interaction between absorber and backscatterer is via an effective anharmonic Einstein potential

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

which includes anharmonicity parameter k_3 and effective spring constant k_{eff}. The contributions of a small cluster are taken by the sum i which is over absorber (i=0) and backscatterer (i=1) and by the sum j which over all their near neighbors excluding the

absorber and backscatterer themselves. The latter [8] contributions are described by the term U(x), and $\hat{R}$ is unit bond length vector.

Using the Morse-pair potential as interacting potential between each pair of atoms and Eqs.(1-3) we derived

$$k_{eff} = c_1(D\alpha^2 + c_2 a k_3) = \mu\omega_E^2; \quad k_3 = -5D\alpha^3/4 \quad ; \tag{4}$$

$$\delta U_E(y) = (c_1 D\alpha^2 a + 3k_3 a^2)y + k_3 y^3 \approx c_1 D\alpha^2 a y + k_3 y^3 \quad ,$$

where D, α are the Morse potential parameters, ω_E is Einstein frequency, and

$$c_1 = \begin{cases} 5, & \text{fcc} \\ 11/3, & \text{bcc} \end{cases} ; \quad c_2 = \begin{cases} 6/5, & \text{fcc} \\ 18/11, & \text{bcc} \end{cases} \tag{5}$$

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.,

$$y = \sigma^0(\hat{a} + \hat{a}^+) \quad ; \qquad \sigma^0 = (\hbar/2\mu\omega_E)^{1/2} \tag{6}$$

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

As the results of applying the first-oder thermodynamic perturbation theory [6,8,14] we get the second cumulant or DWF

$$\sigma^2 = \sigma_0^2 \frac{1+z}{1-z} \quad ; \quad \sigma_0^2 = \frac{\hbar\omega_E}{2c_1 D\alpha^2} \, . \tag{7}$$

By describing the temperature variable z in terms of σ^2

$$z = e^{-\theta_E/T} = \frac{\sigma^2 - \sigma_0^2}{\sigma^2 + \sigma_0^2} \quad ; \qquad \theta_E = \frac{\hbar}{k_B}\left[\frac{c_1}{\mu}(D\alpha^2 + c_2 a k_3)\right]^{1/2} , \tag{8}$$

where k_B is Boltzmann's constant, and θ_E is correlated Einstein temperature, we obtain the first cumulant or net thermal expansion

$$\sigma^{(1)} = a = \frac{\sigma_0^{(1)}}{\sigma_0^2}\sigma^2; \quad \sigma_0^{(1)} = \frac{15\alpha}{4c_1}\sigma_0^2 \, , \tag{9}$$

the third cumulant

$$\sigma^{(3)} = \sigma_0^{(3)} \frac{3(\sigma^2)^2 - 2(\sigma_0^2)^2}{(\sigma_0^2)^2}; \quad \sigma_0^{(3)} = \frac{5\alpha}{2c_1}(\sigma_0^2)^2 \quad , \tag{10}$$

the thermal expansion coefficient

$$\alpha_T = \alpha_T^0 \left(\frac{c_1 D\alpha^2\sigma^2}{k_B T}\right)^2 \left[1 - \left(\frac{\sigma_0^2}{\sigma^2}\right)^2\right] \quad ; \quad \alpha_T^0 = \frac{15k_B}{4c_1^2 D\alpha r} \quad ; \quad \lim_{T\to\infty} \alpha_T = \alpha_T^0 , \tag{11}$$

and their relation

$$\frac{\sigma^{(1)}\sigma^2}{\sigma^{(3)}} = \frac{1}{2 - (4/3)(\sigma_0^2/\sigma^2)^2} \quad ; \quad \lim_{T\to\infty} \frac{\sigma^{(1)}\sigma^2}{\sigma^{(3)}} = \frac{1}{2} \, . \tag{12}$$

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

Table I: Our calculated values of k_{eff}, ω_E, θ_E, and measured results $\theta_E^{exp.}$ [11]

Sample	Bond	k_{eff}(N/m)	ω_E ($\times 10^{13}$ Hz)	θ_E(K)	$\theta_E^{Expt.}$(K)
Ag	Ag-Ag	49.891	2.353	176	167(2)
Cu	Cu-Cu	50.748	3.092	236	232(5)
Fe	Fe-Fe	47.275	3.184	243	---

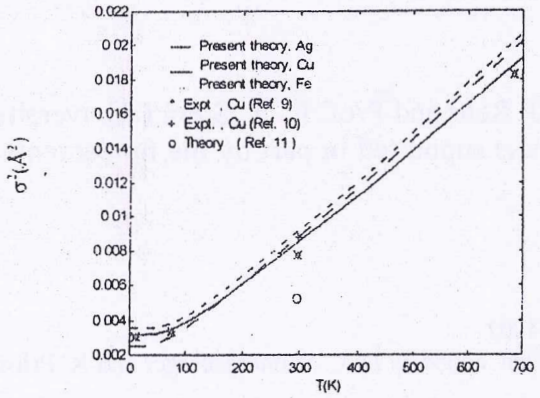

Fig.1: Temperature dependence of our calculated DWF for Ag, Cu, Fe, in comparison with experiment [1,10] and with another theory [12].

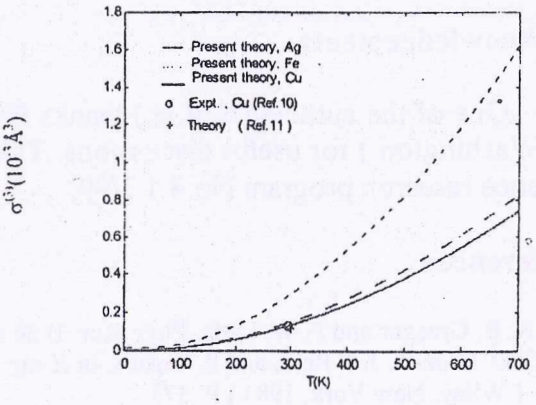

Fig.2: Temperature dependence of our calculated third cumulant $\sigma^{(3)}$ for Ag, Cu, Fe, in comparison with experiment [10] and with another theory

3. Numerical results and discussion

The expressions (4,5,7-12) are applied to numerical calculations for Ag, Cu, and Fe, where D, α are taken from Ref.13. In Table I we present our calculated values of k_{eff}, ω_E, θ_E for Ag, Cu, Fe, and θ_E^{exp} as measured results of θ_E [11]. They show a good agreement of our calculated values θ_E with those from the experiment. Fig.1 illustrates the temperature dependence of our calculated second cumulant or DWF σ^2 for Ag, Cu, Fe in comparison with the experimental values [1,10] and another theoretical result [12] at 295K, calculated by full lattice dynamical method for Cu. The good agreement at low temperature and small differences at high temperature between our results and the measured values are reasonable. Fig. 2 shows the temperature dependence of our calculated third cumulant $\sigma^{(3)}$ for Ag, Cu, Fe, in comparison with the measured [10] and theoretical [12] values. Our results of Cu agree well with the experimental ones. The temperature dependence of our calculated thermal expansion coefficient α_T for Ag, Cu, Fe, and comparison with the measured values [9] for

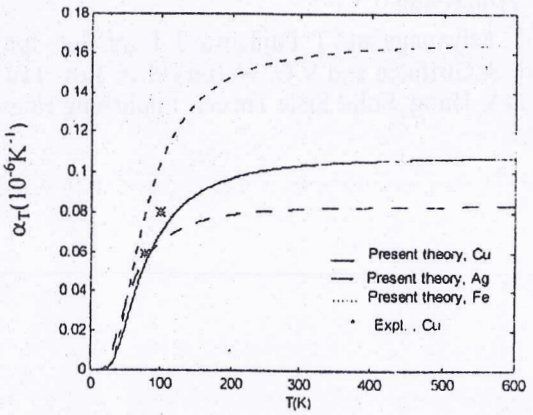

Fig. 3: Temperature dependence of our calculated thermal expansion coefficient α_T for Ag, Cu, Fe, in comparison with the experiment [9] for Cu

Cu are shown in Fig.3. Our results at 77K and 100K are close to the experimental values. Moreover, our α_T have the form of specific heat C_v, reflecting the fundamental of solid state theory [14], that $\alpha_T \sim C_v$. Our σ^2 is proportional to T and $\sigma^{(3)}$ to T^2 at high temperature as concluded by other theories [3,6,12], but the anharmonic single-particle potential model [3] does not give an accurate description of the situation because it ignores correlated motion; the single-bond model [6] has limitations because spring constant $k_s = 2D\alpha^2 = 20.3$ N/m is much smaller than the value 27.9 N/m to approximate the observed phonon spectra; and Figs. 1, 2 show that our results are more close to the experiment than those from Ref. 12 calculated intensively by the full lattice dynamical method [12]. Note that the approach of relation $\sigma^{(1)}\ \sigma^2/\sigma^{(3)}$ to 1/2 reflects the conclusion of classical method and experiment [4,5]; and our description of all the above thermodynamic parameters in term σ^2 is convenient, since determination of σ^2 allows one to predict the other values, thus reducing the numerical calculations and measurements.

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