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Hà Nội, 25 - 11 - 2000

Mục lục

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Anhamonic correlated Einstein model cumulants and XAFS spectra of fcc crystals

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A new analytical procedure for calculation and analysis of cumulants and x-ray Absorption Fine Structure (XAFS) including anharmonic effects of fcc crystals has been formulated. The theory is derived based on anharmonic correlated Einstein model and Morse potential as atomic pair potential. The obtained expressions approach to classical theory at high temperature and contain quantum effects at low temperature. Numerical calculations have been carried out for fcc crystals Cu and W. They show good agreement with experimental resutls.

1. Introduction

It is known that the XAFS spectra and their Fourier transform magnitude provide information on structure of the substances, and therefore, XAFS becomes an powerfull structural analysis technique. At low temperature the harmonic calculating procedures work well [1]. But as the temperature increases the XAFS structural information becomes uncertain [2,3]. The famous treatment of these uncertainties is based on the cumulant expansion approach [4,5], in which the XAFS function is described by

$$\chi(k) = F(k)\,\mathrm{Im}\left\{e^{i\Phi(k)}\exp\left[2ikR_0 + \sum_n \frac{(2ik)^n}{n!}\sigma^{(n)}\right]\right\} \qquad (1)$$

where k, Φ, R_0, F(k) are the wave number, phase change, atomic bond length at equilibrium, real amplitude, respectively, and $\sigma^{(n)}$ are the cumulants.

Main applications of this approach are developed to interpret the measured XAFS spectra at high temperature [6]. Some progresses have been made to approximate the cumulants [6,7,8], but each procedure has a limitation.

In this work using the anharmonic correlated Einstein model [9] and treating some limitations of our previous procedure [3,10], which contains some imperical parameters, to calculate cumulants and to derive the analytical expressions of anharmonic Debye-Waller factor and XAFS spectra of fcc crystals including anharmonic contributions at high temperature. Numerical resutls are compared with experimental data. Their good agreement shows the advantages of present procedure.

2. Theory

From Eq.(1) the XAFS function contains the exponential factor in the form

$$\chi(k) \sim e^{w(k)}, \quad w(k) = 2ik\sigma^{(1)} - 2k^2\sigma^{(2)} - \frac{4ik\sigma^{(2)}}{R}\left(1+\frac{R}{\lambda}\right) - \frac{4}{3}ik^3\sigma^{(3)} + \ldots, \qquad (2)$$

where R is the radius of atomic shell , λ is mean-free path of photoelectron, $\sigma^{(2)}$ is second cumulant or Debye-Waller factor σ^2 . The 1st cumulant $\sigma^{(1)}$ and 3rd cumulant

$\sigma^{(3)}$ are anharmonic parameters, which describe net thermal expansion and XAFS phase change due to anharmonicity, respectively.

We consider the correlated anharmonic vibration between absorber and backscatter with taking into account the contribution of their immediate neighbors. The expressions have been derived based on quantum statistical theory so that the anharmonicity is included by phonon interaction with the mechanism of creation and annihilation operators and high order of atomic interaction potential. The calculations have been carried out based on quasi-harmonic approximation, in which the Hamiltonian of the system is written as a harmonic term with respect to the equilibrium position at a given temperature, plus an anharmonic perturbation. Physical parameters are derived by an averaging procedure, using the density matrix. As the results we obtain the effective spring constant

$$k_{eff} = 5D\alpha^2\left(1-\frac{3}{2}a\alpha\right), \qquad a = < R - R_0 >, \tag{3}$$

correlated Einstein frequency ω_E and Einstein temperature θ_E

$$\omega_E = \left[\frac{5}{\mu}D\alpha^2\left(1-\frac{3}{2}a\alpha\right)\right], \quad \theta_E = \frac{\hbar}{k_B}\left[\frac{5}{\mu}D\alpha^2\left(1-\frac{3}{2}a\alpha\right)\right]^{1/2}, \tag{4}$$

where D, α are the Morse potential parameters, μ is reduced mass of the absorbing and backscattering atoms, and k_B is Boltzmann's constant.

The cumulants are given by

$$\sigma^{(1)} = a = \frac{3\hbar\omega_E}{40D\alpha}\frac{1+e^{-\theta_E/T}}{1-e^{-\theta_E/T}}, \tag{5}$$

$$\sigma^{2} = \frac{\hbar\omega_E}{10D\alpha^2}\frac{1+e^{-\theta_E/T}}{1-e^{-\theta_E/T}}, \tag{6}$$

$$\sigma^{(3)} = \frac{(\hbar\omega_E)^2}{200D^2\alpha^3}\frac{1+10e^{-\theta_E/T}+e^{-2\theta_E/T}}{1-e^{-\theta_E/T}}. \tag{7}$$

From Eq.(5) we obtain the thermal expansion coefficient

$$\alpha_T = \frac{3k_B\theta_E^2 e^{-\theta_E/T}}{20D\alpha R[T(1-e^{-\theta_E/T})]^2}. \tag{8}$$

For the K-edge the XAFS function (1) is given by

$$\chi(k) = \sum_j \frac{N_j S_0^2}{kR_j} F_j(k) e^{-2R_j/\lambda(k)} e^{-2k^2(\sigma^2+\sigma_A^2)} \sin\left[2kR_j + \delta(k) + \Phi_A^j(k)\right], \tag{9}$$

where S_0^2 is the square of many body overlap term, N is the atom number on a shell, F is the backscattering amplitude, and the sum is over all atomic shells.

The anharmonic contribution σ_A^2 to Debye-Waller factor (DWF) σ^2 is taken into consideration by an anharmonic factor [3, 11]. Based on the anharmonic correlated Einstein model this factor has the form

$$\beta(R,T) = \frac{3k_B}{8D}\left(\frac{3}{4}-\frac{\hbar\omega_E}{10D\alpha^2\sigma^2}\right)\left[(2T-\theta_E)+\frac{3k_B}{16D\alpha R}(2T-\theta_E)^2+\left(\frac{3k_B}{16D\alpha R}\right)^2(2T-\theta_E)^3\right], \tag{10}$$

and the anharmonic contribution to XAFS oscillation phase is given by

$$\Phi_A(k,T) = 2k\left[\sigma^{(1)} - 2\Delta\sigma^2\left(\frac{1}{R} - \frac{1}{\lambda}\right)\right] - \frac{4}{3}\sigma^{(3)}(T)k^3 \qquad (11)$$

where σ^2 is calculated by Eq.(6), $\sigma^{(1)}$ by Eq.(5), $\sigma^{(3)}$ by Eq.(7), ω_E and θ_E by Eq.(4) and $\sigma_A^2 = \beta\sigma^2$.

3. Numerical resutls

Now we apply the above theory to numerical calculations for the fcc crystals Cu and W. The parameters D and α were taken from [12]. The resutls for k_{eff}, ω_E, and θ_E in comparison with experimental value $\theta_E^{expt.}$ [13] are given in table I.

Table I: The values of k_{eff}, ω_E, and θ_E compared $\theta_E^{expt.}$ [13]

Crystal	Bond	k_{eff}(N/m)	ω_E(x10^{13}Hz)	θ_E(K)	$\theta_E^{expt.}$
Cu	Cu-Cu	50.748	3.092	236	232(5)
W	W-W	115.959	2.748	210	.....

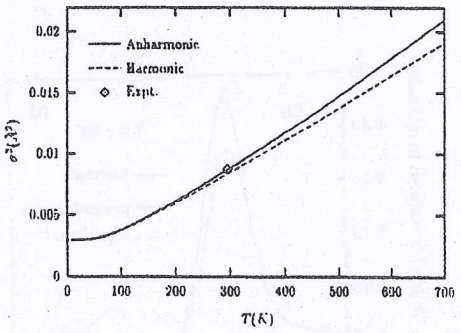

Fig. 1: *Harmonic and anharmonic Debye-Waller factor of Cu*

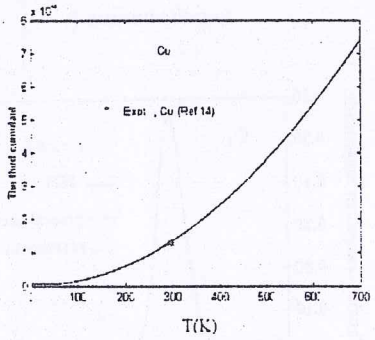

Fig.2: *3rd cumulant of Cu compared with experiment*

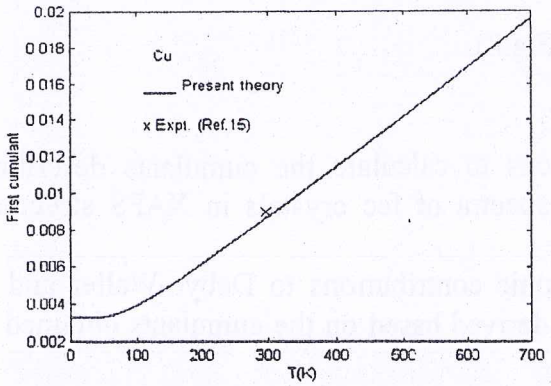

Fig. 3: *First cumulant of Cu*

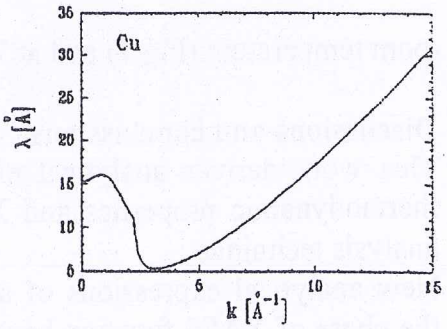

Fig.4: *Mean-free path of Cu*

Fig.1 shows the temperature dependence of harmonic and anharmonic Debye-Waller factor of Cu in comparison with experimental value [14]. Fig. 2 shows the temperature dependence of the third cumulant of Cu in comparison with experimental resutls [14]. Fig. 3 shows the temperature dependence of the first cumulant of Cu in

comparison with experimental value [16]. Fig. 4 shows the mean-free path of Cu. Fig. 5 shows the anharmonic contribution to XAFS oscillation phase of Cu for different temperatures. Fig. 6 shows the XAFS function of Cu at 700K calculated by harmonic procedure FEFF [1] and by present anharmonic theory. Fourier transform magnitudes of the XAFS function of Cu calculated by present anharmonic theory are compared with those calculated by harmonic procedure [1] and with experimental results [15] at

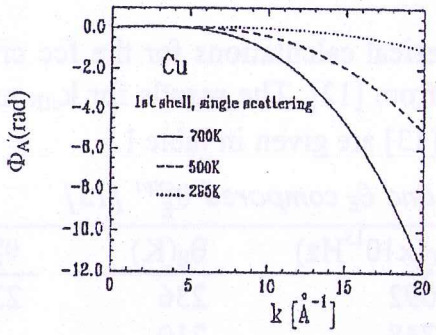

Fig. 5: *XAFS phase change due to anharmonicity*

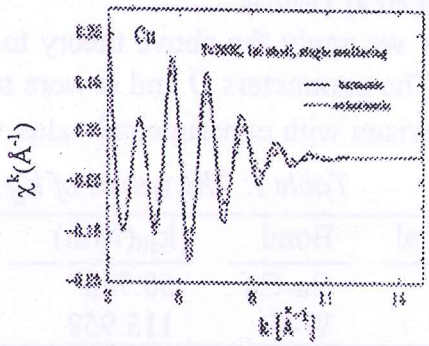

Fig.6: *Harmonic and anharmonic XAFS*

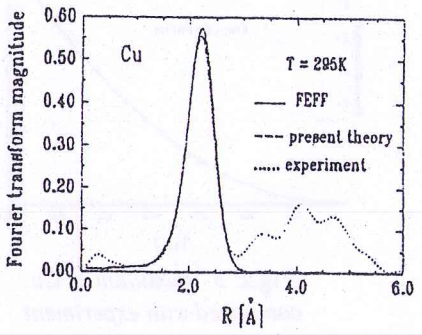

Fig. 7: *Fourier transform magnitude at 295K*

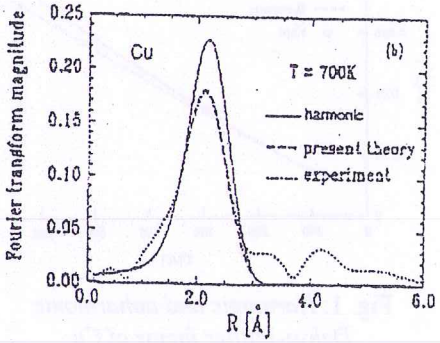

Fig. 8: *Fourier transform magnitude at 700K*

at room temperature (Fig.7) and at 700K (Fig.8).

4. Discussions and conclussions

- This work derives analytical expressions to calculate the cumulants describing thermodynamic properties and XAFS spectra of fcc crystals in XAFS structural analysis technique.
- New analytical expressions of anharmonic contributions to Debye-Waller and to the phase of XAFS function have been derived based on the cumulants obtained in present procedure.
- The theory is valid at low temperature where the harmonic procedure works well and at high temperature where anharmonic contribution must be included. The expressions contain quantum effects such as zero point contribution at low temperature.

- The good agreement of our calculated resutls with experimental values illustrated in the above figures and table denote some advantages of present procedure in XAFS theory.

Acknowledgment

One of the authors (N.V.H.) thanks Prof. J. J. Rehr for useful comments and Dr. L. Tröger for providing the data of high-temperature XAFS of Cu. This work is supported in part by the VNU-Hanoi research program QT-00-06 and the fundamental science research program No. 410 801.

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