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ANHARMONIC CONTRIBUTIONS TO DEBYE-WALLER FACTOR AND XAFS SPECTRA OF FCC CRYSTALS

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Abstract. *New analytical expressions for anharmonic factor and for phase change of X-ray Absorption Fine Structure (XAFS) spectra due to anharmonic effects have been derived. They contribute to getting anharmonic Debye-Waller factor and anharmonic XAFS spectra at high temperature which are transformed into those of harmonic model at low temperature. The cumulants contained in our new formulas are calculated by anharmonic correlated Einstein model, and the theory is applied to fcc crystals. Numerical calculations have been carried out for Cu, Ag, Pb, and the results agree well with experimental data.*

I. INTRODUCTION

It is known that the XAFS spectra and their Fourier transform magnitudes provide informations on the atomic number and the shell radius of the substances, respectively. Therefore, XAFS becomes an powerful structural analysis technique. At low temperature the harmonic procedures for XAFS calculation work well [1]. But as the temperature increases the structural information from the XAFS becomes uncertain, i.e., they are different at different high temperatures [2,3]. The famous treatment of these uncertainties is based on the cumulant expansion approach [4,5], according to which the XAFS oscillation function is described by

$$\chi(k) = F(k)\, Im\left\{ e^{i\Phi(k)} exp\left[2ikr_0 + \sum_n \frac{(2ik)^n}{n!}\sigma^{(n)} \right] \right\}, \qquad (1)$$

where $k, \Phi, F(k)$ are the wave number, net phase shift, real scattering amplitude, repectively, and $\sigma^{(n)}$ $(n = 1, 2, 3,)$ are the cumulants, which appear due to the thermal averaging of the function in which r is the spontantaneous bond length of the two neighboring atoms and r_0 is its value at the equilibrium.

Main applications of this approach have been developed to fit the high-temperature XAFS and to interpret the anharmonic effects in these spectra [2, 4, 6, 7]. Some progresses have been made to approximate the cumulants [7-9], but each of these procedures has a limitation, which was discussed elsewhere [10]. An anharmonic factor has been introduced [3,11,12] to take into account the anharmonic contributions to Debye-Waller factor and to the XAFS spectra, but this factor still contains a fitting parameter, and the cumulants were obtained by an extrapolation procedure from the experimental data.

The purpose of this work is to derive a new anharmonic factor, which overcomes the limitations of the previous one, and a new formula expressing the phase change of XAFS spectra due to the anharmonicity. The cumulants contained in these formulas are calculated using the anharmonic correlated Einstein model [13]. Finally, we get the XAFS function which include anharmonic effects at high temperature and is transformed into the one of the harmonic model [1] at low temperature. Numerical calculations have been carried out for fcc crystals Cu, Ag, Pb. The results are compared with those measured in the experiment [14,15]. They show a good agreement between theoretical and experimental results.

II. THEORY

Developing further Eq.(1) we obtain the XAFS oscillation function which contains an exponential factor in the form

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

where $R = \langle r \rangle, \lambda, \sigma^{(1)}, \sigma^{(2)} = \sigma^2$, and $\sigma^{(3)}$ are the thermally averaged radius of atomic shell, the mean-free path of photoelectron, the first cumulant or net thermal expansion, the second cumulant or Debye-Waller factor, and the third cumulant, respectively.

Using Eqs. (1,2) we derived the anharmonic XAFS function which is given by

$$\chi(k) = \sum_j \frac{S_0^2 N_j}{kR_j} F_j(k)\, e^{-\left(2k^2\sigma^2_{tot}+2R_j/\lambda\right)} \sin\left[2kR_j + \Phi_j + \Phi_A^j\right] \tag{3}$$

where S_0^2 and N_j are the many body overlap term and the atomic number of each shell, respectively, the other parameters have the same meanings as defined above, and the sum is over all the atomic shells. In this equation the total Debye-Waller factor $\sigma^2_{tot}(T)$ at temperature T consists of the harmonic contribution $\sigma^2_H(T)$ and the anharmonic one $\sigma^2_A(T)$ [7,11]

$$\sigma^2_{tot}(T) = \sigma^2_H(T) + \sigma^2_A(T) \tag{4}$$

and Φ_A denotes the phase change of XAFS spectra due to anharmonic contribution.

Our next step is the definition of $\sigma^2_A(T)$ and Φ_A. We can use an argument analogous to the one given by [16] for the change of Debye-Waller factor due to the temperature increasing to show that [7, 11]

$$\Delta\sigma^2 = \Delta\sigma^2_H\left[1 + 2\gamma_G\frac{\Delta V}{V}\right], \tag{5}$$

where γ_G is Grüneisen parameter and $\Delta V/V$ is the relative volume change due to thermal expansion. Considering that the temperature T increases from the initial point at $0K$ and taking into account Eq.(4), we generalize Eq.(5) to the form

$$\sigma_{tot}^2 = \sigma_H^2 + \sigma_A^2 = (1+\beta)\,\sigma_H^2 \tag{6}$$

The anharmonic effect is expected to be equivalent to a system having an asymmetric radial pair distribution function. To model the asymmetry we replaced the harmonic potential by a Morse potential [17]

$$U\left(x\right) = D\left(e^{-2\alpha x} - 2e^{-2x}\right) \tag{7}$$

where x is the deviation of instantaneous bond length between the two atoms from equilibrium, D is the dissociation energy and $1/\alpha$ corresponds to the width of the potential. The cumulants applied to this work have been calculated using the anharmonic correlated Einstein model [13], and they are given by

$$\sigma^{(1)} = a = \frac{3\hbar\varpi_E}{40D^2\alpha}\frac{1+e^{-2\theta_E/T}}{1-e^{-2\theta_E/T}} \tag{8}$$

$$\sigma^2 = \frac{\hbar\varpi_E}{40D\alpha^2}\frac{1+e^{-2\theta_E/T}}{1-e^{-2\theta_E/T}}, \tag{9}$$

$$\sigma^{(3)} = \frac{\left(\hbar\varpi_E\right)^2}{10D^2\alpha^3}\frac{1+10e^{-2\theta_E/T}+e^{-2\theta_E/T}}{\left(1-e^{-2\theta_E/T}\right)^2} \tag{10}$$

where the correlated Einstein frequency ϖ_E and the correlated Einstein temperature θ_E are as follows

$$\varpi_E = \left[\frac{5D\alpha^2}{\mu}\left(1-\frac{3}{2}a\alpha\right)\right]^{1/2}, \theta_E = \frac{\hbar}{k_B}\left[\frac{5D\alpha^2}{\mu}\left(1-\frac{3}{2}a\alpha\right)\right]^{1/2} \tag{11}$$

In these expressions M is the reduced mass of absorber and backscatterer, and k_B is the Boltzmann's constant.

Using the net thermal expansion a in Eq.(8) we calculated γ_G and $\Delta V/V$, and then, based on Eqs.(5,6) we derived a new anharmonic factor for a single bond R for temperature dependence

$$\beta\left(T\right) = \frac{9\eta k_BT}{16D}\left[1+\frac{3k_BT}{8D\alpha R}\left(1+\frac{3k_BT}{8D\alpha R}\right)\right], \tag{12}$$

$$\eta\left(T\right) = \frac{2(e^{-\theta_E/T}-e^{-\theta_E})}{\left(1-e^{-\theta_E}\right)\left(1+e^{-\theta_E/T}\right)}. \tag{13}$$

According to Eq.(6) the anharmonic contribution to Debye-Waller factor at a given temperature is determined by $\sigma_A^2 = \beta\sigma_H^2$, so that from Eq.(2) we derived a new expression for anharmonic contribution to the phase of XAFS spectra

$$\Phi_A(T) = 2k\left[\sigma^{(1)}(T) - 2\beta\sigma_H^2(T)\left(\frac{1}{R} - \frac{1}{\lambda}\right)\right] - \frac{4}{3}\sigma^{(3)}(T)\,k^3. \tag{14}$$

From this equation it is clear that ~~A~~ Φ_A will disappears at low temperature, where the anharmonic values $\sigma^{(1)}, \beta, \sigma^{(3)}$ are negligibly small.

III. NUMERICAL RESULTS AND DICUSSIONS

Now we apply the expressions derived in previous section to numerical calculations for some fcc crystals. The Morse potential parameters D and α were obtained using experimental values for the energy of sublimation, the compressibility, and the lattice constant [18]. Figure 1 shows the temperature dependence of our calculated anharmonic factor for Cu, Ag, Pb. In the case of Cu it has the value 2.7% at 300K and 8.4% at 700K which agree well with those obtained by an imperical procedure [13,19]. They are negligibly small at low temperature and increase strongly from the temperature which is higher than Einstein temperature where $\theta_E = 94K$ for Pb, $\theta_E = 176K$ for Ag and $\theta_E = 236K$ for Cu.

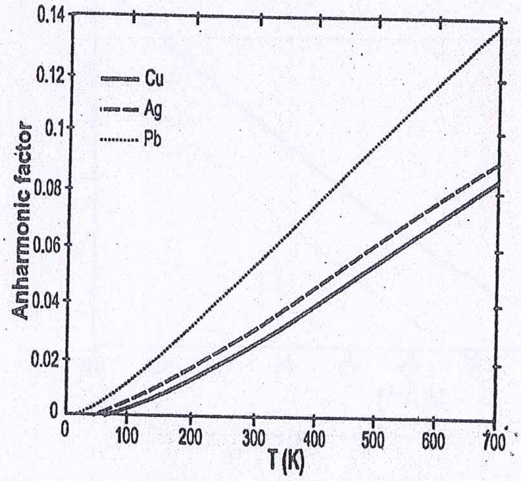

Fig. 1: Temperature dependence of anharmonic factor $\beta(T)$ for Cu, Ag, Pb.

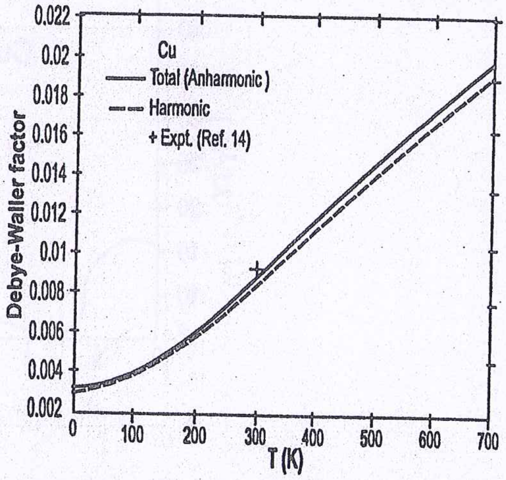

Fig. 2: Teperature dependence of total Debye-Waller factor σ_{tot}^2(anharmonic) compared with the harmonic one and with an experimental value [14].

Figure 2 illustrates the temperature dependence of our calculated total Debye-Waller factor σ_{tot}^2 (anharmonic) compared with the harmonic one σ_H^2 and with the experimental result. Our anharmonic value at 295K agree well with the measured data [14]. Figure 3 shows our calculated phase change of XAFS spectra of Cu due to anharmonicity. They are different at different temperatures 295K, 500K and 700K, and the differences are very strong at high temperature and high k-values. Figure 4 shows significant difference between the XAFS spectrum at 700K of Cu calculated by the harmonic FEFF code [1] and by our method including the anharmonic contribution.

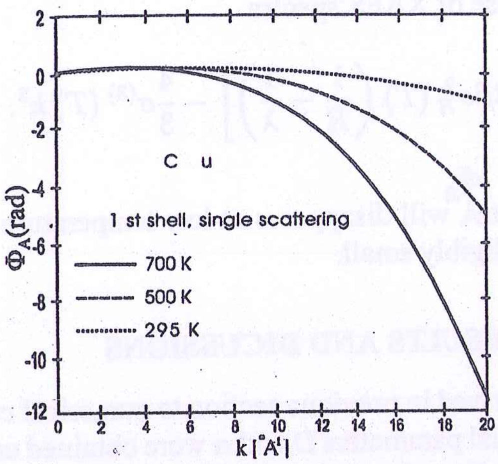

Fig. 3: Phase change Φ_A of XAFS spectra of Cu due to anharmonicity at 295K, 500K and 700K.

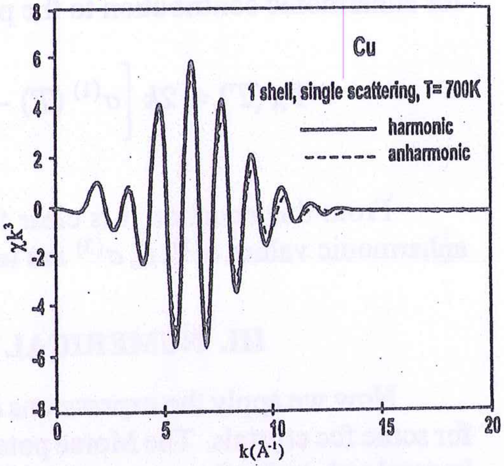

Fig. 4: Our calculated anharmonic XAFS spectra of Cu at 700K compare with those calculated by harmonic model.

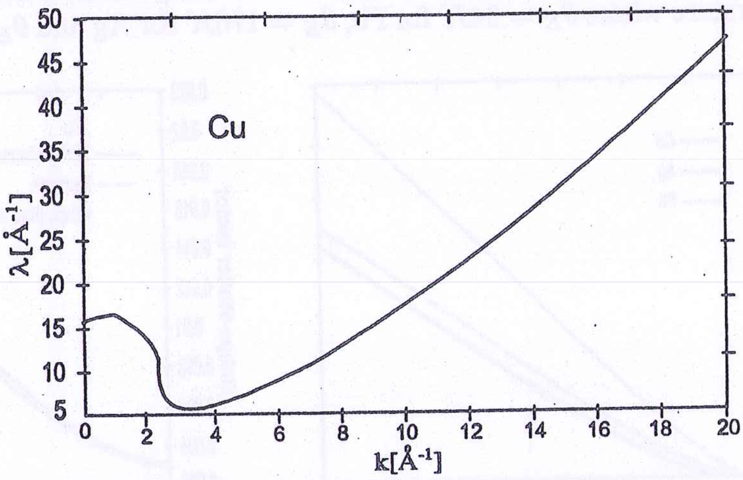

Fig. 5: The k-dependence of mean-free path $\lambda(k)$ of photoelectron of Cu

The anharmonic spectrum is shifted to the left and damped especially at high k-values in comparison with the harmonic one. Figure 5 illustrates the k-dependence of mean-free path of photoelectron, used in this work. Fourier transform magnitudes of XAFS spectra of Cu calculated by our anharmonic theory are compared with those calculated by harmonic FEFF [1] and with the experimental results [15] at 295K (Figure 6) and at 700K (Figure 7). Our calculated values including anharmonic contributions agree well with the measured ones. From these results our extracted uncertainties of structural information on the bond length due to anharmonicity are as follows: 0.009(± 0.001)Å at 295K and at 0.048(± 0.002)Å at 700K.

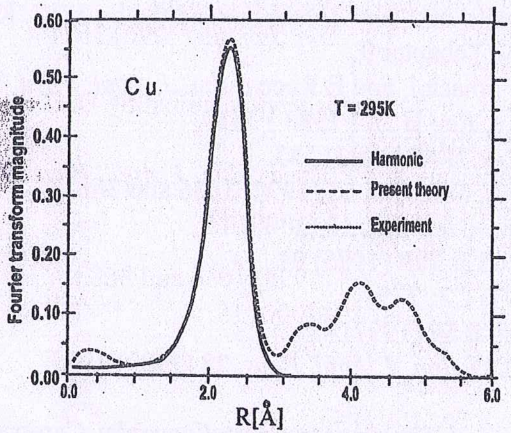

Fig. 6. Comparison of Fourier transform magnitude of our calculated anharmonic XAFS spectrum of Cu at 295K with those of harmonic model and of experiment [15].

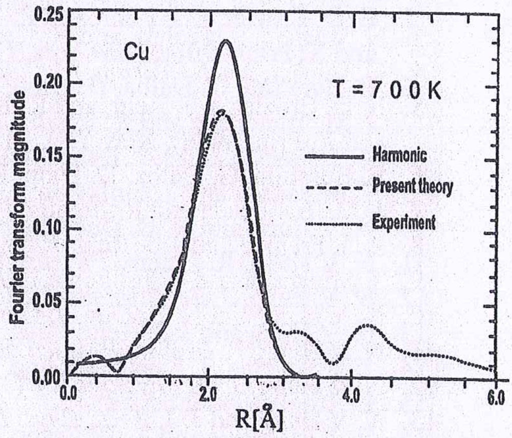

Fig. 7. Comparison of Fourier transform magnitude of our calculated anharmonic XAFS spectrum of Cu at 700K with those of harmonic model and of experiment [15].

IV. CONCLUSIONS

In this work the new analytical expressions for anharmonic factor and for phase change of XAFS spectra due to anharmonicity have been derived. The anharmonic contribution to Debye-Waller factor is obtained by a multiplification of the harmonic one with our anharmonic factor. The cumulants contained in our new derived expressions are calculated by anharmonic correlated Einstein model.

Our anharmonic factors are negligibly small at low temperature and increase strongly from the temperature higher than Einstein temperature, thus describing the temperature dependence of anharmonic effects in XAFS theory.

The good agreement of our calculated results for Cu with the experimental values denotes the advantages and efficiency of our new anharmonic procedure in XAFS data analysis theory. Our new derived expressions include anharmonic contributions at high temperature but they are automatically transformed in to those of harmonic model at low temperature.

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