Hội nghị KH Trường ĐH KH TN - ĐHQG Hà Nội
Lần thứ 3

Theory of Anharmonic Extended X-ray Absorption Fine Structure in Single-shell Model

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Abstract: *A new theory of the Extended X-ray Absorption Fine Structure (EXAFS) including anharmonic contributions has been developed based on the cumulant expansion and the single-shell model. Analytical expressions for the anharmonic contributions to the amplitude and to the phase of the EXAFS have been derived. The EXAFS function contains anharmonic effects at high temperature and approaches the one of the harmonic model at low temperature. Numerical results for Cu agree well with the experimental values. Peaks in the Fourier transform of our calculated anharmonic EXAFS and of the experimental one at 295K and 700K are shifted significantly compared to the harmonic model results.*

I. Introduction

The harmonic approximation in EXAFS calculations works very well[1] at low temperatures because the anharmonic contributions to the atomic thermal vibrations can be neglected. But at different high temperatures the EXAFS spectra provide apparently different structural information[2-17] due to the anharmonicity, and these effects need to be evaluated. The formalism for including anharmonic effects in EXAFS is often based on the cumulant expansion approach,[3,5] and the anharmonic effects in EXAFS have been valuated by the ratio methods.[3-9] Another way is the direct calculation and analysis of EXAFS and its parameters including anharmonic effects at any temperature.[10-12] Limitation of this procedure is that the expressions for the anharmonic factor and for the phase change of the EXAFS due to anharmonicity contain a fitting parameter, and the cumulants were obtained by an extrapolation procedure from the experimental data.

The purpose of this work is to develop an anharmonic theory of EXAFS by deriving analytical expressions for the anharmonic factor determining the anharmonic contributions to the amplitude and for the anharmonic contributions to the phase of the EXAFS, which overcome the limitations of the previous ones.[10-12] To calculate the cumulants contained in the derived expressions the quantum statistical approach with the anharmonic correlated Einstein model[13] has been used in which the parameters of the anharmonic effective potential are based on a Morse potential that characterizes the interaction between each pair of atoms, and the anharmonicity is described by the cumulants obtained by the calculation of the phonon-phonon interaction process.[13,14] Numerical results for Cu are discussed and compared to the experimental data.[17,19]

II. Formalism

According to the cumulant expansion approach the EXAFS oscillation function is given by

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

where $F(k)$ is the real atomic backscattering amplitude, Φ is the net phase shift, k and λ are the wave number and the mean free path of the photoelectron, respectively, and $\sigma^{(n)}$ (n = 1,2,3, ...) are the cumulants. They appear due to the thermal average of the function $\exp(i2kr)$ in

which the asymmetric terms are expanded in a Taylor series about $R = \langle r \rangle$ with r as the instantaneous bond length between absorbing and backscattering atoms and then are rewritten in terms of cumulants.

This EXAFS oscillation function including anharmonic effects contains the Debye-Waller factor $e^{-W(k,T)}$ accounting for the effects of the thermal vibrations of atoms. Based on the analysis[4,13] of cumulant expansion we obtain

$$W(k,T) = 2ik\sigma^{(1)}(T) - 2k^2\sigma^{(2)}(T) - 4ik\sigma^{(2)}(T)\left(\frac{1}{R} - \frac{1}{\lambda(k)}\right) - \frac{4}{3}ik^3\sigma^{(3)}(T) + \frac{2}{3}\sigma^{(4)}(T)k^4 + \cdots, \quad (2)$$

where $\sigma^{(1)}$ is the first cumulant or net thermal expansion; $\sigma^{(2)}$ is the second cumulant which is equal to the mean square relative displacement (MSRD) σ^2; $\sigma^{(3)}$ and $\sigma^{(4)}$ are the third and the fourth cumulants, respectively. The higher cumulants are not included due to their small contributions.[3,5]

To consider anharmonic contributions to the MSRD we used an argument analogous to the one[15] for its change due to the temperature increase and obtain

$$\sigma^2(T) - \sigma^2(T_o) = (1 + \beta(T))\left[\sigma_H^2(T) - \sigma^2(T_o)\right], \qquad \beta(T) = 2\gamma_G \frac{\Delta V}{V}. \quad (3)$$

where γ_G is Grüneisen parameter, and $\Delta V/V$ is the relative volume change due to thermal expansion. T_o is a very low temperature so that $\sigma^2(T_o)$ is a harmonic MSRD. This result agrees with the one in another consideration[4] on the change of the MSRD. Deriving further Eq. (3) we obtain the total MSRD

$$\sigma^2(T) = \sigma_H^2(T) + \beta(T)\left[\sigma_H^2(T) - \sigma^2(T_o)\right] \quad . \quad (4)$$

It is clear that the MSRD approaches the very small value of zero-point contribution σ_0^2 when the temperature approaches zero, i. e.,

$$\sigma^2(T_o) \to \sigma_0^2 \quad for \; T_o \to 0.$$

Hence, it can be seen in Eq. (4) that the total MSRD $\sigma^2(T)$ at a given temperature T consists of the harmonic contribution $\sigma_H^2(T)$ and the anharmonic one $\sigma_A^2(T)$

$$\sigma^2(T) = \sigma_H^2(T) + \sigma_A^2(T), \quad \sigma_A^2 = \beta(T)\left[\sigma_H^2(T) - \sigma_0^2\right]. \quad (5)$$

This separation will help us to determine the anharmonic contribution to the EXAFS amplitude.

In the present approach we apply the anharmonic correlated Einstein model[13] to the calculation of the cumulants where the effective interaction potential is given by

$$V_{cn}(x) \cong \frac{1}{2}k_{cn}x^2 + k_3x^3 + \cdots = V(x) + \sum_{i=j} V\left(\frac{\mu}{M_i}x\hat{\mathbf{R}}_{12}\cdot\hat{\mathbf{R}}_{ij}\right), \mu = \frac{M_1M_2}{M_1 + M_2}. \quad (6)$$

Here x is the deviation of instantaneous bond length between two atoms from equilibrium, $\hat{\mathbf{R}}$ is the bond unit vector, k_{cn} is effective spring constant, and k_3 the cubic parameter giving an asymmetry in the pair distribution function. The correlated Einstein model may be defined as a oscillation of a pair of atoms with masses M_1 and M_2 (e.g., absorber and backscatterer) in a given system. Their oscillation is influenced by their neighbors given by the last term in the left side of Eq. (6), where the sum i is over absorber ($i = 1$) and backscatterer ($i = 2$), and the sum j is over all their near neighbors, excluding the absorber and backscatterer themselves whose contributions are described by the term $V(x)$.

To model the asymmetry we replaced the harmonic potential by an anharmonic one, e. g., a Morse potential with parameters D and α charactrizing the intraction of each pair of atoms.

Applying it to the effective potential of the system of Eq. (6) (ignoring the overall constant) we obtain

$$k_{eff} = 5D\alpha^2\left(S - \frac{3}{2}\alpha u\right) = \mu\omega_E^2 ; \quad k_3 = -\frac{5}{4}D\alpha^3 ; \quad \theta_E = \frac{\hbar\omega_E}{k_B}. \tag{7}$$

where k_B is the Boltzmann constant: ω_E, θ_E are the correlated Einstein frequency and temperature; the structural parameter S = 5 for fcc and S =11/3 for bcc structure.

Using the above results in first-order thermodynamic perturbation theory[13,14] with consideration of the phonon-phonon interaction for taking into account the anharmonicity we obtain the cumulants

$$\sigma^{(1)}(T) = \sigma_0^{(1)}\frac{1+z}{1-z}, \quad \sigma_0^{(1)} = \frac{15\alpha}{4S}\sigma_0^2, \quad z = e^{-\theta_E/T} \tag{8}$$

$$\sigma^2(T) = \sigma_0^2\frac{1+z}{1-z}, \quad \sigma_0^2 = \frac{\hbar\omega_E}{2SD\alpha^2}, \tag{9}$$

$$\sigma^{(3)}(T) = \sigma_0^3\frac{1+10z+z^2}{(1-z)^2}, \quad \sigma_0^{(3)} = \frac{5\alpha}{2S}\left(\sigma_0^2\right)^2. \tag{10}$$

where $\sigma_0^{(1)}, \sigma_0^2, \sigma_0^{(3)}$ are the zero-point contributions to the first, second and third cumulant, respectively.

Based on the derived cumulants and correlated Einstein frequency we calculated the relative volume change due to thermal expansion and Grüneisen parameter. By substituting the obtained results in Eq. (3) we derived an anharmonic factor

$$\beta(T) = \frac{9\eta(T)k_BT}{16D}\left[1 + \frac{3k_BT}{8D\alpha R}\left(1 + \frac{3k_BT}{8D\alpha R}\right)\right], \quad \eta(T) = \frac{2e^{-\theta_E/T}}{1+e^{-\theta_E/T}}. \tag{11}$$

This factor is proportional to the temperature and inversely proportional to the shell radius, thus reflecting a similar property of anharmonicity obtained in an experimental catalysis research[2] if R is considered as particle radius.

The anharmonic contribution to the EXAFS phase at a given temperature is the difference between the total phase and the one of the harmonic EXAFS. On the left side of Eq. (2) the 2nd and the 5th terms contribute to the EXAFS amplitude. Only the 1st, the 4th terms and the anharmonic contribution to the MSRD in the 3rd term are anharmonic contributions to the phase. Therefore, from this equation we obtain

$$\Phi_j(T,k) = 2k\left[\sigma^{(1)}(T) - 2\sigma_j^2(T)\left(\frac{1}{R} - \frac{1}{\lambda(k)}\right) - \frac{2}{3}\sigma^{(3)}(T)k^2\right]. \tag{12}$$

The 4th cumulant is often very small.[13,14,17] This is why we obtained from Eqs. (1, 2), taking into account the above results, the temperature dependent K-edge EXAFS function including anharmonic effects as

$$\chi(k,T) = \sum_j \frac{S_0^2 N_j}{kR_j^2} F_j(k) e^{-\left(2k^2\sigma_j^2(T) + 2R_j/\lambda(k)\right)} \sin\left(2kR_j + \Phi_j(k) + \Phi'_j(k,T)\right). \tag{13}$$

which by including Eq. (5) is resulting in

$$\chi(k,T) = \sum_j \frac{S_0^2 N_j}{kR_j^2} F_j(k) e^{-\left(2k^2\left[\sigma_H^2(T) - \sigma_j^2(T)\right] + 2R_j/\lambda(k)\right)} \sin\left(2kR_j + \Phi_j(k) + \Phi'_j(k,T)\right). \tag{14}$$

where S_0^2 is the square of the many body overlap term, N_j is the atomic number of each shell, the remaining parameters were defined above, the mean free path λ is defined by the imaginary part of the complex photoelectron momentum $p = k + i/\lambda$, and the sum is over all atomic shells.

It is obvious that in Eq. (14) $\sigma_A^2(T)$ determines the anharmonic contribution to the amplitude characterizing the attenuation, and $\Phi_A(k,T)$ is the anharmonic contribution to the phase characterizing the phase shift of EXAFS spectra. They are calculated by Eq. (5) and Eq. (12), respectively. Their values characterize the temperature dependence of the anharmonicity, but the anharmonicity is described by the cumulants given by Eqs. (8 - 10) obtained by consideration of the phonon-phonon interaction process. That is why they also characterize the temperature dependence of the phonon-phonon interaction in the EXAFS. At low temperatures these anharmonic values approach zero and the EXAFS function Eq. (14) is reduced to the one of the harmonic model.

III. Discussion of numerical results and comparison with experiment

We applied the expressions derived in the previous section to numerical calculations for fcc crystal Cu. The Morse potential parameters[18] D, α; calculated effective spring constant k_{eff}; correlated Einstein frequency ω_E and temperature θ_E are written in Table I, where our

Table I: *Morse potential parameters D, α ; calculated effective spring constant k_{eff} ; correlated Einstein frequency ω_E and temperature θ_E of Cu.*

Crystal	$D(eV)$	$\alpha(A^{-1})$	$k_{eff}(N/m)$	$\omega_E(\times 10^{13} Hz)$	$\theta_E(K)$
Cu	0.3429	1.3588	50.7478	3.0889	235.9494

calculated value $\theta_E \approx 236\,K$ for Cu agrees well with the measured one of 232 (5) K.[9] Figure 1 shows the temperature dependence of our calculated anharmonic factor $\beta(T)$ for Cu. It has the

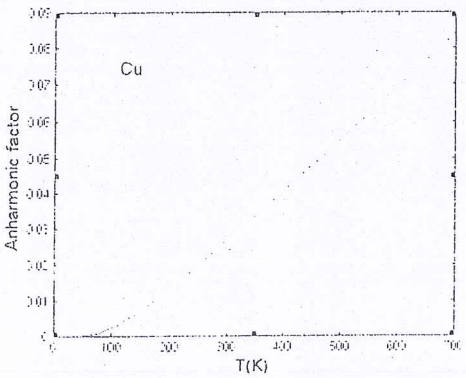

Figure 1: *Temperature dependence of the calculated anharmonic factor $\beta(T)$ for Cu.*

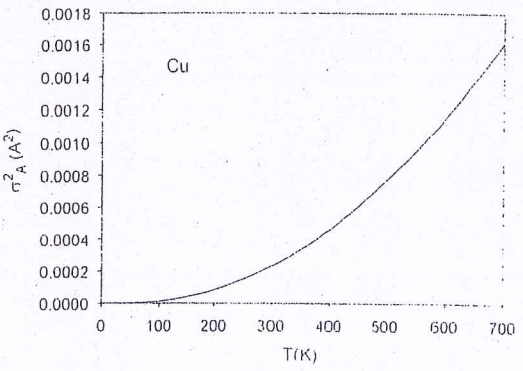

Figure 2: *Temperature dependence of the calculated anharmonic contribution $\sigma_A^2(T)$ of Cu to the EXAFS amplitude*

values 0.28 at 300 K and 0.84 at 700 K which agree well with those obtained by the other studies.[11,16] Figure 2 shows the temperature dependence of our calculated anharmonic contribution $\sigma_A^2(T)$ to the MSRD determining the anharmonic contribution to the EXAFS amplitude of Cu. It is small at low temperatures and then increases strongly at high temperatures This result also shows that below 100 K no anharmonic effect in the EXAFS of Cu is expected. It agrees well with our previous prediction[11,12] and with the experimental results.[2,17] Therefore, $\sigma_A^2(T)$ also makes it possible to determine the temperature above which the anharmonic effects

or the phonon-phonon interaction are visible. For Cu this temperature is about 100 K. Figure 3 illustrates the temperature dependence of our calculated total MSRD $\sigma^2(T)$ of Cu compared to

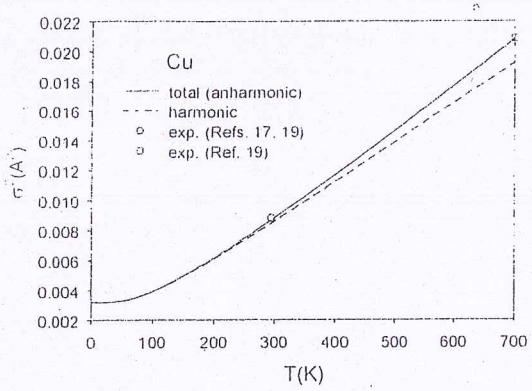

Figure 3: *Temperature dependence of the calculated total MSRD or DWF* $\sigma^2(T)$ *for Cu compared to the harmonic one* $\sigma_H^2(T)$ *and to the measured values at 295 K*[17,19] *and at 700 K.*[19]

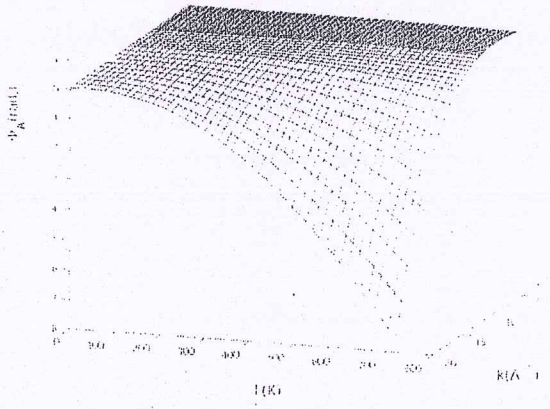

Figure 4: *Temperature and k-dependence of the calculated anharmonic contribution* $\Phi_A(k,T)$ *to the phase of the EXAFS of Cu.*

its harmonic one $\sigma_H^2(T)$ and to the experiment.[17,19] The calculated values of the total anharmonic MSRD agree well with the measured results at 295 K[17,19] and 700 K.[19] Figure 4 illustrates the temperature and k-dependence of our calculated anharmonic contribution $\Phi_A(k,T)$ to the EXAFS phase of Cu for the first shell for single scattering. These contributions are especially large at high temperatures and high k-values. Figure 5 shows the significant difference between the EXAFS spectrum χk^3 of Cu at 295K and 700K calculated by the harmonic FEFF code[1] and the one including the anharmonic contributions. The

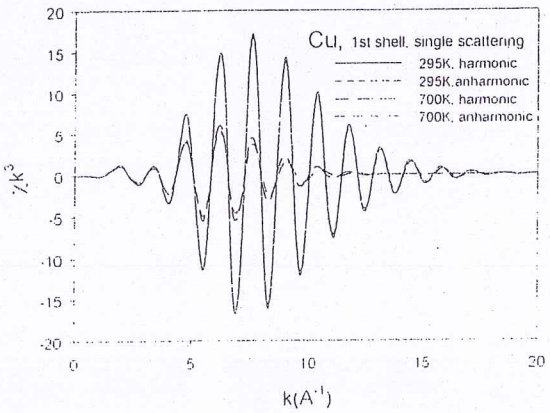

Figure 5: *Comparison of the harmonic EXAFS of Cu with those calculated by our anharmonic theory at 295K and 700K.*

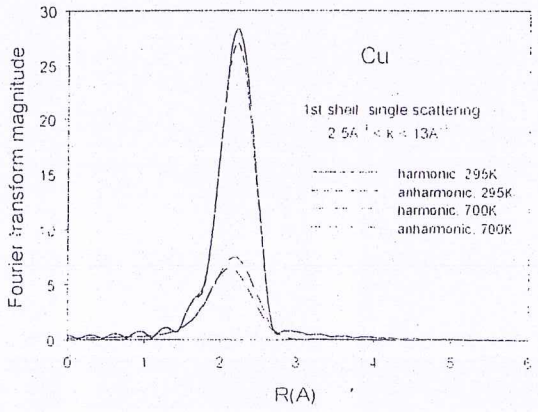

Figure 6: *Comparison of the Fourier transform magnitudes of the EXAFS spectra from Figure 5.*

anharmonic spectrum is shifted to the left and attenuated especially at high k-values. Fourier transform magnitudes over the range 2.5 $Å^{-1} < k < 13\ Å^{-1}$ of these EXAFS spectra of Cu are illustrated in Figure 6. Our calculated EXAFS Fourier transform magnitudes of Cu including anharmonic contributions for the first shell agree well with the measured ones.[19] They are shifted to smaller distances by 0.03 Å at 295 K and by 0.07 Å at 700 K in comparison to the

harmonic model results. as well as yielding apparently different structural information at the different high temperatures.

IV. Conclusions

We have developed an anharmonic theory of EXAFS containing the derived expressions for the anharmonic contributions to its amplitude determined by a new derived anharmonic factor and for the anharmonic contributions to its phase based on the cumulant expansion and the single-shell model. The total MSRD is the sum of the harmonic and the anharmonic ones.

Advantage of the present procedure is that these anharmonic contributions can be calculated and analyzed for any temperature and for any k-value. Moreover, based on the anharmonic contribution to the EXAFS amplitude we also can predict the temperature above which the anharmonicity or the phonon-phonon interaction in the EXAFS is visible.

The anharmonic effects in the present model are obtained as corrections which can be added to a harmonic model like the well-known FEFF code[1] to modify it into the anharmonic one. Our expressions derived for the EXAFS and its parameters include anharmonic contributions at high temperatures and are approaching those of the harmonic model at low temperatures. They can be calculated ab initio as they have been tested for the case of Cu.

The good agreement between the calculated results and experiment shows the advantage and efficiency of this new procedure for the analysis of anharmonic contributions to the EXAFS.

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