EVALUATION OF XAFS SPECTRA WITH INFLUENCE OF ANHARMONICITY

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Abstract. *In this work the X-ray Absorption Fine Structure (XAFS) spectra with influence of anharmonicity have been evaluated to get correct structural information. The temperature above which the anharmonic effects must be included is identified with Einstein temperature and as the third cumulant calculated by anharmonic-correlated Einstein model. Debye-Waller factor and XAFS spectra of Cu calculated by present procedure are different from those calculated by harmonic model and agree very well with experimental values. Using this agreement several important physical parameters are extracted from experiment. They agree very well with theoretical or by other methods extracted results.*

I. Introduction

The most important and meaningful task of XAFS technique is to describe and interpret the XAFS spectra and then is to extract physical parameters by comparison between theoretical and experimental results. It was discovered and that the XAFS spectra are different at different high temperatures, so that they provide different structural information [1, 2]. Some recent works [2, 3] are successful in describing the changes of amplitude and phase of XAFS spectra in terms of anharmonic contributions as the temperature T increases where the anharmonic effect is taken into account by an anharmonic factor. But in these considerations the temperature T_0 above which the anharmonicity must be included is only a fitting parameter and the third cumulant was taken from experiment.

This work is devoted to calculation of the third cumulant [4] and the temperature T_0 basing on the anharmonic - correlated Einstein model [5] where T_0 is identified with Einstein temperature. They are applied to calculation of Debye-Waller factors and XAFS spectra including anharmonic contributions of atomic vibration. The numerical results of Cu are compared with experimental values. Thanks to their very good agreement several physical parameters are extracted from the experiment.

II. Formalism

In the single-shell model the XAFS function, providing structural information through its Fourier transform magnitude, is given by [2, 3]

$$\chi(k) \sim F(k) \exp\left(-\frac{2R}{\lambda}\right) \exp\left[-2k^2(\sigma_H^2 + \sigma_A^2)\right] \sin(2kR + \delta(k) + \phi_A(k)), \qquad (1)$$

where k is wave vector, $F(k)$ is scattering amplitude, R is shell radius, λ is electron mean-free-path, σ_H^2 is harmamic contribution to Debye-Waller factor (DWF) and $\delta(k)$ is total phase shift.

The anharmonic contribution to SWF is given by

$$\sigma_A^2(R,T) = \beta(R,T)\sigma_H^2(R,T). \tag{2}$$

in which the anharmonicity is taken into consideration by the anharmonic factor

$$\beta(R,T) = \frac{18\eta\gamma_G}{(8D\alpha)^3}[(8D\alpha)^2\xi + 24D\alpha\xi^2 + 3\xi^3]. \tag{3}$$

$$\eta = \frac{[\sigma_H^2(T) - \sigma_H^2(T_0)]}{\sigma_H^2(T)};\ \ \xi = \frac{k_B(T-T_0)}{R}. \tag{4}$$

and the phase change due to anharmonicity is given by

$$\phi_A(k,T) = 2k\left[\Delta R(T) - 2\Delta\sigma^2\left(\frac{1}{R} - \frac{1}{\lambda}\right)\right] - \frac{3}{4}\sigma^{(3)}(T)k^3. \tag{5}$$

$$\Delta\sigma^2(T) = \sigma_H^2(T) + \sigma_A^2(T) - \sigma_H^2(T_0);\ \ \Delta R(T) = \frac{3k_B(T-T_0)}{8D\alpha} \tag{6}$$

where D and α are the Morse potential parameters and γ_G is Gruneisen Parameter.

Now we use the anharmonic-corretated Einstein model to calculate the temperature T_0 and the cumulants. The first $\sigma^{(1)}$, second $\sigma^{(2)}$, third $\sigma^{(3)}$ cumulant and thermal exapnsion coefficient α_T are given by [4]

$$\sigma^{(1)} = a = \frac{3\hbar\omega_E}{40D\alpha}\frac{1+z}{1-z}. \tag{7}$$

$$\sigma^{(2)} = \frac{\hbar\omega_E}{10D\alpha^2}\frac{1+z}{1-z}. \tag{8}$$

$$\sigma^{(3)} = \frac{(\hbar\omega_E)^2}{200D^2\alpha^3}\frac{1+10z+z^2}{(1-z)^2}, \tag{9}$$

$$\alpha_T = \frac{3k_B}{20D\alpha r}\frac{z(\ln z)^2}{(1-z)^2}. \tag{10}$$

where $z = \exp(-\theta_E/T)$, ω_E and θ_E are Einstein frequency and temperature.

$$\omega_E = \left[\frac{5}{\mu}D\alpha^2\left(1 - \frac{3}{2}\alpha a\right)\right]^{1/2}. \tag{10}$$

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

Here μ is reduced mass of absorbing and backscattering atoms.

It is easy from eqs. (7-9) to get the following relation

$$\frac{\alpha_T r T\sigma^2}{\sigma^{(3)}} = \frac{3z\ln(1/z)(1+z)}{(1-z)(1+10z+z^2)}, \tag{12}$$

which approaches from the $theta_E$ to the constant value 1/2. Moreover, the relation $\alpha_T r T\sigma^2/\sigma^{(3)} = 1/2$ in classical limit [1], i.e., at high temperatures, where the anharmonicity must be included. Therefore, the temperature T_0 in eqs. (3 - 6) is identified with

the Einstein temperature calculated by eq. (11), and the second and third cumulants used in eqs. (2-6) are calculated by eqs. (8 - 9).

III. Comparison between Experiment and Extraction of physical parameters

Now we use the formulas presented in previous section to calculate SWF and other parameters as well as XAFS spectra with influence of anharmonicity of atomic vibration. That means, at any temperatures Fig. 1a shows the values of DWF of Cu calculated by present procedure in harmonic and anharmonic model in comparison with an experimental value [6] at 295K. Fig. 1b presents the Fourier transform magnitude of XAFS spectrum from the first shell of Cu at 295K calculated by present anharmonic procedure in comparison with those calculated by harmonic model and with the result measured recently in the HASYLAB at DESY [2]. In both figures the values calculated by present anharmonic procedure agree very well with experimental result and are different from those calculated by harmonic model.

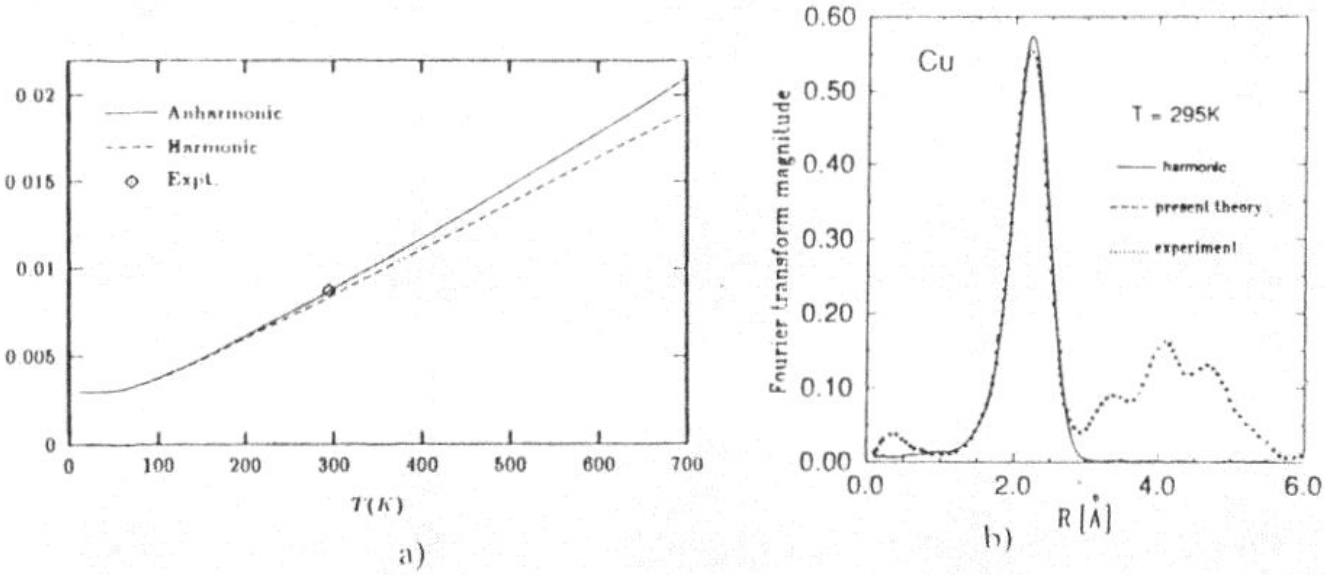

Fig. 1a. DWF of Cu calculated by present anharmonic procedure (solid) in comparison with those calculated by harmonic model (dashed) and those of experiment [6] (□).
Fig. 1b Fourier transform magnitude of SAFS spectrum of Cu calculated by present anharmonic procedure (dashed) in comparison with those calculated by harmonic model solid) and those of experiment (dots) [2].

Thanks to this agreement several physical parameters of Cu are extracted. They are presented in Table 1. The values of α, D and γ_G agree very well with those obtained using experimental values for the energy of sublimation, the compressibility and the lattice constant [7]. The values of $k_{eff}, \sigma^{(3)}$ and θ_E agree very well with theoretical results of ref. 1 and θ_D agrees very well with the one of ref. 8.

$\alpha(Å^{-1})$	D(eV)	γ_G	k_{eff}(N/m)	$\sigma^{(3)}(10^{-3}$ Å$^3)$	θ_e(K)	θ_D(K)
1.359	0.343	2.108	50.748	0.131	236	315

Table 1. The values of $\alpha, D, \sigma^{(3)}, \theta_E$ effective spring constant k_{eff} and Debye temperature θ_D of Cu extracted from experiment by present procedure.

In conclusion, present anharmonic procedure can serve as an effective procedure not only for calculation of DWF and XAFS spectra with anharmonic contributions of atomic vibration providing structural information at any temperatures but also for extraction of several physical parameters from the experiment.

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ĐÁNH GIÁ CÁC PHỔ XAFS VỚI ẢNH HƯỞNG CỦA DAO ĐỘNG PHI ĐIỀU HOÀ

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Trong bài này các phổ cấu trúc tinh tế của hấp thụ tia X (XAFS) với ảnh hưởng của dao động phi điều hoà đã được đánh giá để nhận các thông tin chính xác về cấu trúc của vật thể. Nhiệt độ mà trên nó các hiệu ứng dao động phi điều hoà phải bổ sung được đồng nhất với nhiệt độ Einstein và cũng như cumulant bậc ba được tính theo mô hình Einstein tương quan phi điều hoà. Hệ số Debye-Waller và các phổ XAFS của Cu tính bằng phương pháp này khác với các phổ tính theo mô hình điều hoà và trùng rất tốt với các kết quả thực nghiệm. Nhờ sự trùng hợp này mà một số tham số vật lý đã được rút ra từ thực nghiệm. Chúng trùng tốt với các kết quả lý thuyết hay thực nghiệm được rút bằng phương pháp khác.