EVALUATION OF TEMPERATURE AND SHELL SIZE DEPENDENCE OF ANHARMONICITY IN EXAFS OF Cu

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Abstract : In this work we evaluated the anharmonic effects in Extended X-ray Absorption Fine Structure (EXAFS) of Cu in the Single-Shell model. They are proportional to the temperature and inversely proportional to the radius of the spherical shell. The anharmonic EXAFS spectra are compared with the harmonic ones showing significant differences. Our anhrmonic spectra at T=700K agree very well with the measured ones and are much better than the results calculated by the harmonic model.

I. INTRODUCTION

No crystal is exactly harmonic. But the harmonic model can work because the most of EXAFS spectra were measured at low temperature where the anharmonicity can be neglected. For some aspects like catalysis research the EXAFS studies carried out at low temperature may not provide a correct structural picture and the high-temperature EXAFS is necessary [1]. The aim of this paper is to use the theory presinted in [2] to evaluate the anharmonic effects in EXAFS of Cu. They are included in the Mean-Square-Relative-Displacement (MSRD). The anharmonic contribution is taken into consideration by multiplying the harmonic one with an anharmonic factor. The results calculated by our anharmonic model are compared with the ones calculated by the harmonic code [3] at the same temperature. They show significant differences and our anharmonic results agree very well with the measured ones.

II. THEORY

For a crystalline material the K-edge EXAFS spectrum is described by:

$$\chi(k) = \sum_j \frac{S_o^2 N_j}{k R_j^2} F_j(k) \exp\left[-2(R_j/\lambda) - 2\sigma_j^2 k^2 + C_{ej}(k) \right] \times$$
$$\times \sin\left[2k R_j + \delta_j(k) + C_{oj}(k) \right] \qquad (1)$$

here

$$C_{ej}(k) = \frac{2}{3}\sigma_j^{(4)} k^4 + \dots \qquad (2)$$

$$C_{oj}(k) = \frac{4\sigma_j^2 k}{R_j}[1 + R_j/\lambda] - \frac{4}{3}\sigma_j^{(3)} k^3 + \dots \qquad (3)$$

k is photoelectron wave number, S_o^2 is square of the many-body overlap term, λ is the electron mean free path, F(k) is the atomic backscattering amplitude, δ(k) is a net shift and the sum is over the coordination shells of neighbors of the absorbing atom. In this case one expands the asymmetric terms in the brack-ets in a Taylor serie about $R_j = <r_j>$ and rewrite the thermal everage in terms of cumulants $\sigma^{(n)}{}_j$ [5] defined by the equation :

$$< e^{2ikr} > = \exp\left\{ \sum_{n=1}^{\infty} [(2ik)^n / n!] \sigma^{(n)} \right\} \qquad (4)$$

When phonon-phonon interactions are important the terms given in Eqs. (2) and (3) are required to give an accurate description of the EXAFS. The term of Eq. (1) including σ^2 desribes Debye-Waller factor. We assume that at temperature To the system is in a equilibrium and the nearest neighbor separation between two atoms is Ro and the harmonic approach is valid. So at temperature T>To the anharmonicity appears and it must be considered. At temperatures above the Debye temperature the classical model works well [6] and the MSRD σ^2(T) including the harmonic contribution $\sigma^2{}_H$(T) and the anharmonic one σ^2 (T) has been calculated [2] and desribed by:

$$\sigma^2(T) = [1 + \beta (T_i R_o) \sigma_H^2 \quad ; \quad \sigma_A^2(T) = \beta(T, R_o) \sigma_H^2(T) \qquad (5)$$

Where the anharmonic contribution is valued by the anharmonic factor:

$$\beta(T_i R_o) = \frac{\Delta \sigma_H^2(T)}{\sigma_H^2(T)} = \frac{18\gamma}{(8D\alpha)^3} \left[(8D\alpha)^2 \frac{k_B \Delta T}{R_o} + 24D\alpha \left(\frac{k_B \Delta T}{R_o} \right)^2 + 3 \left(\frac{k_B \Delta T}{R_o} \right)^3 \right] \qquad (6)$$

$$\Delta \sigma_H^2(T) = \sigma_H^2(T) - \sigma_H^2(T_o) \quad ; \quad \Delta T = T - T_o \qquad (7)$$

In this anharmonic model the harmonic potential is replaced by the Morse pair potential [7]:

$$U(R) = D\{ \exp [-2\alpha(R-R_o)] - 2\exp [-\alpha(R-R_o)] \} \qquad (8)$$

Where α and D are constants with dimensions of reciprocal distance and energy, respectively, k_B is Boltzmann constant. The anharmonic contribution causes also a phase change. Therefore, to include the anharmonicity the phase of EXAFS spectra is corrected by :

$$\Delta\Phi(T) = 2k \left[\Delta R_1 - 2\Delta\sigma^2 \left(\frac{1}{R} - \frac{1}{\alpha} \right) \right] - \frac{4}{3} \sigma^{(3)}(T) k^3 \qquad (9)$$

$$\Delta\sigma^2 = \sigma^2(T) - \sigma^2(T_o) \quad ; \quad \Delta R_1 = R(T) - R_o = 3k_B \Delta T / 8D\alpha \qquad (10)$$

Where $\sigma^{(3)}$ is the therd cumulant [4]

III. RESULTS OF CU

Cu has fcc structure with the lattice constant of 3.61 $\overset{o}{A}$ which was used to calculate the coordinations of the neighbor atoms. Cu has comparatively large anharmonic vibrations even at room temperature, but at T=80K no anharmoniceity was measured [8] that is why the value T_o=100K was used. Debye temperature T_D is temperature dependent, but for T≥100K it is about constant at T_D= 315K which was used in our calculation. The values γ= 2. 18 ; D = 0.3429eV; α= 1.3588^{-1} were taken from [7]. All calculated values are called

harmonic if only the harmonic MSRD was used and called anharmonic if besides the harmonic MSRD the anharmonic contribution was involved. The anharmonic factor of Cu calculated with the help of Eq. (6) is proportional to the temperature and inversely proportional to the radius of the spherical shell (Fig.1). These qualities are the same in the case of anharmonic contribution σ^2_A calculated with the help of Eq. (5) and illustrated in Fig.2.Because in our theory the single-shell model was used then R_0 is also the radius of the outer shell that is why the above are similar to the ones discovered in a experiment [1] that the anharmonicity of motion of crystal atoms increases with desreasing particle size and with increasing temperature. Certainly, in the case of particle surface-effects have to be included and the anharmonic contribution must be stronger. The anharmonic MSRD have been calculated with the help of Eq. (5) and compared with the harmonic ones for the first and the second shell (Fig.3). It shows increasing of the anharmonic MSRD especially at high temperature. The calculated anharmonic MSRD value of 0.91×10^{-2} $\overset{\circ}{A}{}^2$ for the first shell at T = well with the measured one of $0.876 \times 10^{-}$ $\overset{\circ}{A}{}^2$ [6] that is why the use of percent theory can be extended for the room temperature. The mean = free path is k-dependent (Fig.4) influencing on the anharmonic correction of the phase of EXAFS spectra. To

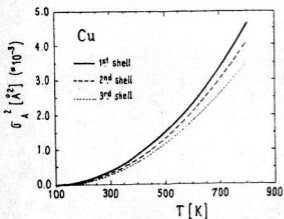Fig 1. Temperature and shell size dependence of anharmonic factor

Fig 2. Anharmonic contribution to the MSRD

receive $\sigma^{(3)}$ (T) (Fig.5) for Cu we extrapolated its measured of value 0.13×10^{-3} [8] according to its proportionlity to the square of temperature [4,6]. The temperature dependence of the phase corrections of the anharmonic EXAFS spectra is included in ΔR_t, $\Delta\sigma^2$ and $\sigma^{(3)}$, while the shell size dependence is only in the term $\Delta\sigma^2/R$, that is why, the temperature dependence of $\Delta\phi$ is stronger than its shell size dependence. The harmonic and anharmonic EXAFS spectra have been calculated using muffin-tin potential for the absorbing and back scattering atoms. Because extrinsic and losses involve the same final states , interference between these
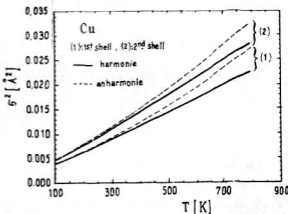

Fig 3. Comparison of harmonic MSRD with anharmonic one of the first and the second shell

processes must also be considered. The intrinsic losses and interference tend to compensate each other, considerably reducing the net effect of the intrinsic processes alone, these loss terms are simply lumped into a constant reduction factor S^2_0 [3]. The major contribution to the EXAFS is from the first shell. We compare in Fig.7 the harmonic EXAFS spectrum with the anharmonic one for the first shell at T = 700K. In calculation of these spectra the value $S^2_0=0.9$ [3] was used. In the EXAFS teehque the Fourier transform provides structural information. Fig.8 compares the of Fourier transform of the harmonic and anharmonic EXAFS spectra of the first shell at three
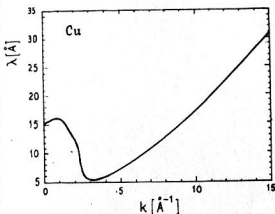
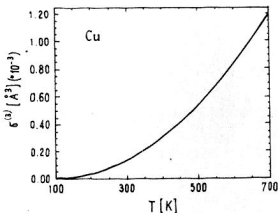Fig 4. k - dependence of the mean-free path

temperature. Fig.9. illustrates the damping and the shifting to the right of the anharmonic EXAFS spectra with increasing temperature especially at high k-values. Fig.7 and Fig.8 show significant differences between the harmonic and the anharmonic case. The behaviors of calculated anharmonic EXAFS spectra (Fig.9) are similar to the ones of the measured results [9]. Fig.10 shows that our calculated anharmonic result very well with the measured one and is must better than the curve calculated by the harmonic code [3]. From the above results we can see the necessity of the anharmonic corrections in the EXAFS spectra calculated by the harmonic model as well as their temperature and shell size dependence.
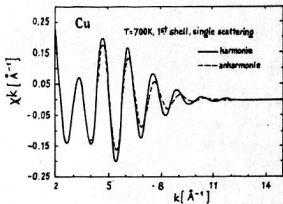
Fig 5. Temperature dependence of the third cumulant.
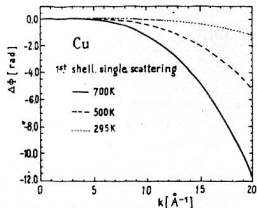
Fig 6. Phase corrections due to anharmonicity at three temperatures

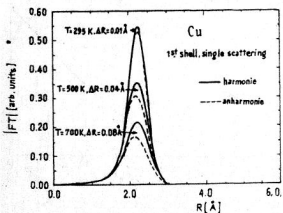Fig 7. Harmonic and anharmonic EXAFS spectra of the first shell at T=700K

Fig 8. Fourier transform magnitudes of harmonic and anharmonic EXAFS spectra of the first shell at three temperatures
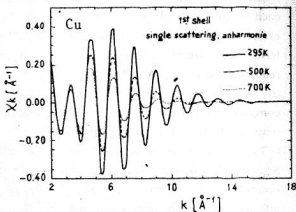

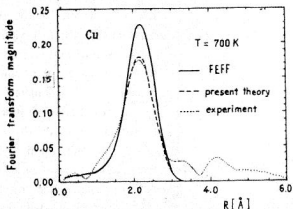Fig 9. Anharmonic EXAFS spectra at three temperatures

Fig 10. Comparison of measured fourier transform magnitude with the one calculated by our anharmonic model and by FEFF

IV.CONCLUSIONS

The anharmonic effects discovered in the measurement of EXAFS of Cu have been calculated. They are proportional to the temperature and inversely proportional to the radius of the shell. The calculated results afree well with the measured ones even at room temperature showing the necessity of the anharmonic corrections in the EXAFS spectra calculated by the harmonic model. Including the anharmonic contribution in our model can widen the use of the famous code FEFF of Prof. John Rehr et al [3] for calculating EXAFS spectra at high temperature.

LITERATURES

1. B.S Clausen, L. Graback, H. Topsoe, L.B.Hansen, P.Stolze, J.K. and O.H.Nielsen, J.Catal.141, p.368 (1993).

2. N.V.Hung and R.Frahm, the 8th Int. Conf. On XAFS, Berlin (1994) and Physica B.

3. J.J.Rehr, J.Mustre de Leon, S.I.Zabinsky and R.C.Albers J.Am.Chem.Soc. 113, p.5135 (1991).

4. J.M.Tranquada and R.Inglls, Phys. Rev. B 28, p.3520 (1993).

5. G.Bunker, Nucl. Instrum. Methods 207, p.473 (1983)

6. T.Fujikawa and T.Miyanaga, J.Phys.Soc.Jpn.62, p.4108 (1993).

7. L.A. Girifalco and V.G.Weizer, Phys. Rev. 114, p. 687 (1959).

8. T Yokoyama, T.Sasukawa and T.Ohta, Jpn. J. Appl. Phys. 28, p. (1989).

9. E.A. Stern, P.Lavins and Zhe Zhang, Phys. Rev. B 43, p.8850 (1991).

ĐÁNH GIÁ SỰ PHỤ THUỘC NHIỆT ĐỘ VÀ KÍCH THƯỚC LỚP CỦA TÍNH PHI ĐIỀU HÒA TRONG EXAFS CỦA Cu

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Trong công trình này chúng tôi đã đánh giá các hiệu ứng phi điều hòa trong phần cấu trúc tinh tế của phổ hấp thụ Rơn-ghen (EXAFS) của Cu với mô hình đơn lớp. Các ảnh hưởng phi điều hòa được tìm thấy tỷ lệ thuận với nhiệt độ và tỷ lệ nghịch với bán kính của lớp cầu. Các phổ EXAFS phi điều hòa đã được so sánh với các phổ điều hòa và cho thấy sự khác nhau rõ rệt giữa chúng. Các phổ phi điều hòa tính theo mô hình của chúng tôi ở nhiệt độ 700K đã rất trùng với kết quả thực nghiệm và sự trùng hợp này tốt hơn các phổ tính theo mô hình điều hòa rất nhiều.