Positive or Negative Thermal Expansion in Anharmonic Vibrational Systems in EXAFS study

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Abstract. An EXAFS expression was introduced for analysis of positive or negative thermal expansion. The EXAFS parameters were directly related to the interatomic potential. Also, it was shown that the sign of anharmonic potential parameter $k_3$ depends on the sign of thermal expansion coefficient. Simulation works showed that the positive or negative thermal expansion can be sensitively measured by EXAFS study.

1. Introduction

Bond stretching, causing the local thermal expansion of chemical bond, occurs frequently in molecules or lattice relaxed with the thermal disturbance beyond the harmonic vibrational limit. Recently the negative thermal expansion has been extensively studied for the practical application to the non-expandable alloys \cite{1, 2, 3, 4, 5}. The positive/negative thermal expansion is relevant to the bond stretching/contraction configuration, severely subjected to the interatomic potential of atoms in solid \cite{6, 7, 8, 9}. Although these local thermal expansion phenomena have been investigated in EXAFS study, considerable progress has not been made yet because of experimental limitation and theoretical difficulties \cite{10, 20, 12, 13}. It has been shown that the local thermal expansion occurs in the anharmonic vibrational systems \cite{8, 9} which can be related to an asymmetric pair distribution \cite{14}.

In this study, we demonstrated a simple criterion to identify the bond stretching/contraction in a theoretical manner, using a pair distribution function applicable to the positive/negative thermal expansion \cite{9}.

2. EXAFS expression for thermal variational systems

The volume of solid materials can be expanded or contracted according to the characteristics of bonding configuration and effective potential between constituent atoms. The structures of solids are more or less deformed by changing lattice parameters as temperature increases. This means that the origin of positive or negative thermal expansion may cause the apparent deformation of amplitude and phase of EXAFS spectra. The deformed spectra require a proper EXAFS expression, explicitly indicating the positive/negative thermal expansion.

In anharmonic system, the EXAFS equation can be expressed for both positive and negative thermal expansion by
\[ \chi(k) = \frac{N F(k) S_0^2(k) e^{-2R/k}}{k R^2} A_c(k) \sin(2kR + \varphi(k) + \phi_c(k)) \]  

(1)

where

\[ A_c = (1 + (2k\delta)^2)^{-\frac{\sigma^2}{2\pi^2}} \]  

(2)

and

\[ \phi_c(k) = \frac{\sigma^2}{2\delta^2} (\tan^{-1}(2k\delta) - (2k\delta)) \approx (-\frac{8}{3} \sigma^2 \delta k^3 + \cdots) \]  

(3)

where \( N \) is the number of neighbor atoms, \( R \) is the average interatomic distance, \( \sigma^2 \) is the Debye-Waller parameter, and \( \delta \) is the parameter of thermal expansion. The backscattering amplitude \( F(k) \) and the phase \( \varphi(k) \) are available from FEFF [15, 16, 17]. Yet, asymmetric pair distribution function is implicit, even though it can be demonstrated in terms of anharmonic potential. Here, \( \delta \) is valued with polarity of thermal expansion, either positive or negative. Look how Debye-Waller parameter \( (\sigma^2) \) and thermal expansion parameter \( (\delta) \) are related to the parameters of anharmonic potential

\[ V(r) = \frac{1}{2} k_0 (r - r_0)^2 - k_3 (r - r_0)^3 + k_4 (r - r_0)^4 \]  

(4)

where \( r_0 \) is the equilibrium distance, \( k_0 \) is the force constant in attraction, \( k_3 \) is the skew parameter ascribing the local environments of solid atoms, and \( k_4 \left( = \frac{9k_3^2}{2k_0^2} \right) \) is the extra constraint for the anharmonic vibrational model. As well as \( \delta \)-parameter, \( k_3 \) indicates the positive or negative thermal expansion. By setting \( \delta = R - r_0 \), we have the following relationship between \( \sigma^2 \), \( \delta \), \( k_0 \), and \( k_3 \) [8, 18]

\[ \sigma^2 = \frac{k_B T}{k_0} \]  

(5)

and

\[ \delta = \frac{3k_3}{k_0^2} k_B T. \]  

(6)

where \( k_B \) is Boltzmann constant and \( T \) is absolute temperature.

The relevant thermal expansion coefficient (\( \alpha \)) can be expressed by

\[ \alpha = \frac{\Delta \delta}{r_0 \Delta T}. \]  

(7)

The anhamonic potential gives a pair distribution function as follows

\[ g(r) = \frac{e^{-\frac{V(r)}{k_B T}}}{\int_0^{\infty} e^{-\frac{V(r)}{k_B T}} dr}. \]  

(8)

The general EXAFS spectrum is convoluted with the pair distribution \( g(r) \) by

\[ \chi(k) = \int_0^{\infty} \frac{N F(k) S_0^2(k) e^{-2r/k}}{k r^2} g(r) \sin(2kr + \varphi(k)) dr. \]  

(9)

From the anharmonic pair distribution function (Eq.8), we can see the explicit variation of the EXAFS spectrum. Without such explicit representation of \( g(r) \) function, we may use the EXAFS equation (Eq.1) instead in case for slightly anharmonic system (e.g. \( \delta < 0.03 A \)).
3. EXAFS simulation for positive and negative thermal expansion

Let us consider the case of positive thermal expansion with the potential parameters of \( k_0 = 47 \text{N/m} \) and \( k_3 = +2.56 \times 10^{11} \text{N/m}^2 \), bond distance is \( R = 2.54 \text{Å} \). Fig.1 shows the temperature dependence of pair distributions for positive thermal expansion. Fig.2 shows the EXAFS spectra of a copper calculated by Eqs.4, 8, and 9, respectively, for 300 K, 500 K and 700 K. As apparently shown, the amplitude is decreasing and the phase of EXAFS spectra is relatively expanded as temperature increases. This is a dilemma about the polarity of thermal expansion, less indicating that the bond is positively expanded as temperature increases.

![Figure 1. Pair distribution function for positive thermal expansion.](image1)

![Figure 2. Simulated EXAFS spectra for positive thermal expansion.](image2)

![Figure 3. Pair distribution function for negative thermal expansion.](image3)

![Figure 4. Simulated EXAFS spectra for negative thermal expansion.](image4)

When the simulated spectra were fitted to Eq.1, we have \( \delta = 0.0148 \text{Å} \) for the spectrum at 300K, and \( \delta = 0.0252 \text{Å} \) at 500K. As expected, \( \delta \)s are all positive indicating that this material is positively expanded as temperature increases. The estimated value of the thermal expansion coefficient is \( \alpha = 20.47 \times 10^{-6}/\text{K} \). It is obvious that \( \delta \) is positive for the positive thermal expansion. On the contrary, let us consider negative simulation with negative thermal expansion. EXAFS spectra for NTE was simulated with the potential parameters of \( k_0 = 47 \text{N/m} \) and \( k_3 = -2.56 \times 10^{11} \text{N/m}^2 \), bond distance is \( R = 2.54 \text{Å} \). Fig.3 shows the pair distributions for negative thermal expansion. Fig.4 shows the simulated spectra, respectively, for 300 K, 500 K and 700 K. As apparently shown, the decreasing amplitude is the same but the phase is reversed compared to the case of PTE. Simply, this reverse phenomenon in phase feature indicates the
the negative thermal expansion. When the simulated spectra in Fig. 4 were fitted to Eq. 1, we obtained $\delta = -0.0155\AA$ for the spectrum at 300 K and $\delta = -0.0273\AA$ at 500 K. The values of $\delta$ are all negative. Also, the estimated thermal expansion coefficient is $\alpha = 23.9 \times 10^{-6}/K$.

Analytically, because negative thermal expansion is the reverse direction of positive thermal expansion, the modified EXAFS equation (Eq.1) works for the practical analysis.

As discussed with our computation simulation, the EXAFS spectra are very sensitive for the local structural variation. The origin of negative thermal expansion was not interpreted in our study. We only elucidated the numerical validity associated with the unusual case of negative thermal expansion. Without doubt, EXAFS is a powerful tool to quantitatively characterize the positive or negative thermal expansions. In a theoretical aspect, although the modified EXAFS expression (Eq.1) is practically useful to analyze the anharmonic vibrational system, the correction phase term ($\phi_c(k)$ in Eq.3) is the artificial strangeness, lacking interpretation of interatomic potential. To avoid such an ambiguity, we need to perform the inverse computation with establishing the measurement error bar. Our study of STIC (Synthesized Topological Inverse Computation) [19] is promising to make a progress for general cases, even highly disordered configurations such as amorphous or non-crystalline materials - complex multicomponent systems.

In summary, quantitatively we mentioned that the modified EXAFS expression is valid only for slightly anharmonic system (i.e. $\delta < 0.03\AA$). Also, we elucidated the structural insight of positive or negative thermal expansion under establish anharmonic potential. It was clearly simplified that the sign of anharmonic potential parameter $k_3$ determines the trend of the positive or negative thermal expansion.

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