Anharmonic correlated Einstein-model Debye-Waller factors

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(Received 28 January 1997)

An anharmonic correlated Einstein model is derived for local vibrational amplitudes in x-ray-absorption fine structure (XAFS) that takes into account all near neighbors of absorber and backscattering atoms. The model is based on quantum thermodynamic perturbation theory and includes anharmonic effects based on empirical potentials. Calculations are presented for the second and third cumulants in XAFS as well as the net thermal expansion and thermal expansion coefficient. This model avoids full lattice dynamical calculations yet provides reasonable agreement with experiment. The generalization to displacement-displacement correlation functions and multiple-scattering Debye-Waller factors is also discussed. [S0163-1829(97)03125-1]

I. INTRODUCTION

The Debye-Waller (DW) factor $e^{-w(p)}$ accounts for the effects of the thermal vibration of atoms in the theory of x-ray-absorption fine structure (XAFS). The dominant term $w(p) = 2p^2\sigma^2$ depends on the mean square relative displacement (MSRD) σ^2 of the bond between absorber and backscattering atoms,[1–3] where p is the photoelectron wave number. Anharmonicity in the potential yields additional terms in the DW factors, which if ignored can lead to non-negligible errors in structural parameters[4–11] derived from XAFS spectra. The formalism for including anharmonic effects in XAFS is often based on the cumulant expansion,[7] where the even cumulants contribute to the amplitude and the odd ones to the phase of XAFS spectra, i.e., $w(p) = 2ip\sigma^{(1)} - 2p^2\sigma^2 - (4/3)ip^3\sigma^{(3)} + \cdots$. Many efforts have been made[7–18] to develop this approach in order to include such anharmonic contributions. At high temperatures the classical approach can work well.[5–11] But this approach cannot be valid at low temperature due to zero-point vibration.[14] Recent work by Frenkel and Rehr[12] (FR) derived relations between XAFS cumulants using a correlated Einstein model and first-order thermodynamic perturbation theory. Their discussion is based on a local vibration picture that includes near-neighbor correlations, but phonon dispersion is neglected. It is not obvious that such an Einstein model can reasonably approximate anharmonic cumulants in solids.[14] Works by Miyanaga and Fujikawa[14] have been carried out using a more sophisticated, full lattice dynamical approach, but this approach requires extensive calculations. More recently, an equation of motion (EM) approaches has also been used.[19] On the other hand, a correlated Einstein model is local and should be a reasonable approximation when correlations are short ranged.

This work is a next step to the approach of FR (Ref. 12) for approximating cumulants in XAFS. Our further development is the derivation of an anharmonic correlated Einstein model for a small cluster. Our present model includes only near-neighbor interactions between absorber and backscattering atoms and their immediate neighbors. These interactions are described by an effective pair potential instead of a single-bond model[12] and must be summed to get the net potential for a single bond. The parameters of our anharmonic

potential are based on a phenomenological potential (e.g., Morse potential) that characterizes the interaction between each pair of atoms. The results of quantum thermodynamic perturbation theory[12,20] are then used to obtain the net thermal expansion (or first cumulant) and the thermal expansion coefficient (given by the derivative), as well as the second and third cumulants. Numerical results for Cu are found to be in good agreement with experiment[3,15,23] and with those calculated by other theories.[1,2,14,19] This illustrates the advantage and simplicity of the present correlated Einstein model in describing anharmonic effects in XAFS. We also discuss how the displacement-displacement correlation functions and multiple-scattering DW factors can be obtained with similar Einstein models.

II. ANHARMONIC CORRELATED EINSTEIN MODEL

We consider the anharmonic correlated Einstein model characterized by an effective potential

$$V_E(x) \cong \frac{1}{2}kx^2 + k_3 x^3 + \cdots, \tag{1}$$

where x is deviation of instantaneous bond length between the two atoms from equilibrium, k is effective spring constant, and k_3 the cubic anharmonicity parameter. The presence of k_3 gives an asymmetry or skew in the pair distribution function. The correlated Einstein model may be defined as the oscillation of a single bond 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. In the center-of-mass frame of this bond the anharmonic Einstein model is defined by the effective single spring potential

$$V_E(x) = V(x) + \sum_{j \neq i} V\left(\frac{\mu}{M_i}x\hat{\mathbf{R}}_{12}\cdot\hat{\mathbf{R}}_{ij}\right), \tag{2}$$

where $\mu = M_1 M_2/(M_1+M_2)$, $\hat{\mathbf{R}}$ is the bond unit vector; 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. The latter contributions are described by the first term in the left side of this

equation. Thus in the second term of Eq. (2) only part of the value x contributes to the interaction potential.

In this paper we will present the results for an anharmonic Morse potential,[22,26] which is appropriate for metals like Cu. Expanded to third order about its minimum this model becomes

$$V(x) = D(e^{-2\alpha x} - 2e^{-\alpha x}) \cong D(-1 + \alpha^2 x^2 - \alpha^3 x^3 + \cdots), \quad (3)$$

where x is the same value defined above, D is the dissociation energy, and $1/\alpha$ corresponds to the width of the potential. It is usually sufficient to consider weak anharmonicity (i.e., first-order perturbation theory) so that only the cubic term in this equation must be kept.

We will illustrate the theory for a simple fcc crystal (e.g., Cu), though the generalization to other structures or longer-range interactions is straightforward. Applying the Morse potential of Eq. (3) to first-near-neighbor bond vibrations, the effective interacting Einsten potential of Eq. (2) (ignoring the overall constant) is given by

$$V_E(x) \cong D\left(\frac{5}{2}\alpha^2 x^2 - \frac{5}{4}\alpha^3 x^3 + \cdots\right). \quad (4)$$

Using Eqs. (1) and (4) as well as the definition[12] $y = x - a$ as the deviation from the equilibrium value of x at temperature T we derive k and k_3,

$$k = 5D\alpha^2\left(1 - \frac{3}{2}\alpha a\right) = \mu\omega^2, \quad k_3 = -\frac{5}{4}D\alpha^3, \quad (5)$$

where a is net thermal expansion or first cumulant $\sigma^{(1)}$. Following FR (Ref. 12) and using the above results in first-order thermodynamic perturbation theory we obtain

$$a = \sigma^{(1)} = \sigma_0^{(1)}\frac{1+z}{1-z} = \frac{\sigma_0^{(1)}}{\sigma_0^2}\sigma^2, \quad \sigma_0^{(1)} = \frac{3\alpha}{4}\sigma_0^2, \quad (6)$$

where $\sigma_0^{(1)}$ and σ_0^2 are zero-point contributions to $\sigma^{(1)}$ and σ^2, respectively, and $z = e^{-\theta_E/T}$ with θ_E as the Einstein temperature. Thus the ratio $\sigma^{(1)}/\sigma^2$ is a constant, independent of
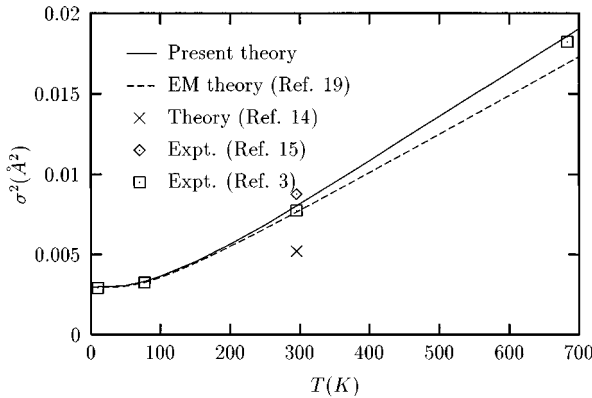

FIG. 1. Temperature dependence of our calculated second cumulant σ^2 (solid), in comparison with experimental values (Ref. 3) ($\square$) and (Ref. 15) ($\diamond$) as well as EM approach results (Ref. 19) (dashed) and another theoretical value (Ref. 14) ($\times$). Our σ^2 is proportional to T at high temperatures and contains zero-point contributions at low temperatures.

TABLE I. Formulas of $\sigma^{(1)}$, σ^2, $\sigma^{(3)}$, and α_T in low-temperature ($T\to 0$) and high-temperature ($T\to\infty$) limits.

	$T\to 0$	$T\to\infty$
$\sigma^{(1)}$	$\sigma_0^{(1)}(1+2z)$	$3k_B T/20D\alpha$
σ^2	$\sigma_0^2(1+2z)$	$k_B T/5D\alpha^2$
$\sigma^{(3)}$	$\sigma_0^{(3)}(1+12z)$	$3(k_B T)^2/50D^2\alpha^3$
α_T	$\alpha_T^0 z(\ln z)^2(1+2z)$	α_T^0

temperature, which is proportional to the anharmonic parameter $\alpha \sim k_3/k$. The second cumulant is given by

$$\sigma^2 = \sigma_0^2\frac{1+z}{1-z}, \quad \sigma_0^2 = \frac{\hbar\omega}{10D\alpha^2}. \quad (7)$$

Following Rabus[21] we may describe the temperature variable $z = e^{-\theta_E/T}$ in terms of σ^2,

$$z = \frac{\sigma^2 - \sigma_0^2}{\sigma^2 + \sigma_0^2}. \quad (8)$$

From Eq. (6) we derive the thermal expansion coefficient

$$\alpha_T = \alpha_T^0\left(\frac{5D\alpha^2}{k_B T}\right)^2(\sigma^2)^2[1 - (\sigma_0^2/\sigma^2)^2], \quad \alpha_T^0 = \frac{3k_B}{20D\alpha r}, \quad (9)$$

and will see later that α_T becomes α_T^0 at high temperatures, where k_B is Boltzmann's constant. Our third cumulant is given by

$$\sigma^{(3)} = \sigma_0^{(3)}\frac{3(\sigma^2)^2 - 2(\sigma_0^2)^2}{(\sigma_0^2)^2}, \quad \sigma_0^{(3)} = \frac{\alpha}{2}(\sigma_0^2)^2, \quad (10)$$

where $\sigma_0^{(3)}$ is the zero-point contribution to $\sigma^{(3)}$. From the above results we obtain a simple relation between cumulants in terms of σ^2,

$$\frac{\sigma^{(1)}\sigma^2}{\sigma^{(3)}} = \frac{1}{2 - (4/3)(\sigma_0^2/\sigma^2)^2}. \quad (11)$$

The above formulas at low and high temperatures are presented in Table I. Note that Eq. (11) approaches the classical expression[10] of 1/2 at high temperatures.

III. RESULTS AND DISCUSSION

We now apply the formulas derived in the previous section to numerical calculations of XAFS cumulants for fcc Cu. The parameters $D = 0.343$ eV (i.e., 3980 K) and $\alpha = 1.359$ Å^{-1} of the Morse potential were taken from Ref. 22; they were obtained using experimental values for the energy of sublimation, the compressibility, and the lattice constant. The Morse potential parameters of Ref. 22 agree with these values within about 10%. However the single spring constant[12] obtained with these parameters $k_s = 2D\alpha^2 = 20.3$ N/m is significantly smaller than the value 27.9 N/m needed to approximate the observed phonon spectra with a single parameter. These differences are indicative of the limitations of a single spring constant model[12] and the possible importance of next-neighbor interactions. The
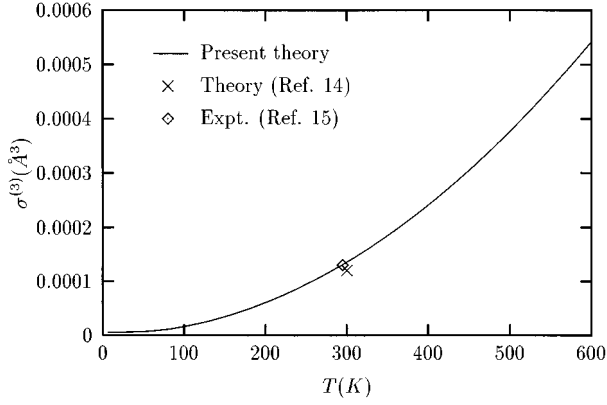
FIG. 2. Temperature dependence of our calculated third cumulant $\sigma^{(3)}$ (solid), in comparison with an experimental result (Ref. 15) ($\diamond$) and another theoretical value (Ref. 14) ($\times$). Our $\sigma^{(3)}$ is proportional to T^2 at high temperatures and contains zero-point contributions at low temperatures.
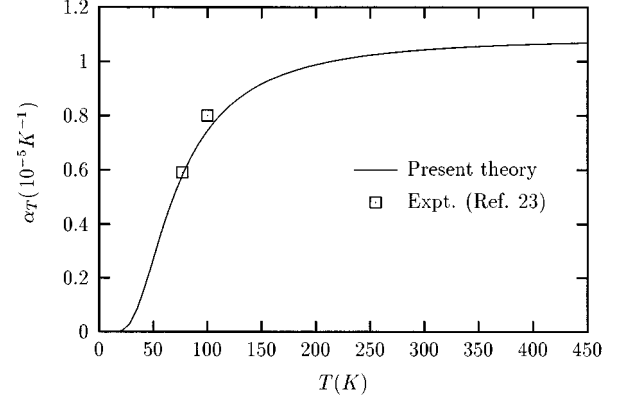

FIG. 3. Temperature dependence of our calculated thermal expansion coefficient α_T (solid), in comparison with experimental values (Ref. 23) ($\square$). Our α_T becomes constant at high temperatures and is very strongly temperature dependent at low temperatures.

Morse potential parmeters yield from Eq. (5) an effective spring constant $k_{\text{eff}} = 50.7$ N/m and, hence, a correlated Einstein temperature $\theta_E \cong 218$ K at 295 K. For completeness, the temperature dependence of k_{eff} was included in Eq. (5), but this dependence for Cu is very small. For example, $k_{\text{eff}} = 50.7$ N/m at 30 K and 49.9 N/m at 295 K. Figure 1 shows the temperature dependence of our calculated second cumulant σ^2, in comparison with the experimental values,[3,15] as well as with the results of the EM approach calculation[19] and another theoretical value[14] at 295 K. The good agreement at low temperatures and small differences at high temperatures between our results and the measured values are reasonable, given the simplicity of the method. However, anharmonic second order terms in perturbation theory become important at high temperatures and yield a correction to σ^2 given by a factor[6] $1 + 36k_3^2 k_B T/k^3 \cong 1 + 9k_B T/20D$, which is an increase of about 3% at 295 K and 8% at 700 K. This explains why at 10 K and 77 K the agreement is better than at high temperatures, and also suggests that the phonon fit spring constant 27.9 N/m may give a better fit than the value 20.3 N/m from single-bond compressibility data. In any case the value of k can also be used as a fitting parameter. Figure 2 illustrates the temperature dependence of our calculated third cumulant $\sigma^{(3)}$, in comparison with measured[15] and theoretical[14] values. Our result at 295 K agrees well with the experimental value. The temperature dependence of our calculated thermal expansion coefficient α_T and comparison with measured values[23] are shown in Fig. 3. Our results for α_T at 77 K and 100 K are close to the experimental values.[23] This temperature dependence has the same form as the specific heat.[12,23,24] We also present in Table II several values of σ^2, $\sigma^{(3)}$, and α_T at different temperatures calculated by our theory and those extracted from experiments[3,15,23] or calculated by other theories.[14] The second cumulant σ^2 describing MSRD and DW factors is primarily a harmonic effect plus small anharmonic contributions which appear only at high temperatures. But $\sigma^{(3)}$ is entirely an anharmonic effect, which is small and difficult to see at low temperatures (Fig. 2).

By using similar Einstein models, we can calculate the mean-square vibrational amplitudes at a given site $u^2 = \langle u_i^2 \rangle$ and the displacement-displacement correlation function $c_R = 2u^2 - \sigma^2 = \langle u_0 u_R \rangle$. At high temperature c_R amounts to roughly 40% of u^2, as in the Debye model,[1,2] and our value 0.21 at 14 K of c_R/u^2 is close to the result[2] 0.20 at 4 K. Multiple-scattering DW factors σ_Γ^2 can be obtained by expanding the effective path length in XAFS to linear order in the fluctuation $\mathbf{u}_i$ at each site i,[25]

TABLE II. Comparison of the thermal expansion coefficient and second and third cumulants of Cu calculated here in this work with those extracted from experiments and calculated by other theories.

T (K)	σ^2 ($\times 10^{-2}$ Å^2)			$\sigma^{(3)}$ ($\times 10^{-3}$ Å^3)			α_T ($\times 10^{-5}$ K^{-1})	
	Present	Expt.[a]	Other[b]	Present	Expt.[c]	Other[b]	Present	Expt.[d]
10	0.298	0.292						
77	0.333	0.325		0.010			0.584	0.59
100	0.365			0.014			0.745	0.80
295	0.803	0.774	0.520	0.131	0.13		1.070	
300	0.817			0.136		0.12	1.072	
683	1.858	1.823					1.090	

[a]Reference 3.
[b]Reference 14.
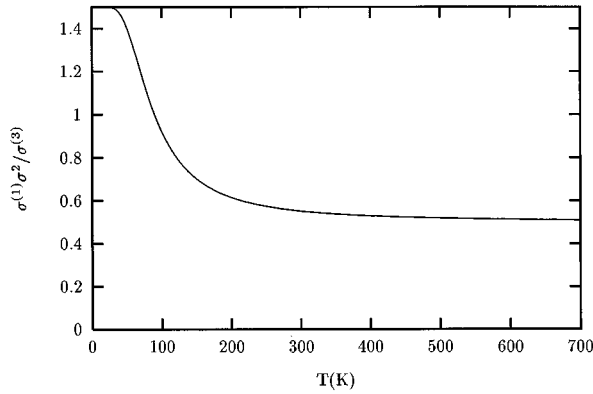[c]Reference 15.
[d]Reference 23.

FIG. 4. Temperature dependence of the relation $\sigma^{(1)}\sigma^2/\sigma^{(3)}$ as a criterion to identify the temperature above which this relation approaches the classical expression (Ref. 10) of 1/2 and the classical limit is applicable. For Cu this temperature is about correlated Einstein temperature ($\theta_E = 218$ K).

$$\sigma_\Gamma^2 = \frac{1}{4}\sum_{ij}\ \langle(\mathbf{u}_i - \mathbf{u}_{i'})\cdot\hat{\mathbf{R}}_{ii'}(\mathbf{u}_j - \mathbf{u}_{j'})\cdot\hat{\mathbf{R}}_{jj'}\rangle,$$

$$i' = i+1, \quad j' = j+1, \quad (12)$$

which contain the components $\langle u_i u_j\rangle\hat{\mathbf{R}}_{ii'}\cdot\hat{\mathbf{R}}_{jj'}$. Therefore, we can obtain σ_Γ^2 in terms of the displacement-displacement correlation functions $\langle u_i u_j\rangle$ calculated above. Thus the correlated Einstein model can also be applied to calculations of multiple-scattering DW factors.

The quantum theory works for any temperature, but reduces to the classical limit at high temperature when $\sigma^2 \gg \sigma_0^2$. Our relation $\sigma^{(1)}\sigma^2/\sigma^{(3)}$ approaches the classical result [10] of 1/2 at high temperatures. Therefore, we can use this relation as a criterion to identify the temperature above which the classical approach is applicable. Figure 4 shows that below the Einstein temperature ($\theta_E = 218$ K) the classical result loses validity.

By using the above formulas and cumulants extracted from XAFS experiment we can derive information about θ_E as well as anharmonic potential parameters. Our description of the anharmonic parameters in terms of σ^2 is convenient, since determination of σ^2 allows one to predict the other cumulants. This correlated Einstein model also avoids extensive full lattice dynamical calculation. The good agreement between our numerical results and experiment to within experimental uncertainty about 20% shows the advantage and simplicity of present model in approximating cumulants and other anharmonic parameters in XAFS.

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