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Extended x-ray-absorption fine-structure Einstein frequency and moments of the phonon spectrum: An experimental and theoretical study

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Extended x-ray-absorption fine-structure measurements of the nearest-neighbor mean-square relative displacements (MSRD) for the fcc materials Ni, Cu, Yb, Pt, Au, Pb, and Th are presented. It is shown experimentally that the temperature dependence of the MSRD is well characterized by a single parameter ω_E, the Einstein frequency. This frequency was found to be equal to the square root of the second moment of the phonon density of states $\langle \omega^2 \rangle^{1/2}$ in all cases studied. Theoretical calculations are presented which show that if nearest-neighbor interactions dominate, ω_E should equal $\langle \omega^2 \rangle^{1/2}$ to within 5%.

INTRODUCTION

We have measured the temperature dependence of the extended x-ray-absorption fine structure (EXAFS) on a large number of fcc materials. For harmonic solids the temperature dependence of EXAFS data is describable by a temperature parameter,[1-3] often called a Debye-Waller factor, in analogy with the x-ray diffraction temperature parameter. Whereas in x-ray diffraction the mean-square displacement of a given type of atom is measured, the relevant quantity in EXAFS measurements is the mean-square relative displacement (MSRD) of the central atom relative to its neighbors. The MSRD, for a pair of atoms at sites l and l' is defined by

$$\sigma_{ll'}^2 = \langle [(\mathbf{u}_l - \mathbf{u}_{l'}) \cdot \hat{\mathbf{R}}_{ll'}]^2 \rangle \; , \tag{1}$$

where $\mathbf{u}_l$ is the displacement of an atom at site l from its equilibrium position $\mathbf{R}_l$, $\hat{\mathbf{R}}_{ll'}$ is a unit vector in the direction $\mathbf{R}_l - \mathbf{R}_{l'}$, and $\langle \cdots \rangle$ denotes a thermal average. Previous work[3,4] has indicated that an Einstein model quite accurately describes the temperature dependence of the MSRD for nearest neighbors. The Einstein model for the nearest-neighbor MSRD gives

$$\sigma^2(T) = \frac{\hbar}{2\mu\omega_E} \coth \left[\frac{1}{2} \frac{\hbar\omega_E}{kT} \right] , \tag{2}$$

where μ is the reduced mass for the atom pair (l,l') and ω_E is the Einstein frequency.

We have measured the MSRD for the first shell of neighbors for the fcc metals $_{28}$Ni, $_{29}$Cu, $_{70}$Yb, $_{78}$Pt, $_{79}$Au, $_{82}$Pb, and $_{90}$Th at a large number of temperatures in the range 20—400 K. The value of ω_E was determined for each metal by least-squares fitting, e.g., (2) to the $\sigma^2(T)$ data; the results are listed in Table I. In Fig. 1 the data are plotted in the dimensionless form $\sigma^2(T)/\sigma^2(0)$ vs T/Θ, where $\Theta_E = (\hbar/k)\omega_E$; the solid lines represent the least-squares fits. Note that for all elements the Einstein model gives a very good fit to the data.

CONNECTION WITH HEAT CAPACITY DATA

One of the earliest methods of measuring phonon properties was to measure the heat capacity as a function of temperature and this method is still widely used. It can be easily shown that certain moments of the phonon density of state (DOS) can be found directly from heat capa-

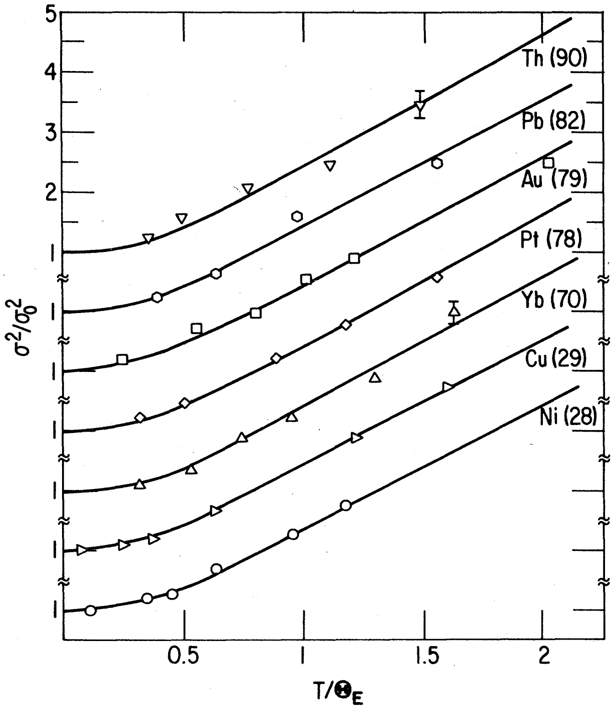

FIG. 1. The normalized MSRD versus reduced temperature for the indicated elements. The normalization parameters are $\sigma_0 = \hbar/2\mu\omega_E$ and $\Theta_E = \hbar\omega_E/k$. Here the ω_E parameters are found by least-square fits of the indicated data and are given in Table I.

TABLE I. A comparison of the Einstein frequency derived from the EXAFS technique [Eq. (2)] and the second moment of the phonon spectra derived from heat capacity [Eq. (3)].

	Einstein frequency from EXAFS (THz)	(second moment)$^{1/2}$ from heat capacity (THz)
$_{29}$Cu	30.0	31.0
$_{70}$Yb	11.0	10.7
$_{78}$Pt	22.8	23.0
$_{79}$Au	17.5	17.5
$_{82}$Pb	9.3	9.2
$_{90}$Th	15.9	16.0

city data. In particular, by making accurate measurements near the Debye temperature, the second moment $\langle \omega^2 \rangle$ can be found[5,6] from fitting the data to the expression for heat capacity, C, at high temperatures, which is

$$C = 3R \left[1 - \frac{\hbar^2 \langle \omega^2 \rangle}{12(kT)^2} + \cdots + (A+\gamma)T \right] . \tag{3}$$

Here R is the gas constant, A is a small anharmonic contribution, and for metals γ is the electronic contribution.[6] In Table I, ω_E and $\langle \omega^2 \rangle^{1/2}$ are shown for all the materials we studied except Ni [for which Eq. (3) does not hold because the magnetic transition gives an additional contribution to the electronic term]. Note the almost exact agreement between the second moment and ω_E. In the next section we discuss the theory of the MSRD and show how this result can be explained.

THEORY

In this section we will derive an expression for ω_E in terms of the moments of the phonon density of states. The presentation will be kept as general as possible, although parts of the discussion will be limited to the case of a monatomic Bravais lattice. This restriction is made only for clarity and simplicity of notation, and the arguments can be modified to give the final result a more general validity, as will be discussed below.

We start by considering the harmonic part of the potential energy for a solid, which can be written in the general form

$$V = \tfrac{1}{2} \sum_{\substack{l,l',\\ \mu,\nu}} u_{l\mu} D_{\mu\nu}(l,l') u_{l'\nu} , \tag{4}$$

where $u_{l\mu}$ is the μth Cartesian coordinate of $\mathbf{u}_l$ and $D_{\mu\nu}(l,l')$ is the dynamical matrix. The MSRD for nearest neighbors, which can be thought of as the mean-square compression of a bond, should depend mainly on the nearest-neighbor central force constant. Hence we choose to express $D_{\mu\nu}(l,l')$ in terms of central pair potentials. After some rearrangement of terms, the thermal average of the harmonic potential energy can be written

$$\langle V \rangle = \tfrac{1}{4} \sum_{l,l'} \alpha_{ll'} \sigma_{ll'}^2 . \tag{5}$$

The double sum over atomic sites can be rewritten in terms of a single sum over coordination shells, and, separating out the first shell term, we get

$$\langle V \rangle = \frac{N}{4} z_1 \alpha_1 \sigma_1^2 + \frac{N}{4} \sum_{j>1} z_j \alpha_j \sigma_j^2 , \tag{6}$$

where z_j is the coordination number for the jth shell and N is the number of atoms in the solid.

In many materials the nearest-neighbor central force constant is an order of magnitude larger than all other force constants, and for such solids we expect the second term on the right-hand side of Eq. (6) to be small compared to the first. Assuming this term to be small (as will later be verified for the case of fcc metals), we can replace it with an approximation. To do so, we note that as j increases the correlation of atomic motions decreases and, for a pair of atoms with one at the origin and the other at site l in shell j, σ_j^2 approaches its limiting value of $[(\mathbf{u}_0 \cdot \hat{\mathbf{R}}_{01})^2] + [(\mathbf{u}_l \cdot \hat{\mathbf{R}}_{01})^2]$. Ignoring anisotropy in the mean-square displacements and assuming a monatomic lattice, there is a single limiting value for σ_j^2, which will be labeled σ_∞^2. This quantity is not only an upper limit, but is also a good approximation for σ_j^2 when $j>1$. Calculations[3] of σ_2^2 and σ_3^2 for some fcc and bcc metals show that the magnitudes of these quantities are typically 70% to 90% of σ_∞^2. Hence, to approximate the term in question, σ_j^2 will be replaced by σ_∞^2. If we also define a (small) parameter λ which characterizes the contribution to the potential energy of higher coordination shells relative to the first, with

$$\lambda = \sum_{j\,(>1)} z_j \alpha_j / z_1 \alpha_1 , \tag{7}$$

we obtain the result

$$\sigma_1^2 \approx \frac{4}{N z_1 \sigma_1} (V) - \lambda \sigma_\infty^2 . \tag{8}$$

If we now use Eq. (4) to determine the equations of motion for the atoms and look for normal mode solutions, we obtain the eigenvalue equation

$$\omega^2 u_{l\mu} = \frac{1}{M} \sum_{\nu,l'} D_{\mu\nu}(l,l') u_{l'\nu} . \tag{9}$$

Since the trace of $D_{\mu\nu}(l,l')$ is equal to the sum of its eigenvalues, we can write

$$3N\overline{\omega^2} = \frac{1}{M} \sum_{\mu,l} D_{\mu\mu}(l,l) , \tag{10}$$

where we have defined the nth moment of the frequency spectrum by

$$\overline{\omega^n} = \frac{1}{3N} \sum_a \omega_a^n . \tag{11}$$

In terms of the central force constant model, the second moment is given by

$$\overline{\omega^2} = \frac{1}{3M} \sum_j z_j \alpha_j , \tag{12}$$

which can be rearranged to give

$$Z_1\alpha_1 = \frac{3}{(1+\lambda)} M\overline{\omega^2} \, . \tag{13}$$

Substitution into Eq. (8) yields

$$\sigma_1^2 = \frac{4(1+\lambda)}{3NM\overline{\omega^2}} \langle V \rangle - \lambda\sigma_\infty^2 \, . \tag{14}$$

Now we consider the temperature dependence of the factors $\langle V \rangle$ and σ_∞^2 in Eq. (14). It follows from the virial theorem that $\langle V \rangle = \frac{1}{2}\langle H \rangle$ for a system of harmonic oscillators, and hence

$$\langle V \rangle = \frac{1}{4} \sum_a \hbar\omega_a \coth\left[\frac{1}{2}\frac{\hbar\omega_a}{kT}\right] . \tag{15}$$

The limiting value of σ_∞^2, assuming cubic symmetry, is equal to $2\langle u_\alpha^2 \rangle = \frac{2}{3}\langle u^2 \rangle$, and its temperature dependence is given by

$$\sigma_\infty^2 = \frac{\hbar}{3NM} \sum_a \frac{1}{\omega_a} \coth\left[\frac{1}{2}\frac{\hbar\omega_a}{kT}\right] . \tag{16}$$

Substitution of Eqs. (15) and (16) into Eq. (14) yields

$$\sigma_1^2 = \frac{\hbar}{3NM\overline{\omega^2}} \sum_a \left[\omega_a + \lambda\left[\omega_a - \frac{\overline{\omega^2}}{\omega_a}\right]\right] \coth\left[\frac{1}{2}\frac{\hbar\omega_a}{kT}\right] , \tag{17}$$

and in the low- and high-temperature limits this becomes

$$\sigma_1^2 = \frac{1}{M\overline{\omega^2}} \times \begin{cases} \hbar\bar{\omega}\left[1+\lambda\left[1-\dfrac{\overline{\omega^2}\,\overline{\omega^{-1}}}{\bar{\omega}}\right]\right], & T \simeq 0 \, , \\ 2kT[1+\lambda(1-\overline{\omega^2}\,\overline{\omega^{-2}})], & T \gg \dfrac{\hbar}{k}\omega_{\max} \, . \end{cases} \tag{18}$$

Comparing these results to the high- and low-temperature limits of Eq. (2), we observe that

$$\omega_E \simeq (\overline{\omega^2})^{1/2} \times \begin{cases} [(\overline{\omega^2})^{1/2}/\bar{\omega}]\left[1+\lambda\left[\dfrac{\overline{\omega^2}\,\overline{\omega^{-1}}}{\bar{\omega}} - 1\right]\right], & T \simeq 0, \\ [1+\frac{1}{2}\lambda(\overline{\omega^2}\,\overline{\omega^{-2}} - 1)], & T \gg \dfrac{\hbar}{k}\omega_{\max} \, . \end{cases} \tag{19}$$

Although we have derived it only for a monatomic Bravais lattice, our formula for ω_E has a more general validity. The derivation can easily be modified for the case of a lattice with a two-atom basis. Furthermore, a crystalline lattice is not required. By introducing configuration averages, one can obtain the same result for ω_E for a monatomic amorphous solid and for diatomic amorphous solids with sufficient symmetry. For some materials, especially covalent solids, angular three-body forces may be significant; however, the nearest-neighbor central force should always dominate, and the first term in (19) should be a reasonable first approximation for ω_E.

We can estimate the moments in Eq. (19) using the Debye model. The result is

$$\omega_E \simeq (\overline{\omega^2})^{1/2} \times \begin{cases} \sqrt{16/15}(1+\frac{1}{5}\lambda), & T \simeq 0, \\ (1+\frac{2}{3}\lambda), & T \gg \dfrac{\hbar}{k}\omega_{\max} \end{cases} \tag{20}$$

with $(\overline{\omega^2})^{1/2} = \sqrt{3/5}\,\omega_D$. If we ignore force constants beyond the second shell, $\lambda = z_2\alpha_2/z_1\alpha_1$. For fcc metals, $z_2/z_1 = \frac{1}{2}$ and $\alpha_2/\alpha_1 \sim 0.1$,[7] and hence one would expect to find $\omega_E \simeq (\overline{\omega^2})^{1/2}$ with a correction factor of approximately 5%.

It is interesting to connect these results with the interpretation of the MSRD in terms of a projected density of modes,[3] $\rho_1(\omega)$, contributing to relative motion,

$$\sigma_1^2 = \frac{\hbar}{2\mu} \int \rho_1(\omega) \frac{1}{\omega} \coth\left[\frac{1}{2}\frac{\hbar\omega}{kT}\right] d\omega \, . \tag{21}$$

The expression (17), with only nearest-neighbor central forces, is equivalent to this with[8]

$$\rho_1(\omega) = \frac{\omega^2}{\overline{\omega^2}} \rho_0(\omega) \, , \tag{22}$$

where $\rho_0(\omega)$ is the normalized phonon density of states. Thus the above analysis also suggests a way to relate the projected density of states to the phonon spectrum and its moments.

DISCUSSION

We have seen experimentally and theoretically that there is a close connection between EXAFS measurements and thermodynamic measurements of the second moment of the phonon density of states for fcc metals. Is this result applicable to more complex solids? To check, we have also compared ω_E to the second moment of NiO and found agreement to within 10%. In more complex solids with more than one kind of near-neighbor some weighting of the various ω_E values for the various pairs of atoms must be done to compare with the second moment. It is not clear exactly how this should be done. In another paper[9] on soft modes in some C-15 compounds a simple optic-mode weighting scheme was used and agreement to within 10% was again found.

The measurement of the MSRD is quite easy and can be done on almost any material. Only small quantities of sample are necessary. If a material shows interesting soft modes the MSRD is sensitive to it. Clearly the EXAFS technique is a valuable tool for studies of average phonon properties of materials.

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