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Temperature and polarization dependence of extended x-ray absorption fine-structure spectra

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The temperature and polarization dependence of the extended x-ray absorption fine structure (EXAFS) is calculated within the framework of a simple approximate form for the theory. A discussion of the microscopic information contained in such dependences is given, and a specific application to the polarization-dependent EXAFS in zinc is made.

I. INTRODUCTION

In the past few years there has been renewed interest[1] in the interpretation and analysis of the so-called extended x-ray absorption fine structure (EXAFS). This revival of interest stems from the dramatic improvement in the intensity of tunable x-ray sources *vis-à-vis* synchrotron radiation and the realization that such experiments give important microscopic information about the local environment surrounding a definite atomic species. The interplay between recent theories of EXAFS and measurements on simple molecular systems have shown how it is possible to extract structural information from measurements on a variety of quite complex systems; more specifically, near-neighbor distances can be extracted. Ideally one would like to characterize the local environment as completely as possible, i.e., we would in principle like to determine the position, type, and number of the central-atom neighbors and to determine such interesting properties as the relative vibrational amplitudes and force constants of these neighbors.

It is the purpose of this paper to discuss in detail the temperature, and to a lesser extent polarization dependence of EXAFS. We will show that an analysis of this dependence gives important information about the local modes of vibration around the central atom. In particular we will show that it is possible to learn a great deal about the mean amplitude of vibrations and force constants of the near neighbors in a harmonic system. We will apply these ideas to an analysis of the polarized anisotropic EXAFS spectrum in zinc.[2]

II. THEORETICAL FORMULATION OF THE PROBLEM

In the simplest theory[3] of EXAFS the oscillatory part of the absorption coefficient χ_0 for a long wavelength photon of frequency ω and polarization vector $\hat{\epsilon}$ is given by

$$\chi_0(\omega,\hat{\epsilon}) = -\sum_j \frac{1}{kR_j^2}\,\mathrm{Im}\left[e^{2ikR_j+2i\delta_1'}f_j(\pi)\right]e^{-2\gamma R_j}(\hat{\epsilon}\cdot\hat{R}_j)^2\,. \tag{1}$$

Here $k=[2m(\omega-\Omega_{\mathrm{th}})]^{1/2}$ is the wave vector of the free electron promoted above threshold (Ω_{th}) to the continuum from the K shell by the photon. The angular dependent factor correctly accounts for the emission probability of an electron from a spherically symmetric ground state to a plane wave propagating in the direction R_j.[3]

Equation (1) describes the modification of the final state as the photoelectron propagates outwards and is backscattered by the jth atom located at $\vec{R}_j$ and then propagates back towards the origin. The spherical outgoing wave has been approximated by a plane wave and $f_j(\pi)$ is the complex backscattering amplitude. The phase shift δ_1' describes the effect of the potential of the excited atom. The isotropic damping factor γ takes into account inelastic scattering of the electron from other electrons.

At any finite temperature the positions $\vec{R}_j$ of the atoms are smeared by thermal vibrations. In all treatments of EXAFS the effect of this vibrational smearing has been included in Eq. (1) by setting R_j equal to its equilibrium value (R_j^0) and multiplying each term in Eq. (1) by a factor $e^{-2k^2\sigma_j^2}$. Since this factor is meant to account for the thermal vibrations of the atoms about their equilibrium sites R_j^0, one usually assumes that the quantity σ_j^2 is identical with the atomic mean-square displacement of the atoms.[4]

The simple formulation of EXAFS, expressed concisely in Eq. (1), explicitly neglects multiple-scattering effects and implicitly hides all of the many-body effects associated with the dynamic response of the many-electron system to the presence of the excited electron and hole in the parameters δ_1', $f_j(\pi)$, γ, and σ_j^2. All but the final one, σ_j^2, are taken to be functions of k, while the quantities δ_1' and $f_j(\pi)$ may be determined empirically from EXAFS measurements on simple molecules.[5] Given these two quantities it is then possible to unambiguously determine structural information, i.e., the positions R_j^0 assuming only that the quantity $\gamma(k)$ is a nonoscillatory function.

The exponential falloff with energy of the oscillatory part of the amplitude is clearly related to the quantities γ and σ_j^2. Since γ characterizes the electronic loss processes (for example, plasmon emission) it is expected to be temperature independent and for most solids, to be roughly isotropic in space. The quantity σ_j^2, on the other hand, since it characterizes the relative oscillatory motion of nearby atoms, is expected to be temperature dependent and anisotropic with respect to the incoming photon polarization vector.

The fact that a quantity of the form $e^{-2k^2\sigma_j^2}$ represents the effect of thermal motion of atoms has been quite widely accepted in even the most refined theories of EXAFS. The precise definition of σ_j^2 and the validity of such an expression, however, has not been thoroughly investigated.[6]

To see the origin of $e^{-2k^2\sigma_j^2}$ we start from Eq. (1) and replace $\vec{R}_j$ by $\vec{R}_j^0+\vec{u}_j-\vec{u}_0$ and retain all the leading terms in $|\vec{u}_j-\vec{u}_0|/R_j^0$. Here $\vec{u}_j$ and $\vec{u}_0$ are, respectively, the jth atom and central-atom displacement vectors. With this replacement, Eq. (1) represents the EXAFS due to an instantaneous configuration, since $\vec{u}_j$ and $\vec{u}_0$ are functions of the time. To obtain the observed EXAFS, we must average over a period which is short on a microscopic scale, but which is long compared with the period of vibration of the atoms. It is simpler, however, to evaluate the ensemble average of Eq. (1) over a canonical ensemble defined by the Hamiltonian of the system, rather than to take a time average. The EXAFS spectrum is then given by

$$\chi=\chi_0\langle e^{2ik\Delta_j}\rangle\,, \tag{2}$$

where $\Delta_j=\hat{R}_j^0\cdot(\vec{u}_j-\vec{u}_0)$.

The exponential in Eq. (2) cannot be expanded, as $k\Delta_j$ is usually much greater than one even for $\Delta_j/R_j^0\ll 1$, so that an evaluation of the temperature dependence of the EXAFS requires the evaluation of

$$\langle e^{2ik\Delta_j}\rangle\equiv\mathrm{Tr}(e^{-\beta H}e^{2ik\Delta_j})\,. \tag{3}$$

In general, such averages cannot be carried out. However, in many cases of interest the vibrations of the atoms are described by a harmonic or quadratic Hamiltonian. This is the case for almost all solids and molecules at low temperature and will be the situation assumed to be true here. In this case we make use of the well-known relation[7]

$$\langle e^{2ik\Delta_j}\rangle=e^{-2k^2\langle\Delta_j^2\rangle} \tag{4}$$

and obtain

$$\chi=\chi_0e^{-2k^2\langle\Delta_j^2\rangle}\,. \tag{5}$$

Thus, only if we assume small harmonic vibrations and if we set

$$\sigma_j^2=\langle\Delta_j^2\rangle\,, \tag{6}$$

do we get the usual form of the EXAFS thermal damping factor.

It is important to note that it is *not* necessary to assume *isotropic* Gaussian atomic displacements. In fact $\langle\Delta_j^2\rangle$, is the mean-square *relative* displacement (MSRD) along $\vec{R}_j$ or, in molecular spectroscopy terminology, the mean-square amplitude of vibration.

In Sec. III, using Eqs. (5) and (6), we discuss what can be learned about the force fields of a system from a study of the temperature dependence of the EXAFS. In Sec. IV, we introduce an approximate method to calculate the temperature-dependent damping of the EXAFS in anisotropic crystals. Finally, we apply this approximate scheme to zinc and compare it with recent experiments.[2]

III. EXAFS AND FORCE FIELDS

For molecules, the possibility of measuring directly the MSRD between atom pairs is of great interest. In modern techniques of molecular structure determination (electron diffraction, microwave, infrared, and Raman) it is important to distinguish between the equilibrium internuclear distance and various kinds of average distances. In particular, for the interpretation of electron diffraction experiments, it is necessary to calculate the MSRD for each atom pair in the molecule to be studied. The calculations are very laborious and always make use of assumptions about the nature of the force-fields. Conversely, the calculated MSRD are used to determine (harmonic) force fields, if they can be obtained by an independent measurement. Presently this can be done only by using electron diffraction. The necessary accuracy can be obtained only in very few cases, by an extremely elaborate experimental procedure.[8]

The utility of EXAFS as a tool in measuring MSRD has yet to be tested. Nevertheless, it is worthwhile to examine in more detail its potential usefulness. In EXAFS experiments it is possible to measure, quite straightforwardly, the MSRD at various temperatures. We will see that it is possible to directly relate the *temperature dependence of the MSRD to the molecular force fields*, themselves.

Let us consider a polyatomic molecule. The treatment[9] of the harmonic vibrations problem involves the secular equation for the normal frequencies ω_n^2. This equation may be written in the form

$$|\underline{G}\underline{F} - \omega^2\underline{1}| = 0\,, \tag{7}$$

where $\underline{G}$ is the inverse "mass" matrix, $\underline{F}$ is the potential energy matrix, and $\underline{1}$ is the unit matrix. The matrices $\underline{G}$ and $\underline{F}$ are specified by a complete set of internal displacement coordinates (e.g., bond lengths and angle displacements). This set of coordinates we represent by the column matrix $\underline{S}$. The MSRD amplitude matrix is defined by[10]

$$\underline{\Sigma} = \langle \underline{S}\,\underline{S}^{+}\rangle\,, \tag{8}$$

where $\langle\cdots\rangle$ means thermal averaging. The diagonal elements of $\underline{\Sigma}$ are the MSRD of vibrations, i.e., we can choose a coordinate system such that $\langle\Delta^2{}_j\rangle = \Sigma_{jj}$. Transforming $\underline{S}$ to normal coordinates $\underline{Q}$ using the matrix $\underline{L}$

$$\underline{S} = \underline{L}\,\underline{Q}\,, \tag{9}$$

we obtain

$$\underline{\Sigma} = \underline{L}\langle\underline{Q}\,\underline{Q}^{+}\rangle\underline{L}^{+}\,, \tag{10}$$

where

$$\langle Q\,Q^{+}\rangle_{nn'} = [(\hbar/2\omega_n)\coth\tfrac{1}{2}\beta\hbar\omega_n]\delta_{nn'} \tag{11}$$

and $\beta = 1/kT$.

In the high-temperature region one can derive a simple relationship between Σ and the molecular force fields. Using the well-known relations

$$\begin{aligned}(\underline{L}^{+}\underline{F}\,\underline{L})_{nn'} &= \omega_n^2\delta_{nn'}\,,\\ \underline{L}\,\underline{L}^{+} &= \underline{G}\end{aligned} \tag{12}$$

and expanding the hyperbolic cotangent in Eq. (11):

$$\coth\tfrac{1}{2}\beta\hbar\omega_n = 2/\beta\hbar\omega_n + \tfrac{1}{8}\beta\hbar\omega_n\,, \tag{13}$$

we obtain

$$\underline{\Sigma} = (1/\beta)\underline{F}^{-1} + \tfrac{1}{16}\hbar^2\beta\underline{G}\,. \tag{14}$$

If we choose the internal coordinate system so that the diagonal element Σ_{jj} is the MSRD of the jth bond (i.e., the bond length between the central atom and the atom at $\vec{R}_j$), we have

$$G_{jj} = 1/\mu\,. \tag{15}$$

Here μ is the reduced mass of the pair of atoms forming the jth bond. Finally, from Eqs. (14) and (15), we obtain

$$\langle\Delta_j^2\rangle = \Sigma_{jj} = (1/\beta)F_{jj}^{-1} + \tfrac{1}{16}\hbar^2(\beta/\mu)\,. \tag{16}$$

In a typical EXAFS experiment, it would be a simple matter to deduce F_{jj}^{-1} from the slope of the high-temperature values of $\langle\Delta_j^2\rangle$. This measured value could then be used to *test* the force-field model on which the $\underline{F}$ matrix is based. In electron diffraction measurements[11] of $\langle\Delta_j^2\rangle$ there have been, to date, no temperature-dependent measurements. Such a situation arises because of the complexity of performing such measurements.

IV. MEAN-SQUARE RELATIVE DISPLACEMENTS IN CRYSTALS

For perfect cyrstals it is convenient to rewrite the MSRD $\langle\Delta_j^2\rangle$ in terms of the *mean-square displacements* (MSD) $\langle(\vec{u}_j\cdot\vec{R}_j)^2\rangle$, $\langle(\vec{u}_0\cdot\hat{R}_j)^2\rangle$ and the *displacement correlation function* (DCF) $\langle(\vec{u}_0\cdot\hat{R}_j)(\vec{u}_j\cdot\hat{R}_j)\rangle$; i.e.,

$$\langle\Delta_j^2\rangle = \langle(\vec{u}_0\cdot\hat{R}_j)^2\rangle + \langle(\vec{u}_j\cdot\hat{R}_j)^2\rangle - 2\langle(\vec{u}_0\cdot\hat{R}_j)(\vec{u}_j\cdot\hat{R}_j)\rangle\,. \tag{17}$$

This form is useful as we wish to discuss separately the role played by the MSD and by the DCF.

In a monoatomic crystal we have[12]

$$\langle\Delta_j^2\rangle = \frac{\hbar}{NM}\sum_{\vec{q}\lambda}(\hat{e}_{\vec{q}\lambda}\cdot\hat{R}_j)^2\frac{1}{\omega_{\vec{q}\lambda}} \times (\coth\tfrac{1}{2}\beta\omega_{\vec{q}\lambda})[1-\cos(\vec{q}\cdot\vec{R}_j)]\,, \tag{18}$$

where N is the number of atoms of mass M, and $\hat{e}_{\vec{q}\lambda}$ is the polarization vector for phonons of momentum $\vec{q}$, polarization λ, and frequency $\omega_{\vec{q}\lambda}$. The first term on the right-hand side of Eq. (18) is twice the MSD which is independent of the central atom neighbor distance and determines the decrease in the EXAFS amplitude as a result of the "total" thermal motion of the atoms along $\hat{R}_j$. When this term is inserted in Eq. (5) the resulting expression is formally identical to the Debye-Waller factor with $2k\hat{R}_j$ replacing the x-ray momentum transfer.

The second term in Eq. (18) ensures that only *out-of-phase* thermal motion of the atoms along $\hat{R}_j$ determines the decrease in the EXAFS amplitude. This term is most interesting as it also determines the R_j dependence of the damping factor and it can be computed, e.g., if a lattice-dynamical force model is available.

In anisotropic crystals a study of the various components of the MSD in the principal directions gives one a good experimental test of dynamical force models. Similarly, an experimental determination of MSRD would reflect directly on the stretching of various near-neighbor bonds in a crystal. While there have been many calculations of MSD,[7] to our knowledge there have been no calculations of MSRD. This situation is undoubtedly due to the lack of good experimental data. In the absence of such calculation of the DCF based on a lattice-dynamical force model it is not unreasonable to approximately evaluate the relative importance of the DCF versus the MSD by using a simple

Debye model of the lattice vibrations.

For the moment, let us restrict our attention to a monoatomic cubic crystal. In this case we can replace $(\hat{e}_{\vec{q}\lambda}\cdot\hat{R}_j)^2$ in Eq. (18) with $\frac{1}{3}$. Then, using the Debye approximation for the density of states it is straightforward to show that

$$\langle\Delta_j^2\rangle=\frac{3\hbar}{M\omega_D}\left[\frac{1}{4}+\left(\frac{T}{\Theta_D}\right)^2\Phi_1\right]-\frac{3\hbar}{M\omega_D}\left\{\frac{1-\cos(q_DR_j)}{2(q_DR_j)^2}+\left(\frac{T}{\Theta_D}\right)^2\left[\Phi_1-\frac{1}{3!}\left(q_DR_j\frac{T}{\Theta_D}\right)^2\Phi_3+\frac{1}{5!}\left(q_DR_j\frac{T}{\Theta_D}\right)^4\Phi_5-\cdots\right]\right\}, \tag{19}$$

where

$$\Phi_n=\int_0^{\Theta_D/T}dx\frac{x^n}{e^x-1}. \tag{20}$$

In this expression ω_D, Θ_D, and q_D are the Debye frequency, temperature, and wave vector, respectively. The first term on the right-hand side is twice the MSD while the second term is twice the DCF. To get a rough idea of the relative size of the various forms we have numerically computed the ratio of the first shell DCF to the MSD for bcc and fcc lattices as a function of temperature. The results are shown in Fig. 1. The most interesting feature is the magnitude of the DCF term which amounts to roughly 40% of the MSD at high temperature in both cases. Although this conclusion is reached within an approximate model we have an indication that the use of the measured MSD for σ_j^2, as is usually the case, is incorrect.

We would like to make a comparison of those theoretical ideas to recent experiments in zinc. Since zinc is anisotropic we cannot use a simple Debye model. As an artifice, however, a directional Debye temperature originally proposed by Gruneisen and Goens,[12] can be introduced in order to give a good rough parameterization of the actual spectra. In essence, for an anisotropic system a directional Debye temperature is associated with the component of the MSD in a given direction, as if the system were isotropic and all the atoms vibrated with the particular component of the MSD associated with that direction; e.g., in the x direction

$$\langle u_x^2\rangle=(3\hbar/M\omega_D)[\tfrac{1}{4}+(T/\Theta_{Dx})^2\Phi_1]. \tag{21}$$

For zinc the MSD parallel to the basal plane and perpendicular to it are known from thermodynamic and inelastic neutron data and have been calculated by Barron and Munn.[13] Thus we can determine the Debye temperatures $\Theta_{D\parallel}, \Theta_{D\perp}$ and use the results of Fig. 1 for an fcc lattice (which has $q_DR_1=4.37$ as for hcp) to determine, at each temperature, the value of the ratios of the DCF to the MSD parallel and perpendicular to the basal plane.[14] This is a hybrid scheme in which the MSD are accurately known (from experiment and lattice-dynamical force models), while the relative weight of the DCF is calculated on the basis of the anisotropic Debye model. The results for the MSRD parallel $(\sigma_\parallel^2)$ and perpendicular $(\sigma_\perp^2)$ to the basal plane are

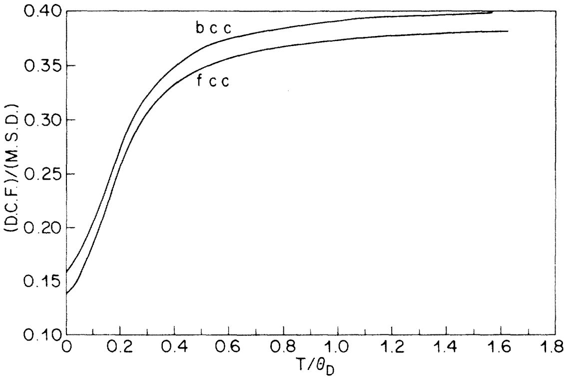

FIG. 1. Temperature dependence of the ratios of the displacement correlation function (DCF) $\langle\vec{u}_0\cdot\hat{R}_1)(\vec{u}_1\cdot\hat{R}_1\rangle$ and the mean-square displacement (MSD) $\langle(\vec{u}_0\cdot\hat{R}_1)^2\rangle$. Results are obtained within the Debye model for fcc and bcc crystals and refer to the first shell only.

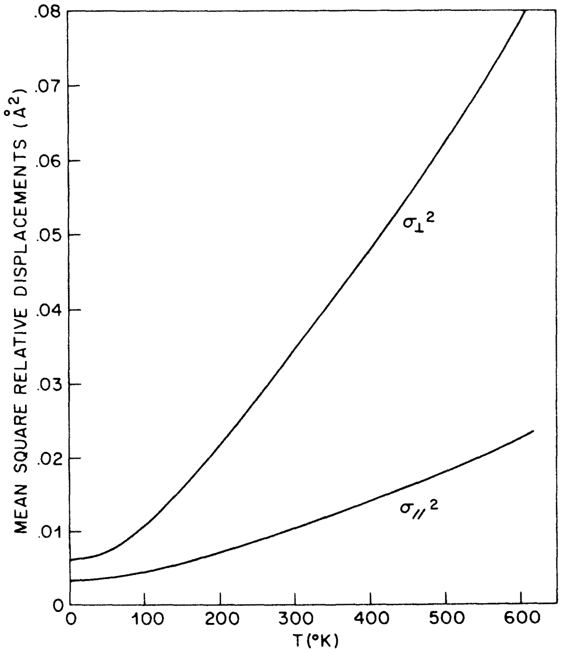

FIG. 2. Temperature dependence of the mean-square relative displacements of zinc parallel $(\sigma_\parallel^2)$ and perpendicular $(\sigma_\perp^2)$ to the basal plane. Results refer to the first shell only.

shown in Fig. 2. Here we have plotted $\sigma_{\parallel}^2$ and $\sigma_{\perp}^2$ as a function of temperature for the first shell only. The theoretical result based on this simple model clearly predicts a large anisotropy in the EXAFS damping factor. It is also important to point out that the calculated MSRD values are considerably smaller than twice the MSD.

At room temperature the preliminary data[2] for $\sigma_{\parallel}^2$ and $\sigma_{\perp}^2$ in zinc are

$$\sigma_{\perp}^2 = 0.04 \pm 0.005\,\text{Å}^2, \quad \sigma_{\parallel}^2 = 0.015 \pm 0.005\,\text{Å}^2 ,$$

which are in semiquantitative agreement with the theory. Thus, although our scheme only takes into account the DCF in an approximate way, we may conclude that in many materials such considerations are important.

V. CONCLUSION

In this paper we have examined a few related aspects of the temperature dependence of the EXAFS spectra. We have shown that the thermal vibrations of the atoms about their equilibrium positions can simply be taken into account by using Eq. (2) as long as one assumes harmonic displacements. For molecular systems we were then able to show that the temperature dependence of σ_j^2 is simply related to the force field of the system. Such a relation can be used to test force-field models provided enough accuracy on σ_j^2 is available. In addition we have discussed the actual evaluation of σ_j^2 in perfect crystals. With increased experimental accuracy it may become necessary to calculate the DCF from a detailed lattice force model. In this paper we have, instead, introduced an approximation scheme of evaluating σ_j^2 which can be used both in isotropic and anisotropic crystals, if the Debye-Waller factor is known. We have applied this hybrid scheme to the case of zinc and we find a semiquantitative agreement with the experiments. In this respect the most interesting result is the large contribution of the displacement correlation function to σ_j^2. This indicates the inadequacy of identifying measured mean-square displacements with the σ_j^2, even at a very approximate level.

EXAFS is still in the process of being explored as a potential tool for structural analysis. The accuracy of the information obtainable is still very uncertain. As far as the temperature dependence is concerned, the situation is even more obscure, owing to the scarcity of experimental data. In our discussion we have made numerous approximations. For example, we have completely neglected anharmonicity and restricted the formulation to the approximation given by Eq. (1). We feel, however, that much remains to be done before more detailed theoretical comparisons can really be made meaningful.

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