PHYSICAL REVIEW B VOLUME 20, NUMBER 12 15 DECEMBER 1979

Extended x-ray absorption fine structure Debye-Waller factors. I. Monatomic crystals

E. Sevillano and H. Meuth
Aerospace and Energetics Research Laboratory, University of Washington, Seattle, Washington 98195

J. J. Rehr
Department of Physics, University of Washington, Seattle, Washington 98195
(Received 24 May 1979)

Debye-Waller factors in the extended x-ray absorption fine structure (EXAFS) are related to the mean-square fluctuations in interatomic distances, σ_R^2. Monte Carlo calculations of σ_R^2 based on lattice-dynamical models are presented for crystalline Cu, Fe, and Pt. The results are compared with correlated Einstein and Debye models, with experimental data and with the mean-square vibrational amplitudes $u_{\hat{q}}^2$ which enter the Debye-Waller factor in x-ray diffraction.

I. INTRODUCTION

The analysis of the extended x-ray absorption fine structure (EXAFS) has become an important technique for determining the microscopic structure of molecules and solids.[1] The success of this technique is due in part to a relatively simple parameterization of the EXAFS spectra,[2]

$$\chi = \sum_R \frac{N_R f_R A_R}{kR^2} \sin(2kR + \delta_R) e^{-\lambda R} e^{-2\sigma_R^2 k^2} , \quad (1)$$

in terms of such structural quantities as interatomic distances R, their mean-square fluctuations σ_R^2, and the coordination numbers N_R of the shell at radius R. The remaining parameters in Eq. (1) include the photoelectron wave number k, a backscattering amplitude f_R, an amplitude reduction factor[3] A_R, a net phase shift[4,5] δ_R, and a decay constant λ.

Although studies of various terms in Eq. (1) have been carried out,[2–5] relatively little attention has been directed at precise calculations of the Debye-Waller factors $e^{-2\sigma_R^2 k^2}$. A knowledge of σ_R^2 is important both for testing our fundamental understanding of EXAFS and for precise determinations of coordination numbers from EXAFS. Beni and Platzman[6] have discussed the theory of σ_R^2 in general terms and have developed an approximate Debye model which includes correlations. An earlier treatment also based on the Debye approximation is given by Shmidt.[7] A thorough discussion of methods for calculating σ_R^2 within the harmonic approximation is given in a forthcoming paper.[8]

The purpose of this note is to compare several theoretical calculations of σ_R^2 among themselves and with experimental data.[9,10] In particular we present calculations of $\sigma_R^2(T)$ for crystalline Cu, Fe, and Pt, as a function of temperature, for several multiparameter force-constant models fit to the observed phonon spectra.[10-15] We have chosen crystalline Cu since it is one of the standard substances used to test theories of EXAFS[2–4] and because its vibrational properties are well known.[10–12] For comparison we have examined Pt, a more complex fcc crystal,[13] and Fe,[14,15] which has a bcc crystal structure.

II. CALCULATION

By definition the mean-square atomic vibrational amplitudes $u_{\hat{q}}^2$ and the mean-square fluctuations in interatomic distances σ_R^2 are given, respectively, by

$$u_{\hat{q}}^2 = \langle (\vec{u}_{\vec{R}} \cdot \hat{q})^2 \rangle \quad (2)$$

and

$$\sigma_R^2 = \langle [(\vec{u}_{\vec{R}} - \vec{u}_{\vec{0}}) \cdot \hat{R}]^2 \rangle , \quad (3)$$

where the brackets refer to a thermal average and $\vec{u}_{\vec{R}}$ is the displacement vector at lattice point $\vec{R}$. For monatomic, Bravais crystals, an expansion of $\vec{u}_{\vec{R}}$ in Eq. (3) in normal modes (assuming the validity of the harmonic approximation[16]) leads to the expression

$$\sigma_R^2 = \frac{\hbar}{MN} \sum_{\vec{k},\lambda} (\hat{\epsilon}_{\vec{k},\lambda} \cdot \hat{R})^2 \frac{(1 - \cos\vec{k}\cdot\vec{R})}{\omega_{\vec{k},\lambda}} \coth(\beta\hbar\omega_{\vec{k},\lambda}/2) . \quad (4)$$

Here $\vec{k}$ runs over a Brillouin zone, $\lambda = 1$, 2, and 3 is a polarization index, $\omega_{\vec{k},\lambda}^2$ and $\hat{\epsilon}_{\vec{k},\lambda}$ are, respectively, the eigenvalues and eigenvectors of the dynamical matrix, $\beta = 1/k_B T$, M is the atomic mass, and N is the number of atoms in the crystal. The expression for $u_{\hat{q}}^2$ is similar except that the factor $(1 - \cos\vec{k}\cdot\vec{R})$ is replaced by $\frac{1}{2}$. For the monatomic, cubic crystals of interest here, $u_{\hat{q}}^2 \equiv u^2$ is independent of $\hat{q}$ and $\sigma_R^2 \equiv \sigma_j^2$ ($j = 1,2,\ldots$) is the same for all atoms in a given shell j.

Equation (4) is equivalent to the more convenient integral expression,

$$\sigma_R^2 = \frac{\hbar}{M} \int d\omega\, \rho_R(\omega) \frac{\coth(\beta\hbar\omega/2)}{\omega} . \tag{5}$$

Here

$$\rho_R(\omega) = \sum_{\vec{k},\lambda} (\hat{\epsilon}_{\vec{k},\lambda} \cdot \hat{R})^2 (1 - \cos \vec{k} \cdot \vec{R}) \delta(\omega - \omega_{\vec{k},\lambda}) \tag{6}$$

is the normalized, projected density of modes contributing to relative vibrational motion, which can be calculated once and for all for a given shell. The analogous expression for u^2 is similar except that $\rho_R(\omega)$ in Eq. (5) is replaced by $\frac{1}{2}\rho(\omega)$, where $\rho(\omega)$ is the total density of modes per atom; this quantity is given by Eq. (6) with a factor $\frac{1}{3}$ replacing $(\hat{\epsilon}_{\vec{k},\lambda} \cdot \hat{R})^2 (1 - \cos \vec{k} \cdot \vec{R})$. A spherical average in Eq. (6) leads to a closed form expression for $\rho_R(\omega)$ appropriate for the correlated Debye model

$$\rho_R(\omega) = \frac{3\omega^2}{\omega_D^3} \left[1 - \frac{\sin \omega R/c}{\omega R/c} \right] , \tag{7}$$

where $\omega_D = k_B \Theta_D / \hbar$ is derived from the Debye temperature Θ_D, and $c = \omega_D / k_D$ where $k_D = (6\pi^2 N/V)^{1/3}$, and V is the crystal volume. The use of Eq. (7) in Eq. (5) simplifies the calculation of σ_R^2 with the Debye model, in that only a single Bose integral is required at each temperature.[17]

III. RESULTS AND DISCUSSION

We have evaluated $\rho_R(\omega)$ in Eq. (6) by a Monte Carlo sampling technique using between 2000 and 10 000 points in a Brillouin zone for a number of force-constant models[10–15] representative of Cu, Fe, and Pt. Plots of $\rho(\omega)$ and $\rho_R(\omega)$ for the first and second shells of Cu and Fe are presented in Fig. 1; for comparison $\rho(\omega)$ and $\rho_R(\omega)$ are also given for the Debye model for Cu. Our results for σ_R^2 and u^2 from 10 000 point runs are given in Table I; the statistical error in these results is of order 1%. We have found that different force-constant models give results differing by 5–10%; this is illustrated for Cu in Fig. 2 using the models of Svensson *et al.*[10] (model A), Nicklow *et al.*[12] (model B), and a single, central-force-constant model (model C). Representative points extracted from experimental data[9] by the *ratio method* are included for comparison, and we refer the reader to those papers for additional details. Briefly this method is based on a plot of $\ln[\chi_R(T_1)/\chi_R(T_2)]$ vs k^2, where χ_R is the contribution in Eq. (1) to χ from shell R; if the plot yields a straight line its slope is taken to be $2[\sigma_R^2(T_2) - \sigma_R^2(T_1)]$. The results indicate that models B and C fit the data somewhat better than model A does below 500 K.

A comparison of these results with those obtained from the Einstein and Debye approximations is difficult, owing to the arbitrariness in the choice of Ein-

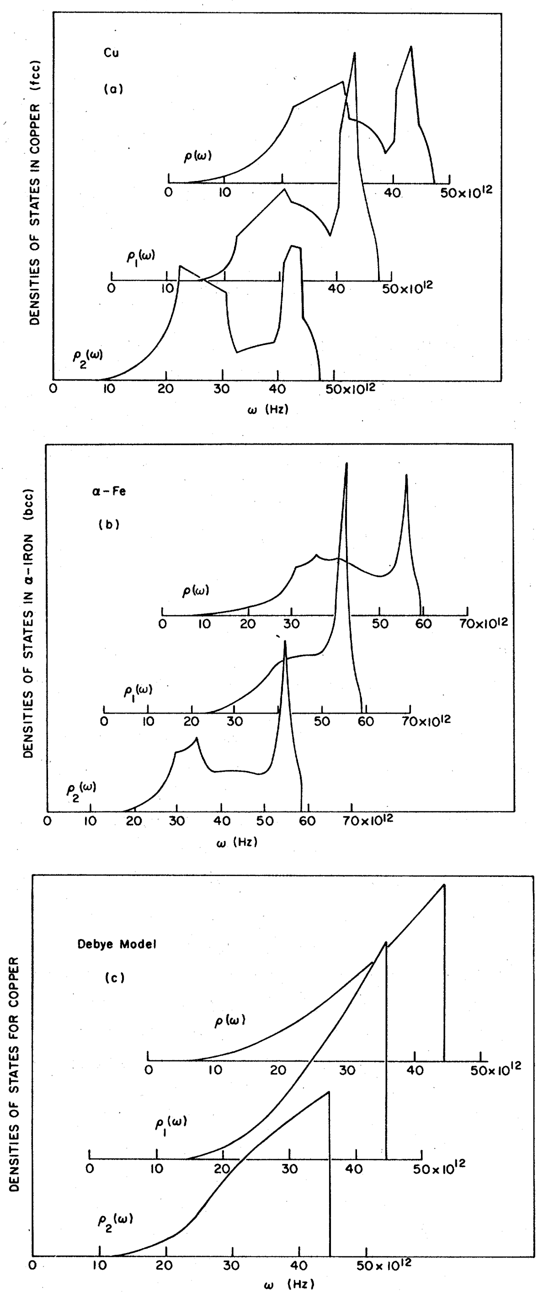

FIG. 1. Total density of modes $\rho(\omega)$ and projected densities of modes for shells 1 and 2, $\rho_i(\omega)$, vs frequency ω for (a) Cu and (b) α-Fe, from smoothed Monte Carlo calculations, and (c) for the Debye model for Cu.

TABLE I. Mean-square vibrational amplitudes u^2 and σ_R^2 in units of 10^{-3} Å^2 calculated with force-constant models for Cu (Ref. 12), Fe (Ref. 15), and Pt (Ref. 13).

T	Cu (fcc)				Fe (bcc)			Pt (fcc)		
(K)	u^2	σ_1^2	σ_2^2	σ_3^2	u^2	σ_1^2	σ_2^2	u^2	σ_1^2	σ_2^2
4	1.77	2.95	3.43	3.34	1.55	2.51	2.85	0.83	1.33	1.57
10	1.78	2.95	3.43	3.34	1.56	2.51	2.85	0.84	1.33	1.57
20	1.80	2.96	3.44	3.34	1.57	2.51	2.85	0.86	1.34	1.59
40	1.89	2.99	3.53	3.41	1.64	2.52	2.87	0.98	1.40	1.73
77	2.29	3.28	4.08	3.88	1.86	2.61	3.07	1.36	1.71	2.28
150	3.44	4.50	5.99	5.61	2.61	3.19	4.00	2.30	2.67	3.75
295	6.19	7.70	10.62	9.87	4.49	5.06	6.60	4.33	4.86	6.99
400	8.26	10.18	14.13	13.13	5.94	6.51	8.65	5.83	6.50	9.39
700	14.27	17.44	24.37	22.60	10.18	10.97	14.73	10.15	11.25	16.31

stein and Debye temperatures. We have found that the correlated Debye model,[6,7] referred to as model D [Eqs. (7) and (5)], with Debye temperatures quoted in the literature[18] [$\Theta_D \simeq 315$ K (Cu), 225 K (Pt), and 420 K (Fe)] yields results for σ_R^2 and u^2 which are close to those from the force-constant models. Considering the simplicity of the Debye model and the differences between the results for models $A-C$ and experiment, the Debye model has much to recommend itself, especially for the nearly isotropic systems studied here.

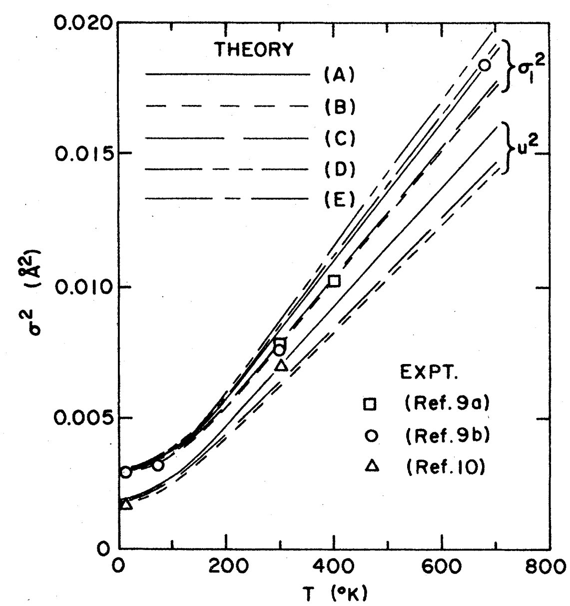

FIG. 2. Mean-square vibrational amplitudes u^2 and σ_1^2 for the first shell of Cu vs temperatures as calculated from various force-constant models [A (Ref. 10), B (Ref. 12), and C (single parameter)], from the Debye model (D), and from the Einstein model (E), and as determined from experiment in Refs. 9 and 10.

In the Einstein approximation (model E), which is adequate for many purposes, ρ_R is replaced by a δ function,

$$\rho_R(\omega) = \delta(\omega - \omega_E(R)) \ . \tag{8}$$

and hence σ_R^2 has a very simple form,

$$\sigma_R^2(\omega) = \frac{\hbar}{M\omega_E} \coth(\beta\hbar\omega_E/2) \ . \tag{9}$$

As discussed in Ref. 8, the Einstein frequency appropriate for EXAFS is intermediate between $(\mu_{-1})^{-1}$ and $(\mu_{-2})^{-1/2}$, depending on the temperature range of interest, where μ_p are the power moments of the exact density $\rho_R(\omega)$ in Eq. (6). These moments can be calculated exactly for the correlated Debye model and averaged, which is the approach adopted here. In terms of the Debye frequencies $\omega_D = k_B\Theta_D/\hbar$, the approximate values,

$$\omega_E(u^2) \simeq \tfrac{3}{5}\omega_D \tag{10}$$

and

$$\omega_E(\sigma_1^2) \simeq \tfrac{3}{4}\omega_D \ , \tag{11a}$$

$$\omega_E(\sigma_2^2) \simeq \tfrac{2}{3}\omega_D(\text{fcc}) \ , \ \text{or} \ \tfrac{7}{10}\omega_D \ (\text{bcc}) \ , \tag{11b}$$

in Eq. (8), with the Debye temperatures noted above, yield results comparable to those from the Debye model over a wide temperature range (Fig. 2).

An additional comparison of these theories is provided by the difference between $2u^2$ and σ_R^2, which is twice the radial displacement-displacement correlation function,[6] $c_R = \langle \vec{u}_0 \cdot \hat{R} \ \vec{u}_R \cdot \hat{R} \rangle$. The ratio c_R/u^2 tends to a model-dependent constant at large and small temperatures, which we have compared in Table II. Note that the Debye model tends to un-

TABLE II. Correlation function c_R/u^2 calculated with force-constant models for Cu (Ref. 12), Fe (Ref. 14), and Pt (Ref. 13), and with correlated Einstein (Ref. 8) and Debye (Ref. 6) models.

Temp. (K)	Model	Shell	Cu 1	Cu 2	Fe 1	Fe 2	Pt 1	Pt 2
4	Force const.		0.178	0.032	0.196	0.082	0.197	0.051
	Debye		0.146	0.001	0.163	0.068	0.148	0.002
	Einstein		0.2	0.10	0.2	0.14	0.2	0.10
700	Force const.		0.415	0.167	0.468	0.276	0.446	0.218
	Debye		0.387	0.232	0.405	0.324	0.387	0.233
	Einstein		0.36	0.18	0.36	0.26	0.36	0.18

derestimate the correlations slightly, the Einstein approximation is worse. With present experimental precision, however, the differences are not easily distinguishable.

In conclusion, we find that for the first few shells of monatomic cubic crystals, all of the models examined (Einstein, Debye, and single or multiparameter force-constant models) can provide a reasonable fit to the experimental data. Given the discernable differences between the various calculations and experiment, however, we believe that EXAFS can provide a useful test of the validity of a given force-constant model.

ACKNOWLEDGMENTS

We thank F. Lytle, B. Greegor, and P. Rabe for informing us of their experimental results prior to publication, and D. M. Bylander for advice on Monte-Carlo integration routines. This work was supported in part by NSF Grants Nos. DMR76-82112 and DMR79-07238.

[1]E. A. Stern, Contemp. Phys. 19, 289 (1978).

[2]E. A. Stern, Phys. Rev. B 10, 3027 (1974); P. A. Lee and J. B. Pendry, *ibid.* 11, 2795 (1975); C. A. Ashley and S. Doniach, *ibid.* 11, 1279 (1975).

[3]J. J. Rehr, E. A. Stern, R. L. Martin, and E. R. Davidson, Phys, Rev. B 17, 560 (1978).

[4]P. A. Lee and G. Beni, Phys. Rev. B 15, 2862 (1977).

[5]B. K. Teo and P. A. Lee, J. Am. Chem. Soc. 101, 2815 (1979).

[6]G. Beni and P. M. Platzman, Phys. Rev. B 14, 1514 (1976).

[7]V. V. Shmidt, Bull. Acad. Sci. USSR, Ser. Phys. 25, 998 (1961); 27, 392 (1963); a summary of this work is given by D. E. Sayers, Ph.D. thesis (University of Washington, 1971) (unpublished).

[8]J. J. Rehr (unpublished).

[9]W. Böhmer and P. Rabe, J. Phys. C 12, 2465 (1979); R. B. Greegor and G. W. Lytle, this issue, Phys. Rev. B 20, 4902 (1979).

[10]E. C. Svensson, B. N. Brockhouse, and J. M. Rowe, Phys. Rev. 155, 619 (1967).

[11]P. A. Flinn, G. M. McManus, and J. A. Rayne, Phys. Rev. 123, 809 (1961).

[12]R. M. Nicklow, G. Gilat, H. G. Smith, L. J. Raubenheimer, and M. K. Wilkinson, Phys. Rev. 164, 922 (1967).

[13]G. G. E. Low, Proc. Phys. Soc. 79, 479 (1962).

[14]V. J. Minkiewicz, G. Shirane, and R. Nathans, Phys. Rev. 162, 528 (1967).

[15]D. H. Dutton, B. N. Brockhouse, and A. P. Miiller, Can. J. Phys. 50, 2915 (1972).

[16]A. A. Maradudin, E. W. Montroll, G. H. Weiss, and I. P. Ipatova, *Theory of Lattice Dynamics in the Harmonic Approximation,* 2nd ed. (Academic, New York, 1971).

[17]A HP-25 program for calculations of σ_R^2 with the Debye model is available from the authors.

[18]F. H. Herbstein, Adv. Phys. 10, 313 (1961).