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ABSTRACT

We present an exact and efficient method to calculate both thermal and structural damping of the multiple scattering (MS) contributions to the x-ray absorbtion coefficient. Our method, which accouts for the correlations, gives some results which indicate that only for the EXAFS signal the dominat damping is given by a simple Debye-Waller type of correction in the amplitude. In the higher order contribution to total cross section phase effects become important and can alter the effective damping. In the case of structural disorder we show how the MS signal is capable of providing new structural information in such a way to allow us to distinguish between various amorphous structural model.

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We present an exact and efficient method to calculate both thermal and structural damping of the multiple scattering (MS) contributions to the x-ray absorbtion coefficient. Our method, which accouts for the correlations, gives some results which indicate that only for the EXAFS signal the dominat damping is given by a simple Debye-Waller type of correction in the amplitude. In the higher order contribution to total cross section phase effects become important and can alter the effective damping. In the case of structural disorder we show how the MS signal is capable of providing new structural information in such a way to allow us to distinguish between various amorphous structural model.

Recently several attempts have been made in order to extract from a XAS spectrum of different systems the multiple scattering (MS) contributions (proportional to the higher order correlation functions) leading to encouraging results [1,2].

A focal point which has to be clarified at the theoretical level is the effect of the thermal vibrations of the atoms and structural disorder on the various contributions χ_n to the multiple scattering series.

Using a high temperature expansion for the vibrational correlation function [3,4], we obtain the correlation matrices, among the coordinates of the atoms connected by multiple scattering paths, which define the widths of the gaussian peak in the N-body strucural correlation function. In this way we can calculate the effects of the thermal and structural disorder on the MS contributions simply evaluating the quantity [5]:

$$\langle \chi_n(k) \rangle = \int d\mathbf{r} \frac{e^{-\frac{1}{2}(\mathbf{r}, M^{-1}\mathbf{r})}}{(2\pi)^{\frac{N}{2}} \, \mathrm{Det}(M)^{\frac{1}{2}}} \; A(k, \mathbf{r}) \; \sin(kR_p + \phi(k, \mathbf{r}))$$

We have done this using two methods: a monte carlo simulation over the distribution of displacements and a Taylor expansion, truncated to the first order, around the equilibrium position of the atoms in the path. Both methods have been used obtaining the same results. In the expression written above R_p is the total lenght of the n-th path, $A(k, \mathbf{r})$ and $\phi(k, \mathbf{r})$ are the amplitude and the phase associated to the MS signal related to the path under consideration [5] and M is the correlation matrice. This matrix is calculated by the method of the high-temperature-expansion as described in the Refs. 3,4.

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The Taylor expansion is suitable for structural purposes. After simple algebra we have obtained the first order correction to the MS signal which turned out to be [4]:

$$\langle \chi_n(k) \rangle = A_0 \sqrt{1 + \frac{(A_1, M\psi_1)^2}{A_0^2}}\; e^{-\frac{1}{2}(\psi_1, M\psi_1)} \sin\left(kR_p + \phi_0 + \frac{(A_1, M\psi_1)}{A_0} \right)$$

In this expression ψ_1 is the first order in the Taylor expansion of the total phase ψ (k, r) = A (k,**r**) + ϕ (k,**r**), while A_0, A_1 are the coefficients of the expansion of the amplitude and ϕ_0 is the backscattering phase at equilibrium position. The dominant term is the exponential factor which reduces to the usual Debye-Waller factor in the case of χ_2 and constant ϕ. Normally the other correction are small. For a deeper discussion see Ref. 4.

As an application we present some results relative to thermal vibration on crystal silicon. Indeed we have calculated the EXAFS contribution coming from second shell, the χ_3 signal coming from the 3-path joining the atoms belonging to the first and second shell and the χ_4 contribution due to the 4-path, involving first and second shell, which returns to the photoabsorber through a further first-shell atom in staggered position with respect to the atom of second shell. In Fig.1 we report the logarithm of the ratio of the damped amplitudes with the undamped amplitudes versus k^2 for these three signals (continuous lines). The dotted lines represent the damping coming from the fluctuation of the total path lenght only, neglecting all the phase corrections: the so called "geometrical contribution". These calculations indicate that for the χ_2 signal the damping is only given by a Debye-Waller type of correction in the amplitude [4,6] while for χ_3 and χ_4 signals the phase effects become important and can alter the effective damping. This result seems to be a general situation in agreement with exact calculation of Ref. 6 and with the approximate treatment given in Ref.4. An other interesting result is that the real damping for χ_n (n > 2) is surprisingly smaller than the one of second shell EXAFS. An explanation of this non evident behaviour lies in the fact that in our χ_3 the strongly vibrating second shell bond is counted only once while the same bond enters twice in the second shell χ_2.

This method is quite general and can be used to study the effect the structural disorder. The investigation on the same system using two different structural model of amorphous silicon (Biswas and Wiener models) [4] indicates that the different behaviour of the damping in the multiple scattering contributions can be used in a clear way to distinguish between different models. For this purpose we have calculated the second shell χ_2 signal and the χ_{3A} and χ_{3B} signals. The χ_{3A} signal comes from the 3-path within the tetrahedron while the second comes from the already considered 3-path. In Fig.2 the total signal $\chi_2 + \chi_{3A} + \chi_{3B}$ is reported, as continuous line for the Winer model and dashed line for Biswas model. Each signal has been also damped with the usual exponential decay factor which accounts approximately for the inelastic losses. The two signal are quite different and we want to underline that the level of the signal is at least one order of magnitude higher than the usual signal to noise ratio obtained by means of absorption spectroscopy.

This fact can open the way to the use of the x-ray absorption spectroscopy as a means for understanding the local order in amorphous system and discriminate between different models for amorphous structures.

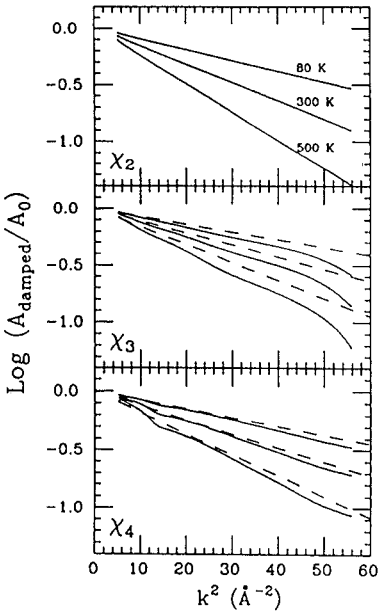

Fig.1

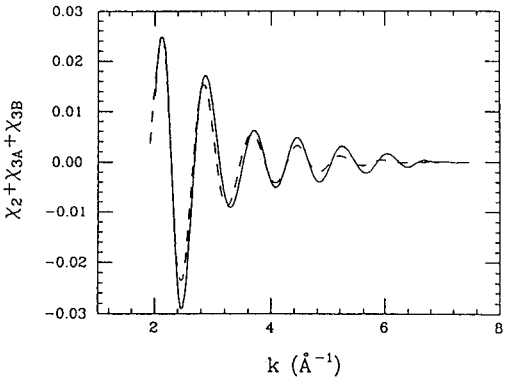

Fig.2

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