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SPHERICAL WAVES EXAFS AND MULTIPLE SCATTERING EFFECTS IN XANES OF THE K-EDGE SPECTRUM OF SILICON

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Abstract: A theoretical calculation of the K-edge spectrum of silicon was performed. A good fit with the experimental EXAFS spectrum has been obtained by using the spherical wave formalism, the actual values of the mean free path and the Debye-Waller terms. The relevant multiple scattering contribution in the first 70 eV of the spectrum has been obtained by subtraction of a simulated EXAFS spectrum from the experimental one.

INTRODUCTION. - In order to establish the role of the basic physical processes in the EXAFS and XANES parts of K-edge absorption spectra such as inelastic losses, thermal vibration and multiple scattering we have performed a careful quantitative analysis of the silicon K-edge absorption spectrum. A good fitting of the EXAFS oscillations from 50 to 450 eV above the absorption threshold (in the range of wave vector 4-11 Å⁻¹, with \( E_T = 1838 \) eV) has been obtained using spherical waves \(^1_,^2\). The spectrum of the mean free path \( \lambda(E) \) of the photoelectron has been determined from photoemission experiments \(^3\) and it has been included in the EXAFS calculations. The EXAFS Debye-Waller factors \(^4\) have been also considered. They have been calculated for each shell using a dispersive model of lattice vibrations of Walker and Keating \(^5\) starting from X-ray diffraction measures on vibrational amplitudes in Silicon \(^6_,^7\). An investigation on multiple scattering effects has been carried out by subtracting the calculated spectrum from the experimental one; the difference spectrum shows an oscillation which can be explained considering the first path of multiple scattering.

EXPERIMENTAL. - The experimental spectrum was recorded at the storage ring ACO (Orsay) by Lagarde and Flank \(^8\) in transmission mode using a double InSb (111) crystal monochromator and ionization chamber detectors.

RESULTS AND DISCUSSION. - The modulation of the atomic absorption has been extracted by subtracting from the experimental spectrum a polynomial fitting that simulates the smooth atomic contribution to the absorption \(^9\): \( X(k) = p(k) - p_0(k)/p_0(k) \). The EXAFS calculation following the spherical waves formalism of Lee and Pendry \(^1\) (SWLP) has been performed by using the EXAFS program kindly allowed by SRS-Daresbury Laboratory. A parallel calculation has been performed by using the spherical waves approximation (SWA) developed by Natoli and Benfatto \(^2\).

Coordination numbers and distances of the shells of silicon are well-known from literature; the mean free path damping factor \( \exp(-2R_i/\lambda) \) has been evaluated using information \(^1\); in the calculation of \( k \) we have inserted the finite life time of the core hole \( (\tau_h = 0.4 \) eV) \(^10\) following the relation \(^11\):

\[
\Gamma_{\text{eff}}(E) = \Gamma_{\text{h}} + h(2E/m)^{1/2}2\pi \lambda(\Gamma_{\text{h}}(E)) \quad \text{and} \quad \lambda_{\text{eff}}(E) = h(2E/m)^{1/2}2\pi \Gamma_{\text{h}}(E)
\]

Starting from the calculation of Walker and Keating for the Debye-Waller relative factors \( \sigma^2_R = (|u_R - u_0|^2/R^2) \) =2M\(\gamma\)(R) and assuming a linear-chain model of dispersion of elastic waves (with only nearest-neighbour interactions) we have evaluated a reasonable approximation for the actual values of the EXAFS Debye-Waller factors (fig.2). It is easy to see that the combined action of these two damping terms (\( \exp(-2\sigma^2_R - 2R/\lambda) \)) quenches the contribution of the remote shells starting from 70 eV above the absorption threshold. The EXAFS calculation shows that the first three shells give the major contribution and the further shells give a contribution to the spectrum only up to 70 eV. In order to compare the theoretical spectrum with the experimental one an appropriate value of \( E_0 \) has been chosen. The best fit has been obtained including seven shells in the spherical wave calculation (fig.3,4). The fact that there is a contribution due to the distant shells was observed by Lagarde \(^8\). We show that in the photoelectron energy range 50-130 eV the spherical waves...
The photoelectron mean free path calculated from photoemission measurements gives a better fitting than the plane wave one which is smaller in amplitude and out of phase in this energy range (fig. 5). These results are also confirmed by the Fourier transform approach. The FT calculations were performed by taking into account the calculated phase shifts and the backscattering amplitudes. In this way we have to find the peaks of the FT spectrum in the real space at the right crystallographic positions. By performing the Fourier transform in the single scattering range (50-470 eV) it is possible to discriminate from the noise only three shells; a similar calculation has been performed on the theoretical spectrum where there are only window effects: also in this case the signals of the distant shells are convolved and it is impossible to distinguish one shell from another (fig. 6). A similar analysis performed on the whole range (5-470 eV) shows that there is a contribution from the fourth and fifth shells but it is still impossible to separate them (fig. 7).

The silicon crystal exhibits no atoms in collinear configuration if we look to a cluster formed by 7 shells around the central absorbing atom. Therefore it provides an ideal system to test the presence of multiple scattering of type 2(12). In the fcc crystalline copper it was pointed out that there are negligible multiple scattering contributions (13). The absorption coefficient for x-ray absorption spectra can be expressed by the series

\[ \mu(k) = \mu_0(k)(1 + \Sigma_{n=2}^{\infty} X_n(k)) \]

where \( \mu_0(k) \) is the single scattering term (14-16). The multiple scattering term \( X_{MS} = \Sigma_{n=3}^{\infty} X_n(k) \) can be extracted from the experimental spectrum by subtracting from the experimental \( X(k) \) the calculated single scattering contribution in spherical waves (15). We have measured \( X_{MS} = X_2(k) - X_2(k) \) and it is plotted in fig. 8. The same result has been obtained by using two independent methods, the SWLP and the SWA, for calculating \( X_2(k) \) as described above. The \( X_{MS} \) spectrum has been compared with the theoretical calculations of the triple scattering term \( X_3(k) \) for multiple
scattering pathways involving two neighbour atoms within the first two shells. The first path of double scattering has an effective radius $R=1/2(R_1+IR_2-R_1+R_2)=4.27 \text{ Å}$. There are 36 equivalent paths runned through by the photoelectron and it is expected to be the most important contribution. The calculated $\chi_3$ using the multiple scattering theory (14-15) is shown in fig.9. The theoretical calculation is close to the experimental oscillation $\chi_{MS}$.
We observe a high amplitude contribution at low k values and a frequency similar to the experimental $\chi_{MS}$. The differences between $\chi_{MS}$ and the theoretical $\chi_3$ which become more important at low energy can be assigned to higher orders of multiple scattering. From the Fourier analysis it is not possible to separate a specific peak due to multiple scattering in fact the extracted $\%S$ is near in frequency and out of phase with the oscillation due to the sum of the contributions of the second and third shells. This effect combined with the low number of oscillations of the $\chi_{MS}$ spectrum, explains the failure of the Fourier transform method used to recovering the multiple scattering signal. This result shows that the multiple scattering contribution in the first 70 eV of silicon K-edge is important and could be used as a direct probe of the triplet correlation function. A tentative explanation for the weak multiple scattering contributions in copper can be due to a negative interference effect between higher multiple scattering terms like that observed in octahedral clusters(14,16).

**Fig. 8** The difference spectrum between the spectra shown in fig.5, cleaned by the low frequency of the residual first shell contribution.

**Fig. 9** The calculated spectrum $\chi_3(k)$ for the shortest ($d \sim 2x4.27$ Å) double scattering pathway in silicon.

**References:**


2) M. Benfatto and C. R. Natoli, *Proc. of this conference*


8) P. Lagarde, A. M. Flank, *Journal de Physique, to be published*


