LNF-90/094

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Estratto da: Conf. Proc. Vol. 25 XSR-89, A. Balerna, E. Bernieri, S. Mobilio (Eds.)
SIF Bologna, Pag. 31 (1990)

Conference Proceedings Vol. 25
«2nd European Conference on Progress
in X-Ray Synchrotron Radiation Research»
A. Balerna, E. Bernieri and S. Mobilio (Eds.)
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FULL MULTIPLE SCATTERING THEORY APPLIED TO THE DETERMINATION OF PHOTOELECTRON MEAN-FREE PATHS IN ZINCBLENDE AND SILICON.

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ABSTRACT

It is of importance to determine the region that is probed by the photoelectron of an X-ray absorption experiment. We show that this region depends on the photoelectron kinetic energy through its effective mean-free path. To assert these ideas ab-initio calculations are applied to semiconducting and insulating compounds.

I - Introduction

X-ray absorption cross sections of solids has been calculated in the scheme of the full multiple scattering theory. We first checked the validity of the theory for semiconducting and insulating compounds such as crystalline silicon or zincblende where we performed calculations for the K-edges of silicon, sulfur and zinc. The calculated spectra are in good agreement with the experiments and were presented elsewhere [1,2]. In former communications, we outlined the influence of the free parameters that are to be chosen when the multiple-scattering equations are solved in a non-self-consistent muffin-tin potential. The muffin-tin radii are set so as to minimize the discontinuity of the potential between two adjacent spheres and there is no overlap between neighbouring spheres. The potential of the final state with a core-hole on the absorbing atom is a self-consistent atomic potential of the Z+1 element with only one electron on the 1s orbital and one additional electron on the upper orbital. The multielectronic interactions are taken into account through different formulations of the exchange and correlation potential : exchange potential X-α with α determined by Schwartz [3], exchange potential of Dirac in the formulation given by Hara[4] and the complex exchange and correlation potential of Hedin-Lundqvist [5]. The best results are obtained with the Dirac-Hara potential although at high photoelectron energy Dirac-Hara and Hedin-Lundqvist potentials produce essentially the same results. Here we concentrate on the influence of the cluster size, i.e. on the region that is probed by the photoelectron.

II - Mean-free path

At the sulfur K-edge in ZnS a 8 shell cluster is needed to reproduce the whole experimental spectrum while at the zinc K-edge a 5 shell cluster is enough. At the silicon K-edge in c-Si a 8 shell cluster is needed too. Nevertheless a two or three shell cluster already reproduces the region beginning $\approx$20 eV above the edge. These results are in agreement with former spherical and plane wave calculations where it was shown that the eighth shell takes part to the single scattering process in c-Si [6,7]. The zincblende and diamond (c-Si) structures are highly symmetrical and the atoms of the eighth shell are colinear with the atoms of the second shell and the absorbing atom. This considerably enhances the effective scattering

power of the eighth shell by a focussing effect. The eighth shell around zinc atoms does not play an important role such as around silicon and sulfur atoms. A first reason is the faint scattering power of zinc atoms. However we are going to show that the regions probed by the photoelectron are different in the three cases.

In the common picture of the absorption process the photelectron is emitted by the absorbing atom, scattered by the surrounding neighbours and it comes back to the site of the absorbing atom. The contribution of one particular path is related to the scattering amplitudes of all the atoms in the path and to the propagation amplitude between the successive scattering atoms. These amplitudes are reduced due to inelastic scattering of the photoelectron by the electrons of the compound. The inelastic interactions are mainly interactions with the less bound electrons and result from collective excitations of the valence electrons at a definite energy, the plasmon energy, which is related to the electronic density. In ZnS and c-Si plasmon energy values are about 15 eV. Then when the photoelectron energy is less than the plasmon energy the photoelectron is not energetic enough to interact inelastically with valence electrons. On the other hand when the photoelectron is more energetic than the plasmon energy, $\hbar\omega_p$, it is partially inelastically scattered by valence electrons. This reduces much its inelastic mean-free path, λ_{in}, and makes the contribution from distant shells negligible. The contributions to the mean-free path of other excitations such as electron-hole excitations are negligible here and are not considered. Moreover in an X-ray absorption experiment the core-hole lifetime is related to a "core-hole mean-free path", $\lambda_{c\text{-}h}$, since the longer is the core-hole lifetime, the larger is the region explored by the photoelectron. The effective mean-free path of the photoelectron λ_{eff} is obviously given by $1/\lambda_{eff} = 1/\lambda_{in} + 1/\lambda_{c\text{-}h}$.

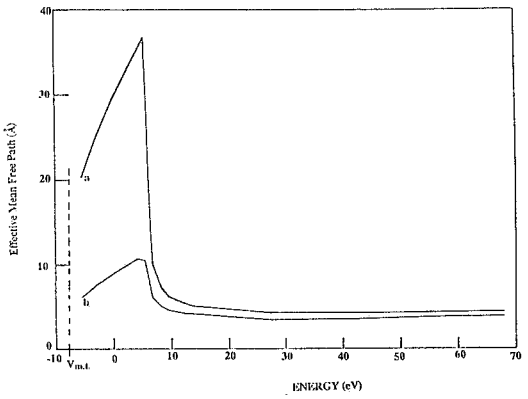

Figure 1. Effective mean-free path in ZnS.
a - at sulfur K-edge; b - at zinc K-edge.

The effective mean-free paths for 1s core-holes in silicon, sulfur and zinc have been computed. The computation of $\lambda_{c\text{-}h}$ is straightforward when the core-hole width, Γ_h, is known [8]. From Penn λ_{in} is expressed as a function of the imaginary part of the self-energy Σ of the photoelectron $\lambda_{in} = \frac{h^2 k}{2m} \frac{1}{|\,\mathrm{Im}\,\Sigma(k,r_s)\,|}$ [9]. To calculate the self-energy of an electron of momentum k in a electron gas of density $\frac{3}{4\pi r_s^3}$ we followed the approach of Hedin-Lundqvist where the dielectric function is written in the plasmon pole approximation. The calculated values of the effective mean-free path in crystalline silicon are in good agreement with the experimental data [2]. The values of the effective mean-free path in zincblende for photoelectrons originating from either sulfur or zinc 1s shell are plotted in figure 1. The plasmon energy clearly appears as a steep decrease of λ_{eff}. In our calculation it is roughly situated 15 eV above the interstitial potential of the muffin-tin potential.

III - Comparison with experiments

To check the region that is experienced by the photoelectron we performed full multiple scattering calculations in various clusters. The spectra were calculated with the real exchange potential of Dirac-Hara and then convoluted by a Lorentzian function whose width is related to λ_{eff}. The size of the cluster is progressively increased so as to relate the appearence of each feature in the absorption cross section to a specific cluster size. We also performed multiple scattering calculations with a complex potential. Both methods lead to essentially the same spectra. This proves that in the complex potential theory the damping factor is well taken into account. We particularly want to underline that the damping factor is an averaged sum of the damping factors originating from the imaginary part of the scattering amplitudes and the damping factor of the propagator in the interstitial region. This means that there is a cancellation of the terms coming from the damping of the propagator inside the muffin tin spheres.

Si K-edge cross sections for a series of clusters of increasing size are plotted in figure 2. The spectra can be divided into two regions. When the photoelectron energy is more than $h\omega_p$, λ_{eff} is much reduced. In this region a one shell cluster already gives the rough shape of the absorption cross-section. The increase of the cluster size only leads to modulations in the one shell signal. With a five shell cluster the calculated spectrum is very similar to the experimental spectrum and farther shells do not change any more the calculated spectra. The fifth shell is 5.9 Å far from the absorbing atom and λ_{eff} is $\approx$ 5 Å above $h\omega_p$. This means that the damping factor for an electron backscattered by the fifth shell is $\approx$ 90%. For higher order scattering the damping factor is even higher. When the photoelectron energy is less than $h\omega_p$, λ_{eff} is only limited by Γ_h. Since Γ_h=0.4 eV for a 1s core-hole in silicon, the damping is faint and λ_{eff} is large (more than 20 Å). In this region the spectra are modified by the addition of shells until the eighth shell. This is well understood since the reduction factor of the amplitude is never more than $\approx$ 50 %.

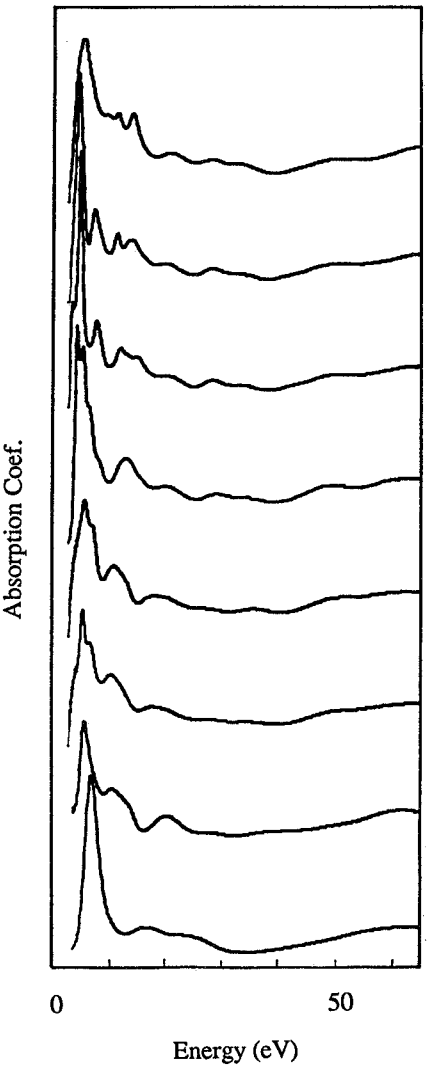

Figure 2. Full multiple scattering calculations at Si K-edge for clusters of increasing size; the bottom spectrum is for a one shell cluster and the top spectrum for a eight shell cluster.

The same conclusions can be drawn at the sulfur K-edge since the core-hole lifetimes are similar. On the other hand at the zinc K-edge the core-hole is large (Γ_h = 1.64 eV) and the

effective mean-free path before the plasmon energy stays between 5 and 10 Å. The region after the plasmon energy can receive the same interpretation as in the case of c-Si since in this region the effective mean-free path does not depend strongly on the core-hole width. In the region before the plasmon energy, the effective mean-free path is low and it is not surprising to see that a 5 shell cluster calculation produces a cross section in good agreement with the experiment (Fig.3). The calculated spectra have been performed with the real part of the exchange and correlation potential of Hedin-Lundqvist. As expected they present a contraction of the energy scale in comparison to the experimental spectra [2].

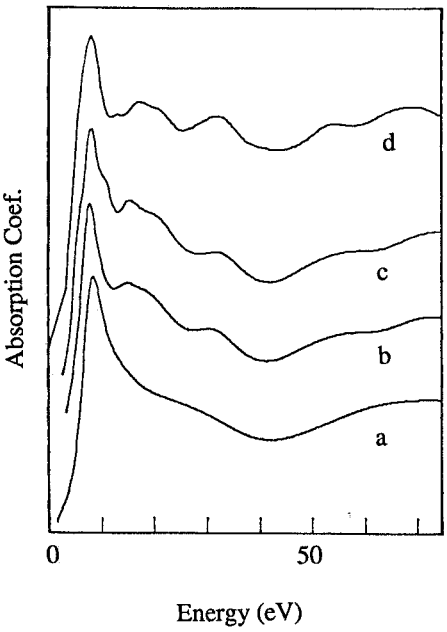

Figure 3. Full multiple scattering calculations at zinc K-edge in ZnS : a - one shell cluster; b - three shell cluster; c - five shell cluster; d - experimental spectrum.

IV - Conclusion

We outline that the photoelectron probes a region around the absorbing atom that depends on both the plasmon energy of the compound and the core-hole lifetime of the absorbing atom. It is related to the common fact that, although the overall resolution is better at the K-edges of light elements, the spectra only present sharp features in the vicinity of the edge. Moreover the mean-free path calculations allow an estimate of the correctness of the plasmon pole approximation that is used in the computation of the Hedin-Lundqvist exchange and correlation potential. This gives a good support to further calculations performed in the frame of the multiple-scattering theory with a complex potential.

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