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M. Benfatto, C.R. Natoli, A. Bianconi, J. Garcia, I. Davoli, A. Marcelli  
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A NEW PROBE OF HIGHER ORDER CORRELATION FUNCTION IN  
AMORPHOUS SEMICONDUCTORS

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**XANES (X-RAY ABSORPTION NEAR EDGE STRUCTURE): A NEW PROBE OF HIGHER ORDER CORRELATION FUNCTION IN AMORPHOUS SEMICONDUCTORS**

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**ABSTRACT**

The higher order correlation function of local distribution in amorphous semiconductors have been probed directly by XANES (x-ray absorption near edge structure) experiments using synchrotron radiation. We show that unique structural informations on the geometry of local atomic arrangements in amorphous vanadium oxide semiconductor and in silica glasses can be obtained. The multiple scattering theory has been applied to interpret the data.

**1. - INTRODUCTION**

Interest in local structure determination beyond the pair distribution function has recently stimulated the growing of x-ray absorption near edge structure (XANES)<sup>(1-6)</sup>. The low energy part of x-ray absorption spectra is sensitive to the geometrical arrangement of the environment surrounding the absorbing atom because of the strong scattering power, for the low energy photoelectrons, favors multiple scattering (MS) processes. At high energies such that the atomic scattering power becomes substantially small a single scattering (SS) regime take place, where

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the modulation in the absorption coefficient (EXAFS)<sup>(1)</sup> is substantially due to the interference effect of the outgoing photoelectron wave from the absorbing atom and the backscattered wave from each surrounding atom. Hence this latter part of the spectrum provides information about the pair correlation function. By decreasing the photoelectron kinetic energy a gradual turn over occurs from the EXAFS (SS) regime to the XANES full multiple scattering (FMS) regime<sup>(2-5)</sup> where all the MS pathways which begin and end at the absorbing atom contribute to the total absorption cross section.

By making the expansion of the total cross section, in the energy region where it is possible, it has been shown<sup>(6)</sup> that the contributions of successive scattering orders to the total absorption cross section can be identified.

Here we report a study of the site structure of amorphous semiconducting  $V_2O_5$  and silica glasses. Amorphous  $V_2O_5$  exhibits semiconducting properties arising from the hopping of small polarons between vanadium ions<sup>7,8</sup>, but the random structure of the glass leads to an Anderson localization of the charge carriers<sup>(9)</sup>. Both polaron formation and Anderson localization lead to distortions of the lattice at vanadium sites. It is therefore important, in the study of semiconducting properties of amorphous vanadium oxide, to establish detailed information on site structure and its distortions. Information on the geometry of  $V^{4+}$  sites, 1% of the total amount of vanadium, have been obtained by ESR spectroscopy<sup>(10)</sup> but no information can be obtained on silent  $V^{5+}$  ions and diffraction experiments probing the pair distribution function have obtained contradictory results<sup>(11)</sup>.

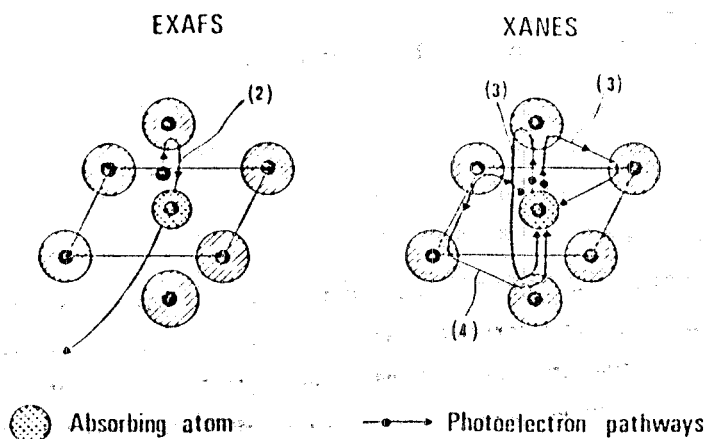


FIG. 1 - Pictorial view of the multiple scattering pathways in the EXAFS single scattering regime and in the XANES multiple scattering regime.

## 2. - EXPERIMENTAL

The experiment has been performed at the Frascati synchrotron radiation facility. The high resolution K-XANES of vanadium is achieved by using a Si(220) monochromator and an entrance slit of 0.5 mm. The amorphous  $V_2O_5$  has been obtained by ultra fast quenching from the melt (splat cooling). The oxygen K-XANES of  $SiO_2$  glass has been measured using the "grasshopper" soft xray beam line. In the data analysis the pre-edge absorption back-ground has been subtracted.

## 3. - RESULTS AND DISCUSSION

In Fig. 2 the experimental XANES of amorphous semiconducting  $V_2O_5$  and the fit of the XANES using the multiple scattering (MS) theory<sup>(6)</sup> are shown. The theoretical spectrum has been obtained for a cluster formed by the central vanadium and six neighbouring oxygens forming a bipyramidal cluster. Peaks A and C are due to MS normal to the layers and peak B is due to MS in the plane. The splitting of peak B is due to a small distortion of the base of pyramids but smaller than in the crystal. This results show that amorphous  $V_2O_5$  is formed by layers of square pyramids, like in crystal, but with topological disorder.

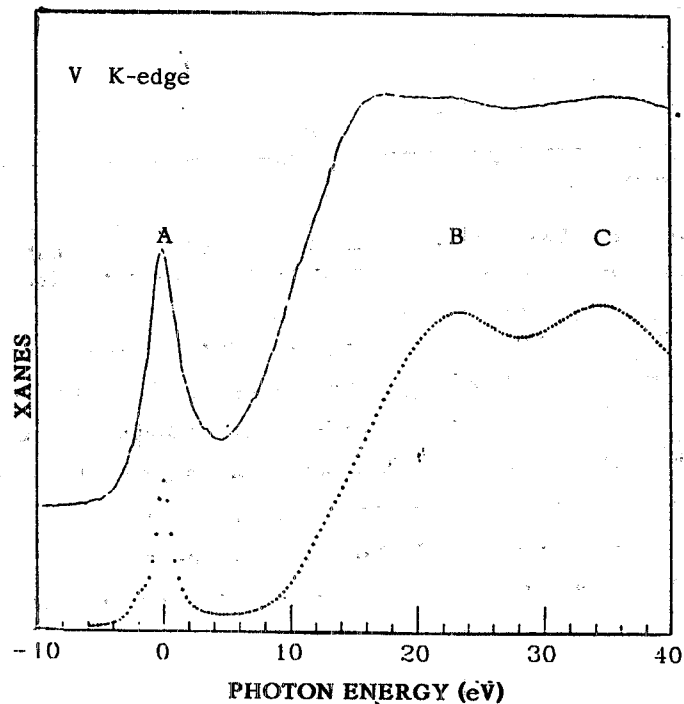


FIG. 2 - K-XANES of vanadium in amorphous  $V_2O_5$  and theoretical multiple scattering calculations for a bipyramidal cluster with a one short double bond at 1.58 Å, a sixth atom at 2.8 Å and the four atoms in the plane at 1.82 Å.

In Fig. 3 we show the oxygen K-XANES of amorphous SiO<sub>2</sub> (fused quartz) and a preliminary MS calculation for a small cluster formed by two silicons around a central oxygen<sup>(12)</sup>. We have found that the expansion of the total cross section is feasible above threshold<sup>(6)</sup>

$$a_t = a_a (1 + \sum_{n=2}^{\infty} \chi_n)$$

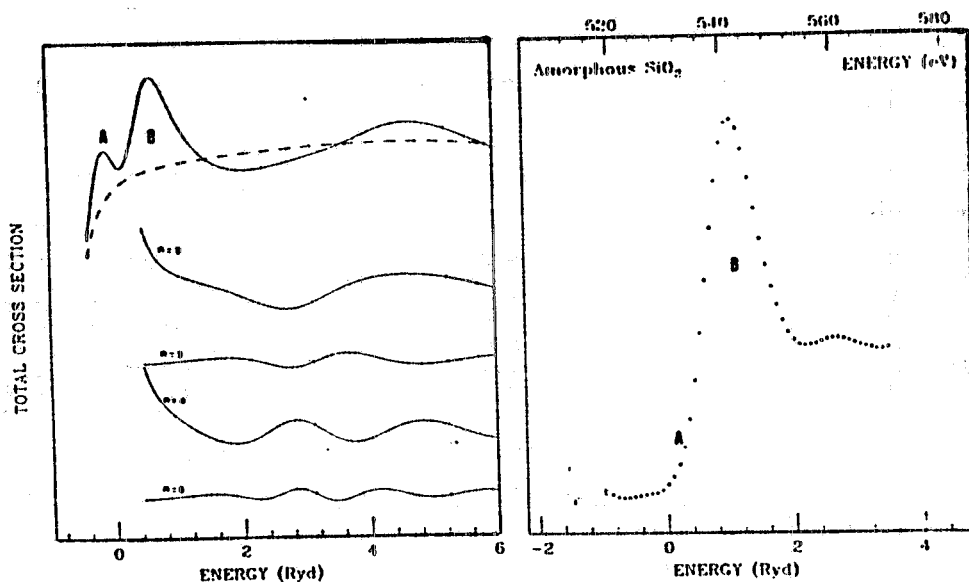


FIG. 3 - Oxygen K-XANES of SiO<sub>2</sub> glass and the XANES calculation, showing the  $\chi_2$  (XANES),  $\chi_3$ ,  $\chi_4$ ,  $\chi_5$  higher order contribution to the total absorption.

where  $a_a$  is the atomic absorption and  $\chi_n$  are the contributions due to successive orders of scattering pathways (see Fig. 1) which are shown in Fig. 3. A qualitative agreement with the experiment has been found. The main resonance B, in the continuum, is due to MS pathways and it is dependent on the bridging bond angle. In other silica glasses we have determined a variation of the average bridging bond angle with glass preparation procedures<sup>(12)</sup>.

In conclusion we have shown that XANES spectroscopy is a new probe of higher order correlation functions for unique structural information on amorphous systems.

**REFERENCES**

- (1) Proc. of Intern. Conf. "EXAFS and Near Edge Structure", Springer Series in Chem. Phys. vol. 27, Eds. A. Bianconi, L. Incoccia, S. Stipcich (Springer-Verlag, 1983).
- (2) A. Bianconi, Appl. of Surface Science 6, 392 (1980).
- (3) M. Belli, A. Scafati, A. Bianconi, S. Mobilio, L. Palladino, A. Reale and E. Burattini, Solid State Commun. 35, 392 (1980).
- (4) A. Bianconi, S. Doniach and D. Lublin, Chem. Phys. Lett. 59, 121 (1978).
- (5) A. Bianconi, M. Dell'Ariceia, P.J. Durham and J.B. Pendry, Phys. Rev. B26, 6502 (1982).
- (6) M. Benfatto, C.R. Natoli, A. Bianconi, J. Garcia, A. Marcelli and I. Davoli, Phys. Rev. B, to be published and Frascati Report LNF-85/26 (1985).
- (7) I.J. Austin and N.F. Mott, Adv. Phys. 18, 41 (1978).
- (8) F.P. Koffyberg and F.A. Benko, Phil. Mag. B38? 357 (1978).
- (9) P.W. Anderson, Phys. Rev. 109, 1942 (1958).
- (10) O. Kahn, J. Livage and R. Collongues, Phys. Stat. Sol. A26, 175 (1974).
- (11) A.C. Wright, Phil. Mag. B50, L23 (1984).
- (12) A. Marcelli, I. Davoli et al., J. de Physique (1985) to be published.