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VANADIUM SITE STRUCTURE IN V_2O_5 GEL BY POLARIZED EXAFS AND XANES

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The polarized X-ray absorption spectra of vanadium pentoxide gel have been studied. The V_2O_5 gels form a new class of materials[1,2] which show electronic properties and can be applied for switching devices and anti-static coatings. We have investigates the site structure of dilute solutions and of spontaneous dehydrated solid with approximate formula V_2O_5-1.6 H_2O. They are formed by layers of square pyramids which have five oxygens on the corner and one vanadium just above the center of the square basis. The polarized EXAFS in the direction of the axis of the pyramids gives the short double bond length. Polarized EXAFS in the plane gives the distances from oxygen nearest neighbours and from vanadium in the second shell in the layer plane. Polarized XANES spectra have been measured and exhibit large variations with the change of the angle between the electric field and the axis of the pyramids. In Fig. 1 we compare the XANES spectra of vanadium K-edge obtained with non polarized radiation (lower curve) with the absorption spectra measured with the electric field of the radiation parallel and perpendicular (upper curves) to the square basis of the vanadium pentoxide gel structure.

The multiple scattering XANES calculations have been performed for several geometries to find the best agreement with experiment. In Fig. 2 we report the theoretical partial cross section calculation of the vanadium pentoxide in two different tetragonal pyramid clusters with a neighbour double oxygen bond and one long oxygen bond. We show the partial theoretical multiple scattering calculation in the case of vanadium atom in the plane formed by 4 oxygens (lower part) and the same calculation with the small displacement of the vanadium atoms out of the plane (upper curve). Comparing experimental XANES spectra with theoretical calculations we obtain evidence of one long oxygen bond that is not detected by EXAFS and the distance of this oxygen, due to the water molecules bellow the basis of the pyramids has been determined.

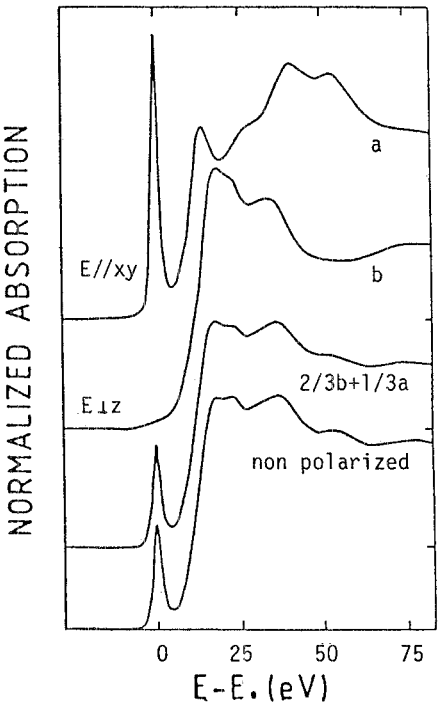

Fig. 1 - The absorption V K-edge with polarized radiation (a and b spectra). The third curve is obtained by the weighing sum of the a and b spectra and is compared with the non polarized radiation experiment (lower curve).

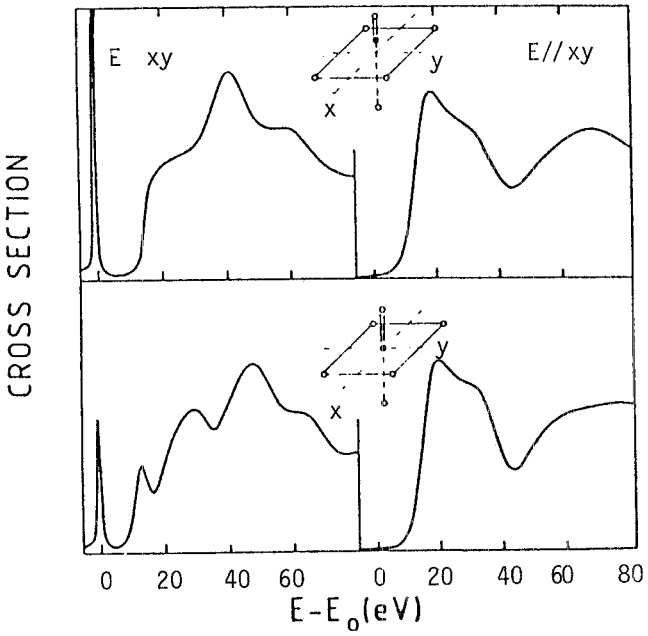

Fig. 2 - Theoretical partial multiple scattering calculation for vanadium pentoxide structure in two different geometries. We show the sensitivity of the calculation to small displacement of the vanadium atom out of the oxygen plane.

Finally we show that: i) it is possible by XANES to determine fine geometrical details such as vanadium displacement from the square oxygen basis; ii) the spectra of the gel in solution are found to be similar to amorphous solid V_2O_5; and iii) the characteristic EXAFS spectrum of vanadium oxides which exhibit a suppression of the amplitude is due to the negative interference between scattering along the axis and the one on the plane[3].

References:

(1) J.J.Legendre and J.Livage, J. of Colloid and Interface Sci. 94, 75 (1983).

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(3) S.Stizza, M.Benfatto, I.Davoli, O.Gwozski and G.Mancini, Amorphous to Crystalline Phase Transition of V_2O_5 Glass Studied by EXAFS and XANES Analysis, presented at the "XIV Intern. Congress on Glass", New Delhi, India (1986).