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ON THE BASIC STRUCTURAL UNIT OF AMORPHOUS \( V_2O_5 \) FROM XANES AND EXAFS

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Résumé - Des échantillons de pentoxyde de vanadium amorphe ont été étudiés par XANES. Les spectres ont été analysés à partir de modèles de diffusion multiple. Des structures locales en forme de pyramides tétragonales semblent exister. La cristallisation par chauffage a aussi été étudiée et des distorsions de la cellule de base au cours de la transformation ont été mises en évidence.

Abstract - XANES (X ray absorption near edge structure) spectra of rapid-quenched amorphous vanadium pentoxide have been measured using synchrotron radiation. The spectra have been analyzed with the multiple scattering theory. Evidence for tetragonal pyramids has been found. The transition from glass to crystalline state with temperature has been studied and the small distortions of the basic structural unit related with the transition has been found.

1 - INTRODUCTION

Vanadium pentoxide is a component of semiconducting oxide glasses which exhibit hopping conductivity. Amorphous \( V_2O_5 \) can be obtained by rapid-quenching techniques. The basic structural unit of this glass is not well established\(^1\) in fact in the first X ray diffraction work\(^2\) the interatomic distance V-O was found to be 1.85 Å, on the contrary large angle X ray scattering \(^3\) experiment found the V-O distance 1.75 Å and on the basis of the pair correlation function the hypothesis of tetrahedra sharing corners as structural units of this glass has been advanced. A similar controversy concerns the basic structural units of liquid vanadium pentoxide.\(^4,5\)
Here we report the study of the basic structural unit of V$_2$O$_5$ glass by XANES (x-ray absorption near edge structure) and EXAFS. XANES spectroscopy has been used to study local structure in vanadium phosphate glasses\(^{(6-8)}\) and vanadium oxide crystalline compounds\(^{(9)}\). XANES spectroscopy probes the local geometry via the photoelectron multiple scattering.\(^{(10)}\) The total absorption cross section can be factorized in an atomic part $\alpha_a$ and in a part due to the modulations of the multiple scattering processes with neighbouring atoms. In principle all multiple scattering pathways which begin and end at the vanadium site, classified according with the number of scattering events from $n=2$ (EXAFS) to $n=3,4,5,...$ contribute to XANES in the full multiple scattering region. In the energy range where the expansion is possible\(^{(11)}\) the total cross section is given by

$$\alpha_t = \alpha_a \left( 1 + \sum_{n=2} \chi_n \right)$$

Therefore XANES provides information on higher correlation functions and joint with EXAFS, which gives the pair correlation function are an ideal method to establish the local structure in glasses.

II - EXPERIMENTAL METHODS

EXAFS and XANES spectra were recorded at the Frascati synchrotron radiation facility using the storage ring Adone operated at 50 mA and 1.5 GeV. A Si(220) channel-cut crystal was used as monochromator with a 0.5 mm exit slit and the resolution at V K-edge was about 0.8 eV. The samples were prepared at Gdansk Technical University by rapid quenching technique. The experiment has been repeated several times and the crystallization of glasses has been realized by heating treatment.

III - RESULTS AND DISCUSSION

In fig. 1 we report the XANES spectra of V$_2$O$_5$ glass of the same sample at different temperatures. Above $T_c=220^0$ the amorphous sample crystallizes and the XANES spectrum becomes the characteristic spectrum of crystalline V$_2$O$_5$\(^{(7-9)}\). The main variation in the spectra appears at the first two features after the absorption jump edge. The EXAFS spectra are shown in fig. 2 where in the upper (lower) panel the EXAFS of the crystalline (amorphous) spectrum is reported. EXAFS analysis has been carried out and average V-O distance has been found to remain at about 1.85 Å, the second shell at about 2.8 Å shows a contraction of 0.02 Å in the glass. Only a small decrease of the intensity of further shells in the Fourier transform has been found in the glass.
Fig. 1. XANES spectra of vanadium pentoxide glass at various temperatures. The intensity scale of the spectra above the crystallization temperature at $220°C$ has been changed.

Fig. 2. EXAFS spectra of amorphous (lower panel) and of crystalline (upper panel) $V_2O_5$. 
The fact the EXAFS spectra are very similar is an indication that the pair distribution function is only little affected by the transition from the crystal to the amorphous state and therefore the amorphous oxide is formed by layers of tetragonal pyramids as in crystalline $V_2O_5$. The differences observed in the XANES between the two forms is therefore due to a small variation of the site structure geometry. In the crystal there is short double bond of 1.58 Å and the atoms on the basis of the pyramid are at 1.78 Å, 1.87 Å, 1.87 Å, 2.02 Å; a sixth atom is at 2.8 Å. We have performed multiple scattering calculations of the XANES spectra of the structural unit of vanadium pentoxide. We have found a good fit of the experimental XANES spectrum of the glass with a cluster where all atoms on the pyramid basis are at the same distance. The first peak after the absorption jump has been found to be due to scattering in the plane of the pyramid base, and therefore the main variations between glass and crystal are due to a rearrangement of the atoms of the basis in a less distorted way in the glass than in the crystal. The white line has been found to be due to the multiple scattering pathways along the axis of the pyramid and therefore depends on the positions of the atoms at 1.58 Å, and 2.8 Å. In conclusion the XANES and EXAFS show that the structural basic unit of the glass is similar to that of the crystal.
Fig. 4 Total theoretical absorption spectrum for the tetragonal pyramid cluster in agreement with the experimental XANES spectrum of amorphous V$_2$O$_5$.

REFERENCES