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Talk given at the "Third Intern. Conf. on
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ON THE BASIC STRUCTURAL UNIT OF AMORPHOUS V_2O_5 FROM XANES AND EXAFS(*)

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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 difraction 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

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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_2O_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[6,7,8] 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 α_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=3,5,5,... 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

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

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.

2.- 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 repeted several time and the crystallization of glasses has been realized by heating treatment.

3.- RESULTS AND DISCUSSION

In Fig. 1 we report the XANES spectra of V_2O_5 glass of the sample at different temperatures. Above Tc=220° the amorphous sample crystallizes and the XANES spectrum becomes the characteristic spectrum of crystalline V_2O_5[7,8,9]. 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

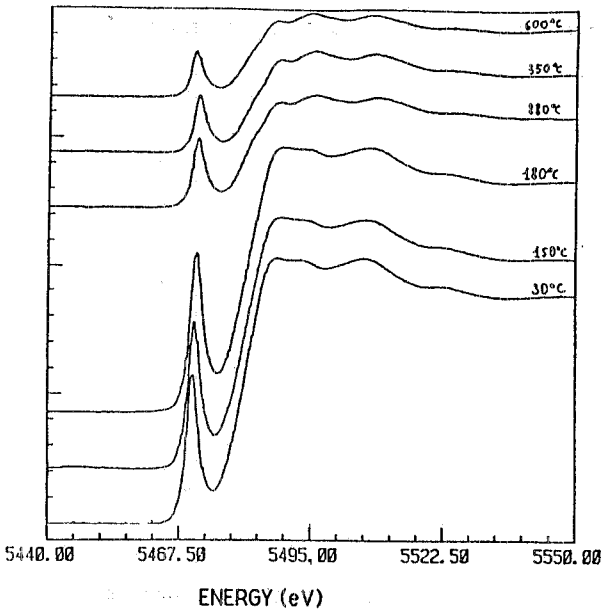

Fig. 1 - XANES spectra of vanadium pentoxide glass at various temperatures. The intensity scale of the spectra above the crystallization temperature at 220°C has been changed.

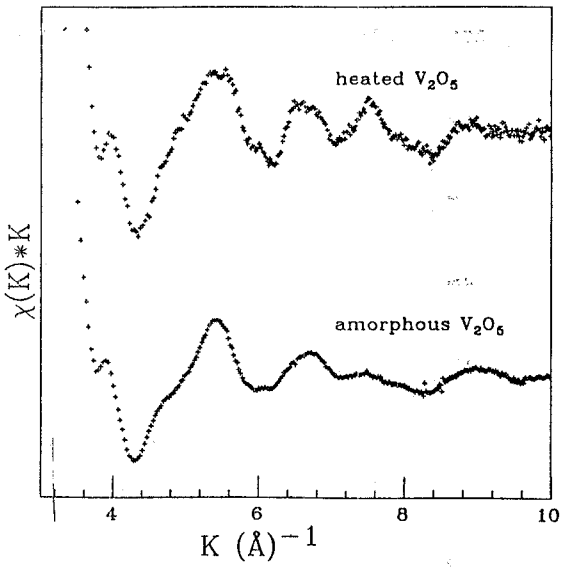

Fig. 2 - EXAFS spectra of amorphous (lower panel) and of crystalline (upper panel V_2O_5.

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.

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. In Fig. 3 we report the results of polarized theoretical calculations. 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 (see Fig. 4). 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.

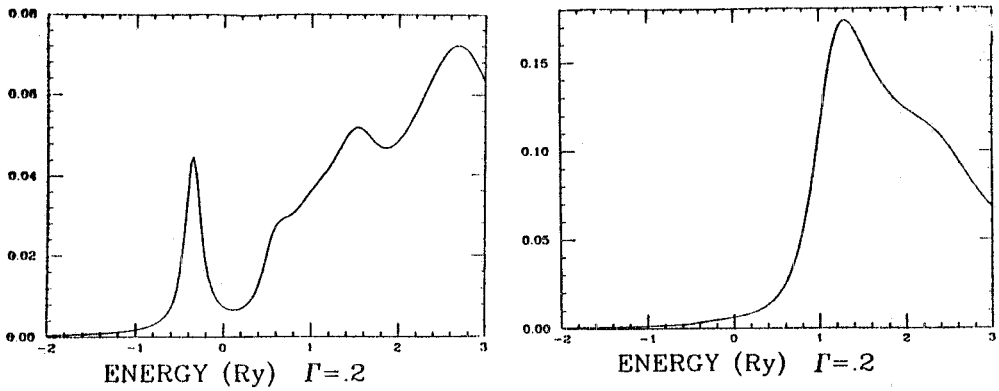

Fig. 3 - Polarized theoretical multiple scattering calculations of vanadium XANES for a tetragonal pyramid cluster. In the left (right) panel the spectrum with the polarization vector along the pyramid axis (basis) are reported.

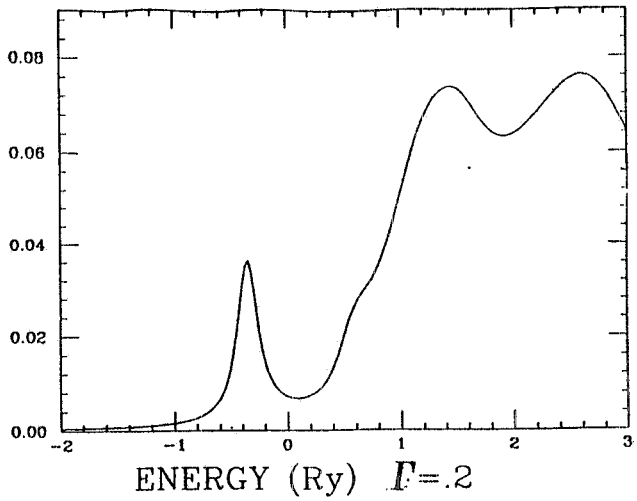

Fig. 4 - Total theoretical absorption spectrum for the tetragonal pyramid cluster in agreement with the experimental XANES spectrum of amorphous V_2O_5.

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