

ISTITUTO NAZIONALE DI FISICA NUCLEARE  
Laboratori Nazionali di Frascati

LNF-82/2(R)  
19 Gennaio 1982

A. Bianconi, I. Davoli, A. Giovannelli, O. Gzowski, L. Murawski,  
S. Stizza and L. Palladino: XANES (X-RAY ABSORPTION NEAR  
EDGE STRUCTURE) OF V IN VANADIUM-IRON PHOSPHATE  
GLASSES.

XANES (X-RAY ABSORPTION NEAR EDGE STRUCTURE) OF V IN VANADIUM-IRON  
PHOSPHATE GLASSES

A. Bianconi, A. Giovannelli  
Istituto di Fisica dell'Università di Roma, 00185 Roma

I. Davoli, S. Stizza, L. Palladino  
Istituto di Fisica dell'Università di Camerino, 62032 Camerino

O. Gzowski, L. Murawski  
Institute of Physics, Technical University, 80-952 Gdansk (Poland).

ABSTRACT.

The X-ray Absorption Near Edge Structure (XANES) of vanadium-iron phosphate glasses ( $50 \text{ P}_2\text{O}_5 + (50-x)\text{FeO} + x\text{V}_2\text{O}_5$ ) have been measured. The effective charge of V ions in glasses has been determined. At low  $\text{V}_2\text{O}_5$  concentration ( $x \sim 5$ ) only  $\text{V}^{4+}$  with 6-fold coordination is present on the contrary a static mixed valence state ( $\text{V}^{4+}$ ,  $\text{V}^{5+}$ ) has been found at high concentrations  $20 \leq x \leq 50$ . The results explain the electron hopping conductivity effects at high  $\text{V}_2\text{O}_5$  concentration ( $x \sim 50$ ) involving  $\text{V}^{4+} - \text{V}^{5+}$  pairs and at low  $\text{V}_2\text{O}_5$  concentration ( $x \sim 10$ ) involving  $\text{V}^{4+} - \text{Fe}^{3+}$  pairs.

1. - INTRODUCTION.

Amorphous oxides have been object of study using synchrotron radiation spectroscopy since many years because of the unique character of X-ray absorption spectroscopy to give information on the local structure around a selected atom<sup>(1)</sup>. From the early studies<sup>(2)</sup> it has been shown that the near edge structures extending over 30-40 eV above the absorption threshold are characteristic of the local structure in amorphous oxides. It has been demonstrated that the local structure of amorphous oxides of simple metals like  $\text{Al}_2\text{O}_3$ <sup>(2, 3)</sup>,  $\text{SiO}_2$ <sup>(3, 4)</sup> and  $\text{SiO}$ <sup>(4)</sup> or transition metal oxides of Mn<sup>(5)</sup> and Fe<sup>(6)</sup> can be determined from

the measure of XANES<sup>(1,5)</sup> (X-ray Absorption Near Edge Structure).

In this work, we have studied the XANES of vanadium ions in semiconducting phosphate glasses. The electrical conductivity in such glasses is realized by the hopping of the electron between transition metal ions in the two valency states e. g.  $V^{4+} \rightarrow V^{5+}$ <sup>(7)</sup>. When the glass contains two different transition metal oxides the situation is more complex because one can not exclude the electron hopping of  $Fe^{2+} \rightarrow V^{5+}$  or  $V^{4+} \rightarrow Fe^{3+}$  type. We have studied the XANES of the glass of composition  $50P_2O_5 + (50-x)FeO + xV_2O_5$  (in mole) to find out the local structure of vanadium sites. The information about the coordination of iron ions in these glasses have been obtained from the Mössbauer studies. It was concluded that iron exists in octahedral configuration, and that as the Fe oxides are replaced by the vanadium oxide, the number of  $Fe^{2+}$  ions rapidly decreases<sup>(8)</sup>. At 10% mole of  $V_2O_5$  in the ( $x = 10$ ) glass the ratio  $Fe^{2+}/Fe_{tot}$  is 0.04 and a minimum of conductivity has been observed<sup>(9,10)</sup> but since there is no information yet about vanadium ions, the explicit interpretation of the observed phenomena is almost impossible.

X-ray absorption spectra can be separated in three parts: 1) Edge; 2) XANES; 3) EXAFS. EXAFS is widely used as a method to determine the interatomic distances also in disordered systems<sup>(11)</sup>. Severe limitations of EXAFS in amorphous systems both for determination of the coordination numbers and distances<sup>(12)</sup> are due to the fact the EXAFS gives only the first-order pair-correlation-function and therefore does not contain information on coordination geometry. We have measured the XANES spectra<sup>(1,5)</sup> where the observed peaks are due to multiple scattering resonances (MSR) and therefore contain information on the relative positions of the atoms within  $\sim 4 \text{ \AA}$  around the central atom<sup>(13-15)</sup>. In fact from XANES of glasses we can obtain information on coordination geometry. The limitations of XANES in presence of several different V sites are shown in this paper.

The analysis of the first peak at the K-threshold in the "edge region" in a range of  $\sim 5 \text{ eV}$  allows determination of the effective charge of V ions which in these glasses cannot be determined by Mössbauer technique. Moreover the intensity of this transition to V-3d-derived molecular orbitals is strongly sensitive to coordination geometry and it is the more sensitive probe of the presence of different local coordination geometries of V in oxide glasses.

## 2. - EXPERIMENTAL.

The glasses were melted in air atmosphere at 1500 °K for 3 hours in alumina crucibles. They were made up from reagent grade materials  $V_2O_5$ ,  $Fe_2O_3$  and  $NH_4H_2PO_4$  by quenching from the melt.

The XANES experiments were carried out at the synchrotron radiation facility PULS at the Frascati Laboratories. Synchrotron radiation emitted by the ADONE storage ring, working at 1.5 GeV and about 50 mA was monochromatized by a Si(220) channel cut single crystal monochromator. The absorption coefficient has been calculated from transmission data T

using the formula  $\alpha = -(1/d)\ln T$  where  $d$  is the thickness of the sample. The samples were in the form of a layer of powder, few microns thick, on a Kapton tape. The stated energy differences between two absorption peaks in the derivative of absolute spectra are accurate to  $\pm 0.1$  eV. Data acquisition and elaboration were done using a PDP/11 computer. The absorption scale of each spectrum was normalized to the high energy value of the absorption continuum (in the EXAFS region at  $\hbar\omega = 5520$  eV i.e. 50 eV above the threshold peak). This normalization procedure allows the study of the intensity variation of peaks between different glasses and compounds.

### 3. - RESULTS AND DISCUSSION

#### 3.1. - XANES.

Fig. 1 shows the X-ray absorption spectra of vanadium-iron-phosphate glasses compared with crystalline  $V_2O_5$ . The multiple scattering resonances appear as peaks A, B and C in the energy range 5480 eV 5510 eV (10-40 eV above  $E_1$ ). The XANES of  $V_2O_5$ , characteristic of V

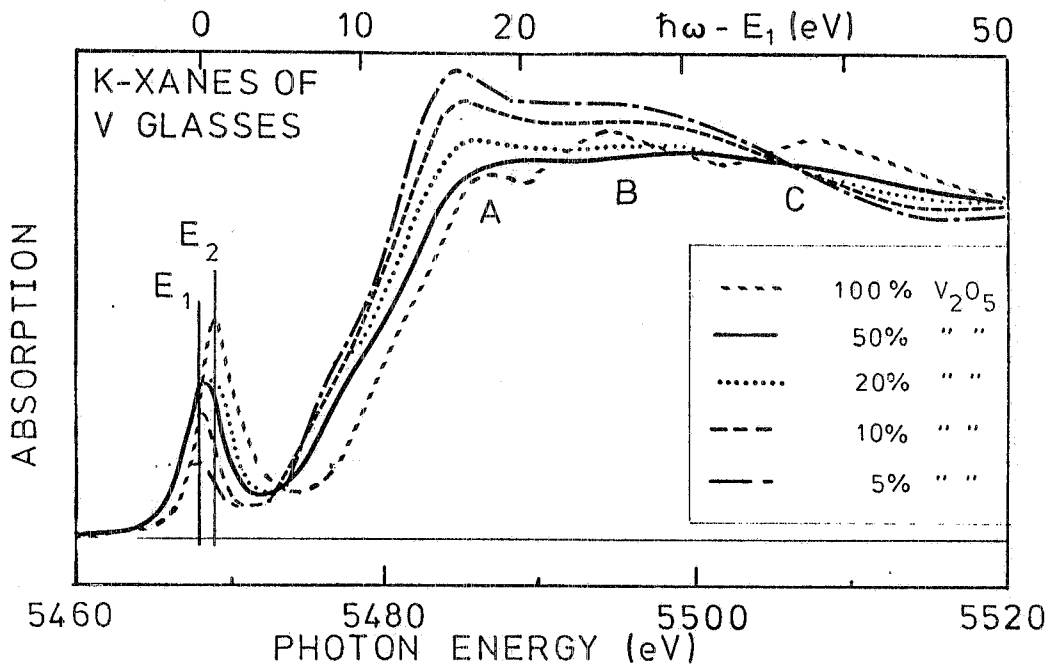


FIG. 1 - XANES of vanadium in crystalline  $V_2O_5$  and in semiconducting glasses  $50 P_2O_5 + (50 - x)FeO + xV_2O_5$  with different  $V_2O_5$  percentage  $x$  from 5% to 50%.

ion coordinated by 5 oxygen atoms, shows the peak A weaker than the B and C peaks. The XANES of the 5%  $V_2O_5$  glass is very similar to the measured XANES of crystalline  $V_2O_5$ <sup>(16)</sup>. This XANES spectrum is characteristic of a 6-fold coordinated transition metal (Ca, V, Ti)

compound<sup>(5, 13)</sup>. The peak A is at lower energy than in  $V_2O_5$  and is stronger than the broad peak corresponding to peaks B and C therefore the XANES of the  $x = 5$  glass shows that the local structure of the vanadium sites is formed by  $VO_6$  units.

The XANES of glasses with higher  $V_2O_5$  concentration show weak broad structures. However there is a trend from the flat spectrum of 50%  $V_2O_5$  glass (close to the smooth average absorption of the model compound  $V_2O_5$ ) toward the XANES of the 5%  $V_2O_5$  glass. These

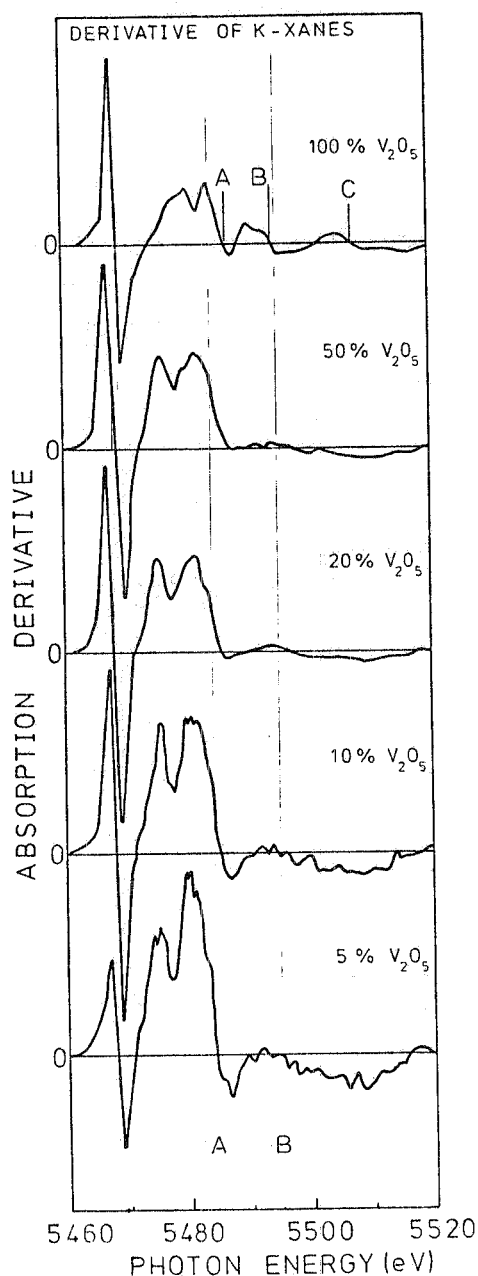


FIG. 2 - Derivative of XANES spectra reported in Fig. 1.

featureless XANES spectra can be explained as a result of the average of XANES of V ions in different coordination geometries. The trend of the XANES spectra approaching the XANES of 6-fold coordinated vanadium with decreasing  $V_2O_5$  percentage is interpreted as evidence of increasing number of V ions in 6-fold-coordination (C. N. 6).

Fig. 2 shows the derivative spectra of XANES of the semiconducting oxide glasses. The derivative spectra show that the energy positions of peaks A and B shift toward higher energy increasing the  $V_2O_5$  percentage. The peak C is not observed in the glasses.

### 3.2. - Edge.

Fig. 3 shows the "edge region" of the glasses and of the  $V_2O_5$  model compound. The first weak peak E at the K-threshold is plotted. Fig. 4 shows the derivative curves of the same peak E due to the  $1s \rightarrow t_{2g}$  or  $1s \rightarrow t_2$  transitions in 6-fold or in 4-fold coordination respectively. In perfect 6-fold octahedral coordination  $1s \rightarrow t_{2g}$  transition is dipole forbidden. The observed intensity is therefore due to the presence of p-components in the final state due to mixing with p-orbitals of neighbor atoms and/or to quadrupole transitions. In the 4-fold coordination the  $t_2$  final state has on the contrary a large p-character and therefore appears as strong as the dipole-allowed peaks at higher energy. In the case of  $V_2O_5$ , the 5-fold coordination of V with oxygen atoms gives practically a molecular final state similar to the  $t_2$  orbital and therefore we observe in Fig. 1 and 3 a strong peak E.

Let us now discuss the edge spectra of each glass.  $x = 5$  glass. - The intensity and energy position ( $\hbar\omega = 5468$  eV) of peak E in the glass with the lowest vanadium

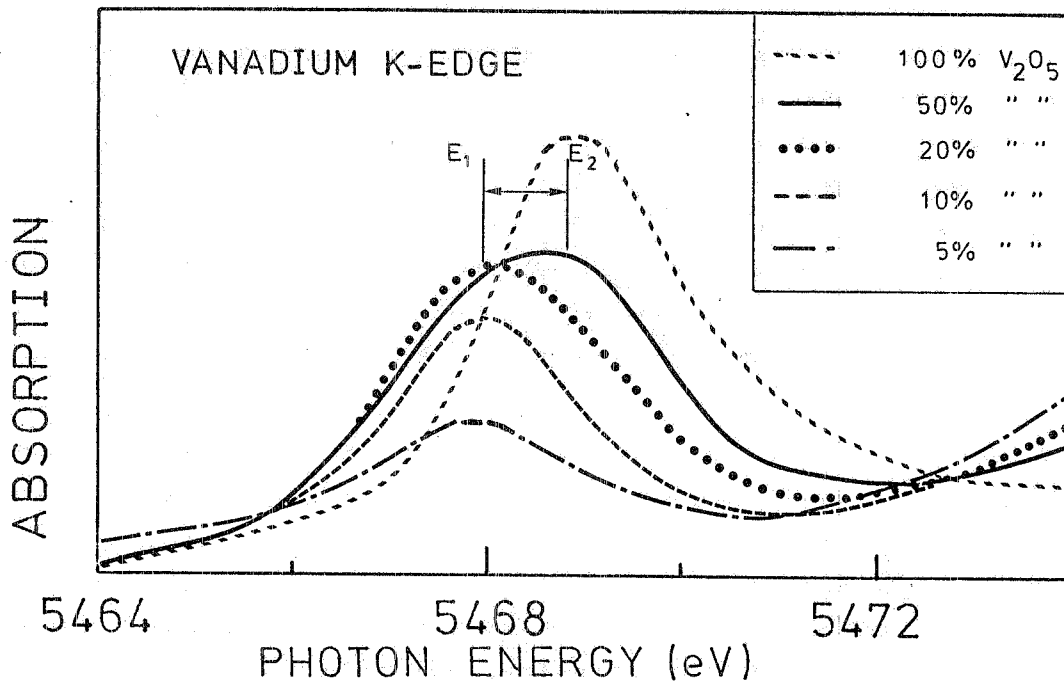


FIG. 3 - K edge of V in the semiconducting glasses and the crystalline V<sub>2</sub>O<sub>5</sub>. The figure shows the first peak at threshold E splitted (E<sub>1</sub>, E<sub>2</sub>) and shifted as function of V<sub>2</sub>O<sub>5</sub> concentrations.

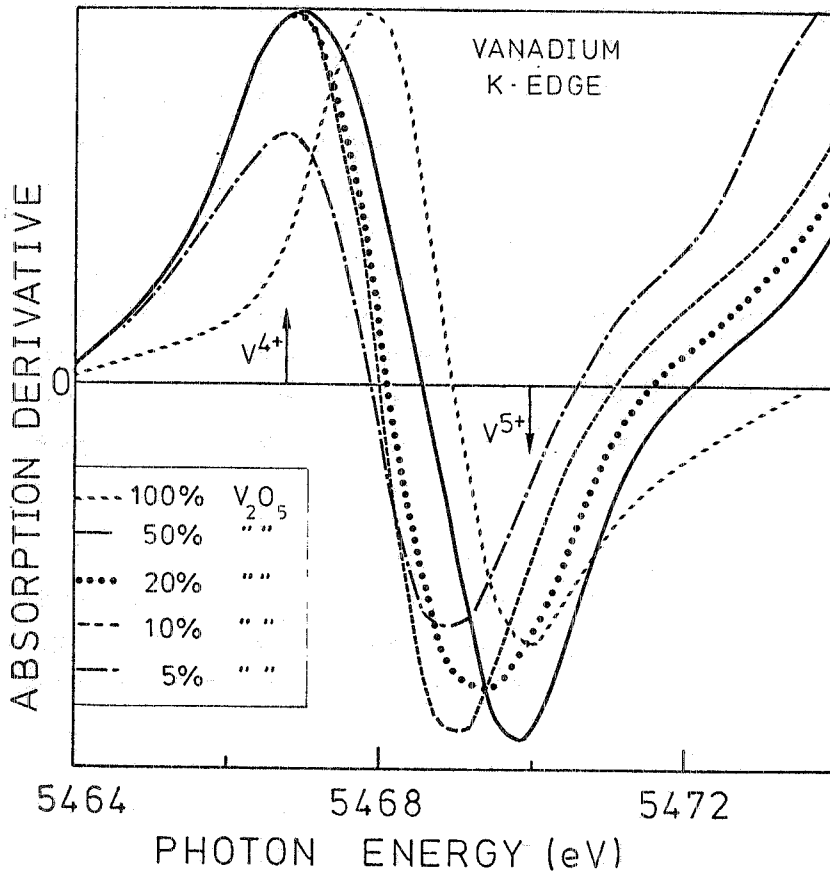


FIG. 4 - Derivative of the first peak at the K edge of vanadium glasses.

concentration (5%  $V_2O_5$ ) confirm the conclusions obtained from XANES analysis. In fact it is as weak as the corresponding peak in other vanadium and manganese oxides<sup>(5, 13, 16)</sup> with 6-fold coordination. The energy of the E peak in the lowest vanadium concentration is at 0.9 eV below the E peak in crystalline  $V_2O_5$ . This is the expected chemical shift of the binding energy of the 1s initial state going from  $V^{5+}$  of  $V_2O_5$  to  $V^{4+}$  of  $VO_2$ , as it has been measured by X-ray photoemission experiments<sup>(17)</sup>. We conclude that the V ions of this glass at low vanadium oxide concentration are  $V^{4+}$  ions coordinated by 6 oxygens ( $V^{4+}$  C.N. 6). This is the more common coordination for  $V^{4+}$  and it is the expected configuration of ions acting as "modifiers" in the glass network<sup>(18)</sup>.

x = 50 glass. - At the highest concentration we have studied (50%  $V_2O_5$ ), in absence of FeO, the E peak is splitted and two peaks  $E_1$  and  $E_2$  (see Fig. 3, 4). The derivative spectrum (solid line) has the maximum at the same energy of the spectrum of 5%  $V_2O_5$  glass characteristic of  $V^{4+}$  charge state, while the negative minimum is at the same energy of the spectrum of the model compound  $V_2O_5$ , characteristic of  $V^{5+}$  charge state. We conclude from this analysis that in the 50%  $V_2O_5$  glass V is in a mixed valence state with the presence of both  $V^{5+}$  and  $V^{4+}$ .

x = 10 glass. - Decreasing the  $V_2O_5$  concentration the intensity of peak  $E_2$ , at  $V^{5+}$  energy position, decreases and finally disappears (Fig. 3). The minima of the derivative spectra in Fig. 4 shift toward lower energy. In the 10%  $V_2O_5$  glass the presence of the peak  $E_2$  (the  $V^{5+}$  component) is hard to be observed. Also the energy position of the negative minimum in Fig. 4 in the derivative spectrum of the 10%  $V_2O_5$  glass is at the same energy as the 5%  $V_2O_5$  glass, suggesting that there is no more vanadium in the  $V^{5+}$  effective charge state. The high intensity of the  $E_1$  peak in Fig. 3 for the 10%, 20%, 50%  $V_2O_5$  glasses indicate that part of the vanadium ions has not a 6-fold-coordination. This can be an indication that part of vanadium ions are 4-fold coordinated. This very unusual coordination for  $V^{4+}$  ions can be explained if part of the vanadium ions substitute phosphorus ions and participate as "network formers" in the structure of the these oxide glasses. The largely different ionic effective charges and coordination of vanadium in these glasses show this ion has an intermediate character and can be both a "modifier" and a "network former" in different situations. In conclusion in the x = 10, x = 20 glasses we find  $V^{4+}$  C.N. 6 and  $V^{4+}$  C.N. 4 configurations where the last configuration disappears decreasing x.

### 3. 3. - Hopping conductivity and local structure.

The study of XANES of vanadium-iron phosphate glasses permits not only to specify directly the configuration of vanadium ions, but also allows to draw certain conclusions concerning the existence of respective electron transitions in the conductivity process in the above mentioned glasses.

XANES results show that the glass with 50% mole of  $V_2O_5$  is a mixed valence system of  $V^{4+}$  and  $V^{5+}$  with coordination numbers CN = 4 and CN = 5 respectively. In this case the electrical conductivity is simply due to the electron transition  $V^{4+} \rightarrow V^{5+}$ .

In the 20%  $V_2O_5$  glass we find some  $V^{4+}$  ions with C.N. 4, some with C.N. 6 and comparatively lower number of  $V^{5+}$  ions. The Mössbauer spectra of iron in this glass showed that the concentration of  $Fe^{2+}$  ions is about 2%<sup>(8)</sup> and therefore the conductivity is still dominated by  $V^{4+} \rightarrow V^{5+}$  electron transition.

In the 10%  $V_2O_5$  glass we find only  $V^{4+}$  in two coordination geometries characterized by C.N. 4 and C.N. 6. The Mössbauer spectra of iron for this glass show that the number of  $Fe^{2+}$  ions is about 6%. If the  $V^{5+}$  ions really are not present the electrical conductivity would be due to the electron transition  $Fe^{2+} \rightarrow Fe^{3+}$  and eventually  $V^{4+} \rightarrow Fe^{3+}$ . The existence of both these transitions is suggested by the results of internal friction studies for these glasses<sup>(9)</sup>, in fact this method allows to observe the considered electronic transitions<sup>(19)</sup>.

In the 5%  $V_2O_5$  glass we find only  $V^{4+}$  with C.N. 6. Because Mössbauer studies show that the concentration of  $Fe^{2+}$  is about 12% one can expect two electron transitions of  $Fe^{2+} \rightarrow Fe^{3+}$  and  $V^{4+} \rightarrow Fe^{3+}$ . For this glasses two characteristic peaks in the spectra of the internal friction were observed<sup>(6)</sup>.

One can not directly compare the results of structural studies of vanadium-iron phosphate glasses with those of binary vanadium-phosphate glasses, but some of results show an agreement with Jordan and Calvo<sup>(20, 21)</sup> suggestions based on density studies of binary glasses. They suggested that the glass containing more than 50 mole %  $V_2O_5$  exhibited two basic types of vanadium environment. These are tetrahedral  $VO_4$  groups and tetragonal pyramids of  $VO_5$  composition with a long and thus a weak V-O interaction completing the octahedral environments in half of these cases. Our results giving a mixed valence state for the 50%  $V_2O_5$  glass, formed by  $V^{4+}O_4$  and  $V^{5+}O_5$  microscopic units, are in agreement with their suggestions.

#### 4. - CONCLUSION.

XANES spectra of phosphate glasses with two transition metal oxides (iron and vanadium oxides) show that to explain the electrical conductivity results one must assume the existence of  $V^{4+} \rightarrow Fe^{3+}$ . The mixed valence state of 50 mole %  $V_2O_5$  glass has been determined. Both the presence of  $V^{4+}$  and  $V^{5+}$ , ionic state and the coordination geometries of these oxide glasses have been obtained by a joint analysis of "edge" and "XANES" regions of the absorption spectra. The coordination geometry and the ionic state of vanadium strongly dependent on  $V_2O_5$  concentration.  $V^{4+}$  ions exhibit two coordination geometries characterized by C.N. 4 and C.N. 6. The C.N. 4 configuration disappears at low  $V_2O_5$  concentrations. This is an indication that vanadium acts mostly as a "modifier" at low concentrations while it participates as a oxide "network former" in the glasses at higher concentration.



#### ACKNOWLEDGMENTS.

Thanks are due to the Director and all members of the staff of the Project for the utilization of synchrotron radiation "PULS" and to the "ADONE" machine group. This research was realized in the frame of the cooperation agreement between the University of Camerino and technical University of Gdansk.

#### REFERENCES.

- (1) - A. Bianconi, *Appl. Surf. Science* 6, 392 (1980).
- (2) - A. Balzarotti, A. Bianconi, E. Burattini, M. Grandolfo, R. Habel and M. Piacentini, *Physica Status Solidi (b)* 63, 77 (1974).
- (3) - A. Bianconi, *Surf. Science* 89, 41 (1979).
- (4) - A. Bianconi and R. S. Bauer, *Surf. Science* 99, 76 (1980).
- (5) - M. Belli, A. Scafati, A. Bianconi, S. Mobilio, L. Palladino, A. Reale and E. Burattini, *Solid State Commun.* 35, 355 (1980).
- (6) - G. Calas, P. Levitz, J. Petiau, P. Bondot and G. Loupilas, *Rev. Phys. Appl.* 15, 1161 (1980).
- (7) - N. F. Mott, *J. Non-Cryst. Solids* 1, 1 (1968).
- (8) - L. Murawski, C. H. Chung and J. D. MacKenzie, *J. Non-Cryst. Solids* 32, 91 (1979).
- (9) - O. Gzowski, L. Murawski, W. Lizak, H. Binezycka and J. Sawicki, *J. Phys. D* (in print).
- (10) - W. Chomka, D. Samatowicz, O. Gzowski and L. Murawski, *J. Non-Cryst. Solids* (in print).
- (11) - D. Raoux, J. Petiou, P. Bondot, G. Calas, A. Fontaine, P. Lagarde, P. Levitz, G. Loupilas and A. Sadoc, *Rev. Phys. Appl.* 15, 1079 (1980).
- (12) - P. Eisenberger and B. Lengeler, *Phys. Rev.* B22, 3551 (1980).
- (13) - A. Bianconi, in "EXAFS for Inorganic Systems", ed. by C. D. Garner and S. S. Hasnain, Daresbury Report SCI/R17 (1981), p. 13, and references therein.
- (14) - A. Bianconi, S. Doniach and L. Lublin, *Chem. Phys. Letters* 59, 121 (1978).
- (15) - P. J. Durham, J. B. Pendry and C. H. Hodges, *Solid State Commun.* 38, 159 (1981); G. N. Greaves, P. J. Durham, G. Diakun and P. Quinn, *Nature* 294, 139 (1981).
- (16) - A. Bianconi, to be published.
- (17) - R. J. Colton, A. M. Guzman and J. W. Rabalais, *J. Appl. Phys.* 49, 409 (1978).
- (18) - R. F. Pettifer, in "EXAFS for Inorganic Systems", ed. by C. D. Garner and S. S. Hasnain, Daresbury Report SCI/R17 (1981).
- (19) - W. Chomka, O. Gzowski, L. Murawski and D. Samatowicz, *J. Phys.* C11, 3081 (1978).
- (20) - B. D. Jordan and C. Calvo, *Can. J. Phys.* 55, 436 (1977).
- (21) - C. Calvo and B. D. Jordan, *Phys. Chem. Glasses* 17, 220 (1976).