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XANES COMPARATIVE STUDY OF RUTILE SOLID SOLUTIONS : (Ti,V)O₂, (Ti,Nb)O₂ AND (Ti,Ta)O₂

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Résumé

On a mesuré l'absorption au seuil K du titane, au seuil K du vanadium et L du tantale dans les solutions solides (Ti,V)O₂, (Ti,Nb)O₂ et (Ti,Ta)O₂. Par comparaison des solutions entre elles, on a montré l'existence d'un transfert de charge partiel entre Ti et Nb. On a par ailleurs, déterminé les variations du champs de ligandes et de la taille de l'octaèdre de coordination. Enfin, on a détecté la présence d'un pic excitonique aux seuils du titane et du vanadium pour toutes les solutions solides.

Abstract

We have measured the absorption at Ti K edge, V K edge and Ta L edge in (Ti,V)O₂, (Ti,Nb)O₂ and (Ti,Ta)O₂ solid solutions. Comparison of the edge spectra of these compounds shows evidence of a partial charge transfer between Ti and Nb and variations of the ligand field and the size of the coordination octahedron. Lastly, we have detected the presence of an excitonic peak at Ti or V edge in all solid solutions.

Introduction

Comparison of K-edge absorption spectra of substitutional solid solutions involving Ti should help clarify the origin of the changes occurring on the Ti K edge at around 5Kev. The chosen compounds are such that only a few electrons are present around the Fermi level: zero or one for Ti or Nb atoms, one for vanadium and zero for tantalum. We will examine here four points: electron transfer, ligand field strength, variation of the size of the coordination octahedron and excitonic effects. The procedures for collecting, smoothing and deriving the spectra and full results are published elsewhere (/1/ and in submitted publications: XANES in (Ti,V)O₂ to Phys. Rev. B15; XANES in (Ti,Ta)O₂ to Physica Status Solidi). Experimental K edge spectra are shown in Fig.1, energy positions of the different features occurring on K edge spectra are plotted on fig.2 and experimental results on Ta L edge are shown on Fig.3.

1-Electron transfer

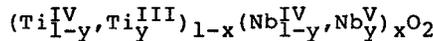
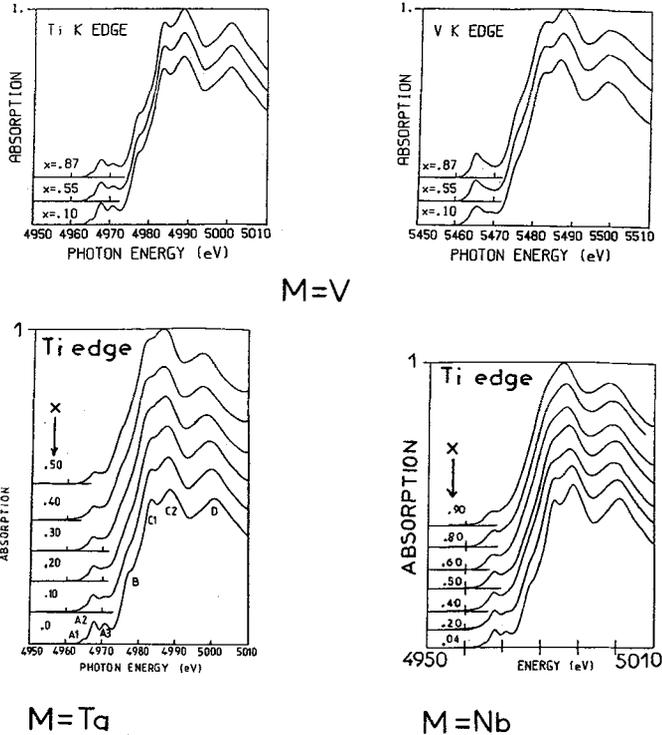
The overall positive energy shift of the edge of absorption is related to an increase of valence on the central atom. This comes from a lower screening of the nucleus attractive potential on the 1s core electron and from a reduction of core Coulomb interaction with all other electrons. Valence change in solid solutions are very useful because it yields the atoms between which an electron transfer occurs.

Nevertheless, the difficulty is to quantitatively appreciate the chemical shift among other effects. Magnetic susceptibility and electrical conductivity measurements have been carried out and indicate that:

- in (Ti,V)O₂, titanium and vanadium atoms have respectively the 3d⁰ and 3d¹ configuration whatever the vanadium content /2/.
- in (Ti,Ta)O₂, titanium atoms have the 3d⁰ or 3d¹ configuration depen-

ding on the tantalum content whereas Ta atoms have the $5d^0$ configuration /3/. Extreme situations are thus available to evaluate the effect of an electron valence change in the same structure and to apply those results to $(Ti,Nb)O_2$ which is intermediate. We think that reliable shifts can be measured on the second dipole forbidden transition (i.e. $1s \rightarrow t_{2g}$). For the upper transitions, chemical shift and other effects mix. It seems that the chemical shift is around 0.7-0.8eV per valence charge increase. It is the same order in $(Ti,Nb)O_2$ but from TiO_2 to NbO_2 . This indicates that a partial charge transfer occurs leading to the following formula:

Fig1: $Ti_{1-x}M_xO_2$ K edge spectra



in which y is unknown but significantly non-zero. We have shown elsewhere /2/ that y is related to the occurrence of electron pairings along the c axis on the niobium atoms.

2-ligand field

t_{2g} and e_g wave functions corresponding to A2 and A3 peaks are essentially composed by 3d metallic orbitals. They are empty or occupied by one electron. Some of the $1s \rightarrow 3d$ transitions are dipole forbidden but quadrupole allowed, absorption coefficient is therefore not negligible and give rise to features with a tenth of magnitude of allowed transitions. A2-A3 splitting allows evaluation of the strength of the crystal field in O_h symmetry. We have found:
 3.1eV around Ti^{4+} in $(Ti,V)O_2$ and in $(Ti,Ta)O_2$
 2.1eV around Ti^{3+} in $(Ti,Ta)O_2$ and 2.3eV in $(Ti,Nb)O_2$
 The weakening of the crystal field is probably due to the screening of the ligand field by d electron.
 3.9eV around V^{4+} in vanadium poor $(Ti,V)O_2$ solid solutions
 2.8eV around V^{4+} in vanadium rich $(Ti,V)O_2$ solid solutions
 There is no electronic transfer in these solid solutions but there are antiferromagnetic electron couplings along the c axis. The proportion

of paired electrons increases with the vanadium content as mentioned by Horlin et al. /2/. Consequently, the weakening of the ligand field is related to these electronic changes. Lastly, transitions $2p_{3/2} \rightarrow t_{2g}$ and e_g indicate a high ligand field around Ta^{5+} in $(Ti,Ta)O_2$

3-Size of the coordination octahedron

On the base of the analysis made by Natoli /5/ to link the mean oxygen-metal bond length and energy difference between peaks t_{2g} and an allowed transition, we have observed the following variations.

Ti-O mean distance in $(Ti,V)O_2$ seems to decrease by 2pm (picometer) from its value in TiO_2 (195.7pm).

V-O mean distance in the same solid solutions, seems to increase by 4pm from its value in VO_2 (193.3pm). These variations of the size of the coordination octahedron are due to a steric effect and are related to the difference of the ionic radii: V^{4+} 63pm, Ti^{4+} 68pm.

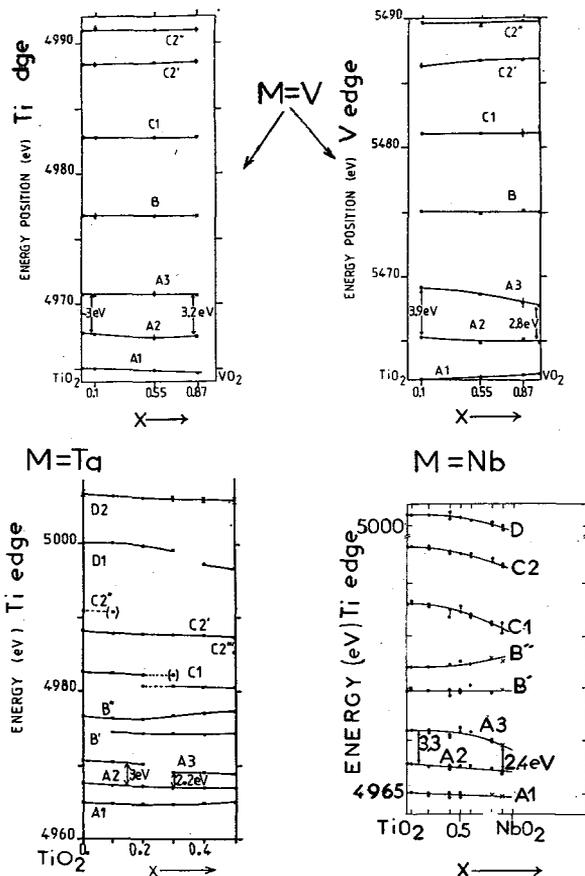
Ti-O mean distance in $(Ti,Nb)O_2$ increases by 11pm from TiO_2 . It is the same magnitude in $(Ti,Ta)O_2$. This comes probably from the increase of the titanium ionic radii because of charge transfer (Ti^{3+} 76pm) and simultaneous screening.

4-Exciton peak

A Frenkel exciton peak is well defined at Ti K edge of TiO_2 . It is the excited electron which remains bound to the core hole. It is not mobile in the structure and is well localized. The binding energy can be evaluated as 1.1eV and the FWHM is of the order of the experimental resolution i.e. 1.3eV. In solid solution, at the Ti K edge, exciton binding energy is independent on V content whereas it is weakly dependent on Nb content (decreasing from 1.1 to .9eV) but strongly dependent on Ta content (decreasing from 1.1 to .6eV). The intensity of the exciton line follows the same dependence. This seems to be highly correlated with the d electron density on Ti atoms.

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Fig2: $Ti_{1-x}M_xO_2$, peak positions



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