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THERMODYNAMIC, SPECTROSCOPIC, X-RAY, ELECTRONIC AND MAGNETIC STUDY OF 
(Ti$_{1-x}$Nb$_x$)O$_2$ SOLID SOLUTIONS VERSUS TEMPERATURE AND COMPOSITION

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réssumé - Diverses propriétés physiques ou physico-chimiques des solutions solides 
(Ti,Nb)O$_2$ ont été étudiées en fonction de la température et de la composition de 
manière à déterminer l'évolution de la structure électronique. La présence de nio-
bium à l'état 4d$^1$ modifie largement le comportement électrique et la structure de 
defauts de TiO$_2$. Les niveaux de niobium s'acumulent au voisinage de la bande de 
conduction du Ti. L'écart à la stoechiométrie du matériau change de signe quand 
la concentration de niobium augmente, cette modification est à relier à l'occupation 
particelle des niveaux 4d du niobium. Aux concentrations de niobium élevées des 
interactions antiferromagnétiques entre les niobium ou les titane porteurs d'élec­
trons se développent. Les électrons sont alors plus localisés que dans TiO$_2$ et la 
mobilité est thermiquement activée.

**Abstract** - We have studied different physical or physico-chemical properties of 
(Ti,Nb)O$_2$ solid solutions versus temperature and composition in order to sift our 
the evolution of the electronic structure. The substitution of titanium by niobium 
in the 4d$^1$ state changes largely the electrical behaviour and the defect structure 
of TiO$_2$. The 4d electronic levels of niobium pile up close to the bottom of the 
conduction band. The departure from stoichiometry changes of sign for the niobium 
contents $>$ 4%, this would be related to the partial occupation of 4d levels. For 
higher niobium content, antiferromagnetic interaction occurs on the niobium or on 
the titanium atoms. Electrons are then more localised than in TiO$_2$ and their mobility 
in thermally activated.

**I - THERMODYNAMIC PROPERTIES**

By means of thermogravimetric mea-
surements, it has been possible to 
obtain informations on the nature of 
intrinsic and extrinsic defects of 
Nb$_x$Ti$_{1-x}$O$_{2+y}$ solid solutions. Pure TiO$_2$ 
is an oxygen-deficient oxide. The main 
defects are oxygen vacancies, doubly 
ionized V$_{O}^-$ or singly ionized V$_{O}^+$ and 
interstitial titanium Ti$_{i}^+$. NbO$_2$ is a 
metal-deficient oxide. The main defects 
are niobium vacancies. The solid solu-
tions may be divided into two groups. 
If $x$ $>$ 0.04, the behaviour is analogous to 
that of NbO$_2$ with the same defects, but 
the width of the homogeneity range de-
creases with the titanium content and 
Nb$_{0.04}$Ti$_{0.96}$O$_2$ is a stoichiometric 
oxide. If $x$ $<$ 0.04, the oxides are both 
metal-deficient and oxygen-deficient 
according to the oxygen partial press-
Measure. In the oxygen-deficient domain, the main defects are oxygen vacancies. In the metal-deficient domain, the main defects are metal vacancies $V_{\text{M}}^\text{M}.$

### II-X-RAY ABSORPTION SPECTROSCOPY /2/

The K-edge spectra of titanium in $(\text{Ti},\text{Nb})\text{O}_2$ was recorded on the synchrotron radiation at Lure-DCI-Orsay. Only the near edge structures have been analyzed. They show the energy position of the band maxima of unoccupied levels if we assume the one electron approximation valid. The analysis of the second derivatives leads to three important conclusions.

First, a partial electron transfer occurs from $\text{Nb}4d$ to $\text{Ti}3d$ wave function with increasing niobium content. This implies close energies for these wave functions.

Second, the crystal field splitting which is the splitting between the levels arising from $t^2_g$ and $e_g$ decreases from 3.3eV to 2.5eV when niobium content increases. This is related to the screening by the d-electrons and the increase of the oxygen-metal bond length.

Third, the change of the shape of the Ti spectra with niobium content indicates that modifications occur around the titanium continuously from $\text{TiO}_2$ to $\text{NbO}_2$. Hence the solid solutions are probably disordered.

### III-ELECTRON TRANSPORT IN $\text{(Ti}_{1-x}\text{Nb}_x)\text{O}_2$ FOR $x>0.8$ /6/

The analysis of electrical conductivity and thermopower yields different conclusions as for pure or doped $\text{TiO}_2$ where a large polaron was pointed out /4,5/. In the present case, the experimental results are consistent with a small polaron model. Mobilities shown on the opposite figure are thermally activated whatever the niobium content. Thermopower (not shown here but in /6/) indicates that polarons are bound to larger species with an energy greater than 0.1eV increasing with the niobium content. However, it seems that mobile species would be single small polarons only for low temperatures, because of the high calculated energy at high temperature for the associated phonon according to the small polaron theory. Hence we have proposed the existence of bipolaron or tripolaron for higher niobium content or high temperature. This assumption accounts for the high temperature thermopower and the variation of the activation energy of the mobility with the temperature for $x<0.5$. For $\text{NbO}_2$, owing to the magnitude of the thermopower ($-80\mu\text{V/K}$), a small polaron transport may still be assumed, but with a higher orbital degeneracy and the possibility of two electrons on the same site.

### IV-X-RAY DIFFRACTION STUDY

We have measured by means of X-ray diffraction on powder, the "a" and "c" parameters of the rutile phases (D$\text{4h}$) or pseudo rutile phases (C$\text{4h}$) versus the temperature and the niobium content.

Plots of variations of c and a parameters relatively to $\text{TiO}_2$ are...
shown on the opposite figure versus the composition for room and 1300K. We have noticed as other authors that a tetragonal-rutile transition occurs for higher niobium content and near 1000K but without discontinuity of the parameters.

The influence of $x$ is much greater than that of $T$. The "a" parameter increases faster than the "c" parameter and follows a Vegard law. It is not the case on the "c" parameter which becomes approximately constant for $x>50\%$ for all temperatures.

From that, we have concluded that a relative compression stands along c. This is related to antiferromagnetic interactions along the c axis between adjacent sites.

With increasing $T$, the thermal expansion of TiO$_2$ is isotropic, on the contrary, NbO$_2$ thermal expansion is strongly anisotropic, as "a" is almost $T$ independent and "c" has the same dependence as TiO$_2$ (this is not shown here but in a subsequent paper).

These observations leads to the conclusion that interaction between adjacent sites occurs even at high temperatures and essentially along the "c" axis. Because of the disappearance of long range order but without discontinuity on the parameters, we conclude to a thermal disorder of electron pairings.

V-MAGNETIC PROPERTIES /7-8/

A-EXPERIMENTAL

Magnetic susceptibility was measured with three different apparatus: a liquid helium magnetometer for $4K<T<300K$, a gaseous helium magnetometer for $300K<T<600K$ and an argon magnetometer for $400K<T<1250K$. The different results are very well consistent with each other.

B-RESULTS

We have shown on the opposite figure the squared Bohr magneton number versus the temperature and the niobium content. The analysis will be made by comparison with the results obtained previously on (Ti,- Ta)O$_2$ and (Ti,V)O$_2$ solid solutions.

In the case of (Ti,V)O$_2$ the increase of magneton number is related to the monoclinic-tetragonal transition occurring at about 350K for vanadium contents larger than 0.8. For lower vanadium contents there is no transition and the increase of magneton number is related to the effect of temperature on the antiferromagnetic interactions in vanadium clusters.

The same phenomenon is noticeable in (Ti,Nb)O$_2$ for niobium contents larger than .5 and consequently we conclude to the existence of such clusters in these solid solutions. Nevertheless we notice that the transition occurs at much higher temperature ($T>1100K$).

The (Ti,Ta)O$_2$ solid solutions are limited to tantalum contents smaller than .5, the results are known for $T<300K$. For this range of temperatures and tantalum contents, no transition is visible. Nevertheless (Ti,Nb)O$_2$ solid solutions look alike to (Ti,Ta)O$_2$ for low
temperature and for low niobium content. We notice in the both cases that the magneton number is non-zero and independent of x for T=0. It is quite different in (Ti,V)O₂.

**C-DISCUSSION**

For x<.45

In the case of (Ti,V)O₂ the magnetic properties are related to the antiferromagnetic coupling between half spins with quenched orbital momentum in linear cluster along the c axis. Because of the different magneton numbers at low temperature between (Ti,V)O₂ and other solid solutions we conclude that there is no S=1/2 centers in (Ti,Nb)O₂. A better explanation of the non zero magneton number for T=0 is a partial balance of spin momentum and orbital momentum through the spin-orbit coupling and the distortion around metallic sites. This leads to stabilize an orbital singlet but the spin orbit coupling mixed different wave functions and thus effective momentum has not the spin only value neither the zero value at 0K. Therefore it can be deduced that the squeezing of the metallic octahedron along the c axis is greater than the tetragonal distortion. This effect appears either for (Ti,Nb)O₂ or for (Ti,Ta)O₂. So effective momentum at very low temperature comes from electrons on titanium.

Moreover for higher temperatures a comparison between the magnitude of effective momentum of Ti₈Nb₂O₁₂ and Ti₈Ta₂O₁₂ shows that the first is smaller than second one. Because in (Ti,Ta)O₂ electrons are principally trapped on the titanium sites, in (Ti,Nb)O₂ a part of electrons are located on niobium sites and probably with a larger antiferromagnetic coupling. However this conclusion is valid only for rather low temperatures. For higher temperatures electrons becomes mobiles as indicated by the temperature dependence of the thermopower. Thus they can be located on the titanium sites partly isolated or in clusters.

For T>750K for Ti₈Nb₂O₁₂ the thermopower becomes constant. This implies that the number of electronic mobile species does not change anymore, that is to say all electrons are mobiles. No break was observed on the temperature dependence of the effective magnetic momentum. We thus can conclude that no change of magnetic properties appears such as the formation of a triplet state coming from the localization of two electrons on the same site. On the other hand, if all mobile species were monoelectronic we would find an effective momentum approximately constant since electrons are frequently on titanium sites and the spin-orbit coupling is rather small (150cm⁻¹). Consequently, the assumption of polyelectronic mobile species at high temperature is rather likely.

For x>.45

For T=0, the magneton number is zero, consequently the orbital momentum may balance the spin momentum everywhere there is no cluster and the distortion of the metallic site may stabilize an orbital doublet or triplet. This does not exclude antiferromagnetic couplings occuring elsewhere since they lead again to a zero effective magnetic momentum.

As mentioned previously, the low magneton number for intermediate temperatures comparing to spin only formula, implies a large number of spin pairings. Those ones are destroyed with increasing temperature leading to an increase of the Bohr magneton number.

Nevertheless, in NbO₂ at high temperature the effective momentum is considerably lower than the spin only value with S=1/2 or than the value obtained by taking into account the spin orbit coupling. Thus, exchange couplings are still preserved but probably on the same site. Since the thermopower is independent of T, the polyelectronic species are still mobile.

**VI—CONCLUSION**

As a conclusion, we will proposed tentatively the following evolution of the electronic structure near the conduction band versus the composition and the temperature.
The different point defects of TiO$_2$ appearing in the gap are replaced by titanium vacancies when niobium is added. The Nb levels stands 0.2eV below the conduction band. As the niobium content increases antiferromagnetic chains are created, their length depending on the amount of niobium. However, it remains single electrons on Nb or Ti for x<50% for all temperatures. For x>50%, the amount of single electrons is very small at low temperatures. It increases again at high temperatures when the density of states of electrons in clusters decreases.

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