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The influence of titanium and oxygen vacancies on the chemical bonding in titanium oxide†

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Abstract. The three TiO phases, α -, β - and γ -TiO, with stoichiometric composition, contain about 15% vacancies on both the Ti and the O sublattices. The low-temperature modification α -TiO, which is stable below 940 °C, crystallises in a monoclinic structure corresponding to the formal composition $\text{Ti}_{0.833}\text{O}_{0.833}$. In order to study the influence of the Ti and O vacancies on the chemical bonding in TiO, the related NbO structure, of formal composition $\text{Ti}_{0.75}\text{O}_{0.75}$ (Ti_3O_3), has been chosen as a model for the much more complicated real structure of TiO. This choice is based on the assumption that the model shows the essential effects with less computational effort. A self-consistent LAPW band structure calculation has been performed for the hypothetical TiO having the NbO structure. The calculated density of states and the local partial densities of states are compared with the corresponding data for stoichiometric TiO containing no vacancies, and for a model structure of $\text{TiO}_{0.75}$ containing ordered O vacancies. A characteristic feature in Ti_3O_3 is the occurrence of an additional band caused by the O vacancies and of three further bands with predominant d character, in the energy region between the 'p band' and the 'd band' of TiO. This effect leads to the disappearance of the band gap between the 'p band' and the 'd band' existing in stoichiometric TiO. The splitting off of four bands below the remaining metal d bands was previously predicted by Andersen and Satpathy. The bonding situation is discussed on the basis of electron density plots. The introduction of Ti vacancies, \square_{Ti} , in ordered $\text{TiO}_{0.75}$ causes an increase of the strength of the Ti- \square_{O} -Ti bonds across the oxygen vacancies, \square_{O} . The ionicity of the remaining Ti-O σ bonds is reduced. The Ti-O π bonds are strengthened, whereas the Ti-Ti σ bonds along the edges of the Ti octahedra around the O vacancies remain practically unchanged. The O- \square_{Ti} -O interaction of the rather localised O 2p orbitals across the Ti vacancies does not lead to an effective bond formation. The superposition of the Ti- \square_{O} -Ti bonds and the Ti-Ti σ bonds leads to a 'd band' electron density in the (111) plane that is directed towards the centres of the triangles formed by neighbouring Ti atoms. A similar electron density was obtained by Andersen and Satpathy assuming metal three-centre bonds.

1. Introduction

In a recent paper (Schlapansky *et al* 1989), the influence of O vacancies, \square_{O} , on the electronic structure of cubic TiO was studied by performing a self-consistent LAPW band structure calculation for the composition $\text{TiO}_{0.75}$, whereby a hypothetical or-

† This paper is dedicated to the memory of the late Professor O E Polansky.

dered defect structure $\text{Ti}_3^{[4]}\text{Ti}^{[6]}\text{O}_3\Box_{\text{O}}$ (Schlapansky *et al* 1989) was assumed†. The results were compared to similar calculations for $\text{TiC}_{0.75}$ (Redinger *et al* 1985, 1986) and $\text{TiN}_{0.75}$ (Herzig *et al* 1987). In contrast to these two systems, however, $\text{TiO}_{0.75}$ is reported to contain 5% vacancies on the Ti sublattice sites (Banus *et al* 1972).

At the stoichiometric composition, all three TiO phases, γ -, β -, and α -TiO (Murray and Wriedt 1987), accommodate approximately 15% vacancies on both the Ti and O sublattices. The high-temperature form, γ -TiO, is stable between 1250 °C and the melting point. It crystallises in the sodium chloride structure and has a wide homogeneity range caused by vacancies. About 15% vacancies are randomly distributed over each the Ti and the O sublattice (Banus *et al* 1972). In the temperature range between 1250 °C and 940 °C β -TiO is stable. This phase exhibits a cubic superstructure with vacancies on particular lattice sites which are randomly occupied (Murray and Wriedt 1987). The structure of the low-temperature α -TiO phase (below 940 °C) of formal composition $\text{Ti}_{0.833}\text{O}_{0.833}$ is monoclinic. Its unit cell contains 10 Ti and 10 O atoms occupying 10 of 12 lattice sites of each sublattice of the NaCl structure (Watanabe *et al* 1967). This structure can also be derived from linear chains of octahedral Ti_6O_{12} clusters around the O vacancies (Burdett and Hughbanks 1984).

If not only two, but all six Ti atoms of one cluster are connected to other clusters, the three-dimensional network of the NbO structure results, with 25% vacancies on both the Ti and O sublattices (Simon 1981). The unit cell of the NbO structure can be derived from the unit cell of ordered $\text{Ti}_3^{[4]}\text{Ti}^{[6]}\text{O}_3\Box_{\text{O}}$ by leaving the $\text{Ti}^{[6]}$ lattice sites vacant. In agreement with thermodynamic calculations of the defect formation and interaction energies in TiO (Boureau and Tetot 1987), there are neither unlike vacancies at first neighbour lattice sites nor vacancies of the same type on second nearest lattice positions in the model structure. While for NbO, the NbO structure is more stable than the NaCl structure by 1 eV (Schwarz 1987), both structures seem to be of equal stability for TiO, which crystallises in the more complicated defect structure of α -TiO at low temperatures.

In the present work, a self-consistent LAPW band structure calculation was undertaken for a hypothetical $\text{Ti}_{0.75}\text{O}_{0.75}$ crystallising in the NbO structure. This model structure should show the essential effects of both Ti and O vacancies on the chemical bonding in TiO, but it requires much less computational effort than the related, but much more complicated, superstructure of α -TiO. The influence of the Ti vacancies on the stabilisation of Ti- and O-deficient titanium oxide can be investigated separately by comparing the results of the present band structure calculation for ordered $\text{Ti}_{0.75}\text{O}_{0.75}$ with the recently published calculation for ordered $\text{TiO}_{0.75}$ (Schlapansky *et al* 1989). The present paper is intended to complement this publication.

The influence of both Ti and O vacancies on the stability of titanium oxide has already been investigated theoretically by various authors.

Earlier publications, such as the non-self-consistent APW-VCA (virtual crystal approximation) band structure calculations for Ti- and O-deficient titanium oxides by Schoen and Denker (1969), exclude the possibility of vacancy states, which, meanwhile, have been proved to be of crucial importance for the stability of vacancy-containing transition metal carbides, nitrides and oxides (Redinger *et al* 1985, 1986, Herzig *et al*

† A model structure of this compound is obtained by removing an O atom from the centre of the cubic unit cell for the NaCl structure. Then, the Ti atoms ($\text{Ti}^{[4]}$) at the face centres are surrounded by only four instead of six nearest O neighbours and are no longer equivalent to the $\text{Ti}^{[6]}$ atoms at the cube corners, the latter retaining the octahedral coordination of the NaCl structure with six nearest O neighbours.

1987, Schlapansky *et al* 1989).

Huisman *et al* (1980) were the first to stress the importance of vacancy states for the energetic stabilisation of defects in TiO. Besides a simple tight-binding model Hamiltonian calculation of the densities of states, they determined the cohesive energy of TiO as a function of the vacancy contents by means of the non-selfconsistent KKR-ATA (average T-matrix approximation) method. The authors obtained vacancy states in the gap between O p and Ti d band. They identified these vacancy states with Ti conduction band states from presumptive clusters of O vacancies. In these clusters, the Ti conduction band states of s or p symmetry are not shifted to higher energies by the repulsive action of the O s and p valence states as in TiO without defects. However, neither Huisman *et al* (1980) nor later *ab initio* band structure calculations for Ti- and O-deficient titanium oxide (Schwarz 1987, Hörmandinger *et al* 1988) entered into a more detailed discussion of the influence of vacancies on the chemical bonds in TiO.

In contrast, Andersen and Satpathi (1984) discussed the chemical bonding in the ordered metal oxide defect structures Nb₃O₃ and Ti₅O₅ in terms of four localised metal d hybrid orbitals per metal atom. The lobes of these hybrid orbitals point towards the centres of the triangular faces of the metal octahedra building up these defect structures. The localised orbitals originate from the muffin-tin orbitals of an LMTO-ASA band structure calculation by transforming them into a tight-binding basis of metal d and oxygen p states. If metal-non-metal p-d π bonding is neglected, only the metal $d_{x^2-y^2}$ states are involved in nearest neighbour p-d σ bonding. Therefore metal d_{z^2} and d_{xy} , d_{xz} , d_{yz} orbitals are available for the formation of four equivalent hybrid orbitals per metal atom. In the Nb₃O₃ structure with three metal atoms per unit cell, four states per unit cell are lowered in energy. Using the basis of Andersen and Satpathy, these four states are bonding linear combinations of d^4 hybrid orbitals leading to metal three-centre bonds.

Burdett and Hughbanks (1984) also discussed thoroughly the influence of vacancies on the chemical bonds in TiO and NbO, but they argued only with results from semi-empiric extended Hückel band structure calculations.

Gubanov *et al* (1984) compared the atomic orbital populations, the Mulliken and the valence charges for titanium oxide clusters of 27 atoms without vacancies and with either a Ti or an O vacancy in the centre of the cluster. In addition to some problems concerning the embedding of the cluster and the cluster charge, their model does not allow for any interaction between the O and Ti vacancies and, therefore, cannot completely describe TiO with both vacancies present at the same time.

2. Computational aspects

The self-consistent LAPW method (Andersen 1975, Koelling and Arbman 1975) has been used for the calculation of the electronic structure of Ti_{0.75}O_{0.75} crystallising in the NbO structure (Ti₃□_{Ti}O₃□_O). The unit cell for the NbO structure is shown in figure 1 and contains the two different cuts in the (100) plane and the cut in the (111) plane for which electron density plots will be displayed later on. Both the Ti and O atoms are in a square-planar crystal field of four nearest O (Ti) neighbours resulting in D_{4h} point group symmetry for the Ti and O lattice sites. In a local coordinate system with the z axis pointing towards the nearest vacancy, the atomic p and d states of both O and Ti split according to the D_{4h} symmetry. The d states split into the four components d_{z^2} , $d_{x^2-y^2}$, d_{xy} and (d_{xz} , d_{yz}). In an octahedral crystal field the first

two components correspond to the twofold degenerate e_g states and the last two to the threefold degenerate t_{2g} states. The three degenerate p states in O_h split into p_z and (p_x, p_y) states with the p_z states pointing towards the Ti or O vacancy.

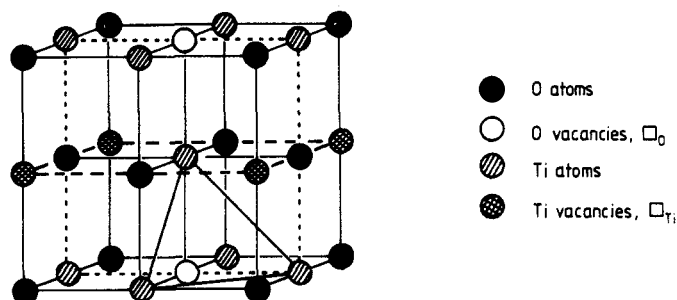


Figure 1. Cubic unit cell for $Ti_{0.75}O_{0.75}$ crystallising in the NbO structure. ---, (100) plane (cut 1); ·····, (100) plane (cut 2); —, (111) plane.

The lattice parameter and muffin-tin radii of stoichiometric TiO (Schlapansky *et al* 1989) used as input for the present band structure calculation are listed in table 1. As in the work by Schlapansky *et al* (1989), the k expansion of the LAPW wave functions was extended over 350 k vectors. An energy mesh of 10 k points in the irreducible part of the Brillouin zone (IBZ) was used in the SCF procedure. After having reached self-consistency, eigenvalues for the finer mesh of 256 k points in the IBZ were calculated in order to obtain the densities of state (DOS) by means of the tetrahedron method (Lehmann and Taut 1972).

Table 1. Input parameters for the LAPW band structure calculation of ordered $Ti_{0.75}O_{0.75}$ (in au).

Quantity	Region	$Ti_{0.75}O_{0.75}$
Lattice parameter		7.89274
Muffin-tin sphere radii	Ti, \square_{Ti}	2.14175
	O, \square_O	1.80462

More information on details of the band structure calculation can be found in the paper by Schlapansky *et al* (1989).

3. Results

3.1. Band structure and DOS

Figure 2 displays the band structure of ordered $Ti_{0.75}O_{0.75}$ in three symmetry directions of the simple cubic Brillouin zone. Due to the presence of three oxygen atoms in the unit cell, three O 2s bands at about -0.7 Ryd and nine O 2p bands between 0.1 and about 0.43 Ryd are found in the band structure. In the energy range from about 0.43 to 1.1 Ryd 16 bands follow. In the lower part of this energy region, a band is

observed which is caused by the oxygen vacancies. The corresponding states, which show a significant amount of s-like charge in the oxygen vacancy sphere and d_{z^2} charge in the Ti sphere, will be called oxygen vacancy states further on. They are encircled in figure 2. A similar vacancy band has also been observed in $\text{TiC}_{0.75}$ (Redinger *et al* 1985, 1986), $\text{TiN}_{0.75}$ (Herzig *et al* 1987), $\text{TiO}_{0.75}$ (Schlapansky *et al* 1989) and NbO (Wimmer *et al* 1982). In CPA calculations, these vacancy states correspond to virtual bound states (Marksteiner *et al* 1986). The remaining 15 bands arise from the d states of the three titanium atoms in the unit cell. In the following, the above-mentioned 16 bands are referred to as 'd band'.

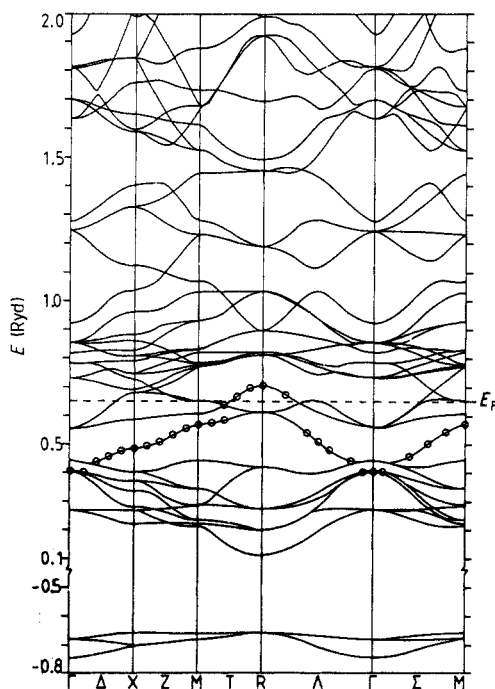


Figure 2. Band structure of ordered $\text{Ti}_{0.75}\text{O}_{0.75}$. The so-called O vacancy states are encircled. Energies with respect to the constant muffin-tin potential between the spheres.

The vacancy band and three d bands with mainly Ti d_{z^2} , and (d_{xz} , d_{yz}) character are separated by a pseudogap at 0.69 Ryd (with respect to the muffin-tin zero) from the remaining d bands at higher energies. A comparison with the band structure of TiO without vacancies and of $\text{TiO}_{0.75}$ with only O vacancies shows that the above-mentioned four bands (denoted as vacancy induced bands further on) completely fill the gap between the O 2p band and the Ti 3d band of TiO and $\text{TiO}_{0.75}$.

Figures 3 and 4 display the DOS and the large components of the local partial DOS for TiO, ordered $\text{TiO}_{0.75}$ and ordered $\text{Ti}_{0.75}\text{O}_{0.75}$ (in electrons $\text{Ryd}^{-1}/\text{cubic unit cell}$). The DOS curves are shifted to coincide at the bottom of the lowest band where the partial local O 2s DOS ('s band') dominates. The gap between the 'p band' (where the local partial O 2p DOS dominates) and the 'd band' (with mainly Ti 3d DOS) is characteristic for TiO and, to a lesser extent, for $\text{TiO}_{0.75}$, but it does not appear in

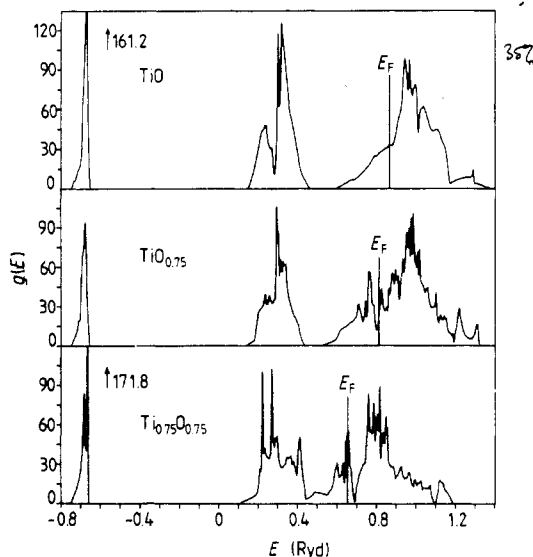


Figure 3. Total DOS for TiO and ordered TiO_{0.75} (Schlapansky *et al* 1988), and for ordered Ti_{0.75}O_{0.75} (present work) in units of electrons Ryd⁻¹/ cubic unit cell. (The cubic unit cell of TiO contains four formula units.) The curves are shifted to coincide at the bottom of the O 2s band.

Ti_{0.75}O_{0.75}. The two vacancy induced peaks in the DOS (at energies between about 0.43 and 0.69 Ryd with respect to the muffin-tin zero) correspond to the four vacancy induced bands. In Ti_{0.75}O_{0.75}, the Fermi level drops considerably compared to TiO and TiO_{0.75}, and is found in the second vacancy induced peak immediately below the pseudogap. This position at a high DOS is energetically unfavourable and can be attributed to the highly ordered NbO structure causing the sharp peaks in the DOS and also to the higher vacancy concentration compared to the real structure. A slight disorder of the vacancies or a small change of composition would smear out the peaks and would locate the Fermi level at a more favourable position, as can be deduced from a KKR-CPA DOS calculation for disordered Ti_{0.85}O_{0.85} (Hörmandinger *et al* 1988).

Because of the reduced symmetry of the O lattice sites compared to the NaCl structure, the O *p_z* states are no longer equivalent to the O *p_x* and O *p_y* states. Hence, the peaks in the 'p band' split, thus changing its shape considerably. In particular, a new sharp peak emerges at the top of the 'p band' which consists of states with O 2*p_z* symmetry. A similar peak has been found in the DOS of NbO crystallising in the same structure (Wimmer *et al* 1982).

In table 2, the band gaps and band widths are tabulated for TiO and TiO_{0.75} (Schlapansky *et al* 1989), Ti_{0.85}O_{0.85} (Hörmandinger *et al* 1988), and Ti_{0.75}O_{0.75}. Introduction of both Ti and O vacancies leads to a successive reduction and the eventual disappearance of the p-d gap apart from a narrowing of the occupied range of the 'd band', which is caused by the considerable lowering of the Fermi level.

Further information on the influence of the Ti and O vacancies on the chemical bonding in titanium oxide can be obtained from the local partial DOS in the corresponding vacancy spheres and from the local partial Ti 3d, Ti 4p, O 2s and O 2p DOS.

The upper part of figure 5 shows the total DOS and the local DOS with s and p

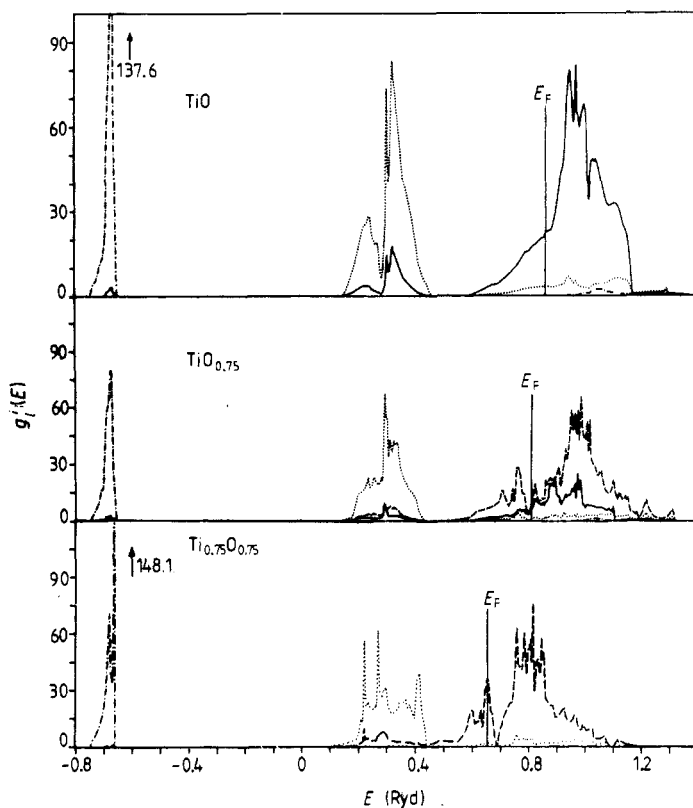


Figure 4. Main partial local DOS components for TiO and TiO_{0.75} (Schlapansky *et al* 1988), and for Ti_{0.75}O_{0.75} (present work). The same units and conventions as in figure 3 are used. — · — ·, O 2s DOS; · · · · ·, O 2p DOS; —, Ti^[6] 3d DOS or Ti 3d DOS in TiO; - - -, Ti^[4] 3d DOS or Ti 3d DOS in Ti_{0.75}O_{0.75}.

Table 2. Band widths and band gaps (in Ryd) for TiO and TiO_{0.75} (Redinger *et al* 1985, 1986), Ti_{0.75}O_{0.75} (present calculation) and Ti_{0.85}O_{0.85} (Hörmandinger *et al* 1988).

	Band	TiO	TiO _{0.75}	Ti _{0.75} O _{0.75}	Ti _{0.85} O _{0.85}
Band width	s	0.13	0.09	0.09	
	p	0.33	0.30	0.33	0.32
	Occupied d (+ vacancy)	0.30	0.29	0.22	0.22
Band gap	s-p	0.72	0.80	0.77	
	p-d	0.13	0.09	—	0.03
E_F (with respect to bottom of s band)		1.65	1.55	1.40	
E_F (with respect to bottom of p band)		0.76	0.64	0.54	0.57
E_F (with respect to muffin-tin zero)		0.95	0.83	0.65	

symmetry within the \square_{O} sphere. Analogous to $\text{TiC}_{0.75}$ (Redinger *et al* 1985, 1986), $\text{TiN}_{0.75}$ (Herzig *et al* 1987), and $\text{TiO}_{0.75}$ (Schlapansky *et al* 1989), the first vacancy induced peak (at about 0.16 Ryd below the Fermi level) is dominated by the partial local \square_{O} s DOS. The second vacancy induced peak contains a large fraction of p-like DOS in the \square_{O} sphere.

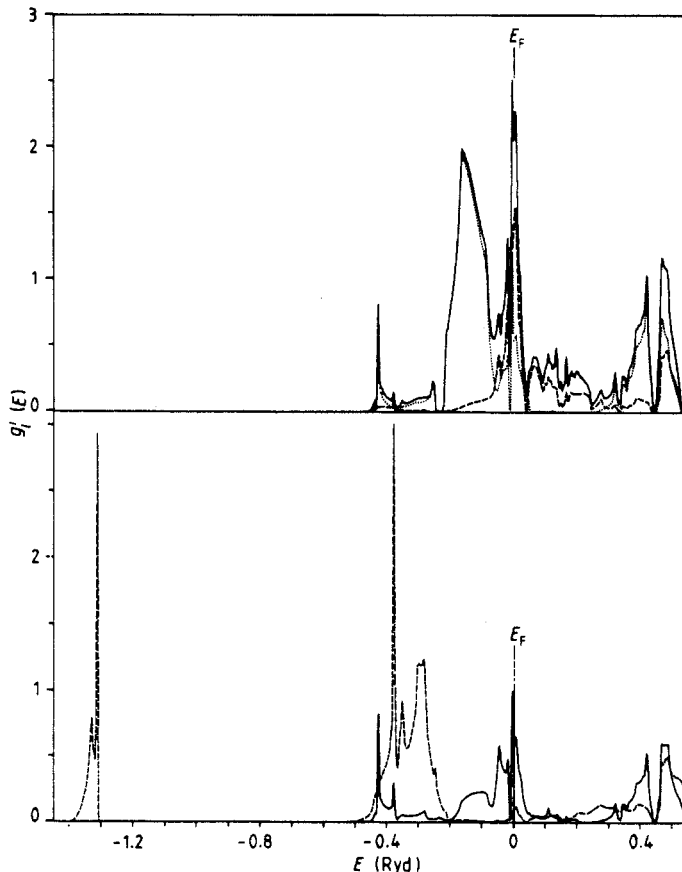


Figure 5. Top: DOS in the O vacancy sphere of ordered $\text{Ti}_{0.75}\text{O}_{0.75}$. —, total DOS; ·····, s-like DOS; ---, p-like DOS. Bottom: split of the Ti p-like DOS. —, p_z component; ---, (p_x, p_y) component.

In figure 6, the local partial Ti 3d DOS is split into its 'e_g'-like components d_{z^2} and $d_{x^2-y^2}$ (upper part) and into its 't_{2g}'-like components d_{xy} and (d_{xz}, d_{yz}) (lower part). The $d_{x^2-y^2}$ component appears in the 'p band' and, together with the O 2p DOS, in the 'd band' above the Fermi level, corresponding to bonding O-Ti p-d σ and antibonding O-Ti p-d σ^* interactions, respectively. It does not contribute to the vacancy induced peaks where the Ti d_{z^2} DOS dominates which, on the other hand, is quite small in the p band.

The partial local Ti d_{xy} DOS appears in the 'p band' and is fairly large above the Fermi level in the 'd band' indicating bonding p-d π and antibonding p-d π^* interactions. The Ti d_{xy} states cannot form d-d σ bonds in the NbO structure, and only a small number of them is found in the vacancy induced peaks. The present calculation shows that the Ti d_{xy} states do not coincide energetically with the Ti

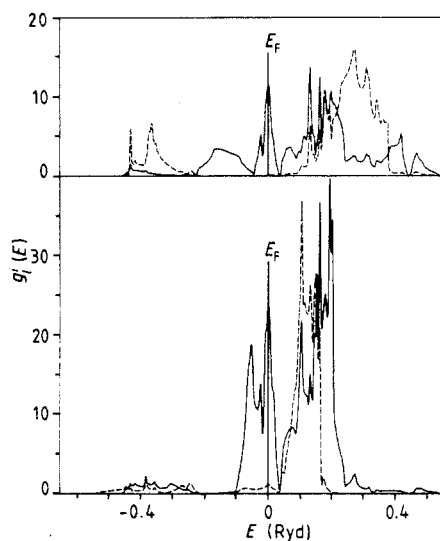


Figure 6. Split of the partial Ti 3d DOS in ordered $\text{Ti}_{0.75}\text{O}_{0.75}$. Top: Ti d_{z^2} (—) and Ti $d_{x^2-y^2}$ (---) DOS. Bottom: Ti (d_{xz} , d_{yz}) (—) and Ti d_{xy} (---) DOS. The same units as in figure 3 are used.

d_{z^2} and (d_{xz} , d_{yz}) states. This means that the prerequisites for the formation of d^4 hybrid orbitals consisting of d_{z^2} , d_{xz} , d_{yz} and d_{xy} orbitals in equal portions are not fulfilled. Such hybrids have been assumed to be important for the stability of Nb_6O_{12} and Ti_6O_{12} clusters (Andersen and Satpathy 1984).

The p_z and (p_x , p_y) components of the local partial Ti p DOS are shown in the lower part of figure 5. The most important feature is the relatively large amount of Ti p_z DOS in the vacancy induced peaks. The Ti p_z DOS in the region of the vacancy induced bands leads to an additional peak in the Ti K emission spectra (KES) just below the Fermi level (Tsutsumi *et al* 1977) which cannot be explained by the local partial Ti p DOS for TiO without vacancies (Hörmandinger *et al* 1988). No vacancy induced bands exist for the latter compound and the Fermi level is situated in the lower part of the 'd band' where no Ti 4p states can be found. The occurrence of the additional peak of the Ti p DOS below E_F is independent of any assumption concerning the ordering of the vacancies, as it is also found in the KKR-CPA calculation by Hörmandinger *et al* (1988) for $\text{Ti}_{0.85}\text{O}_{0.85}$ which assumes complete disorder of the vacancies on both the Ti and the O sublattices. Whereas the shape of the Ti K emission spectrum is well reproduced by the calculation of Hörmandinger *et al* (1988), the peak separation is too small by 2 eV, which is attributed to the local density approximation on which the calculation is based. We did not calculate any spectra because we are treating a hypothetical defect structure. Nevertheless, from our Ti 4p DOS, we would certainly get the correct double peak structure of the Ti KES. The main effect of the vacancies on the spectra seems to be quite independent of their degree of order. Therefore, we are convinced that our conclusions concerning their influence on the chemical bonding should also be valid for real TiO with its relatively complicated defect structure.

The local \square_{Ti} DOS is shown in the top part of figure 7 together with its partial s and p components. The largest peaks of the \square_{Ti} DOS are found in the 'p band'. The

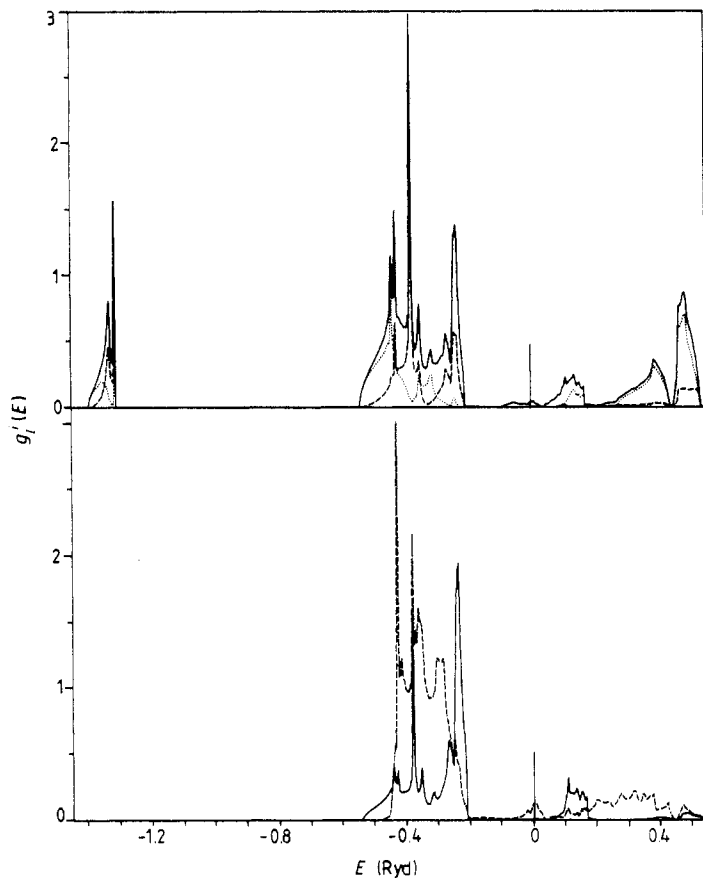


Figure 7. Top: partial local DOS in the Ti vacancy sphere of ordered $\text{Ti}_{0.75}\text{O}_{0.75}$. —, total DOS; \cdots , s-like DOS; ---, p-like DOS. Bottom: split of the partial O 2p-like DOS. —, p_z component; ---, (p_x, p_y) component.

partial local \square_{Ti} DOS of p (and d, mostly e_g) symmetry exceeds the partial local \square_{Ti} s DOS in almost the whole energy range.

The lower part of figure 7 shows the split of the O 2p DOS into its p_z and (p_x, p_y) components. The distinct peak at the top of the 'p band' originates from p_z states.

3.2. Partial charges

The charge analysis for some of the vacancy states can be found in table 2. The vacancy states (encircled in figure 2) mainly possess Ti 3d charge of d_{z^2} symmetry together with a large fraction of s-like charge in the \square_{O} sphere. The charge in the vacancy sphere is remarkably higher than the charge in each one of the Ti spheres. The charge in the vacancy sphere indicates the bonding $\text{Ti}-\square_{\text{O}}-\text{Ti}$ $d_{z^2}-d_{z^2}$ interaction which has been discussed previously by Redinger *et al* (1985, 1986), Herzig *et al* (1987), and by Schlapansky *et al* (1989). In the energy region of the vacancy induced bands, states are found which exhibit a p-like charge in the O vacancy. A few of them are listed in the bottom part of table 3. They can be considered as antibonding $\text{Ti}-\square_{\text{O}}-\text{Ti}$ $d_{z^2}-d_{z^2}$ states. However, the p-like charge in the \square_{O} sphere can also be

Table 3. Charge analysis (in percent) for some O vacancy states of ordered Ti_{0.75}O_{0.75}. For O and Ti the figures refer to three muffin-tin spheres. Upper part, bonding states; lower part, antibonding states with respect to □_O.

Irr. rep.	E (Ryd)	O spheres			Ti spheres							□ _O sphere			q _{out}
		Total	s	p	d	d _{z²}	d _{x²-y²}	d _{xy}	(d _{xz} , d _{yz})	Total	s	p	Total		
Γ ₁	0.400	0.92	8.24	—	31.22	31.22	—	—	—	39.46	24.44	—	24.44	35.03	
Δ ₁	0.443	10.52	4.77	0.64	34.40	33.32	1.08	—	—	39.81	20.64	0.23	20.87	28.31	
X ₁	0.483	2.87	4.25	2.13	37.63	36.23	1.40	—	—	44.01	23.00	—	23.00	29.71	
Z ₁	0.516	2.70	3.48	3.13	38.53	37.59	0.65	0.30	—	45.14	21.99	0.48	22.65	29.24	
M ₁	0.568	1.68	2.31	5.81	35.98	35.98	—	—	—	44.10	23.44	—	23.44	30.17	
T ₁	0.586	3.36	1.43	2.48	52.71	34.28	—	18.43	—	56.62	10.68	2.68	13.36	26.15	
R ₁	0.705	1.00	—	18.80	—	—	—	—	—	18.80	32.06	—	32.06	47.94	
A ₁	0.506	4.59	3.55	2.28	39.38	38.43	—	0.12	0.83	45.21	20.01	1.23	21.24	28.66	
Σ ₁	0.475	5.34	4.29	1.61	37.46	36.74	0.52	0.12	0.08	43.36	21.33	0.62	21.95	29.05	
S ₁	0.546	3.23	2.70	3.15	42.36	38.42	0.20	—	3.73	48.21	18.36	1.58	19.94	28.19	
M _{2'}	0.651	3.02	1.53	0.49	66.69	36.16	0.93	—	29.61	68.71	—	5.08	5.08	22.69	
X _{4'}	0.727	1.18	1.75	0.78	73.71	73.71	—	—	—	76.64	—	6.06	6.06	16.04	
R ₁₅	0.897	10.38	1.16	—	84.38	46.32	—	—	38.06	85.54	—	1.18	1.18	2.44	

produced by the overlap of Ti d_{xz} and d_{yz} states involved in d-d σ bonds along the edges of the Ti octahedra surrounding the \square_{O} vacancy.

If the local partial charges for the valence states are summed over the energy range of the 's', 'p' and the occupied part of the 'd band' of $\text{Ti}_{0.75}\text{O}_{0.75}$, the LAPW local partial charges of table 4 are obtained, which will be compared with the corresponding results for TiO and $\text{TiO}_{0.75}$ (Schlapansky *et al* 1989). All charges either refer to one muffin-tin sphere or, for the interstitial region, to one quarter of the interstitial volume of the cubic unit cell (which is identical to the interstitial volume of the rhombohedral cell of the NaCl structure). The Ti atoms of $\text{Ti}_{0.75}\text{O}_{0.75}$ correspond to the $\text{Ti}^{[4]}$ atoms of $\text{TiO}_{0.75}$.

In both vacancy-containing titanium oxides, the interstitial charge in the 'p band' is reduced with respect to TiO without vacancies because of the reduced number of O-Ti p-d bonds. Nevertheless, the Ti 3d charge in the p band of $\text{Ti}_{0.75}\text{O}_{0.75}$ almost reaches the value of TiO because the remaining O-Ti p-d bonds are stronger than in TiO. Moreover, the Ti vacancies favour O-Ti p-d π bonds between the O p_z and Ti d_{xy} states, because the latter are no longer involved in $\text{Ti}^{[4]}$ - $\text{Ti}^{[6]}$ d-d σ bonds. The charge components in the \square_{Ti} sphere are dominated by those of p and e_g symmetry, which means that no net bonding across the Ti vacancy takes place.

The lowering of the Fermi level in going from $\text{TiO}_{0.75}$ to $\text{Ti}_{0.75}\text{O}_{0.75}$ leads to a reduction of the Ti 3d and O 2p charges in $\text{Ti}_{0.75}\text{O}_{0.75}$. The $\text{Ti}^{[4]}$ - $\text{Ti}^{[6]}$ bonds of $\text{TiO}_{0.75}$ do not exist in $\text{Ti}_{0.75}\text{O}_{0.75}$ and the loss of these bonds shows up in a decrease of the interstitial valence charge in the 'd band'.

Table 4. LAPW partial charges for ordered $\text{Ti}_{0.75}\text{O}_{0.75}$ (in electrons/muffin-tin sphere). The differences between the total self-consistent LAPW charges and the atomic superposed charges are also indicated.

Band		$\text{Ti}_{0.75}\text{O}_{0.75}$				
		Ti	\square_{Ti}	O	\square_{O}	Interstitial
s	s	0.01	0.02	1.69	—	
	p	0.02	0.03	—	—	
	d	0.03	0.01	—	—	
	Total	0.07	0.07	1.69	—	0.16
p	s	0.08	0.13	0.01	0.04	
	p	0.11	0.15	3.83	0.01	
	d	0.55	0.07	0.01	—	
	Total	0.76	0.37	3.85	0.05	0.94
d (+ vacancy)	s	0.03	—	—	0.41	
	p	0.04	—	0.09	0.10	
	d	1.14	—	0.01	0.02	
	Total	1.20	0.01	0.10	0.58	0.39
Occupied valence	s	0.12	0.15	1.71	0.45	
	p	0.17	0.18	3.92	0.10	
	d	1.72	0.09	0.02	0.02	
	Total	2.04	0.44	5.64	0.58	1.49
Charge differences		-0.20	-0.13	0.30	0.09	-0.07

The differences between the total LAPW charges and the superposed atomic charges in the interstitial and in the muffin-tin spheres for ordered $\text{Ti}_{0.75}\text{O}_{0.75}$ are tabulated in the bottom part of table 4. The atomic superposed charges were calculated for the valence electron configurations $3d^2 4s^2$ for Ti and $2s^2 2p^4$ for O. As for TiO and $\text{TiO}_{0.75}$ (Schlapansky *et al* 1989), charge is shifted from the Ti to the O sphere during the SCF procedure. The \square_{Ti} sphere loses charge, because most of the oxygen states below the Fermi level with some charge in the \square_{Ti} sphere are non-bonding or antibonding. Contrarily, the O vacancy sphere gains charge because of the bonding character of the Ti d_{z^2} states.

The split of the Ti 3d and the O 2p charges into their components according to the D_{4h} point group symmetry is shown in table 5.

Table 5. Split of the partial Ti 3d and O 2p charges in ordered $\text{Ti}_{0.75}\text{O}_{0.75}$ (in electrons/muffin-tin sphere).

Band	Ti						O	
	d_{z^2}	$d_{x^2-y^2}$	' e_g '	d_{xy}	(d_{xz}, d_{yz})	' t_{2g} '	(p_x, p_y)	p_z
p	0.05	0.25	0.30	0.11	0.13	0.24	2.51	1.32
d (+ vacancy)	0.37	—	0.37	0.04	0.72	0.76	0.07	0.02
Occupied valence	0.43	0.28	0.71	0.15	0.85	1.00	2.58	1.34

In the 'p band', the Ti $d_{x^2-y^2}$, d_{xy} and (d_{xz}, d_{yz}) charges, which measure the strength of the Ti-O d-p σ and d-p π bonds in these materials, all increase from $\text{TiO}_{0.75}$ to $\text{Ti}_{0.75}\text{O}_{0.75}$. In the occupied part of the 'd band' only the Ti d_{z^2} charge remains constant, while all ' t_{2g} '-like charge components are reduced. This effect results from the lowering of the Fermi level to the second vacancy induced peak. Overall, the Ti ' e_g '-like charge now exceeds the Ti ' t_{2g} '-like charge, in contrast to TiO and $\text{TiO}_{0.75}$ (Schlapansky *et al* 1989).

3.3. Electron density and chemical bonding

Unsymmetrised LAPW wave functions were used for the calculation of the valence electron density of $\text{Ti}_{0.75}\text{O}_{0.75}$, closely following the approach described by Redinger *et al* (1986).

Figure 8 shows the valence electron density of $\text{Ti}_{0.75}\text{O}_{0.75}$ for the two inequivalent cuts in the (100) plane (shown in figure 1). One clearly recognises the ' e_g '-like charge distribution around the Ti atoms.

Also in figure 8, the separate electron density contributions of the 'p' and 'd band' are depicted for the two cuts in the (100) plane. The electron density from the 'p band' illustrates the O-Ti p-d σ bonds. The 'd band' electron density plot (cut 2) reveals the existence of a Ti-Ti d_{z^2} - d_{z^2} bond across the O vacancy. The importance of Ti- \square_{O} -Ti d_{z^2} - d_{z^2} interactions, which clearly emerges from the present band structure calculation, has been postulated by Burdett and Hughbanks (1984) from their semi-empirical Extended-Hückel band structures. The contribution of this Ti- \square_{O} -Ti bond exceeds the contribution of the Ti-Ti d-d (' t_{2g} '-like) σ bond which is predominant in TiO and $\text{TiO}_{0.75}$. These features of the Ti-Ti bonding in $\text{Ti}_{0.75}\text{O}_{0.75}$ can again be explained by the fact that the vacancy induced states with (d_{xz}, d_{yz}) symmetry are only partially occupied.

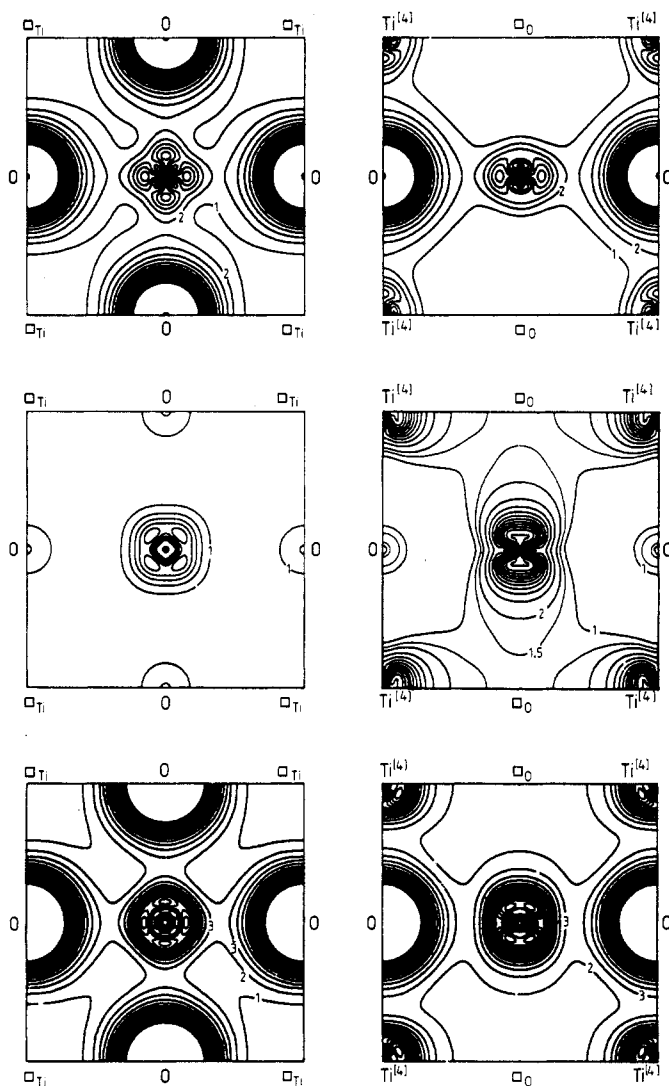


Figure 8. Valence electron densities in the (100) plane of $\text{Ti}_{0.75}\text{O}_{0.75}$ in units of $10^{-1} e \text{ \AA}^{-3}$. Left, cut 1; right, cut 2. Top, 'p band' states only; centre, 'd band' states only; bottom, all occupied valence states.

Almost all of the \square_{O} states possess a certain amount of Ti s and p charge (table 3), thus augmenting their degree of delocalisation and increasing the effectiveness of the long-range Ti- \square_{O} -Ti d_{z^2} - d_{z^2} bonds. This result entirely confirms the findings of Burdett and Hughbanks (1984). In contrast to Huisman *et al* (1980), however, the \square_{O} states of the present calculation cannot be classified as pure Ti conduction band states of s and/or p symmetry exclusively, since they possess predominantly d_{z^2} and (d_{x^2} , d_{y^2}) symmetry.

The corresponding antibonding d_{z^2} - \square_{O} - d_{z^2} interactions are found in the second vacancy peak (at the Fermi level) with a large fraction of p-like DOS in the \square_{O} sphere.

In contrast to $\text{TiO}_{0.75}$, however, not all these antibonding states are occupied in $\text{Ti}_{0.75}\text{O}_{0.75}$.

Analogous to the Ti d_{z^2} states, the rather delocalised Ti p_z states participate in bonding and antibonding $\text{Ti}-\square_{\text{O}}-\text{Ti}$ p_z-p_z interactions across the vacancy.

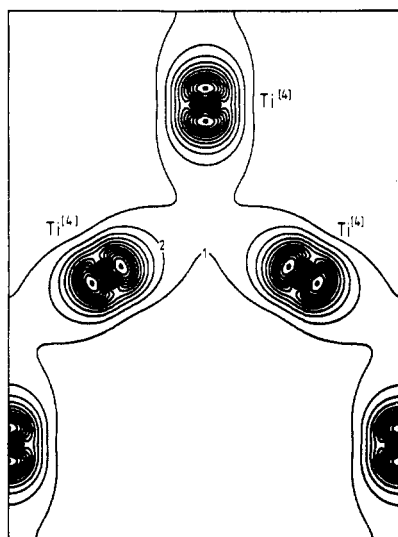


Figure 9. Electron density of the occupied part of the 'd band' in the (111) plane of $\text{Ti}_{0.75}\text{O}_{0.75}$ in units of $10^{-1} e \text{ \AA}^{-3}$.

Figure 9 shows the electron density plot of the occupied 'd band' for the (111) plane in $\text{Ti}_{0.75}\text{O}_{0.75}$. The maxima of the electron density are directed towards the centre of the triangle formed by Ti atoms octahedrally surrounding the oxygen vacancy. This electron distribution results from the superposition of the electron densities of the $\text{Ti}-\text{Ti}$ (d_{xz}, d_{yz})-(d_{xz}, d_{yz}) σ bonds and the $\text{Ti}-\square_{\text{O}}-\text{Ti}$ $d_{z^2}-d_{z^2}$ bonds. The d_{xy} contribution can be neglected in this energy region (see table 5). A similar electron density distribution can be generated by using d^4 hybrid orbitals. This concept has been used by Andersen and Satpathy (1984).

The removal of the $\text{Ti}^{[6]}$ atoms of $\text{TiO}_{0.75}$ leads to a redistribution of electron density in $\text{Ti}_{0.75}\text{O}_{0.75}$, which can be seen in figures 10 and 11, where the differences of the electron densities between $\text{Ti}_{0.75}\text{O}_{0.75}$ and $\text{TiO}_{0.75}$ are plotted in the (100) and (111) planes. Full lines indicate a higher electron density and broken lines a lower electron density in $\text{Ti}_{0.75}\text{O}_{0.75}$ compared to $\text{TiO}_{0.75}$.

In addition to the obvious loss of electron density within the Ti vacancy sphere, the following effects can be seen in the difference electron density plots.

Within the O sphere, electronic charge is shifted from the $\text{O}-\text{Ti}$ to the $\text{O}-\square_{\text{Ti}}$ direction creating an anisotropic difference electron density for the O atom. This can also be deduced from table 5, where the O p_z charge component was found to be slightly predominant. Net bonding interactions of the O p_z states across the Ti vacancy can be excluded because of the localised character of the O $2p_z$ orbitals and the negative charge transfer in the Ti vacancy sphere (table 4). Therefore, the redistribution of the electronic charge within the O sphere must be attributed to additional p_z-d_{xy} π bonds with the neighbouring Ti atoms. These bonds should

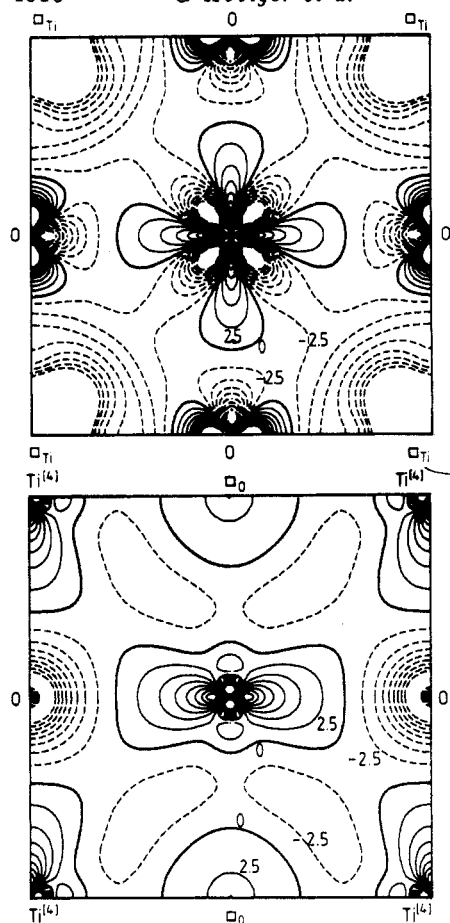


Figure 10. Difference between the valence electron densities of $\text{Ti}_{0.75}\text{O}_{0.75}$ and $\text{TiO}_{0.75}$ (omitting the O 2s band) for the two different cuts in the (100) plane in units of $10^{-2} e \text{ \AA}^{-3}$.

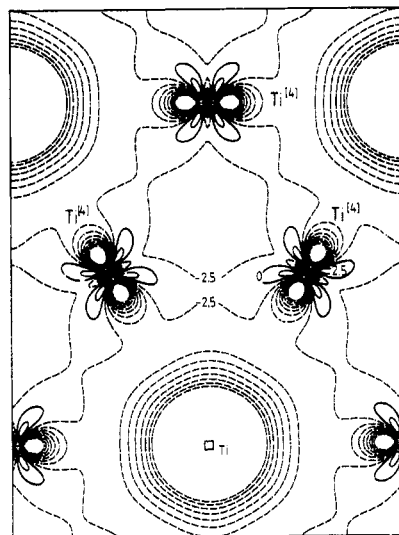


Figure 11. Difference between the valence electron densities of $\text{Ti}_{0.75}\text{O}_{0.75}$ and $\text{TiO}_{0.75}$ (omitting the O 2s band) in the (111) plane in units of $10^{-2} e \text{ \AA}^{-3}$.

also lead to an increased ' t_{2g} '-like charge in the Ti sphere. This increase, however, cannot be observed, because it is overcompensated by the simultaneous elimination of $\text{Ti}^{[4]}-\text{Ti}^{[6]}$ d-d σ bonds.

In the O-Ti direction, the decrease of electron density in the O sphere and a certain increase in the Ti sphere indicate a lower ionicity of the O-Ti bond in $\text{Ti}_{0.75}\text{O}_{0.75}$ compared to $\text{TiO}_{0.75}$.

Inspection of the electron density differences between $\text{TiO}_{0.75}$ and TiO (see Schlapsky *et al* 1989) shows that the O-Ti^[6] and the Ti^[4]-Ti^[6] bonds are weakened by the introduction of the O vacancies. The thus destabilised Ti^[6] atoms are removed in going from ordered $\text{TiO}_{0.75}$ to ordered $\text{Ti}_{0.75}\text{O}_{0.75}$. The Ti-O-Ti $d_{z^2}-d_{z^2}$ bonds of $\text{TiO}_{0.75}$ are strengthened when additional Ti vacancies are introduced. Whereas, in $\text{TiO}_{0.75}$, the O vacancies alone weaken the Ti-Ti bonds along the edges of the Ti octahedra, the additional presence of Ti vacancies in $\text{Ti}_{0.75}\text{O}_{0.75}$ does not significantly influence these bonds. The electron density distribution for a state which is involved in this type of bonding has been given for $\text{TiN}_{0.75}$ by Herzig *et al* (1987) (figure 13).

Overall, stabilising and destabilising effects of the Ti and O vacancies approximately compensate each other in $\text{Ti}_{0.75}\text{O}_{0.75}$ crystallising in the NbO structure as

has been shown by Schwarz (1987), who demonstrated $\text{Ti}_{0.75}\text{O}_{0.75}$ to be equally stable as TiO without vacancies crystallising in the NaCl structure. However, ordered $\text{Nb}_{0.75}\text{O}_{0.75}$ was found in the same calculation to be more stable than NbO by 1 eV. This additional stabilisation of the Nb compound can easily be understood from the more delocalised nature of the Nb 4d states. A comparison with the APW calculation of $\text{Nb}_{0.75}\text{O}_{0.75}$ (Wimmer *et al* 1982) shows that, for $\text{Nb}_{0.75}\text{O}_{0.75}$, more charge from states of the 'd band' is accumulated in the O vacancy sphere and in the interstitial, because the Nb 4d states are capable of forming more efficient bonds across the O vacancy or along the edges of the metal octahedra than the Ti 3d states.

4. Conclusion

The results of the present investigation together with the findings of Schlapansky *et al* (1989) can be summarised as follows:

(i) In the gap between the p and the d band of TiO four bands appear in $\text{TiO}_{0.75}$ and $\text{Ti}_{0.75}\text{O}_{0.75}$. One of these bands is generated by the O vacancies while the other three bands are d bands which are shifted into this energy region by the interaction with the vacancies. The states of the vacancy band mainly have s-like character in the vacancy sphere and d_{z^2} -like character in the Ti sphere. The p-d gap of TiO completely disappears in $\text{Ti}_{0.75}\text{O}_{0.75}$.

(ii) The relatively weak O-Ti bonds in TiO are partly replaced by stronger $\text{Ti}-\square_{\text{O}}-\text{Ti}$ $d_{z^2}-d_{z^2}$ bonds in ordered $\text{TiO}_{0.75}$. The $\text{Ti}^{[6]}-\text{Ti}^{[4]}$ and $\text{Ti}^{[6]}-\text{O}$ bonds are weakened.

(iii) The removal of these destabilised $\text{Ti}^{[6]}$ atoms of $\text{TiO}_{0.75}$ leads to stronger $\text{Ti}-\square_{\text{O}}-\text{Ti}$ $d_{z^2}-d_{z^2}$ bonds for ordered $\text{Ti}_{0.75}\text{O}_{0.75}$. The Ti-Ti bonds along the edges of the Ti octahedra around the O vacancies remain essentially unchanged. The additional presence of titanium vacancies leads to stronger O-Ti p_z-d_{xy} π bonds, whereas the formation of $\text{O}-\square_{\text{Ti}}-\text{O}$ bonds is unfavourable because of the rather localised O $2p_z$ states. In both defect structures, the O-Ti p-d σ bonds are stronger than in TiO without vacancies. The ionicity of this bond decreases from $\text{TiO}_{0.75}$ to $\text{Ti}_{0.75}\text{O}_{0.75}$.

(iv) The interactions of the Ti d_{z^2} states across the O vacancy lower the energy of these states in both defect structures considerably and they are shifted to the p-d gap below the d band of TiO. The p-d gap completely disappears for $\text{Ti}_{0.75}\text{O}_{0.75}$ and the Fermi level with respect to the bottom of the s band is lowered by as much as 3.4 eV.

(v) The results of our band structure calculations agree well with the predictions of the d^4 model of Andersen and Satpathy. Some discrepancies arise, however, in the interpretation of the electron density. In our calculation, the d band electron density in the (111) plane (figure 9) results from the superposition of $\text{Ti}-\square_{\text{O}}-\text{Ti}$ $d_{z^2}-d_{z^2}$ bonds and $\text{Ti}-\text{Ti}$ $(d_{xz}, d_{yz})-(d_{xz}, d_{yz})$ σ bonds, whereas the similar electron density distribution of Andersen and Satpathy is due to metal three-centre bonds.

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