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Abstract

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ON SOME RESULTS OF AN X-RAY SPECTRAL INVESTIGATION OF THE CHEMICAL BOND IN TITANIUM OXIDES OF VARIABLE COMPOSITION ($TiO_{0.85}$—$TiO_{1.20}$)

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In work ([1]), an experimental study was carried out of the X-ray titanium $K\beta_5\beta''$ emission bands in the lower oxides with a cubic structure within the homogeneity range of this phase. In a further development of these works, the corresponding X-ray K-absorption spectra were studied. In the present communication an attempt is made at a quantitative interpretation of the results obtained, on the basis of their comparison with the recently calculated ([2]) band structure of titanium monoxide. The conditions for obtaining the X-ray spectra were analogous to those described in ([1]). The method of preparing absorbers was the same as in ([4]). The X-ray K-absorption spectra and the last titanium $K\beta_5\beta''$ emission bands in the oxides of variable composition investigated by us are compared on a single energy scale in Fig. 1. In Table 1 an attempt is made to interpret the experimental results obtained for $TiO_{1.026}$ by comparing them with the predictions of theory ([2]). Consideration of these data makes it possible to arrive at the following conclusions.

The structure of the X-ray emission $K\beta_5\beta''$ bands and the titanium K-absorption edges in monoxide throughout the entire homogeneity range of this phase is in good agreement with the conclusions following from analysis of the band structure of the compound. This makes it possible to verify, refine, and extend the ideas expressed earlier ([1,3,4]) about the nature of the different maxima of intensity or of the absorption coefficient in the X-ray spectra of the metal in these and other compounds. From Fig. 1 and Table 1 it is seen that the $K\beta''$ band observed in the titanium spectra in oxides, lying at a distance of 22 eV from the Fermi boundary, is due to the transition of electrons between the 1s-level of the metal and a group of levels predominantly of s-symmetry with a small ($\sim$ 4—9%) admixture of p-functions in the sphere of the titanium atom. The energy position of the maximum of this line is determined mainly by the energy of the 2s-level in the anion sphere, corresponding to the irreducible representation L_1. This explains the previously observed ([5]) dependence of

the position of the $K\beta''$ band in different compounds of one metal on the nature of the anion. However, owing to the selection rules, the intensity of the $K\beta''$ band will be determined by the percentage of p-electrons in the titanium sphere that populate the group of levels under consideration and that undergo, in the emission process, a dipole transition to the $1s$-levels of the metal atom. It is obvious, therefore, that the shape and intensity of the $K\beta''$ band cannot correctly reflect the density of the distribution of electrons on the $2s$-levels of the anion; however, the energy position of this band can serve as a kind of reference point for determining the relative position on the energy scale of the anion (oxygen) $2s$-band. In an analogous way one may conclude that the appearance in the spectrum of the shoulder $K\beta_5^{\mathrm{III}}$ is due to the existence in the energy spectrum of TiO of another group of levels, among which the largest role is played by the level corresponding to the irreducible representa-

···to the $X_{4'}$ splitting, with the greatest relative density of p-states in the titanium sphere. A competing process in this case may be the overlap transition of the anion $2p$-electrons, whose density at the levels under consideration is fairly large (40-50%). The fact that, as the relative oxygen content in the oxide increases, the relative intensity of the $K\beta_5^{\mathrm{III}}$ band increases (Fig. 1) shows that the contribution of this process is comparable to, or even exceeds, the contribution of the direct transition. If this is so, then the experimentally observed shift of the energy of the band maximum toward lower energies (close to 11 eV), in comparison with the maximum corresponding to the energy of the $X_{4'}$ level, becomes understandable. The group of levels forming the $K\beta_5^{\mathrm{II}}$ band is populated mainly by $2p$-electrons in the oxygen sphere (50-70%) and by $3d$-electrons in the titanium sphere ($\sim$ 10-20%). The theoretical maximum of this band* agrees well with that observed experimentally. As in the case of the $K\beta_5^{\mathrm{III}}$ band, the linear increase in the intensity of the $K\beta_5^{\mathrm{II}}$ band indicates the predominant contribution made to its formation by overlap dipole transitions of oxygen $2p$-electrons to the titanium $1s$-levels. The change in the probability of this transition in various oxides, which may be associated with a regular change in the lattice constant, apparently plays a subordinate role. The energy of the maximum of the $K\beta_5^{\mathrm{II}}$ band, as we assumed earlier ([1]), thus characterizes the energy of that part of the $3d$-electrons relatively strongly bound to titanium which take part in covalent bonds of the absorbing atom with the atoms forming its nearest environment in the crystal lattice of the compound. In contrast to this, the levels from which electron transitions take place in the formation of the $K\beta_5^{\mathrm{I}}$ band in the titanium sphere are populated mainly by $3d$-electrons. The fraction of functions of p-symmetry in the wave functions describing the behavior of the electrons occupying these levels is relatively small ($\sim$ 16-20% in the oxygen sphere). Therefore the appearance of the $K\beta_5^{\mathrm{I}}$ band is almost entirely due to the direct quadrupole transition of the least strongly bound, so-called collectivized, $3d$-electrons to the $1s$-levels of the metal. With increasing index n for oxygen in TiO_n, the intensity of this band decreases ([1]). This evidently corresponds to a decrease in the fraction of $3d$-electrons participating in metal-like bonds in the compound and to an increase in their number in Me–

Fig. 1. X-ray K-absorption spectra (right curves) and $K\beta_5\beta''$ emission bands (left curves) of titanium in oxides of different composition

Figure 1: Fig. 1. X-ray K-absorption spectra (right curves) and $K\beta_5\beta''$ emission bands (left curves) of titanium in oxides of different composition

O bonds. This is indicated by

Fig. 1. X-ray K-absorption spectra (right curves) and $K\beta_5\beta''$-emission bands (left curves) of titanium in oxides of different composition

* The positions of the maxima of $K\beta_5^{\mathrm{II}}$ (as well as $K\beta_5^{\mathrm{I}}$) were determined from the maxima of the density of states calculated in ([2]).

Table 1

Comparison of the energies of the extrema of the fine structure of the titanium X-ray spectra in rutile ($TiO_{1.026}$) with the results of a theoretical calculation of the band structure of this compound ([2])

Irreducible representation	O^- sphere: $2s$	O^- sphere: $2p$	O^- sphere: $3d$	Ti^+ sphere: $4p$	Ti^+ sphere: $3d$	Type of genetic transition	Level energy, Ry	Level energy, eV	Band maximum energy, eV	Experimental data: emission or absorption maximum	Experimental data: energy, eV
Emission											
Δ_4	74.5	0.02	0.01	3.9	1.4	dip. quad.	−1.672	−22.7	−22.0	$K\beta''$	−22.4
X_1	78.7	–	–	–	5.9	quad.	−1.667	−22.6	−22.0	$K\beta''$	−22.4
W_1	78.6	–	0.01	3.4	4.4	dip. quad.	−1.641	−22.3	−22.0	$K\beta''$	−22.4
Σ_1	76.6	0.02	–	6.8	1.4	dip. quad.	−1.629	−22.2	−22.0	$K\beta''$	−22.4
L_1	77.1	–	–	9.5	–	dip.	−1.621	−22.0	−22.0	$K\beta''$	−22.4
L_2'	–	40.9	–	–	10.1	dip. quad.	−0.817	−11.1	−9.5	$K\beta_5^{\mathrm{III}}$	−11.4
Σ_1	–	47.8	0.02	0.8	10.1	dip. quad.	−0.744	−10.1	−9.5	$K\beta_5^{\mathrm{III}}$	−11.4
X_4'	–	52.4	–	16.0	–	dip.	−0.696	−9.5	−9.5	$K\beta_5^{\mathrm{III}}$	−11.4
Δ_1	–	52.8	0.01	2.3	10.0	dip. quad.	−0.694	−9.4	−9.5	$K\beta_5^{\mathrm{III}}$	−11.4

Irreducible representation	O^- sphere: $2s$	O^- sphere: $2p$	O^- sphere: $3d$	Ti^+ sphere: $4p$	Ti^+ sphere: $3d$	Type of genetic transition	Level energy, Ry	Level energy, eV	Band maximum energy, eV	Experimental data: emission or absorption maximum	Experimental data: energy, eV
W_3	–	50.6	0.1	11.7	6.1	dip. quad.	−0.650	−8.8	−7.7	$K\beta_5^{II}$	−7.2
W_2'	–	61.5	–	–	11.2	dip. quad.	−0.632	−8.6	−7.7	$K\beta_5^{II}$	−7.2
L_3'	–	59.6	–	–	20.3	dip. quad.	−0.622	−8.4	−7.7	$K\beta_5^{II}$	−7.2
Σ_3	–	53.6	0.2	8.1	9.5	dip. quad.	−0.621	−8.4	−7.7	$K\beta_5^{II}$	−7.2
Σ_4	–	62.5	–	0.5	18.0	dip. quad.	−0.615	−8.4	−7.7	$K\beta_5^{II}$	−7.2
X_5'	–	70.2	–	7.1	–	dip.	−0.527	−7.2	−7.7	$K\beta_5^{II}$	−7.2
Δ_5	–	70.3	0.04	4.5	3.8	dip. quad.	−0.520	−7.1	−7.7	$K\beta_5^{II}$	−7.2
Γ_{15}	–	79.4	–	2.1	–	dip.	−0.486	−6.6	−7.7	$K\beta_5^{II}$	−7.2
X_3	–	–	2.1	–	56.6	quad.	−0.352	−4.8	−2.1	$K\beta_5^{I}$	−1.6
Δ_2'	–	–	2.0	–	61.8	quad.	−0.248	−3.4	−2.1	$K\beta_5^{I}$	−1.6
Γ_{25}'	–	–	1.8	–	76.4	quad.	−0.101	−1.4	−2.1	$K\beta_5^{I}$	−1.6
W_3	–	16.2	1.0	0.07	57.3	quad. dip.	−0.053	−0.7	−2.1	$K\beta_5^{I}$	−1.6
Σ_3	–	20.5	0.8	0.2	52.6	quad. dip.	−0.029	−0.4	−2.1	$K\beta_5^{I}$	−1.6
Absorption											
Δ_1	–	25.5	0.24	4.0	45.1	quad. dip.	0.058	0.8	1.7	A	1.7
Δ_2	–	–	2.4	–	89.9	quad.	0.096	1.3	1.7	A	1.7
L_3'	–	59.6	–	–	20.3	dip. quad.	0.109	1.5	1.7	A	1.7
L_1	77.1	–	–	9.5	–	dip.	0.128	1.7	1.7	A	1.7
X_1	78.7	–	–	–	5.9	quad.	0.161	2.2	1.7	A	1.7
W_1	78.6	–	0.01	3.4	4.4	dip. quad.	0.163	2.2	1.7	A	1.7
W_2'	–	61.5	–	–	11.2	dip. quad.	0.263	3.6	1.7	A	1.7

Irreducible representation	O^- sphere: $2s$	O^- sphere: $2p$	O^- sphere: $3d$	Ti^+ sphere: $4p$	Ti^+ sphere: $3d$	Type of genetic transition	Level energy, Ry	Level energy, eV	Band maximum energy, eV	Experimental data: emission or absorption maximum	Experimental data: energy, eV
Σ_4	–	62.5	–	0.5	18.0	dip. quad.	0.312	4.2	6.1	B	8
L'_3	–	59.6	–	–	20.3	dip. quad.	0.321	4.2	6.1	B	8
X'_4	–	52.4	–	16.0	–	dip.	0.447	6.1	6.1	B	8

* 100% corresponds to the number of electrons needed to populate the given level. The table does not include $4s$-, $4f$-electrons, or electrons whose state is described by a plane wave.

** dip. –dipole transition; quad. –quadrupole transition.

*** The origin of the energy scale was taken as the Fermi surface, whose position on the experimental curves was assumed to approximately coincide with the point of intersection of the contour of the isolated component $K\beta_5^{\mathrm{I}}$ with the contour of the absorption edge.

This is evidenced by the fact that, with an almost constant number of valence electrons in all oxides in the homogeneity range ([6,7]), the Fermi surface, within experimental error, remains unchanged. The energy of the center of gravity of the $K\beta_5$ band agrees satisfactorily with that calculated theoretically. Agreement between theory and experiment is also observed in the energy region of unoccupied states, which appear in the absorption spectra. As can be seen, the most intense absorption, in accordance with theoretical predictions, occurs at the levels corresponding to irreducible representations L_1 (max A) and X'_4 (max B).

The theoretical calculations of the band structure of TiO were carried out ([2]) under the assumption that the effective charge concentrated on the titanium atom is equal to unity (on oxygen, correspondingly, -1), and that the lattice of the compound is defect-free. As for the first assumption, it is in good agreement with estimates of the magnitude of the charge on the metal atom that can be made on the basis of data on the magnitude of the shift of the $K\alpha_{1,2}$- and $K\beta_1$-lines in these compounds ([8,9]), is confirmed by the good agreement between theory and experiment demonstrated in the present work, but contradicts the

notions of the coexistence of nonequivalent titanium atoms in these oxides ([10]). The second assumption is indeed fulfilled in real crystals ([11]), which is reflected in the x-ray spectra. Of the maxima observed in the x-ray spectra, the energies of the maxima of the $K\beta_5^{\mathrm{I}}$- and $K\beta_5^{\mathrm{II}}$-emission bands can be determined most reliably. The data of Table 1 show that the experimentally observed distance of these maxima from the Fermi boundary is $\sim 0.5 \pm 0.2$ eV smaller than the theoretical value*. This can be explained by a shift of the Fermi energy due to the defectiveness of TiO and corresponds, according to our estimates**, to a decrease in the number of delocalized electrons by $\sim 0.8 \pm 0.5$ electron. The authors express their gratitude to S. M. Blokhin and L. M. Mazalov for useful discussions and to L. I. Perevalova for assistance in carrying out the experiment.

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* According to the approximate estimate ([7]), this value should be ~ 1.7 eV.

** The estimate was based on the condition, adopted in ([2]), that the total area bounded by the curve $N(E)$ for TiO, TiN, and TiC corresponds respectively to 10, 9, and 8 delocalized electrons. These data could be somewhat refined by a more accurate experimental determination of the Fermi surface according to ([12]).

Note: Figure translations are in progress. See original paper for figures.