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O.Yu. Khyzhun, Ya.V. Zaulychny, V.D. Dobrovolsky

X-RAY EMISSION AND ABSORPTION SPECTRA OF SUBSTOICHIOMETRIC TANTALUM NITRIDES SYNTHESIZED AT HIGH PRESSURE

I.M. Frantsevych Institite for Problems of Materials Science, National Academy of Sciences of Ukraine, 3 Krzhyzhanovsky st., UA-252142 Kyiv, Ukraine

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The X-ray emission spectroscopy (XES) and X-ray absorption spectroscopy (XAS) methods have been used to study the electronic structure of substoichiometric tantalum mononitrides synthesized at high pressures. Cubic (NaCl structure) and hexagonal (WC structure) tantalum nitrides were obtained using the method of self-spreading high-temperature synthesis (pressures up to 0.1 GPa) or at conditions of high temperature – high pressure treatment (pressures 7 to 10 GPa). Both the Ta $L\beta_5$ and N $K\alpha$ X-ray emission spectra of cubic nitrides TaN_x (NaCl structure, $0.81 \leq x \leq 1.172$) and hexagonal nitrides $TaN_{0.99}$ (CoSn structure) and $TaN_{0.90}$ (WC structure) have been derived and compared in a single energy scale. The Ta L_{III} XAS spectra of the above cubic nitrides TaN_x were investigated. In all the tantalum nitrides studied the Ta 5d-like and N 2p-like states are strongly hybridized, and the charge transfers from Ta atoms to N atoms. In the series TaN (CoSn structure) → TaN (WC structure) → TaN (NaCl structure) a decrease of the XES N K_α band half-width was observed. In the most substoichiometric on the metal sublattice cubic tantalum mononitrides ($1.134 \leq x \leq 1.172$) a creation of the subband of non-binding N 2p-like states arranged in the region of the energy gap between the Ta 5d – N 2p- and Ta 5d-like bands has been detected.

1. Introduction

Transition metal (TM) carbides and nitrides are of great interest because these compounds exhibit an unusual combination of a number of physical and chemical properties (high hardness and high melting points, good electrical and thermal conductivity, superconductivity, etc. [1,2]). The chemical bond in these compounds is a superposition of covalent, metallic, and ionic component, which make an interpretation of their electronic structure very difficult. The above compounds exhibit wide regions of homogeneity within the limits of which they contain a considerable number of structural vacancies. Nonstoichiometry effects are greatly important in TM carbides and nitrides, because they strongly influence the properties of the mentioned compounds [1]. Some of properties of the substoichiometric carbides and nitrides can be understood by considering the electronic structure of these materials.

The electronic structure of substoichiometric binary TM carbides and nitrides with vacancies on their non-metal sublattices has been studied in detail (see, *e.g.*, Refs. [3–7]). The understanding of the electronic structure of substoichiometric on the metal sublattice binary refractory compounds has also been of quite some interest. The influence of metal vacancies on the electronic structure of binary TM compounds has been theoretically studied for Ti_yC and Ti_yO by Gubanov et al. [8]; for the compounds M_3N_4 (M = Ti, Zr, Hf) by Schwarz et al. [9]; for carbides, nitrides, and oxides of Ti and V by Ivanovsky et al. [10]; for the zirconium nitride $Zr_{0.75}N$ by the authors [11,12]. The X-ray photoelectron spectroscopy (XPS) method has been used by Ihara et al. [13] to study the XPS valence-band spectra of the MoN_x films, with x over the range $0.5 \leq x \leq 1.8$.

The X-ray emission spectroscopy (XES) and X-ray absorption spectroscopy (XAS) methods have not been used so far for investigation of the electronic structure of TM carbides and nitrides with vacancies on the metal sublattice (see, *e.g.*, monographs [5,14,15]). Moreover, while the electronic structure of stoichiometric cubic tantalum mononitride was investigated in a series of theoretical [16–20] and experimental [21–23] works, the substoichiometric cubic tantalum nitride in the region of its homogeneity was not studied [5,14,15]. The electronic structure of substoichiometric hexagonal tantalum mononitrides with the WC-type structure was ivestigated by Tsvyashchenko *et al.* [24] by means of the non-self-consistent symmetrized augmented plane wave method. The XES investigations of hexagonal (CoSn structure) stoichiometric tantalum mononitride have been carried out in Refs. [21–23, 25].

In the present paper we have performed the XES investigations of cubic tantalum mononitride TaN_x (NaCl structure) with vacancies on the non-metal sublattice or on the metal one ($0.81 \leq x \leq 1.172$). For comparison the XES Ta 5*d*-like and N 2*p*-like spectra of the hexagonal nitrides $TaN_{0.99}$ (CoSn structure) and $TaN_{0.90}$ (WC structure) have been studied.

2. Experimental

The technique of the present XES and XAS investigations of the electronic structure of substoichiometric tantalum nitrides are analogous to those described elsewhere [26–28]. Therefore, in this paper only the main details of the experiment are described.

The N $K\alpha$ emission bands ($K \rightarrow L_{II,III}$ transition) reflecting the energy distribution of filled valence states of *p*-symmetry of nitrogen in tantalum nitrides were measured with an RSM-500 ultrasoft X-ray spectrometer. The dispersing element was a diffraction grating with 600 lines/mm and a radius of curvature of R = 6000 mm. The detector was a secondary electron multiplier with a CsI photocathode. The X-ray chamber was evacuated to $1 \cdot 10^{-6}$ Pa. The resolution of the RSM-500 spectrometer was about 0.3 eV.

The fluorescent X-ray emission Ta $L\beta_5$ bands ($L_{III} \rightarrow O_{IV,V}$ transition) reflecting primarily the occupied Ta 5*d*-like states were measured with a DRS-2M spectrograph in the second order of reflection from the (0001) plane of a quartz crystal prepared according to Johann (for more detailed information see Refs. [15,26]). The resolution of the DRS–2M spectrograph was also about 0.3 eV. The BHW–7 X-ray tube with gold anode was used as a source of primary radiation. The accumulation times for the Ta $L\beta_5$ spectra were about 130 to 150 hrs.

The Ta L_{III} absorption spectra (empty Ta 5*d*-like states) were measured in the first order of reflection from $(13\,\bar{4}\,0)$ plane of a quartz crystal using the method of "a variable field of

absorption" (see Refs. [26,29,30]). For the comparison of the absorption coefficient $\mu(E)$ in substoichiometric cubic tantalum mononitrides the Ta L_{III} absorption edges were reduced to a single effective thickness d of absorber as described in Refs. [26,28]. The N $K\alpha$ absorption spectra in tantalum nitrides could not be investigated, probably, as the result of strong screening of the N atoms by the Ta atoms [15,28].

The Ta $L\beta_5$ bands were normalized to one and the same peak intensities of the X-ray Ta $L\beta_9$ lines. The relative intensities of the N K_α bands were not measured because there was not a standard X-ray line in the range of energies corresponding to the energy of the N K_α band [15,31]. A comparison of the Ta $L\beta_5$ and N K_α emission bands in a single energy scale was realized on the basis of the XPS Ta 4*f* and N 1*s* core-level binding energies which were measured with an ES-2401 spectrometer [32,33].

The substoichiometric cubic tantalum nitrides and the hexagonal nitride $TaN_{0.90}$ (WC structure) investigated in the present paper were synthesized from the initial hexagonal nitride $TaN_{0.99}$ (CoSn structure) by high pressure – high temperature treatment (at 1000–2400°C and 7–10 GPa) or by means of the method of "self-spreading high-temperature synthesis of refractory inorganic compounds" (at pressures up to 0.1 GPa, for more detailed information see Refs. [28,33]). All the tantalum nitrides studied were single-phase specimens. The X-ray diffraction analysis data and lattice parameters of the tantalum nitrides investigated in the present work were reported in Refs. [28,32,33].

3. Results and discussion

3.1. *Tantalum nitrides with vacancies on the non-metal sublattice*

The results of comparison in a single energy scale of the Ta $L\beta_5$ and N $K\alpha$ emission bands of cubic tantalum nitrides TaN_x with vacancies on the non-metal sublattice ($x < 1.00$) are presented in Fig. 1. For comparison the results of XES investigations of the hexagonal tantalum nitrides $TaN_{0.99}$ and $TaN_{0.90}$ with the structures of CoSn-type and WC-type, respectively, are also shown in the mentioned figure. As one can see from Fig. 1, in all the cubic and hexagonal tantalum nitrides investigated the main peaks "*b*" of the X-ray Ta $L\beta_5$ and N $K\alpha$ bands coincide with each other within experimental errors in the single energy scale (Table 1). Therefore, as it was detected for tantalum carbides [26,27], the metal 5*d*-like and non-metal 2*p*-like states in tantalum nitrides investigated are also strongly hybridized.

Fig. 1 shows that the transformation of the electronic structure of cubic TaN owing to creation of new vacancies on its non-metal sublattice as a whole is analogous to that of cubic TaC with vacancies on its C-sublattice. The maxima "*b*" of the Ta $L\beta_5$ and N K_α bands reflect the hybridized Ta 5*d*-like and N 2*p*-like states responsible for the formation of the direct Ta-N bonds [32,33]. The removal of nitrogen atoms from the non-metal sublattice of cubic TaN leads to breaking of some Ta-N bonds. Therefore, the number of the hybrid Ta 5*d*-like and N 2*p*-like states is decreased with the increasing number of N-vacancies. Consequently, part of the Ta 5*d*-like states, which do not take part in the formation of covalent d_{Ta}–p_N bonds owing to Ta 5*d* – N2*p*-like hybridization, will be located in the high-energy region, about 1–2 eV below the Fermi energy E_f, mainly as Ta 5*d*-like states of t_{2g}-symmetry [33]. The mentioned redistribution of the Ta 5*d*-like states due to the creation of vacancies on the non-metal sublattice of cubic TaN_x is reflected on the changes of the

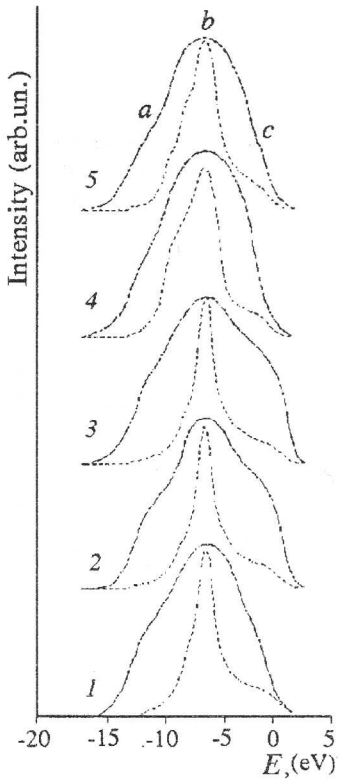


Fig. 1. A comparison in a single energy scale of the Ta $L\beta_5$ (solid curve) and N $K\alpha$ (dashed curve) emission bands of cubic tantalum nitrides TaN_x with $x < 1.00$: *1* – $x = 0.97$; *2* – $x = 0.88$; *3* – $x = 0.81$. For comparison the spectra of the hexagonal nitrides $TaN_{0.99}$ (CoSn structure) (*4*) and $TaN_{0.90}$ (WC structure) (*5*) are also shown

Table 1

Energy position, in eV, of maxima of the XTS and XAS spectra in tantalum nitrides investigated (in a single energy scale)

Compound	Structure type	Ta$L\beta_5$ band	N $K\alpha$ band	Ta L_{III} absorption edge ("white line")
$TaN_{0.99}$	CoSn	-5.7	-5.8	+2.7
$TaN_{0.90}$	WC	-5.5	-5.6	+2.6
$TaN_{0.81}$	NaCl	-5.8	-5.8	2.8
$TaN_{0.88}$	NaCl	-5.8	-5.9	3.3
$TaN_{0.97}$	NaCl	-5.9	-5.9	3.2
$TaN_{1.095}$	NaCl	-5.9	-5.8	2.7
$TaN_{1.109}$	NaCl	-6.0	-5.8	3.0
$TaN_{1.134}$	NaCl	-6.0	-5.9	3.4
$TaN_{1.144}$	NaCl	-5.8	-5.9	3.3
$TaN_{1.172}$	NaCl	-5.9	-5.8	3.6
Uncertainty	-	±0.2	±0.2	±0.3

normalized Ta $L\beta_5$ spectra of these compounds (unfortunately, as mentioned, the N $K\alpha$ bands could not be normalized). As one can see from Fig. 1, the normalization of the Ta $L\beta_5$ bands with respect to the corresponding Ta $L\beta_9$ lines shows that the intensity of the Ta $L\beta_5$ spectra decreased in the row $TaN_{0.97} \rightarrow TaN_{0.81}$. One can observe the increase of the Ta 5*d*-like density of states about 1–2 eV below E_f in going from $TaN_{0.97}$ to $TaN_{0.81}$. Fig. 2 shows that the ratio I_c/I_b monotonously increases for the Ta $L\beta_5$ band in the mentioned row. The above redistribution of the Ta 5*d*-like states due to the creation of vacancies on the non-metal sublattice of TaN_x results in appreciable broadening of the Ta $L\beta_5$ band in the direction $TaN_{0.97} \rightarrow TaN_{0.81}$ (Table 2).

The creation of vacancies on the non-metal sublattice of cubic TaN_x does not change the shape of the N $K\alpha$ band (Fig. 1). As one can see from Fig. 2 and Table 2, with an increase of the number of nitrogen vacancies in cubic tantalum nitride both the N $K\alpha$ band half-widths and the ratios I_c/I_b of the band remain unchanged. Figs 1 and 3 show that the N $K\alpha$ bands in substoichiometric cubic tantalum nitrides are narrower than the analogous spectra of hexagonal tantalum nitrides with close content of vacancies in their non-metal sublattices (compare, *e.g.*, dashed curves *1* and *4* or *2* and *5* in Fig. 1). In contrary to the N $K\alpha$ bands, the Ta $L\beta_5$ band half-widths of the hexagonal nitrides $TaN_{0.99}$ and $TaN_{0.90}$ are somewhat smaller in comparison with those of cubic TaN_x with close content of N-vacancies (Fig. 3).

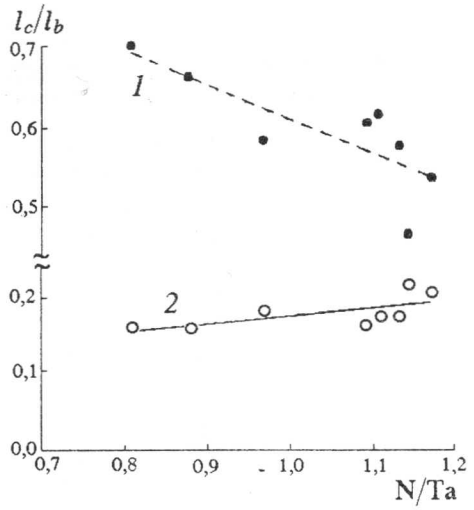


Fig. 2. Relative intensities of the near-Fermi features "*c*" of the Ta $L\beta_5$ (*1*) and N $K\alpha$ (*2*) emission bands *vs* nitrogen-to-tantalum ratios *x* in the substoichiometric cubic tantalum nitrides

Table 2

Half-width ($W_{1/2}$), in eV, of the XES spectra in cubic tantalum mononitrides

Compound	Ta $L\beta_5$ band	N $K\alpha$ band
$TaN_{0.81}$	11.2	2.32
$TaN_{0.88}$	10.0	2.38
$TaN_{0.97}$	9.2	2.46
$TaN_{1.095}$	9.1	2.46
$TaN_{1.109}$	9.0	2.52
$TaN_{1.134}$	9.1	2.73
$TaN_{1.144}$	8.6	2.91
$TaN_{1.172}$	8.5	3.02
Uncertainty	±0.2	±0.06

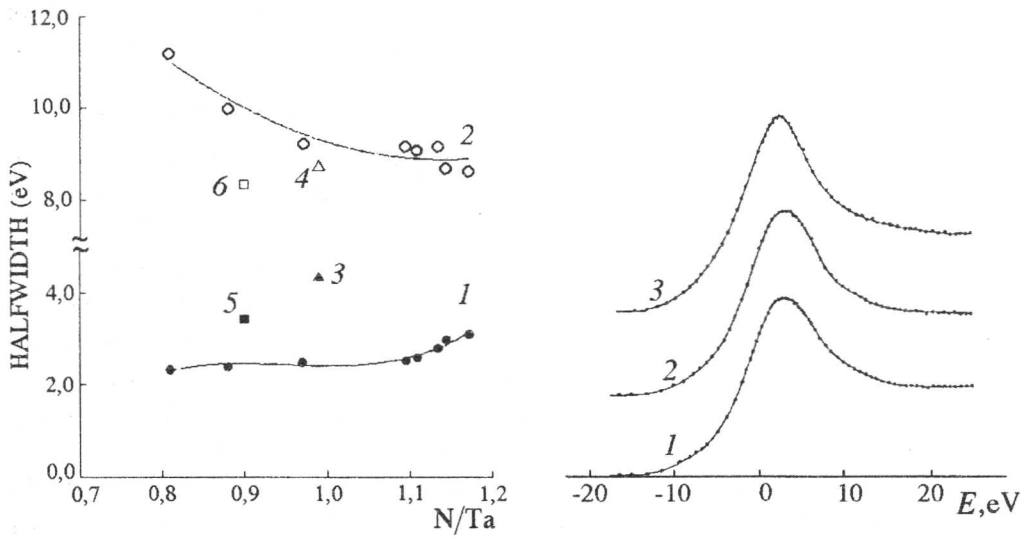


Fig. 3. The XES band half-widths *vs* the nitrogen-to-tantalum ratios *x* in cubic tantalum nitrides: *1* – N $K\alpha$ band and *2* –Ta $L\beta_5$ band. The results of analogous investigations of the hexagonal nitrides $TaN_{0.99}$ (CoSn structure) and $TaN_{0.90}$ (WC structure) are shown by data (*3,4*) and (*5,6*), respectively

Fig. 4. The normalized Ta L_{III} absorption spectra of cubic TaN_x with vacancies on the non-metal sublattice: *1* – x = 0.97; *2* – x = 0.88; *3* – x = 0.81

The results of the XAS investigations of cubic tantalum nitrides with vacancies on the non-metal sublattice are shown in Fig. 4. As one can see from Fig. 4, the creation of vacancies on the nitrogen sublattice of cubic TaN_x does not result in the formation of fine structures on the Ta L_{III} absorption spectra. Fig. 4 shows that an increase of intensity of the normalized Ta L_{III} spectra is only observed in the row $TaN_{0.97} \rightarrow TaN_{0.81}$ (for more detailed

information see Refs. [32,33]). The increase of the absorption coefficient $\mu(E)$ in the region of "white" line of the Ta L_{III} absorption spectrum going from $TaN_{0.97}$ to $TaN_{0.81}$ is connected with increasing relative number of tantalum atoms in cubic TaN_x in the mentioned row. Earlier analogous results were detected for substoichiometric cubic TaC_x and hexagonal W_2C_x carbides with vacancies on their non-metal sublattices [26,34].

3.2. Cubic tantalum nitrides with vacancies on the metal sublattice

The results of comparison in a single energy scale of the Ta $L\beta_5$ and N $K\alpha$ emission bands of cubic tantalum mononitrides with vacancies on the metal sublattice ($x > 1.00$) are shown in Fig. 5. Fig. 5 shows that the another changes of the shape of the emission bands are observed owing to introduction of vacancies on the metal sublattice of cubic tantalum mononitrides. Both the shapes and half-widths of the Ta $L\beta_5$ band remain almost constant in going from $TaN_{1.095}$ to $TaN_{1.172}$ (see Figs 3 and 5). Only a decrease of the ratio I_c/I_b of the Ta $L\beta_5$ band was observed in the mentioned sequence (Fig. 2). But the N $K\alpha$ band half-width increases in the row $TaN_{1.095} \rightarrow TaN_{1.172}$ (Table 2), and the creation of an additional feature "*d*" of the N $K\alpha$ band has been detected in the most substoichiometric on the metal sublattice cubic tantalum nitrides (with $x = 1.134$ to $x = 1.172$, Fig. 5). As one can see from Fig. 5, the energy position of the subband "*d*" is in the energy gap between the Ta5*d*- N2*p*-hybridized band (feature "*b*" of the Ta $L\beta_5$ and N $K\alpha$ emission spectra) and the Ta 5*d*-like band (feature "*c*" of the Ta $L\beta_5$ spectra). The relative intensity of the feature "*d*" of the N $K\alpha$ band (I_d/I_b ratio) increases in the row $TaN_{1.134} \rightarrow TaN_{1.172}$ (Fig. 5). As shown in Refs. [32,33], the creation of the feature "*d*" of the N $K\alpha$ band in the most substoichiometric on the metal sublattice cubic tantalum mononitrides is due to the formation of the subband of the non-binding N 2*p*-like states in these compounds. The creation of the subband of the non-binding X 2*p*-like states (X = C, N) has been predicted by theoretical calculations of the electronic structure for group IV*b* and V*b* carbides and nitrides contained structural vacancies on their metal sublattices [9–12]. The above theoretical calculations indicate that the creation of the subband of the X 2*p*-like non-binding states in substoichiometric on the M-sublattice compounds M_yX ($y < 1.00$; X = C, N, O) should lead to some broadening of the X 2*p*-like bands with increasing number of metal vacancies in the mentioned compounds. This was true for cubic tantalum nitrides TaN_x (with $x > 1.00$) investigated in the present work (Figs 3 and 5). As one can see from Fig. 2, an increase of the relative intensity of the feature "*d*" of the N $K\alpha$ band with increasing number of the M-vacancies in TaN_x leads to some increase of the relative intensity of the near-Fermi feature "*c*" of the N 2*p*-like XES spectra.

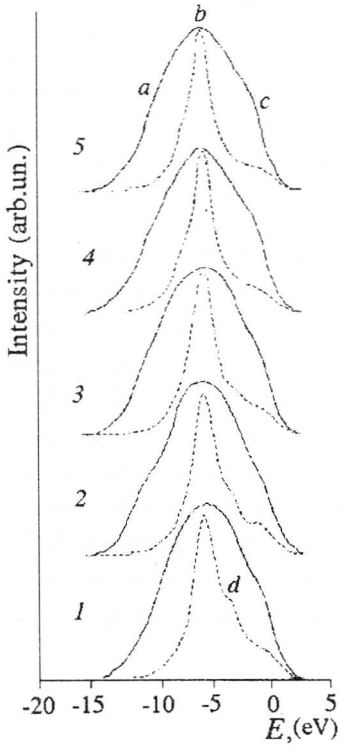
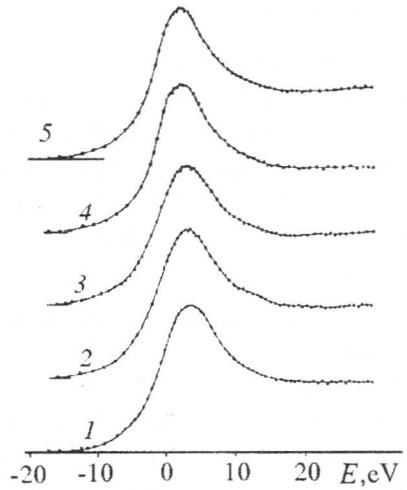


Fig. 5. A comparison in a single energy scale of the Ta $L\beta_5$ (solid curve) and N $K\alpha$ (dashed curve) emission bands of cubic tantalum nitrides TaN_x with $x > 1.00$: *1* – $x = 1.172$; *2* – $x = 1.144$; *3* – $x = 1.134$; *4* – $x = 1.109$; *5* – $x = 1.095$

The results of the XAS studies of cubic tantalum

mononitrides with vacancies on the metal sublattice are presented in Fig. 6. Like in cubic TaN_x with N-vacancies, the creation of vacancies on the tantalum sublattice does not result in any changes of the shape of the Ta L_{III} absorption spectra. But as one can see from Fig. 7, inflection points of the Ta L_{III} absorption spectra monotonously shifted towards E_f in the sequence $TaN_{0.81} \rightarrow TaN_{0.97} \rightarrow TaN_{1.095} \rightarrow TaN_{1.172}$.



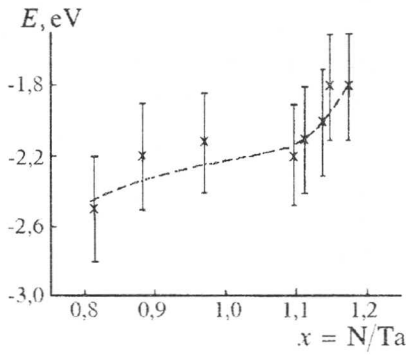


Fig. 6. The normalized Ta L_{III} absorption spectra of cubic TaN_x with vacancies on the non-metal sublattice: *1* – x = 1.172; *2* – x = 1.144; *3* – x = 1.134; *4* – x = 1.109; *5* – x = 1.095

Fig. 7. Energy positions (with respect to the Fermi level) of the inflection points of the Ta L_{III} absorption spectra *vs* nitrogen-to-tantalum ratios x in the substoichiometric cubic tantalum nitrides

It should be noted that the integral intensities of the Ta $L\beta_5$ bands in all the tantalum nitrides investigated (with vacancies on the N-sublattice as well as on the Ta-sublattice) are 15–28% (±7%) smaller than in pure metallic tantalum. Besides, as it was detected in Refs. [28,32,33], in the investigated specimens TaN_x the XPS Ta 4*f* core-level binding energies increase compared with the Ta 4*f* binding energy of pure Ta_{met}. The above facts indicate that when tantalum atoms and nitrogen atoms combine to form tantalum nitrides, the charge transfers from Ta atoms to N atoms. Our results confirm the data of theoretical band calculations [18–20], which indicate that in cubic tantalum nitrides the charge transfers in the direction Ta → N. The almost monotonous shift towards E_f of the inflection points of the Ta L_{III} absorption spectra in the row $TaN_{0.81} \rightarrow TaN_{1.172}$ points out that an increase of the positive effective charge on the tantalum atoms is observed when going from $TaN_{0.81}$ to $TaN_{1.172}$.

4. Conclusions

The X-ray emission data indicate that in all the studied substoichiometric cubic (NaCl structure) nitrides TaN_x ($0.81 \leq x \leq 1.172$) as well as in the hexagonal compounds $TaN_{0.99}$ (CoSn structure) and $TaN_{0.90}$ (WC structure) the Ta 5*d*-like and N 2*p*-like states are strongly hybridized. In the sequence $TaN_{0.99}$ (CoSn structure) → $TaN_{0.90}$ (WC structure) → TaN_x (NaCl structure) the N $K\alpha$ band half-width decreases. The creation of new vacancies on the

non-metal (metal) sublattice of cubic TaN_x increases the Ta 5*d*-like (N 2*p*-like) band half-width. In TaN_x studied the charge transfers from Ta atoms to N atoms. In the row $TaN_{0.81} \rightarrow TaN_{1.172}$ the positive effective charge on the tantalum atoms increases.

Acknowledgments

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1. *L.E. Toth*, Transition metal carbides and nitrides, Academic Press, New York–London (1971).
2. *G.V. Samsonov and I.M. Vinitskii*, Refractory Compounds, Metallurgia, Moscow (1976) (in Russian).
3. *J.-L. Calais*, Adv. Phys. **26**, 847 (1977).
4. *E.A. Zhurakovsky and V.F. Nemchenko*, Kinetic Properties and Electronic Structure of Interstitial Phases, Naukova Dumka, Kyiv (1989) (in Russian).
5. *A.L. Ivanovsky, V.P. Zhukov and V.A. Gubanov*, Electronic Structure of Refractory Carbides and Nitrides of Transition Metals, Nauka, Moscow (1990) (in Russian).
6. *A. Neckel*, Intern. J. Quantum Chem. **23**, 1317 (1983).
7. *P. Marksteiner, P. Weinberger, A. Neckel, R. Zeller and P.H. Dederichs*, Phys. Rev. **B33**, 812 (1986), ibid **33**, 6709 (1986).
8. *V.A. Gubanov, A.L. Ivanovsky, G.P. Shveikin and D.E. Ellis*, J. Phys. Chem. Solids **45**, 719 (1984).
9. *K. Schwarz, A.R. Williams, J.J. Cuomo. J.H.E. Harper and H.T.G. Hentzell*, Phys. Rev. **B32**, 8312 (1985).
10. *A.L. Ivanovsky, V.I. Anisimov, D.L. Novikov, A.I. Lichtenstein and V.A. Gubanov*, J. Phys. Chem. Solids **49**, 465 (1988).
11. *P. Marksteiner, P. Weinberger, A. Neckel, R. Zeller and P.H. Dederichs*, J. Phys. F: Met. Phys. **16**, 1495 (1986).
12. *V.I. Ivashchenko, E.P. Trofimova, A.A. Lisenko and E.A. Zhurakovsky*, Phys. Metals **10**, 18 (1990).
13. *H. Ihara, Y. Kimura, K. Senzaki, H. Kezuka and M. Hirabayashi*, Phys. Rev. **B31**, 3177 (1985).
14. *E.Z. Kurmaev, V.M. Cherkashenko and L.D. Finkelstein*, X-Ray Emission Spectra of Solids, Nauka, Moscow (1988) (in Russian).
15. *A. Meisel, G. Leonhardt and R. Szargan*, R-Ray Spectra and Chemical Binding, Springer, Berlin, Heidelberg (1989).
16. *E.S. Alekseev, R.G. Arkhipov and S.V. Popova*, Phys. stat. sol. (b), **90**, K133 (1978).
17. *P. Weinberger, C.P. Mallett, R. Podloucky and A. Neckel*, J. Phys. C: Solid State Phys. **13**, 173 (1980).
18. *V.P. Zhukov, A.L. Ivanovsky, V.A. Gubanov, G.P. Shveikin and J. Weber*, Zh. Neorgan. Khim. **25**, 318 (1980) (in Russian).
19. *V.L. Bekenev, A.A. Ostroukhov and I.N. Frantsevich*, Fiz. Tekhn. Vysok. Davl. № 13, 67 (1983) (in Russian).
20. *E.M. Gololobov, N.N. Dorozhkin and V.B. Novysh*, Fiz. Tverd. Tela **31**, 290 (1989) (in Russian).
21. *E.A. Zhurakovsky, Ya.V. Zaulychny, S.V. Popova and V.S. Mainashev*, Fiz. Tekhn. Vysok. Davl. № 9, 54 (1982) (in Russian).

22. *E.A. Zhurakovsky, Ya.V. Zaulychny and A.Yu. Garmash*, Izv. Vuzov: Fizika **31**, 114 (1988) (in Russian).
23. *O.Yu. Khyzhun, Ya.V. Zaulychny and E.A. Zhurakovsky*, in: Influence of High Pressures upon Materials, A.V. Kurdyumov (ed.), IPMS Academy of Sciences of Ukraine (1994), p. 19 (in Russian).
24. *A.V. Tsvyashchenko, S.V. Popova and E.S. Alekseev*, Phys. stat. sol. (b), **100**, 99 (1978).
25. *A.S. Shulakov, Ph.D. Thesis*, Leningrad State University, Leningrad (1974).
26. *O.Yu. Khyzhun, E.A. Zhurakovsky, A.K. Sinelnichenko and V.A. Kolyagin*, J. Electron Spectrosc. Related Phenom. **82**, 179 (1996).
27. *O.Yu. Khyzhun*, Ukr. J. Phys. **42**, 173 (1997).
28. *O.Yu. Khyzhun, Ya. V. Zaulychny, E.A. Zhurakovsky and V.B. Shipilo*, Met. Phys. Adv. Tech. **16**, 457 (1997).
29. *Ya.V. Zaulychny, O.Yu. Khyzhun, E.A. Zhurakovsky and V.D. Dobrovolsky*, Phys. Metals **10**, 672 (1991).
30. *O.Yu. Khyzhun, Ya. V. Zaulychny and E.A. Zhurakovsky*, J. Alloys Comp. **244**, 107 (1996), and references therein.
31. *J.A. Bearden*, X-Ray wavelengths, Oak Ridge Atomic Energy Commission, Tennessee (1964).
32. *O.Yu. Khyzhun, Ph.D.* Thesis, Institute of Metal Physics of the Academy of Sciences of Ukraine, Kyiv (1992).
33. *O.Yu. Khyzhun*, Metallofiz. Nov. Tekhnol. **19** (No.6), 1 (1997) (in Russian).
34. *O.Yu. Khyzhun, E.A. Zhurakovsky and Ya.V. Zaulychny*, Sov. Powder Metal. and Metal Ceramics **29**, 732 (1990).