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A.A. Lavrentyev¹, B.V. Gabrelian¹, V.B. Vorzhev¹, I.Ya. Nikiforov¹,
O.Yu. Khyzhun², J.J. Rehr³

X-RAY SPECTROSCOPY STUDIES OF THE ELECTRONIC
STRUCTURE AND BAND-STRUCTURE CALCULATIONS OF CUBIC
TaC_xN_{1-x} CARBONITRIDES

¹Department of Physics, Don State Technical University
Gagarin Sq. 1, Rostov-on-Don, Russian Federation
E-mail: alavrentyev@dstu.edu.ru

²Frantsevych Institute for Problems of Materials Science,
National Academy of Sciences of Ukraine
3 Krzhyzhanivsky str., 03142 Kyiv, Ukraine
E-mail: khyzhun@ipms.kiev.ua

³Department of Physics, University of Washington
Seattle, WA 98195-1560, USA

The electronic structure of almost stoichiometric cubic (NaCl structure) tantalum carbonitrides TaC_xN_{1-x} synthesized under high pressure–high temperature conditions (7–10 GPa and 2100–2400°C) was studied employing X-ray photoelectron spectroscopy (XPS), X-ray emission spectroscopy (XES) and X-ray absorption spectroscopy (XAS). The XPS valence-band and core-level spectra, the XES Ta Lβ₅, C Kα and N Kα bands (reflecting energy distributions of mainly the Ta 5d-, C 2p- and N 2p-like states, respectively), as well as the XAS Ta L_{III} edges (unoccupied Ta d-like states) were derived and compared on a common energy scale for the compounds TaC_{0.98}, TaC_{0.52}N_{0.49} and TaN_{0.97} obtained under the mentioned high pressure–high temperature conditions. To investigate the influence of substitution of carbon atoms by nitrogen in the cubic TaC_xN_{1-x} system, the cluster self-consistent calculations of the electron density of states for cubic TaC, TaC_{0.5}N_{0.5} and TaN compounds were carried out with the FEFF8 code. In the present work a rather good agreement of the experimental and theoretical results for the electronic structure of the TaC_xN_{1-x} system under consideration was obtained.

Introduction

It is well known that almost all transition metal (TM) carbides and nitrides form unlimited solid solutions with each other [1,2]. Some physical and chemical properties of such TM carbonitrides are non-monotonous as a function of the

MC/MN ratio (M denotes a transition metal) and in many cases they depend strongly on a ternary compound composition. The properties of TM carbonitrides can be understood by considering their electronic structure. Additionally, the understanding of the electronic structure of TM carbonitrides is also of great technical interest because alloying the sublattices of the compounds with atoms of a different type is one of the most promising methods for modification of service characteristics of materials [2,3].

Concerning the TaC–TaN system, the synthesis of a continuous cubic (NaCl structure) solid solution by conventional powder metallurgy methods is not possible using as precursors usual forms of tantalum mononitride (CoSn structure) and monocarbide (NaCl structure) [1,2]. As Weber [4] has revealed, a phase transition from the fcc to the hcp structure occurs in the TaC_xN_{1-x} carbonitrides near $x = 0.4$. A continuous nonstoichiometric cubic TaC_xN_y ($x + y \neq 1$) solid solution was first derived by Avakyan et al. [5] using the method of self-spreading high temperature (SSHT) synthesis. However, the SSHT method does not allow to obtain stoichiometric TaC_xN_y system (with $x + y \approx 1$). The above problem was solved by Gololobov et al. [6,7] employing high temperature–high pressure conditions for obtaining the almost stoichiometric TaC_xN_{1-x} system.

However, it is interesting to study the influence of substitution of carbon atoms for nitrogen on the electronic structure of the TaC–TaN system. The aim of this work was to employ both experimental and theoretical methods for solution of the above task. Series of theoretical band-structure calculations were devoted either to TaC [8–12] or to TaN [13–16] compounds, however, to the best of our knowledge, previously there were no attempts for theoretical investigation of the electronic structure of a ternary TaC_xN_{1-x} system. For the above system, in the present paper we have used also three experimental methods providing information about the electronic structure of solids, namely, X-ray photoelectron spectroscopy (XPS), X-ray emission spectroscopy (XES) and X-ray absorption spectroscopy (XAS).

2. Experimental

Cubic tantalum carbonitride $TaC_{0.52}N_{0.49}$ and mononitride $TaN_{0.97}$ investigated in the present work were synthesized under high pressure–high temperature conditions (7–10 GPa and 2100–2400°C) using the following powdered materials as precursors: hexagonal mononitride $TaN_{0.99}$ (CoSn structure), cubic monocarbide $TaC_{0.98}$ (NaCl structure), and metallic tantalum. According to the data of a conventional chemical analysis and XPS measurements [17], the tantalum mononitride under consideration contains some admixtures of carbon and the analytical formula $TaC_{0.04}N_{0.97}$ can be ascribed to the compound. The synthesis method, the calculation of the burden's chemical composition and of content of the nitrogen-containing heterocyclic compounds in the burdens (melamine ($C_3H_6N_6$), 5,6-dimethylbenzimidazole ($C_9H_{10}N_2$), γ , γ' -dipyridyl ($C_{10}N_2H_8$))

were discussed previously [17]. By the data of the chemical analysis and tests with a Microscan-5 X-ray microanalyser, an ES-2401 electron spectrometer, a JAMP-10 Auger scanning electron microscope («JEOL», Japan), and a CS-244 carbon analyser («Leco», Germany) oxygen content in the studied tantalum carbonitrides was lower than 0.3 wt%, unbonded carbon was either absent or its content was < 0.1 wt% [17].

Measurements of the XPS valence-band and core-level spectra were carried out in an ion-pumped chamber of an ES-2401 spectrometer having a base pressure less than $5 \cdot 10^{-8}$ Pa. In the mentioned spectrometer, the Mg $K\alpha_{1,2}$ radiation ($E = 1253.6$ eV) was used as a source of spectra excitation. The binding energy (BE) of 84.00 ± 0.05 eV of the XPS Au $4f_{7/2}$ core-level spectrum was used as a reference. The surfaces of the studied specimens were prepared by Ar^+ bombardment (1700 V, $30 \mu\text{A}/\text{cm}^2$, 10 min) with subsequent mechanical cleaning in the spectrometer chamber, as reported in Refs. [17,18].

The X-ray C $K\alpha$ and N $K\alpha$ emission bands ($K \rightarrow L_{\text{II,III}}$ transition) reflecting the energy distribution of the C $2p$ - and N $2p$ -like states, respectively, in the tantalum carbonitrides under consideration were derived with the energy resolution ΔE_{min} of about 0.3 eV using an RSM-500 spectrometer. A diffraction grating with 600 lines/mm and a radius of curvature $R = 6026$ mm was used as a dispersing element in the RSM-500 spectrometer. The detector was a secondary electron multiplier VEU-6 with a CsI photocathode. The X-ray chamber was evacuated to $1 \cdot 10^{-6}$ Pa. The C $K\alpha$ and N $K\alpha$ spectra were recorded under conditions of oil-free evacuation practically eliminating impact of hydrocarbon vapours on the target. In addition, the surfaces of the tantalum carbonitrides under consideration were prepared by Ar^+ bombardment in the spectrometer chamber (2100 V, $50 \mu\text{A}/\text{cm}^2$, 10 min). The fluorescent X-ray Ta $L\beta_5$ emission bands ($L_{\text{III}} \rightarrow O_{\text{IV,V}}$ transition) reflecting primarily the Ta $5d$ -like states in the above materials were obtained using a DRS-2M spectrograph (the resolution was estimated to be $\Delta E_{\text{min}} \approx 0.4$ eV) in the second order of reflection from the (0001) plane of a quartz crystal prepared according to Johann [19]. An X-ray BKhV-7 tube with gold anode was used as a source of spectra excitation.

The X-ray Ta L_{III} absorption spectra (unoccupied Ta d -like states) were obtained using a KRUS-1 spectrometer. The method of «a variable field of absorption» was employed for recording the spectra and a quartz crystal with the (13 $\bar{4}$ 0) reflecting plane and a radius of curvature $R = 872$ mm was used as a dispersing element. The absorber covering half of the rotating sample cell was made in the form of a thin film of the investigated substance with a wax binder. Our attempts for investigating quantum yields of the X-ray photoeffect in the area of the C K and N K absorption edges in the tantalum carbonitrides were unsuccessful, probably, as a result of strong screening of the carbon and nitrogen atoms by the heavier tantalum atoms. An X-ray diffraction analysis employing Cu $K\alpha$ radiation has revealed that the tantalum carbonitrides studied in the present work were single-phase materials [17].

Calculation procedure

Cluster self-consistent calculations of the total density of states (DOS) and the partial Ta $5d$ -, N $2p$ - and C $2p$ -like DOS were carried out with the FEFF8 program [20] for TaC, TaC_{0.5}N_{0.5} and TaN compounds possessing the structure of NaCl-type. The *ab initio* calculations employing the FEFF8 program are carried out in the approach of multiple scattering theory for clusters in real space, i.e. without any restrictions on symmetry and periodicity of a crystal lattice. Relativistic atomic charge densities are calculated at the very beginning and the phase shifts derived with relativistic corrections using the above procedure are used on the next steps of calculations of the self-consistent muffin-tin potential in the approach of full multiple scattering for clusters consisted of approximately 45 atoms.

During the self-consistency procedure, a new electron density is calculated; the number of 10 to 20 iterations is necessary to reach a coincidence of the Fermi energy within 0.003 eV. Clusters consisted of approximately 200 atoms are used for calculations of the total and partial DOS. Energy resolution (accuracy) of the DOS calculations is restricted by (i) final dimensions of the clusters, (ii) life-time of a core-level hole, (iii) a distinction of the muffin-tin potential from the total potential. However, such integral characteristics as the total DOS, the Fermi energy and charge transfer values are almost insensitive to the above-mentioned peculiarities of the FEFF8 program employed in the present work for calculations of the electronic structure of cubic tantalum carbonitrides [20].

4. Results and discussion

Figure 1 represents a comparison of the Ta $L\beta_5$, C $K\alpha$ and N $K\alpha$ emission bands and the XPS valence-band spectra for the cubic TaC_xN_{1-x} carbonitrides under consideration provided that a common energy scale is used. It is obvious that, instead of the main maximum *B*, the presence of the very prominent high-energy near-Fermi feature *C* and the low-energy feature *A* is characteristic of all the spectra presented in Fig. 1. In accordance with results of Refs. [21,22], the main maximum *B* of the Ta $L\beta_5$ band in tantalum carbides and nitrides is created by the Ta $5d$ -like states taking part in the formation of the covalent $d_{\text{Ta}}-p_{\text{C(N)}}$ bonds due to Ta $5d$ -C(N) $2p$ -like hybridization, while the near-Fermi feature *C* of the band is created by the Ta $5d$ -like states taking part in forming the metallic component of the chemical bonding. Therefore, an increase of the relative intensity of the near-Fermi feature *C* of the Ta $L\beta_5$ band, when going from tantalum monocarbide to tantalum mononitride through the intermediate tantalum carbonitride, indicates that the metallic component of the chemical bonding increases when going from TaC_{0.98} to TaN_{0.97}. As Fig. 1 reveals, increasing the relative intensity of the near-Fermi feature *C* of the Ta $L\beta_5$ band in the sequence TaC_{0.98} → TaN_{0.97} leads to broadening the band (i.e., to increasing the full width at half-maximum of the band) in the mentioned sequence of compounds.

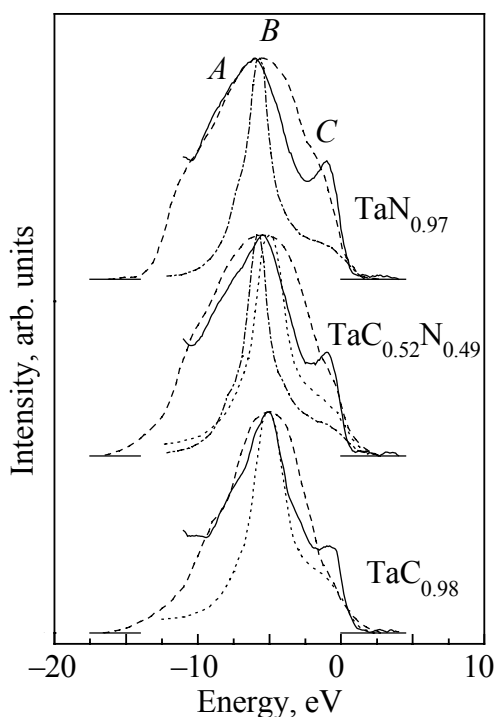


Fig. 1. Comparison on a common energy scale of the X-ray emission Ta $L\beta_5$ (---), N $K\alpha$ (- · - · -), C $K\alpha$ (· · · ·) bands and the XPS valence-band spectra (—) for the cubic tantalum carbonitrides under investigation (zero of energy corresponds to the position of E_F of an ES-2401 spectrometer energy analyzer)

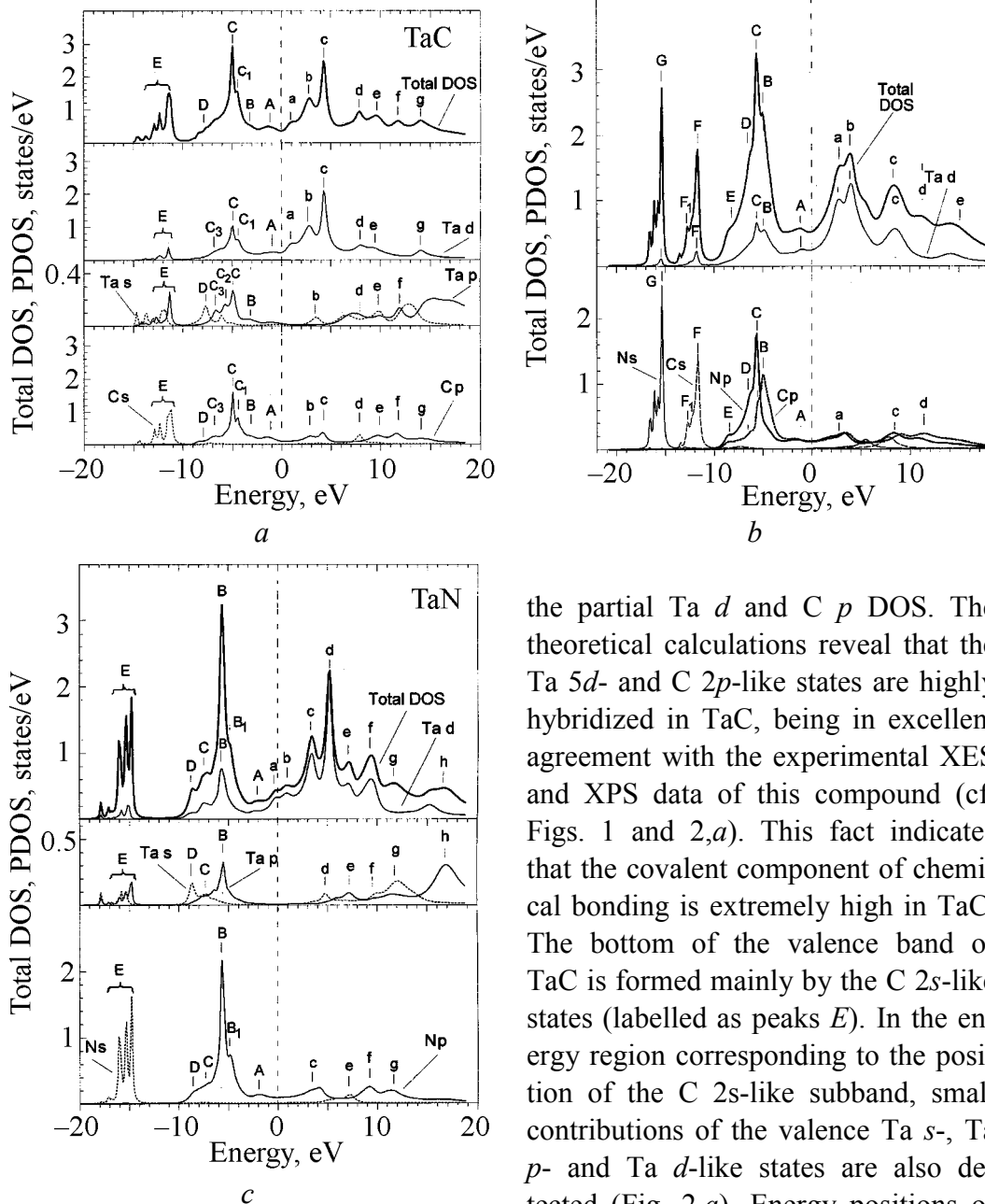
tantalum mononitride. Therefore, the strong Ta $5d$ -C(N) $2p$ -like hybridization is characteristic of the TaC_xN_{1-x} carbonitrides under consideration.

The energy position of the main maximum B of the C $K\alpha$ band remains constant (within accuracy of the experiment) with respect to the Fermi level when going from $TaC_{0.98}$ to $TaC_{0.52}N_{0.49}$, as well as that of the N $K\alpha$ band in the sequence $TaN_{0.97} \rightarrow TaC_{0.52}N_{0.49}$. Additionally, the shape of the C $K\alpha$ (N $K\alpha$) band does not change in the sequence $TaC_{0.98} \rightarrow TaC_{0.52}N_{0.49}$ ($TaN_{0.97} \rightarrow TaC_{0.52}N_{0.49}$). The above facts indicate the absence of the C $2p$ -N $2p$ -hybridization in the cubic TaC_xN_{1-x} system. As seen from Fig. 1, half-widths of the C $K\alpha$ and N $K\alpha$ bands and relative intensities of their near-Fermi features C do not change within experimental errors when carbon atoms are substituted for nitrogen atoms in the cubic TaC_xN_{1-x} system under study.

The above-mentioned experimental results on studies of the electronic structure of cubic tantalum carbonitrides are in a rather good agreement with the theoretical calculations presented in Fig. 2. In Fig. 2,*a*, the main occupied part of the valence band of cubic tantalum monocarbide is formed mainly by contributions of

Since changes of shapes of the XPS valence-band spectra of substoichiometric cubic and hexagonal tantalum carbides resemble changes of those observed for the Ta $L\beta_5$ band [21], we can expect similarity of changes of the XPS valence-band and XES Ta $L\beta_5$ spectra when carbon atoms are substituted for nitrogen atoms in the cubic TaC_xN_{1-x} system. This is observed in fact in the present experiments. As one can see from Fig. 1, similar to that observed for the Ta $L\beta_5$ band, the relative intensity of the near-Fermi feature C of the XPS valence-band spectra and their half-widths increase somewhat when going from $TaC_{0.98}$ to $TaN_{0.97}$. Additionally, energy positions of the main peaks B of the Ta $L\beta_5$ band and the XPS valence-band spectra, coinciding with the position of the main peak B of the C $K\alpha$ band in tantalum monocarbide within accuracy of the experiments, shift by about $(0.7-0.8) \pm 0.2$ eV away from E_F when going from $TaC_{0.98}$ to $TaN_{0.97}$, coinciding with the main peak B of the N $K\alpha$ band in

Fig. 2. Calculated total and partial density of states of cubic TaC (a), TaC_{0.5}N_{0.5} (b) and TaN (c) (zero of energy corresponds to the Fermi energy)



the partial Ta *d* and C *p* DOS. The theoretical calculations reveal that the Ta 5*d*- and C 2*p*-like states are highly hybridized in TaC, being in excellent agreement with the experimental XES and XPS data of this compound (cf. Figs. 1 and 2,*a*). This fact indicates that the covalent component of chemical bonding is extremely high in TaC. The bottom of the valence band of TaC is formed mainly by the C 2*s*-like states (labelled as peaks *E*). In the energy region corresponding to the position of the C 2*s*-like subband, small contributions of the valence Ta *s*-, Ta *p*- and Ta *d*-like states are also detected (Fig. 2,*a*). Energy positions of

the main maxima *C* and of the near-Fermi shoulders *A* of the theoretical partial C *p* and Ta *d* DOS (Fig. 2,*a*) well correspond to the positions of the fine-structure features *B* and *C* of the XES C *K*α and Ta *L*β₅ bands, respectively (see Fig. 1). The energy positions of the maxima *B* (C *p*-like DOS) and *C* (N *p*-like DOS) of the TaC_{0.5}N_{0.5} carbonitride coincide with those of the main maxima *B* of the experimental C *K*α and N *K*α bands of the TaC_{0.52}N_{0.49} compound (cf. Figs. 1 and 2,*b*).

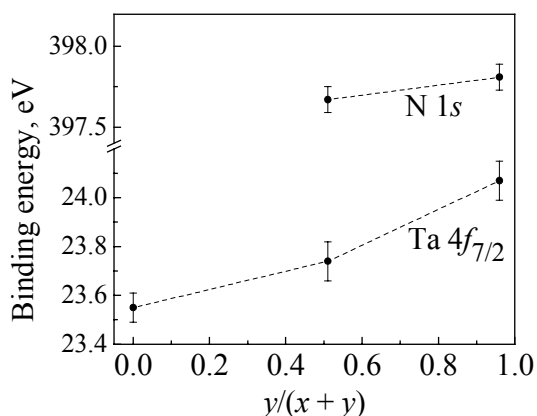


Fig. 3. Dependence of the XPS Ta 4f_{7/2} and N 1s core-level binding energies upon content of carbon and nitrogen atoms in the cubic TaC_xN_{1-x} carbonitrides studied

It should be noted that the theoretical curves of the partial C *p*- and N *p*-like DOS reveal an extremely weak C 2*p*-N 2*p*-hybridization within the main part of the valence band of TaC_{0.5}N_{0.5}, being in excellent agreement with the experimental results for the TaC_{0.52}N_{0.49} compound (see Fig. 1). As Fig. 2,*b* shows, the C 2*s*- and N 2*s*-like states form *F* and *G* subbands on the curves representing the above partial DOS of TaC_{0.5}N_{0.5}. The mentioned subbands are well separated from each other as well as from C 2*p*- and N 2*p*-like bands of the TaC_{0.5}N_{0.5} carbonitride

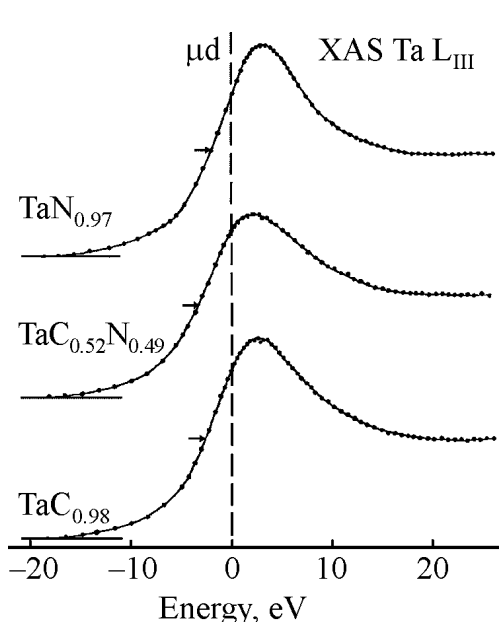


Fig. 4. The X-ray Ta *L*_{III} absorption edges of the cubic TaC_xN_{1-x} carbonitrides under consideration (zero of energy corresponds to the position of *E*_F of an ES-2401 spectrometer energy analyzer)

Furthermore, from the theoretical curves presented in Fig. 2,*c*, it is obvious that the energy positions of the maxima *B* of the N *p*- and Ta *d*-like DOS of TaN correspond to those of the maxima *B* of the experimental N *K*α and Ta *L*β₅ bands of the TaN_{0.97} compound (see Fig. 1). Additionally, similar to the experimental observations (Fig. 1), the main maximum of the valence band formed mainly by contributions of the C(N) 2*p*- and Ta 5*d*-like states shifts in the direction opposite to the position of the Fermi energy when going from TaC to TaN.

(Fig. 2,*b*).

Dependences of the Ta 4*f* and N 1*s* core-level BEs on content of carbon and nitrogen atoms in the TaC_xN_{1-x} system are presented in Fig. 3. An increase of the XPS Ta 4*f* core-level BE in the TaC_{0.98} → TaC_{0.52}N_{0.49} → TaN_{0.97} sequence indicates that the substitution of carbon atoms by nitrogen atoms leads to increasing the positive effective charge of tantalum atoms. Therefore, in the TaC_{0.82} → TaC_{0.05}N_{0.78} sequence the ionic component of chemical bonding increases. It was difficult to evaluate changes of charge states of carbon and nitrogen atoms when going from TaC_{0.98} to TaN_{0.97}. Fig. 3 shows that the XPS N 1*s* core-level BE decreases slightly when going from TaC_{0.97} to TaC_{0.52}N_{0.49}. Nevertheless, as discussed in Refs. [17,18], the XPS N 1*s* core-level spectra

superimpose on the Ta $4p_{3/2}$ spectra in tantalum carbonitrides. Additionally, the XPS C $1s$ core level spectrum in the tantalum carbide and carbonitride under study ($E_{BE} \sim 283$ eV) superimposes on the C $1s$ line of carbon- and hydrogen-containing admixtures ($E_{BE} \sim 285$ eV). The above difficulties do not allow to make precise measurements of the XPS N $1s$ and C $1s$ core-level BEs in the cubic TaC_xN_{1-x} carbonitrides.

The X-ray Ta L_{III} absorption edges of the cubic tantalum carbonitrides studied are presented in Fig. 4. From the above figure, it is obvious that the substitution of carbon atoms by nitrogen atoms in the TaC_xN_{1-x} system does not lead to any changes of shapes of the Ta L_{III} absorption spectra measured in the near-edge region. However, in the sequence $TaC_{0.98} \rightarrow TaC_{0.52}N_{0.49} \rightarrow TaN_{0.97}$ the inflection point of the edges (marked by the arrows in Fig. 4) shifts by about 0.7 eV towards higher energies. The above fact indicates the growth of the positive effective charge of tantalum atoms in the mentioned sequence of compounds. This result confirms the results of XPS Ta $4f$ core-level BE measurements presented in Fig. 3.

5. Conclusions

A rather good agreement of the experimental (XPS, XES and XAS measurements) and theoretical (using the FEFF8 program) results for the electronic structure of the TaC_xN_{1-x} system has been obtained in the present paper. The results indicate that a strong hybridization of the Ta $5d$ - and C(N) $2p$ -like states is characteristic of the TaC_xN_{1-x} compounds studied, while the hybridization of the C $2p$ -like and N $2p$ -like states is absent.

It has been established that the substitution of carbon atoms by nitrogen atoms in the TaC_xN_{1-x} carbonitrides reveals increasing both a half-width of the XPS valence-band spectrum and a relative intensity of the near-Fermi subband created mainly by contributions of the Ta $5d$ -like states. When going from $TaC_{0.98}$ to $TaN_{0.97}$ through the carbonitride of intermediate composition, the energy position of the inflection point of the X-ray Ta L_{III} absorption edge shifts towards higher energies, while the main maximum of the XPS valence-band spectrum shifts in the direction opposite to the position of the Fermi level, E_F . Additionally, in the above sequence of compounds the XPS Ta $4f$ core-level binding energies increase. Comparison on a common energy scale reveals that energy positions of the C $K\alpha$ and N $K\alpha$ bands do not change with respect to E_F when substituting carbon atoms for nitrogen atoms in the TaC_xN_{1-x} carbonitrides.

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