

## Photoemission study of the electronic structure of stoichiometric and substoichiometric TiN and ZrN

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The electronic structure of stoichiometric and substoichiometric titanium nitride (TiN) and zirconium nitride (ZrN) have been studied with ultraviolet and x-ray photoelectron spectroscopy. The valence-band spectrum of stoichiometric TiN is compared with calculations of the density of states. Peak positions and widths agree quite well, whereas photon-energy-dependent intensity variations do not seem to follow the trends expected from the atomic photoionization cross sections. The more tightly bound metal core lines are shifted to higher binding energies by about 1.4 eV in the compounds compared to those in the pure metals. In contrast to earlier investigations of similar compounds, no difference in the binding energies of the metal core lines could be detected as a function of stoichiometry. Discrepancies were found between the experimental results and a coherent-potential-approximation calculation of the effects of substoichiometry in TiN. Neither the strong increase of states at the Fermi level nor the predicted shift of the valence-band peak could be detected. An extra peak around 2-eV binding energy was found in the substoichiometric TiN and ZrN samples and assigned to an occupied defect state. For  $\text{TiN}_{1-x}$  the peak intensity is comparable to that of the peak at the Fermi level, whereas for  $\text{ZrN}_{1-x}$  this peak is broader and less pronounced.

### I. INTRODUCTION

The refractory transition-metal carbides and nitrides exhibit many interesting physical and chemical properties.<sup>1,2</sup> They are all metallic, some having very high electrical conductivities comparable to that of copper, while some are superconductors with transition temperatures of up to 18 K. The extremely high melting points and hardness of these compounds has led to their use as cutting tools, for coatings, and as a high-temperature material. All of these physical properties are related to the electronic structure of the refractory compounds and experimental investigations using techniques such as photoelectron spectroscopy which

probe the electronic density of states are thus of great interest. The importance of the electronic structure, coupled with the fact that the refractory compounds crystallize in the relatively simple rock-salt structure also make them attractive for theoretical investigation.

Interest in the bonding of the refractory compounds has stimulated a number of band-structure calculations during the last few decades. Since the pioneering work by Bilz<sup>3</sup> which used a tight-binding method, many different methods have been applied, the most useful appearing to be the augmented-plane-wave (APW) approach.<sup>4-6</sup> An excellent summary of the band-structure calculations carried out before 1977 has been given in a review article by Calais.<sup>7</sup> All of the band-structure

calculations show that the valence-band region ( $\sim 5$  eV below the Fermi energy) is built up from metal  $d$  states which are strongly hybridized with the carbon or nitrogen  $2p$  states, whereas the nonmetal  $2s$  states are well separated from the valence band at about 11 eV below the Fermi energy for the carbides and around 15 eV for the nitrides. Many experimental studies using different techniques such as x-ray and ultraviolet photoemission spectroscopy<sup>8-15</sup> (XPS and UPS), soft x-ray emission spectroscopy,<sup>16-18</sup> and optical spectroscopy<sup>19</sup> have found this picture to be at least qualitatively correct. Recent angle-resolved photoemission studies carried out on TiC (Ref. 20) and TiN (Refs. 21 and 22) single crystals were able to give a more detailed answer about the location of some critical points in the band structure and about the energy-band dispersion along some of the symmetry lines in the crystal.

Another remarkable property of the refractory compounds is their tendency to form nonstoichiometrically; indeed it is virtually impossible to produce some of them as single phase with their nominal formula. They can be prepared so that up to 40% of the nonmetal sites in the crystal are empty while the metal sites are fully occupied. It is known that many of the physical properties of these compounds, e.g., superconductivity, specific heat, and paramagnetic susceptibility, are strongly effected by the vacancies.<sup>1,2</sup> Different theoretical approaches have been used recently in order to arrive at a better understanding of the electronic structure of the vacancies in refractory compounds.<sup>23-29</sup> So far the vacancy problem cannot be solved exactly and appropriate approximations have to be made. Klima<sup>24,25</sup> has used the coherent-potential approximation (CPA) in a linear combination of atomic orbitals basis to calculate the partial and total density of states (DOS) of  $\text{TiC}_{1-x}$  and  $\text{TiN}_{1-x}$  with  $0 \leq x \leq 0.4$ . The same method has also been used by Klein *et al.*<sup>26</sup> to calculate the electronic density of states for  $\text{NbC}_{1-x}$ ,  $\text{TaC}_{1-x}$ , and  $\text{HfC}_{1-x}$  with  $0 \leq x \leq 0.3$ .

The results of both CPA calculations verify simple arguments based on the rigid-band model. A blind application of this model, however, leads to an unrealistic picture of the electronic effect of the vacancy in which only the Fermi energy is altered. Removing, for instance, a carbon atom from the system leaves one extra electron behind because roughly five states are taken away but only four electrons are removed. The electron is transferred back to the metal atom and fills up empty  $d$  states

above the position of the Fermi level in the stoichiometric material.

Quite a different way of investigating the vacancy problem has been developed by Schwarz and Rösch<sup>27</sup> for NbC and by Ries and Winter<sup>28</sup> for NbC and VN. They have performed cluster calculations in the multiple-scattering self-consistent-field (SCF)  $X\alpha$  approximation. Schwarz and Rösch used a cluster size of 27 atoms, whereas Ries and Winter used a cluster of 203 atoms in 14 shells surrounding a central carbon atom or a vacancy. In both cases the results for the perfect cluster are in good agreement with self-consistent APW calculations by Schwarz.<sup>30</sup> The effect of a vacancy on the SCF  $X\alpha$  electronic density of states<sup>27,28</sup> is quite different from that obtained with the CPA method of Klima.<sup>24,25</sup> On the vacancy site a narrow peak with a half-width of  $\sim 0.27$  eV appears in the DOS. This peak, which is associated with states which have mainly  $s$ -like symmetry, is located in the valley between the Fermi level and the strong valence-band peak which consists of metal  $d$  and nonmetal  $p$  states. To fill up these states, the vacancy attracts a charge of roughly 0.8 electrons from the six adjacent metal atoms. From these cluster calculations, the strong suppression of the superconducting transition temperature was found to be due only partly to disappearance of the soft modes with increasing vacancy concentration. Changes in the electronic part of the electron-phonon coupling have also to be taken into account. As has been outlined above, the results given for the same class of materials obtained with different theoretical model calculations are very contradictory.

Only a few experimental investigations of the vacancy problem in refractory transition-metal compounds have been carried out.<sup>11,31-34</sup> The results of these are also contradictory. One of the most direct experimental methods to test the different predictions of the various model calculations is photoelectron spectroscopy. This paper reports the experimental results of a photoemission (XPS and UPS) investigation of well-characterized stoichiometric and substoichiometric samples of TiN and ZrN and compares them with theoretical predictions.

In the following section we give a short description of the method of sample preparation and of the experimental procedure. Results obtained for the stoichiometric samples are discussed in Sec. III A and effects related to the substoichiometry of the samples are presented in Sec. III B.

## II. EXPERIMENTAL

### A. Sample preparation

Single crystals of nearly stoichiometric TiN and ZrN were made using the chemical vapor deposition (CVD) method. The starting materials used were liquid  $\text{TiCl}_4$  and solid  $\text{ZrCl}_4$  for the growth of TiN and ZrN, respectively, with a mixture of equal amounts of nitrogen and hydrogen gas. A constant gas stream (2 l/h) transported the metal tetrachlorides to an induction-heated molybdenum tube where at temperatures between 1400 and 1500°C the metal nitrides, as the only solid reaction products, start to grow. In order to obtain a good growth rate, the  $\text{ZrCl}_4$  powder had to be heated to about 200°C, whereas the room-temperature vapor pressure of  $\text{TiCl}_4$  of about 10 Torr is large enough for good growing conditions. Compared to zone-melted single crystals, those prepared by the CVD method have well-structured growth areas and fewer defects.

Substoichiometric single crystals of TiN and ZrN were prepared by a modified traveling-solvent method. The starting materials for this method were high-purity metal rods with a diameter of about 12 mm and a length of 20 cm. The rods were heated with an induction coil under a pressure of 19.2-bar nitrogen. The formation of this nitride, which starts at the surface, raises the melting point considerably (e.g., Ti: 1668°C to TiN: 2950°C). By carefully increasing the temperature, it is possible to keep the surface region solid while the inner part of the rod is liquid and able to take up the nitrogen which diffuses through the surface. Further details of the preparation methods are described elsewhere.<sup>35</sup>

The samples were characterized by a chemical analysis of nitrogen, oxygen, and carbon. The nitrogen analysis was made with a vacuum hot-extraction method as well as with the Dumas

method. Values of the chemical analysis are given in Table I. The determination of the lattice constants and the structure of the samples was made with x-ray diffraction using monochromated  $\text{Cu K}\alpha_1$  radiation. No segregation of the transition metal or evidence of a mixture of different phases could be detected. The total vacancy concentration was determined by measuring the mass density. A comparison of these results with the data obtained from an x-ray density measurement shows that more than 99% of the metal lattice sites are occupied even in the substoichiometric samples, and nearly all vacancies are on nitrogen sites. It is known that the superconducting transition temperature of the refractory compounds is strongly affected by the stoichiometry and homogeneity of the crystals. To demonstrate the high quality of the crystals grown with the methods described above, we also list in Table I the superconducting transition temperatures  $T_c$  measured with an induction bridge. The width  $\Delta T_c$ , which gives an indication of the homogeneity of the samples, was determined using the conventional method of measuring the temperature difference between the 10% and 90% points of the step in the inductance curve.

### B. Experimental procedure

The photoelectron spectra were measured using two different photoelectron spectrometers. The UPS experiments were carried out in a Vacuum Generators ADES 400 angle-resolved spectrometer. The photoemission spectra were taken using Ne I ( $h\nu=16.85$  eV), He I (21.22 eV), and the He II (40.82 eV) photons from a differentially pumped discharge lamp. The spectrometer was operated with an energy resolution of 0.3 eV. The samples studied were polycrystalline and no angular dependence of the photoemission spectra could be detect-

TABLE I. Chemical analysis, lattice constant  $a$ , superconducting transition temperature  $T_c$ , width of the superconducting transition region  $\Delta T_c$ , and the work function  $\phi$  for the samples studied. Numbers given in parentheses represent the estimated uncertainty in the last figure.

Sample	Chemical analysis	$a$ (Å)	$T_c$ (K)	$\Delta T_c$ (K)	$\phi$ (eV)
TiN <sub>0.99</sub>	TiN <sub>0.994</sub> C <sub>0.0025</sub> O <sub>0.0037</sub>	4.2366(9)	6.09	0.04	3.79(5)
TiN <sub>0.80</sub>	TiN <sub>0.802</sub> C <sub>0.001</sub> O <sub>0.0063</sub>	4.2301(6)	< 0.02		3.66(5)
ZrN <sub>0.97</sub>	ZrN <sub>0.97</sub> C <sub>0.002</sub> O <sub>0.0007</sub>	4.5722(5)	10.54	0.02	3.58(5)
ZrN <sub>0.82</sub>	ZrN <sub>0.82</sub> C <sub>0.007</sub> O <sub>0.0048</sub>	4.5748(6)	2.45	0.25	3.38(5)

ed by measuring at different emission angles, so all UPS spectra presented in this paper are measured under normal emission with an acceptance cone of  $3^\circ$ . The base pressure in the vacuum chamber was  $2 \times 10^{-10}$  Torr. The XPS spectra were taken with a modified Hewlett Packard 5950A ESCA spectrometer using a monochromatized Al  $K\alpha$  source ( $h\nu = 1486.7$  eV) for excitation. The experimentally determined resolution function of the spectrometer is a Gaussian with a full width at half maximum of 0.6 eV.<sup>36</sup> The vacuum was  $3 \times 10^{-10}$  Torr in the sample-preparation chamber and  $2 \times 10^{-11}$  Torr in the measuring chamber.

Prior to the measurements the surfaces of the samples were cleaned *in situ* by filing with a diamond file. This very simple but effective method has been used successfully in investigations of other refractory transition-metal compounds<sup>10,11</sup> and does not seem to produce undesirable changes in the surface composition. Clean surfaces cannot be prepared by argon-ion sputtering because preferential sputtering of the nonmetal atom is a strong effect in this class of materials.<sup>10,20</sup> High-temperature *in situ* flashings have been used previously to clean single-crystal surfaces of some transition-metal carbides and nitrides.<sup>12,13,15,21,22</sup> This procedure is not appropriate in our study because we are not only interested in the stoichiometric compounds but also in the electronic properties of substoichiometric samples. It has been shown recently by Weaver *et al.*<sup>20</sup> and Oshima *et al.*<sup>37</sup> that stoichiometric surfaces can be prepared by high-temperature flashing of highly substoichiometric samples which have been Ar-sputtered. After our procedure of diamond filing no surface contamination from oxygen or carbon could be detected by measuring the core lines of these elements with XPS.

### III. RESULTS AND DISCUSSION

#### A. Stoichiometric samples

A comparison of the experimental electron distribution curves (EDC's) obtained from a photoemission experiment with the electronic DOS may be misleading if one focuses only on the results obtained with a single photon energy. Spurious effects arising from enhanced surface sensitivity, from the energy dependence of the photoionization cross section or from final-state effects can be separated out by carrying out the measurements for different values of the photon energy.

The valence-band EDC's of TiN obtained with different photon energies are shown in Fig. 1. The background arising from secondary electrons has been subtracted from these curves so that the intensity modulations due to the change in photon energy can be discussed. In the lower part of Fig. 1 we show the valence-band region of the partial DOS calculation by Neckel *et al.*<sup>5</sup> The N 2s DOS which occurs at a binding energy of about 16 eV is not shown here but will be discussed later. It can be seen that there is good agreement between the calculated DOS and the experimental results for the peak at the Fermi energy, the valley around 2.5 eV, and the strong valence-band peak around 5.5 eV. The two shoulders in the calculated valence band at  $\sim 3.5$  and 6.5 eV also appear in the spectra. As the photon energy varies, the position of these shoulders remains fixed and the overall shape of the peak near the Fermi energy is unaffected. This behavior suggests that final-state effects are less important for these features. Intensity variations, on the other hand, do occur. There is a loss of intensity on the low-binding-energy side of the main valence-band peak as the photon energy increases and a gain on the high-binding-energy side. These effects give the appearance of a shift of the center of gravity of the main peak to higher binding energies. Although final-state effects could play a role, it is also possible that the intensity variations are caused by the energy dependence of the N 2p and Ti 3d differential photoionization

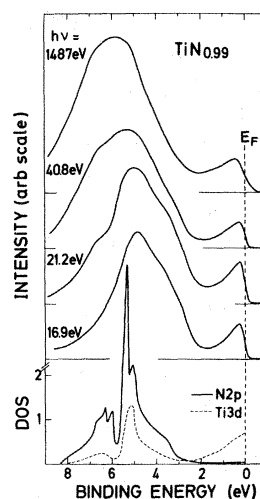


FIG. 1. Valence-band photoemission spectra of  $\text{TiN}_{0.99}$  obtained with different photon energies. The background arising from secondary electrons has been subtracted. Partial density of states from Ref. 5 are shown in the lower part of the figure.

cross sections. The observed trend of an increase in the intensity arising from  $d$  states relative to that arising from  $p$  states as  $h\nu$  becomes larger, agrees in principle with theory.<sup>38</sup> The changes seen, however, are much weaker, than those calculated from the partial DOS using differential cross sections  $\sigma$  and asymmetry parameters extrapolated from the calculations by Goldberg *et al.*<sup>38</sup> In particular a gain in intensity of the peak near the Fermi energy relative to the main valence-band peak by a factor of  $\sim 1.5$  is expected as the photon energy increases from 21.2 to 1487 eV. The spectra, however, show no significant change in relative intensities. It is clear that while such a simple model may explain trends in the data it is unable to completely describe the observed behavior.

The ratio of the intensity of the 16.7-eV (N 2s) peak to that of the 5-eV valence-band peak does not have the energy dependence expected from the calculation. The ratio expected from a superposition of the partial DOS weighted by the atomic photoabsorption cross sections is similar for  $h\nu=40.8$  and 1487 eV. The experiment, however, shows the N 2s peak to have roughly the same intensity as the peak near the Fermi energy for  $h\nu=1487$  eV but to have no observable intensity for  $h\nu=40.8$  eV. This discrepancy is difficult to understand because the peak near 16 eV in the calculated DOS is very atomiclike, having only a few percent of Ti 3d states mixed with the N 2s. Our

results for TiN are in general agreement with the previous work of Johansson *et al.*<sup>15</sup> These authors found that the N 2s peak in the spectrum grew with increasing photon energy and had an intensity of roughly one-half that of the main valence-band peak for  $h\nu=190$  eV (the maximum photon energy used).

Photoemission spectra of the isoelectronic substance ZrN show the same features as TiN. Besides a shift in the maximum of the valence band of about 0.5 eV towards the Fermi energy, the valence-band peak is sharper and the XPS-band width is reduced by at least 1.5 eV. The narrowing and sharpening of the valence band which we see on going from TiN to ZrN has also been observed by Ihara *et al.*<sup>8,9</sup> in the XPS spectra of TiC and ZrC.

Ihara *et al.*<sup>39</sup> suggested that the differences between the valence-band widths of the two carbides is the result of stronger localization of the metal  $d$  electrons in ZrC than in TiC. Stronger localization suggests that the bonds become more ionic, i.e., there is a greater charge transfer from the metal to nonmetal atom. A charge transfer such as this can be investigated by examining the core-level binding energies in the compound and comparing them with those in the pure material.<sup>40</sup> The binding energies of several core lines from TiN, ZrN, Ti, and Zr have been determined and are listed in Table II. The energy shifts  $\Delta E_B$  between the binding ener-

TABLE II. Core-level binding energies for Ti, TiN, Zr, and ZrN from XPS measurements. The differences in binding energies  $\Delta E_B$  between the compound and the element are given in the third column. Because the spin-orbit splitting is not resolved for Ti 3p and Zr 4p, the position of these core levels was taken as the midpoint at half maximum.

Core level	Binding energies (eV)		$\Delta E_B$ (eV)
	Ti	TiN	
Ti 3p	33.2	35.0	1.8
Ti 2p <sub>3/2</sub>	453.6	455.1	1.5
Ti 2p <sub>1/2</sub>	459.7	461.0	1.4
N 1s		397.4	
N 2s		16.7	
	Zr	ZrN	
Zr 4p	27.8	29.7	1.9
Zr 3d <sub>5/2</sub>	178.5	179.8	1.3
Zr 3d <sub>3/2</sub>	181.0	182.2	1.2
Zr 3p <sub>3/2</sub>	329.3	330.8	1.5
Zr 3p <sub>1/2</sub>	342.8	344.3	1.5
N 1s		397.5	
N 2s		16.7	

gies in the element and that in the compound are the same, being equal to 1.4 eV within the experimental uncertainty of 0.1 eV for the deeper core levels in ZrN and TiN. Under the assumption of equal relaxation energies this result means that the charge transfer is roughly the same for both materials. A shift of 1.5 eV has been seen for Ti  $2p_{3/2}$  and previously<sup>31</sup> for TiN. The relationship between core-level shifts and charge transfer is also discussed by Sheludchenko *et al.*<sup>41</sup> for compounds of Ti and V. The greater difference between the shifts observed for the weaker bound Ti  $3p$  and Zr  $4p$  levels can be explained by a stronger interaction of the  $4p$  level with the valence electrons and should not be used to discuss the problem of charge transfer.

### B. The effect of nonstoichiometry

Spectra from the valence-band region of  $\text{TiN}_x$  are compared in Fig. 2 with the total DOS calculated with the CPA method by Klima.<sup>25</sup> The effect of nonstoichiometry is seen in the calculation as an increase in the DOS around the Fermi energy and a decrease in the DOS near the rising edge of the valence band at a binding energy of about 4 eV. The spectra for the substoichiometric sample

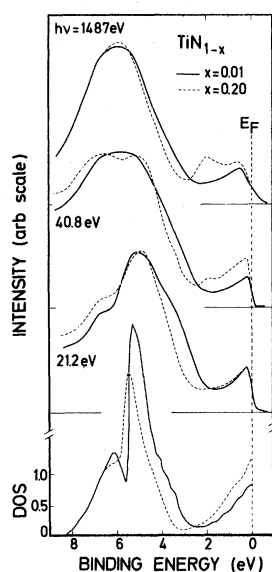


FIG. 2. Valence-band photoemission spectra of  $\text{TiN}_{0.99}$  (solid line) and  $\text{TiN}_{0.8}$  (dashed line) obtained with photon energies of  $h\nu=1487$ , 40.8, and 21.2 eV. The lower part of the figure shows the total density of states for stoichiometric TiN (solid line) and substoichiometric  $\text{TiN}_{0.8}$  (dashed line) from Ref. 25.

exhibit a strong intensity variation in the region near the Fermi energy. For  $h\nu=21.2$  eV both spectra are the same within 2 eV of the Fermi energy but at  $h\nu=40.8$  eV, the intensity in this region is 50% greater for the substoichiometric sample than for TiN. In addition a small peak appears near 2 eV in the spectrum of  $\text{TiN}_{0.8}$ . When the photon energy is increased to 1487 eV, this small peak grows to become stronger than that at the Fermi energy, the latter having roughly the same strength for TiN as for  $\text{TiN}_{0.8}$ . The intensity in the region around 3–4 eV is lower for the substoichiometric sample for all photon energies, the maximum difference occurring at  $h\nu=21.2$  eV.

At a first glance, these overall effects in the experimental spectra are consistent with the calculated changes in the DOS for the substoichiometric sample. In particular the increase in the DOS near the Fermi energy reflects the behavior seen in the experiment. The most important effect in the calculation is the upward shift in the Fermi energy because every missing nitrogen atom contributes an electron to the Ti  $3d$  states. For comparison with experiment the DOS are aligned at the Fermi energy. The intensity difference around 3–4 eV is seen in both experiment and theory but the peak seen in the experiment near 2 eV is not present in the CPA calculation.

The same trends as described above for the valence-band spectra of substoichiometric TiN are also found for the electronically equivalent system ZrN. Valence-band spectra of  $\text{ZrN}_{1-x}$  are shown in Fig. 3 for photon energies of 21.2, 40.8, and 1487 eV. The intensity around the Fermi level in-

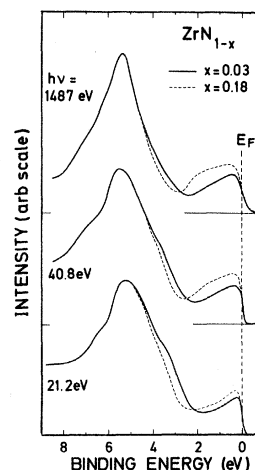


FIG. 3. Valence-band photoemission spectra of  $\text{ZrN}_{0.97}$  (solid line) and  $\text{ZrN}_{0.82}$  (dashed line) obtained with photon energies of  $h\nu=1487$ , 40.8, and 21.2 eV.

creases with increasing photon energy for the substoichiometric sample and the decrease in intensity at the valence-band edge around 3.5 eV is strongest for the lowest photon energy. The appearance of a second peak in the region below the Fermi level is not as pronounced as it was for the substoichiometric TiN sample but nevertheless a broad structure is present near 2 eV in the  $h\nu=1487$  eV spectrum.

Summarizing our results for substoichiometric TiN, we come to the conclusion that the CPA calculations of Klima<sup>25</sup> exhibit the correct trends in the data but do not show the peak near 2 eV. All of the spectra show the intensity decrease near 3 eV which is predicted for the substoichiometric sample. This effect was also seen for ZrN and appears to have its origin in a reduction of N  $2p$ -derived states in this region. An experimental verification of this conclusion is shown in Fig. 4 where the addition of  $10^3$  L of  $N_2$  to the surface of  $ZrN_{0.82}$  is seen to alter the spectrum so that it looks more like that for the nearly stoichiometric sample. The CPA calculation<sup>25</sup> indicates that the DOS at the Fermi energy should increase by a factor of 1.6 on going from TiN to  $TiN_{0.8}$ . XPS spectra yield the most reliable comparison for this kind of effect because intensity normalization can be made at core lines and surface effects are de-emphasized. The experimental data shown at the top of Fig. 2 show a smaller increase by a factor of 1.2 when the spectra are normalized to the Ti  $3p$  core line.

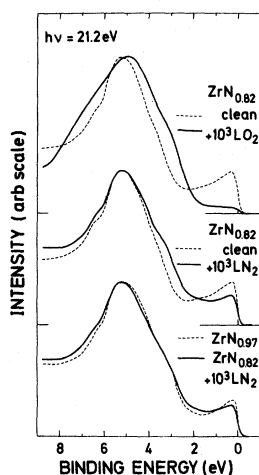


FIG. 4. Effect of adsorption of  $10^3$  L (Langmuir) of oxygen (upper part) and of  $10^3$  L of nitrogen (middle part) on the valence-band photoemission spectra of  $ZrN_{0.82}$ . In the lower part of the figure the spectrum of  $ZrN_{0.82}$  with  $10^3$  L nitrogen is compared to the spectrum of the nearly stoichiometric  $ZrN_{0.97}$ .

The appearance of a peak in the dip between the strong valence-band peak and the conduction band for the substoichiometric samples is not expected from the calculations.<sup>25</sup> Before concluding that this peak corresponds to an occupied defect state, we must rule out other possibilities, namely that surface segregation of the metal atom occurs, or that substoichiometric samples adsorb oxygen at the vacancy sites. Surface segregation of Ti or Zr atoms could give rise to extra emission from the pure-metal  $d$  states which have strong peaks near this binding energy.<sup>42</sup> Careful analysis of the core-line spectra, however, has failed to reveal the presence of pure-metal-derived features which would be expected at binding energies which are 1.4 eV smaller than the Ti or Zr core lines in TiN and ZrN (see Table II). The additional emission at 2 eV may not be attributed to some slight oxidation of the substoichiometric sample for the following reasons. After cleaning of the sample, no trace of oxygen could be found by monitoring the O  $1s$  signal. In addition, exposure of the sample to oxygen considerably reduced the intensity of the spectrum in the region in question, and broadened the valence band as illustrated in the top part of Fig. 4.

Assignment of the peak at 2 eV binding energy to a vacancy state is possible because removal of a nitrogen atom has the effect of adding an extra electron to the conduction band. At least some of these electrons may be bound at the vacancy with a binding energy of 2 eV. An extra peak has also been found in an XPS investigation of NbC,<sup>11</sup> a compound which has a similar electronic structure to TiN and ZrN. The peak, which appeared in the dip between the valence band and the Fermi energy in spectra of substoichiometric NbC, occurs at roughly the same energy as a localized vacancy state predicted by cluster calculations.<sup>27,28</sup> According to the results of Winter and Ries<sup>28</sup> the vacancy state should have mainly  $s$  symmetry but there is also a smaller  $d$  contribution from the six neighboring metal atoms.

The question as to whether the symmetry of the vacancy state is  $s$ - or  $p$ -like as suggested by Schwarz and Rösch<sup>27</sup> for NbC cannot be answered by our experiment. We have found a resonant enhancement of the emission at the Fermi level using a synchrotron radiation source. Consequently a direct comparison of the intensities of the vacancy and the emission at the Fermi level with the energy dependence of the atomic cross sections may be misleading.

The core-level spectra were also compared with those for the stoichiometric compounds. For both substoichiometric  $\text{TiN}_{1-x}$  and  $\text{ZrN}_{1-x}$  no shifts were seen in the core-line binding energies relative to those of TiN and ZrN. These results are in contrast to those of an earlier XPS investigation of  $\text{TiC}_{1-x}$  by Ramquist *et al.*<sup>32</sup> These authors found that the  $\text{Ti } 2p_{3/2}$  peak shifted to lower binding energies by 0.6 eV when the carbon content decreased to  $1-x=0.6$ , whereas the  $\text{C } 1s$  energy was independent of  $x$ . It is possible that the different behavior seen by Ramquist *et al.* is related to the different methods of sample preparation. It is known that the hot-pressing method produces many more vacancies on the metal sublattice compared to the CVD and traveling-solvent methods used to prepare the samples for this investigation. Compared to our spectra the linewidth of their  $\text{Ti } 2p_{3/2}$  peak is much broader and no distinct loss spectra are seen; these are strong indications of inhomogeneous Ti distribution. It should be noted that the spectra given by Ramquist *et al.*<sup>32</sup> show a second  $\text{C } 1s$  peak originating from contamination by hydrocarbons which is three times stronger than the  $\text{C } 1s$  peak coming from the TiC.

#### IV. CONCLUSIONS

Valence-band spectra of stoichiometric TiN can be explained with a partial DOS obtained with the APW method. The intensity variation of the  $\text{N } 2s$  peak, however, is stronger than expected from the atomic-cross-section behavior. For both ZrN and TiN, the metal core levels shifted by the same amount from their positions in pure Zr and Ti indicating similar charge transfer in the two compounds.

For the substoichiometric compounds we saw a change in the shape of the top of the valence band and an occupied defect state at a binding energy of about 2 eV. This state is another example of experimentally determined vacancy states in refractory compounds. Calculations currently in progress by Pecheur *et al.*<sup>43</sup> indicate that such vacancy states are common for the whole family of transition-metal carbides and nitrides but that the energy and width of such states depend strongly on the particular compound. In view of this second point it may not be surprising that the vacancy peak detected in  $\text{ZrN}_{1-x}$  is weaker and much broader than that in  $\text{TiN}_{1-x}$ .

There are several possible reasons why this feature has not been seen in previous investigations.<sup>12,13,15,21,22</sup> The first is that many earlier studies have used flash cleaning to prepare surfaces for photoemission measurements but it is now known that this method leads to a stoichiometric surface layer.<sup>20,37</sup> The second reason is that the choice of photon energy is important. In work recently carried out using a synchrotron radiation source we have found a strong resonance in the peak near the Fermi level.<sup>44</sup> Whereas the Ti or Zr  $d$  states are enhanced, the defect state is not and can be "buried" in the background.

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