An electron energy loss and ultraviolet photoemission study of VN\(_x\), NbN\(_x\) and ZrN\(_x\)

William Kent Schubert

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AN ELECTRON ENERGY LOSS AND ULTRAVIOLET PHOTOEMISSION STUDY OF VANADIUM-NITRIDE(X), NiOBium-NITRIDE(X), AND ZIRCONIUM-NITRIDE(X)

Iowa State University

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An electron energy loss and ultraviolet photoemission study of VN$_x$, NbN$_x$, and ZrN$_x$

by

William Kent Schubert

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of the Requirements for the Degree of DOCTOR OF PHILOSOPHY

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LIST OF SYMBOLS AND ABBREVIATIONS

TMNC's  transition metal nitrides and carbides
ELS  electron energy loss spectroscopy
UPS  ultraviolet photoemission spectroscopy
AES  Auger electron spectroscopy
ω  frequency
a₀  cubic lattice parameter (or the Bohr radius in Eq. 27 of Chapter III)
x  nonmetal-to-metal ratio
Tₐ  superconducting transition temperature
EDC  photoelectron energy distribution curve
DOS  density of states
JDOS  joint density of states
Eₚ  Fermi energy
Eₖ  final state energy
ϕ  photoelectric work function energy
ω_p  free electron volume plasma frequency
ε(ω)  complex dielectric function
−Im(1/ε)  volume loss function
−Im(1/ε + 1)  surface loss function
E_p  primary or incident electron energy
I. INTRODUCTION

The transition metal nitrides and carbides (TMNC's) have been of considerable interest for many years due to their unusual combination of physical properties and the technical applications taking advantage of these properties. A brief review of these properties will be given here. More extensive discussions are found in References 1-3.

The most extensively used property of the TMNC's is their great hardness. The carbides in particular are among the hardest materials known, with microhardness values between those of sapphire and diamond (2-4). This hardness has led to widespread use in cutting tools and similar applications. The nitrides, being slightly less hard, have been used less in this type of application. In conjunction with their extreme hardness, the TMNC's generally exhibit a high degree of brittleness at room temperatures (brittle-to-ductile transitions occur at elevated temperatures (2)).

High melting (or decomposition) temperatures are another characteristic of the TMNC's. Again, the carbides are superior to the nitrides with TaC holding the highest mark at 3983°C. TiC, the most frequently studied of the TMNC's, melts at \( \approx 3070°C \). The nitrides generally exhibit somewhat lower decomposition temperatures. In a nitrogen atmosphere, ZrN decomposes at \( \approx 2980°C \), while two other nitrides of interest in the present study, VN and NbN, show decomposition temperatures (\( \approx 2180°C \) and \( \approx 2200°C \) respectively) very similar to the parent transition metal melting temperature.
The crystal chemistry of the TMNC's is fairly complex. However, carbon and nitrogen are typically located in interstitial sites of a transition metal sublattice, and the complex structures can often be built from relatively simple coordination polyhedra. The mononitrides of interest in the present study crystallize in the rocksalt structure with the nitrogen atoms occupying octahedral interstitial sites within a face-centered-cubic transition metal lattice.

As a general rule, the TMNC's are chemically stable at room temperature. Some evidence exists (this will be discussed further in later chapters) that the compounds are weakly unstable with respect to oxygen.

In combination with the above mechanical and chemical properties, the TMNC's generally display metallic electrical, magnetic, and optical properties, typically similar to the transition metals. Many of these parameters are imperfectly known and large differences appear in reported values (2), probably due to their strong dependence on the nonmetal-to-metal ratio, impurity levels, and overall defect structure.

Finally, and of particular importance to this work, many TMNC's exhibit relatively high temperature superconductivity. While the highest demonstrated transition temperature ($T_c$) is $\sim 23$K (for Nb$_3$Ge of the A-15 family), many of the TMNC's compare quite favorably. NbN has shown $T_c$'s up to $\sim 17$K and some NbN based alloys have extended this to nearly 18K. ZrN and VN are also respectable superconductors with maximum $T_c$'s of 10.2K and 9K respectively.

In addition to the properties mentioned above, the defect structure of the TMNC's is one of their most important and yet subtle aspects.
Exact stoichiometry is rare and the materials are often stable over exceptionally wide composition ranges. When large numbers of nonmetal vacancies exist, there is evidence that they are sometimes ordered (5). In fact, there is some evidence that even in some stoichiometric samples there may be a considerable number of vacancies on both metal and nonmetal sublattices (2). This defect structure, whether ordered or unordered, plays an important role in determining the nature of nearly all of the properties discussed above. Even different processing techniques used to fabricate samples of the same composition can result in different defect structures and thus different mechanical, electrical and superconducting properties. These subtle influences of the defect structure and the difficulties in separating them from composition effects have undoubtedly been responsible for much of the confusion found in the literature on the TMNC's.

The TMNC's have been popular subjects for theoretical and experimental investigations due to the unusual combination of properties mentioned above. In particular, the nature of the chemical bonding is of interest. The rocksalt crystal structure is usually identified with ionically bonded compounds. The properties of hardness and brittleness are often found in covalent materials. On the other hand, the high thermal and electrical conductivities suggest the importance of metallic bonding. These seemingly disparate properties have led to some controversy among early theoretical and experimental investigations.

One subject of this controversy was the placement of the nonmetal 2p states and the metal d states with respect to E_F, and the resulting
direction of charge transfer (see Fig. 1). Placement of a large part of the nonmetal 2p states below the Fermi level would emphasize metal-nonmetal bonds and lead to a charge transfer toward the nonmetal atoms. Conversely, placement of the nonmetal 2p states above $E_F$ would tend to emphasize metal-metal bonds and the nonmetal atoms would simply donate electrons into the transition metal d bands. This later picture would result in a band structure very similar to the parent metal.

Depending on the particular property, or combination of properties they were attempting to explain, early investigators lined up on one side or the other of this controversy. Crystal structures and interatomic distances in the monocarbides and nitrides led Rundle (6) to concentrate on the nonmetal-metal bonding contributions and favor charge transfer from metal to nonmetal atoms. Bilz (7) came to essentially the same conclusions and stated that by adjusting the density of states at the Fermi level according to the valence electron concentration (VEC), one could explain the various properties of the TMNC's. Conversely, other workers supported strong metal-metal bonding contributions. Kiessling (8) took this stand based on crystallographic, magnetic and thermodynamic evidence and claimed that the nonmetal atoms donated electrons to the transition metal d bands. Samsonov and Umanskiy (9) and Umanskiy (10), along with Coste and Conte (11) also favored this picture. Dempsey (12) was led to the same conclusions by the metallic resistivities and melting points which he felt were very similar to the transition metals.
Figure 1. Schematic representations of two proposed bonding pictures in the TMNC's. In (a), a large part of the nonmetal (NM) 2p states are filled and there is charge transfer from transition metal (TM) to nonmetal atoms. In (b), the nonmetal 2p states lie above the Fermi level and simply donate charge into the transition metal d bands. The model depicted in (a) is supported by recent APW calculations and is now generally accepted.
Later workers tried to simultaneously account for the contributions of covalent, ionic and metallic bonding, but for a time confusion persisted about the direction of charge transfer. Lye and Logothetis (13) used optical reflectivity data from TiC to adjust the parameters of their semi-empirical tight binding calculation of the energy bands and the density of states. Their results were somewhat intermediate with the bottom of the C 2p bands extending just below the Fermi level. Small nonmetal to metal charge transfer was predicted. At about the same time, Ern and Switendick (14) carried out nonself-consistent augmented plane wave (APW) calculations and obtained very different results predicting metal to nonmetal charge transfer. Conklin and Silversmith (15), also using the APW method, but with different initial configurations for the atomic potentials, found results generally similar to those of Ern and Switendick.

More recent calculations (16-21) have also supported qualitatively the results of Ern and Switendick. Some differences remain in terms of bandwidths and the ordering of particular bands, but it is now certain that in the monocarbides and nitrides the nonmetal 2p states lie a few electron volts below $E_F$, and the metal atoms donate small amounts of electronic charge into the nonmetal atom spheres. The self-consistent APW calculations of Neckel et al. (17) and Schwarz (21) cover a large number of the TMNC's and are a good representative of the more recent calculations. Calais (22) has compared the various band calculations for many of the TMNC's and related compounds and provides a good overall picture of the similarities and differences.
The calculations discussed above apply to the stoichiometric compounds. However, because of the wide range of stability and the concomitant changes in the physical parameters displayed by these materials, it is of considerable interest to examine the effects of an increasing number of nonmetal vacancies on the electronic structure. One obvious and often used approach is the application of the rigid-band model to account for the decreasing number of valence electrons as nonmetal atoms are removed. From this simplistic approach, one can make straightforward predictions about the dependence of the valence bandwidth and the density of states at $E_F$ on the nonmetal concentration.

More sophisticated calculations on $\text{VC}_x$ have been carried out by Zbasnik and Toth (23) and by Neckel et al. (24). Both groups employed the APW-Virtual Crystal Approximation (25) but arrived at rather different results. Assuming randomly distributed vacancies as carbon was removed, Zbasnik and Toth found an elevation (with respect to $E_F$) of the carbon 2s states and the strongly hybridized (C 2p) - (V 3d) states, while the more localized V 3d states showed only a narrowing. Considerable reshaping of the fine structure in the hybridized region was also observed. On the other hand, Neckel et al. found an upward shift of the entire band structure as carbon was removed. Relative separations of the various peaks from $E_F$ changed very little ($\approx 0.1$ eV) and the fine structure remained fairly constant throughout the valence band. Unlike Zbasnik and Toth, Neckel et al. observed a monotonic increase in the density of states at the Fermi level as carbon was removed.
Another recent approach to this problem has been the cluster calculation (26,27). However, this method is best applied to very dilute vacancy concentrations and is perhaps not a good approach to the present situation where large vacancy concentrations are common.

Yet another approach to the vacancy problem in the TMNC's is the coherent potential approximation (CPA). Klima (28) applied this method to TiC$_x$ for $0.6 \leq x \leq 1.0$. The results were quite different from rigid-band expectations. As the carbon content decreased, the partial C 2p DOS also decreased throughout the band and appeared significantly smoother due to increased scattering of electrons on vacant sites. The occupied part of the hybridized Ti 3d plus C 2p valence band was found to widen slightly as carbon was removed (the rigid-band model predicts a narrowing of the occupied valence band). Both models predict that the density of states at the Fermi level should increase as carbon is removed because in the stoichiometric material $E_F$ lies in a minimum of the DOS.

Among TMNC's, TiC is the most extensively studied experimentally. This can be attributed to its recognition as a prototype of the whole class of materials and also the relative ease of fabricating suitable samples. Most of the work has been spectroscopic in nature with x-ray photoemission spectroscopy (XPS) (19,20,29-38), x-ray emission spectroscopy (XES) (39-42), and ultraviolet optical work (13,16,43) being the most prominent techniques.

Considerable disagreement is found among the optical results on TiC (13,16,43). The most recent are those of Lynch et al. (43), which
show good qualitative agreement with the APW calculations of Neckel et al. (17), but detailed interband assignments have not been made. The data of Lye and Logothetis (13) show reasonable agreement with that of Lynch et al. at higher photon energies, but are quite different below 5 eV. The spectra of Alward et al. (16), obtained from an in situ sputter etched sample, reveal more structure than either of the other two studies. The spectra for samples of various compositions evolve in a smooth manner in the work of Lynch et al., lending more credibility to their results. Increased carbon vacancy concentration generally resulted in broadened structures due to loss of symmetry and increased scattering of electrons from vacancies. Carbon related peaks in the optical conductivity weakened as carbon was removed. Straightforward evidence for a rigid-band shift of $E_F$ was not observed. Lynch et al. (43) also calculated the volume and surface electron loss functions (see Chapter III) and found a free-electron-like volume plasmon whose energy reflected the changing valence electron densities in samples of different composition.

The XPS studies have examined the valence band density of states and the core level energies (19,20,29-38). For the most part, qualitative agreement with the calculated DOS of Neckel et al. (17) has been found. Fairly typical of recent XPS work on TiC is that of Johansson et al. (29) where the valence band and core level spectra were examined for samples of various compositions. The Ti 2p$_{3/2}$ binding energy was found to be $\sim$0.9 eV larger in TiC$_{0.97}$ than in Ti metal. The carbon 1s level remains constant in binding energy over this composition range.
No composition related changes were observed in the valence band spectra, but this could be due to the relatively low resolution of the XPS experiment.

Ultraviolet photoemission spectroscopy (UPS) work by Hagström et al. (44,45) showed better resolution of the valence band spectra, however, oxygen contamination caused some problems in interpretation. Again, generally good agreement with the APW calculations was observed and no x-dependences were found, either in terms of shifts or reshaping of the hybridized Ti 3d-C 2p valence band.

Quite recently, more refined experiments have emerged. The angle-resolved UPS measurements on TiC using synchrotron radiation by Weaver et al. (46) represent the first attempts at sorting out the ordering of particular bands. In principle, this type of experiment can map energy band dispersions in high symmetry directions. The results of this work again confirmed the general results of the APW calculations, but indicated that some of the bands (particularly the carbon 2s) actually lie somewhat deeper and are considerably broader than predicted.

While typical of the TMNC's in many ways, TiC is not suitable for the present study because it fails to exhibit superconductivity. To date, the only superconducting TMNC's to be studied spectroscopically are TiN (47) and NbC (48). In both cases, angle-integrated UPS measurements were reported on single samples.

In their TiN measurements, Johansson et al. (47) again found reasonable agreement with the APW calculations (17). As expected theoretically, TiN shows stronger photoemission at the Fermi level than
TiC due to the greater density of localized Ti 3d states. A double peaked valence band with a minimum 2.5 eV below $E_F$, a peak and a shoulder at $-5.3 \pm 0.3$ eV and about $-7.0$ eV respectively, and a hybridized Ti 3d–N 2p bandwidth of approximately 9.0 eV were observed for TiN (47). As with TiC, the nonmetal 2s states were observed deeper than predicted in the APW calculations (17). Photon energy related intensity modulations within the valence band were quite similar in TiC and TiN. The relative intensity of the nonmetal 2s peaks increased with the photon energy reflecting the behavior of the atomic photo-ionization cross sections (49). Within the hybridized portion, the intensity modulations were stronger in TiN than in TiC. This can be partially, but not entirely, explained by the different shapes of the Ti 3d and N 2p partial densities of states (17). (The Ti 3d and C 2p partial densities of states are very similar in shape, in contrast to the situation in TiN.) An understanding of final state roles will probably be required to fully understand these intensity modulations.

The NbC experiments of Weaver and Schmidt (48) are similar in content to the above TiN experiments. Again, a double peaked valence band is observed which resembles closely the calculated DOS (21,50,51). Also, as in the TiC and TiN studies, the nonmetal 2s states were observed to be slightly deeper and broader than theoretically predicted.

Comparison of the above theoretical and experimental studies suggests that the APW band structures and densities of states are at least qualitatively correct, assuming that the angle-integrated photoemission experiments give primarily density of states information. More detailed
comparison of experiment and theory will require mapping of the individual energy bands by further use of angle-resolved UPS measurements.

In addition to the work reviewed above, several recent neutron scattering studies have produced data relevant to the present investigation. Phonon anomalies have been observed in the acoustic branches of the dispersion curves for several transition metals and their compounds (52-58). A one-to-one correspondence exists between the appearance of these anomalies and superconductivity in the materials.

Several rather different theoretical explanations for the phonon anomalies and their correlation to superconductivity have been proposed. These models are of interest to the present study to the extent that they make certain assumptions about the electronic structure. General arguments for screening resonances at phonon wave vectors in the Brillouin zone interior have been proposed by Sinha and Harmon (59) and by Hanke et al. (60). Other groups have suggested that the topology of the electronic density of states near the Fermi level plays an important role in determining the existence and the k-space location of the phonon anomalies (61-67). Their assumptions require a high density of primarily metal d states just below $E_F$ and nonmetal 2p states just above $E_F$.

Of particular interest is the neutron scattering study by Weber et al. (55) on VN$_x$ samples of various compositions. The strength and position of the phonon anomalies appeared to be related to the amount of nitrogen in the sample and thus the superconducting transition
temperature (see Chapter II). Employing the theory of Varma and Weber (65-67), this behavior could be explained by assuming a rigid-band shift of $E_F$ to account for the changing number of valence electrons.

Yet another experimental work giving indirect evidence for possible rigid-band effects is the measurement of the magnetic susceptibility of VN$_x$ $(0.75 \leq x \leq 1.00)$ between 77K and 300K by Ajami and MacCrone (68). A marked increase in $\chi$ with the nitrogen concentration and a nearly linear increase in $\chi$ with temperature were interpreted as consistent with a rigid-band model applied to a double peaked valence band density of states with a high density of (mainly) vanadium d states near $E_F$.

As is apparent from the above discussion, the TMNC's provide fertile ground for investigation of phonon and electronic properties and their relation to superconductivity. Considerable work has already been done on the class of materials, but most involves nonsuperconducting members of the group. Several neutron scattering studies of superconducting TMNC's have been carried out, but spectroscopic investigations of the electronic structure have been limited to TiN and NbC.

This thesis describes an investigation of the electronic structure of the superconducting mononitrides of vanadium, niobium and zirconium using reflection electron energy loss spectroscopy (ELS) and angle-integrated ultraviolet photoemission spectroscopy. An attempt has been made to study the compositional dependences of the electronic structure. Our work is believed to be the first application of ELS to any of the transition metal nitrides or carbides and the first use of UPS to study VN, NbN and ZrN. The following chapters will provide
further background on superconductivity in the three compounds and on
the theoretical aspects of ELS and UPS as they are applied in this
study. Next, the experimental procedures for fabricating, characterizing
and studying the samples will be discussed in detail and the basic
aspects of the ultrahigh vacuum surface analysis chamber will be
presented. Finally, the experimental results will be presented and
discussed for the three compounds in light of the previous (related)
work reviewed above.
II. MATERIALS

A. Phase Relationships

The mononitrides of V, Nb, and Zr of interest in the present study all exist in the B1 (rocksalt) crystal structure (2,69-75) shown in Fig. 2. The nitrogen atoms occupy octahedral interstitial sites within a face-centered cubic (fcc) transition metal atom sublattice.

Although a complete phase diagram is not available for the vanadium-nitrogen system, it has been fairly well-investigated (2,3). Initially, nitrogen is incorporated into the body centered cubic (bcc) vanadium lattice in solid solution, up to a composition of about VN$_{0.15}$. Hexagonal, or β-phase VN is present as a single phase from about VN$_{0.35}$ to VN$_{0.49}$ (69,70). Then from about VN$_{0.49}$ to VN$_{0.70}$ a two phase region is observed which consists of the β-phase and the mononitride δ-phase. Finally, the B1 crystal structure δ-phase exists as a single phase from VN$_{0.71}$ to VN$_{1.00}$ (69). Over this wide stability range for δ-VN, the lattice parameter increases almost linearly from $a_0 = 4.0662$ Å for VN$_{0.72}$ to 4.1398 Å for VN$_{1.00}$ (69). This behavior of the lattice constant is shown in Fig. 3. The reaction of V metal in N$_2$ requires reaction temperatures above 1200°C (76).

VN$_x$ reportedly decomposes at ~2180°C under one atmosphere of nitrogen pressure (2), although considerable nitrogen is lost at lower temperatures when heated under vacuum.

The phase diagram for NbN$_x$ (72,73) is much less accommodating for the production of the desired δ-phase (see Fig. 4). Several nonsuperconducting, interrelated phases exist in the same composition range,
ROCKSALT (B1) CRYSTAL STRUCTURE

● TRANSITION METAL ATOMS
X NITROGEN ATOMS

Figure 2. The rocksalt (B1) crystal structure found in VN\textsubscript{x}, NbN\textsubscript{x} and ZrN\textsubscript{x}. The nitrogen atoms fill octahedral interstitial sites within an fcc transition metal atom sublattice.
Figure 3. The dependence of the lattice constant $a_0$ on the nitrogen-to-vanadium atomic ratio ($x$) for $\delta$-VN (data from Ref. 69)
Figure 4. Proposed phase diagrams for the Nb-N system. (The lower diagram is from Ref. 72 while the upper diagram is a modification by Ref. 73.)
complicating the fabrication of single phase samples. \(\beta\)-NbN is the hexagonal crystal structure equivalent to \(\beta\)-VN discussed earlier. 

\(\gamma\)-NbN is a tetragonal distortion of the rocksalt structure found in \(\delta\)-NbN. \(\epsilon\)-NbN is of hexagonal crystal structure, and forms at the same compositions but at lower reaction temperatures. The \(\delta'\)-NbN also seen in Fig. 4 is apparently a metastable phase that occurs in the \(\delta \rightarrow \epsilon\) transition (73). Apparently, nitriding temperatures above 1300°C are required to produce \(\delta\)-NbN, and the stable composition range appears to be about \(\text{NbN}_{0.86}\) to \(\text{NbN}_{1.062}\) (72,73). The nitrogen rich samples are prepared at very high nitrogen pressures (\(\sim 240\) Atm).

Over the stable composition range for the \(\delta\)-phase, the lattice constant displays rather unusual behavior (see Fig. 5). In nitrogen deficient samples, \(a_0\) increases almost linearly with \(x\), much as in \(\text{VN}_x\), but by a much smaller percentage. The lattice constant reaches a maximum near stoichiometry and then decreases as more nitrogen is forced into the lattice (77).

\(\text{NbN}_x\) decomposes at about 2200°C under one atmosphere of nitrogen pressure (2), but loses considerable nitrogen at lower temperatures when heated under vacuum.

The phase diagram for \(\text{ZrN}_x\) is shown in Fig. 6 (from Ref. 74). The exact phase boundaries are not well-established. The \(\text{ZrN}_x\) system differs from \(\text{VN}_x\) and \(\text{NbN}_x\) in that only one intermediate phase is known, forming in the rocksalt structure. This is similar to \(\text{TiN}_x\) (2), another compound where the parent transition metal is hexagonal rather than cubic (as V and Nb). Nitrogen initially enters the hexagonal
Figure 5. The dependence of the lattice parameter ($a_0$) on the $N/Nb$ atomic ratio ($x$) for $\delta$-NbN (data from Ref. 77)
Figure 6. Proposed phase diagram for the Zr-N system (from Ref. 74)
α-Zr lattice in solid solution, up to a concentration of just over 20 atomic percent. Then, as the x value increases further, (B1) ZrN\textsubscript{x} begins to form. The rocksalt structure exists as a single phase over a broad range from about 36 atomic percent nitrogen to the stoichiometric compound. Preparation by nitriding Zr in N\textsubscript{2} allows only compositions where x ≤ 1.0 (2). Apparently ZrN can be formed at much lower reaction temperatures than either δ-VN or δ-NbN.

The variation of the lattice constant for ZrN\textsubscript{x} is unusual and unexplained. At substoichiometric compositions, the lattice expands slightly as nitrogen is removed (78–80), as shown in Fig. 7. The percentage change in a\textsubscript{0} is very small compared to that in the VN\textsubscript{x} system.

ZrN reportedly decomposes at about 2980°C when under one atmosphere of nitrogen (2), although it loses considerable nitrogen at lower temperatures when heated under vacuum.

B. Superconductivity in VN\textsubscript{x}, NbN\textsubscript{x} and ZrN\textsubscript{x}

As mentioned in Chapter I, VN\textsubscript{x}, NbN\textsubscript{x} and ZrN\textsubscript{x} are members of an interesting class of superconducting materials. NbN has one of the highest T\textsubscript{c}'s known (~17K) while VN and ZrN are lower temperature superconductors (~9K and 10.2K respectively).

It has long been known that in the transition metal nitrides and carbides, the superconducting transition temperature demonstrates a strong dependence on the nonmetal-to-metal ratio (x). This led to contradictory early reports for T\textsubscript{c}'s in some of these compounds. Röegner (81) made important contributions in clarifying this confusion in his
Figure 7. The dependence of the cubic lattice parameter $a_0$ on the nitrogen concentration in ZrN$_x$. Single phase ZrN$_x$ (B1) exists only to the right of the vertical dashed line (from Ref. 80)
work on NbN_x. Later investigations showed similar behavior for NbC_x (82,83), TaC_x (82-84), TiN_x (71), VN_x (71,85,86) and HfN_x (87,88). For most of these compounds, T_c is a maximum near the stoichiometric composition and then decreases rapidly as nitrogen (or carbon) is removed.

This strong dependence of T_c on x is apparently inconsistent with the concept of favorable electron/atom ratios as promoted by Matthias (82,89). Defect structure is known to play a role in determining T_c. Studies on TiO by Doyle et al. (90) indicated the detrimental effects of lattice vacancies on T_c. By reducing the number of vacancies in a stoichiometric sample, they were able to increase T_c from 0.7K to 2.3K. Similar studies have not been carried out on the nitrides and carbides, so compositional and defect effects have not been separated with any degree of certainty.

Impurity concentration also affects the T_c's of these materials. Interstitial impurities, such as oxygen, are particularly troublesome because they are extremely difficult to avoid and they degrade the T_c (91,92). The susceptibility of a particular sample to oxygen contamination is probably a function of the nonmetal-to-metal ratio. This ratio affects the elemental chemical activities and limits the amount of oxygen which can be incorporated (2). The transition temperature T_c tends to be strongly dependent upon the fabrication process, another indication that impurities (or defects) are playing a role.

The particular dependences of T_c on x for VN_x and NbN_x are shown in Fig. 8(a and b). In VN_x, the transition temperature increases smoothly
Figure 8(a). The dependence of the superconducting transition temperature $T_c$ on the N/V atomic ratio $x$ for δ-VN (data from Ref. 2)
Figure 8(b). The dependence of $T_c$ on the N/Nb atomic ratio $x$ for $\delta$-NbN (data from Ref. 93)
from 2K at \( x = 0.76 \) to 9K at \( x = 1.00 \) (2). This wide composition range and the strong increase in \( T_c \) make VN\(_x\) a particularly interesting material to study. There is some confusion about the dependence of \( T_c \) on \( x \) for NbN\(_x\). Horn and Saur (93) found that \( T_c \) peaked near 16.5K at a composition of about \( \text{NbN}_{0.95} \), while Williams et al. (94) show a steady increase in \( T_c \) up to 17.3K at \( \text{NbN}_{0.95} \). Some of this confusion may lie in the difficulties of accurate chemical analysis for these materials. A careful study of \( T_c \) vs. \( x \) apparently does not exist for ZrN\(_x\).

C. The Need for Characterization

As is apparent from the above discussions of the phase relationships and superconductivity in the TMNC's, sample characterization is essential in studies of these materials. Careful studies on samples of unknown composition are of limited usefulness.

Several pertinent characteristics should be determined as fully as possible, although not all of those listed below are important for every experiment. Among these characteristics are: (1) the crystal structure and lattice constant, (2) chemical composition, including the \( x \) value and the impurity levels (particularly oxygen), (3) sample homogeneity, and (4) the overall defect structure including vacancy concentration, grain size, and dislocation structure.

In the present study of the electronic structure and its relationship to the composition and the superconducting properties, factors 1-3 listed above are especially important. These characteristics have been evaluated for each of the samples studied, by methods that will be discussed further in Chapter IV.
III. THEORY OF UPS AND ELS

A. UPS

UPS has been used extensively to study the electronic structure of a wide range of materials. It is useful for this purpose because the photoemitted electrons retain information about the distribution of initial electronic energy states. For the present experiments (angle-integrated measurements on polycrystalline samples), the well-known three-step model (95,96) for photoemission is sufficient to understand the data. The three-step model includes photoexcitation of the bound electrons, transport of the excited electrons to the surface of the material (with or without scattering), and escape from the material. The model has been developed and discussed in detail previously (95-98) and will only be briefly reviewed here.

The photocurrent \( J(E,\hbar \omega) \), measured by a detector at an energy \( E \), due to excitation of electrons by photons of energy \( \hbar \omega \), can be written in an independent-particle approximation as (97,99)

\[
J(E,\hbar \omega) = \left( \frac{2\pi e}{\hbar} \right) \sum_{i_f} |M_{fi}|^2 \delta(E_f - E_i - \hbar \omega) \delta(E - E_f) .
\]  

(1)

\( E_i \) is the initial (occupied) state energy and \( E_f \) is the final excited state energy of the electron in the metal. Both energy levels are eigenstates of the unperturbed Hamiltonian \( \hat{H}_o \),

\[
\hat{H}_o = \frac{\hat{p}^2}{2m} + V(\hat{r})
\]

(2)

where \( \hat{p} \) is the momentum operator and \( V(\hat{r}) \) is a self-consistent screened
potential including the surface. The details of the excitation process are contained in the transition matrix element \( M_{fi} \) between the initial and final eigenstates.

\[
M_{fi} = \langle f | \hat{H}' | i \rangle
\]  

\( \hat{H}' \) is the interaction Hamiltonian, given in the dipole approximation as

\[
\hat{H}' = \frac{e}{2mc} (\hat{A} \cdot \hat{p} + \hat{p} \cdot \hat{A}) = \frac{e}{mc} (\hat{A} \cdot \hat{p}).
\]  

\( \hat{A} \) is the electromagnetic vector potential. The final step in Eq. (4) neglects local field corrections to \( \hat{A} \) and assumes that the two operators commute. A sum is taken over all initial states and the first delta-function establishes energy conservation. The sum over final states and the second delta-function sets the final state energy \( E_f \) equal to the energy window \( E \) of the detector.

The eigenfunctions \( |i\rangle \) and \( |f\rangle \) must be written in the form of a two-dimensional Bloch wave parallel to the surface because the three-dimensional periodicity is destroyed by the sample surface (99).

\[
|f\rangle = \exp(i\hat{k}_\parallel \cdot \hat{\rho}) \phi_f(\hat{\rho}, z, E)
\]  

Here \( \hat{\rho} = (x, y) \) and \( z \) is chosen perpendicular to the surface. The electron wavevector \( \hat{k} \) is written as

\[
\hat{k} = \hat{k}_\parallel + \hat{k}_\perp
\]  

where \( \hat{k}_\perp \) and \( \hat{k}_\parallel \) are normal and parallel to the surface respectively.
The final state wavefunction $\phi_f(\rho, z, E)$ can be conveniently viewed as a time-reversed LEED (low energy electron diffraction) wavefunction (100-102). In a reduced zone picture,

$$\phi_f(\rho, z, E) = \sum_n T_n(E) \exp(ik|z) f_n(\rho, z, k_\parallel, E)$$

(7)

where the propagating functions $f_n$ are periodic in $\rho$ and $z$ for $z < 0$ (i.e., inside the material). The coefficients $T_n(E)$ arise from matching conditions at the surface and represent the amplitudes of the transmitted waves $f_n$. To include inelastic scattering effects during transport to the surface, the normal component of the electron wavevector can be considered complex,

$$k_\parallel = k^{(1)}_\parallel + ik^{(2)}_\parallel$$

(8)

where $k^{(2)}_\parallel$ will describe the damping of the wavefunction inside the solid.

If the damping is not too large, so that bulk photoemission is possible, the photocurrent can be written in the more transparent form often used for the three-step model (97).

$$J(E, \hbar \omega) = T(E)L(E) \sum_{\text{if}} |M_{fi}|^2 \delta(E_F - E_i - \hbar \omega) \delta(E - E_F)$$

(9)

$T(E)$ is the effective electron escape probability and $L(E)$ is the inelastic electron mean free path.

Momentum conservation effects are included via the matrix element $M_{fi}$. In a direct-transition model (i.e., vertical transitions between bands) for angle-integrated UPS measurements on polycrystalline samples,
three-dimensional $\mathbf{k}$-conservation occurs during excitation, but the observed energy distribution curve (EDC) is averaged over all $\mathbf{k}$-values. The bulk spectrum is then determined by the optical joint density of states (JDOS) of the band structure for a particular excitation energy $\hbar \omega$ \cite{99,103}. This is an integral in $\mathbf{k}$-space over the surface of constant vertical ($\mathbf{k}$-conserving) energy separation $\hbar \omega$ between bands.

In the "nondirect" transition model of Spicer \cite{104}, used in some early work, one assumes that $\mathbf{k}$-conservation is fully relaxed. In this case, the EDC reflects the product of the initial and final state densities modulated by an energy dependent (only) matrix element. Here, all structure shifting rigidly with the photon energy must arise from the initial state density. Later work \cite{105} showed that the direct-transition model is probably more correct, and better describes the data, especially that taken at $\hbar \omega > 10.7$ eV.

In summary, the sum over initial states in the expression for the photocurrent leads one to conclude that the observed photoemission spectrum is determined primarily by the initial state density, with each state $E_\uparrow$ contributing as energy conservation allows, and with an intensity modulated by the square of a matrix element. If the matrix element can be regarded as constant and the density of final states is sufficiently high, the observed EDC will reflect the initial density of states. (This is most rigorously true at x-ray photon energies.) As $\hbar \omega$ decreases, the density of available final states decreases. For bulk excitation with small damping, $\mathbf{k}$-conservation plays a role and the EDC reflects the energy distribution of the JDOS.
In this study, the observed EDC's are compared directly with the calculated initial densities of states. Structure correlations between the EDC and the initial DOS are expected, but there may not be a one-to-one correspondence because of additional structure unique to the JDOS, or because of vanishing matrix elements. Manifestations of direct transitions are sometimes observed as photon energy dependent intensities and positions of various structures within the EDC's.

For a particular photon energy $\hbar \omega$, the electron will be excited from the initial state of energy $E_i$ ($E_i < E_F = 0$) to a final state of energy $E_f$ ($E_f = \hbar \omega + E_i > E_F = 0$). However, only those excited electrons with enough energy to overcome the surface potential barrier will have a chance to escape into the vacuum (see Fig. 9). Therefore, the kinetic energy in the vacuum $E^*$ is given by $E_f - \phi_s$ where $\phi_s$ is the sample work function energy. To be detected, the electron must be collected by the collector of the energy analyzer whose work function energy is represented by $\phi_c$. From Fig. 10(a), we see that the measured energy $E$ will be given by

$$E = E^* - (\phi_c - \phi_s) = E_f - \phi_s - (\phi_c - \phi_s) = E_f - \phi_c \quad . \quad (10)$$

Those electrons emitted from the Fermi level ($E_i = E_F = 0$) will have the maximum kinetic energy measured by the energy analyzer,

$$E_{\text{max}} = \hbar \omega - \phi_c \quad . \quad (11)$$

The lowest energy electrons able to escape into the vacuum ($E_f = \phi_s$) will have a kinetic energy measured by the analyzer to be
Figure 9. A schematic representation of photoemission from a hypothetical transition metal

\( \hbar \omega \) photon energy

\( E_F \) Fermi energy (\( E_F = 0 \))

\( E_i \) initial state energy of the excited electron (\( E_i < 0 \))

\( E_f \) final state energy of the excited electron inside the metal (\( 0 < E_f < \hbar \omega \))

\( \phi_S \) surface work function energy of the sample

\( E^* \) kinetic energy of the excited electron in the vacuum (\( E^* = E_f - \phi_S \))
Figure 10. Energy diagrams depicting the relationship of the sample and the collector of the energy analyzer. $\phi_s$ and $\phi_c$ are the surface work function energies while $E_{F_S}$ and $E_{F_C}$ are the Fermi energies of the sample and collector respectively. In (a), the sample and collector are both grounded ($E_{F_S} = E_{F_C} = 0$). In (b), the sample is biased negatively ($eV < 0$) with respect to the collector ($E_{F_S} = eV > E_{F_C}$).
If $\phi_s$ is less than $\phi_c$ (true for all of the samples used in this study), the EDC will be artificially cut off at $E = 0$. To observe the low energy end of the EDC, the sample must be biased negatively with respect to the collector of the energy analyzer, as depicted in Fig. 10(b). This increases the detected kinetic energy $E$ by the magnitude of the bias voltage. The energy width of the EDC is given by

$$E_{\text{max}} - E_{\text{min}} = \hbar \omega - \phi_c - (\phi_s - \phi_c) = \hbar \omega - \phi_s,$$

and provides a good measure of the sample work function energy (106).

B. ELS

Electron energy loss spectroscopy (ELS) of solids was first demonstrated by Rudberg (107) in the reflection of low energy electrons from crystal surfaces. Ruthemann (108) demonstrated the technique for the transmission of high energy electrons through thin films. Many of the theoretical aspects of ELS have been reviewed by Pines (109), and reviews of the entire field of ELS have been compiled by Raether (110, 111). Only a brief review of the particular aspects important in the present work will be given here.

The incident electrons in an ELS experiment can interact with the solid through both single electron excitations and collective excitations. The single electron (intraband and interband) excitation energies are determined by the electron energy band structure of the material being probed. The collective excitations, on the other hand,
are longitudinal density fluctuations of the valence electrons of the solid, and their characteristic energies are determined primarily by the density of the electrons participating in the collective motion. For a free electron gas, it is easy to show (112) that the quanta of this collective oscillation (called a plasmon) will have a characteristic frequency $\omega_p$ given by

$$\omega_p = \left(\frac{4\pi ne^2}{m}\right)^{1/2}$$

(14)

where $n$ is the density of electrons participating and $m$ and $e$ are the electron mass and charge respectively. For high density plasmas ($10^{22}-10^{23}$ cm$^{-3}$), the above expression yields plasmon energies $\hbar\omega_p$ of $\sim 10$ eV.

The best available description of ELS up to now has been the classical "dielectric theory" (110,111,113-115). In this theory, the scattering cross section is related to the dielectric response of the system and the kinematics of the interaction are not explicitly considered. The system is described by a complex dielectric function (115)

$$\varepsilon(\hat{q},\omega) = \varepsilon_1(\hat{q},\omega) + i\varepsilon_2(\hat{q},\omega)$$

(15)

where $\hbar\omega$ and $\hbar\hat{q}$ are the energy and momentum (respectively) transferred to the target. This function represents the response of a system of atoms to a transverse electromagnetic wave (i.e., light) due to its effect on the bound electrons. The response function is frequency dependent and unique to the system being described.
Application of this theory to ELS assumes that the "transverse" dielectric function $\varepsilon_{\text{trans}}$ mentioned above is identical to the longitudinal dielectric function $\varepsilon_{\text{long}}$ which is involved for the longitudinal electric field created by a moving electron. The relationship between $\varepsilon_{\text{long}}$ and $\varepsilon_{\text{trans}}$ can be written (111)

$$\varepsilon_{\text{long}} \propto \frac{\varepsilon_{\text{trans}}}{1 + q^2}. \quad (16)$$

It is apparent that for small $q$ (i.e., small momentum transfer), $\varepsilon_{\text{long}}$ and $\varepsilon_{\text{trans}}$ are essentially identical. This identity is demonstrated by the good agreement between loss spectra calculated from optical experiments and those observed in ELS at $q \sim 0$ (111).

The model for the scattering process is as follows. The Coulomb field of the scattering electron interacts, during its approach, with the electron gas of the solid via long-range dipole fields. The interaction produces a time- and space-dependent polarization field which damps the motion of the electron. The polarization field can be decomposed by a Fourier expansion into plane waves which are damped inside the solid proportional to $\varepsilon_2$. Energy is transferred to the medium during the relaxation of the scattering electron.

For an electron gas with damping, the dielectric function can be shown (111) to have the form

$$\varepsilon(\omega) = 1 - \left(\frac{\omega \rho^2}{\omega^2}\right)\left(\frac{1}{1 - (i\omega \tau_c)^{-1}}\right) \quad (17)$$

where $\tau_c$ is the relaxation time describing the damping. The $q$ dependence has been ignored in Eq. (17). The real and imaginary parts
of $\varepsilon(\omega)$ can thus be written

$$\varepsilon_1 = 1 - \frac{\omega_p^2}{\omega^2} \left( \frac{1}{1 + (\omega^2 \tau_c^2)^{-1}} \right)$$

(18)

$$\varepsilon_2 = \frac{1}{\omega \tau_c} \left( \frac{\omega^2}{\omega_p^2} \right) \left( \frac{1}{1 + (\omega^2 \tau_c^2)^{-1}} \right) .$$

(19)

The dielectric theory shows that the conditions for a (bulk) plasmon are satisfied when $\varepsilon(\omega) = 0$. From Eq. (17), we see that for negligible damping ($\omega_p \tau_c \gg 1$ or $\varepsilon_2 \gg 0$), the dielectric function vanishes when $\omega = \omega_p$, the free electron plasma frequency.

In a solid with bound electrons and characteristic energy bands, interband transitions will affect the form of the dielectric function. Defining the interband transition energies as

$$\hbar \omega_{\ell m} = E_{\ell} - E_m$$

(20)

and assuming negligible damping ($\omega \tau_{\ell m} \gg 1$), the dielectric function may be written (111)

$$\varepsilon \sim \varepsilon_1 = 1 - \frac{4\pi e^2}{m} \sum_{\ell} \sum_{m} \frac{f_{\ell m}}{\omega^2 - \omega_{\ell m}^2} .$$

(21)

The sums over $\ell$ and $m$ include all transitions from occupied initial states $m$ to unoccupied final states $\ell$. The $f_{\ell m}$ are the oscillator strengths for the transitions involved. Analysis of Eq. (21) reveals that low-lying interband transitions ($\hbar \omega_{\ell m} < \hbar \omega_p$) tend to increase the observed plasma frequency above the calculated free-electron-like
value, while high-lying interband transitions tend to decrease the observed plasma frequency (111,116). If the free-electron-like value of \( \omega_p \) and the interband frequencies are well-separated, the effect on the observed plasma frequency is very small.

The perturbation caused by the electric field of the incoming electron causes it to lose energy to excitations of the electrons of the solid. The time-averaged rate of energy loss from the scattering electron can be written

\[
< \frac{dW}{dt} > = < \int \mathbf{J}(\mathbf{r},t) \cdot \mathbf{E}(\mathbf{r},t) d^3r >
\]

(22)

where \( \mathbf{J} \) is the current density of the incident electron and \( \mathbf{E} \) is the electric field strength in the solid due to the incident electron. Fourier transforming \( \mathbf{J} \) and \( \mathbf{E} \) and carrying out the time average yields

\[
< \frac{dW}{dt} > = \frac{1}{(2\pi)^4} \int d\omega \int d\omega' \int d^3q \int d^3q' J(q,\omega)E(q',\omega')
\]

\[
\times \int \int e^{-i(\omega+\omega')t} e^{i(q+q') \cdot \mathbf{r}} d^3r dt \times \frac{1}{J dt}
\]

\[
= \int d\omega \int d^3q J(q,\omega) \cdot \mathbf{E}^*(q,\omega)
\]

\[
= \int d\omega \int d^3q \left( -\frac{i\omega}{4\pi} \right) \epsilon(q,\omega) \mathbf{E}^*(q,\omega)
\]

(23)

where a scalar \( \epsilon(q,\omega) \) has been assumed and the relations

\[
\mathbf{J} = \sigma \mathbf{E} = -\frac{i\omega}{4\pi} \epsilon \mathbf{E}
\]

have been used. \( < \frac{dW}{dt} > \) is real, while the right hand side of Eq. (23) is complex due to \( \epsilon = \epsilon_1 + i\epsilon_2 \). Equating the real parts and using the
relation \( \mathbf{E} = \mathbf{D}/\varepsilon \), one obtains for the bulk case

\[
\langle \frac{dW}{dt} \rangle = \int d\omega \int d^3q \left( \frac{\omega}{4\pi} \right) \frac{e_2}{|\varepsilon|^2} DD^* .
\]

\( \mathbf{D} \) is given by \( \mathbf{D} \cdot \mathbf{D} = 4\pi\rho \) where \( \rho \) for the incident electron of velocity \( \mathbf{v} \) is \( e\mathbf{r}(r - vt) \). Since \( \mathbf{D} \) is determined by the incident electron, the crucial factor in the energy loss is

\[
\frac{e_2}{|\varepsilon|^2} = \frac{e_2}{\varepsilon_1^2 + e_2^2} = - \text{Im} \left( \frac{1}{\varepsilon} \right) ,
\]

which is sometimes referred to as the volume loss function (111,117).

The damping is proportional to \( e_2 \) while the screening of the field intensity is proportional to \( 1/|\varepsilon|^2 \).

In the presence of a surface, the development is the same except that the field intensity inside the solid due to the scattering electron outside the solid is screened by \( 1/|\varepsilon + 1|^2 \). This leads to the definition of the surface loss function (111,117)

\[
\frac{e_2}{|\varepsilon + 1|^2} = \frac{e_2}{(\varepsilon_1 + 1)^2 + e_2^2} = - \text{Im} \left( \frac{1}{\varepsilon + 1} \right) .
\]

This leads to a shift of the plasma frequency (now determined by \( \varepsilon + 1 = 0 \) (118)) to \( \hbar\omega_p/\sqrt{2} \) for a free electron gas with a planar surface bounded by vacuum.

The differential cross section for energy transfer \( E = h\omega \) and (small) momentum transfer \( h\mathbf{q} \) can be written for single bulk losses (110) as
\[
\frac{d^2\sigma}{dE d\Omega} = \left( \frac{m}{\pi^2 n a_0} \right) \left( \frac{1}{\hbar^2 q^2} \right) \left( -\text{Im} \left( \frac{1}{\varepsilon} \right) \right)
\]  

(27)

where \( a_0 \) is the Bohr radius and \( n \) the electron density.

The volume and surface loss functions describe completely the fundamental structure of the loss spectra because they contain all information about the dielectric behavior of the medium. The \( q \)-dependence of \( \varepsilon(q,\omega) \) is of little importance when the primary electron energy and momentum are much larger than the transferred energy and momentum (117).

The loss functions can exhibit maxima which arise from either peaks in \( \varepsilon_2 \) or poles due to the denominator (\( \varepsilon = 0 \) or \(-1\) for the volume and surface cases, respectively). The single-electron excitations give rise to peaks in \( \varepsilon_2 \) and appear in the loss functions reduced in intensity by \( 1/|\varepsilon| \) (bulk) or \( 1/|\varepsilon+1| \) (surface), and slightly displaced in energy compared to the \( \varepsilon_2 \) curve which describes optical absorption. The conditions for the poles in the loss functions are exactly the conditions stated earlier for the excitation of plasmons, indicating that plasmons should give rise to strong peaks in the loss functions.

The assumptions of small momentum transfer and \( E_p \gg \hbar \omega \), implicit in Eq. (27), are most rigorously satisfied in transmission ELS experiments. Generally, in these experiments, the experimenter need only make sure that the loss spectrum is not dependent upon the primary electron energy, the film thickness and so on.

In reflection ELS, only electrons scattered back from the sample are detected. These electrons must undergo inelastic scattering preceded or followed by a large-angle elastic diffraction (117). The
assumptions of Eq. (27) that $E_p \gg \hbar \omega$ and $q \ll k_p$ ($k_p =$ primary electron wavevector) may not be fulfilled for the lower primary energies $(100 \text{ eV} \leq E_p \leq 2000 \text{ eV})$ used in reflection experiments or for loss processes involving atomic core levels. Therefore, it is important to insure that the observed loss energies do not depend strongly upon the primary electron energy used. If strong $E_p$-dependence is observed, $E_p$ must be increased. The good agreement of reflection ELS with transmission ELS and optical determinations of the loss functions, such as demonstrated in Ref. 119, indicates that a significant fraction of the scattered electrons can be associated with single inelastic events occurring in combination with a purely elastic reflection.

One should also note that in reflection ELS, one measures some sort of weighted average of the volume and surface loss functions (117). The coupling of electrons to volume and surface plasmons has been treated theoretically by several authors (118,120-122). Not unexpectedly, it is found that electrons near the surface excite mainly surface plasmons while electrons deeper inside the material are more likely to excite volume plasmons. As the primary electron energy is increased, the scattering electrons create a smaller fraction of surface plasmons compared to volume plasmons. The calculations are more complicated than simply an energy dependent penetration depth effect, but the result is the same. This phenomenon has been observed experimentally by several workers (123-127).

Also, to determine the detailed behavior of $\varepsilon_1$ and $\varepsilon_2$ from the observed loss spectrum and Eq. (27), one must measure the absolute
value of the scattering cross section, implying that the incident and scattered beam intensities and the detected volume are known. This is feasible only in transmission ELS where the intensities can be measured and the film thickness is known. In reflection ELS, the observed spectrum is typically reported in arbitrary units, and $\varepsilon_1$ and $\varepsilon_2$ are not readily available from the data. Because the conditions for a plasmon ($\varepsilon_2 \ll 1$ and $\varepsilon_2 \cong \varepsilon_1 = 0$ or $-1$ for the bulk or surface respectively) cannot be verified directly in reflection ELS, plasmon identifications must be considered somewhat tentative in such work.

Collective excitations are experimentally always observed to dominate electron energy loss spectra, especially at lower loss energies ($\leq 30$ eV) (119,127,128,129). The intensity of scattered electrons decreases rather rapidly at higher loss energies. The low energy region can also contain interband excitations, but these often seem to be masked somewhat by the strong collective contributions. At higher loss energies, $\varepsilon_2 \ll 1$ and $\varepsilon_1 \cong 1$, implying that $\text{Im}(-\frac{1}{\varepsilon}) \approx \varepsilon_2$. This indicates that one should observe primarily single-electron excitations at loss energies greater than about 30 eV.
IV. EXPERIMENTAL

A. Ultrahigh Vacuum Surface Analysis Apparatus

The experimental ultrahigh vacuum (UHV) surface analysis chamber used for most sample fabrication and all Auger electron (AES), ultraviolet photoemission (UPS) and electron energy loss spectroscopy (ELS) measurements is shown schematically in Fig. 11. Base pressures \( \leq 1 \times 10^{-10} \) Torr (as measured with a nude ion gauge) are regularly attained in this chamber after baking at \( \approx 150^\circ C \) to \( \leq 1 \times 10^{-6} \) Torr into a liquid nitrogen trapped, two inch diffusion pump followed by evaporation of Ti onto a large surface area, liquid nitrogen cooled bellows. A baffle blocks any straight line path from the Ti source to the upper half of the chamber, thus protecting the various vacuum inserts during Ti evaporation. Residual gas analysis reveals the combination of background gases typical in such UHV chambers, namely hydrogen, methane, and water vapor. Under usual operating conditions, oxygen, nitrogen, carbon monoxide and carbon dioxide levels are below the detection limits of the gas analyzer.

The various other vacuum inserts will be mentioned and discussed in later paragraphs as the techniques are outlined.

B. Sample Fabrication Techniques

The surface sensitivity of the spectroscopic measurements to be made, and the high susceptibility of the transition metal nitrides to oxygen contamination, make necessary extra precautions to provide suitably pure and clean samples. Two fabrication methods, designed to
Figure 11. The top view of the ultrahigh vacuum surface analysis apparatus

Ar ultrahigh vacuum leak valve connected to a high purity Ar gas cylinder
CMA cylindrical mirror electron energy analyzer (double pass) used for AES, ELS and UPS
E grazing incidence electron gun used for AES and ELS
I ion bombardment gun used for sputter etching
IG nude ion gauge
N₂ ultrahigh vacuum leak valve connected to a high purity N₂ gas cylinder
P pumping line connected through an ultrahigh vacuum valve to a liquid nitrogen trapped diffusion pump and a mechanical roughing pump
RGA residual gas analyzer
S sample connected to a precision manipulator
UV ultraviolet light source
W window
minimize oxygen exposure were adopted: (1) \textit{in situ} nitriding (i.e., within the UHV chamber), and (2) external nitriding in a mullite tube furnace. These methods and their respective advantages and disadvantages are discussed below.

The primary motivation for the \textit{in situ} fabrication method was the desire to avoid oxygen exposure at any step during the fabrication or spectroscopic measurements. A commercially obtained high purity transition metal foil (1 cm x 11 cm x 0.01 cm) was initially electropolished to remove surface carbon and to obtain a smooth and shiny surface. The foil was then sequentially boiled and ultrasonically cleaned in acetone and methanol before being mounted in the stainless steel clamps of the precision sample manipulator and inserted into the UHV chamber. Following the usual 150°C bakeout, and at a pressure $<1 \times 10^{-10}$ Torr, Auger analysis always revealed considerable oxygen and some carbon as major surface contaminants. Small traces of residual chlorine left from the electropolishing were also sometimes detected.

The next major step involved producing a clean transition metal foil for nitriding. In the cases of Nb and Zr, this was accomplished through straightforward high temperature outgassing at pressures $<1 \times 10^{-9}$ Torr. The oxides of Nb become volatile at temperatures above 2000°C (106,130) and a clean surface is obtained by heating to these temperatures in a vacuum better than $1 \times 10^{-9}$ Torr. The clean Nb surface is verified through Auger analysis and even more rigorously with UPS (106,130,131). UPS is found to be much more sensitive to oxygen contamination via the appearance of the oxygen 2p states (5-8 eV
below $E_p$) in the experimental EDC and the determination of the photoelectric work function from the total energy width of the EDC \((106,130,131)\). The extensive high temperature treatment also promotes the growth of large \((1-3\,\text{mm})\) single crystal grains \((131)\) and allows carbon to diffuse into the bulk.

Simple heat treatments also clean Zr, but the mechanism is different than for Nb. AES indicates a clean Zr surface after relatively mild \((\sim 1000\,\text{°C})\) outgassing. The surface carbon and oxygen apparently diffuse quickly into the bulk becoming too dilute at the surface to be detected with AES. However, as with Nb, the oxygen 2p states appear in the UPS results long after AES indicates a clean surface. Extensive heating to \(\sim 1550\,\text{°C}\) at pressures \(\leq 1 \times 10^{-9}\) Torr minimizes the oxygen contribution in the EDC (see Chapter V) and as with Nb, results in the growth of large single crystal grains.

V presents a much more difficult cleaning problem than either Nb or Zr. High temperature heat treatments can be used to drive off surface oxides, but they also cause surface segregation of bulk impurities (such as P or S) present at parts per million levels. Several hours of heating to temperatures just below the melting point remove the S (as well as subliming considerable V) but the P still remains. Sputter cleaning easily removes the segregated P layer, but subsequent reheating to temperatures above 1200°C causes its reappearance.

In order to obtain ELS and UPS data from clean V, the following procedure was adopted. The foil was outgassed to temperatures near
the melting point at pressures $\approx 1 \times 10^{-9}$ Torr for \n1 hour. Ar$^+$ ion etching was used to remove the surface-segregated S and P. The sputter-induced surface damage was annealed by heating for several minutes to \n1000°C. Several repetitions of the sputtering and low temperature annealing resulted in a sample whose Auger spectra showed no P, S or O. Invariably, however, UPS results revealed the oxygen 2p states (see Chapter V). This cleaning procedure has been found to give reliable reflection ELS results (119).

After a clean transition metal foil was obtained, ELS and UPS measurements could be taken (as outlined in later sections) for comparison with the nitride results.

The next step in the in situ fabrication was to convert the foil to the nitride by heating in pure nitrogen. The UHV chamber was sealed at a pressure of $\leq 4 \times 10^{-9}$ Torr and filled with high purity (99.999%) nitrogen directly from a gas cylinder through a previously baked, stainless steel line and an UHV leak valve. Pressures between 0.001 Atm. and approximately 1.3 Atm. were used, depending on the type of transition metal and the desired final composition. The foil was then nitrided by heating with an alternating current for times from one to fifteen hours. Longer times were gradually adopted in an attempt to improve sample homogeneity. Nitriding temperatures used were in general agreement with those found in the literature (2,68,71,93). Temperatures of 1200°C or greater were required for VN and greater than 1300°C for NbN. ZrN can be formed at lower temperatures, but this was generally done in our work at \n1200°C. The particular nitriding
pressures, temperatures and times that we used are listed in Tables 1-3.

After nitriding, UHV was restored to perform ELS and UPS measurements. AES results generally indicated that the *in situ* samples were free of oxygen and carbon contamination.

The strong point of the *in situ* procedure is the avoidance of oxygen contamination. However, the samples fabricated *in situ* did suffer from varying degrees of inhomogeneity (as discussed in the next section). Further, it was found in practice that one could not predict, with any degree of precision, what the final nitrogen concentration would be for particular fabrication parameters.

In an attempt to overcome some of these drawbacks, some samples were fabricated more conventionally in a mullite tube furnace. The procedures used here follow those outlined in the work of Ajami and MacCrone (68) on VNₓ, although some modifications have been implemented to minimize oxygen exposure during nitriding.

As with the *in situ* procedure, clean transition metal foil rectangles (1.0 cm x 1.0 cm x 0.01 cm) were prepared through UHV outgassing (and sputtering) techniques. The foils were necessarily exposed to air before being placed in the 3" diameter mullite tube furnace, so surface oxide layers and adsorbed carbon were undoubtedly present, although the bulk should remain clean.

The basic arrangement of the tube furnace is shown in Fig. 12. The system is designed to provide a continuous steady flow of high purity nitrogen over the hot transition metal foil in a completely
<table>
<thead>
<tr>
<th>Sample</th>
<th>Nit. Time (hrs)</th>
<th>Nit. Press. (Atm)</th>
<th>Nit. Temp. (°C)</th>
<th>a₀ (Å)</th>
<th>x</th>
<th>T_c (K)</th>
<th>ΔT_c a (°K)</th>
<th>% of Sample b</th>
</tr>
</thead>
<tbody>
<tr>
<td>VN-2</td>
<td>1</td>
<td>0.001</td>
<td>1300</td>
<td>-</td>
<td>β-VN</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>VN-4</td>
<td>1</td>
<td>0.02</td>
<td>1500</td>
<td>4.077</td>
<td>0.76</td>
<td>4.5</td>
<td>2.0</td>
<td>100</td>
</tr>
<tr>
<td>VN-5</td>
<td>1</td>
<td>0.05</td>
<td>1530</td>
<td>4.088</td>
<td>0.80</td>
<td>8.35</td>
<td>0.4</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.9</td>
<td>0.9</td>
<td>70</td>
</tr>
<tr>
<td>VN-6</td>
<td>1</td>
<td>0.10</td>
<td>1560</td>
<td>4.098</td>
<td>0.84</td>
<td>8.22</td>
<td>0.7</td>
<td>65</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5.68</td>
<td>0.5</td>
<td>35</td>
</tr>
<tr>
<td>VN-7</td>
<td>3</td>
<td>0.40</td>
<td>1560</td>
<td>4.101</td>
<td>0.85</td>
<td>8.4</td>
<td>0.4</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6.1</td>
<td>0.6</td>
<td>70</td>
</tr>
<tr>
<td>VN-9</td>
<td>7</td>
<td>0.8</td>
<td>1450</td>
<td>4.119</td>
<td>0.92</td>
<td>7.8</td>
<td>0.9</td>
<td>100</td>
</tr>
<tr>
<td>VN-10 c</td>
<td>15</td>
<td>0.8</td>
<td>1230</td>
<td>4.123</td>
<td>0.94</td>
<td>8.4</td>
<td>1.4</td>
<td>100</td>
</tr>
<tr>
<td>VN-11</td>
<td>14.5</td>
<td>1.0</td>
<td>1330</td>
<td>4.125</td>
<td>0.94</td>
<td>8.25</td>
<td>0.7</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5.4</td>
<td>1.5</td>
<td>55</td>
</tr>
<tr>
<td>VN-F6</td>
<td>106</td>
<td>50 cc/min</td>
<td>1220</td>
<td>4.129</td>
<td>0.96</td>
<td>8.65</td>
<td>0.3</td>
<td>65</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>5.4</td>
<td>2.3</td>
<td>35</td>
</tr>
<tr>
<td>VN-F2 d</td>
<td>100</td>
<td>45 cc/min</td>
<td>1450</td>
<td>4.114</td>
<td>0.90 d</td>
<td>8.8</td>
<td>0.3</td>
<td>5</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6.7</td>
<td>0.5</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.4</td>
<td>1.0</td>
<td>45</td>
</tr>
</tbody>
</table>

aΔT_c is the superconducting transition width as determined from 10% complete to 90% complete.

b% of sample is estimated from the relative height of the steps in the inductive T_c curves as measured on finely ground powders. Note that since no sample other than VN-10 gave indication of other than a single phase or composition from careful x-ray measurements, these numbers may overestimate the amount of competing phase present. See text for details.

cSample VN-10 showed ≤5% β-VN in the x-ray diffraction pattern.

dSample VN-F2 contained considerable oxygen in the bulk. The composition is estimated to be VN_{0.70.2}. 
Table 2. Fabrication parameters and resulting characteristics for NbN\textsubscript{x} samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nit. Time (hrs)</th>
<th>Nit. Press. (Atm)</th>
<th>Nit. Temp. (°C)</th>
<th>( a_0 ) (Å)</th>
<th>Composition</th>
<th>( T_c ) (K)</th>
<th>( \Delta T_c ) (K)</th>
<th>% of Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>NbN-1\textsuperscript{a}</td>
<td>13.1</td>
<td>0.17</td>
<td>1280-1370</td>
<td>-</td>
<td>( \delta, \beta, \epsilon, \gamma )-NbN</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NbN-2\textsuperscript{b}</td>
<td>15.0</td>
<td>0.82</td>
<td>1510</td>
<td>4.381</td>
<td>NbN\textsubscript{0.79}\textsuperscript{0.04}\textsuperscript{0.03}</td>
<td>13.6</td>
<td>1.5</td>
<td>60</td>
</tr>
<tr>
<td>NbN-3</td>
<td>14.5</td>
<td>1.3</td>
<td>1500</td>
<td>4.386</td>
<td>NbN\textsubscript{0.8}\textsuperscript{0.05}\textsuperscript{0.05}</td>
<td>14.3</td>
<td>1.3</td>
<td>50</td>
</tr>
<tr>
<td>NbN-F1</td>
<td>100</td>
<td>45</td>
<td>1451</td>
<td>4.383</td>
<td>NbN\textsubscript{0.8}\textsuperscript{0.1}</td>
<td>14.1</td>
<td>0.6</td>
<td>65</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Sample NbN-1 showed almost equal parts \( \delta, \epsilon, \gamma \) and \( \beta \)-NbN in x-ray diffraction results.

\textsuperscript{b}Sample NbN-2 showed \( \approx 10\% \) \( \epsilon \)-NbN in addition to \( \delta \)-NbN in x-ray diffraction results.
Table 3. Fabrication parameters and resulting characteristics for ZrN\textsubscript{x} samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nit. Time (hrs)</th>
<th>Nit. Press. (Atm)</th>
<th>Nit. Temp. (°C)</th>
<th>(a_0) (Å)</th>
<th>Composition</th>
<th>(T_C) (K)</th>
<th>(\Delta T_C) (K)</th>
<th>% of Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrN-1\textsuperscript{a}</td>
<td>14.1</td>
<td>1.1</td>
<td>1200-1300</td>
<td>4.578</td>
<td>(\alpha)-Zr + ZrN\textsubscript{x}</td>
<td>&lt; 0.6</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>ZrN-2\textsuperscript{b}</td>
<td>14.5</td>
<td>1.3</td>
<td>1320</td>
<td>4.584</td>
<td>(\alpha)-Zr + ZrN\textsubscript{0.5}\textsuperscript{0.1}\textsuperscript{0.01}</td>
<td>7.8</td>
<td>2.9</td>
<td>50</td>
</tr>
<tr>
<td>ZrN-F1\textsuperscript{c}</td>
<td>100</td>
<td>45 cc/min</td>
<td>1451</td>
<td>4.574</td>
<td>ZrN\textsubscript{0.8}\textsuperscript{0.07}\textsuperscript{0.03}</td>
<td>10.3 (\sim 9)</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>ZrN-F2\textsuperscript{c}</td>
<td>106.5</td>
<td>50 cc/min</td>
<td>1220</td>
<td>4.577</td>
<td>ZrN\textsubscript{0.72}\textsuperscript{0.15}\textsuperscript{0.03}</td>
<td>10.4 (\sim 9)</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Sample ZrN-1 showed about equal parts \(\alpha\)-Zr with nitrogen in solid solution and (B1) ZrN\textsubscript{x} in x-ray diffraction results. All data presented for ZrN-1 is for \(\alpha\)-Zr (see text for details).

\textsuperscript{b}Sample ZrN-2 also showed about equal parts \(\alpha\)-Zr and (B1) ZrN\textsubscript{x} in x-ray diffraction results. All data presented from ZrN-2 is for (B1) ZrN\textsubscript{x} (see text for details).

\textsuperscript{c}Samples ZrN-F1 and ZrN-F2 were single phase (B1) ZrN\textsubscript{x} with reasonably sharp x-ray diffraction patterns. The superconducting onset occurred above 10K, but the transition was spread over \(\sim 9\)K°.
Figure 12. A schematic drawing of the external sample fabrication apparatus. In the purifying section, the prepurified N₂ passes from the flow meter (FM) to the drying column (DC) and then to the small getter oven (O) filled with Cu screen and Zr foil. From the purifying section, the gas flows into the mullite tube furnace (TF) containing the sample (S). From the nitriding section the gas passes to the exhaust section where it is expelled through two beakers (B), the first of which is partially filled with mineral oil to avoid backstreaming of air into the nitriding section.
sealed system. The essential elements of the apparatus are a controlled flow of gas, a purifying section, the nitriding oven and the exhaust section.

Prepurified (99.9%) \(N_2\) is passed through a flow regulator (at 10 to 100 cc/min) into the purifying section. This consists of a drying column and an 800°C getter oven filled with Cu screen and Zr foil. The hot Cu and Zr effectively remove oxygen from the flowing gas. During a typical run, the copper screen on the inlet side turns black (indicating formation of \(CuO\)) over a small fraction of its length and the Zr foil turns gold (indicating formation of ZrN) with a black inlet edge (indicating formation of ZrO). The outlet end of the Zr foil is consistently bright gold in color and the Cu screen on the outlet end is unchanged in appearance, indicating that the \(O_2\) has been removed. From the getter cleaning section, the \(N_2\) flows directly into the 3" diameter mullite tube furnace whose ends are O-ring sealed. The furnace (nitriding) temperature is sensed with a thermocouple and regulated by a microprocessor controller to \(\pm 1.0^\circC\). The gas passes from the tube furnace to the exhaust section where it is bubbled through mineral oil to avoid the backstreaming of air into the nitriding furnace.

Before placing the transition metal foils in the tube furnace, they are wrapped in successive layers of Mo, Zr and Ta foil to provide further gettering protection against oxygen contamination. The inner Mo wrap is relatively inactive, picking up only a small amount of nitrogen (it becomes slightly brittle) and more importantly, protecting
the transition metal sample from the extremely reactive surrounding Zr layer. The Zr wrap should further getter out any remaining oxygen (or carbon) in the flowing gas. Obviously, it also picks up large amounts of nitrogen and indeed, these protective Zr wraps were consistently converted to nearly stoichiometric ZrN. Even when nitrided, the Zr foil should preferentially getter oxygen. The outside Ta wrap also provides some gettering action and appears to be converted to Ta₂N.

Nitriding temperatures used in the external process were the same as those in the in situ method. The improved uniformity of the nitriding temperature in the external process presumably promotes sample homogeneity. Longer nitriding times (up to 160 hours) were also adopted in attempts to improve the homogeneity. These nitriding times are about 100 times longer than those used by Ajami and MacCrone (68), presumably due to the additional protective wrappings. Even with the long nitriding times, homogeneity problems sometimes persisted (see discussion in the next sections).

C. Sample Characterization

As was mentioned in earlier chapters, sample characterization is essential when working with the TMNC's. The characteristics of primary importance in the present study are the crystal structure, nitrogen-to-transition metal ratio (x), impurity levels (particularly oxygen) and compositional homogeneity. The major techniques used to evaluate these characteristics were Auger electron spectroscopy, x-ray diffraction and AC inductive superconducting transition temperature measurements.
AES was used for **in situ** monitoring of the surface composition. This allows one to follow the progress of cleaning procedures and to determine if these procedures are continually depleting the nitrogen content of the sample. However, AES is not sufficiently precise for determining the absolute nitrogen content from one sample to the next. Although UPS can be used as a very sensitive check for oxygen on the pure transition metals, it is less valuable for the TMNC's in this respect because of the overlap of the 2p states from the different nonmetal atoms. Hence, one must rely totally on AES to monitor the oxygen contamination. Unique difficulties arise here for vanadium and VN$_x$ due to the overlap of the vanadium and oxygen AES signatures. This problem is discussed in detail in Chapter V.

X-ray diffraction was used to determine the crystal structure and lattice constant for each sample studied. This allows a positive check for the rocksalt structure characteristic of the mononitrides and also provides a moderately sensitive (down to approximately 5%) check for alternate phases of different crystal structure. Further, the cubic lattice constant provides a measure of the nitrogen-to-transition metal ratio $x$ through comparison with data already published in the literature (see Chapter II). This is especially effective for VN$_x$, where the lattice constant changes by about 2% over the stable composition range. The sharpness of the x-ray diffraction peaks and the resolution of the Cu $K\alpha_1$ and $K\alpha_2$ doublets provide a mild check on the sample homogeneity. One must be careful to obtain diffraction results from several parts of the sample to insure a true check on the homogeneity.
The final characterization tool was a standard AC inductive superconducting transition temperature measurement. Knowledge of $T_c$ gives another check on the $x$ value through comparison with the literature (see Chapter II). In materials like the TMNC's, where $T_c$ depends on the composition, the transition width provides a sensitive check of the sample homogeneity. To avoid confusion due to shielding effects, $T_c$'s were measured on samples ground to a fine powder. In the absence of shielding effects, inductive $T_c$ measurements should reveal the relative amounts of material contributing to any structures present in the $T_c$ curve.

For externally fabricated samples, mass increases due to the nitriding treatment were also measured. By assuming all mass gain is due to nitrogen uptake, one can calculate an average $x$ value for the sample. This method is accurate only to a few percent, and within these limits, it indicated $x$ values in agreement with those determined from the lattice constant.

The resulting sample characteristics, along with the relevant fabrication parameters, are shown in Tables 1, 2, and 3 for $VN_x$, $NbN_x$, and $ZrN_x$ respectively. Samples fabricated in situ are labeled, for example, as VN-11, indicating the eleventh $VN_x$ sample fabricated in the UHV chamber. Samples fabricated in the tube furnace have an additional $F$ in the notation (e.g., VN-F6).

As expected, one of the major problems in fabricating these mononitride samples is achieving compositional homogeneity. However, the precise degree of inhomogeneity, although small, is unclear. As an
example, consider sample VN-11. X-ray diffraction revealed fairly
sharp, well-resolved doublets and indicated a single lattice parameter
\( a_0 = 4.125 \, \text{ Å} \) and thus a single composition \( x = 0.94 \). However, the
inductive \( T_c \) measurement done on the powdered sample revealed two steps
in the transition (\( \sim 45\% \) went superconducting at 8.25K while 55\% went
superconducting at 5.4K). These two "\( T_c \)'s" imply two distinct composi­
tions that would have lattice constants differing by 0.5%, easily
resolvable by the diffractometer. Yet, as mentioned, no hint of this
behavior was found in careful diffraction measurements. Because of this
apparent discrepancy between the x-ray diffraction and \( T_c \) results, some
of the samples studied are regarded as unsuitable for examination of
compositional dependences. As we will see, ELS and UPS results from
these samples are certainly representative of the compound at the x-ray
inferred composition, but the presence of small contributions from a
different composition cannot be ruled out.

We have been unable to develop a complete and consistent explana­
tion for the above-mentioned discrepancies. Attempts to verify the
possibility of shielding effects in the inductive \( T_c \) measurements proved
negative. (\( T_c \) results for shattered samples of 1-2 mm dimensions were
essentially the same as those from powdered samples.) Attempts to
locate possible high \( T_c \) regions of different compositions using AES
and depth profiling techniques also proved fruitless.

Among the VN\(_x\) samples, VN-4 \( (x = 0.76) \), VN-9 \( (x = 0.92) \), and
VN-10 \( (x = 0.94) \) showed suitably homogeneous superconducting transi­
tions to be used for compositional comparisons. VN-10 also showed
\( \lesssim 5\% \) \( \beta \)-VN in the x-ray diffraction results.
The NbN\textsubscript{x} and ZrN\textsubscript{x} samples show greater problems with homogeneity, as is apparent in Tables 2 and 3. The phase diagram for NbN\textsubscript{x} is less forgiving in that several alternate crystal structures are possible at the same composition, depending upon the reaction temperature used. The desired δ-NbN must be formed at temperatures >1300°C and the stability range is much narrower than for δ-VN. NbN-1 was reacted at ~1300°C and shows evidence of β-NbN (Nb\textsubscript{2}N), ε-NbN, γ-NbN and the desired δ-NbN (see Chapter II). Consequently, higher nitriding temperatures were used for the later NbN\textsubscript{x} samples in an attempt to preferentially form δ-NbN. Even at the higher temperatures, NbN-2 still showed approximately 10% ε-NbN in the x-ray diffraction results. Some of the ε-phase may form during cleaning procedures which utilize lower temperatures. Later samples nitrided at higher nitrogen pressures showed single phase δ-NbN in the x-ray results, but appeared to be inhomogeneous in the inductive T\textsubscript{c} results. Consequently, compositional comparisons cannot be made from this study for NbN\textsubscript{x}, although representative spectra have been determined.

The ZrN\textsubscript{x} samples proved to be the most troublesome. Although the phase diagram is simpler than for either VN\textsubscript{x} or NbN\textsubscript{x}, insurmountable problems for the present fabrication techniques were encountered. It proved impossible to fabricate in situ single phase ZrN of the B1 crystal structure. Even at nitrogen pressures up to ~1.3 Atm., the samples were found to be approximately 50% α-Zr with nitrogen in solid solution, and 50% ZrN of the rocksalt structure. These in situ samples (ZrN-1 and ZrN-2) exhibited very large grains (1-3 mm), and
small composition differences were detectable from grain to grain using AES. ELS and UPS also showed different spectra for different grains. The externally fabricated ZrN samples were single phase, but inductive \( T_c \) measurements showed a continuous, broad transition starting at \( \sim 10.2 \text{K} \) and extending down to \( \sim 1.4 \text{K} \). In addition, it proved impossible to completely clean the surfaces of the externally fabricated ZrN samples (this is discussed further in the following section). Consequently, the ZrN\(_x\) results presented here are actually from ZrN\(_x\)C\(_{y}\)O\(_z\) samples with \( y \leq 0.15 \) and \( z \leq 0.05 \). The results should be representative of ZrN in general shape, but some alteration of the ELS and UPS curves must be assumed.

D. Sample Surface Cleaning

Before meaningful UPS and ELS measurements could be taken, it was necessary to obtain the cleanest possible surface as determined by AES measurements. Ideally, the Auger results should show only the desired transition metal and nitrogen.

For the \textit{in situ} VN\(_x\) samples, this was a fairly simple matter because the samples were never exposed to air and picked up little or no oxygen during the nitriding process. Relatively mild outgassing (\( \leq 1000 \text{C} \)) of the nitride foil was usually adequate to insure a clean Auger spectrum. The same was true for \textit{in situ} ZrN\(_x\) and to a lesser extent NbN\(_x\) samples (some sputter cleaning was required for \textit{in situ} NbN\(_x\) samples).

However, for samples made externally, the cleaning problems were more severe and more elaborate cleaning procedures were required. It
has been recently reported by Johansson et al. (47) that repeated flash heating to high temperatures resulted in clean TiC and TiN surfaces without altering the surface composition. This technique was attempted on the compounds used in the present study with little success. We find that high temperature treatments continually deplete the nitrogen content (as indicated by residual gas analysis and AES), apparently due to the lower decomposition temperatures of these particular compounds.

To minimize such depletion of nitrogen from the samples during cleaning, lower temperature cleaning processes were adopted. First, to remove the surface oxide layer grown when the externally nitrided sample was exposed to air, 3 KeV Ar$^+$ ion sputtering was used until Auger analysis indicated that no oxygen was present (or a minimum oxygen signal in the case of some NbN or ZrN samples). Second, the sample was further sputter-cleaned while heated to temperatures <1200°C. In this procedure, externally made samples were crimped into a previously outgassed Ta foil that was used for support and heating. In most cases, this treatment caused an initial rise in the oxygen AES signal which again, eventually disappeared (or reached a minimum). Finally, the sputter treatment was ended and the samples were heated to ~1000°C to anneal sputter-induced surface damage. Sputtering invariably resulted in a nitrogen deficient surface (the nonmetal-to-metal ratio typically decreased by ~25%), but the final annealing usually restored the sample surface to nearly the original nonmetal-to-metal ratio.
The above three-step cleaning procedure was effective for VN$_x$ samples, but somewhat less so for NbN$_x$ and ZrN$_x$ samples. The surface oxide was relatively thin for VN and NbN and could be removed rather easily. Oxygen incorporation into the bulk proved to be somewhat of a problem for NbN. For ZrN, the surface oxide layer was typically estimated to be ~100 Å thick from depth profiling measurements. In fact, Auger results often showed no nitrogen contribution prior to sputtering (i.e., the samples appeared to be ZrO$_x$). It proved to be nearly impossible to completely remove this oxide layer. The long sputtering times required also caused other problems. Under the influence of the sputtering beam, a significant amount of ZrC$_x$ was formed. Neither continued sputtering nor heat treatments could remove this carbide layer. This last problem seemed to be unique to the ZrN$_x$ samples.

Examples of AES curves from "clean" externally nitrided foils will be discussed in Chapter V.

AES was also used to monitor the surface composition of the samples throughout the course of the ELS and UPS measurements. Periodic outgassing (approximately every 15 minutes) to about 1000°C was required to maintain suitably clean surfaces.

E. UPS Measurements

The angle-integrated UPS curves obtained in this study were recorded using a differentially pumped, windowless, microwave excited, noble gas discharge lamp and the double-pass CMA in a preretarding mode.
All curves reported are the average of several (five to ten) traces, individually normalized with respect to the peak intensity near the Fermi edge. This insures that the EDC's are truly representative of the material and also provides an improvement in the signal-to-noise ratio. In an individual EDC, the signal-to-noise ratio is typically better than 15:1. Count rates were generally \( \sim 10^4 \) CPS for the first ionization lines of He and Ne.

The windowless discharge lamp (see Fig. 13) was built after the fashion of Rowe et al. (132). The three differentially pumped sections are separated by stainless steel capillary tubes (\( \sim 0.08 \) mm inner diameter and 8-10 cm in length). The discharge is maintained in a quartz tube (\( \sim 1.27 \) cm in diameter and 10-15 cm in length). The noble gas pressure in the discharge region is typically 1.0 to 2.0 Torr for the Ne I (\( \tilde{\hbar}\omega = 16.8 \) eV) and He I (\( \tilde{\hbar}\omega = 21.2 \) eV) ionization lines and \( 10^{-2} \) Torr for the Ne II (\( \tilde{\hbar}\omega = 26.9 \) eV) and He II (\( \tilde{\hbar}\omega = 40.8 \) eV) lines. A weak axial magnetic field was applied following the method of Vorburger et al. (133) to stabilize the low pressure discharges required for the Ne II and He II lines. A Welch 1397 mechanical pump (17.7 CFM) reduces the pressure in the first differentially pumped stage to \( \lesssim 10^{-3} \) Torr, while a liquid nitrogen trapped four-inch oil diffusion pump reduces the pressure in the second stage to \( \lesssim 10^{-7} \) Torr. When using Ne I or He I photons, the pressure in the main UHV chamber rises to \( \lesssim 2 \times 10^{-9} \) Torr, while for Ne II and He II conditions, the chamber pressure is typically \( \lesssim 7 \times 10^{-10} \) Torr. In both cases, the noble gas is continuously pumped out through port P (see Fig. 11) by
Figure 13. A schematic diagram of the differentially pumped, windowless, microwave excited, noble gas discharge lamp used for UPS experiments. The noble gas discharge is maintained in the quartz tube by a clip-on microwave (2450 MHz) cavity powered by a modified Raytheon CMD-5 diathermy unit. The pressure in the discharge region is typically 10-2000 mTorr. Stainless steel capillary tubes separate the differentially pumped stages. The first stage ($\approx 1 \times 10^{-3}$ Torr) is connected through a 4 inch diameter hose to a 17.7 cfm mechanical pump. The second stage ($\approx 1 \times 10^{-7}$ Torr) is connected by a 4 inch diameter stainless steel tube to a liquid nitrogen trapped, 4 inch oil diffusion pump. The mechanical pump also serves as the forepump for the diffusion pump. A 1500 Å thick Al (1% Si) filter is mounted near the end of the final capillary tube to remove the hydrogen alpha line. The UHV isolation valve seals the main chamber from the lamp when desired. Chamber pressures during UPS experiments are typically $\approx 2 \times 10^{-9}$ Torr.
the small diffusion pump. Residual gas analysis confirms our expecta-
tion that the increased chamber pressure during photoemission is
tively due to the noble gas streaming into the main chamber from the
UPS lamp.

The microwave power required to maintain the discharge is supplied
to a 2450 MHz Evenson cavity (134) by a modified Raytheon CMD-5
diathermy unit capable of providing up to 100 Watts. The unit was
power regulated as described by Brandenburger (135) in order to insure
constant light intensity for a given gas pressure. The gas pressure
was set using a precision metering valve.

Finally, a 1500 A thick Al (1% Si) filter (136) was placed near
the end of the final stainless steel capillary tube within the UHV
chamber. The filter removes the unavoidable hydrogen alpha line at
10.8 eV, providing a wider range of useful energies below the Fermi
edge in the Ne I and He I spectra.

To perform Ne I and He I measurements, the CMA pass energy was set
to 25 eV. Theoretically, the CMA resolution is 0.7% of the pass
energy (i.e., ~0.18 eV for a pass energy of 25 eV), but in practice it
is somewhat larger. The instrumental resolution was estimated from
the half-width of the Fermi-edge in the clean vanadium UPS results,
and is <0.40 eV for a pass energy of 25 eV. To offset lower count
rates resulting from lower photon fluxes when using the Ne II or the
He II lines, the pass energy was increased to 50 eV and 100 eV
respectively, thus decreasing the resolution somewhat. One should also
note the presence of a $\hbar \omega = 27.6$ eV shoulder in the Ne II curves
reported here (see Chapter V).
For all of the metals and compounds studied here, the Fermi level can be easily located by the midpoint of the initial sharp rise in the photoelectron intensity. As discussed in Chapter III, this rise occurs at a kinetic energy of $\hbar \omega - \phi_c$ ($\phi_c$ is the CMA collector work function energy, consistently found to be 4.9 eV). The energy distribution curves are shown with the energies measured with respect to $E_p = 0$ eV, and indicate the initial state energy below $E_p$.

In order to determine the sample work function energy using the methods discussed in Chapter III, it was necessary to bias the samples a few volts below ground potential. This shifts the entire EDC to higher kinetic energies and allows one to measure the entire curve even though the sample work function energy is less than $\phi_c$.

**F. ELS Measurements**

All energy loss measurements were taken using a grazing incidence electron gun and the double-pass CMA in the preretarding mode (137). Primary electron energies ($E_p$) between 100 eV and 1000 eV were used. The loss energies reported are the average of several measurements taken at $E_p = 500$ eV. Loss energies taken using other $E_p$ values were essentially identical. The full width at half maximum (FWHM) of the primary beam decreased from $\sim 0.7$ eV for $E_p = 1000$ eV to $\sim 0.4$ eV for $E_p = 100$ eV. Beam currents ranged from 10 $\mu$A at $E_p = 1000$ eV to $< 1$ $\mu$A at $E_p = 100$ eV. The energy loss curves are shown with the energy measured relative to $E_p$ (i.e., an energy loss of 25 eV implies $E_p - 25$ eV is the kinetic energy actually measured).
The undifferentiated loss spectra N(E) were recorded in a pulse counting mode. Typical count rates were $10^6$ CPS in the elastic peak and $10^4$ CPS in the maximum of the secondary electron spectrum. For N(E) spectra, the CMA pass energy was set to 15 eV for scaling convenience in recording the curves on an x-y recorder. The resolution in these N(E) spectra is thus limited by the FWHM of the primary electron beam. N(E) spectra were recorded primarily for intensity information and its dependence on $E_p$.

To more accurately resolve and locate the energies of the different loss peaks, derivative spectra were recorded using standard synchronous detection methods. For dN/dE, 25 KHz, 0.5 volt peak-to-peak modulation was applied to the outer CMA cylinder and a pass energy of 50 eV was used. Electron excitations from core levels to the Fermi level typically give rise to a kink or step-like shape in N(E) (119) and can be located by a step or peak respectively in dN/dE. The second derivative, $-d^2N(E)/dE^2$, was recorded at 2 volt peak-to-peak modulation. Electron excitation of collective (plasmon) oscillations of the valence electrons leads to peaks in the low energy region (energy loss $\leq$30 eV) of the loss curve and can be located by peaks in the negative second derivative curve, a measure of the curvature in N(E). Such a measurement discriminates against shifts due to smoothly varying background contributions to N(E).

These techniques for obtaining reflection ELS curves have been proven reliable in previous work on several pure transition metals (119), giving loss energies in good agreement with both transmission ELS and ultraviolet optical experiments.
V. RESULTS AND DISCUSSION

A. Vanadium and VNₓ

Before proceeding to the VNₓ results, it will be simplest and most efficient to first review completely the results for vanadium. As mentioned in Chapter IV, vanadium turns out to be an extremely difficult material to clean at the level required for these spectroscopic measurements. The high temperatures required to boil off surface oxides also cause surface segregation of bulk impurities (present at ppm levels) that cannot be removed by simple heating at temperatures below the melting point (1890°C) of vanadium.

The best efforts (see Chapter IV for the techniques involved) resulted in apparently "clean" Auger spectra (see Fig. 14). However, the overlap of the V-L₂,₃VV peak (∼510 eV) and the O-KL₂,₃L₂,₃ peak (∼513 eV) make the unambiguous identification of small amounts of oxygen on vanadium very difficult (138). One must resort to the O-KL₁L₂,₃ peak (∼493 eV) which is typically much less intense than the O-KL₂,₃L₂,₃ contribution. The detection of oxygen present in small amounts on vanadium is demonstrated by the "dirty" Auger spectra shown in Fig. 14. A less noticeable indication of the oxygen is a slight broadening of the V-L₂,₃VV peak.

Photoemission results for a "clean" vanadium foil are shown in Fig. 15. The calculated density of states of Boyer et al. (139) is shown in Fig. 16 for comparison. Although the AES results show no oxygen contamination, the O 2p levels are easily recognized in the photoemission results. There is little correlation between the EDC's
Figure 14. Two Auger curves demonstrating the detection of a small amount of oxygen on vanadium. The major oxygen peak (O-KL_{23}L_{23}) overlaps the highest energy vanadium peak, forcing one to rely on the less intense O-KL_{23}L_{23} peak at ~493 eV to estimate the oxygen concentration.
Figure 15. Photoelectron EDC's from "clean" vanadium taken at $E_0 = 16.8$ and 21.2 eV. The structure centered around -6.6 eV is due to 0 2p states, even though AES results indicated an oxygen-free surface. The curves are normalized with respect to the peak near $E_F = 0$ eV.
Figure 16. The calculated density of states for vanadium of Boyer et al. (139)
and the calculated DOS because of the 0 2p states centered at about -6.6 eV. Experimentally, strong photoemission is seen at $E_F$ with only a shoulder at about -1.5 eV. The V 3d bandwidth appears to be approximately 3.0 eV, but it is difficult to be more precise due to the interference of the 0 2p states.

To verify oxygen as the origin of the -6.6 eV peak, EDC's were recorded from freshly sputtered, unannealed foils (see Fig. 17). Only a hint of the oxygen peak remains as a broad hump centered around -6.0 eV (the rise above the dashed line is the estimate of the remaining 0 2p contribution). The agreement with the calculated DOS actually improves slightly, but sputter-induced artifacts are probably present so Fig. 17 should not be considered representative of clean, annealed vanadium.

At any rate, it may be concluded that the "clean" vanadium foil is actually partially covered with oxygen. Although the oxygen is easily seen in UPS results, the amount must be small ($\lesssim 1\%$ of a monolayer) since it cannot be detected with AES. The much higher sensitivity of UPS (versus AES) to oxygen is not unusual, as will be discussed in reference to Nb and Zr.

The ELS results for vanadium (shown in Fig. 18) have been published previously (119). A brief review will facilitate later comparisons with VN$_x$ results. In the collective, or low energy region (energy losses $\lesssim 30$ eV) four peaks were observed in $-d^2N/dE^2$. These structures were identified through comparison with optical results (140,141), as the volume and surface contributions of two sets of
Figure 17. Photoelectron EDC's from unannealed, sputter cleaned vanadium taken at $\hbar \omega = 16.8$ and 21.2 eV. Note the reduction of the O 2p contribution (estimated as the rise above the dashed background curve) relative to Fig. 15. However, sputter-induced artifacts are probably present in these spectra. The curves are normalized with respect to the peak near $E_F = 0$ eV.
Figure 18. ELS results for "clean" vanadium taken at $E_p = 690$ eV (from Ref. 119)
collective electron oscillations (plasmons). A free electron plasmon energy calculation using the V 3d and 4s electrons matches fairly well the highest energy peak in the collective region (22.3 eV calculated versus 21.5 eV experimental). The associated surface plasmon for the same group of electrons occurs experimentally at 14.8 eV. A set of "lowered" plasmons (140,141) is observed at 9.6 eV and 5.3 eV (volume and surface respectively). Analysis of the optical data (140,141) allowed identification of these peaks as due to collective oscillations, but more damped than the free-electron-like plasmons. A microscopic model explaining the origin of these "lowered" plasmons is apparently not available, although they are observed in many of the transition metals (119). Plasmon identifications from the present reflection ELS results alone must be considered tentative since the behavior of \( \varepsilon_1 \) and \( \varepsilon_2 \) cannot be readily determined (see Chapter III).

In the higher energy loss region (loss energies \( \gtrsim 30 \) eV), one observes the excitations of the V 3p and 3s core levels (at \( \sim 36.6 \) eV and \( \sim 66.9 \) eV respectively) in dN/dE. These numbers are close to the x-ray atomic energy levels (142) and XPS determined core level energies of V (138). In addition to the core levels associated with the V 3p threshold, one observes structure extending to \( \sim 20 \) eV higher loss energies. This type of additional structure is observed in nearly all of the transition metals and many of their compounds, both by ELS (129, 143-146) and by x-ray absorption measurements (147,148). Several alternate explanations have been proposed (see Ref. 119), and recently, considerable progress has been realized especially for those metals
with nearly filled d-bands (149-152). A review of much of this
work is presented in Ref. 153. However, for metals with less than half
full d-bands, the problem becomes more complex due to the large number
of possible final state configurations. The additional structure
apparently is related to the unfilled states just above $E_F$, but not in
a simple fashion.

A typical Auger spectrum for a δ-VN sample is shown in Fig. 19.
As mentioned in Chapter IV, AES does not give a good absolute determi­
ation of the nitrogen-to-vanadium atomic ratio ($x$) from sample to sample.
It is useful for monitoring changes in $x$ on a single sample during
cleaning processes, and also gives a good indication of the surface
impurities. The spectrum, shown in Fig. 19, shows no carbon (which
would appear at $\sim$270 eV) or oxygen (the O-KL$\alpha_1$ peak would appear at
$\sim$493 eV), the two most common impurities when working with the nitrides.

There are differences in the vanadium Auger signature which can
be understood in terms of the chemical environment in the nitride.
Most noticeable is the reshaping of the V-L$_{2,3}$M$_{2,3}$ peak at $\sim$472 eV.
In the nitride, this peak actually shows two contributions, with the
new peak lying about 5 eV lower in energy, and appearing as a kink in
the region of maximum negative slope (the resolution is not sufficient
to completely resolve the two peaks). The two peaks arise from those
present in the VN hybridized valence band (to be discussed below)
through the last step in the V-L$_{2,3}$M$_{2,3}$ V Auger decay. Similar
behavior is seen in Auger spectra from various vanadium-oxides where,
again, two major peaks are seen in the valence band (138).
Figure 19. A typical Auger spectrum for a clean \( VN_x \) sample (shown here for \( VN-F6 \)). Note that there is no evidence of a carbon peak at \( \approx 270 \) eV or the \( 0-KL_{1,2,3} \) peak at \( \approx 493 \) eV.
UPS results for a nearly stoichiometric δ-VN sample are shown in Fig. 20. The calculated DOS for stoichiometric VN of Neckel et al. (17) is shown for comparison in Fig. 21. The experimental EDC's display a double peaked valence band about 8.5 eV wide with a minimum at about -2.0 eV. Strong intensity is observed near $E_F$ while the second peak (at $\sim$5.2 eV) exhibits a shoulder at $\sim$6.8 eV in the 21.2 eV spectrum, but not in the 16.8 eV spectrum. All of these features are at least qualitatively confirmed in the calculated DOS. There the predicted minimum ($\sim$2.7 eV) and the second peak ($\sim$5.8 eV) are somewhat deeper than observed experimentally, but the predicted bandwidth ($\sim$8.5 eV) and the shoulder ($\sim$7.0 eV) agree very well with experiment. The calculation predicts (17) that the states near $E_F$ are primarily ($\sim$80%) of V 3d character. The peak at -5.8 eV seems to be comprised of almost equal parts of V 3d and N 2p states (i.e., very strongly hybridized), while the -7.0 eV shoulder is $\sim$75% N 2p in character. The calculated DOS also shows the N 2s states about 16 eV below $E_F$, but these are too deep to be observed in the present experiments. The full energy widths of the two EDC's both predict a work function energy of 4.1 eV $\pm$ 0.1 eV for VN-11.

The strongly hybridized region exhibits some residual angular dependences as shown in Fig. 22. The apparatus used for these experiments does not allow independent variation of the incidence and collection angles, and the meaning of "most normal incidence" (MNI) and "most grazing incidence" (MGI) in the present context is shown in the inset to Fig. 22. For every δ-VN sample studied, better resolution of
Figure 20. Photoelectron EDC's for sample VN-11 (x = 0.94) taken at $\hbar\omega = 16.8$ and 21.2 eV. The curves are normalized with respect to the peak near $E_p = 0$ eV.
Figure 21. The calculated density of states for VN$_{1.00}$ of Neckel et al. (17). Dotted curve: N 2s states; dashed curve: N 2p states; solid curve: V 3d states
Figure 22. Photoelectron EDC's from sample VN-11 demonstrating the angular dependence of the intensity from -4 to -8 eV for $\hbar \omega = 21.2$ eV. The inset shows the meaning of "most normal incidence" (MNI) and "most grazing incidence" (MGI) in the present context.
the peak and shoulder (at -5.3 eV and -7.0 eV respectively) was obtained at the MNI setting, yet the peak position and the bandwidth remained constant. The exact meaning of this angular dependence is difficult to determine from the present data alone. It could represent simply penetration depth effects or it could result from an actual dispersion of the bands involved in the -7.0 eV shoulder. An angular dispersion is possible even though these are angle-integrated measurements, because the samples display large (1-2 mm) grains and the CMA does not integrate over all emission angles.

Figure 23 shows EDC's at four photon energies for sample VN-9 (x = 0.92). The 26.9 eV spectrum shows a shoulder at E_p and an artificial low energy broadening of the -5.2 eV peak due to the neon satellite line at 27.6 eV. Note also that the resolution is lower for the 26.9 eV and 40.8 eV curves because the CMA pass energy was increased from 25 eV to 50 eV and 100 eV respectively to offset the smaller signal strengths. All four curves are normalized with respect to the peak near E_p. As the photon energy increases, the minima and peak positions, as well as the hybridized bandwidth, remain fairly constant. The -7.0 eV shoulder grows in intensity as \( \hbar \omega \) increases. The shoulder is never observed (for samples of any x-value) at \( \hbar \omega = 16.8 \) eV and is nearly as intense as the major peak (at -5.2 eV) for \( \hbar \omega = 40.8 \) eV. As mentioned above, this peak is primarily N 2p in character in the DOS, suggesting that the observed intensity increase is related to the N 2p photoexcitation cross section. Similar intensity variations have been observed in TiN (47), but results at higher \( \hbar \omega \) suggested that final state effects might also be important.
Figure 23. Photoelectron EDC's for sample VN-9 (x = 0.92) taken at $\hbar \omega = 16.8, 21.2, 26.9$ and 40.8 eV. The spectra are normalized with respect to the peak near $E_F = 0$ eV. The resolution decreases for $\hbar \omega = 26.9$ and 40.8 eV because the CMA pass energy was increased to offset smaller signal strengths. The shoulder above $E_F = 0$ and the broadening of the left side of the $-5.0$ eV peak in the $\hbar \omega = 26.9$ curve are due to a near satellite line at $\hbar \omega = 27.6$ eV.
Along these lines, it is found that the observed valence band consistently appears narrower in the $\hbar \omega = 16.8$ eV EDC's than for those taken at higher $\hbar \omega$. This is apparently due to the lack of suitable final states at the lower photon energy.

A major goal of this work has been to study the effects of the nitrogen-to-vanadium atomic ratio ($x$) on the electronic structure. UPS results for samples of several different $x$ values are shown in Figs. 24 and 25 and are listed in Table 4. As mentioned in Chapter IV, samples VN-4 and VN-9 should be relied upon most heavily for compositional comparisons in the experimental data. Again, the curves are normalized with respect to the peak near $E_F$. As discussed in Chapter I, several different theoretical approaches to this problem have been tried, with little agreement among the different results (23,24,27,28, 154). The rigid-band model is particularly tempting because of its simplicity, and makes several predictions relative to the present results. First, as $x$ decreases, the Fermi level should shift downward through the rigid bands and the occupied portion of the hybridized bands would narrow. The peaks and minimum should appear nearer $E_F$. The experimental results presented in Figs. 24 and 25 lend little support to the rigid-band model. In Fig. 24, the hybridized band is only very slightly narrower for $x = 0.76$ than for $x = 0.92$ (~0.2 eV). The minimum lies slightly deeper for VN$_{0.76}$ than for VN$_{0.92}$, and the second peak also lies deeper for VN$_{0.76}$, both trends opposite to the rigid-band predictions. The -7.0 eV shoulder disappears almost completely at $x = 0.76$ (this was not due to the angular dependence shown
Figure 24. Photoelectron EDC's taken at $\hbar \omega = 21.2$ eV for several VN$_x$ samples ($0.76 \leq x \leq 0.96$). The curves are normalized with respect to the peak near $E_p = 0$ eV. Samples VN-4 ($x = 0.76$) and VN-9 ($x = 0.92$) should be relied upon most heavily for compositional comparisons.
Figure 25. Photoelectron EDC's taken at $\hbar \omega = 16.8$ eV for several $\delta$-$\text{VN}_x$ samples ($0.76 \leq x \leq 0.96$) plus a $\beta$-VN sample. The curves are normalized with respect to the peak near $E_F = 0$ eV. Samples VN-4 ($x = 0.76$) and VN-9 ($x = 0.92$) should be relied upon most heavily for compositional comparisons within the $\delta$-phase.
Table 4. UPS results for \( \text{VN}_x \)

<table>
<thead>
<tr>
<th>Sample</th>
<th>( x )</th>
<th>( E_D ) (eV)</th>
<th>EDC Peaks (eV)</th>
<th>EDC Minimum (eV)</th>
<th>Bandwith (eV)</th>
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<tr>
<td>VN-4</td>
<td>0.76</td>
<td>16.8</td>
<td>-0.3 5.4</td>
<td>-2.2 7.8</td>
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<tr>
<td></td>
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<td>21.2 -0.3 5.5</td>
<td>-2.3 8.3</td>
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<td>-2.3 7.7</td>
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<td>21.2 -0.3 5.5</td>
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<tr>
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<td>-2.0 8.5</td>
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<td>40.8 -0.3 5.3</td>
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<td>VN-10(^a)</td>
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<td>-1.9 8.0</td>
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<td>VN-11</td>
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<tr>
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<td>-2.1 8.5</td>
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<tr>
<td>VN-F6</td>
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<td>-2.2 8.1</td>
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<td>-2.0 8.5</td>
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<tr>
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<td>( E_F )</td>
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<td>VN-F2(^b)</td>
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<td>21.2 -0.25 5.5</td>
<td>-2.5 8.9</td>
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\(^a\)Sample VN-10 showed approximately 5% \( \beta \)-VN in the x-ray diffraction pattern.

\(^b\)Sample VN-F2 contained considerable oxygen but still showed reasonable superconducting characteristics. AES results indicated an approximate composition of \( \text{VN}_{0.70.2} \).
in Fig. 22), but is present at larger x values. The results for $\hbar \omega = 16.8$ eV shown in Fig. 25 show essentially the same behavior, except that the -7.0 eV shoulder is never visible.

Some of the experimental observations are more in line with the theoretical predictions of Klima (28) (see Chapter I). Since Klima worked with TiC$_x$, some details of his predictions would undoubtedly be different for VN$_x$, because the details of the TiN and VN band structures are different. Some general results should be common to both compounds. In particular, the reduction of the nonmetal 2p contribution to the DOS as x decreases seems to be observed in the disappearance of the -7.0 eV shoulder (due primarily to N 2p states) in sample VN-4 (x = 0.76). The shift of the minimum and the second peak to deeper binding energy as x decreases is also consistent with Klima's calculations.

The present results are in qualitative agreement with optical (43) and UPS (44,45) studies of TiC$_x$ (see Chapter I) where, again, no definitive rigid-band evidence was found. Apparently, the compositional changes induce a more complicated reshaping of the valence band rather than a simple rigid-band shift of $E_F$.

For reference, it is informative to present UPS results from a badly oxygen-contaminated $\delta$-VN sample (note that the sample still displayed respectable superconducting characteristics). Figure 26 shows the AES results while Fig. 27 shows the EDC's. The oxygen effects are readily discernible in the photoemission curves. Most obvious is the increased bandwidth (by $\sim 0.4$ eV) and the loss of structure within the second major peak. The minimum and peak positions also move to
Figure 26. Auger spectrum from an oxygen contaminated $\delta$-VN sample (VN-F2). Note the presence of the O-KL$_{1}$L$_{2,3}$ peak at $\approx$493 eV and the alteration of the shape of the highest energy structure relative to that for an oxygen-free VN$_x$ sample (see Fig. 19)
Figure 27. Photoelectron EDC's from an oxygen contaminated 6-VN sample (VN-F2) taken at $\hbar\omega = 16.8$ and 21.2 eV
slightly (~0.3–0.4 eV) deeper binding energies than for an oxygen-free sample. These changes might be anticipated when one compares the calculated densities of states for VN and VO (17).

ELS results for sample VN-11 (x = 0.94) are shown in Fig. 28. The following comparisons can be made with the vanadium ELS results shown in Fig. 18. In $dN/dE$, the V 3p and 3s core levels are observed to shift to greater binding energy in the nitride (36.6 eV → 39.5 eV for the V 3p and 66.9 eV → 68.0 eV for the V 3s). This shift is consistent with, but not proof of, a charge transfer from the vanadium atoms to the nitrogen atoms. The additional structure extending ~20 eV beyond the V 3p threshold is observed to change shape in the nitride. As mentioned previously, this structure is poorly understood in the loss spectra of vanadium. If it is somehow related to the unfilled states just above $E_F$, the hybridization of the valence band in the nitride would lead one to expect a change in shape, but details cannot be predicted.

In the low energy region (loss energies ~30 eV) of $-d^2N(E)/dE^2$, the differences between V and VN are more striking. First, one observes the shift of the free-electron-like volume plasmon from 21.5 eV in V to ~25.2 eV in VN-11, reflecting the increased valence electron density. (Free electron calculations including the V 3d and N 2p electrons yield 24.9 eV for stoichiometric VN.) The identification of the free-electron-like surface plasmon is more difficult for VN. Two possibilities exist in either the shoulder at ~21.0 eV or the peak near 15.6 eV. (The surface plasmon occurred at 14.8 eV in V.) More will be said about this in later paragraphs.
Figure 28. ELS results for sample VN-11 (x = 0.94) taken at $E_p = 500$ eV
The "lowered" plasmons of vanadium seem to persist in δ-VN, also shifting to higher energies (9.6 eV and 5.3 eV in V to ~11.0 eV and ~6.9 eV for VN-11 for the volume and surface components respectively).

Besides the collective oscillations mentioned above, one also observes an extremely sharp peak at ~2.8 eV energy loss in VN that was not present in V. The loss is tentatively labeled as due to interband transitions involving states near E_F. Several possibilities appear in the band structure (17) but an exact assignment is not possible solely from the present experiments.

To gain more insight into the volume versus surface nature of the various losses, it is helpful to examine the loss intensities as a function of the primary energy E_p. Generally, one expects volume contributions to dominate at higher primary energies E_p, and surface contributions to become more prominent at lower E_p (see Chapter III). The results of such work are shown in Fig. 29 for sample VN-11 (x = 0.94). Primary energies from 100 eV to 1000 eV have been used and the light vertical lines mark the loss energies determined at E_p = 500 eV from the derivative spectra. The loss energies do not exhibit strong E_p dependences, indicating that the assumptions of the dielectric theory (see Chapter III) are not being badly violated. The curves are normalized with respect to the elastic peak shown (at reduced gain) at zero energy loss. No attempt has been made to remove the multiple scattering background which is quite evident in the E_p = 100 eV spectrum. (A sharply rising background starting at about 50 eV kinetic energy is always present in these experiments.) Note the improved
Figure 29. ELS N(E) spectra for sample VN-11 (x = 0.94) recorded at several different primary energies (100 eV ≤ E_p ≤ 1000 eV). Volume contributions should dominate at higher E_p values while surface contributions should be more prominent at lower E_p values. The curves are normalized with respect to the elastic peak shown (reduced by 33.3 times) at zero loss energy. The light vertical lines mark the loss energies determined from \( \frac{dN(E)}{dE} \) and \( -\frac{d^2N(E)}{dE^2} \) at \( E_p = 500 \) eV.
resolution of the low energy side of the 2.8 eV peak as $E_p$ decreases. This is due to the reduction in the primary beam energy width at smaller $E_p$ values (see Chapter IV).

The additional structure associated with the V 3p threshold decreases in intensity as $E_p$ decreases. This may indicate an energy dependence for the cross sections for these excitations.

The volume nature of the 25.3 eV plasmon is evident. At $E_p = 1000$ eV, this plasmon is the dominant feature of the loss curve. As $E_p$ decreases, the intensity of this peak drops until, at $E_p = 100$ eV, the weight of the peak seems to have shifted to the 21.0 eV shoulder. This also provides evidence for identifying the shoulder as the free-electron-like surface plasmon (rather than the 15.3 eV loss peak).

Evidence also exists for the proposed surface origin of the 7.0 eV peak. As $E_p$ decreases, the intensity increases in this region of $N(E)$ (between the 2.8 eV peak and the 11.0 eV peak). This causes poorer resolution of the high energy loss side of the 2.8 eV peak in spite of the improving instrumental resolution mentioned earlier.

No other ELS data on TMNC's (other than that to be discussed later in this work) are available for comparison. Loss functions calculated from optical work on $\text{TiC}_x$ (43) do provide a point of reference. These optical results reveal qualitatively similar features. Two sets of collective oscillations are observed with the highest energy peak corresponding to the free-electron-like volume collective oscillation of the valence electrons. No corresponding low energy peak is seen in the optical results, but reflection ELS experiments can violate the
dipole selection rules governing optical excitations. These similarities and the success of previous ELS work on the pure transition metals (119) give us reasonable confidence in the results presented here.

Compositional dependences within the ELS curves are depicted in Fig. 30 and the corresponding loss energies are tabulated in Table 5. Also included in Fig. 30 are the ELS curves for V and $\beta$-VN. The $\beta$-VN sample is easily distinguished from the $\delta$-VN samples both in $dN/dE$ and in $-d^2N/dE^2$. The V 3p and 3s core levels appear to shift almost immediately to the greater binding energy (i.e., no monotonic increase within the $\delta$-phase is apparent as x increases). The relatively low resolution of this experiment may prevent the observation of shifts of only a few tenths of an electron-volt. Monotonic increases have been observed for deeper titanium core levels in XPS work on TiC$_x$ (29), but the magnitude was $\approx 0.2$ eV. One would also expect the volume plasmon frequency to reflect changes in x via the valence electron density. Such behavior was observed in the optical experiments on TiC$_x$ (43). For $\delta$-VN, the free-electron plasmon energy should shift from $24.2 \text{ eV}$ at VN$_{0.72}$ to $24.9 \text{ eV}$ at VN$_{1.00}$. For the x range covered in the present experiment, a 0.4 eV shift is expected. However, no such trend is observed and, in fact, a small shift in the opposite direction is found. These differences may again be within the experimental uncertainty.

B. Nb and NbN$_x$

As with V and VN$_x$, I will first present the results for pure Nb and then move on to NbN$_x$. As discussed in earlier chapters, clean Nb can
Figure 30. ELS curves recorded at $E_p = 500$ eV for several $VN_x$ samples ($0.76 \leq x \leq 0.96$) plus V and $\beta$-VN. (a) The first derivative curves. (b) The negative second derivative curves.
Table 5. Loss energies for VN \(_x\) (\(E_p = 500\) eV)

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<th>Sample</th>
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<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
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\(\hbar \nu_p\)  

24.9

\textsuperscript{a}The loss values reported here and in later tables are the average of several measurements. The standard deviation is given in parentheses.

\textsuperscript{b}This sample showed approximately 5\% \(V_2N\) in the x-ray diffraction pattern.

\textsuperscript{c}Free electron volume plasmon energy calculated including the V 3d and N 2p electrons for \(VN_1.00\). Inclusion of N 2s electrons yields 27.8 eV.
be obtained through simple high temperature (>2000°C) outgassing at low pressures ($\leq 1 \times 10^{-9}$ Torr). Both Auger and UPS spectra from samples cleaned in this manner showed no evidence of oxygen, carbon or other contaminants. It is well-known (106,130,131) that UPS is much more sensitive than AES to oxygen on Nb, and usually considerable additional outgassing was required to obtain oxygen-free UPS results even after AES indicated a clean sample.

EDC's taken at $\hbar \omega = 16.8$ eV and 21.2 eV are shown in Fig. 31, along with the calculated DOS (155). These results are in excellent agreement with those found in the literature (106,130,131) and the agreement with the calculated DOS is obvious. The observed valence bandwidth of about 3.9 eV is in good agreement with the $\sim 4.0$ eV calculated bandwidth. A strong peak near $E_F$ (-0.4 eV) is observed, as is common for many of the early d-band transition metals. In the angle-resolved work of Smith (131), this peak has been associated with the local minimum between $\Gamma$ and N where the $\Sigma_1$ band crosses the Fermi level (156). Two other structures are easily discernible, i.e., the shoulder at -1.1 to -1.3 eV and the second strong peak at -2.3 to -2.8 eV. These two structures show strong dependence upon the photon energy, indicating that direct transitions are playing an important role. In addition, the shoulder intensity was observed to vary strongly with the emission and incidence angles (see the inset to Fig. 22). This peak in the calculated DOS (155,156) arises from states near $N_2$ in the band structure (N is the center of the 110 face in the bcc Brillouin zone). Well outgassed and recrystallized Nb foils have been shown (131) to grow large single crystal grains preferentially oriented with the 110
Figure 31. Photoelectron EDC's for Nb taken at $\hbar \omega = 16.8$ and 21.2 eV. The dashed curve shows the shape of the theoretical density of states calculated by Mattheiss (155).
direction normal to the foil surface. In the angle-resolved UPS work, Smith (131) proposed an $N_1$ final state for this structure. Dipole selection rules would normally forbid this transition (157), but angle-integrated measurements would relax this restriction. It therefore seems appropriate to associate this shoulder with the $E_2$ band. The second major peak can be related to the lowest lying $E_1$ band (156). The shift of the peak to deeper binding energy, as the photon energy increases, is consistent with the shape of this band and the associated final state $N_1$ band proposed by Smith (131). However, it lies somewhat closer to $E_F$, and shows more dispersion with $\hbar \omega$ than observed in those angle-resolved measurements. Also worth noting is the constant position of the minimum at -1.8 eV, regardless of the photon energy. This minimum is attributed to the gap between bands one and two (131,156) in the calculated DOS.

ELS results for clean Nb are shown in Fig. 32. These results are identical to those published previously (119) except that two additional peaks have been resolved at loss energies below 5 eV. These results were shown in Ref. 119 to be in excellent agreement with the optically determined volume and surface loss functions of Weaver et al. (141).

As with V, a free-electron-like volume plasmon is observed, this time at 20.8 eV. A free electron calculation including the Nb valence electrons yields 19.6 eV. Optical experiments (141) also located the volume plasmon at 20.8 eV, indicating that the plasmon energy has been pushed up due to interband absorption at lower energies. The associated surface plasmon appears in the present work at 18.3 eV and is found to be 17.7 eV optically (141).
Figure 32. ELS results for Nb taken at $E_p = 500$ eV. The arrows mark the plasmon and "lowered" plasmon energies determined from the optical work of Weaver et al. (141)
One observes the "lowered" plasmons also found in V. In Nb, these were located optically at 9.7 eV (volume) and 9.0 eV (surface) (141). In the present results, one observes a single peak at 9.6 eV, indicating that the volume and surface components were not resolved. The optically determined plasmon energies are marked by the arrows in Fig. 32.

Some confusion persists in the literature about the identification of the volume plasmon in Nb. Several investigators (158-161) identify the peak at 9.6 eV as the volume plasmon while attributing the higher energy loss peaks to multiple plasmon losses. Experimentally, this is often justified by pointing out that the 9.6 eV peak is the dominant feature in the dN/dE spectra. This can be misleading, however, and one should rely on the undifferentiated loss curve N(E) to gather intensity information. It is apparent in Fig. 32 that the peak centered around 20 eV dominates N(E), yet the narrower (and less intense in N(E)) structure at 9.6 eV is most prominent in dN/dE. In addition, the detailed behavior of $\varepsilon_1$ and $\varepsilon_2$ as determined from the optical results (141), supports the identification of the 20.8 eV peak as the volume plasmon. The 9.6 eV structure shows collective behavior, but is more strongly damped than the higher energy peak (thus, its identification as a "lowered" plasmon).

The low energy peaks (2.8 eV and 4.9 eV loss energies) could arise from some unspecified interband excitations. Reference 141 showed much fine structure in the low energy region of the calculated loss functions which correlated well with peaks in $\varepsilon_2$. Interband transitions between the filled states below $E_F$ and a high density of unfilled states
centered about 3 eV above $E_F$ could give rise to the above mentioned loss peaks.

At higher loss energies, one observes the Nb 4p (30.3 eV) and 4s (57.9 eV) core level thresholds in $dN(E)/dE$. From UPS work at higher photon energies, on Nb foils prepared in much the same manner, Miller (130) located the 4p core levels at 30.8 eV ($j = 3/2$) and 32.5 eV ($j = 1/2$) below $E_F$. The splitting is not seen in the present ELS results, but the energy agreement with the lowest lying 4p state is reasonable. The atomic 4p energy level has been reported at 33.9 eV while the atomic 4s level is 58.1 eV (142). As with V, one observes additional structure extending some 20 eV beyond the 4p threshold. Once again, this cannot be simply explained in terms of the density of final states.

As mentioned in Chapter IV, the NbN$_x$ samples presented more difficulties than VN$_x$ in terms of homogeneity and surface cleanliness. The earliest in situ samples contained considerable amounts of impurity phases while later samples, although single phase, were all of approximately the same composition, displayed broad $T_c$'s and contained small amounts of carbon and oxygen (at least in the surface region). The externally fabricated sample NbN-F1 also showed regions of differing $T_c$ and contained oxygen as a bulk impurity. Due to these sample limitations, the effect of the x value on the electronic structure of $\delta$-phase NbN$_x$ cannot be determined from the present results.

A typical Auger spectrum is shown in Fig. 33 for sample NbN-F1. The sum total of nitrogen and oxygen is estimated roughly from comparison
Figure 33. Auger curve for a δ-NbN sample (NbN-Fl). The inset shows the Nb Auger signature of the pure metal for comparison. Structures involving valence band states are altered in shape due to the new chemical environment in the nitride. This sample contained oxygen as a bulk impurity.
of the lattice constant and data already in the literature (see Chapter II), while the Auger intensities are used to determine the relative amounts of nitrogen and oxygen. As with VN\textsubscript{x}, the Nb signature displays differences from the pure metal spectrum (shown as an inset in Fig. 33), reflecting the new chemical environment. In particular, all Auger peaks involving the valence band states now show two contributions due to the double peaked valence band DOS of the nitride (see the M\textsubscript{4,5}N\textsubscript{1}V structure at ~142 eV, the M\textsubscript{4,5}N\textsubscript{2,3}V structure at ~167 eV and the M\textsubscript{4,5}VV structure at ~197 eV). This also causes an apparent reduction in intensity in the dN/dE spectrum of these peaks. This is at least part of the reason that the published sensitivity factors (Ref. 162) yield very poor results in determining the absolute nonmetal-to-metal ratio (a nitrogen-rich composition relative to that determined by other methods is always indicated) for these compounds. Not understood, is the apparent increase in relative intensity (compared to Nb) of the M\textsubscript{4,5}N\textsubscript{1}N\textsubscript{2,3} structure at ~105 eV.

Figure 34 shows UPS results for NbN-3 (NbN\textsubscript{0.8C0.05}O\textsubscript{0.05}) at h\omega = 16.8 and 21.2 eV, while Fig. 35 shows for comparison the DOS for stoichiometric NbN calculated by Schwarz (21). As with VN\textsubscript{x}, a double peaked valence band is experimentally observed, with the peaks occurring near E\textsubscript{F} (~0.4 eV) and -5.8 eV, separated by a minimum at -2.6 eV. The hybridized valence bandwidth is seen to be ~8.7 eV. The calculation indicates that the states near E\textsubscript{F} should be ~90% Nb 4d in character, while the second peak (predicted at -5.7 eV) is ~85% N 2p in character. This indicates somewhat less hybridization than in VN\textsubscript{x}. The calculated
Figure 34. Photoelectron EDC's taken at $\hbar \omega = 16.8$ and $21.2$ eV for sample NbN-3 ($\text{NbN}_{0.8}\text{C}_{0.05}\text{O}_{0.05}$). The curves are normalized with respect to the peak near $E_F = 0$ eV.
Figure 35. The calculated density of states for NbN \textsubscript{1.00} of Schwarz (21). Dotted curve: N 2s states; dashed curve: N 2p states; solid curve: Nb 4d states.
minimum position (-3.5 eV) and the bandwidth (~9.0 eV) are somewhat larger than observed experimentally.

The calculated DOS also indicates weak shoulders on either side of the second peak that are not really observed experimentally. Several things could be preventing the detection of this fine structure. First of all, the presence of C and O would tend to wash out details. Secondly, the samples are fairly substoichiometric and inhomogeneous, both of which would possibly smear the spectra. Recent UPS results on NbC (48) also showed rather broad spectra, quite similar to the NbN results. The inherently broad EDC's may simply reflect the greater difficulties in preparing homogeneous, clean, stoichiometric NbN samples (compared to VN).

Comparison of the \( \hbar \omega = 16.8 \) eV and 21.2 eV spectra reveals several interesting features. First, the 16.8 eV spectrum indicates a narrower bandwidth than the higher photon energy. As with VN, this is apparently related to the availability of suitable final states. Secondly, the relative intensity of the second peak is consistently higher in the 16.8 eV spectra. Further work with a wider range and finer adjustment of \( \hbar \omega \) will be required to understand the origins of the intensity changes.

The \( \hbar \omega = 16.8 \) eV results for NbN show an additional peak (relative to the 21.2 eV curves) lying above the minimum in the valence band density of states. The position and width of this peak are sample dependent, as seen in Fig. 36. Its energetic position does not correspond well with any feature in the initial DOS, and no corresponding peak was observed in VN.
Figure 36. Photoelectron EDC's taken at $h\omega = 16.8$ eV for several $\delta$-NbN samples plus Nb and a mixed phase sample. Note that sample NbN-2 also contained $\leq 10\%$ $\epsilon$-NbN. The position and width of the structure at about $-1.1$ eV is very sample dependent. In addition, this structure does not appear in the $h\omega = 21.2$ eV curves for $\delta$-NbN (see Fig. 37) and it does not correspond well with any features in the calculated DOS (see Fig. 35). The curves are normalized with respect to the peak near $E_F = 0$ eV.
Figures 36 and 37 show EDC's for samples of various compositions. These results are listed in Table 6. The Nb spectra are also shown for comparison. In both the \( E_\omega = 16.8 \) eV and 21.2 eV results, sample NbN-1 stands out from the other nitride samples. Recall that this sample contained almost equal parts of \( \beta, \epsilon, \gamma \) and \( \delta \)-NbN (see Chapter IV). It is not possible to identify exactly which differences are due to what phase, but it is clear that there are significant differences between the band structures describing the various different phases. NbN-2 also contained a small amount (\( \approx 10\% \)) of \( \epsilon \)-NbN, and small differences in shape between the UPS results from it and the single phase samples NbN-3 and NbN-F1 are also discernible.

In Fig. 37 one notes that the shape of the second peak centered around -5.8 eV is different for each sample. This may be a reflection of the differing amounts of interstitial impurities (i.e., carbon and oxygen) which would change the shape of the filled DOS. The variability of the second peak seems greater at \( E_\omega = 21.2 \) eV than at \( E_\omega = 16.8 \) eV. The minimum position seems nearer \( E_F \) when carbon is present (as in NbN-3). This is consistent with the different DOS of NbC (21), where the carbon 2p levels lie at slightly shallower binding energy than the nitrogen 2p states. The hybridized bandwidths observed here are all slightly narrower than found in the calculations (21), in spite of the presence of oxygen which should serve to increase the bandwidth.

ELS results from sample NbN-3 are shown in Fig. 38. The general shape is somewhat similar to that reported for VN\( _x \). The free-electron-like volume plasmon again shifts to higher energy than in the parent
Figure 37. Photoelectron EDC's taken at $\hbar \omega = 21.2$ eV for several $\delta$-NbN samples, plus Nb and a mixed phase sample. Note that sample NbN-2 also contained $\approx 10\%$ $\epsilon$-NbN. The curves are normalized with respect to the peak near $E_F = 0$ eV.
Table 6. UPS results for NbN\textsubscript{x}

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>( \hbar \omega ) (eV)</th>
<th>EDC Peaks (eV)</th>
<th>EDC Minimum (eV)</th>
<th>Bandwidth (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NbN-2\textsuperscript{a}</td>
<td>NbN\textsubscript{0.79C0.04O0.03}</td>
<td>16.8</td>
<td>-0.3</td>
<td>-1.1</td>
<td>-5.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>21.2</td>
<td>-0.4</td>
<td>-6.3</td>
<td>-2.9</td>
</tr>
<tr>
<td>NbN-3</td>
<td>NbN\textsubscript{0.8C0.05O0.05}</td>
<td>16.8</td>
<td>-0.5</td>
<td>-1.25</td>
<td>-5.9</td>
</tr>
<tr>
<td></td>
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<td>21.2</td>
<td>-0.5</td>
<td>-5.8</td>
<td>-2.7</td>
</tr>
<tr>
<td>NbN-F1</td>
<td>NbN\textsubscript{0.8O0.1}</td>
<td>16.8</td>
<td>-0.4</td>
<td>-1.1</td>
<td>-5.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>21.2</td>
<td>-0.3</td>
<td>-5.5</td>
<td>-2.8</td>
</tr>
<tr>
<td>Schwarz</td>
<td>NbN\textsubscript{1.00}</td>
<td>( E_F )</td>
<td></td>
<td>-6.0</td>
<td>-3.5</td>
</tr>
<tr>
<td>Ref. 21</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Sample NbN-2 showed \( \leq 10\% \) c-NbN in x-ray diffraction measurements.
Figure 38. ELS results for sample NbN-3 (NbN$_{0.8}$O$_{0.05}$_C$_{0.05}$) taken at $E_p = 500 \text{ eV}$.
metal, reflecting the increased valence electron concentration. Its energy (23.5 eV) agrees fairly well with that determined from a free electron calculation including the Nb 4d and N 2p electrons (22.7 eV for stoichiometric NbN). Inclusion of the N-2s electrons (lying ~14 eV below $E_F$ and well-separated from the Nb 4d and N 2p electrons) leads one to expect the volume plasmon at about 25.4 eV, considerably higher than our experimental value. The experimental peak at about 20.4 eV in $-d^2N(E)/dE^2$ is tentatively identified as the associated surface plasmon. This too lies at higher energy than observed in Nb metal (18.3 eV).

Several more structures are observed at lower loss energies whose identifications are more tenuous. The unresolved "lowered" plasmons seen at 9.6 eV in Nb seem to persist in NbN$_x$, now resolved and appearing at 15.0 eV and 12.1 eV for the volume and surface components respectively. (More will be said about these identifications in the discussion of Fig. 39 that follows.) At even lower energies, peaks appear in $-d^2N/dE^2$ at 7.5 eV and 3.4 eV. The peak centered around 7.5 eV may actually be two peaks lying close together as will be discussed in reference to other samples. The sharp 3.4 eV loss peak is reminiscent of the 2.8 eV peak so prominent in the VN$_x$ spectra (see Fig. 28). The similarity to the VN$_x$ peak leads one to consider a similar origin, however, specific interband assignments have not been possible in either case.

In the core level region one again observes the Nb 4p and 4s core level thresholds in $dN/dE$, now appearing at 32.9 eV and 59.0 eV respectively. This represents a shift to deeper binding energy in the nitride
compared to the pure metal. These shifts (30.3 eV → 32.9 eV and 57.9 eV → 59.0 eV) are about the same magnitude as seen in VN^x, and again are consistent with, but not proof of a charge transfer from the metal to the nonmetal atoms. Once again, the poorly understood additional structure extending about 20 eV beyond the 4p threshold is observed, changed in shape from the Nb results.

To aid in the above identifications, Fig. 39 shows the dependence of N(E) on E_p. Again the curves are normalized with respect to the elastic peak intensity at zero energy loss and no attempt has been made to remove the diffuse multiple scattering background. In the collective region, two peaks seem to display volume origin, increasing in intensity as E_p increases. The structure at 15.0 eV loss energy increases from an asymmetric broadening to the peak at 12.1 eV when E_p = 100 eV, to a separate peak of almost equal intensity (to the 12.1 eV peak) when E_p = 500 eV. The composite peak at loss energies just above 20 eV shows similar behavior. These observations seem to support the identifications proposed earlier of the free-electron-like plasmons at 23.5 eV (volume) and 20.4 eV (surface) and the "lowered" plasmons at 15.0 eV (volume) and 12.1 eV (surface). There does not seem to be any strong E_p dependence for the peak intensities at the lower loss energies.

The ELS results for several NbN_x samples and for Nb are depicted in Fig. 40(a and b). These results are tabulated in Table 7. In the core level region of dN/dE, it is easy to see the shifting of the Nb 4p and 4s thresholds to deeper binding energy. Particularly in the 4p case, the shape of the threshold changes significantly as nitrogen is
Figure 39. ELS N(E) curves for sample NbN-3 recorded at $100 \text{ eV} \leq E_p \leq 500 \text{ eV}$. The curves are normalized with respect to the elastic peak at zero energy loss (shown reduced by 33.3 times). The light vertical lines mark the loss energies determined from the derivative spectra recorded at $E_p = 500 \text{ eV}$. Volume related losses should be more prominent at higher $E_p$ values while surface related losses should become more prominent at lower primary energies.
Figure 40(a). ELS $dN(E)/dE$ curves recorded at $E_p = 500$ eV for several $\delta$-NbN samples plus Nb and a mixed phase sample. Note that sample NbN-2 also contained $\leq 10\%$ $\epsilon$-NbN. The curve for the mixed phase sample NbN-1 is easily distinguishable from those for the $\delta$-phase samples.
$E_p = 500\text{eV}$

$\text{NbN}_x$

$\text{NbN-1}$

$\beta, \gamma, \epsilon$ and $B$ - NbN

$\text{NbN-2}$

$(\text{NbN}_{0.79}\text{C}_{0.04}\text{O}_{0.03})$

$\text{NbN-3}$

$(\text{NbN}_{0.80}\text{C}_{0.05}\text{O}_{0.05})$

$\text{NbN-F1}$

$(\text{NbN}_{0.80}\text{O}_{0.1})$

$\frac{dNIEV}{dE}$ (ARBITRARY UNITS)

ENERGY LOSS (eV)
Figure 40(b). ELS $-d^2 N(E)/dE^2$ curves recorded at $E_p = 500$ eV for several $\delta$-NbN samples plus Nb and a mixed phase sample. Note that sample NbN-2 also contained $\leq 10\%$ $\epsilon$-NbN. The curve for the mixed phase sample NbN-1 is easily distinguishable from those for the $\delta$-phase samples.
Table 7. Loss energies for NbN$_x$ ($E_p = 500$ eV)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>A (eV)</th>
<th>B (eV)</th>
<th>C (eV)</th>
<th>D (eV)</th>
<th>E (eV)</th>
<th>F (eV)</th>
<th>G (eV)</th>
<th>H (eV)</th>
<th>J (eV)</th>
<th>K (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NbN-1</td>
<td>$\delta, \varepsilon, \gamma$ and $\beta$-NbN</td>
<td>4.2</td>
<td>5.9</td>
<td>8.3</td>
<td>12.3</td>
<td>19.8</td>
<td>23.1</td>
<td>32.7</td>
<td>40.1</td>
<td>58.9</td>
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<tr>
<td></td>
<td>(0.1)</td>
<td></td>
<td></td>
<td>(0.1)</td>
<td>(0.1)</td>
<td>(0.6)</td>
<td>(0.1)</td>
<td></td>
<td>(0.2)</td>
<td>(0.4)</td>
<td></td>
</tr>
<tr>
<td>NbN-2$^a$</td>
<td>NbN$<em>{0.79}$C$</em>{0.04}$O$_{0.03}$</td>
<td>3.5</td>
<td>6.7</td>
<td>12.2</td>
<td>15.0</td>
<td>20.0</td>
<td>24.0</td>
<td>33.1</td>
<td>35.5</td>
<td>41.0</td>
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<tr>
<td></td>
<td>(0.1)</td>
<td></td>
<td></td>
<td>(0.1)</td>
<td>(0.1)</td>
<td>(0.1)</td>
<td>(0.2)</td>
<td>(0.1)</td>
<td>(0.3)</td>
<td>(0.2)</td>
<td>(0.3)</td>
</tr>
<tr>
<td>NbN-3</td>
<td>NbN$<em>{0.8}$C$</em>{0.05}$O$_{0.05}$</td>
<td>3.4</td>
<td>7.5</td>
<td>12.1</td>
<td>15.0</td>
<td>20.4</td>
<td>23.5</td>
<td>32.9</td>
<td>35.8</td>
<td>40.6</td>
<td>59.0</td>
</tr>
<tr>
<td></td>
<td>(0.1)</td>
<td></td>
<td></td>
<td>(0.1)</td>
<td>(0.1)</td>
<td>(0.3)</td>
<td>(0.2)</td>
<td>(0.3)</td>
<td>(0.4)</td>
<td>(0.2)</td>
<td>(0.3)</td>
</tr>
<tr>
<td>NbN-F1</td>
<td>NbN$<em>{0.8}$O$</em>{0.1}$</td>
<td>3.6</td>
<td>6.5</td>
<td>12.0</td>
<td>15.0</td>
<td>19.7</td>
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<td>40.9</td>
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<tr>
<td></td>
<td>(0.1)</td>
<td></td>
<td></td>
<td>(0.1)</td>
<td>(0.1)</td>
<td>(0.1)</td>
<td>(0.1)</td>
<td>(0.4)</td>
<td>(0.2)</td>
<td>(0.4)</td>
<td>(0.3)</td>
</tr>
</tbody>
</table>

$^{b}$$\hbar\omega$$_p$ 22.7

$^{a}$Sample NbN-2 showed $\approx$10% $\varepsilon$-NbN in addition to the $\delta$-phase in x-ray diffraction results.

$^{b}$$\hbar\omega$$_p$ is the volume plasmon energy resulting from a free electron calculation including Nb 4d and N 2p electrons for NbN$_{1.00}$. Inclusion of N 2s electrons yields 25.4 eV.
added to the metal. The sharp initial edge present in Nb is more rounded in the NbN_x samples. This could be explained in terms of varying core level shifts, depending on the Nb atom's local chemical environment (i.e., the various numbers of N, C, O and vacancies among its nearest neighbors). Such considerations may apply to these samples and could explain the smearing of the threshold.

The sample of mixed phase (NbN-1) is easily distinguishable from the single phase samples even in the core level region. Sample NbN-2 (which contains a small amount of ε-NbN) looks quite similar to the single phase samples.

In the low energy region, the negative second derivative displays some obvious changes as nitrogen is added. The increase in the volume and surface free-electron-like plasmon energies is evident. The lowered plasmons that were unresolved in Nb (and in NbN-1) shift to higher energy and split into resolved volume and surface contributions in the single phase (and NbN-2) samples. One also observes the growth of the lowest energy peak at about 3.5 eV as nitrogen is added. Again, sample NbN-1 is easily distinguished from the other NbN_x samples.

As mentioned earlier, the structure centered around 5-8 eV shows evidence of two contributions. In the single phase NbN_x samples, the shape of the structure in -d^2N/dE^2 is quite variable in this region, but always shows an asymmetric broadening on either the high or low energy side.
C. Zr and ZrN$_x$

As with Nb, clean Zr foils were prepared using extensive high temperature (>1550°C) outgassing at low pressures (<1 x 10$^{-9}$ Torr). This allows surface carbon to diffuse into the bulk and depletes the oxygen content of the foil, and also promotes recrystallization into large single crystal grains. Both AES and UPS indicate a clean foil surface after such treatment.

An EDC for clean Zr taken at $h\omega$ = 21.2 eV is shown in Fig. 41, while for comparison, the calculated DOS is shown in Fig. 42 (163). There is moderately good agreement between the experiment and theory. The sharp minimum in the calculation at about -0.3 eV appears only as a kink in the present results. Correspondence exists between the experimental peak (at -1.0 eV) and shoulder (at about -2.2 eV) and the gross features of the calculation. The fine structure of the calculation cannot be resolved in the present experiment. The EDC shows weak contributions extending to about 4.0 eV below $E_F$. The calculation shows a weak tail down to <-5.0 eV, but the strength is less than 10% of its maximum value by -4.0 eV.

One can also still detect a weak oxygen 2p signal in Fig. 41 giving rise to the broad hump centered about 5 to 6 eV below $E_F$. The dashed line is an estimation of the contribution of secondary electrons in the region, implying that the rise above this line is due to the presence of a very small amount of oxygen.

ELS results for Zr taken at $E_p$ = 500 eV are shown in Fig. 43. In the high energy region, one readily observes the Zr 4p and 4s core
Figure 41. Photoelectron EDC for clean Zr taken at $\hbar \omega = 21.2$ eV. The rise above the dashed curve in the vicinity of -6.0 eV is an estimation of the 0 2p contribution.
Figure 42. The shape of the calculated DOS for Zr (from Ref. 163)
Figure 43. ELS results for Zr recorded at $E_p = 500$ eV
level thresholds at 27.1 eV and 51.1 eV respectively in $dN(E)/dE$. These
energies are close to the x-ray atomic energy levels reported at 28.7 eV
and 51.3 eV for the 4p and 4s (142). As with the other transition metals,
additional structure appears extending about 20 eV beyond the 4p thresh­
old. In $N(E)$, this appears to peak just below 40 eV, while $dN(E)/dE$
indicates a sharp rise at about 33.6 eV.

Four peaks are resolved in the low energy region (in $-d^2N(E)/dE^2$) at
17.0, 13.3, 7.4 and 3.5 eV. Following the previous results for V, Nb,
Mo and Ta (119), these are tentatively identified in order as the free-
electron-like volume and surface plasmons and the "lowered" volume and
surface plasmons. Optical experiments and resulting calculations of the
loss functions by Lynch et al. (164) also identified four peaks in the
low energy region. However, the agreement is poor in terms of overall
shape and the loss energies. The optically derived loss functions
showed much higher intensity in the "lowered" plasmons and also reported
a lower volume plasmon energy (14.6 eV). These results and those of
other workers are collected in Table 8.

Agreement with recent transmission ELS experiments (165) is somewhat
better. In these results, Frandon et al. corrected for multiple scat­
tering and surface contributions to the loss function $Im(-1/\varepsilon)$, so they
did not report the surface plasmon energies. The shape of their loss
function is very similar to the present results except there is less
strength below the volume plasmon peak (this should be expected since
the surface contributions have been removed). Their reported plasmon
energy (16.9 eV) is in very good agreement with the present results.
Table 8. Loss energies for Zr \((E_p = 500 \text{ eV})\)

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
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</thead>
<tbody>
<tr>
<td><strong>Present Work</strong></td>
<td>3.5 (0.1)</td>
<td>7.4 (0.1)</td>
<td>13.3 (0.2)</td>
<td>17.0 (0.1)</td>
<td>27.1 (0.2)</td>
<td>33.6 (0.2)</td>
<td>51.1 (0.2)</td>
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<tr>
<td>Ref. 165</td>
<td>8.0</td>
<td>16.9</td>
<td>27.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ref. 128</td>
<td></td>
<td></td>
<td></td>
<td>15.6</td>
<td></td>
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<tr>
<td>Ref. 164</td>
<td>5.2</td>
<td>5.7</td>
<td>13.4</td>
<td>14.6</td>
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<tr>
<td>Ref. 142</td>
<td></td>
<td></td>
<td>28.7</td>
<td>51.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\hbar\omega_p^a)</td>
<td></td>
<td></td>
<td>(N_{2,3})</td>
<td>(N_1)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(\hbar\omega_p^a\) The free-electron-like plasmon energy calculated including the Zr valence electrons.
They also reported structure near 8 eV, but interpreted this as the envelope of unresolved interband transitions rather than the "lowered" plasmon (calculations of $\varepsilon_1$ in their work did not indicate $\varepsilon_1 = 0$ in this energy region, contrary to the optical results). Frandon et al. also reported the Zr 4p threshold at 27.5 eV, in good agreement with the present results.

The apparent discrepancies between the loss energies determined optically and the ELS results apparently are due to sample surface cleanliness. Zr is a very strong getter for oxygen and its presence would affect loss energies. This has been observed previously in comparisons between optical and ELS results for V (119).

As mentioned earlier, the ZrN$_x$ samples presented special difficulties in regard to surface cleanliness and homogeneity. The $x$-dependence of the electronic structure for the $\delta$-phase cannot be studied from the present results. Comparisons will be made between Zr metal, Zr metal with nitrogen in solid solution (sample ZrN-1) and (B1) ZrN$_x$. Sample ZrN-1 actually was about 50% $\alpha$-Zr with nitrogen in solution and 50% (B1) ZrN$_x$. Using AES, one could easily recognize two distinct compositions. The higher nitrogen regions were associated with the ZrN$_x$ while the lower nitrogen content areas were identified as the solid solution. To avoid confusion, all of the ZrN-1 results presented here are from the solid solution, although good ZrN$_x$ data were also obtained from this sample.

A typical Auger spectrum is shown in Fig. 44 for a single phase, externally fabricated sample ZrN-F1. (Recall from Chapter IV that even
Figure 44. Auger curve for sample ZrN-Fl. The carbon peak at ~270 eV increased during sputter cleaning treatments. The oxygen was present as a bulk impurity. The inset shows the Zr signature from the pure metal for comparison. Valence band related structures are altered in shape due to the new chemical environment in the nitride.
the single phase ZrN\textsubscript{x} samples showed very broad superconducting transitions.) Considerable carbon and oxygen are present, at least in the surface region. Note that the carbon signature is that of the carbide, rather than the graphitic signature typical of sorbed carbon containing gases (162). The sum total of the nitrogen, carbon and oxygen has been roughly estimated from the lattice constant (see Chapter II), while the relative amounts of N, C and O are estimated from the Auger intensities in dN/dE and the published (162) sensitivities for these elements.

As in VN\textsubscript{x} and NbN\textsubscript{x}, the transition metal signature exhibits changes reflecting the new chemical environment of the nitride. Those Auger peaks involving valence band states split due to the double peaked valence band DOS and appear less intense (the pure metal signature is shown in the inset to Fig. 44). Again, this causes difficulties in determining the x value from the Auger intensities.

EDC's for ZrN-F1 are shown in Fig. 45 for \( \hbar \omega = 16.8 \) and 21.2 eV. Apparently, no calculated DOS for ZrN exists in the literature. Not surprisingly, the UPS experiments indicate a double peaked valence band density of states very similar to VN or NbN. Major peaks occur at \( E_F \) and -5.4 eV and are separated by a minimum centered at -2.5 eV. The hybridized Zr 4d and N 2p bandwidth is observed to be about 8.6 eV. The second peak was consistently more intense for \( \hbar \omega = 16.8 \) eV than for \( \hbar \omega = 21.2 \) eV (similar to the case with NbN). There is an apparent shoulder (or at least asymmetry) on the high energy side of the second peak that appears stronger at \( \hbar \omega = 21.2 \) eV.
Figure 45. Photoelectron EDC's for sample ZrN-F1 taken at $\hbar \omega = 16.8$ and 21.2 eV
Figures 46 and 47 compare EDC's from ZrN-1 (solid solution of nitrogen in α-Zr) and ZrN-Fl. These and results from other samples are found in Table 9. Both ZrN-1 and ZrN-Fl display the N 2p states in the region centered about 5 eV below E_p. The occupied bandwidth is narrower for ZrN-1 (7.9 eV as compared to 8.6 eV for ZrN-Fl), and the minimum separating the two peaks lies at slightly deeper initial state energy (-2.9 eV as compared to -2.5 eV for ZrN-Fl). The relative intensity of the second peak is also much less for the solid solution sample (ZrN-1). As with NbN, no fine structure around the second peak is observed. The presence of the C and O may wash out any fine structure that might be present in the DOS.

Table 9. UPS results for ZrN_x

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>ω (eV)</th>
<th>ECD Peaks (eV)</th>
<th>EDC Minimum (eV)</th>
<th>Bandwidth (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrN-1</td>
<td>α-Zr + N</td>
<td>16.8</td>
<td>-0.4</td>
<td>-5.3</td>
<td>-3.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>21.2</td>
<td>-0.3</td>
<td>-5.3</td>
<td>-2.8</td>
</tr>
<tr>
<td>ZrN-2</td>
<td>ZrN_{0.50.10.01}</td>
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<td>-0.35</td>
<td>-5.35</td>
<td>-2.4</td>
</tr>
<tr>
<td>ZrN-Fl</td>
<td>ZrN_{0.80.070.03}</td>
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<td>-0.2</td>
<td>-5.4</td>
<td>-2.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>21.2</td>
<td>-0.25</td>
<td>-5.4</td>
<td>-2.6</td>
</tr>
<tr>
<td>ZrN-F4</td>
<td>ZrN_{0.720.150.03}</td>
<td>16.8</td>
<td>-0.35</td>
<td>-5.3</td>
<td>-2.4</td>
</tr>
</tbody>
</table>

Both ZrN-1 and ZrN-2 showed both α-Zr plus N in solid solution and (B1) ZrN_x in x-ray diffraction results. See text for details.

The ELS results for ZrN-Fl (taken at E_p = 500 eV) are shown in Fig. 48. In the first derivative curve, the low energy structure
Figure 46. Photoelectron EDC's taken at $\hbar \nu = 16.8 \text{ eV}$ comparing (B1) ZrN$_x$ with nitrogen in solid solution in $\alpha$-Zr.
Figure 47. Photoelectron EDC's taken at $\hbar \omega = 21.2$ eV comparing (B1) $\text{ZrN}_x$ with nitrogen in solid solution in $\alpha$-Zr.
Figure 48. ELS results for sample ZrN-F1 recorded at $E_p = 500$ eV. The first structure in $dN(E)/dE$ is shown off scale so that the core level region is seen with sufficient detail.
shown off scale so that the core level contributions appear with suitable strength.

The Zr 4p and 4s core levels shift to deeper binding energies in the nitride, appearing at 28.7 eV and 53.2 eV respectively for ZrN-Fl. (They appeared at 27.1 eV and 51.1 eV respectively in Zr metal.) The 4s core level shift is unexpectedly greater than the 4p shift. This is reversed from the observations on VN\textsubscript{x} and NbN\textsubscript{x}. One also observes the additional structure associated with the 4p threshold, altered in shape relative to the Zr results.

In the low energy region of the loss curves, results fairly similar to VN and NbN are found. The volume free-electron-like plasmon (calculated to be about 20.0 eV for ZrN) is observed at about 21.1 eV. The associated surface plasmon appears to occur at 18.4 eV. Again one observes what was identified in Zr as the "lowered" plasmons. The volume contribution appears at 13.5 eV giving rise to a very sharp peak in both N(E) and \(-\frac{d^2N(E)}{dE^2}\). The lowered surface plasmon could be identified as either of the two peaks occurring at 6.1 or 8.6 eV. From the present results, it is impossible to be more precise. (One of the two must also be identified as an interband transition.) Finally, the characteristic, sharp low energy peak is observed at about 2.9 eV.

To study the volume versus surface nature of the various losses, the primary energy dependence was observed for N(E). Primary energies from 250 eV to 1000 eV were used, as shown in Fig. 49. The curves are normalized with respect to the elastic peak shown at zero energy loss at reduced gain. The light vertical lines indicate the loss energies
Figure 49. ELS N(E) curves for sample ZrN-Fl recorded at primary energies of 250, 500, and 1000 eV. The curves are normalized with respect to the elastic peak shown (reduced by 33.3 times) at zero energy loss. The light vertical lines mark the loss energies determined from the derivative spectra recorded at $E_p = 500$ eV. Volume related losses should be more prominent at higher primary energies, while surface related losses should become more prominent at lower primary energies.
ZrN–FI
(ZrN$_{0.8}^0C_{0.07}^0O_{0.03}$)

N(E) (ARBITRARY UNITS)

ENERGY LOSS (eV)
determined from the derivative spectra at $E_p = 500$ eV. The volume and surface origins of the plasmons at 21.1 eV and 18.4 eV respectively are readily apparent in the shift of the weight of the broad peak in this region to the lower loss energy as $E_p$ decreases. There may also be a slight decrease of the relative intensity of the "lowered" volume plasmon at 13.5 eV as $E_p$ decreases. No additional information is obtained to help in identifying the "lowered" surface plasmon.

Comparisons of ELS results for Zr metal, nitrogen in solution in Zr, and (Bl) ZrN$_x$ are shown in Fig. 50(a-c) and listed in Table 10. The solid solution sample ZrN-1 is easily distinguished from both Zr and ZrN$_x$. The additional structure associated with the Zr 4p threshold displays distinctive shape (in $dN(E)/dE$) for each of the three types of samples. The 4p core level shift is slightly less for ZrN-1 than for the ZrN$_x$ samples, but the 4s shift seems to be about the same. The plasmon energies are also nearly constant from ZrN-1 to the higher nitrogen content samples, with the exception of the surface plasmon (17.7 eV rather than $\approx$18.4 eV). Although the shape of the low energy region is dramatically altered in $N(E)$ for the nitrogen containing samples, the second derivative spectra look very similar. In particular, in $N(E)$, the relative intensities of the volume plasmon and the low energy interband peak increase noticeably as the nitrogen content increases. Finally, one notes in $-d^2N(E)/dE^2$ a shift of the peak at 7.1 eV in ZrN-1 to 6.1 eV in the ZrN$_x$ samples. (The low energy interband peak behavior parallels this shift, although the magnitude is less.)
Figure 50(a) ELS N(E) curves for Zr, α-Zr and (B1) ZrNₓ recorded at \( E_p = 500 \) eV. The curves are normalized with respect to the elastic peak at zero energy loss (shown reduced by 33.3 times).
Figure 50(b). ELS $dN(E)/dE$ curves for Zr, $\alpha$-Zr and (B1) ZrN$_x$ recorded at $E_p = 500$ eV
Figure 50(c). ELS $-d^2N(E)/dE^2$ curves for Zr, α-Zr, and (B1) ZrN recorded at $E_p = 500$ eV
Table 10. Loss energies for $\text{ZrN}_x$ ($E_p = 500$ eV)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>J</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrN-1(^a)</td>
<td>$\alpha$-Zr + N</td>
<td>3.4</td>
<td>7.1</td>
<td>8.8</td>
<td>13.5</td>
<td>17.7</td>
<td>21.2</td>
<td>28.3</td>
<td>36.9</td>
<td>53.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.2)</td>
<td>(0.1)</td>
<td>(0.2)</td>
<td>(0.1)</td>
<td>(0.1)</td>
<td>(0.1)</td>
<td>(0.2)</td>
<td>(0.2)</td>
<td>(0.3)</td>
<td></td>
</tr>
<tr>
<td>ZrN-2</td>
<td>$\text{ZrN}_{0.5}^{0.1}^{0.01}$</td>
<td>3.0</td>
<td>6.1</td>
<td>8.8</td>
<td>13.6</td>
<td>18.2</td>
<td>21.4</td>
<td>28.8</td>
<td>32.5</td>
<td>37.3</td>
<td>53.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.1)</td>
<td>(0.1)</td>
<td>(0.1)</td>
<td>(0.2)</td>
<td>(0.1)</td>
<td>(0.1)</td>
<td>(0.5)</td>
<td>(0.2)</td>
<td>(0.5)</td>
<td></td>
</tr>
<tr>
<td>ZrN-F1</td>
<td>$\text{ZrN}_{0.8}^{0.07}^{0.03}$</td>
<td>2.9</td>
<td>6.1</td>
<td>8.6</td>
<td>13.5</td>
<td>18.4</td>
<td>21.1</td>
<td>28.7</td>
<td>32.0</td>
<td>37.5</td>
<td>53.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.1)</td>
<td>(0.1)</td>
<td>(0.1)</td>
<td>(0.2)</td>
<td>(0.2)</td>
<td>(0.1)</td>
<td>(0.2)</td>
<td>(0.2)</td>
<td>(0.1)</td>
<td></td>
</tr>
<tr>
<td>ZrN-F4</td>
<td>$\text{ZrN}_{0.72}^{0.15}^{0.03}$</td>
<td>3.0</td>
<td>6.2</td>
<td>8.5</td>
<td>13.6</td>
<td>18.5</td>
<td>21.5</td>
<td>28.9</td>
<td>32.3</td>
<td>37.2</td>
<td>53.1</td>
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<td></td>
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<td>(0.2)</td>
<td>(0.1)</td>
<td>(0.1)</td>
<td>(0.1)</td>
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<td>(0.2)</td>
<td>(0.1)</td>
<td>(0.3)</td>
<td>(0.1)</td>
<td>(0.3)</td>
</tr>
</tbody>
</table>

$\hbar \omega_p$\(^b\) 20.0

\(^a\) Both samples ZrN-1 and ZrN-2 contained both $\alpha$-Zr and (B1) ZrN$_x$; however, ZrN-2 was a superconductor while ZrN-1 was not above $\sim 0.6$K. See text for more details.

\(^b\) Free electron volume plasmon energy calculated including the Zr 4d and N 2p electrons for ZrN$_{1.00}$. Inclusions of the N 2s electrons yields 22.7 eV.
D. Comparisons of VN$_x$, NbN$_x$ and ZrN$_x$

It is informative to summarize the similarities and differences in the above results for the three different compounds. In the UPS results, the expected double peaked valence band density of states was observed experimentally for all three compounds. Only relatively fine details (e.g., the $-7.0$ eV shoulder in VN$_x$ or the $-1.1$ eV peak in the NbN$_x$ results at $h\omega = 16.8$ eV) appeared unique to a particular compound. The hybridized valence bandwidth was slightly less for VN$_x$ than for NbN$_x$ (in agreement with theoretical results). The width of the second peak in the EDC appeared to be $\sim 0.3$ eV wider in VN$_x$ than for the other materials. This perhaps could be interpreted as an indication of increased hybridization in VN$_x$ (in agreement with the theoretical results).

In the ELS results, there are general similarities in the overall shape for the three compounds, most noticeably, the presence of the sharp low energy peak ($2.8$ eV in VN, $\sim 3.5$ eV in NbN and $2.9$ eV in ZrN). The possibility of an interband transition (originating from near $F_F$) causing these peaks seems obvious. The peak in the unfilled DOS does lie closer to $E_F$ in VN than in NbN (see Figs. 21 and 35), but the energy agreement is not particularly impressive.

Each of the compounds exhibits the volume free-electron-like plasmon at an energy very close to the calculated value including the transition metal 3d or 4d electrons and the N 2p electrons. Both experiment and theory indicate that the valence electron density increases in order from ZrN to NbN to VN. This lends more credence to arguments supporting this interpretation of these excitations. It should also be noted that
inclusion of the N 2s electrons in the free electron calculation results in a plasmon energy considerably higher than observed experimentally for each case. It is also found that the ratio of the free-electron-like volume and surface plasmon energies is very nearly identical for each of the three compounds (the ratio is between 1.15 and 1.20 for all samples). This does not agree with the naive $\sqrt{2}$ theoretical expectation for free electron materials, but this was also violated in the pure metals (119). The similarity of this ratio for the three compounds could be interpreted as evidence of their similar electronic structures.

Each of the compounds seems to exhibit the "lowered" plasmons characteristic of so many of the transition metals and their compounds. The collective nature of these excitations can only be speculated upon from the present results, as explained earlier.

In the core level region, interesting comparisons can be made for the shape of the additional structure associated with the 3p (in VN) and 4p (in NbN or ZrN) thresholds. From $dN/dE$ in Figs. 18, 32 and 43, one can see that the gross shape is quite similar in Nb and Zr, but dissimilar for V. From Figs. 28, 38 and 48, we can see that the same relationships hold true for the nitrides of these metals. This may be related to membership in a particular transition metal series.
VI. CONCLUSIONS

This thesis represents the application of reflection electron energy loss spectroscopy and angle-integrated ultraviolet photoemission spectroscopy to the study of the electronic structure and the collective electron behavior of the superconducting mononitrides of V, Nb and Zr. Several carefully fabricated samples of each compound have been studied to insure the reliability of the results reported.

Suitably clean samples of these materials are very difficult to obtain, so rather time consuming, in situ fabrication techniques have been developed and used for most of the samples studied. The in situ methods worked fairly well for VN\textsubscript{x}, where samples spanning essentially the entire stable composition range of the \( \delta \)-phase have been investigated. Unfortunately, for NbN and ZrN, reaction of the metal in a static partial pressure of N\textsubscript{2} proceeds best at pressures greater than could be tolerated by the UHV chamber. Only rather substoichiometric NbN, and multiple phase ZrN could be produced in situ, so less clean, externally made samples had to be relied upon. Consequently, it should be noted that the NbN and ZrN results reported here are somewhat affected by the presence of oxygen and carbon.

The UPS experiments provide primarily information about the initial density of states and indicate that the chemical bonding in the mononitrides occurs basically as predicted by the APW calculations of Neckel et al. (17) and Schwarz (21). The major part of the N 2p electronic states are located roughly 5-6 eV below the Fermi level. There is considerable hybridization of the N 2p and transition metal d states.
and significant metal to nonmetal charge transfer is predicted. The experimental results indicate similarly shaped valence band densities of states for the three compounds and show good agreement with the calculated results for VN and NbN. Each compound exhibited a double peaked valence band with strong photoemission occurring near $E_F$ and 5-6 eV below $E_F$, and a minimum lying 2-3 eV below the Fermi level. The occupied bandwidth was observed to be ~8.5 eV in VN, in good agreement with the calculation. Bandwidths for NbN and ZrN were observed to be 8.5-8.7 eV and ~8.6 eV respectively. These are probably affected by the presence of oxygen (which should tend to increase the occupied bandwidth), but even so, the NbN value is a few tenths of an electron-volt less than predicted.

The ELS experiments have provided considerable useful information regarding the collective electron behavior for these compounds. Like the parent transition metals, each nitride exhibits free-electron-like collective oscillations of the valence electrons. The volume plasmon energy is found to be ~25.2 eV for VN, ~23.5 eV for NbN and ~21.1 eV for ZrN. In each case, the volume plasmon is observed at just slightly higher energy than the free electron value calculated by including the transition metal 3 or 4d electrons and the N 2p electrons. The "lowered" plasmons of unknown origin common to so many of the transition metals and their compounds are also observed. Finally, a prominent, sharp low energy (interband) excitation at ~3.0 eV is found to be characteristic of all the nitrides studied.

The ELS experiments also provided information on the locations of the low-lying, transition metal core states. These core states
consistently shifted to deeper binding energy in the nitride as compared to the parent metal. This shift is 2-3 eV for the 3 or 4p core levels, \( \approx 1 \) eV for the V 3s and Nb 4s levels, and \( \approx 2 \) eV for the Zr 4s level. Such results are consistent with the direction of charge transfer suggested by the APW calculations and the UPS results.

The ELS curves are also found to provide a good "fingerprint" for the nitride compounds. Competing phases within the samples are easily distinguishable from the desired \( \delta \)-phase. For \textit{in situ} fabrication, this possibility provided a valuable check on the sample quality (i.e., whether the sample was entirely of the desired phase).

For VN, results were also obtained for the compositional dependence of the electronic structure. In particular, the UPS results provide little support for the simple rigid-band picture of the \( x \)-dependent electronic structure which has often been assumed \( (55, 65-68, 154) \). Although the occupied valence band does narrow very slightly \( (\approx 0.2 \) eV) as \( x \) decreases from 0.92 to 0.76, the minimum and second peak in the EDC move to deeper initial state energy, a shift opposite to rigid-band expectations. These results, plus the reduction in intensity of N 2p related structure as \( x \) decreases, provide some qualitative support for the more sophisticated coherent potential approximation approach to this problem used by Klima \( (28) \).

In conclusion, the combination of the \textit{in situ} fabrication and characterization by AES, ELS and UPS has provided some reliable data about the electronic structure and collective electron behavior of some interesting superconducting transition metal nitrides which have traditionally been difficult experimental subjects. This represents
the first use of UPS on VN, NbN or ZrN, and the first use of ELS to investigate any of the TMNC's.
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