A study of the electronic structure of $\alpha$-$\text{NaV}_2\text{O}_5$ using angular-resolved soft X-ray spectroscopy

Gerald Woods

University of Tennessee

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To the Graduate Council:

I am submitting herewith a dissertation written by Gerald Woods entitled "A study of the electronic structure of α-NaV$_2$O$_5$ using angular-resolved soft X-ray spectroscopy." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Physics.

Tom Callcott, Major Professor

We have read this dissertation and recommend its acceptance:

David Mandrus, Marianne Breinig, Bob Compton

Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)
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We have read this dissertation and recommend its acceptance:

Marianne Breining
Dean E. Mandl
Robert U. Compton

Accepted for the council:

Vice Provost and Dean of Graduate Studies
A STUDY OF THE ELECTRONIC STRUCTURE OF
\( \alpha' \)-NaV\(_2\)O\(_5\) USING ANGULAR-RESOLVED SOFT X-RAY
SPECTROSCOPY

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Gerald Woods
December, 2001
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First of all, I would like to thank my major professor, Dr. Thomas A. Callcott, for his guidance through my graduate study. The opportunity he has given me has certainly been a rewarding experience, which will always be remembered and appreciated.

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Finally, I would like to thank my family, my wife Lilia and son Dennis, and the good Lord above. They gave me inspiration and patience when I needed it the most. I dedicate this thesis to them.
ABSTRACT

In this dissertation, we use soft x-ray spectroscopy to investigate the electronic structure of the highly anisotropic, strongly correlated transition-metal oxide \( \alpha' \)-NaV\(_2\)O\(_5\). Band structure calculations and theoretical modeling of V-V correlation effects were employed to assist in the interpretation of the experimental data. Our results show that NaV\(_2\)O\(_5\) is a Mott-Hubbard insulator in which the V \( d \)-band spanning the Fermi level is split into lower and upper Hubbard bands by strong correlation effects. Resonance inelastic x-ray scattering (RIXS) measurements provide a direct measure of the \( d-d^* \) excitations between the bands and show that the distance between the centroids of the bands is \( 1.55 \pm 0.05 \) eV. Using a theoretical model of the correlated system, the on-site Coulomb repulsion term is found to be \( U = 3.0 \pm 0.2 \) eV, in good agreement with some other estimates.

Except for the \( d \)-band at the Fermi level, the valence and conduction band states of the system are found to be derived from hybridization of V-\( d \) and O-\( p \) orbitals and to be accurately described by band theory without correlation corrections. The O-\( K \) and V-\( L_3 \) absorption and fluorescence spectra from these bands vary strongly as the polarization vector of the exciting x-rays is varied with respect to the crystalline orientation. An analysis of this data permits us to determine the spatial direction and ordering of the orbitals of the system. Also, by varying both the energy and the angle of the exciting radiation, we are able to selectively excite the three distinct oxygen sites of the system and to measure the O-\( p \) local partial density of states for each site.
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CHAPTER 1

INTRODUCTION

1.1 Overview

Transition metal oxides (TMO) and other complex compounds containing transition metal and/or rare earth ions are of great current interest in condensed matter physics both for their potential practical applications and for the development of condensed matter theory. Both types of interest are related to the fact that the ground states and elementary excitations in these materials are profoundly affected by the coupling of magnetic, electronic and lattice interactions. It is essential to develop theoretical descriptions that realistically include the effects of screening, localization, correlation and exchange effects if the materials are to be understood well enough to use theory to guide materials development. In materials with partially filled \(d\) and \(f\) bands, magnetic interactions between unpaired spins play an especially important role, and often are critical to the properties of the material. Furthermore, it has been seen that the study of the electronic structure of these materials have contributed to the understanding of their insulating nature.

This dissertation is concentrated primarily on the application of soft x-ray spectroscopy (SXS) to the study of the complex TMO system \(\alpha'\)-NaV\(_2\)O\(_5\). SXS, including absorption, fluorescence and resonant inelastic scattering has proven to have special value for the study of complex materials. When referring to soft x-rays, the energy range is typically between 100-1000 eV. Although much information about the electronic structure of a particular system can be gathered throughout this range, the data
presented in this work was taken between 500 and 600 eV at the oxygen $K\,(1s)$ and vanadium $L_{2,3}\,(2p_{3/2,1/2})$ edges.

Even though $\text{NaV}_2\text{O}_5$ will be the main topic of this dissertation, limited data on other fascinating and widely studied materials, such as NiO, will also be presented to illustrate key experimental and theoretical issues. It is the hope that this thesis will provide insight into the study of complex TMO systems using SXS.

The dissertation is arranged the following manner: Chapter 1 provides introductory information about TMO systems and how they are studied experimentally using SXS techniques. Chapter 2 presents some of the theoretical concepts of SXS, including the methods of calculation that pertain to this dissertation. Chapter 3 provides information about the experimental apparatus and procedures. Finally, chapter 4 will give a thorough description of the electronic structure of $\text{NaV}_2\text{O}_5$ as studied by SXS. Appendices provide additional information concerning interesting features in SXS.

1.2 Introduction to TMO system

$pd$ and $dd$ interactions in TMO systems

In all solid state systems, electrons occupy bands formed by the overlapping atomic orbitals of a periodic array of atoms. In contrast to alkali and other simple metals, due to the smaller radius of the wave function, the $d$ electron systems (e.g. $\text{NaV}_2\text{O}_5$) have smaller overlap, which results in smaller bandwidths [1.1]. In TMO systems, the $d$ wavefunctions overlap with O $2p$ wavefunctions forming bonding/antibonding states. Thus, the $pd$ bandwidths are determined by the hybridization or overlap of the $p$ and $d$ orbitals. Strong hybridization causes the bands to become quite wide, comparable with
the $p$ band. In contrast, weakly hybridized $d$ orbitals (little or no $pd$ overlap) are narrower and their widths are determined by the metal-metal interactions (e.g. V-V, Fe-Fe). In NaV$_2$O$_5$, a narrow $d$ band with dominant V-V interactions spans the Fermi level and plays an important role in its electronic structure.

In TMO systems, the bands are subject to strong crystal field effects, which break the spherical symmetry of atomic potentials [1.1,1.2]. These effects result from both ionic and covalent effects. When a cubic crystal field is applied, the $d$ states of the ion split into two sets of orbitals, the $t_{2g}$ (six-fold degeneracy) and $e_g$ (four-fold degeneracy) orbitals. For NaV$_2$O$_5$ (orthorhombic symmetry), and the 2D perovskite structures [4], the orthorhombic symmetries of the lattice separate the energies of the $e_g$ and $t_{2g}$ orbitals further and the degeneracy associated with these orbitals are lowered as well. These $d$-orbital symmetries are shown in Fig. 1.1. They play a role in the correlation effects, due to V-V interactions, and polarization effects in NaV$_2$O$_5$, due to the bonding/antibonding states they form with the O $2p$ orbitals.

Typically, the "ionic" pictures of crystal field theory are oversimplified. For the case of NaV$_2$O$_5$, our experimental and theoretical results will illustrate that, due to orbital orientation and the resulting crystal field splitting, a $d$ band with $d_{xy}$ symmetry is isolated at the Fermi level from other $d$ bands with different orbital symmetries. Further, our results will show that the $d_{xy}$ band at the Fermi level is half-filled in the ground state. The other $d$ bands separated from the $d_{xy}$ band at the Fermi level, which include another $d_{xy}$ band split by the crystal field potential, form bonding/antibonding states with the O $2p$
Fig. 1.1 The $d$-orbital symmetry lobes in the $x,y,z$ coordinate system. The upper ones are denoted as $t_{2g}$ and the bottom two are denoted as $e_g$. 
orbitals. In the next section, we will see that correlation effects split the V 3d_{xy} band at the Fermi level into upper and lower Hubbard bands.

**A brief introduction to electron correlation in TMO systems**

To illustrate the basic problem with strongly correlated systems, consider a band that is completely filled (valence band) and one that is completely empty (conduction band) as in Fig. 1.2(a). The energy separation $E_{\text{gap}}$ between the two bands is referred as the *band gap* energy and thus the system in an insulator, where the Fermi level is located inside the gap of the material. Now suppose we have a band that is only half filled, such as the 3d band of a Ni ion in NiO. In normal band theory, the system is metallic with a continuous Ni 3d band crossing the Fermi level as seen in Fig. 1.2(b). Actually, NiO is an insulator with a sizeable band gap [1.5]. One of the biggest tasks of theoretical solid state physics was to develop a model to account for the insulating nature of a system like NiO (or NaV$_2$O$_5$).

Much of the work that expanded the current understanding of strongly correlated systems has been outlined thoroughly elsewhere [1.6-1.8]. This dissertation will explore many of those concepts in chapters 2 and 4. It is worth mentioning at this point, however, that strongly correlated (insulating) materials are characterized as either being a charge-transfer (CT) or Mott-Hubbard (MH) type insulators. Each type of insulator is depicted in Fig. 1.3.

On the left hand side of each insulator shown, we see that the uncorrelated $d$ bands are half-filled. When a $d$ electron is excited, the dynamical response of the other
Fig. 1.2 Depiction of an (a) insulator and a (b) metal in a solid state system.
Fig. 1.3 Depiction of both a (a) Mott-Hubbard and a (b) charge-transfer insulator resulting from strong correlation effects.
electrons is such that it raises the energy of the excited electron and lowers the energy of the hole state so that a "correlation (charge) gap" is opened. If the splitting of the $d$ states is small, so that the smallest excitation gap is between filled and empty $d$ states, then the material is a MH insulator. If the splitting of the $d$ states is larger, so that the $d$ states are pushed above a band edge derived from oxygen $2p$ states, then the lowest energy excitation may be from a TM $d$ state to an oxygen $2p$ state so that a so-called CT insulator is formed. Our experimental results will show that NaV$_2$O$_5$ is a classic MH insulator, in which that band gap is between upper and lower Hubbard V $3d$ bands. The interaction that cause these effects is referred to as $U$ in Fig. 1.3.

The study of strongly correlated materials has provided scientists a wealth of experimental observations. For example, the jump in resistivity by two orders of magnitude in Fe$_3$O$_4$ at $T_v = 120$ K, referred to as the Verwey transition [1.9], is still one of the most studied phenomena today [1.10-1.12]. Many other complexities are being thoroughly investigated by a variety of theoretical and experimental techniques. We explore the fascinating material NaV$_2$O$_5$ with SXS, which has a long history and many advantages as described below.

1.3 Introduction to SXS

Historical perspective

Experimental and theoretical studies of the electronic structure of solids have walked side by side in the last century. For SXS, it all started after the discovery of x-rays in 1895. It wasn't until the mid-1940's when the first experiments of SXS on solid samples were performed. During the same period, theoretical calculations of electronic
states of solids were being developed. These methods include the Korringa-Kohn-Rostoker (KKR), Orthogonalized-Plane-Wave (OPW), tight-binding, LCAO, pseudopotential and augmented plane wave methods [1.13-1.18]. Acquiring the technology to perform calculations of extremely large unit cells would come much later, of course. Nevertheless, these remarkable breakthroughs in developing a thorough knowledge of the electronic properties of solid state systems, combined with the experimental progress since 1895, led to the many achievements in technology that is widely used today.

As is always the case, the achievements of the past pave the way for future success. For SXS, other than the progress of electronic structure calculations of the 1960’s, the theoretical work of G. D. Mahan contributed to the interpretation of much of the SXS results. For example, an anomalous peak at the Fermi edge of both emission and absorption spectra of simple metals associated with the many body response of simple metals to the creation of a core hole was predicted by Mahan [1.19]. Further, in a soft x-ray spectroscopic study of Li, an anomalous broadened Fermi edge in the emission spectrum was explained in terms of lattice relaxation occurring on the same time scale as the core hole lifetime by Mahan [1.20] and Almbladh [1.21].

SXS has advanced since the 1940’s. The major recent advances have been the development of intense synchrotron sources of soft x-rays. Insertion devices such as indulators in modern day synchrotron facilities provide extremely high photon flux and brightness compared with conventional sources. A major problem for emission spectroscopies is related to the low radiative yield in the soft x-ray region. Using e-beam
Excitation, the characteristic radiation is often weaker than the Bremsstrahlung from the e-beam. Photon excitation can eliminate the Bremsstrahlung but sources of sufficient intensity were not available before the advent of undulator beamlines at synchrotron sources.

With the advent of third generation synchrotron sources, such as the Advanced Light Source, the flux and brightness have increased by over ten orders of magnitude, as compared to conventional x-ray sources. SXS, with the use of these facilities, improved monochromator and spectrometer efficiencies, and the use of modern day electronic structure calculations has accelerated our understanding of the electronic structure of solid state systems.

**SXS measurements of solids**

This section gives a general view of the types of SXS measurements. In addition, some of the terminology used in this dissertation will be outlined. Additional details of the theory will be given in chapter 2.

Studies of the electronic structure utilizing SXS [1.22] includes both absorption and emission studies. **Soft x-ray absorption** (SXA), in which a measurement of an electronic transition from a core level to an empty conduction band (unoccupied) state is made, provides a measure of the unoccupied part of the density of states (DOS). Absorption processes may be measured by either the total fluorescent yield (TFY) or the total electron yield (TEY) as described fully in chapter 2. **Soft x-ray emission** (SXE) spectra are generated by the radiative transitions from valence states to fill a core hole. If
the excitation source and detected particles are photons, the spectra are referred to as Soft x-ray fluorescence (SXF) spectra. This measurement is sometimes called a photon-in and photon-out measurement. Both SXA and SXF processes are depicted below in Fig. 1.4. In the figure, CB and VB stand for conduction band and valence band respectively.

Advantages of SXS

There are many advantages in using SXS to study the electronic structure of materials. These will be apparent as the data is presented and explained. However, we would like to introduce them to get an idea of the types of issues governing SXS. These advantages include:

1) **Energy selectivity from the monochromatized photons**: Monochromatized light makes it possible to achieve chemical selectivity and sometimes site selectivity. Further, for near threshold excitation, there is insufficient energy for multi-electron excitation, so satellites due to such excitation are suppressed.

2) **Polarization of the x-rays**: This feature is extremely useful when analyzing data from a highly anisotropic system such as NaV$_2$O$_5$. Linear polarization, which is used in these studies, can be used to excite along a specific crystalline axis of anisotropic systems as well as to provide information on the orientation of the magnetic moment in magnetic systems.

3) **Low background**: Bremsstrahlung Suppression due to x-ray excitations as compared to e-beam excitation provides low background in SXS. This facilitates the detection of very weak spectra, such as those from thin surface layers, impurities, and the $M$ and $N$ spectra of heavier transition metal elements.
Fig. 1.4 SXA and SXF processes in solids.
4) **Reduced radiation to samples measured:** Unlike e-beam excitation, radiation damage is minimized. For the case of near threshold photon excitation, the incident power is more efficiently converted to core-hole formation than for energetic electrons. This reduces the power loads for a given excitation rate.

5) **Dipole selection rules:** This allows for angular momentum selectivity.

These advantages give SXS a unique edge to other spectroscopic techniques that the above issues cause concern.

**Disadvantages**

In this dissertation, many of the disadvantages will not be made evident. Therefore, a few should be addressed. These include:

1) **Low radiative yields for some core levels:** Fig. 1.5 shows a plot of fluorescence yield vs. atomic number for the $K$ and $L$ shells. In the plot, we clearly see that the radiative yield for V (atomic number 23) is less than 1%. Thus, the radiative yields are always outweighed by the Auger process. However, the O K spectra provides much more signal and subsequently better resolution.

2) Inadequate resolution in the study of materials with small band gaps at the Fermi level: This fact makes it very difficult to measure superconducting gaps, which are usually on the order of only several meV. Any charge-ordering effects will also be difficult to resolve with our resolution.
Fig. 1.5 Radiative yield vs. atomic number curves in both K and L shell spectra in the soft x-ray regime.
CHAPTER 2

PRINCIPLES AND APPLICATIONS OF SOFT X-RAY SPECTROSCOPY TO TMO SYSTEMS

This chapter of the dissertation describes some very important aspects of SXS. The chapter begins with a discussion of the process of photon absorption in a solid. The theory of electronic transitions is then presented for normal SXF, SXA and resonant inelastic x-ray scattering spectra. Polarization effects in SXS are then described. Lastly, we will describe the electronic structure calculations that were used in the dissertation.

2.1 Elementary excitations in solids

Absorption of a photon in a solid

Before we begin a presentation of the types of transitions that occur in SXS and an outline of the theoretical intensities of both SXA and SXF, we first describe the absorption process of a photon in a solid. Soft x-rays are absorbed to produce a core-hole. This hole may be filled radiatively to produce an emitted photon or non-radiatively to produce an Auger or Coster-Kronig electron. Two measures of the absorption process are in current use. The emitted photons can be collected in a total fluorescent yield (TFY) measurement. Alternatively, the electron plus all secondary electrons produced by subsequent scattering may be collected in a total electron yield (TEY) measurement. As we shall see, these two types of measurements have very different properties.

In either a TFY or a TEY measurement, one measures the total number of decay products, i.e. either fluorescence photons or electrons. If a measurement is to provide an accurate determination of the linear absorption coefficient, \( \mu(\omega) \), two fundamental
conditions must be satisfied: (1) The number of decay products are proportional to the number of core holes and (2) The thickness of the layer that produces the measured signal (i.e. the escaping photons or the secondary electrons) is small compared to the absorption length. These conditions are usually satisfied in the TEY measurement. The secondary electrons are the result of inelastic scattering of the Auger electrons produced after photon absorption. These Auger electrons make their way to the surface scattering off electrons that, with enough kinetic energy, escape from the surface and are measured. The escape depth of the electrons collected is \( \sim 100 \, \text{Å} \), which is usually far less than the typical penetration depth (\( >1000 \, \text{Å} \)). For the TFY, however, in which we measure the fluorescence photons that escape the surface, the second assumption is not fulfilled because the escape depth is generally greater than the absorption depth.

To begin a somewhat quantitative analysis on the TFY measurement, we note that, according to Beer's law, the intensity of a photon beam that penetrates the solid is given by [1]

\[
I = I_0 e^{-\mu(\lambda)x}.
\]  

(2.1)

Thus, the beam decays exponentially with increasing absorption length \( x \). The quantity \( \mu(\lambda) \) is the linear absorption coefficient and \( I_0 \) is the initial intensity. The process for the TFY measurement is depicted in Fig. 2.1. \( \theta_i \) is the angle of incidence of the photon beam, which penetrates a distance \( x_i \) and \( \theta_{out} \) is the angle in which the photon leaves the sample, after traveling a distance \( x_{out} \). Since the beam consists of photons, we can write equation 2.1 as

\[
N = N_0 e^{-\mu(\lambda)x}.
\]  

(2.2)
Fig. 2.1 Schematic view of a TFY experiment. A photon with angular frequency $\omega_i$ is incident at angle $\theta_i$ with respect to the surface. The core hole created by absorption decays by emitting a photon with frequency $\omega_{out}$. 
where \( N \) is the photon flux in the sample at \( x \).

In TFY measurements, our interest is in the radiative yield, which is the number of emitted photons that come out of the sample. To understand this process, we write the number of photons absorbed at a depth \( x \) as

\[
dN_a = -N_0 \mu e^{-\mu x} dx , \tag{2.3}
\]

which is obtained by differentiating Eq. 2 with respect to \( x \). The emitted photons (after absorption) created at \( x \) can be written as

\[
dN = P_R dN_a = N_0 P_R \mu e^{-\mu x} dx , \tag{2.4}
\]

where \( P_R \) is the radiative yield probability. In the soft x-ray regime, this number is typically \( << 1 \). At the end of chapter 1, we showed the yield curve versus atomic number. When measuring the \( L \) shell spectra (see next section), the yield is comparatively small compared to spectra measuring the \( K \) shell.

To determine an expression for the TFY, we re-write Eq. 2.4 as a function of the distance \( z \) from the surface according to Fig. 2.1. Whence,

\[
z = x_i \cos \theta_i = x_{\text{out}} \cos \theta_{\text{out}}, \quad \frac{1}{l_i} = \frac{\mu_i}{\cos \theta_i}, \quad \frac{1}{l_{\text{out}}} = \frac{\mu_{\text{out}}}{\cos \theta_{\text{out}}}. \tag{2.5}
\]

The symbols \( l_i \) and \( l_{\text{out}} \) can be considered as the effective absorption and emission depths, respectively.

Combining the above equations with the change of variables, we can calculate the number of photons out by

\[
N_{\text{out}} (\omega_i, \omega_{\text{out}}, l_i, l_{\text{out}}) \propto N_0 P_R (\omega_i) \int_0^e \frac{1}{l_i (\omega_i)} \frac{1}{l_{\text{out}} (\omega_{\text{out}})} \, dz = N_0 P_R (\omega_i) \frac{l_{\text{out}} (\omega_{\text{out}})}{l_i + l_{\text{out}}}. \tag{2.6}
\]
The TFY is then obtained by integration over the emission energy \( h\omega_{\text{out}} \) i.e.,

\[
\text{TFY} \propto \int_{E_{\text{out}}}^{E_{\text{out}} + \Delta \omega} dN_{\text{out}}(\omega_i, \omega_{\text{out}}, l_i, l_{\text{out}}) d\omega_{\text{out}} = P_R(\omega_i) \int_{E_{\text{out}}}^{E_{\text{out}} + \Delta \omega} \frac{l_{\text{out}}(\omega_{\text{out}})}{l_i(\omega_i) + l_{\text{out}}(\omega_{\text{out}})} d\omega_{\text{out}}.
\]  

(2.7)

From Eq. 2.7, we see that the TFY is proportional to the probability of radiative yield \( P_R(\omega_n) \), which is sensitive to the opening of new channels for emission with increasing probability of radiative decay. Another aspect of Eq. 2.7 is that the TFY is not sensitive to either \( \mu_i \) nor \( l_i \). Near an absorption threshold, which is at a core binding energy of interest, it is often true that \( \mu_i >> \frac{1}{ouz}, \ l_i << l_{\text{out}} \). This is illustrated in Fig. 2.2. Thus, from Fig. 2.2 and the above discussion; we see that the TFY measurement is a good measure of \( P_R \) but not of the absorption coefficient \( \mu \).

A similar analysis can be made for the TEY, in which secondary electrons escape the sample as shown in Fig. 2.3, which depicts the penetration and escape depths for the photons and the secondary electrons. We should note that the escaping electrons do not obey the exponential law. Furthermore, we must integrate over all angles and energies of the inelastic electrons. Thus, for the TEY, we have

\[
\text{TEY} \propto P_{NR}(\omega_i) \int l_{\text{out}}(E) d\Sigma \Omega, \quad (2.8)
\]

where \( P_{NR} \) is the non-radiative yield. Note that \( P_R + P_{NR} = 1 \). In the soft x-ray regime, we typically have that \( P_{NR} \approx 1 \) since \( P_{NR} >> P_R \). Also, \( l_{\text{out}} << l_i \). Thus,

\[
\text{TEY} \approx \frac{1}{l_i(\omega_i)} \int l_{\text{out}}(E) d\Sigma \Omega \approx \mu_i(\omega_i).
\]  

(2.9)
Fig. 2.2 Absorption coefficient versus incident angular frequency. The absorption edge is defined as $E_{\text{threshold}}$. 
Fig. 2.3  Schematic view of both a TEY and TFY experiment. In a TEY experiment, secondary electrons with enough kinetic energy will escape the sample from about a thickness of $\sim 100 \, \text{Å}$. 
Therefore, a TEY measurement is a good measure of the absorption coefficient, providing that $l_{out} \ll l_i$ and $P_{NR} \equiv 1$, as was stated as the underlying assumptions at the start of the discussion.

Electronic transitions in Solids

In chapter 1, it was pointed out that soft x-ray spectroscopy is an excellent tool for studying a variety of compounds because of element and angular momentum selectivity. For the case of TMO systems, this implies that one is able to measure separately the O 2p and the metal 3d/4d local-partial DOS (LPDOS). Results from these measurements may be used to provide useful information about the $pd$ hybridization, correlation effects of the $d$ electrons and the bandlike features from the predominately itinerant O 2p electrons.

The dipole selection rules that govern soft x-ray transitions, for both the absorption and emission processes, are as follows:

$$\Delta n \geq 0, \Delta l = \pm 1, \Delta m = 0, \pm 1, \Delta s = 0,$$

(2.10)

where $n$ is the atomic principal quantum number, $l$ is the angular momentum quantum number of a single electron orbital and $m$ is the magnetic quantum number. Thus, when excitation energies exceed that of a 2p ($l = 1$) core level, and the 2p electron makes a transition to a conduction band state due to photon absorption, we are able to measure the $(s + d)$-LPDOS of empty conduction band states. When the core level is refilled, via a radiative transition, the emission spectra provide a measure of the $(s + d)$-LPDOS of the filled valence states. In this work, that means a measure of both the 3d ($l = 2$) and 4s ($l = 0$) filled states from the transition metal are obtained. Likewise, when the photon energies
exceed the O 1s binding energy in the TMO material, we are able to measure the O 2p LPDOS.

Our notation when describing soft x-ray transitions is illustrated in Fig. 2.4 [2]. Transitions within the metal ions from filled states to the spin-orbit split 2p core levels produces TM-L_{2,3} spectra as shown in the figure. To measure LPDOS information from the O 2p states, transition from the O 2p states to the 1s core level produce O K spectra.

2.2 The electronic structure of solids studied by SXS

SXA and Normal SXF spectra

Normal SXF is produced when a valence electron of particular angular momentum symmetry undergoes a radiative transition into a core hole. One of the aspects of normal emission is that the shape and energy of the recorded spectra are independent of the excitation energy. In most TMO systems, excitations into the conduction band edge produce spectra in which the energy and shape strongly depend on the excitation energy while excitations at energies well above the excitation threshold produce normal SXF spectra. This subsection is restricted to the discussion of normal emission and the principal interpretations of the results.

Two of the main goals in SXS are to obtain information about both the valence and the conduction band states. To achieve this, a number of approximations have to be made. For instance, the many-body aspects are treated separately and thus a simple one-electron picture is used. Normal fluorescence spectra occur due to two independent dipole transitions: The absorption and emission processes are treated as independent dipole transitions [3-5]. Referring to Fig. 1.5, this means that the excitation to a
Fig. 2.4 X-ray notation used in this dissertation. The V $L_3$ spectra is derived from radiative transitions into the $2p_{3/2}$ core level while the O $K$ spectra is derived from radiative transitions into the $1s$ core levels.
conduction band state in SXA is independent of the radiative recombination of the valence electron filling the core hole as seen in SXF. From this independent picture, we can develop an understanding between the matrix elements governing the radiative transitions and the intensity $I(\omega)$ of the SXF spectra.

The intensity of an emitted x-ray with angular frequency $\omega$ is given by,

$$I(\omega) \propto \omega \sum_{v} \left| \langle v | \vec{p} \cdot \vec{A} | c \rangle \right|^2 \cdot \delta(\hbar \omega - E_v + E_c). \quad (2.11)$$

The matrix elements in the brackets are the momentum matrix elements between core and valence states, where $v$ and $c$ represent the valence and core states, respectively. The symbol $\vec{p} \cdot \vec{A}$ term represents the electron-photon interaction. The delta function assures that energy is conserved in the radiative transition from the valence ($E_v$) to the core ($E_c$) states.

In most cases, the $\vec{p} \cdot \vec{A}$ term can be approximated by a dipole term [5]. Converting to dipole matrix elements gives an added frequency factor of $\omega^3$. If the transition matrix elements are constant for transitions between selected core levels and valence states of a particular band and if the dipole selection rules are applied, we may write the intensity of both absorption and emission, in terms of dipole matrix elements as

$$I(\omega) \propto \omega^3 \sum_{G} N_G(E_v) \left| \langle v_{G,jz} | \vec{r} \cdot \vec{E} | c_i \rangle \right|^2. \quad (2.12)$$

$N_G$ is the density of states for the $G$th band, where $G$ stands for reciprocal lattice vectors, at energy $E_v$. $\vec{E}$ is the polarization vector and $\vec{r}$ is the dipole operator. The
angular momentum selection rule for dipole transitions has been made explicit in the matrix element and \( E_v = E_e + h\omega \).

The above equations indicate that the emission process of the x-ray occurs where the valence and core wavefunctions overlap in real space. Core states are highly localized and so in SXS only the DOS in the region of the emitting atom is sampled. Thus, the LPDOS of a particular angular momentum in an insulating or metallic solid state system can be determined for a narrow region around the emitting atom.

**Resonant Inelastic X-ray Scattering (RIXS)**

In all cases of SXS, \( \omega_{\text{in}} \geq \omega_{\text{out}} \), where \( \omega_{\text{in}} \) is the incident angular frequency and \( \omega_{\text{out}} \) is the emitted angular frequency of the photon. In Eq. 2.12, we see that normal SXF spectra represent the LPDOS of a particular site and symmetry independent of the excitation energy or the method of excitation. In RIXS spectra, for excitations near an absorption threshold, the excitation and emission processes are coupled and we observe an inelastic spectrum that tracks the excitation energy in a linear manner [6-10]. The RIXS spectra may be viewed as the result of an *energy loss* process, which occurs in the scattering process. In this section, we provide some background information on the fundamental concepts of RIXS spectra. In chapter 4, RIXS spectra provide crucial information regarding the electronic structure of NaV\(_2\)O\(_5\).

RIXS is a two-photon process in which the dipole selection rules become \( \Delta l = 0, \pm 2 \). RIXS spectra most commonly occur at an absorption threshold. At higher excitation energies, normal emission usually dominates the spectra.
In the inelastic scattering of a photon, the intensity of the RIXS spectra is given by the Kramers-Heisenberg (KH) formula

\[
\frac{d^2\sigma(\omega_m)}{d\omega_{\text{out}} d\Omega} \propto \sum_f \sum_m \frac{\langle f | p \cdot A | m \rangle \langle m | p \cdot A | i \rangle}{E_m - E_i - \hbar \omega_i - i \Gamma_m / 2} \cdot \delta(\hbar \omega_{in} - \hbar \omega_{out} - E_f + E_i). \quad (2.13)
\]

This equation, which is the cross section for inelastic scattering based on second order perturbation theory, includes all of the physics of RIXS spectra. We will discuss some of the most fundamental aspects of this equation that relate to our studies. A more formal view is given in Ma et al. [8]. The \( f \) and \( i \) in the KH formula represent the final and initial state wavefunctions, while \( m \) is one of the many intermediate states. \( p \cdot A \) is the momentum operator and \( \Gamma_m \) represents the lifetime of the intermediate state. Lastly, energy conservation is preserved in the delta function, as was the case in normal emission.

One of the very useful concepts from the KH formula directly related to the interpretation of our data is obtained from the delta function. The delta function implies that the energy losses involve only the energy difference between initial and final states, independent of the intermediate states. Thus, for a single electron excitation, the energy loss is just the energy needed to create an electron-hole pair in the final state so that

\[
\hbar \omega_{in} - \hbar \omega_{out} = E_f - E_i = (E_e - E_h)_f, \quad (2.14)
\]

where \( (E_e - E_h)_f \) is the energy of the electron-hole pair in the final state.

Energy losses measured in SXS are determined solely by the final state energies according to equation 2.14. However, other physics in the scattering are implied by the denominator in the KH formula. Referring to the KH formula, we see that the resonant
denominator is affected by both the energy $E_m$ and lifetime broadening $\Gamma_m$ of the intermediate state. Scattering amplitudes are increased by excitation to energies near the real intermediate state $E_m$. However, it is useful to distinguish between near-resonance excitations, in which we have the inequality $|\hbar \omega_m - E_m + E_f| > \Gamma_m/2$, and on-resonance excitations, in which we have $|\hbar \omega_m - E_m + E_f| < \Gamma_m/2$. For $|\hbar \omega_m - E_m + E_f| > \Gamma_m/2$, the RIXS process dominates the fluorescence and the scattering spectra becomes less intense as the excitations move farther away from the resonant energy. For $|\hbar \omega_m - E_m + E_f| < \Gamma_m/2$, the intermediate state becomes coincident with an accessible real state of the system, so that the scattering process is dominated by excitation energies within $\Gamma_m/2$ of $(E_m - E_f)$.

To illustrate the experimental aspects of the RIXS process; we depict such a process in Fig. 2.5. An incident photon is absorbed by the atom causing an excitation into a conduction band edge or to a virtual state in the gap of the material. The measured energy loss (splitting) between the incident and emitted photon is just equal to the electronic excitation.

While the KH formula (Eq. 2.13) provides a full description of the inelastic scattering process, the detailed nature of the observed spectra depend on the nature of the electronic excitations which contribute to the matrix elements. The properties of the observed spectra are very different, for example, if the electronic excitation is between de-localized band states in which k-vector is conserved (as seen for example in Si, diamond, and graphite [2.9, 2.10]), or results in the creation of a highly localized
Fig. 2.5 The RIXS process in SXS, in which the excitations are at the conduction band edge. The resulting spectra are linearly dependent on $\omega_{in}$. 
excitonic state (as seen for example in BN and many metal oxides [2.11, 2.12]).
Moreover, though the shape of the RIXS emission spectra are related solely to the final state of the scattering process, strong resonances in the intensity of the emission that show up in the TFY absorption spectra can provide valuable information about localization in the intermediate state.

These features make RIXS spectroscopy a powerful tool for the study of the electronic structure of solids. In NaV$_2$O$_5$, we will see that most of the spectral features in both the O K spectra and the V L$_{2,3}$ spectra can be understood in terms of transitions between ordinary band states. The important exception is that in the vanadium spectrum, one small resonant feature gives clear and direct evidence for a $d$-$d^*$ transition between the lower and upper Hubbard bands of a Mott-Hubbard insulator, where correlation effects rather than symmetries of band structure create the band gap at the Fermi level.

**Polarization (angular) dependent spectra in SXS**

**Orbital Orientations of non-cubic crystals**

We show for the first time in this dissertation that the orientation of orbitals in a non-cubic system can be effectively probed using soft x-ray spectra produced by polarized light. To study the orbital orientation of complex TMO systems such as NaV$_2$O$_5$ using SXS, one needs to exploit the system's anisotropic nature. This section is devoted to a basic understanding of how one achieves this by employing SXS.

Polarization studies are of great interest in solid state physics. Photoemission studies of CO absorbed on Ni showed that, with the molecular axis orientated perpendicular to the surface, the $\pi$ orbitals of the CO were selectively excited when the
electric field vector of the photon beam was parallel to the surface [2.13-2.15]. Sophisticated spectroscopic soft x-ray emission studies of CO on Ni have demonstrated that similar molecular orbital information is available from angular resolved SXA and SXF studies. The principles behind the selective excitations in CO are well understood. When the polarization vector $\mathbf{E}$ is along the molecular axis of the CO molecule, only states with $\sigma$ symmetry are excited. Thus, the states with $\pi$ symmetry have zero amplitude. However, with $\mathbf{E}$ perpendicular to the molecular axis, $\pi$ symmetry states are detected.

For single crystals, with well-defined crystalline axes, it is possible to utilize linearly polarized light to selectively excite orbitals with a particular symmetry for SXA studies of non-cubic crystal systems. For cubic systems, the $x$, $y$ and $z$ crystalline directions are equivalent and thus no polarization dependence is detected.

Polarization dependent spectra of highly anisotropic systems are due in principle to the angular part of the matrix elements and the position of the orbital ($2p, 3d, \ldots$) in real (3-D) space and the angular part of the wave functions. We refer now to Fig. 2.6. The figure shows the polarization vector $\mathbf{E}$ scanning the ac-plane making an angle $\theta_E$ with respect to the a-axis. An orbital of $2p$ (2-lobe) character is seen with a position defined by the vector $\mathbf{r}$. From the figure, we write the two unit vectors as

\[
\hat{r} = (\sin \theta \cos \phi) \hat{a} + (\sin \theta \sin \phi) \hat{b} + (\cos \theta) \hat{c},
\]

\[
\hat{e} = (\cos \theta_E) \hat{a} + (\sin \theta_E) \hat{c}.
\]

Thus, the intensity becomes proportional to not only the magnitudes of $\mathbf{r}$ and $\mathbf{E}$, as well as the conduction and valence state vectors, but to the angle $\theta_E$ [2.16]. Whence,
Fig. 2.6 The polarization effect in linearly polarized SXS experiments.
\[ I \propto |r \cdot E|^2 \propto |r|^2 |E|^2 \cos(2\theta_E - 2\gamma) + 1, \]  
where \( \gamma \) can be determined by \( \tan \gamma = \cot \theta \sec \gamma \). Therefore, for highly anisotropic systems such as \( \text{NaV}_2\text{O}_5 \), whose bonding/antibonding \( 2p \) orbitals for each \textit{in-equivalent} oxygen have fixed orientations with respect to the crystalline axes (see chapter 4), by aligning the polarization vector of our photon beam, we selectively excite the different oxygen sites and obtain site-selected, densities of states information for the \( 2p \) orbitals.

**Dichroism in both cubic and non-cubic systems**

In magnetic systems, where a preferred magnetic axis can be established, polarization dependence can also be seen even in cubic systems. These effects have been seen in magnetic systems studied with both linear \((\Delta m = 0)\) and circularly polarized light \((\Delta m = \pm 1)\), where \( \Delta m \) is the change in the magnetic quantum number. This dissertation is restricted to spectra obtained with non-magnetic properties with non-cubic symmetry. However, in Appendix I we present a few examples that illustrate the polarization effects in the magnetic systems \( \text{Fe}_3\text{O}_4 \) and \( \text{Fe}_2\text{O}_3 \).

**X-ray magnetic linear dichroism (XMLD)** studies measure the difference in absorption cross section between light polarized parallel or perpendicular to the magnetic moment. The effect is proportional to the square of the average value of the magnetization of the ions. Thus, XMLD spectra may be strong in any system with collinear magnetic ordering, which can be either ferromagnetic, ferrimagnetic or antiferromagnetic and may provide information on the orientation of the magnetic moment [2.17].
X-ray magnetic circular dichroism (XMCD) is the difference in absorption cross section between left and right circularly polarized light and requires a net magnetization, due to the fact that it is proportional to the local magnetic moment. Thus, it is not a suitable technique in the study of antiferromagnetic systems, since the left and right circularly polarized spectra will cancel out. However, XMCD is a valuable technique for the study ferromagnetic systems, where the determination of the spin-polarization at the Fermi level is crucial to determine the potential application of the material [2.18].

2.3 SXS vs. Other Spectroscopic Techniques

X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a widely used technique in research areas ranging from atomic and solid state physics to chemistry and applied sciences. The chief goal of the measurements is to measure small changes in the core binding energy that are produced by changes in the physical and chemical environments of the atoms. One of the main purposes for utilizing XPS is to identify atomic species at the surface (~10Å). It is also extremely useful for the study of sample impurities. Kai Siegbahn in Uppsala, Sweden developed the XPS technique in the 1960's for which he shared the Nobel Prize in Physics in 1981.

X-ray excitations are generally obtained from either the Mg Kα (hv = 1254 eV) or the Al Kα (hv = 1487 eV). These are the standard energies used when performing XPS experiments. When x-rays with these energies are incident on the surface of a sample, the core electrons, whose binding energies are less than those of the x-rays, will be photoemitted and collected in an energy analyzer with high resolution. The maximum
intensity in the photoelectron spectrum, recorded as the number of electrons versus kinetic energy \((E_K)\), corresponds to the bound electron energy levels in the system. The peak position in the photoelectron spectrum represents the kinetic energy and is related to the binding energy as follows:

\[
E_K = \hbar \nu - E_B - \phi \tag{2.17}
\]

where \(\phi\) is the work function and depends on both the sample and the spectrometer. The principles behind the XPS experiment are fully described and illustrated elsewhere [2.19-2.21].

**Angular-Resolved Photoemission (ARPES)**

The basic result of band theory is the calculation of \(E(k)\) curves, where \(E\) is the energy and \(k\) is a wave vector. Experimentally, one can measure these curves directly using angle-resolved photoemission spectroscopy (ARPES). Table 2.1 illustrates the advantages and disadvantages with this and both XPS and SXS techniques.

In ARPES, an x-ray is absorbed by an atom and an electron is ejected with a certain kinetic energy \(E_K\). If the excited electron escapes through the sample surface without scattering, its emission angle carries information about its momentum at \(k\)-vector. In favorable cases, by measuring the energy and angle of emitted electrons, \(E(k)\) can be measured. The technique is fully described elsewhere [2.22-2.25].

**2.4 Electronic Structure Calculations**

**Introduction**

Between approximately 1940 and the present, a large number of techniques were developed for calculating the electronic states of periodic arrays of atoms in solids. These
Table 2.1 Summary of advantages and disadvantages of SXS, XPS, and APRES

<table>
<thead>
<tr>
<th>METHOD</th>
<th>ADVANTAGES</th>
<th>DISADVANTAGES</th>
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<tbody>
<tr>
<td>SXS</td>
<td>true bulk probe,</td>
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<td></td>
<td>no sample charging,</td>
<td>requires synchrotron</td>
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<td>ARPES</td>
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so-called band structure calculations have been described, for example, by Calloway [2.26]. A very general approach to electronic structure calculations known as density functional theory (DFT) was developed at the end of the 1960's by Hohenburg, Sham, and Kohn [2.27-2.29]. The key to the theory is that all the electronic interactions are approximated by a potential taken to be proportional to the local charge density. The theory has been shown to give an excellent representation of the ground state of the electronic system, but it is known to improperly account for certain correlation effects present in low energy excited states. Many efficient computational methods have been developed to implement DFT for a periodic solid. We have used one of these implementations, the WIEN97 codes, developed at the University of Vienna and subsequently made available for public use [2.30].

The Vienna codes are a full potential, linearized augmented plane wave (FP-LAPW) calculation, that solves the band structure problem by matching [at the boundary of the muffin tin] spherical solutions within a muffin-tin potential surrounding each atom of the structure with symmatrized plane waves in the interstitial regions. The calculations allows all valence states of the system outside of a frozen core region to be treated on an equal footing, and thus has special value for calculations involving partially filled $d$ and $f$ states, which are poorly described by some other methods. The solution is repeated for a large number of points in k-space, and iterated until the potential derived from the solutions agree with the assumed starting potential.
First principles calculations using the WIEN97 code

In addition to the chemical bonding description it provides about a system, the work presented here will touch on other aspects of the calculations employed by this code. For instance, the code itself does not contain explicit terms to deal with excited states, which are very relevant when trying to deal with correlation effects. Coulomb repulsion due to the $d$-$d$ interactions, which must be considered when studying the insulating nature of strongly correlated ($3d$) electron systems, comes into play when an electron in the core level is promoted to a conduction band state (as discussed in previous sections) and thus the system is no longer in the ground state. After an excitation to an excited state, the electrons respond and the interactions that occur are not treated within the WIEN97 code. The failure to treat the Coulomb repulsion between $d$-electrons, when the system is not in the ground state, is most evident in Mott-Hubbard insulators. TMO systems, in which only half of the $3d$-shell is filled, \textit{ab initio} calculations, such as the ones provided by the WIEN97, predict a metal, although optical data may provide evidence to the contrary. Nevertheless, for most semiconducting and weakly correlated materials (e.g. BP [2.31] and MgB$_2$ [2.32]), the results are remarkably accurate. For TMO systems, it describes the itinerant $O$ $2p$ electronic states with near perfection and thus presents itself as a valuable theoretical tool for the study of complex materials using SXS.

The WIEN97 is based on the calculation of a set of single particle equations, known as the Kohn-Sham equations (KS), for a non-interacting electron gas in an external potential. The KS equations are:

$$[K + v_{\text{eff}}(n, \vec{r})]\phi_j(\vec{r}) = \varepsilon_j \phi_j(\vec{r}), \quad (2.18)$$
\[ n(\vec{r}) = \sum_j |\phi_j(\vec{r})|^2 F(\epsilon_j), \]

where \( K \) is the kinetic energy operator, \( F(\epsilon) \) is the Fermi function, \( \nu_{\text{eff}}(n, \vec{r}) \) is the effective potential and \( \epsilon_j (\phi_j) \) are the eigenvalues (eigenvectors). When performing a calculation, the KS equations are solved self-consistently in an iterative process.

To discuss in more detail the prescription for performing a calculation employing this code, we present the flow of the program in Fig. 2.7 and discuss the fundamentals of the calculation.

Before the iterative process begins, in which the KS equations are solved self-consistently, a crystal structure must be defined. Within the structure file, the so-called struct generator, the lattice and lattice constants must be specified. In addition, the number of inequivalent atoms and their atomic positions must also be entered. These parameters, along with the muffin-tin radii, which will be discussed shortly, are the most fundamental input into the code. It is not always trivial. One must refer to the International Table of Crystallography in most cases, especially with complex TMO systems, to gather all of the correct atomic positions. Muffin-tin (MT) radii are the spherical boundaries that surround the atom. It encloses all of the core charge and a portion of the other wavefunctions associated with each orbital. No core charge may "leak out" of the muffin-tin. Thus, the code separates the region of the charge density into two parts; the MT sphere and the interstitial region. Within the MT, the charge density is defined as

\[ n(\vec{r}) = \sum_{l,m} n_{lm} (l \vec{r} - \vec{R} l) Y_{lm} (\vec{r} - \vec{R}) / l \vec{r} - \vec{R} l), \quad (2.19) \]
Fig. 2.7 Flow diagram of the WIEN97 band structure code
where the MT sphere is centered on the nucleus at position $\vec{R}$. Inside the sphere, the wavefunctions are expressed as a linear combination of radial functions times spherical harmonics $Y_{lm}(r)$. Whence,

$$\phi_{ka} = \sum_{lm} [A_{lm} u_i(r,E_i) + B_{lm} \dot{u}_i(r,E_i)] Y_{lm}(\vec{r}),$$

(2.20)

where $u_i(r,E_i)$ is the well-known solution of the radial Schrödinger equation for energy $E_i$ and the spherical part of the potential inside the sphere; $\dot{u}_i(r,E_i)$ is the energy derivative of $u_i$ taken at the same energy $E_i$. Both $u_i$ and $\dot{u}_i$ are obtained by numerical integration of the radial Schrödinger equation on a radial mesh inside the sphere.

A few more points about the MT sphere should be addressed. The spheres that surround each atomic site should not overlap. The program will check this by calculating the nearest neighbor distances for each atom. If there are overlapping spheres, the code will not converge properly due to large charge fluctuations. Another important constraint on the MT spheres is that the different MT radii surrounding each inequivalent atom should not be too different from each other. This will possibly cause so-called "ghost bands", in which there are more eigenvalues than there are electrons.

In the interstitial region, we define the charge density and wavefunctions respectively as,

$$n(\vec{r}) = \sum_\sigma n(\vec{G}) e^{i\vec{G} \cdot \vec{r}}$$

(2.21)

$$\phi_\sigma = \frac{1}{\sqrt{\omega}} e^{i\vec{G} \cdot \vec{r}}.$$
In these equations, \( G \) are reciprocal lattice vectors to be summed. One can see that, in the interstitial region, the charge density and wavefunctions are expansions of plane waves.

The fundamental requirement of the LAPW method is that the amplitude and slope of the solutions within the MT spheres, represented in Eq. 2.20, must match the corresponding plane wave solutions in the interstitial region. All of the process is done numerically within the code.

In addition to the struct generator in the initialization process, the code generates the symmetry operations associated with the space group of the lattice as well as both the number of atoms in the unit cell and the number of electrons (KS equations) in the self-consistency cycle. These values are provided in the output files and was checked for accuracy.

MT radii have been shown to be a very important in the quality of the calculation. Four more extremely important parameters must be implemented in the code for a quality calculation. The first one is the energy that separates the core charge from the valence charge. Valence charge consists of both valence and semi core (local orbitals) electrons. Core charge is calculated from atomic orbitals, in which the energy levels remain roughly fixed from iteration to iteration, except for small changes due to changes in screening by valence electrons. It should be noted that the number of electrons observed in the output of the initialization process represent only the valence + semi core charge and not the core charge. Secondly, one must specify a cut-off parameter, \( R_{mt} K_{\text{max}} \), which sets the number of plane waves and the high-energy limit of calculated electronic states. \( R_{mt} \) is defined as the largest MT radius in the struct file and \( K_{\text{max}} \) is magnitude of the largest \( K \).
vector. For all of the calculations in this thesis, $R_m K_{\text{max}} = 8$. The units are (atomic units*Rydergs). Thirdly, the number of k-points in the first Brilloin zone must be specified. To save computer time with unit cells containing many atoms, one may first iterate the calculation with a small amount of k-points. Then, one can re-converge with as many k-points as computationally possible to obtain accurate densities of states values. Obviously, the more sampling done in the first BZ, the more accurate the crystal properties are. In addition to band diagrams, the WIEN code permits the calculation of the total energy, magnetic moment, bulk modulus, and DOS information.

Finally, in the FP-LAPW method, one must specify the type of approximation used to treat the exchange-correlation part of $\nu_{\text{eff}}(n, \vec{r})$. For all the calculations used in this dissertation, we used the generalized gradient approximation (GGA) [2.33, 2.34]. This approximation takes into account the radial and angular corrections not used in some other approximations. Due to the complexity of the exchange-correlation part of the potential, we will not discuss this further. However, some discussion can be found elsewhere [2.35].

After the initialization has been done successfully, the code will calculate a starting density and potential and is ready to begin solving the KS equations. To briefly summarize the overall picture of the FP-LAPW method for calculating the KS equations based on the input data, we write the equations for expansions of the potential inside and outside the MT boundary as

$$V(r) = \sum_{lm} V_{lm}(r) Y_{lm}(\hat{r}) \quad (\text{inside}), \quad (2.22)$$
\[ V(r) = \sum_{k} V_k e^{iKr} \] (outside).

Inside the MT sphere, the potential is an expansion of spherical harmonics, while outside the MT sphere it is an expansion in plane waves. In our calculation, we usually iterate this solution until the total energy was consistent within 0.0001 Ry.

SXS relies heavily on accurate DOS calculations to help with the interpretation of the results. After the calculation converges, the DOS can be calculated utilizing the tetrahedron method. Partial charges are calculated according to the decomposition of the angular momentum symmetry \( l \) for each site. Accordingly, we are able to obtain LPDOS information for the \( s, p \) and \( d \) symmetries. The states are presented as states/eV/atom.

The input parameters to obtain the LPDOS information of each site are very trivial. Only the atom, the \( l \)-symmetry and energy range need to be specified. All of the eigenvalues and eigenvectors were computed in the self-consistent cycle. Therefore, the entire computational load has been done and a DOS calculation can be performed in a matter of minutes.

In addition to the LPDOS, the WIEN97 code will calculate theoretical x-ray spectra including dipole matrix elements according to Eq. 2.12. Input includes the type of spectra (i.e. \( K, L_{2,3}, \ldots \)), the atom (site) probed, the energy range, type of spectra (absorption or emission) and the broadening parameters. Broadening includes the spectrometer, core or valence broadening. For the O\( K \) spectra, remarkable agreement between theory and experiment is generally reached.

In chapter 4, we will discuss the implementation of correlation effects to \( \text{NaV}_2\text{O}_5 \). Therein, we will present the Hubbard model that describes these effects in the form of on-
site Coulomb interactions, the Hubbard $U$, which are solely the $V_{d-d}$ interactions. The model treats the interactions between the $d$ electrons explicitly without the inclusion of $V$-$O$ interactions. In addition to that discussion, in Appendix II, a comparison between theoretical spectra of the $O K$ LPDOS in NiO utilizing the WIEN97 code and that obtained from an ad hoc calculation, with a systematic treatment of the LDA + $U$ method.

**Pseudopotential method**

The WIEN97 codes are versatile, convenient and accurate, but are computationally demanding and difficult to modify for special purpose calculations. One of our main goals in the analysis of the soft x-ray data from NaV$_2$O$_3$ has been to understand the angular dependences found in the SXA and SXF data taken at the $O K$ edge of this material. For this purpose, the theoretician G. P. Zhang working with our group, has used a LDA, pseudopotential calculation based on previous work of E. L. Shirley at NIST.

The electron states were found by solving the self-consistent Kohn-Sham equation,

$$H \Psi_{nk}(\vec{r}) = \left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(\vec{r}; n) \right] \Psi_{nk}(\vec{r}) = E_{nk} \Psi_{nk}(\vec{r}), \quad (2.23)$$

where $V_{\text{eff}}(r;n) = V_{\text{ion}}(r) + V_h(r;n) + V_{xc}(r;n); n(r) = \Sigma_{nk} | \Psi_{nk}(r)|^2; V_h(r;n) = \int n(r - r')\nu(r - r')n(r')dr'$. For the exchange correlation, the Ceperley-Alder form $V_{xc} = \delta E_{xc}[n]/\delta n(r)$ (analogous to the GGA approximation used in the WIEN97 code). Once the pseudopotential is found, it replaces the external potential in the KS equation.
The method of calculating band structure information using a pseudopotential originated from the orthogonalized plane wave method (OPW). In this approach, the valence wavefunctions are expanded using a basis which consists of plane waves orthogonalized to the lower lying core states. These core states, whose electrons are strongly bound and thus do not respond effectively to the motion of the valence electrons, are treated as fixed states.

In the pseudopotential approximation, the core potential is replaced by a pseudopotential. The determination of the pseudopotential is first done by an atomic calculation, in which the atomic wavefunctions, eigenvalues charge density and potential are calculated using a spherical atomic program. Core radii are selected for each angular momentum quantum number.

The innovation in the work of Shirley et al. [2.36] is the development of an optimized set of basis functions that is significantly smaller than the usual plane wave basis. Nevertheless, is still provides an accurate description of the valence and low energy conduction band states.

After confirming the accuracy of the calculations by comparison with the band structures obtained from the WIEN97 codes, the optimized pseudopotential functions were used to directly calculate the absorption matrix elements, including the angular effects imposed by the linear polarization that enters through the \( \mathbf{r} \cdot \mathbf{E} \) term of the dipole operator in Eq. 2.12, where \( \mathbf{E} \) is the polarization vector of the incident light. These calculations were critical to our understanding of the angular dependences of our SXA
spectra, and for the selection of excitation criteria on both energy and angle that permits us to selectively excite the three different oxygen sites of NaV₂O₅.
CHAPTER 3

EXPERIMENTAL ASPECTS AND SAMPLE PROPERTIES

3.1 Introduction

The experiments reported in this dissertation were carried out on the soft x-ray fluorescence spectrometer end-station of beamline 8.0.1 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. The ALS is a third generation synchrotron facility optimized for an undulator and wiggler insertion devices for the production of photons. This synchrotron facility presents tremendous opportunities for the study of material science, biology, chemistry and protein crystallography.

A few features about this facility should be noted. The stored electron beam energy ranges between 1.3-1.9 GeV, which produces photon beams optimized for tremendous brightness in the vacuum ultraviolet and soft x-ray ranges (10 eV to 1 keV). In this dissertation, all data was collected in the soft x-ray region between 500 eV to 900 eV, at either 1.5 or 1.9 GeV beam energies. Beam spot sizes typically range from about 200 microns to 500 microns. One other thing to note about the ALS is that it produces light in the x-ray region of the electromagnetic spectrum that is twelve orders of magnitude brighter than conventional x-ray sources.

3.2 Description of experimental apparatus (Beamline 8.0)

The soft x-ray fluorescence beamline and endstation is depicted in Fig. 3.1. Beamline 8.0 consists of a 5-cm-period undulator and a spherical grating monochromator, which delivers about 50X light intensity than that of the bending magnetic source.
Fig. 3.1 Beamline 8.0.1 at the Advanced Light Source. The beamline consists of an endstation with a Rowland circle spectrometer soft x-ray fluorescence spectrometer station.
When performing experiments in the soft x-ray range, the desired harmonics of the undulator are the 1\textsuperscript{st}, 3\textsuperscript{rd}, and 5\textsuperscript{th} harmonics. These harmonics cover an energy range of 70 – 1200 eV by adjusting the undulator gap. The monochromator provides resolving powers of $\approx 10,000$. For SXF studies, resolving power of 1,000 or less may be used to increase the excitation flux.

The x-rays generated inside the storage ring enter the beamline and travel down to the endstation where it then hits the sample. It is important to note that the beam of the synchrotron will decay over time. However, this beam decay over time can be normalized by using a monitor, which monitors the incoming flux, $I_0$. This is generally monitored by an electrically floating grid, through which the light passes. Light passes through the grid, which is gold coated. Photoemitted electrons because of light interacting with the grid produce a current (monitored), which is proportional to the photon flux. The emission and absorption data produced in a measurement is usually normalized to $I_0$. After the light passes through the gold-coated grid, it enters the SXF chamber with a spot size on the sample of about 100 µm.

The SXF endstation (STATION 1) consists of a Rowland circle grating spectrometer with a photon counting area detector and an ultrahigh vacuum sample chamber. The grazing incidence spectrometer has a fixed entrance slit rigidly mounted on a flange in the sample chamber. A photon counting area detector is mounted tangent to the Rowland circle and records the spectrum at high resolution. It is scanned on the Rowland circle by a precision XYZ-θ table that permits different Rowland circles to be utilized for high and low energy spectra. In the transverse direction, the long curved
astigmatic image is imaged and sliced into 16 slices. These slices can be translated and added to compensate for curvature and thus to maintain resolution, while collecting as much dispersed radiation as possible. X-ray photons are incident on a 40 mm diameter micro channel plate (MCP) coated with MgF$_2$ to improve the quantum efficiency and resolution. The MCP/resistive sheet detector and readout electronics are commercially available electronics from Quantar Technology. A stack of five MCPs provides about $10^7$ amplification of initial photoelectrons. The charge pulse from the MCPs falls on a resistive sheet detector and flows to its four corners. The charge pulses are summed from these corners to produce analog pulses that gives the X and Y positions, then processed as a gated analog signal for real time readout to a storage oscilloscope. A PC at the end-station controls all the data acquisition electronics via a data acquisition program. In the program, raw data is accumulated in 512 (or 256) by 16 arrays. The 512 slices are in the X (or dispersion) direction and the 16 slices in the Y (or transverse) direction. This raw data is used for all further data manipulation and analysis. Due to optical aberrations in the spectrometer, the spectrum incident on the detector has curvature. By shifting the 16 slices in the Y (or transverse) direction slightly, this curvature is removed. For real time monitoring, the 16 slices, or a selected subset, are then summed to produce a 1D spectrum used for further analysis. For more precise analysis, each bin is multiplied by a transition factor, which compensates for non-uniformities in the detector response. The transmission factor file is determined in a separate experiment. The working pressure is about $1 \times 10^{-9}$. This pressure is monitored on a pressure gauge mounted in an electronic rack away from the beamline.
3.3 Experimental procedures

The energy of the incident photons is determined by the energy setting of the beamline monochromator. The flux is then maximized by adjusting the undulator so that one of its harmonics is co-incident with the monochromator energy. The undulator is controlled by the Labview software LOOM installed on a separate computer other than the PC at the end-station with the data acquisition program installed. LOOM calculates the appropriate gap for the specific photon energy and then is set to that value. After the energy has been set, and the flux optimization is complete, a spectrum at that set energy may be acquired. This completes the work done on STATION 2.

At the end-station, the suggested grating for the desired energy range is selected, and the detector is moved to the position of the desired energy range by specifying its central energy position in the data acquisition program. The sample is aligned to the optimum position by monitoring the analog output from the detector on a voltmeter, and the fluorescence spectrum is collected for a specified time length. Usually, an emission spectrum can be integrated from 600 seconds to 1800 seconds. However, it may be integrated much longer keeping in mind that the storage ring refills periodically.

When sample alignment is complete, one generally measures SXA spectra by selecting the beginning photon energy and the final photon energy at STATION 2. After the SXA spectrum has been performed, emission spectra may be obtained by selecting excitation energies after careful observation of the SXA scan. The reasons will become clear in chapter 4. Typical SXA scans are taken with 0.2 eV/steps/4 seconds. The undulator scans according to this step size as well.
Finally, we briefly explain how angular dependent measurements are performed. The angle of incidence of the incoming light with respect to the sample normal is set by a micrometer at the top of the chamber. This micrometer can be easily adjusted for angular settings between 0° to 90° settings. The detector of course remains fixed. A schematic view is seen in Fig. 3.2. The rotation axis is leads to the top of the chamber where the angle can be adjusted.

3.4 Sample properties

**NaV$_2$O$_5$**

The single crystals of NaV$_2$O$_5$ were prepared at the Oak Ridge National Lab (ORNL). NaVO$_3$ was first prepared by heating Na$_2$CO$_3$ (99.997%) and V$_2$O$_5$ (99.995%) in a platinum crucible for two hours at 800°C. Further VO$_2$ (99%) was added and the sample was further annealed and subsequently cooled in a sealed silica ampoule to form samples of NaV$_2$O$_5$ in a flux of NaVO$_3$. After dissolving the flux with hot water, elongate platelets of approximate dimensions of 1 x 5 x 0.5 mm were obtained. The samples were characterized by x-ray diffraction, specific heat and magnetic susceptibility measurements. The samples were easily cleaved along the c-direction to provide clean and flat [001] surfaces containing the a and b axes. It was found that the long dimension was along the b-direction and the shorter dimension along the a direction.

**Iron oxides**

**Fe$_3$O$_4$**

Both magnetite and hematite were prepared at Commercial Crystal Lab., Inc. The magnetite sample was characterized according to the four-point-probe method, which
Fig. 3.2 Experimental geometry between the beam, sample and detector.
measures resistance vs. temperature. Results of this experiment are displayed in Fig. 3.3. In comparing the Verwey temperature obtained with this sample and the temperature range for Verwey transitions with different amounts of oxygen deficiencies, it has been concluded that this is a high quality stoichiometric sample of Fe$_3$O$_4$. Both the (111) and the (100) face single crystals were characterized with the Verwey transition within limits of oxygen deficiency.

Fe$_2$O$_3$

The single crystals of Fe$_2$O$_3$ were studied with x-ray diffraction to determine the orientation of the c-axis. There were three crystals total. Two of the crystals were held such that the polarization vector E of the photon beam was perpendicular to the c-axis, while the other was mounted such that the c-axis was parallel to the vector at normal incidence.

NiO

The NiO sample was obtained from Tulane University. Both x-ray diffraction and optical experiments confirmed the properties of the sample (i.e. structure, band gap,...). The measured spectra were in good agreement with other published works.
FIG. 3.3 Resistance vs. temperature curve measured on Fe$_3$O$_4$ (111). The Verwey transition is seen at $T_v = 118$ K. The measurement was taken using the four-point probe technique with Cu leads and Ag apoxy.
CHAPTER 4

ELECTRONIC STRUCTURE OF SODIUM VANADATE

4.1 Introduction

This chapter of the dissertation provides a thorough investigation of the electronic structure of \( \alpha' \)-NaV\(_2\)O\(_5\) utilizing SXS on both the V \( L_{2,3} \) and O \( K \) edges. The spectra presented in this chapter consists of both angle and excitation energy dependent data, which provide much insight into the LPDOS of the O \( 2p \) and V \( 3d \) states. The chapter will begin with a description of the structure, which provides crucial insight into the motivation behind the study of this material as well as the interpretation of the data. After both the structure and motivation are briefly outlined, the chapter evolves into the study of strong correlation effects, which is a study of the correlated V \( 3d \) electrons at the Fermi level. Afterwards, we will present and discuss the angular resolved O \( 2p \) and V \( 3d \) LPDOS. We will finish the chapter with some concluding remarks about our observations.

Structure

NaV\(_2\)O\(_5\) is a highly anisotropic compound, which has a primitive orthorhombic lattice with lattice constants \( a = 11.316 \) Å, \( b = 3.611 \) Å, and \( c = 4.797 \) Å at room temperature [1]. The structure of NaV\(_2\)O\(_5\) is shown in Fig. 4.1. V\(_2\)O\(_5\) forms pyramids, with V in the center and O on the four corners of the basal plane and at the apex. There are three inequivalent O sites and one equivalent V site. Double chains of pyramids extend along the b-axis, with the double chains located alternately above and below the ab-plane containing in-equivalent O1 and O2 oxygen sites. O1 atoms bridge the V-O-V
Fig. 4.1 Schematic representation of the room temperature structure of NaV$_2$O$_5$ taken from Ref. 4.21. The top of the figure labeled (a) represents the chain of VO$_5$ pyramids and (b) is a planar view with oxygen sites along the ladder (O$_L$) and rung (O$_R$).
rungs of the ladder along the a-axis. O2 atoms bridge V atoms along the chains and between V atoms in the up and down pyramid chains. O3 atoms are located along the c direction from the V sites and form the apex of the pyramids. The Na atom donates one extra electron to the structure that is shared between the two vanadium atoms, partially filling a band derived from V $d_{xy}$ orbitals [2], which leaves a nominal V$^{4.5+}$ valence on the vanadium site [1]. We will show later what the spectra look like without the inclusion of this extra donated electron in the structurally similar system V$_2$O$_5$. This material has both the same lattice and space group as NaV$_2$O$_5$.

The crystal structure described here is a modification of that proposed by A. Carpy et al. [3]. In this structure, the crystalline lattice is the same as the one described. However, both the valency of the V ions and the space group are not the same. For the structure in Ref. 3, there are two inequivalent V ions with formal valences of (4+ and 5+). Within this structural interpretation, the space group is P2$_1$mn. The new determination of the structure has a space group of Pmmn.

The newly assigned crystal structure has opened the door to many fascinating issues concerning the material. For instance, its configuration leads to an effective $S = 1/2$ 1D Heisenberg antiferromagnetic (AF) spin Hamiltonian, which is due to the strong AF coupling between the V atoms sharing a rung [4]. What is quite fascinating about this quantum spin chain is the very strong interplay between spin, lattice and charge degrees of freedom, which has provided much challenge in the study and understanding of this material.
Motivation

All of the work presented here describing the electronic structure of NaV$_2$O$_5$ was performed at room temperature. Much of the work reported elsewhere on this material has been done at low temperatures, due to a possible spin-Peierls transition Isobe et al. (1996). From their results, in which the magnetic susceptibility drops exponentially at 35 K, they concluded that NaV$_2$O$_5$ is a spin Peierls (SP) system. A SP system undergoes lattice instability at the temperature of the transition and a spin gap opens. For NaV$_2$O$_5$, at 35 K the system undergoes a doubling of the lattice periodicity, which is accompanied by an opening of a gap ($\Delta = 9.8$ meV) measured in the magnetic excitations [5]. The proposal that NaV$_2$O$_5$ was the second SP system in an inorganic solid after CuGeO$_3$ [6] has generated much controversy and debate [7-8]. Our objective, in this dissertation, is to provide as much detail as possible the electronic structure above this transition. In the next two paragraphs we cite recent observations from other experiments concerning the phase transition and discuss what information SXS can provide.

Many different observations from researchers have strongly suggested that transitions, other than a SP transition, occur in NaV$_2$O$_5$ below 35 K. Indeed, it has been reported that this system undergoes a "pure" charge-ordering transition below 35 K, in which the valency on the vanadium ions become 4+ and 5+ [9]. In an NMR study of $\alpha'$-Na$_x$V$_2$O$_5$ ($x = 0.996$), a "pure" charge ordering was ruled out in contradiction to the results in Ref. 9. NMR results show that the valency of the vanadium ions become $V^{4.5-\delta}$ and $V^{4.5+\delta}$, where $\delta << 0.5$ [10]. However, these results also contradict crystal structure
determinations below the phase transition in which the results showed three different valences for the vanadium ions (i.e. 4+, 5+, and 4.5+) [11].

A few comments can be made about future studies of these types of materials by SXS. It is possible to study the orbital orientations of the O 2p and V 3d conduction band states using angular resolved measurements. Unfortunately, a difficulty arises due to charging effects of the sample, which makes the TEY measurements noisy. Further, the opening of gap due to the lattice distortion cannot be resolved by SXS measurements. However, at low temperatures, we are able to study the correlation effects, which is discussed for the room temperature phase in the next section.

4.2 Strong electron correlation in NaV$_2$O$_5$

Introduction

In chapter 1, it was pointed out that band theory predicts that a half-filled d band would produce a metallic system. In the case of NiO, that is not what is observed experimentally and, with the inclusion of correlation effects, it is not predicted theoretically. In this section, we will provide evidence as to the insulating nature of NaV$_2$O$_5$. We will begin the discussion by presenting ab initio calculations of the V 3d projected DOS. That will be followed by a brief description of other spectroscopic experiments performed on NaV$_2$O$_5$ and the presentation of the SXS data.

The calculated V 3d partial-DOS for all d-symmetries are plotted in Fig. 4.2. All of the plots are on the same scale and represent the V 3d partial-DOS of a single V atom in NaV$_2$O$_5$. To discuss the correlation effects in NaV$_2$O$_5$, we will focus on the DOS at the Fermi level, which is set at zero in this plot. The calculations were done
Fig. 4.2 V 3d projected DOS calculated by the WIEN97 code.
using the WIEN97 code [12]. We converged the calculation to total energy within 0.0001 Ry with 512 k-points in the irreducible wedge. In addition, the exchange correlation part of the potential was approximated by the GGA method. [13] Very good agreement was reached with calculations performed using the linear muffin tin approximation (LMTO) [14] and using the linear combination of atomic orbitals (LCAO) [15]. Both the LMTO and LCAO calculations were repeated with an on-site Coulomb correlation repulsion of $U = 2.8$ eV and 3.0 eV respectively to match earlier experimental results [4.16]. Our measurements on NaV2O5 give a result of $U = 3.0$ in good agreement with their calculations. Before proceeding further, it should also be noted at this point that the $x$, $y$, and $z$ notation used here to describe the orbitals in the projected DOS in this work refers to the local basis set. Actually, the crystalline axes $(a,b,c)$ correspond to the $(x,y,z)$ directions of the orbitals of a particular ion.

Referring to Fig. 4.2, the $d_{xy}$ symmetry orbitals (band A in the figure) are seen spanning the Fermi level with a bandwidth of about 0.8 eV. Thus, the calculation produces a metallic solution due to the overlap in the conduction band. To the high-energy side of band A is another empty $d_{xy}$ band, which is separated from band A by a crystal (ligand) field splitting of about 0.3 eV. These bands are the fundamental basis for electronic and magnetic properties of NaV$_2$O$_5$. They, by reasons of symmetry, can only make $\pi$ bonds.

The first spectroscopic study of the valence band was done utilizing ARPES [4.16]. Results of the experiment are displayed in Fig. 4.3. Electrons were collected with
Fig. 4.3 ARPES spectra of NaV$_2$O$_5$ at room temperature with both $k \perp b$ and $k//b$ taken from Ref. 4.16.
both \( k \perp b \) and \( k \parallel b \), where \( k \) is the momentum of the electron and \( b \) refers to the b-axis of the crystal. At a binding energy of \( E_B = 1.5 \) eV, there is a broad peak that is labeled the V 3d band, which is separated from the O 2p band by \( \sim 3.0 \) eV. What is relevant here is that there is no spectral weight at the Fermi level, which is zero on this plot. Therefore, the experiment confirms that the system is insulating.

Using these results, and the results from our \textit{ab initio} calculation, we conclude that the system is an insulator of the Mott-Hubbard type. Strong electron correlation effects in this material will split band A in Fig. 4.2 into lower and upper Hubbard bands (LHB and UHB), respectively. Our experiments will demonstrate the splitting between the LHB and the UHB by measuring the \( d_{xy} \rightarrow d_{xy}^* \) excitations that produce energy losses in RIXS spectra.

Other experimental techniques have had difficulties in confirming the insulating nature of NaV\(_2\)O\(_5\). For instance, optical absorption measurements [17-20] are restricted to the dipole selection rules for SXS normal emission (\( \Delta l = \pm 1 \)) and not the selection rules for a two-photon process such the RIXS spectra (\( \Delta l = 0, \pm 2 \)) measured in SXS. Since the \( d-d \) transitions are forbidden for the optical experiments, these transitions will be very weak if not completely forbidden. Results from a previous optical absorption study concluded that an absorption peak at 1.0 eV was due to a \( d \rightarrow d \) transition [4.20], but later results concluded that this peak was due to bonding/antibonding transitions along the V-O1-V rung [20]. In either case, these results are inconclusive.

Other issues also point to SXS as being a better technique to study correlated systems as opposed to using other spectroscopies such as photoemission and electron
energy loss spectroscopy (EELS) [21]. Photoemission only images the filled states while EELS is sensitive to only the empty states. Combining the two techniques is difficult because they contain different final states. Therefore, we provide the first direct probe of electron correlation in NaV$_2$O$_5$.

**Results of the V L$_{2,3}$ absorption and emission spectra**

In Fig. 4.4, we present the V L$_{2,3}$ absorption spectra of both the total electron yield (TEY) and the total fluorescent yield (TFY). These spectra are normalized to the incident beam current $I_0$. The absorption spectrum is derived from electronic transitions of the V 2$p$ core electrons to empty V 3$d$ states (V 2$p$ $\rightarrow$ V 3$d$). Arrows indicate the excitation energies used to obtain the emission data. The entrance slit width of the beamline monochromator was set at 30µm to obtain a resolution of about 0.3 eV in the energy range around 500 eV. The spin-orbit splitting, which splits the 2$p$ core level into the 2$p_{3/2}$ and 2$p_{1/2}$ contributions, is 7.0 eV, which is about the same as other vanadium oxide materials [22-23]. For each portion of the spectrum, the bandwidth is measured to be $W \approx 4.0$ eV.

We mentioned that the $d_{xy}$ bands can only form $\pi$ bonding/antibonding states and so we have $\pi$ bands around the Fermi level, which are in an ionicity gap of $\sigma$ bands. In NaV$_2$O$_5$, the main interactions at the Fermi level are V-V interactions and so the bandwidths are very narrow around the Fermi level. For the V L$_{2,3}$ emission spectra, we will show that the emission from the top of the band, which is from electrons in $d_{xy}$ orbitals, is well separated from the other bonding $d$ orbitals in the valence band.
Fig. 4.4 $V L_{2,3}$ SXA curves taken at both the TEY and TFY modes.
$V L_{2,3}$ emission spectra are derived from radiative transitions from the $V 3d$ valence electrons to empty $V 2p$ core holes ($V 3d \rightarrow V 2p_{3/2,1/2}$), and provide a measure of the $V 3d$ LPDOS of the valence band. We present the $V L_{2,3}$ SXF spectra versus excitation energy, with the polarization vector $\mathbf{E}$ at a $40^\circ$ angle of incidence with respect to the $b$-axis, in Fig. 4.5. In this plot, the incident photon energies are depicted to the left of each SXF spectrum. These excitation energies are shown on the absorption curve indicated by arrows on the TFY curve as seen in Fig. 4.4. Each emission spectrum was normalized by making the area under the curve proportional to the measured TFY. Our spectrometer entrance slit was set at $50\mu m$, which gave us a spectrometer resolution of about $0.6$ eV.

There are three main features in the fluorescence spectra: Peak P1 (left hand side), peak P2 (right hand side) and P3 (elastic peak) indicated by arrows. What is evident by looking at the SXF spectra is that below an excitation energy of $516.0$ eV, we see that the fluorescence peaks, both P1 and P2, are tracking with the excitation energy. This is characteristic of the RIXS spectra described in chapter 2. In these spectra, there is a fixed energy separation between the incident and emitted photon energies. Above $516.0$ eV, the spectra in peak P1 remain fixed in photon energy. This indicates that, for this spectral feature, the excitation and de-excitation processes are decoupled and normal fluorescence occurs. However, this is not as evident for peak P2, where it appears that the spectra are not fixed in energy and that both normal fluorescence and RIXS spectra are present. Fig. 4.6 plots the emitted photon energies versus incident photon energies. A linear relationship exists between the emitted photon energy and the incident photon energy.
Fig. 4.5 V L$_{2,3}$ SXF spectra at various excitation energies (see Fig. 4.4) with $\theta_i = 40^\circ$. 
Fig. 4.6 Plot of $h\nu_{\text{out}}$ vs. $h\nu_{\text{in}}$ for both peaks P1 and P2. The elastic peak is plotted as well.
when RIXS spectra are present. A slope of 1 is measured for the RIXS spectra of both P1 and P2, and for the elastic peak.

One other thing to note about P2 is that it re-appears at a higher excitation energy of 524 eV. In this excitation energy regime, the transitions are both to the $2p_{3/2}$ and the $2p_{1/2}$ core levels. For the main purpose of this section, it is not necessary to analyze the $L_2$ ($2p_{1/2}$) spectra for correlation effects. All of the information needed is within the $L_3$ emission. It should also be noted that the $2p_{1/2}$ core holes could be filled by other decay mechanisms such as Koster-Kronig decay [24].

Our goal in the rest of this section will be to focus on the characteristics of peak P2, especially around the excitation energy of 516.0 eV, where a strong resonance of P2 is observed. P2 provides specific information concerning the correlation effects in NaV$_2$O$_5$. Two things should be reviewed before proceeding further: (i) P2 is attributed to the electrons donated from the Na atoms, which issues a formal valence of 4.5+ for the V ions and that (ii) the V-O interactions are extremely small thereby only V-V interactions are considered. To briefly address the first point, we refer to Fig. 4.7, where we plot both NaV$_2$O$_5$ and V$_2$O$_5$. Looking at the plot, we can easily conclude that, without the extra electron donated by the Na atoms, P2 would be suppressed (The $d_{xy}$ orbitals would be completely empty.). The second point will be addressed when presenting the O K SXF spectra.

In Fig. 4.8, we plot a blow up of P2 on an energy loss scale. For this scale, we take the emitted photon energy minus the incident photon energy. This can only be achieved if both the monochromator and spectrometer energy scales are accurately
Fig. 4.7 $V L_3$ SXF spectra of NaV$_2$O$_5$ and V$_2$O$_5$ at the indicated excitations.
Fig. 4.8 Energy loss spectra of P2 from Fig. 4.5.
calibrated to each other. We accomplished this by using the elastic peak P3 \( (h\nu_{in} = h\nu_{out}) \). Once this peak is located at the same energy as the incident photon energy, the subtraction can be performed. The two dashed lines, one on the elastic peak, and one aligned on P2, show that a portion of the spectral feature P2 remains fixed in energy loss and this is due to the RIXS process, which strongly suggests a \( d_{xy} \rightarrow d_{xy} \) excitation from the LHB and the UHB. As a result, the final state contains a hole in the valence band and an electron in the conduction band. The process outlined here can be seen in Fig's. 4.9 (a) and (b). Energy loss between the incident and emitted photon energies measures the difference in energy between the UHB and LHB in Fig. 4.9 (a). The smallest energy loss peak corresponds to the lowest excitation between states with \( \Delta l = 0, \pm 2 \). Correlation effects, due to these excitation processes, which split the \( d_{xy} \) subband spanning the Fermi level, are illustrated in Fig. 4.9(b), where on the left is the ground state DOS calculated with the WIEN97 code and on the right is the DOS corresponding to the correlation effects. The next section will test these conclusions with theoretical energy loss spectra with explicit V-V interactions and no V-O interactions.

**Theoretical energy loss spectra including correlation effects**

The energy loss spectra were calculated using a cluster model with eight V atoms, using the Hamiltonian for the Hubbard model \([21, 25-27]\),

\[
H = - \sum_{\langle ij \rangle \sigma} t_{ij} (c_{i\sigma}^\dagger c_{j\sigma} + H.C.) + U \sum_i n_{i\uparrow} n_{i\downarrow} + \sum_{\mu a,b} V^\mu \sum_i n_{i\mu} n_{i\nu}^\mu. \tag{4.1}
\]

In this Hamiltonian, \( \sigma = (\uparrow, \downarrow) \), and \( V_{ij} \) are the inter-site Coulomb interactions, which are either along the rung (a-axis) or the chain (b-axis) directions. The creation (annihilation)
Fig. 4.9 Description of the $d_{xy} \rightarrow d_{xy}^*$ excitation process in the V $L_3$ SXF spectra. (a) A photon is absorbed resulting in a core electron excitation into the UHB and a de-excitation from the LHB filling the core hole.
Continued. (b) The electron-hole pair final state of the RIXS process.
of the single-band electron at site $i$ with spin $\sigma$ is given by $c^\dagger_{i\sigma}c_{i\sigma}$. $n_{i\sigma} = c^\dagger_{i\sigma}c_{i\sigma}$ is the number operator and the hopping term, where the electron effectively hops from one site to another is given by the $t_{ij}$ integrals. $U$ denotes the Coulomb repulsion between electrons on the same site and is given by,

$$U = \int d\vec{r}_1 \int d\vec{r}_2 |\phi(\vec{r}_1 - \vec{R}_j)|^2 \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} |\phi(\vec{r}_2 - \vec{R}_j)|^2. \quad (4.2)$$

This equation for $U$ implies there are two electrons that occupy one site ($j$) and are affected by strong Coulomb repulsion between them.

This calculation provides a very good description for the $d_{xy}$ band of NaV$_2$O$_5$ for a couple of reasons. Firstly, there are (effectively) only 3$d$ bands at the Fermi level and thus the V-O interactions can be neglected. Secondly, there are only a few bands so that correlation effects can be carried out directly for the $d_{xy}$ band, which makes this calculation a very good model for identifying low energy $d$-$d$ excitations.

Nearest neighbor hopping integrals were obtained by fitting a previous $ab$ initio calculation. [Smolinski] For the b-axis, $t^{(b)}(a) = 0.17$ eV and for the a-axis, $t(a) = 0.38$ eV. The inter-site Coulomb interactions $V_{ij}$ between nearest vanadium neighbors on a rung and a ladder are $V_a = 0.72$ eV and $V_b = 0.72$ eV, respectively [27]. We find that an on-site Coulomb repulsion of $U = 3.0$ eV provides the best fit to our data and is consistent with values found by previous workers [27, 28]. Since the number of V atoms is eight, and the system is quarter-filled, the number of electrons in the cluster calculation is four ($N = 4$).

After the Hamiltonian has been diagonalized using the Lanczos recursion method [29], the energy loss spectra are calculated using the KH formula defined in chapter 2 as,
\[ S(\omega, \omega') \propto \sum_f \sum_m \frac{\langle f | p \cdot A | m \rangle \langle m | p \cdot A | GS \rangle^2}{\omega + E_{GS} - E_m - i\Gamma_m / 2} \cdot \delta(E_{GS} - \omega - E_f - \omega'), \quad (4.2) \]

where \( \omega \) and \( \omega' \) are the incident and emitted photon energies, \( \Gamma_m \) is the spectral broadening due to the core hole lifetime in the intermediate state, and \( p \cdot A \) is the transition operator, which is approximated by a dipole operator. \( E_{GS}, E_m, \) and \( E_f \) are the initial, intermediate and final state energies respectively.

The ground state \( |GS\rangle \) contains \( N = 4 \) electrons based on the quarter-filled ladder determination. In the intermediate states \( |m\rangle \), the system contains \( N + 1 \) electrons, due to the excitation of the core electron to an unoccupied band (UHB). The final state \( |f\rangle \) contains \( N \) (four) electrons, where the core hole is filled by a valence electron from the LHB leaving an electron-hole pair behind.

Before we present the results for the theoretical RIXS spectra including correlation effects, we briefly discuss the theoretical RIXS spectra if these correlation effects were omitted. In metals, due to the finite DOS at the Fermi level, RIXS starts from a zero-energy loss. Our LDA (WIEN97) calculations show that without the correlation effects, the experimental \( V L_3 \) SXF spectra are not described accurately, which is due to the metallic solution obtained from the calculation. Thus, the LDA-RIXS spectrum will not provide the band splitting that occurs according to our experiments. This is recovered however when correlation effects are included, as we now show.

Results from the theoretical RIXS calculations, including on-site correlation effects described by the above Hamiltonian are presented in Fig. 4.10. The intensities
Fig. 4.10 Calculated energy loss spectra of P2 from Fig. 4.5.
are on the same scale, which have arbitrary units. The incident energy $\omega$ is labeled from a to d and are shown in the inset of the figure. We used an on-site Coulomb parameter $U = 3.0$ eV for this calculation.

As with the experimental RIXS spectra, we see a linear tracking of the emitted photon energy with the incident photon energy. We also observe a resonant peak (divided by 2.5) with a measured energy loss of -1.55 eV (labeled c). This value is the experimentally measured value of the resonance from the experimental RIXS. Further, variations in $U$ produce a linear change in the energy loss feature. It was determined that a variation of $U = 3.0 \pm 0.2$ eV, corresponds to the experimental uncertainty of the energy loss of $-(1.56 \pm 0.05)$ eV. The result is that, considering only V-V interactions, in which only V $d_{xy}$ states are located at the Fermi level, the experimentally observed RIXS spectra measures a low-energy electronic $d_{xy} \rightarrow d_{xy}^*$ excitation, which leaves a hole in the valence band ($d_{xy}$) and an electron in the conduction band ($d_{xy}^*$). Theoretical calculations including an on-site Hubbard parameter of $U = 3.0$ eV predict an energy loss of -1.55 eV in good agreement with the experimental value of -1.56 eV. This value of $U$ is in good agreement with the estimates and measured values of other authors.

In addition to the energy loss features, the calculation shows two other weak resonances at -2.8 and -1.2 eV. The feature at -2.8 eV is most likely attributed to the continuum edge, where excitations into states above threshold produce normal emission. The second feature at -1.2 eV may be attributed to the cluster size used in the calculation and diminishes when the cluster size increases from the eight atom cluster used in this calculation.
4.3 Angular dependent SXA and SXF of NaV$_2$O$_5$

Introduction and preliminary results

This section of the chapter will exploit the highly anisotropic nature of NaV$_2$O$_5$ by presenting experimental and theoretical calculations of SXA and SXF spectra at both the O $K$ and the V $L_3$ edges. The chapter is arranged as follows: After an introduction to the importance of studying the O 2$p$ LPDOS, as we did in the last section, we will discuss the electronic structure of the O 2$p$ states using both angular dependence and excitation energy dependence. Afterwards, we will return to the V $L_3$ edge and discuss the effects of polarization dependence on the V 3$d$ LPDOS. Included in the rest of this chapter is a discussion of the V 3$d$/O 2$p$ hybridization in this system. In the last section, it was stated that the ARPES and SXS measurements revealed that the system is a Mott-Hubbard insulator, in which strong correlation effects split the $d_{xy}$ subband at the Fermi into a LHB and UHB. Referring again to Fig. 4.3, we see that the ARPES measurements on NaV$_2$O$_5$ also show significant band dispersion when the momentum of the electron is parallel to the b-axis. Note, however, the O 2$p$ band exhibits no dispersion when the momentum of the electron is perpendicular to the b-axis. The result of this ARPES data agrees well with the band structure of NaV$_2$O$_5$. Our goal in this section is to provide further insight into the electronic structure of NaV$_2$O$_5$ using angular dependent spectra. Specifically, we will confirm in detail the validity of conventional band structure calculations for the valence and conduction band states. In addition, we will show that angular resolved measurements can determine the orientation of the bonds in real space. Finally, we will show that, using linearly polarized light, one can obtain a LPDOS of
each O site (O1, O2, O3) simply by varying the angle of incidence of the incident light with respect to a particular crystalline axis, and by excitation energy selection. These results were made possible by a close comparison of our experimental data with the theoretical angular dependent absorption calculations of G. P. Zhang.

Comparison of standard pseudopotential and WIEN97 band structure calculations with band structure calculations implementing explicit V-O and V-V hopping integrals provide useful insights into the bonding of NaV2O5. For example, the dispersion of the V 3d_{xy} band at the Fermi level has been shown to depend explicitly on the V-V interactions and not on V-O interactions [15]. The calculation also demonstrated that pd hybridization is an important aspect of the charge ordered phase of the system, due to its direct effect on the V^{4+} band dispersion.

**Experimental and theoretical O K SXA and SXF spectra**

Angular dependent experimental O K absorption spectra were obtained by rotating the sample about an axis located in the plane of the sample, which is centered with the sample (see chapter 3). For a sample of NaV2O5, we depict the geometry of the experiment in Fig. 4.11. The long dimension of the system is the b-axis, while the short dimension is the a-axis. The material cleaves along the c-axis. The polarization vector of the incident beam is horizontal and thus is p-polarized with respect to the optical plane. Rotation of the sample thus scans the polarization vector from the a(b) axis in the plane to the c-axis normal to the plane.

SXA spectra at the O K edge, as a function of angle, measured by the TEY method are shown in Fig. 4.12. The spectra are derived from O 1s → O 2p transitions.
Fig. 4.11 The experimental geometry of the sample and the polarization vector $E$. 
Fig. 4.12 Experimental O K SXA taken in the TEY mode at several angles of incidence between the polarization vector and the crystalline b-axis.
SXRA spectra were measured at 7.5° intervals for \( \mathbf{E} \) vectors in the a-c and b-c planes. Each spectrum was taken at 0.2 eV intervals with a collection time of about four seconds per interval. Our resolution in this excitation energy regime, with the slits being the same as with the V \( L_3 \) emission spectra, is 0.6 eV.

Referring to Fig. 4.12, we see that peak A decreases in intensity, while the peaks labeled B and C increase in intensity as the angle is rotated from 0° (in-plane) \( \rightarrow \) 75° (out-of-plane), where in-plane refers to the a(b) axis in the basal plane of the pyramid and out-of-plane refers to excitations along the apical (c-axis) direction. Recall that in chapter 2 we discussed the polarization effect between the polarization vector \( \mathbf{E} \) and the orbital orientations in the crystal. It was seen that the intensity of the absorption curves had a \( \cos^2 \theta \) dependence, which results from squaring a \( \cos \theta \) dependence in the matrix elements (see chapter 2). Fig. 4.13 plots the intensity of the experimental peaks with angle of incidence. Very good agreement is reached comparing the intensity with the \( \cos^2 \theta \) fit.

For the purposes of our discussion, we present a breakdown of the experimental spectra in Fig. 4.12. In Fig. 4.14, we plot the data taken at 15°, 45°, and 75° in both the a-c and b-c planes. Both sets of spectra show a very strong initial peak for 15°, which drops dramatically when \( \theta \) increases. Careful examination however reveals that the threshold for the absorption curve at 15° in the b-c plane (b-15°-E) is nearly 1.0 eV lower than the threshold for absorption curve at 15° in the a-c plane (a-15°-E). The initial peak for b-15°-E is centered at 530.6 eV, while the initial peak for a-15°-E is centered at 531.2 eV. Later on, we will discuss the meaning of the symbols \( E_{01}, E_{02}, E_{03}, \) and \( E'_{03} \) when considering emission spectra.
Fig. 4.13 Plot of intensity vs. angle for the spectra in Fig. 4.12.
Fig. 4.14 Experimental O K SXA taken with the TEY mode for polarization directions of 15°, 45°, and 75° with respect to both the a (upper panel) and b (lower panel) axes.
To explain differences in the absorption spectra when the angle of incidence is varied in the a-c and b-c planes, we present theoretical, site-selected, absorption curves and O 2p projected DOS calculations. The O K SXA calculations were performed using the equation for $S(\omega)$ from chapter 2. In calculating absorption, the binding energy of each site was assumed the same. Both experiment and theory indicate that this is a valid assumption within our experimental resolution. In Fig. 4.15(a), we display the theoretical absorption curves at several angles of incidences in the b-c plane [30]. Peaks A, B, and C are analogous to Fig. 4.12. Fig.'s 4.15(b), (c), and (d) plot absorption of the different O sites at various angles. The calculations show that O 1 loses intensity in the initial peak (P1) when excitations deviate from the crystalline b-axis but gain intensity at higher energies around 533 eV (P3). Changes in the O 3 are seen as well. O 3 loses intensity in the initial peak (P1) and gains intensity at higher energies around 532.1 eV (P4). Since this peak is in the same position experimentally for excitations in both planes at 75°, the energy scale of the theoretical spectra were scaled to the energy of this peak. As the angle is rotated out of the plane of the pyramid, absorption of O 2 is located at about the same energy region (532-534 eV) but the shape of the curve changes somewhat.

To break the theoretical results down further, we plot the calculated spectra at 15° and 75° in both the a-c and b-c planes in Fig. 4.16. We clearly see the initial peak at 531.2 eV in the a-c plane drops off as $\theta$ is rotated out of the plane. This peak contains mostly O 3 at the threshold region and includes no contribution from O 1. At higher energies, there is a good mixture of all three O site orbitals in the a-c plane when the angle reaches
Fig. 4.15 Theoretical O K SXA curves with various polarizations of the three O sites: (a) is a composite, (b) is O1, (c) is O2 and (d) is O3.
Fig. 4.16 Calculated O K SXA with polarization directions of 15° and 75° with respect to the a (upper panel) and b (lower panel) axes.
75°. What is very interesting and useful is what we see in the b-c plane at 15° for each site. For the b-c plane, O1 contributes most of the orbital weight at the threshold at an angle of 15°. At an energy of 530.5 eV, the O3 has a small isolated window where it contributes most of the 2p orbital weight. Finally, the O2 orbitals are almost completely isolated at an energy of 533.5 eV.

The calculation gives a good description of the contributions of different sites to the angular resolved SXA spectra. Now we present which p-symmetries are associated with each O site and discuss why the O1 and O3 orbitals are especially affected by the polarization. Plotted in Fig. 4.17 are the O 2p projected DOS of all three p-symmetries. The parameters for the calculation are the same as those for the V 3d DOS calculations presented earlier (see Fig. 4.2). The zero energy is taken at the Fermi level. We should also note at this point that, as with the case of the V 3d orbitals, the x, y, and z orbital symmetries are directed along the a, b, and c axes respectively.

Considering these results, and the theoretical absorption curves, we can say that the low energy spectra from the b-15°-E configuration is derived mostly from O1 2p_y (π*) orbitals (peak A'), which are strongly antibonding with V 3d_{xy} orbitals of the V-O1-V rung (see Fig. 4.2 in the previous section). In fact, the V-d_{xy}/O1-2p_y coupling strength is due to the tilt of the d_{xy} orbitals around the b-axis and indicates coupling of the pd π type. Thus, the O1 2p_y unoccupied orbitals are emphasized when excitations are along the b-axis, perpendicular to both the a and c axes. The remainder of the low energy peak for b-15°-E is derived mainly from O3 2p_y orbitals, which are emphasized due to the polarization aligned in the plane of the pyramid. As the case with the O1 2p_y orbitals,
Fig. 4.17  O 2p projected DOS for all three p-symmetries calculated with the WIEN97 code.

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they do not contribute to the absorption spectra when E is rotated out of the plane, at
which point we see the evolution of the resonance at position 532.3 eV (for both crystal
orientations). This resonance is derived from all three O sites (see Fig. 4.15(a)). Similar
absorption measurements have been carried out on other vanadium oxide materials [22,
23, 31].

We have now all of the information to produce a SXF spectrum of each O site in
the valence band. After careful analysis of the theoretical and experimental absorption
spectra, we conclude that the excitation energies to be used are contained within both the
a-15°-E and the b-15°-E configurations. These excitation energies are labeled (see Fig.
4.14) \( E_{O1} \) (529 eV), \( E_{O2} \) (533.5 eV), and \( E_{O3} \) (530.5 eV) in the b-15°-E configuration and
\( E'_{O3} \) (529.9 eV) in the a-15°-E.

To begin the discussion of the LPDOS of the O sites in the valence band, we
present the O \( K \) SXF experimental spectra of both the b-15°-E and a-15°-E configurations
respectively at different excitation energies determined by the TEY absorption curves in
Fig. 4.14. These emission spectra are plotted in Fig.'s 4.18(a) and (b) respectively. The
transitions from the valence band, which produce the spectra, are O \( 2p \rightarrow O 1s \)
transitions. Emission spectra were normalized according to the method described for the
V \( L_3 \) emission spectra. One important thing should be re-emphasized before proceeding
with the discussion. Since the core states are strongly localized at a particular O site,
excitations occur only to conduction band states, which overlap the site. Thus, O1 core
electrons will be excited to O1 conduction band states and O1 valence electrons will fill
the O1 core holes.
Fig. 4.18 O K SXF for various excitation energies in the (a) b-15°-E configuration.
Fig. 4.18 continued. (b) In the a-15°-E configuration.
For the b-15°-E excitation, two peaks are observed, a broad low energy peak centered at an energy of 522 eV and a structured higher energy peak with a maximum at 524.3 eV. Above an excitation energy of 529.0 eV, the 524.3 eV peak increases rapidly with energy, reaching a maximum intensity at an excitation energy of 530.5 eV. Using the theoretical calculation of Fig. 4.15(b) as a guide, we take the spectrum excited at 530.5 eV as representative of the O3 site. Since the O1 site is not excited at low excitation energies in the a-15°-E configuration, another measure of the O3 fluorescence spectra is provided by excitation at 529.9 eV in this configuration.

For the b-15°-E excitation condition, the very strong emission from the O3 site, identified from the 524.3 eV peak, decreases at low excitation energies and disappears entirely for an excitation energy of 529 eV. We take the spectrum excited at 529 eV as representative of the O1 spectrum, with the O3 spectrum eliminated. Similar representative O1 spectra may be obtained by scaling and subtracting the 530.5 eV spectrum (representing O3) from the composite O1 plus O3 spectra taken at 529.5 eV or 530 eV. A close study of the 529 eV spectrum indicates that its maximum is displaced by about 0.5 eV below the comparable peak in the normal fluorescence spectra excited at higher energies. This shift is characteristic of the RIXS spectra discussed in the previous section and is a result of excitation below an absorption threshold. RIXS spectra at the O K edge have been seen in other TMO systems [32].

In Fig 4.19, we present spectra taken in the b-15°-E configuration for excitation energies in the region where excitation shifts from the O3 to the O2 site (see discussion on absorption spectra). There are clear changes in the shape, structure and position of the
Fig. 4.19 O K SXF for the b-15°-E configuration well above threshold.
spectral features as excitation changes from 530.5 eV, where primarily O3 is excited (see Fig. 4.18(a)), to 533.5 eV, where O2 is primarily excited. We take the 533.5 eV spectrum as representative of nearly pure O2 excitation. O2's maximum peak position is located at a spectrometer energy of 524.8 eV, which is 0.5 eV higher in energy than the O3 peak.

To illustrate our conclusions, we present a LPDOS plot, both experimental and theoretical, for each O site in Fig. 4.20. The experimental emission spectra plotted are those which were identified as a LPDOS spectrum of a specific O site. The theoretical emission presented was calculated (for each O site) with the WIEN97 code. Included in the calculation are broadening (Lorentzian) functions with a spectrometer-broadening factor of 0.5 eV, as is the case with our spectrometer resolution.

Referring to fig. 4.20, we see that very good agreement is obtained between experimental and theoretical curves of the O2 and O3 sites. There is excellent agreement of the location of structural features and moderately good agreement in the relative magnitude of experimental and calculated structural features. The agreement for the O1 is much less satisfactory. Only the low energy peak centered at about 522 eV in the theoretical spectrum is observed as a distinct feature of the experimental spectrum. The strong peak located at about 525 eV in the calculated spectrum is observed only as a featureless sloping shoulder in the experimental spectrum.

The implications of this result can be better understood by considering the projections of the O 2p DOS of the different p-symmetries (x,y,z) of the valence band in Fig. 4.17. The theoretical emission curves in Fig. 4.20 are calculated as normal fluorescence spectra, which do not consider the polarization of the exciting photons, and
Fig. 4.20 Plot of both the experimental and theoretical O 2p LPDOS for each O site.
give equal weight to the $p_x$, $p_y$, and $p_z$ components of the DOS. As noted above, there is good agreement for the O2 and O3 sites, but not for O1. Fig.'s 4.14 and 4.15 make clear that excitation of the O1 site at threshold occurs when the polarization vector of the exciting photons is aligned with the O1-$p\pi$ antibonding orbital ($p_\gamma$-projection) directed along the b-axis of the crystal. In the emission spectra, the low energy peak, which dominates the spectrum, is associated with the O1-$p\sigma$ bond orbital, with $p_x$-projection, which is labeled peak $B'$ in Fig. 4.17, between the bridging oxygen and the adjacent vanadium atoms. The contributions of the $p_y$ and $p_z$ at the top of the valence band in Fig. 4.17 are strongly suppressed in the experimental spectra.

Referring to O2, the very bottom of the band is derived from O2-2$p_x$/V-4s bonding orbitals, while the top of the band is derived from mainly O2 2$p_{x,y}$ orbitals. In addition, to the high energy side of the main O 2$p$ band is a small spectral feature, which is seen at low excitation energies, especially along the b-15°-E configuration. This spectral feature is derived from weakly bonding V-$d_{xy}$/O2-2$p_y$ orbitals, which is due to the slight tilt of the VO$_5$ pyramids. The spectral intensity is seen to move with the excitation energy, indicating that this is a RIXS feature. However, the V-O interactions were negligible when accounting for correlation effects seen in the V $L_3$ spectra (see the discussion in the previous section). Finally, for the O3 spectra, the theoretical and experimental curves are in agreement with contributions from all three $p$-symmetries. The O3 2$p_x$ orbitals, as with the case with O1 2$p_x$, are bonded with V 3$d^2_x$ orbitals.
Experimental and theoretical $V L_3$ SXA and SXF spectra

The last section provides results of the $O K$ SXS data obtained utilizing both angular and excitation dependent techniques. In this section, we present and discuss the angular dependent $V L_3$ SXA and SXF spectra. We will first discuss the experimental and theoretical $V L_3$ SXA spectra and then the emission data, and the effects that $pd$ hybridization has on the $V L_3$ emission.

Experimental angular dependent $V L_3$ spectra are presented in Fig. 4.21. Data were collected at 0.2 eV intervals with a resolution of ~0.3 eV. The same sample geometry with respect to $E$ used for the $O K$ spectra is used here. At first glance, the spectra do not contain much angular dependence in contrast to the $O K$ spectra. There are some variations of shape with angle seen at an excitation energy of 517.2 eV. Comparing the spectra taken at $0^\circ$ ($E \parallel b$) (dark line) and at $75^\circ$ (dashed line), there is clearly a change in the intensity and energy but not nearly as dramatic as the $O K$ absorption spectra.

To understand the implications of this result, we present the theoretical angular dependent $V L_3$ SXA calculations in Fig. 4.22. [30] Recall the dipole selection rules for SXS, $\Delta l = \pm 1$ and $\Delta m = 0, \pm 1$. Unlike the calculations for the $O K$ SXA, the SXA for the $V L_3$ edge have two channels for core holes of $p$-symmetry, $m = 0, \pm 1$. Hence we have two conditions: (1) $l = 1, m = 0$ to $l = 2, m = 0$ and (2) from $l = 1, m = \pm 1$ to $l = 2, m = \pm 1$. The calculated spectra show a clear angular dependence. Fig.4.22(a) plots the calculated spectra with $l = 1, m = 0$, while (b) plots the $l = 1, m = \pm 1$ spectra. However, our measurement is a combination of both. Thus, we plot the total in (c) to compare with
Fig. 4.21  Experimental $V L_3$ SXA taken with the TEY mode and at different polarization directions with respect to the b-axis.
Fig. 4.22 Theoretical $V L_3$ SXA at various polarization direction with respect to the b-axis.
theory. As with the experimental data, these effects are effectively canceled out and no strong angular dependence is detected.

In contrast to the absorption, the SXF spectra for the V L₃ edge have a clear detectable angular dependence. Fig. 4.23 plots the spectra taken at a (a) 15° angle of incidence and (b) a 75° angle of incidence. As the sample is rotated from 15°, there is a clear change in the relative magnitude of the two peaks. After all experimental factors are taken into account, we conclude that the intensity of the RIXS peak changes very little as a function of excitation angle, but that the normal fluorescence peak is greatly reduced at high angles of incidence.

To understand this conclusion, recall that both O₁ and O₃ form bonding states with the V 3dₓ²-ᵧ² orbitals. Contributions from these bonding states are suppressed when excitations are out of the plane, where the O₁ and O₃ orbitals seen in the initial peaks for both the a-15°-E and b-15°-E configurations become less intense when θ increases. This indicates that any contributions from O₁ and O₃ orbitals, especially at energies near the threshold, will be maximized in the plane and nearly vanish otherwise. In fact, O₁ absorption in the a-15°-E configuration, at threshold, does not contribute at all. Therefore, the bonding states formed with these p-orbitals will likewise be less emphasized when E is out of the plane for both configurations, and, for the case of O₁, when exciting in the a-c plane at every angle.

4.4 Conclusions

It has been shown that correlation effects can be directly probed using SXS. By employing the concepts of RIXS spectra, we are able to accurately estimate the on-site
Fig. 4.23 V L₃ SXF at various excitation energies with a polarization direction of (a) 15° with respect to the a-axis.
Continued. (b) At 75° with respect to the a-axis.
Coulomb parameter $U_{dd}$ that specifically deals with the V 3$d$ electron interactions. The spectra illustrate that by varying the excitation energy of the incident photon beam, we can determine energy loss, which is a direct result of $d_{xy} \rightarrow d_{xy}$ excitations. Combined with a solid theoretical approach for calculating the V 3$d$ projected DOS, along with the calculation of the transition matrix elements we measure experimentally, a very good scheme has been developed to study other strongly correlated systems, in which electron correlation manifests itself by opening a gap at the Fermi level. In addition to these successes, we have also shown explicitly that LDA calculations, without these correlation effects due to the V 3$d$ electron interactions, cannot theoretically predict the gap of the material when the system is in the excited state.

In contrast to the correlation effects due to V-V interactions, the bonding/antibonding V-3$d$/O-2$p$ states are well described by the calculations of the projected DOS for both the V and O sites. By varying the angle of incidence of $\mathbf{E}$ with respect to the a(b)-axis in the plane and the c-axis along the apical direction, the V $L_3$ emission is very much effected by the in-plane ($\sigma$) bonding of O1 and the bonding with O3, whose bonding orbitals are approximately parallel to the plane.

When applying angular resolved SXS to the O $K$ edge, excellent agreement was reached when resolving the LPDOS of not just a specific O site, but also $p$ orbital symmetries of the same site. For the case of O1, many fascinating results were obtained. For instance, the absorption of O1 occurs at low energies with respect to the other absorption spectra from O2 and O3 only when excitations occur close to the b-axis. Thus, we conclude that the O1 is strongly hybridized with V 3$d_{xy}$ orbitals to form $\pi$ antibonding
states. Further, we have also opened some questions as to the emission process from the O1 site. When electronic transitions from the valence band to the core holes of the O1 site occur, only electrons in the orbitals that participate in $\sigma$ bonding states with V 3$d_{xz}$ at the bottom of the valence band contributed to the spectra. This result, though not yet fully understood theoretically, makes it clear that combined angle and energy selection enables the selective excitation, not only of different oxygen sites, but also of different orbitals on the same site. Moreover, this selective excitation can have a significant effect on the radiative de-excitation channels that contribute to the fluorescence.

Finally, with a careful comparison of theoretical and experimental absorption, we were able to provide a very good measure of a LPDOS of both O3 and O2 2$p$ states. For the case of O3, a spectrum was obtained in two different orientations of the crystal.

This dissertation has shown that SXS is a very useful and exciting tool to study the electronic structure of the highly anisotropic, strongly correlated TMO system known as NaV$_2$O$_5$. This method proves to be very useful in studying other fascinating materials with either challenging physical properties or practical applications (e.g. high-$T_c$ superconducting materials) or both.
REFERENCES


APPENDIX I

X-RAY MAGNETIC LINEAR DICHROISM

In chapter 2, we pointed out that two factors can affect the shape of the spectra when the sample is rotated with respect to the polarization direction. The first is the orbital orientation in highly anisotropic systems. The second is linear magnetic dichroism (LMD), which occurs in some magnetic materials. We have studied LMD in Fe₃O₄ and Fe₂O₃. We will present some of the x-ray magnetic linear dichroism (XMLD) results from those two systems and compare with other results.

Fe₃O₄ is a ferrimagnetic material which contains a mixed valency of Fe³⁺ and Fe²⁺ ions. The crystal system is an cubic inverse spinel with an FCC lattice. Tetrahedral A sites contain one-third of the ions, which are Fe³⁺, while the octahedral B sites have the remaining two-thirds ions with equal numbers of both Fe³⁺ and Fe²⁺ ions. It has been suggested that the Verwey transition, the jump in resistivity at ≈ 120 K, is a result of an onset of a charge-ordering on the B site ions [A1.1].

To illustrate the polarization dependence of SXA spectra in Fe₃O₄, we turn to Fig. A1.1. Here we plot the normal incidence TEY of Fe₃O₄ with a (111) face as a solid line and with a (100) face as a dotted line. Fig. A1.1 also shows the difference spectrum between the two intensities. The TEY plots have been normalized to the incident beam current. A very weak background signal has been subtracted off. Thus, the absorption is 100 % above the background.
Fig. A1.1 Linear dichroism measured on the Fe $L_{2,3}$ edge in Fe$_3$O$_4$ using SXA in the TEY mode. The difference spectra is seen as the dotted line below the TEY spectra.
The general features of the spectra include the crystal field splitting ($\Delta = 1.3$ eV) between the $t_{2g}(xy, xz, yz)$ and $e_g(x^2-y^2, z^2)$ orbitals. This splitting can be seen in both the $L_2$ and the $L_3$ spectra, which are split by about 12.8 eV due to the spin-orbit interaction on the Fe $2p$ core hole. Other spectra taken at the Fe $2p$ absorption edge on this compound are not as clearly resolved as those presented here, in which the crystal field splitting is very much resolved.

Since Fe$_3$O$_4$ is a cubic system, the difference in the absorption curves emanate from the different ionic character of the Fe ions. This was shown theoretically by Dräger et al., in which the absorption spectra were calculated for both the A sites and the B sites (see chapter 1). The Fe ions on the octahedral sites align ferromagnetically, while the Fe$^{3+}$ ions on the tetrahedral sites align with the opposite magnetization. By aligning the polarization vector $\mathbf{E}$ of the photon beam, with linearly polarized light vector $\mathbf{E}$ of the photon beam, with linearly polarized light, along one magnetization and then along the other, the difference in the spectra at both polarization directions is obtained as linear dichroism. Due to the opposite magnetization direction between the tetrahedrally and octahedrally coordinated Fe$^{3+}$ ions, some of the circular dichroism cancels out, due to the change in magnetic quantum number.

LMD effects have also been seen in Fe$_2$O$_3$. Fe$_2$O$_3$ (alpha phase) undergoes a magnetic phase transition from a weakly ferromagnetic to an antiferromagnetic material at the Morin temperature at $T_M = 260$ K [A1.2]. When this occurs, the magnetic moments (Fe$^{3+}$ ions) align along the crystalline (rhombehedral) c-axis. There are an equal number of spins aligning along the positive c-direction as there are along the negative c-direction.
Thus, the system at the phase transition has a net moment of zero. The alignment of the spins was observed by neutron diffraction in 1951 by Shull et al. [A3.3]. At room temperature (above $T_M$), the spins were perpendicular to the c-axis. Diffractions of the same orientation showed that the spins rotated by 90° to align along the c-axis. Shull et al. won the Nobel prize in physics for their work in this area.

In Fig. A1.2, we plot the TEY spectra of Fe$_2$O$_3$ at $T = 300$ K (above the Morin temperature) and at $T = 200$ K (below the Morin temperature) with the polarization vector parallel to the crystalline c-axis. As with the case of Fe$_3$O$_4$, the spectra show a spin-orbit splitting of about 13.2 eV with a crystal field splitting of $\Delta = 1.4$ eV, which is slightly bigger than Fe$_3$O$_4$.

The difference in the shape of the spectra is most clearly noticed at the $L_2$ edge, where the ratio of both the $t_{2g}$ and $e_g$ peaks are different for each polarization. It has been shown that the difference in shape of the spectra is clearly due to a spin-flip transition of the Fe ions, which were perpendicular to the c-axis above $T_M$, and then align parallel to the c-axis below $T_M$ [A1.4]. However, due to surface effects, the measured dichroism does not agree well with theoretical predictions of 25%.
Fig. A1.2 Linear dichroism measured on the Fe $L_{2,3}$ edge in $\text{Fe}_2\text{O}_3$ using SXA in the TEY mode.
APPENDIX II

CALCULATED DOS AND SPECTRA OF NIO

The purpose of this appendix is to compare calculations that exclude on-site Coulomb interactions (WIEN97) with LSDA + $U$ calculations [A2.1], which include correlation effects. We will briefly illustrate this by using the NiO system. Most of the details may be found in the references but enough background will be provided to illustrate the main points.

In Fig. A2.1, we plot the calculated DOS for both the $3d$ and $2p$ states of a Ni and O ion respectively. For the Ni ion, we display both the majority and minority ($\uparrow\downarrow$) spins. The calculation produces an antiferromagnetic ground state with a band gap of about 1 eV, which is significantly underestimated. To predict the correct band gap in the ground state, many methods have been implemented to account for the strong electron correlation effects attributed to the Ni $3d$ electrons. In this picture, the strong Coulomb interactions introduced by the Hubbard $U$ parameter split the Ni $3d$ band and opens a wider gap than that produced without the implementation of $d$-$d$ Coulomb interaction terms. This method has also been utilized with the calculation of x-ray emission spectra for other strongly correlated systems.

Turning now to Fig. A2.1, we see that the strongest weight of states below $E_F$ are from Ni $3d$. At a binding energy of $\sim$ -4.8 eV, we see that there is strong $pd$ hybridization, especially with the $3d\uparrow$ spin states. In contrast, the $pd$ interactions for unoccupied states involve the $3d\downarrow$ states. For the O $1s$ SXS emission spectra, we should observe very little spectral weight at $E_F$. 

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Fig. A2.1 Plot of the Ni 3d (spin-polarized) and O 2p projected DOS in NiO. The Fermi level is at zero energy on this plot.
We now compare the theoretical and experimental O 1s emission in Fig. A2.2. The experimental spectrum is taken from Fig. 5(b). We see that we are in good agreement in the shape of the spectra. However, the shift in relative peak positions is due to the underestimation of the band gap in the calculation. The difference in the two peaks $P_1$ and $P_2$ are about 1.1 eV. The theoretical emission was broadened with same broadening factors as in the experiment. The broad tail that extends beyond $E_F$ is simply due to the broadening scheme implementing within the code, where a Lorentzian is used as opposed to a Gaussian.

Returning to our previous example of calculating NiO emission spectra using the WIEN97 code, we now demonstrate how the experimental spectra compares to theory when implementing the $L(S)DA + U$ approach [A2.1]. Fig. A2.3 displays the experimental spectrum at excitations above threshold and a theoretical spectrum calculated with an impurity model derived from the $L(S)DA + U$ approach. Unlike the comparison in Fig. A2.2 with the WIEN97 code, the spectral shapes line up almost exactly.

In conclusion, although the spectral features of the WIEN97 code are duplicated well, underestimations of the energy gap fail to predict correct (measured) binding energies of the O 2p filled states. Thus, for the case of NiO, since it is an insulator of the charge-transfer type (see Fig. 1.4) a prediction of the band gap in the system using the WIEN97 code will be underestimated. In contrast, by taking into account the effects of correlation after an excitation process, one can obtain reasonable estimates of the band gap and correct measured binding energies of the electronic states.
Fig. A2.2  Experimental and theoretical O K emission spectra. The calculated spectra was obtained using the WIEN97 code.
Fig. A2.3 Experimental and theoretical O K emission spectra from Ref.A2.1.
VITA

Gerald Woods was born in Knoxville, Tennessee. He graduated from Smyrna High School in 1987. Afterwards, he went on to Middle Tennessee State University and studied physics and math for which he received a Bachelor of Science degree in December of 1992. After working in at Associate laboratories, he then went on to further his studies at the University of Tennessee at Knoxville. He received his Doctorate of Philosophy in August of 2001.