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13. ABSTRACT *(Maximum 200 words)*

This grant was for the purchase of a high resolution x-ray fluorescence spectrometer based on the novel design of Professor Joseph Nordgren of Uppsala University in Sweden. Although initially we planned to construct the instrument, we eventually purchased the first such commercially available spectrometer from Gammadata of Uppsala, Sweden and arrived in December 1996. Purchasing the complete spectrometer had numerous advantages for our program, most notably the delivery of a working, calibrated unit from the group that invented the design. Using both this newly arrived instrument, and an identical spectrometer made available to us via a collaboration with Professor Nordgren, we have performed exploratory experiments on wide band gap semiconductors, organic superconductors, and quasi-low dimensional transition metal oxides. Results of these experiments are very encouraging, and prove the feasibility of our program. In particular, we measured the partial density of states of occupied and unoccupied states in GaN, measured the layer specific electronic structure in selected organic superconductors, and explored the effect of band dimensionality on emission from solids.

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High Resolution Soft X-ray Fluorescence Spectrometer

Final progress report for ARO Grant Number DAAH04-95-0014

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1. Forward

This document is the final report for the ARO DURIP grant awarded for the construction of a very high resolution soft x-ray fluorescence spectrometer. The instrument is fully operational and is one of only three such instruments in the United States. Experiments are underway measuring the detailed electronic structure of wide band gap semiconductors, organic superconductors and quasi-low dimensional transition metal oxides. Highlights of these initial experiments include the first direct observation of hybridization core and valence states in wide band gap semiconductors, and the first use of x-ray emission to study band structure in layered organic conductors. The spectrometer is at the core of two new programs funded by the National Science Foundation and it is anticipated that this instrument will see prolonged and productive use.

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4. Project Report

A. Introduction

X-ray fluorescence spectroscopy is well established as an analytic tool for the identification of the chemical composition of compounds. In this spectroscopy, a solid is exposed to either high energy electrons or photons, resulting in the creation of holes in core states. A fraction of these core holes deexcite via the transition of higher lying core electrons into the hole, resulting in the emission of photons. Since each element will have a unique set of core states, a fingerprint of the presence of specific elements is provided by measuring the spectrum of emitted photons.[1] However, due to a number of serious limitations, conventional x-ray fluorescence spectroscopy has largely been superseded by photoemission spectroscopy as a probe of the detailed electronic structure of solids. Among these limitations have been very low energy resolution, complex spectra that are difficult to interpret, and, in the case of electron-stimulated fluorescence, significant beam damage to nonmetallic samples.

A renaissance of soft x-ray fluorescence spectroscopy is presently underway due to advances in x-ray optics and the availability of synchrotron radiation sources.[2,3] By tuning the incident photon energy, core holes can be selectively created on individual elements in multi-element systems, and thus enhanced chemical specificity can be obtained.[2,3] Additionally, many background problems associated with electron and high energy photon excitation can be removed by using monochromatic photon excitation at a core level threshold. Finally, improvements in x-ray optics and detector technology have made it possible for high energy resolution to be obtained in the soft x-ray regime. Soft x-ray fluorescence (SXF) spectroscopy has several distinct advantages over photoemission under certain circumstances. Most notably, SXF has a sampling depth that is one to two orders of magnitude larger than photoemission, can study insulators with ease, and can make electronic structure measurements when the solid is in an applied electric or magnetic field.

Our proposal was to construct a high resolution soft x-ray fluorescence spectrometer based on the highly successful design of Professor Joseph Nordgren of Uppsala University in Sweden.[4] It consists of three fixed, grazing-incidence diffraction gratings, and a position sensitive x-ray detector that can be moved along the Rowland circle for each grating, thus remaining at the focal point for all energies. The spectrometer is housed in an ultra-high vacuum (UHV) chamber featuring low energy electron diffraction (LEED) optics, and an x-ray photoemission spectroscopy and Auger electron spectroscopy (AES) spectrometer. Samples can be cooled to liquid nitrogen temperatures and heated to approximately 1000°C. Fluorescence will be excited by monochromatic radiation from an undulator at the National Synchrotron Light Source (NSLS). All of the chamber hardware, the ancillary spectroscopies, and much of the spectrometer hardware was purchased using start-up funds from Boston University; the DURIP award was to support purchase of the remaining optical and vacuum components, and support the final assembly of the instrument. The spectrometer will see widespread use in the study of the electronic structure of defects and impurities in electronic materials, particularly wide band gap semiconductors. The spectrometer will also be used to study the growth and stability of metal overlayers on wide band gap semiconductors and on metal oxides, to study the evolution of electronic structure during bulk metal-insulator switching transitions, and to measure the electronic structure of complex organic conductors.

B. Instrumentation History and Progress

The instrument became operational in January of 1997, and the first synchrotron radiation excited spectra from GaN were recorded in mid-February 1997. Figure 1 presents an emission spectrum from thin film wurtzite GaN. The resolution of the instrument is identical to the original Nordgren design. Clearly visible in Fig 1. (see inset) is the emission from the N 2p hybridized states in the Ga 3d core level. Such sensitivity to hybrid states is quite remarkable, and will be discussed below in Section C.

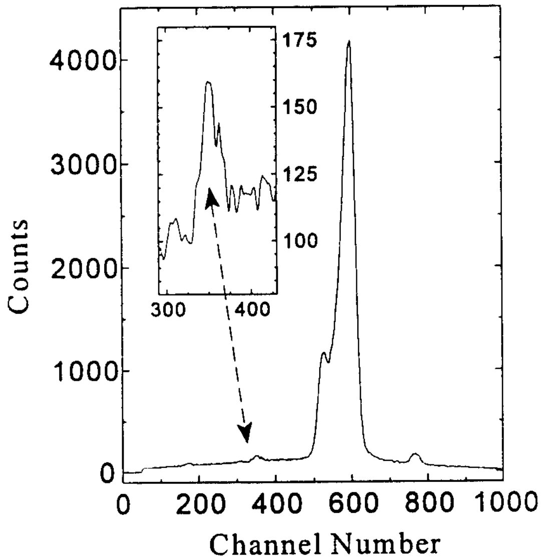

Figure 1: X-ray emission spectrum recorded from GaN with an excitation photon energy of 407.5 eV. 10 channels ≈ 1 eV.

Our initial plan was to assemble the spectrometer from components since a complete unit was not commercially available. However, Professor Nordgren decided to market a version of his spectrometer. Purchasing the complete spectrometer had numerous advantages for our program, most notably the delivery of a working, calibrated unit from the group that invented the design. However, since we had already purchased well over 75% of the components, we agreed that Professor Nordgren would purchase the gratings and vacuum components, we would ship the existing components to Uppsala for assembly and calibration of the spectrometer, and a guaranteed instrument would be shipped back. Negotiations concerning this purchase were prolonged, necessitating a 12 month no-cost extension to the award. Most of the first year was unfortunately spent in these negotiations, primarily between Professor Nordgren and his university concerning financial matters. The purchase order to Uppsala University as the vendor was only written in November 1995, with a 6 month delivery date from receipt of order. The delivery delay was due to the manufacture of the soft x-ray diffraction gratings. However, from a long term programmatic perspective, it was judged that the delay in scientific output was outweighed by the delivery of a calibrated operational instrument. Subsequently, Professor Nordgren entered into an agreement with Gammadata, a company in Uppsala, to manufacture the spectrometer. This required rewriting the purchase order and lead to further delays. The instrument finally arrived mid- December, 1996.

C. Scientific Progress

i) Problems Studied

Despite the fact that our spectrometer has only just arrived, we have nevertheless made significant scientific progress in the use of SXF to study electronic structure in novel materials. This was made possible by entering into a formal collaboration with Professor Nordgren, which allowed us to perform exploratory experiments using an existing spectrometer based at the HASYLAB synchrotron facility, Hamburg, Germany. Our experiments took place in November 1995. Subsequently, we were awarded an International Cooperation grant from the National Science Foundation to cover travel costs associated with these experiments. A second brief set of experiments was performed using another of Professor Nordgren's instruments at the Advanced Light Source in Berkeley, California. Finally, we have just completed two weeks of operations at the NSLS using our own instrument. Three general classes of materials are under investigation: wide band gap semiconductors, organic superconductors, and quasi-low dimensional transition metal oxides. Our goal is to use x-ray emission to study various aspects of the electronic structure in these novel materials. Specifically, we are looking for measurements of hybridization, partial densities of states (PDOS) and band structure. Our initial results are detailed below.

ii) Summary of Results

While the technological importance of refractory III-V nitrides as materials for wide band gap semiconductor devices is clear, there is a significant lack of experimental data concerning the basic electronic structure of such films.[5,6] Only recently have the intrinsic band structure, the density of states, and the electronic properties of surfaces of wide band gap semiconductors come under scrutiny. A fundamental understanding of the electronic structure is required if these materials are to achieve their full technological potential. We have measured the bulk valence band partial density of states by recording Ga L- and N K- x-ray emission spectra. We then compared the x-ray spectra to a recent *ab initio* calculation and found good overall agreement. Figure 2 presents data recorded using the original Nordgren spectrometer for emission following valence electron decay into a N 1s state, while Figure 3 shows similar data for at Ga $2p_{3/2}$ state.[7,8] The emission spectra reveal that the top of the valence band is dominated by N *2p* states, while the x-ray absorption spectra show the bottom of the conduction band as a mixture of Ga *4s* and N *2p* states, again in good agreement with theory.[9] However, due to strong dipole selection rules we can also observe directly for the first time weak hybridization between Ga *4s*- and N *2p*-states in the valence band. This is shown in Figure 4. Furthermore, a component to the N K-emission appears at approximately 19.5 eV below the valence band maximum and can be identified as due to hybridization between N *2p* and Ga *3d* states. The data in Fig. 4 can be compared directly with that shown in Fig. 1. The data in Fig. 1 were obtained using our instrument on beamline X1B at the NSLS, while the data in Fig. 4 were obtained

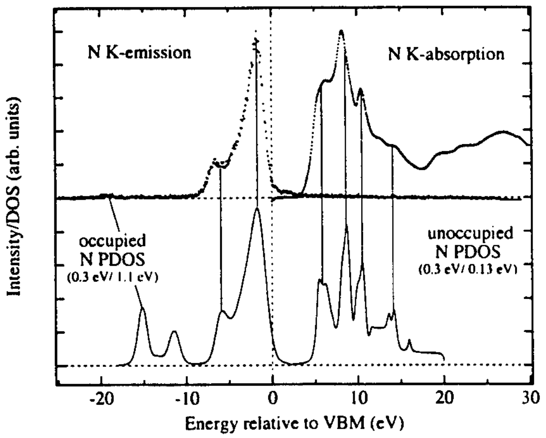

Figure 2: Nitrogen K emission and absorption spectra from GaN (top panel), Ref. 8, and calculated PDOS from Ref. 9 (bottom panel).

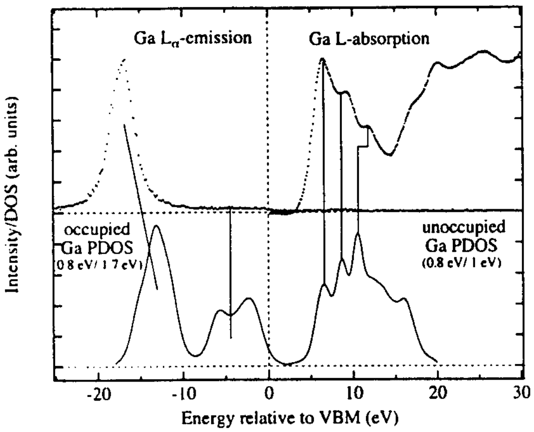

Figure 3: Gallium L emission and absorption spectra from GaN, (top panel), Ref. 8, and calculated PDOS from Ref. 9 (bottom panel).

using the original Nordgren spectrometer on beamline BW3 at HASYLAB, Hamburg.[10] Our instrument is performing superbly, and the hybridization peak is clearly visible in the spectrum. Note that the small peak at higher binding energies above the valence band emission in Fig. 1 is due to elastic scattering of the incoming excitation photons.

Turning to the organic superconductors, we have used the unique properties of x-ray emission spectroscopy to examine aspects of the electronic structure of these materials that are otherwise inaccessible to spectroscopic measurement. Initial experiments have been on the organic superconductors, κ-(BEDT-TTF)$_2$X, where BEDT-TTF = bis(ethylenenedithiolo)tetrathiafulvalene, commonly referred to as "ET". X is an anion, which in our case was Cu[N(CN)$_2$]Br.[11] Fig. 5 shows a series of high resolution x-ray emission spectra from single crystal ET as a function of the energy of the incident excitation photon. The spectra show the emission resulting from a radiative decay from the valence band into a N 1s core hole. As in the GaN experiment, the N 1s core hole is created by the excitation of the N 1s electron into empty states above E_F by monochromatic synchrotron radiation. The narrow peak that moves in emission energy with excitation energy above E_F is simply elastic scattering, namely the emission of a photon due to the de-excitation of the excited N 1s electron back into the N 1s level. Of much more interest is the inelastic scattering, namely the emission due to the valence band density of states. Conventional x-ray emission is considered to give the partial density of states due to the angular momentum conserving dipole selection rule governing the transition. Thus if we create a core hole on the N 1s level, we expect only

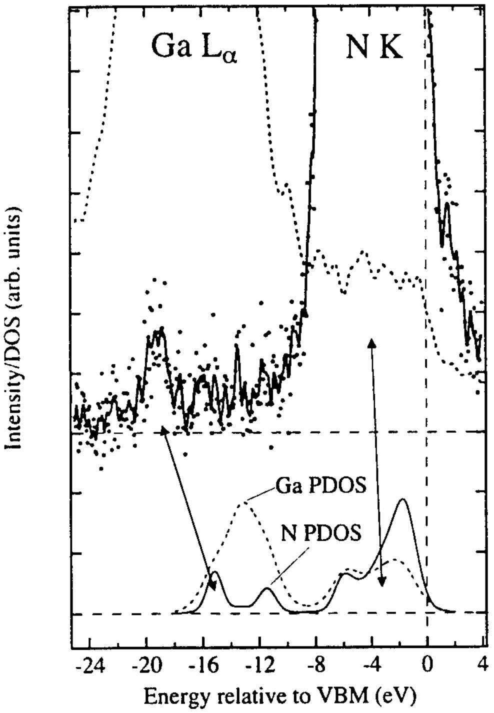

Figure 4: Same emission data as in Figs. 2 and 3, but plotted on an expanded vertical scale, and compared to theory (Ref. 9).

electrons from 2p states to radiatively de-excite to fill the hole. This implies that there should be no dependence of the emission on the energy of the photon used to excite the N 1s hole. However, as is clearly visible in Fig. 5, there is in fact a strong dependence of the emission upon the incident photon energy around the N 1s absorption edge at 395 eV. The explanation for this lies in the conservation of band momentum. The N 1s electron excited above E_F resides in a band state with a well defined k-vector. The valence band electron that falls to fill the core hole must have a k-vector that matches this in order to conserve band momentum, in addition to angular momentum. The data in Fig. 5 show that as the incident photon energy is increased, and the excited electron thus placed in different bands above E_F, the emission spectrum changes dramatically due to the requirement that k be conserved. Thus soft x-ray emission can be used to extract band dispersion information. Similar effects have been reported for graphite.[12] This is an exciting development in the study of electronic structure in organic conductors, since soft x-ray emission is bulk sensitive, elementally specific, applicable in electric or magnetic fields, and now has been shown to be sensitive to band structure effects. Furthermore, since we are measuring only the N-related band structure, and the N atoms are only in the anion layers, we also now have a layer-specific probe. The spectra in Fig. 5 were recorded with the original Nordgren instrument, but identical data were obtained using our instrument.

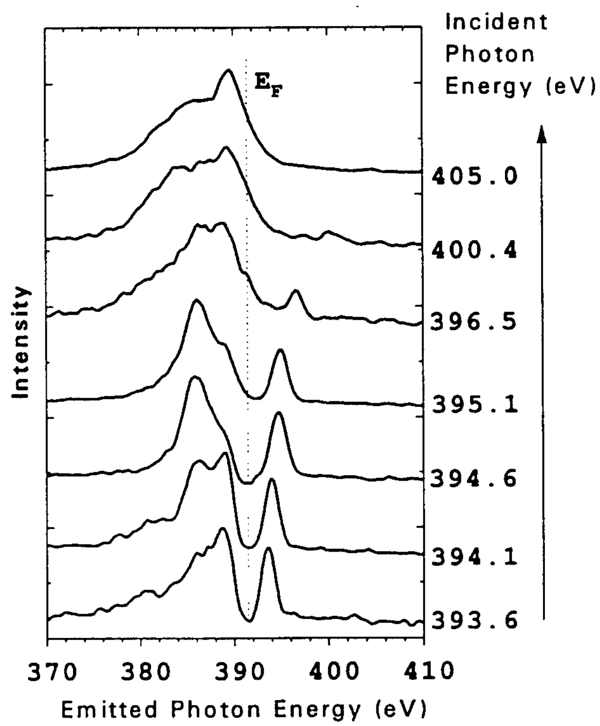

Figure 5: X-ray emission spectra from ET as a function of incident photon energy.

Finally, we have embarked on an exploration of the effects of the dimensionality of bands on x-ray emission from quasi-low dimensional transition metal oxides Initial results are intriguing, and show a much greater sensitivity of x-ray absorption to band dimensionality than x-ray emission.[13]

iii) Publications and Technical Reports

Due to the long construction delays outlined above, no manuscripts with ARO sponsorship have been published during the reporting period. However, three papers are in preparation at the time of writing, and will be submitted shortly. The award of ARO funds for this high resolution SXF spectrometer seeded subsequent success in two proposals to the NSF. In the first of these, I was awarded an NSF CAREER Award (the renamed Presidential/National Young Investigator Award) to use SXF and photoemission to study electronic structure in organic superconductors. This is a five year award, good through the summer of 2000, and provides operating funds and student support. The second award is a regular NSF three year grant to study electronic structure at the surface and in the bulk of wide band gap semiconductors such as GaN. This award funds a postdoctoral research associate based permanently at the NSLS. Success in these proposals would not have been possible without the ARO award, since neither would have provided the funds necessary to complete the SXF spectrometer. Finally, in order to ensure adequate beamtime for our experiments SXF experiments, we have formally joined the research team on the high brightness undulator beamline X1B at the NSLS.

iv) Personnel

This award provides no funds for the support of scientific personnel. No graduate students working with the instrument have yet earned degrees. Note, however, that the PI was awarded an NSF CAREER Award during this reporting period; the CAREER Award is the renamed Presidential/National Young Investigator award.

5) Inventions

No inventions are reported.

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