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Spectroscopic Studies of Oxide-Based Materials in High Magnetic Fields

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Introduction

The overall goal of this work was that presented in the original proposal: to pursue a program of spectroscopic research aimed at the understanding of low-dimensional transition metal oxides in high magnetic fields at the State University of New York at Binghamton. More recently, my research group and I have moved to the University of Tennessee in Knoxville, and my DOE grant has been transferred there.

Summary of Research Results in the Grant Period (November 1998 - July 2001):

Low-Dimensional and Novel Vanadates:

Inorganic Spin Gap Materials: The $\alpha'\text{-NaV}_2\text{O}_5$ system has attracted a lot of attention recently due to the strong charge, spin, lattice interactions. Our experiments have concentrated on a detailed understanding of the electronic structure and how charge degrees of freedom change through the 34 K charge ordering transition. Our measurements identify broad, polarization-dependent electronic structure modifications at $T_c$ (Fig. 1); these features correspond to sidebands on the 1 eV charge transfer excitation in the optical conductivity.

Figure 1: Temperature dependence of zero-field reflectance ratios, $\Delta R$, for the (a) $E||a$ and (b) $E||b$ polarizations. At the center of the spectra, the temperatures are, from top to bottom: $T = 4, 10, 20, 30, 35, 40, 45$ K; at the low energy end, from bottom to top: $T = 4, 20, 30, 40, 45$ K. The inset for each polarization shows the integrated intensities of the $\Delta R$ features versus temperature, with the integration region shown by arrows in the main figure. Empty circles refer to the zero-field data and solid diamonds to the data taken at $H = 28$ T (not shown).

We employed the sensitivity of these high-energy sidebands on the 1 eV absorption band to temperature and applied magnetic field to investigate the phase transition in $\alpha'\text{-NaV}_2\text{O}_5$. Data were collected in steady (45 T) and pulsed (60 T) fields between 4 and 45 K. We used the spectral changes to map the $H-T$ phase diagram and find a temperature-independent phase boundary at $\sim 27$ T which persists above $T_c(0)$, a kink in $T_c(H)$ near $H_c$. 
and $H^2$ behavior of $T_c(H)$ in the high field phase with prefactor $\alpha=0.09$. It is notable that $H_c \approx T_c(0)$. Based upon an analysis of our optical results within a suggested charge-spin-lattice fluctuation model, we propose that the elementary excitation is on-rung intraband hopping with an associated spin-flip and concomitant lattice distortion; coupling of these low-energy excitations with the optically-induced charge transfer yields the high-energy sidebands on the 1 eV band in the optical conductivity. The 34 K phase transition is assigned as a crossover between thermal excitation over the on-rung potential barrier above $T_c$ and tunneling through the barrier below $T_c$, and $H_c$ is associated with a change in the on-rung potential, which modifies the low-energy excitation dynamics and leads to formation of field-induced ferromagnetic domains above 27 T. These results are sure to spur complimentary magnetization and NMR measurements to fully characterize the nature of the ground states of $\alpha'$-NaV$_2$O$_5$ in the vicinity of the 33 T phase boundary.

**Figure 2:** (a) $H$-$T$ phase diagram of $\alpha'$-NaV$_2$O$_5$, mapped out using $E||a$ near-infrared spectral changes. Triangles: steady field optical data; squares: pulsed magnet data. Solid horizontal line: the $H_c$~27 T phase boundary, obtained from the steady field data. Curved solid line (continued as dashed line): $H^2$ fit of the high field phase part ($H > 27$ T) of $T_c(H)$; solid vertical line: low field part ($H < 27$ T) of $T_c(H)$; note the kink in $T_c(H)$. (b) $H^2$ fit of $T_c(H)$, illustrating how we extracted the coupling constant $\alpha$. Triangles with vertical error bars: steady field data; squares with horizontal error bars: pulsed field data. The energy scales of various magnet systems are shown for comparison.

Infrared Investigations of Ti$^{4+}$-Doped $\alpha'$-NaV$_2$O$_5$ In order to compliment our work on the pristine ladder material, we measured the polarized infrared reflectance of Ti$^{4+}$-doped $\alpha'$-NaV$_2$O$_5$ and carried out an analysis of the frequency dependent conductivity. Here, localized doping (achieved via Ti replacement of V) was of special interest; Na underdoping and Ca doping (which results in delocalized spin defects) has been studied in the
past. On-rung impurity incorporation allows us to resolve a number of new rung-polarized vibrational features due to local symmetry breaking. Variable temperature measurements both above and below the charge ordering transition indicate that the majority of zone-folding modes in Ti$^{4+}$ substituted α'-NaV$_2$O$_5$ are a subset of those in the pristine material; minute new folded modes are observed at 46 (E||a), 105 (E||a), and 636 (E||b) cm$^{-1}$. Our results can be understood in terms of disruption of the rung in the vicinity of the Ti$^{4+}$ defect.

Na$_2$V$_3$O$_7$ Nanotubes - A Mesoscopic Analog: In order to compare the electrodynamics of a model ladder material such as α'-NaV$_2$O$_5$ with those of a chemically similar compound with a more localized, tubular morphology, we investigated the infrared and optical properties of Na$_2$V$_3$O$_7$. This material consists of nanotubes made up of edge/corner sharing VO$_5$ square pyramids (Fig. 3); each vanadium site carries a single unpaired spin. While originally thought to be a three-leg ladder system, more recent theoretical work has shown that the spin exchange interactions are best described by six mutually intersecting helical chains.

![Figure 3: Crystal structure of Na$_2$V$_3$O$_7$ nanotubes, showing both a cross section and perspective view of the tubes.](image)

We investigated the electronic and vibrational properties of Na$_2$V$_3$O$_7$ nanotubes and compared the response with other layered and non-layered vanadates. The electronic structure of Na$_2$V$_3$O$_7$ displays a strong similarity to that of non-tubular vanadates. We assign the 1.2 eV band as a V d → d excitation and the 3.3 and 3.9 eV bands as O 2p → V 3d charge transfer structures. Although band structure calculations predict additional fine structure in the density of states due to the tubular morphology, such features are not observed in the absorption spectrum. The vibrational spectrum displays triplet mode splitting due to reduced site symmetry, consistent with the three slightly different vanadium atoms that form the basic structural unit. A low frequency rattling mode is observed in Na$_2$V$_3$O$_7$. This unique characteristic of the Na$^+$-ion intercalated tubes may be connected with the ionic conductivity. Although predicted theoretically, we do not find evidence for a spin gap in the far-infrared. This work was initiated at SUNY-Binghamton and completed at the University of Tennessee.

Far Infrared Investigations of Impurity-Substituted CuGeO$_3$

In order to assess the low-energy excitations in this low-dimensional magnetic materials, we measured far-infrared reflectance of Zn and Si doped CuGeO$_3$ single crystals as a function
of applied magnetic field at low temperature. Overall, the low-energy far-infrared spectra are extraordinarily sensitive to the various phase boundaries in the $H$-$T$ diagram, with the features being especially rich in the low-temperature dimerized state. Zn impurity substitution rapidly collapses the 44 cm$^{-1}$ zone-boundary spin Peierls gap, although broadened magnetic excitations are observed at the lightest doping level (0.2%) and a remnant is still observable at 0.7% substitution. In a 0.7% Si doped sample, there is no evidence of the spin gap. Impurity substitution effects on the intensity of the 98 cm$^{-1}$ zone-folding mode are striking as well. The lightly doped Zn crystals display an enhanced response, and even at intermediate doping levels, the mode intensity is larger than that in the pristine material. The Si doped sample also displays an increased intensity of the 98 cm$^{-1}$ mode in the spin Peierls phase relative to the pure material. The observed trends are discussed in terms of the effect of disorder on the spin gap and 98 cm$^{-1}$ mode, local oscillator strength sum rules, and broken selection rules.

Figure 4: Upper left panel: Far-infrared reflectance of Cu$_{0.998}$Zn$_{0.002}$GeO$_3$ as a function of applied magnetic field at 4.2 K. Upper right panel: Far-infrared reflectance ratios of Cu$_{0.993}$Zn$_{0.007}$GeO$_3$ as a function of applied magnetic field at 4.2 K. Lower left panel: Far-infrared reflectance ratios of Cu$_{0.985}$Zn$_{0.015}$GeO$_3$ as a function of applied magnetic field at 4.2 K. Lower right panel: Far infrared reflectance ratios of Cu$_{0.96}$Zn$_{0.04}$GeO$_3$ as a function of applied magnetic field at 4.2 K. The curves have been offset for clarity in each case.

Understanding the Electronic Structure of $\eta$-Mo$_4$O$_{11}$ in High Magnetic Fields

In order to investigate the dynamic response of two-dimensional density wave compounds, we measured the polarized optical reflectance of $\eta$- and $\gamma$-Mo$_4$O$_{11}$ as a function of temperature and magnetic field. Excitations are assigned and analyzed based upon electronic band structure calculations. The 300 K spectra of $\eta$- and $\gamma$-Mo$_4$O$_{11}$ show charge transfer transitions (O 2$p$ $\rightarrow$ Mo 4$d$) near 4 eV, intraband ($d$ $\rightarrow$ $d$) transitions at $\sim$1.5 eV, and a free carrier response at lower energy. The intraband ($d$ $\rightarrow$ $d$) transition shows strong and unusual anisotropy in the $b$ and $c$ directions, which is directly attributable to the dispersion relations of the lower-lying $d$-block bands. The effect of charge density wave formation on the optical properties of $\eta$- and $\gamma$-Mo$_4$O$_{11}$ is discussed and compared with related materials.
The magnetic field dependence of the optical constants is also determined for $\eta$-Mo$_4$O$_{11}$ and is understood in terms of field effects on the nesting vector and Fermi surface.

**Low-Dimensional Tungsten Bronzes:**

The tungsten monophosphate bronzes, (PO$_2$)$_4$(WO$_3$)$_{2m}$ ($m=2$-14), are another class of layered transition metal oxides that have attracted our attention. These materials are interesting because of their tunable dimensionality. Here, changing the layer thickness ($m$) modulates in-plane “connectivity”, giving rise to a cornucopia of unusual properties including superconductivity and a set of unusual imperfectly nested density wave transitions. We concentrate on a comparison of the $m=2$, 4, and 6 samples, which are the most well-characterized by transport and magnetization techniques. The $m=7$ material is also interesting because it is a density wave superconductor.

**Comparison of the Tungsten Bronze Optical Properties as a Function of Layer Thickness**

We measured the 300 K polarized reflectance spectra and calculated electronic band structures of a series monophosphate tungsten bronzes, (PO$_2$)$_4$(WO$_3$)$_{2m}$, ($m=2$, 4, 6, 7). These materials have several layers of corner-sharing WO$_6$ octahedra separated by one PO$_4$ layer, leading to a “tunable” octahedral layer thickness with $m$. In the optical regime, the spectra of the $m=2$, 4, 6, and 7 materials display an anisotropic electronic excitation, originating from the W intra-$t_{2g}$ $d \rightarrow d$ transition. The intensities and frequencies of the intra-$t_{2g}$ $d \rightarrow d$ excitation vary with the octahedral layer thickness. Several vibrational modes along the interlayer direction of the $m=4$, 6, and 7 compounds also change with $m$ as well. These results are consistent with a softer lattice with increasing $m$. The low-frequency electrodynamics of the monophosphate tungsten bronzes shows a gap or pseudogap feature in the infrared, demonstrating a ubiquitous bound carrier response in these tungsten bronzes.

![Figure 5: Optical conductivities of the $m=2$, 4, 6, and 7 MPTB compounds at 300 K. All data is shown on the same conductivity scale to facilitate comparison. D.C. conductivities for each material are indicated by the solid square at zero frequency.](image)
The Electrodynamics Response of the $m=7$ Density Wave Superconductor

We measured the polarized optical reflectance of P$_4$W$_{14}$O$_{50}$, the only charge density wave superconductor in the monophosphate tungsten bronze family, over a wide frequency range. The 300 K infrared spectra are dominated by a two-dimensional behavior: high reflectance with weak phonons in the conducting $ab$ plane and low reflectance with strong vibrational modes along the interlayer direction. An anisotropic intra-$t_{2g}$ $d \rightarrow d$ excitation ($\sim 10000$ cm$^{-1}$) reveals the "hidden" one-dimensional band structures in P$_4$W$_{14}$O$_{50}$. The variable temperature $ab$-plane spectra clearly show a suppression of the optical conductivity along the $b$-axis below 140 K, giving rise to charge localization and anisotropic density wave gap formation at $\sim 1400$ cm$^{-1}$. Although oscillator strength is redistributed among the free carrier response, charge density wave gap absorption, and $d \rightarrow d$ transition in the density wave states, the spectral weight is largely conserved below the plasma frequency. The $ab$-plane phonons become well-resolved in the CDW states due to reduced screening. Based upon these observations, P$_4$W$_{14}$O$_{50}$ is another example of a superconductor with an unusual normal state.

Figure 6: Optical conductivity of the $m=7$ MPTB compound along the $a$-axis (a) and the $b$-axis (b) at several temperatures. Insets display close-up views of the phonons at several temperatures. Spectra in the insets are offset for clarity. Dash line and arrow indicate how we obtain the optical gap $2\Delta_{\text{optical}}$ at 10 K.

Education and Human Resources

My research program stimulates a broad education in the physical sciences because it crosses the disciplinary boundaries of both Chemistry and Physics. In my lab, students learn how to perform a series of careful physical measurements on a wide variety of novel
electronic and magnetic solid materials. Experimental techniques include polarized far-, middle-, and near-infrared, optical and uv spectroscopies, as well as basic sample handling, high vacuum, and cryogenic techniques. My strong National Laboratory collaborations are a significant benefit to students. We make working visits to the National High Magnetic Field Laboratory in Tallahassee, FL and Los Alamos, NM, and to the National Synchrotron Light Source in Brookhaven, NY several times per year. My move from Binghamton to Knoxville provides opportunities to collaborate at Oak Ridge National Laboratory as well. Regular visits by leading spectroscopists, interaction with very creative synthetic chemists, and strong collaborative ties with theoretical groups provide for a well-rounded experience.

**Students Involved in these Projects**

- High School Student Researchers: Julia Ferris.
- Undergraduate Researchers: Sumit Chowdhary, Scott Oppenheimer.
- Graduate Researchers: ZhengTao Zhu, Barry Jones.
- Postdoctoral Researchers: Virginia Long, Galina Rudko, Andrei Sushkov.

**Key Collaborators on this Work**

We are fortunate to have access to a wide variety of extremely interesting compounds, prepared by some of the world’s leading materials development groups. That we work with interesting and actively studied materials means that our efforts will impact the work of other research groups. At the same time, collaboration with a diverse group of materials preparation groups is an excellent experience for my students, as this interaction requires them to think about the complex relationships between spectroscopy, structure, and exotic electronic and magnetic properties. In fact, it is through this kind of long term joint work and collaboration that we gain the best opportunity to impact the design of new materials.

Over the course of our work, we have also had the opportunity to develop strong collaborations with a number of theoretical groups. In addition to working together to develop a deeper understanding of the experimental results and to solve problems of mutual interest, our interactions frequently inspire new experiments, including investigations on materials we would not have otherwise have studied. Just as with materials synthesists, our collaborations with theorists also provide my students with a stimulating and well-rounded research experience.

- Martha Greenblatt, Rutgers University: prepares tungsten bronze crystals and other bronzes.
- Alexandre Revcolevschi, Université Paris-Sud: grows magnetic oxides single crystals: pure and substituted α'-NaV₂O₅, other materials.
- David Mandrus, Oak Ridge National Labs: grows single crystals of layered magnetic oxides.
- Jean Galy, Université de Toulouse: Na$_2$V$_3$O$_7$ nanotubes.
- Valery Davydov, Russian Academy of Science: prepares novel carbon-based solids and fullerences.
- Hiroshi Negishi, Hiroshima University: Mo$_4$O$_{11}$ crystals.
- Yongjie Wang, National High Magnetic Field Laboratory: User support in high magnetic field infrared spectroscopy.
- Xing Wei, NHMFL, Tallahassee, FL: User support in visible optics in steady magnetic fields.
- Scott Crooker, NHMFL, Los Alamos: User support in optics in pulsed fields.
- Christopher Homes and Larry Carr, Brookhaven National Labs: User support in infrared synchrotron spectroscopy.
- Mike Whangbo, North Carolina State University: provides supporting theory and band structure calculations.
- Gary Adams and John Page, Arizona State University: quantum molecular dynamics theory.

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