Using electronic structure changes to map the $H - T$ phase diagram of $\alpha'$-NaV$_2$O$_5$

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We report polarized optical reflectance studies of $\alpha'$-NaV$_2$O$_5$ as a function of temperature (4-45 K) and magnetic field (0-60 T). Rung directed electronic structure changes, as measured by near-infrared reflectance ratios $\Delta R(H)/R(H=0 \text{ T})$, are especially sensitive to the phase boundaries. We employ these changes to map out an $H - T$ phase diagram. Topological highlights include the observation of two phase boundaries slightly below $T_{SG}$, enhanced curvature of the 34 K phase boundary above 35 T, and, surprisingly, strong hysteresis effects of both transitions with applied field.

After the discovery of a low-temperature spin-gapped phase in $\alpha'$-NaV$_2$O$_5$, there was intense interest in this compound as a possible spin Peierls (SP) material [1, 2, 3]. Reexamination of the 300 K structure showed, however, that the situation is more complex [4]. At room temperature, all vanadium ions have a charge of +4.5 and form chains along the $b$ axis. Chains are connected by V-O-V rungs. The result is a 1/4-filled 2-leg ladder material with low-dimensional chain character and 1 spin per rung [5, 6]. The spin gap (SG) opens at $T_{SG} = 34$ K, as evidenced by an isotropic drop in the susceptibility [5, 6]. The opening of the spin gap is accompanied by unit cell doubling in the $a$ and $b$ directions, and quadrupling in the $c$ direction [7, 17]. According to Lüdecke et al., the low temperature phase of $\alpha'$-NaV$_2$O$_5$ also displays alternating modulated and unmodulated ladder chains [6], although Nakao et al. report a fully zigzag ordered structure, with variable temperature charge disproportionation [8]. Early NMR experiments pointed out the importance of charge ordering (CO) in this material, as evidenced by both $V^{4+}$ and $V^{5+}$ resonances [9]. Zigzag CO is the leading candidate for the low-temperature charge arrangement [6, 12]. More recent NMR experiments have discovered the advent of the charge-ordered phase in $\alpha'$-NaV$_2$O$_5$ at $T_{CO} = 37$ K, slightly above the 34.7 K lattice distortion and spin gap formation [14]. Early thermal expansion measurements also discerned two transitions [20]. The detailed interaction between charge and magnetic ordering in $\alpha'$-NaV$_2$O$_5$ is not understood at this time, although, because of the larger energy scale, CO is expected to dominate. Further, the field dependence of $T_{SG}$ (on a field vs. temperature ($H - T$) phase diagram) is anomalous [21, 22] and does not follow the expected $H^2$ behavior for a SP transition, at least at low applied fields [17, 23, 24]. The nearly vertical field dependence of $T_{SG}$ and the interplay of CO and magnetic effects have been cited as reasons why $\alpha'$-NaV$_2$O$_5$ should not be considered a true SP material.

The electronic structure of $\alpha'$-NaV$_2$O$_5$ has attracted a great deal of attention [20, 22, 39], as have other physical properties [15, 16, 17, 18, 19, 20]. The optical conductivity is strongly polarized, as expected for such an anisotropic material; excitations in the rung direction ($a$) are much stronger than those in the chain direction ($b$). Electronic features are observed near 1 eV, between 3 and 4 eV, and above 4 eV in both polarizations. The 1 eV structure in the $a$ direction has received the most attention and is currently assigned as charge transfer excitation between $V^{4+}$ and $V^{5+}$ on opposite sides of a rung [22]. That changes in electronic structure are sensitive probes of phase boundaries was established by previous work on CuGeO$_3$ and $\alpha'$-NaV$_2$O$_5$, where integrated intensities of reflectance and transmittance ratio features, as a function of temperature or magnetic field, display “breakpoints” at a phase boundary [29, 11, 12]. These inflection points provide a useful tool to locate a transition in $H - T$ phase space. In CuGeO$_3$, the phase diagram obtained in this manner is consistent with that obtained with other techniques [28, 11, 12]. At the same time, the detailed spectral features provide microscopic information on the changes which occur at a phase boundary. In the past, the challenge of accessing the high field phase has prevented general extension of this technique to $\alpha'$-NaV$_2$O$_5$.

In order to provide further information on the electrodynamics of quarter-filled magnetic oxides, we have carried out polarized optical reflectance measurements to probe the high field response of $\alpha'$-NaV$_2$O$_5$. We use these data to generate an $H - T$ phase diagram which shows unusual topology and a number of important differences from traditional SP behavior.

High quality single crystals of $\alpha'$-NaV$_2$O$_5$ were grown in Orsay by the flux method [13]. Typical crystal dimensions were $1.65 \times 2.8 \times 0.25$ mm. The high-field
optical reflectance measurements were performed in the 60 T Long-Pulse magnet at the National High Magnetic Field Lab in Los Alamos, NM. This magnet is powered by a 1.4 GVA motor-generator which provides a very long (2 second), user-definable magnet pulse. We elected to use the flat-top field profile, in which the magnet is held at maximum field (60 T) for a full 100 ms. The sample resides in a vacuum jacket in the bore of the magnet, and data were taken in the range 4 to 45 K, concentrating in the regime around the 34 K phase transition. The temperature was held constant for each shot; the sample was thermally cycled to above 40 K after each magnet pulse to avoid possible hysteresis/fatiguing effects. White light was coupled to the sample via a single 600 µm optical fiber, and thin-film, in-situ linear polarizers selected the desired polarization along the $a$- (rung) or $b$- (chain) direction. The reflected light was collected by another optical fiber, dispersed in an optically fast 0.3 m spectrometer, and collected by a high-speed CCD camera. Because the optical spectra of $\alpha’$-NaV$_2$O$_5$ is modified in broad bands, a 150 line/mm grating was employed. We covered the wavelength range from 350 to 1200 nm. Full spectra were collected every 2.1 ms throughout the entire 2 second magnet pulse, providing for complete field-dependence in a single shot at fixed field $H$. A calibrated coil, mounted on the probe, measured the applied field, which was applied perpendicular to the $ab$ plane.

Small field-induced changes in the polarized optical reflectance were studied by calculating reflectance ratios, $\Delta R(H) = R(H)/R(H=0 \text{ T})$, at a number of fixed temperatures. Reflectance ratios were measured in 1 or 1.5 K steps around $T_{SG}$ (34 K) and at larger temperature intervals further away from the transition. We quantified these reflectance ratio changes with applied field by integrating the spectral area. Inflection points in the integrated area were used to identify phase boundaries in $H - T$ space. Error bars on the location of the high-field phase boundaries vary depending on the sweep; we estimate the largest to be on the order of $\pm 3$ T on the 30 K point near 60 T; other error bars are $\pm 2$ T.

Figure 1 displays the rung-polarized ($a$ axis) near-infrared reflectance ratios of $\alpha’$-NaV$_2$O$_5$ with applied field. As in previous temperature sweep data, the electronic structure is modified in wide bands, with the largest changes occurring in the vicinity of the 1 eV excitation $\alpha'$. That the 1 eV excitation is sensitive to an applied magnetic field is related to the charge transfer from vanadium centers across the V-O-V rung, which also involves a shift of the spin to a new site. Chain-polarized and higher energy rung-polarized spectral signatures were also observed at the phase boundaries; we concentrate our analysis and discussion on the rung-directed near-infrared data because the effects are more pronounced.

In order to quantify the spectral changes in $\alpha’$-NaV$_2$O$_5$ with magnetic field, we calculated the spectral area in the wavelength range of interest and plotted it vs. applied field. Representative data are shown in Fig. 2. The most interesting spectral changes are in the vicinity of the 34 K transition, where there are large hysteresis loops in the integrated area vs. field data below $T_{SG}$. That inflection points in the optical response are different on the up-sweep compared to the down-sweep indicates first-order behavior. Data collected above the 34 K transition temperature does not display hysteresis (Fig. 2). In contrast, CuGeO$_3$ shows second-order character over the majority of $H - T$ phase space with first order behavior only around the critical field ($H_c=12.5$ T) at low temperature, where the spin gap is fully open and the lattice distortion is most pronounced [13,16]. Previous investigations of $\alpha’$-NaV$_2$O$_5$ generally report second-order behavior [17], although these efforts have not explored the $H - T$ diagram in the field regime reported here. The thermal expansion data are an exception in that two transitions are observed [20].

Figure 3 displays the $H - T$ phase diagram for $\alpha’$-NaV$_2$O$_5$ derived from an analysis of the field dependent optical properties. The field dependence of $T_{SG}$ is nearly vertical close to 34 K, softening only above 35 T. Note that previous 28 and 30 T determinations of the transition temperature are in general agreement with this diagram [24,25,29]. Two phase boundaries are clearly observed below $T_{SG}$ in $\alpha’$-NaV$_2$O$_5$. There that are indeed two phase boundaries is supported by the spectral area vs. field data in Fig. 2. Here, two distinct inflection points are seen in both up- and down-field sweeps; the position of these breakpoints changes with temperature, indicating that they are characteristic of $\alpha’$-NaV$_2$O$_5$ and not an experimental artifact [48]. The low-field boundary in Fig. 3 separates two phases directly below $T_{SG}$; it saturates near 33 T. This structure is reminiscent of, but different than, the critical field ($H_c$) boundary that separates dimerized and incommensurate phases in traditional SP materials [4]. The optical signature of the 33 T boundary weakens rapidly away from $T_{SG}$, as indicated on the phase diagram, making the distinction between the two phases short-lived and limiting the range of phase space available for study [54]. In contrast, the optical signature of the high field phase boundary remains strong within the range of our investigation (up to 60 T). The curvature is weaker than that in CuGeO$_3$ [15,16], but stronger than that previously reported for $\alpha’$-NaV$_2$O$_5$ [17,24]. Based upon the three highest field data points and the work of Bulaevski and Cross [21,23] which predicts $H^2$ dependence to the phase boundary, we extract $\alpha$-0.1. The first-order behavior of this (and the 33 T) phase boundary is unexpected and different from CuGeO$_3$ [15,44], although recent theoretical work proposes a framework under which hysteresis might be understood [5].

In summary, we report polarized optical reflectance studies of $\alpha’$-NaV$_2$O$_5$ between 350 and 1200 nm as a function of temperature (4-45 K) and applied magnetic field (0-60 T). Using inflection points in the $a$-axis near-infrared reflectance ratio data, we have identified high-field phase boundaries at a number of different tempera-
tures and mapped out an $H - T$ phase diagram. Highlights include the observation of two phase boundaries slightly below $T_{Sc}$, enhanced curvature of the 34 K phase boundary above 35 T, and, surprisingly, strong hysteresis effects of both transitions with applied field. We hope these experiments will spur complementary magnetization and NMR studies of $\alpha'$-NaV$_2$O$_5$ in the future.

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There are three parts to each shot, each with different field vs. time profiles. Since we collect spectra every 2.1 ms, different field resolutions are therefore obtained over the pulse profile.

Note the absence of breakpoints in the 37 K optical data (Fig. 2).

Possible explanations for this progressive weakening include an extremely wide low-temperature hysteresis (making the transition impossible to follow with only 60 T pulses) or domination of lattice dimerization effects by CO. Clearly, the decay of this boundary is of interest in future work.

Fig. 1. Near-infrared reflectance ratio (ΔR) spectra of α′-NaV₂O₅ at 31 K polarized in the rung (a) direction. The ΔR spectra shown here are presented at three representative fields: 60 T/0 T, 45 T/0 T, and 0 T/0 T, illustrating the different optical response in the three regimes of the $H-T$ phase diagram at this temperature.

Fig. 2. Integrated spectral area of α′-NaV₂O₅ vs. applied magnetic field at four different temperatures below $T_{SG}$ and one temperature above $T_{SG}$. Solid arrows indicate breakpoints; dashed arrows denote the field sweep direction.

Fig. 3. Solid symbols: $H-T$ phase diagram of α′-NaV₂O₅, as obtained from an analysis of inflection points in the reflectance ratio data on the upsweep of the magnet. Symbol size is intended to allow visualization of transition strength. Open star: 28 T data as determined by Long et al. in Ref. [29]; open squares: data as determined by Bompadre et al. in Ref. [24]; open circles: data as determined by Schnelle et al. in Ref. [17]. Dashed lines guide the eye.
Fig. 1, Sushkov et al.

\[ R(H)/R(H=0) \]

H=0 T
H=45 T
H=60 T

\( \alpha'\text{-NaV}_2\text{O}_5 \)
T=31 K, E\text{||a}
Fig. 2, Sushkov et al.
Fig. 3, Sushkov et al.