

Using electronic structure changes to map the H - T phase diagram of α' - NaV_2O_5

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(Received 20 December 2000; published 26 April 2001)

We report polarized optical reflectance studies of α' - NaV_2O_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 $\Delta R(H) = R(H)/R(H=0 \text{ T})$, 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 an additional phase boundary 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.

DOI: 10.1103/PhysRevB.63.220401

PACS number(s): 75.30.-m, 78.20.Ls, 78.67.-n, 75.50.-y

After the discovery of a low-temperature spin-gapped phase in α' - NaV_2O_5 , there was intense interest in this compound as a possible spin Peierls (SP) material.^{1–3} 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 two-leg ladder material with low-dimensional chain character and one spin per rung.^{5,6} The spin gap (SG) opens at $T_{SG}=34 \text{ K}$, as evidenced by an isotropic drop in the susceptibility.^{1–3} 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 α' - NaV_2O_5 also displays alternating modulated and unmodulated ladder chains,⁷ 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.¹⁸ Zigzag CO is the leading candidate for the low-temperature charge arrangement.^{8,12} More recent NMR experiments have discovered the advent of the charge-ordered phase in α' - NaV_2O_5 at $T_{CO}=37 \text{ K}$, slightly above the 34.7 K lattice distortion and spin gap formation.¹⁹ Early thermal expansion measurements also discerned two transitions.²⁰ The detailed interaction between charge and magnetic ordering in α' - NaV_2O_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 and does not follow the expected H^2 behavior^{21,22} for a SP transition, at least at low applied fields.^{17,23–25} The nearly vertical field dependence of T_{SG} and the interplay of CO and magnetic effects have been cited as reasons why α' - NaV_2O_5 should not be considered a true SP material.

The electronic structure of α' - NaV_2O_5 has attracted a great deal of attention,^{26–32} as have other physical properties.^{15,16,23,33–40} 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.³² That changes in electronic structure are sensitive probes of phase boundaries was established by previous work on CuGeO_3 and α' - NaV_2O_5 , where integrated intensities of reflectance and transmittance ratio features, as a function of temperature or magnetic field, display “breakpoints” at a phase boundary.^{29,41,42} 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.^{29,41,42} 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 α' - NaV_2O_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 α' - NaV_2O_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 α' - NaV_2O_5 were grown in Orsay by the flux method.⁴³ Typical crystal dimensions were $1.65 \times 2.8 \times 0.25 \text{ mm}$. 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, New Mexico. This magnet is powered by a 1.4 GVA motor generator which provides a very long (2 sec), 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

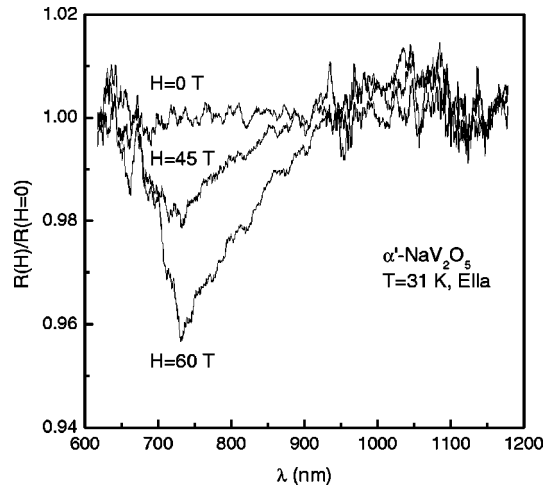


FIG. 1. Near-infrared reflectance ratio (ΔR) spectra of α' - NaV_2O_5 at 31 K polarized in the rung (a) direction. The ΔR spectra shown here are presented at three representative fields: 60 T/0 T, 45 T/0 T, and 0 T/0 T, illustrating the different optical response in the three regimes of the H - T phase diagram at this temperature.

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 charge coupled device (CCD) camera. Because the optical spectra of α' - NaV_2O_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 sec magnet pulse, providing for complete field dependence in a single shot at fixed field.⁴⁴ 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 vs field plot 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 ± 3 T on the 30 K point near 60 T; other error bars are ± 2 T.

Figure 1 displays the rung-polarized (a axis) near-infrared reflectance ratios of α' - NaV_2O_5 at different applied fields. As in previous temperature sweep data, the electronic structure is modified in wide bands, with the largest changes oc-

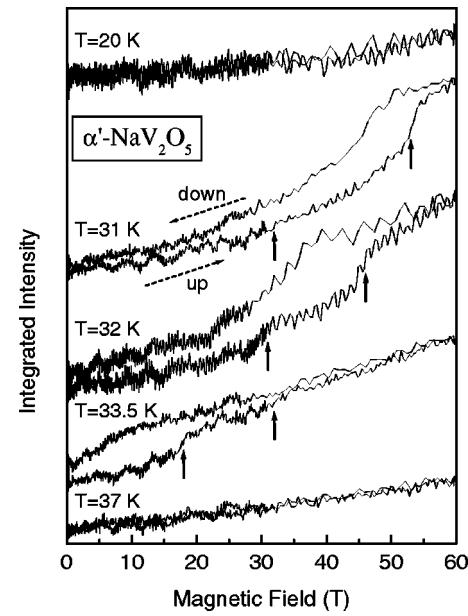


FIG. 2. Integrated spectral area of α' - NaV_2O_5 vs applied magnetic field at four different temperatures below T_{SG} and one temperature above T_{SG} . Solid arrows indicate inflection points in the upsweep data; dashed arrows denote the field sweep direction.

curing in the vicinity of the 1 eV excitation.²⁹ 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 α' - NaV_2O_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 upsweep compared to the downsweep 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.^{45,46} Previous investigations of α' - NaV_2O_5 generally report second-order behavior,⁴⁷ 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 α' - NaV_2O_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 gen-

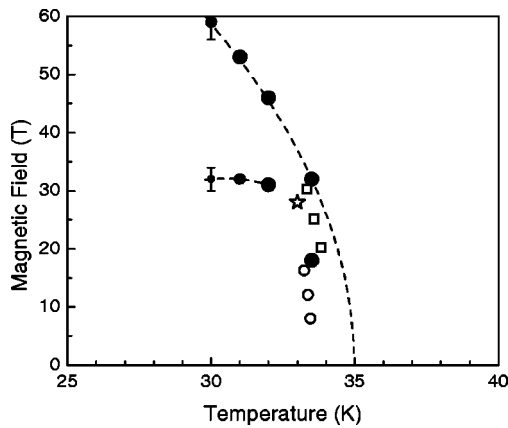


FIG. 3. Solid symbols: H - T phase diagram of α' - NaV_2O_5 , as obtained from an analysis of inflection points in the reflectance ratio data on the upswing of the magnet. Symbol size is intended to allow visualization of transition strength. Open star: 28 T data as determined by Long *et al.* in Ref. 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 show an H^2 fit (right) and a guide to the eye (left).

eral agreement with this diagram.^{24,25,29} Two phase boundaries are clearly observed in the phase diagram of α' - NaV_2O_5 . That there 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 α' - NaV_2O_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.⁴⁹ 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.⁵⁰ 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 ,^{45,46} but stronger than that previously reported for α' - NaV_2O_5 .^{17,24} Based upon the three highest field data points and the work of Bulaevski and Cross^{21,22} which predicts H^2 dependence to the phase boundary, we extract $\alpha \sim 0.11$. The first-order behavior of this (and the 33 T) phase boundary is unexpected and different from CuGeO_3 ,^{45,46} although recent theoretical work proposes a framework under which hysteresis might be understood.⁵¹

In summary, we report polarized optical reflectance studies of α' - NaV_2O_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 temperatures and mapped out an H - T phase diagram. Highlights include the observation of an additional phase boundary 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. We hope these experiments will spur complementary magnetization and NMR studies of α' - NaV_2O_5 in the future.

We are grateful for financial support from the Materials Science Division, Basic Energy Sciences at the U.S. Department of Energy under Grant No. DE-FG02-99ER45741. The National High Magnetic Field Laboratory in Los Alamos, New Mexico, is supported by the National Science Foundation, the State of Florida, and the Department of Energy. We thank Bill Moulton for useful discussions.

- ¹M. Isobe and Y. Ueda, J. Phys. Soc. Jpn. **65**, 1178 (1996).
- ²M. Weiden, R. Hauptmann, C. Geibel, F. Steglich, M. Fischer, P. Lemmens, and G. Güntherodt, Z. Phys. B: Condens. Matter **103**, 1 (1997).
- ³Y. Ueda, Chem. Mater. **10**, 2653 (1998).
- ⁴A. Meetsma, J.L. de Boer, A. Damascelli, T.T.M. Palstra, J. Jegoudez, and A. Revcolevschi, Acta Crystallogr., Sect. A: Found. Crystallogr. **54**, 1558 (1998).
- ⁵H. Smolinski, C. Gros, W. Weber, U. Peuchert, G. Roth, M. Weiden, and C. Geibel, Phys. Rev. Lett. **80**, 5164 (1998).
- ⁶P. Horsch and F. Mack, Eur. Phys. J. B **5**, 367 (1998).
- ⁷J. Lüdecke, A. Jobst, S. van Smaalen, E. Morré, C. Geibel, and H.-G. Krane, Phys. Rev. Lett. **82**, 3633 (1999).
- ⁸H. Nakao, K. Ohwada, N. Takesue, Y. Fujii, M. Isobe, Y. Ueda, M. v. Zimmermann, J.P. Hill, D. Gibbs, J.C. Woicik, I. Koyama, and Y. Murakami, Phys. Rev. Lett. **85**, 4349 (2000).
- ⁹M. Isobe and Y. Ueda, J. Phys. Soc. Jpn. **65**, 1178 (1996).
- ¹⁰Y. Fujii, H. Nakao, T. Yosihama, M. Nishi, K. Nakajima, K. Kakurai, M. Isobe, Y. Ueda, and H. Sawa, J. Phys. Soc. Jpn. **66**, 326 (1997).
- ¹¹H. Seo and H. Fukuyama, J. Phys. Soc. Jpn. **67**, 2602 (1998).
- ¹²M.V. Mostovoy and D.I. Khomskii, Solid State Commun. **113**, 159 (1999).
- ¹³P. Thalmeier and P. Fulde, Europhys. Lett. **44**, 242 (1998).
- ¹⁴S. Nishimoto and Y. Ohta, J. Phys. Soc. Jpn. **67**, 2996 (1998).
- ¹⁵A.N. Vasil'ev, V.V. Pryadun, D.I. Khomskii, G. Dhalenne, A. Revcolevschi, M. Isobe, and Y. Ueda, Phys. Rev. Lett. **81**, 1949 (1998).
- ¹⁶M. Köppen, D. Pankert, R. Hauptmann, M. Lang, M. Weiden, C. Geibel, and F. Steglich, Phys. Rev. B **57**, 8466 (1998).
- ¹⁷W. Schnelle, Yu. Grin, and R.K. Kremer, Phys. Rev. B **59**, 73 (1999).
- ¹⁸T. Ohama, H. Yasuoka, M. Isobe, and Y. Ueda, Phys. Rev. B **59**, 3299 (1999).
- ¹⁹Y. Fagot-Revurat, M. Mehring, and R.K. Kremer, Phys. Rev. Lett. **84**, 4176 (2000).
- ²⁰M. Köppen, D. Pankert, R. Hauptmann, M. Lang, M. Weiden, C. Geibel, and F. Steglich, Phys. Rev. B **57**, 8466 (1998).
- ²¹M.C. Cross, Phys. Rev. B **20**, 4606 (1979).

- ²²L.N. Bulaevskii, A.I. Buzdin, and D.I. Khomskii, *Solid State Commun.* **27**, 5 (1978).
- ²³P. Fertey, M. Poirier, M. Castonguay, J. Jegoudez, and A. Revcolevschi, *Phys. Rev. B* **57**, 13 698 (1998).
- ²⁴S.G. Bompadre, A.F. Hebard, V.N. Kotov, D. Hall, G. Maris, J. Baas, and T.T.M. Palstra, *Phys. Rev. B* **61**, R13 321 (2000).
- ²⁵We were informed recently that a magnetic torsion experiment up to $H=28$ T has been made on α' - NaV_2O_5 [P.H.M. van Loosdrecht (private communication)].
- ²⁶S.A. Golubchik, M. Isobe, A.N. Ivlev, B.N. Mavrin, M.N. Popova, A.B. Sushkov, Y. Ueda, and A.N. Vasil'ev, *J. Phys. Soc. Jpn.* **66**, 4042 (1997); **68**, 318 (1999).
- ²⁷A. Damascelli, D. van der Marel, M. Grüninger, C. Presura, T.T.M. Palstra, J. Jegoudez, and A. Revcolevschi, *Phys. Rev. Lett.* **81**, 918 (1998).
- ²⁸M.N. Popova, A.B. Sushkov, S.A. Golubchik, M.N. Mavrin, V.N. Denisov, B.Z. Malkin, A.I. Iskhakova, M. Isobe, and Y. Ueda, *Zh. Eksp. Teor. Fiz.* **115**, 2170 (1999) [*JETP* **88**, 1186 (1999)].
- ²⁹V.C. Long, Z.T. Zhu, J.L. Musfeldt, X. Wei, H.-J. Koo, M.-H. Whangbo, J. Jegoudez, and A. Revcolevschi, *Phys. Rev. B* **60**, 15 721 (1999).
- ³⁰A. Damascelli, C. Presura, D. van der Marel, J. Jegoudez, and A. Revcolevschi, *Phys. Rev. B* **61**, 2535 (2000).
- ³¹C. Presura, D. van der Marel, A. Damascelli, and R.K. Kremer, *Phys. Rev. B* **61**, 15 762 (2000).
- ³²C. Presura, D. van der Marel, M. Dischner, C. Geibel, and R.K. Kremer, *Phys. Rev. B* **62**, 16 522 (2000).
- ³³E. Ya. Sherman, M. Fischer, P. Lemmens, P.H.M. van Loosdrecht, and G. Güntherodt, *Europhys. Lett.* **48**, 648 (1999).
- ³⁴A.I. Smirnov, M.N. Popova, A.B. Sushkov, S.A. Golubchik, D.I. Khomskii, M.V. Mostovoy, A.N. Vasil'ev, M. Isobe, and Y. Ueda, *Phys. Rev. B* **59**, 14 546 (1999).
- ³⁵S. Luther, H. Nojiri, M. Motokawa, M. Isobe, and Y. Ueda, *J. Phys. Soc. Jpn.* **67**, 3715 (1998).
- ³⁶H. Nojiri, S. Luther, M. Motokawa, M. Isobe, and Y. Ueda, *J. Phys. Soc. Jpn.* **69**, 2291 (2000).
- ³⁷A.N. Vasil'ev, A.I. Smirnov, M. Isobe, and Y. Ueda, *Phys. Rev. B* **56**, 5065 (1997).
- ³⁸M.J. Konstantinović, Z.V. Popović, A.N. Vasil'ev, M. Isobe, and Y. Ueda, cond-mat/9907218 (unpublished).
- ³⁹E. Postolache, D.K. Powell, G. Popov, R.C. Rai, M. Greenblatt, and J.W. Brill, *Solid State Sci.* (to be published).
- ⁴⁰D. Smirnov, P. Millet, J. Leotin, D. Poilblanc, J. Riera, D. Augier, and P. Hansen, *Phys. Rev. B* **57**, 11 035 (1998).
- ⁴¹V.C. Long, J.L. Musfeldt, T. Schmiedel, A. Revcolevschi, and G. Dhalenne, *Phys. Rev. B* **56**, 14 263 (1997).
- ⁴²J. Zeman, G. Martinez, P.H.M. van Loosdrecht, G. Dhalenne, and A. Revcolevschi, *Phys. Rev. Lett.* **83**, 2648 (1999).
- ⁴³M. Isobe, C. Kagami, and Y. Ueda, *J. Cryst. Growth* **181**, 314 (1997).
- ⁴⁴There are three parts to each shot, each with different field vs time profiles. Since we collect spectra over 2.1 ms, different field resolutions are therefore obtained over the pulse profile.
- ⁴⁵M. Hase, I. Terasaki, and K. Uchinokura, *Phys. Rev. Lett.* **70**, 3651 (1993).
- ⁴⁶M. Hase, I. Terasaki, K. Uchinokura, M. Tokunaga, N. Miura, and H. Obara, *Phys. Rev. B* **48**, 9616 (1993).
- ⁴⁷S. Ravy, J. Jegoudez, and A. Revcolevschi, *Phys. Rev. B* **59**, R681 (1999).
- ⁴⁸Note the absence of inflection points in the 37 K optical data (Fig. 2).
- ⁴⁹J.W. Bray, L.V. Interrante, I.S. Jacobs, and J.C. Bonner, in *Extended Linear Chain Compounds*, Vol. 3, edited by J.S. Miller (Plenum, New York, 1983).
- ⁵⁰Possible 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.
- ⁵¹F. Schönfeld, G. Bouzerar, G.S. Uhrig, and E. Müller-Hartmann, *Eur. Phys. J. B* **5**, 521 (1998).