Phase transitions in a magnetic field in V$_{2-y}$O$_3$ ($y = 0$ and 0.04)

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The effect of a magnetic field on the two long-range-ordered magnetic phases, the collinear insulating antiferromagnetic (AFI) and the incommensurate metallic transverse spin density wave (SDW), is investigated for the vanadium sesquioxide system. A field of 18 T has little effect on the AFI phase of a nominal V$_2$O$_3$ sample. The transverse SDW phase of V$_{1.96}$O$_3$ can be suppressed by a 4.6(3)-T magnetic field applied in the plane of spiraling spins, while the same magnetic field applied along the spiral axis has little effect on the SDW phase.

Vanadium sesquioxide (V$_2$O$_3$) has been extensively investigated, as a prototype Mott-Hubbard system exhibiting a metal-insulator transition [1][2]. Stimulated by interest in the Mott-Hubbard system after the discovery of superconductivity in cuprates, a revisit of this classic material has generated exciting new findings: discovery of the static incommensurate spin density wave order [3], spin excitations with completely different spatial correlations between the AFI phase and all other phases [4][5] orbital occupation with $S = 1$ character [6], prominence of orbital contributions to magnetic fluctuations in high temperature metallic phase [7], anomalous resonant x-ray scattering in the AFI phase [8], and high resolution photoemission [9]. These results are inconsistent with previously accepted theoretical models. One outcome is a renewed interest in theoretical investigation on the orbital degree of freedom in correlated $d$-electron systems [10][11].

The V$_2$O$_3$ system is very sensitive to external perturbation. Studies using high pressure and doping with various ions have proven fruitful. For example, the anomaly in physical properties around 500 K in the pure V$_2$O$_3$ is found to be caused by a nearby critical point between the paramagnetic metallic (PM) phase and the paramagnetic insulating (PI) phase, which is uncovered by Cr doping [12] (refer to Fig. 1). The AFM phase, discovered with excess oxygen or Ti doping [13], encourages theoretical investigations of this possibility in the Hubbard model [14][15]. High pressure studies reveal that doping has effects beyond only exerting internal chemical pressure [16]. It also allows investigation into low temperature properties of the paramagnetic metallic phase [17], which is interrupted by phase transitions at ambient pressure.

In this work, we explore new phase space of V$_2$O$_3$ using high magnetic fields. The influence of a static magnetic field (up to 18 T) on the two low temperature magnetic ground states, the AFI and the SDW, was investigated at ambient pressure. While a magnetic field of 18 T is too weak to have a significant effect on the AFI transition of a V$_2$O$_3$ sample, it completely suppresses the transverse SDW phase of a V$_{1.96}$O$_3$ sample.

Single crystals of V$_2$O$_3$ were grown using a skull melter [18]. The as-grown crystal used to study the AFI transition has a slight oxygen excess, which reduced the AFI transition temperature to $T_C \approx 160$ K. Another sliced crystal about 1 mm thick was annealed in a suitably chosen CO-CO$_2$ atmosphere [19] for 2 weeks at 1400°C to adjust the stoichiometry to V$_{1.96}$O$_3$. This sample has an SDW ground state at ambient pressure with $T_N = 8.7$ K.

Magnetization was measured using a vibrating sample magnetometer (VSM) in a 20-T superconducting magnet at the Pulsed Field Facility of the National High Magnetic Field Laboratory at Los Alamos National Laboratory (NHMFL-LANL). The crystal sample was first wrapped in Teflon tape, and then attached to the sample holder at the tip of cold finger by Teflon tape. In this arrangement, the sample could rotate inside the sample holder in response to the applied vertical magnetic field. Reproducible measurements were obtained after...
first ramping the field to 18 T, the maximum magnetic field used in this work.

The effect of magnetic field on the AFI phase transition was first investigated with measurements of magnetization as a function of magnetic field for an as-grown $V_2O_3$ crystal at various temperatures below and above $T_C \approx 160$ K. A few examples are shown in Fig. 2(a). Data at 95 K were taken with the field both ramping up and down. The small difference between the field-up and field-down measurements may not be significant. Clearly, no first-order phase transition between the PM and AFI is detectable in the magnetization curve up to the highest field, $B = 18$ T. In this paper, the $B$ field is always referred to magnetic field outside the sample.

The AFI phase transition was then investigated with magnetization as a function of temperature at various field strengths [refer to Fig. 2(b)]. Thermal hysteresis, due to the first-order PM-AFI phase transition, in data taken on warming and cooling hardly changes with $B$. Thus, we conclude that a magnetic field of 18 T has little effect on the AFI transition for nearly stoichiometric $V_2O_3$.

We now turn to magnetic field effect on the SDW transition. Magnetization of $V_{1.96}O_3$ at various magnetic fields as a function of temperature is shown in Fig. 3(a). The cusp due to the second order SDW phase transition near 8.7 K remains sharp at 1 T. With increasing magnetic field, the cusp moves to lower temperature and becomes less well defined. Phase transition in this portion of the $T$-$B$ phase space can be better determined with measurements of magnetization as a function of the field at various fixed temperatures. Some examples are shown in Fig. 3(b). These measurements complement well the constant field data in Fig. 3(a).

Data points in Fig. 4(a) represent the peak positions in the $M$ vs $T$ or $M$ vs $H$ curves, such as those in Fig. 3. They delineate the phase boundary for the transverse SDW phase. The critical field to suppress the transverse SDW phase is extrapolated to be 4.6(3) T.

The transverse SDW state of $V_{1.96}O_3$ consists of spin spiral with an incommensurate wave vector along the $c$ axis and spin direction rotating in the hexagonal basal plane. Thus, magnetic anisotropy is expected. Additional measurements below 5 T, with sample orientation fixed with respect to the applied field, were conducted using a SQUID magnetometer. Magnetization measurements performed for the field applied along both the $c$ axis (filled symbols) and $a^*$ axis (open symbols) are shown in Fig. 5. For a given magnetic field, the $a^*$-axis magnetization is appreciably larger than the $c$-axis mag-
FIG. 4. A T-B phase diagram for $V_{1.96}O_3$. The magnetic field direction is (a) perpendicular to and (b) parallel to the $c$ axis, respectively.

netization, consistent with previous measurement [19]. Therefore, when the sample is allowed to rotate in the magnetic field, as in the case of our VSM measurement with the 20 T magnet, the measured response is predominantly the $a^*$-axis one. This is confirmed by the similar magnetization data taken in 4 T using VSM (star) and using SQUID with field applied along $a^*$ axis (open triangle) in Fig. 5. Thus, the phase diagram in Fig. 4(a) is for the field in the rotating plane of the spin spiral, i.e., perpendicular to the $c$ axis.

The $c$-axis magnetization (filled symbols) in Fig. 5 shows a inflection around 8.7 K, the zero field Néel point. This behavior is what is expected of a antiferromagnet when the field direction is perpendicular to the spins. While the magnitude of $M/H$ changes appreciably with magnetic field, the inflection point changes little. This behavior in phase transition is in sharp contrast to that in the $a$-axis magnetic response. A different response is also clear in the $M$ vs $B$ curves at 7.5 K in Fig. 3(b). The cusp associating with the SDW phase transition appears only when the field is perpendicular to the $c$ axis. Phase boundary for $B$ parallel to the $c$ axis is shown in Fig. 3(b). There is little detectable effect on $T_N$.

The saturation moment for $V_2O_3$ in the AFI phase is $1.2\mu_B$ [22]. The magnetic energy at 18 T, $1.2\mu_B \times 18T = 1.3$ meV, is only 9% of $k_B T_N$. A much higher magnetic field may be needed to affect this first order transition.

The saturation moments for $V_{1.96}O_3$ in the SDW phase is $0.15\mu_B$ [3]. The magnetic energy for $V_{1.96}O_3$ at the critical field, $0.15\mu_B \times 4.6T = 0.04$ meV, is only 5% of $k_B T_N$. In addition, the induced moment at 4.6 T and zero temperature can be estimated using the value of $M/H$ at low temperature from Fig. 3(a): $2.4 \times 10^{-6} \times 46000 = 110$ emu/mole V = 0.02$\mu_B$/V. This is only a small fraction of the zero field staggered moment. Therefore, it is unlikely that the SDW phase is replaced by a field-induced “ferromagnetic” state above 4.6 T. This is also consistent with the persistence of the SDW state at 5 T when the field is applied along the $c$ axis. In reference to the T-B phase diagram of a common antiferromagnet, the phase above 4.6 T in Fig. 4(a) could be a spin-flop state. In this case, the B-M is comparable to the anisotropic energy, which can be a small fraction of $k_B T_N$. It remains to be seen, using, e.g., neutron diffraction, what happens to the incommensurate magnetic structure of the transverse SDW at high magnetic field and low temperature. A field-induced incommensurate-commensurate transition has been observed in the Dzyaloshinskii-Moriya type [28] incommensurate magnets, such as the itinerant MnSi [24] and localized Ba$_2$CuGe$_2$O$_7$ [30], while the incommensurability is expected to be locked by Fermi surface in Lomer-Overhauser type [31] incommensurate magnets.

Recently, magnetotransport measurements have been conducted by Klimm et al. [32] up to 12 T. Anomalies in their data may be related to the phase transition uncovered here. However, the orientation dependence in their data has yet to be understood in term of the orientation dependence we find in this work.
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