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Metamagnetism and soliton excitations in the modulated ferromagnetic Ising chain CoV$_2$O$_6$

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We report a combination of physical property and neutron scattering measurements for polycrystalline samples of the one-dimensional spin-chain compound CoV$_2$O$_6$. Heat capacity measurements show that an effective $S = 1/2$ state is found at low temperatures and that magnetic fluctuations persist up to $\sim 6T_N$. Above $T_N = 6.3$ K, measurements of the magnetic susceptibility as a function of $T$ and $H$ show that the nearest-neighbor exchange is ferromagnetic. In the ordered state, we have discovered a crossover from a metamagnet with strong fluctuations between 5 K and $T_N$ to a state with a 1/3 magnetization plateau at $2 < T < 5$ K. We use neutron powder diffraction measurements to show that the antiferromagnetic state has incommensurate long-range order and inelastic time-of-flight neutron scattering to examine the magnetic fluctuations as a function of temperature. Above $T_N$, we find two broad bands between 3.5 and 5 meV and thermally activated low-energy features which correspond to transitions within these bands. These features show that the excitations are deconfined solitons rather than the static spin reversals predicted for a uniform ferromagnetic Ising spin chain. Below $T_N$, we find a ladder of states due to the confining effect of the internal field. A region of weak confinement below $T_N$, but above 5 K, is identified which may correspond to a crossover between two- and three-dimensional magnetic ordering.

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I. INTRODUCTION

One-dimensional magnetic materials with quantum ($S = 1/2$) spins have been widely studied as their excitation spectra often consist of continuums of fractionalized particles which have no analogs in higher spin or three-dimensional materials. A particularly elegant example is the Ising spin chain, which in a transverse field undergoes a counterintuitive magnetic structure consisting of CoO$_6$ octahedra running down the $b$ axis interspersed with nonmagnetic V$_6$-like blocks. The magnetic properties of Co-Co distance within the chains is $\sim 3$ Å and the distances between chains are $\sim 4.8$ Å along [001] and $\sim 7.2$ Å along [100]. The chains contain two crystallographically independent sites [Fig. 1(b)], which alternate in the sequence 1, 1, 2, 1, 1, etc. The main magnetic exchange interactions are also shown in Fig. 1(b), with a notable modulation along the chain direction (i.e., $J_1 \neq J_2$). The magnetic properties of several other brannerites have been reported. The isostructural material CuV$_2$O$_6$ is a low-dimensional antiferromagnet, due to Cu$^{2+}$ orbital order, whereas monoclinic MnV$_2$O$_6$ is an isotropic antiferromagnet that shows reduced magnetic coherence lengths due to Mn-V antisite disorder.

II. EXPERIMENT

Polycrystalline samples of CoV$_2$O$_6$ were synthesized using a citrate decomposition method similar to that used for MnV$_2$O$_6$. Stoichiometric quantities of cobalt(II) acetate tetrahydrate (Aldrich, 99%+) and V$_2$O$_5$ (Aldrich, 99.99%) were mixed in distilled water together with a threefold molar excess of acetic acid. The mixture was slowly heated and
FIG. 1. (Color online) (a) Structure of triclinic CoV$_2$O$_6$ showing edge-sharing sites indicated. For clarity, the V$_2$O$_3$ blocks are omitted. The principle exchange interactions in the chain are indicated in (b).

stirred until a gel formed. The gel was allowed to solidify then decomposed at 300°C for 3 h. The resulting solid was ground, pelleted, and heated at 600°C, 630°C, and 650°C for 12, 12, and 72 h, respectively. Powder x-ray diffraction using a Bruker D8-Advance showed a phase pure product. Magnetic susceptibility measurements were performed using a Quantum Design MPMS in varying fields up to 2 T as a function of temperature from 2 to 300 K in field- and zero-field-cooled conditions. Magnetization isotherms were recorded using the ac susceptibility option of a Quantum Design PPMS at temperatures from 2 to 35 K in fields of up to 9 T. This system was also used for specific heat measurements. For these, an additional measurement consisting of the sample mount and a small quantity of grease was performed before a small pellet of CoV$_2$O$_6$ was affixed. We used a variety of neutron powder diffractometers to characterize our samples. High-resolution data were collected at 2 K with wavelengths of 1.79 and 2.8 Å using the E9 instrument at HZB, Berlin. A detector bank consisting of 64 $^3$He detectors arranged at 2.5° intervals was employed. A total of 32 steps of the detector were carried out, resulting in a step size of 0.078° with a resolution minimum of $\Delta d/d \sim 2 \times 10^{-3}$ over a total angular range of 160°. The high-resolution data were refined by the Rietveld method using the GSAS suite of programs. We also performed temperature-dependent measurements using the medium-resolution focusing diffractometer E6, also at HZB. This instrument has a vertically and horizontally bent pyrolytic graphite monochromator and two large position-sensitive detectors giving a high flux at a wavelength of 2.4 Å. For both diffraction measurements, the sample was held in a 6-mm vanadium can and temperature was controlled using a standard Orange helium flow cryostat. Time-of-flight inelastic neutron scattering data were collected with IN5 at the

Institut Laue-Langevin, Grenoble. This instrument is a direct geometry cold neutron spectrometer with a 30-m$^2$ array of position-sensitive detectors. The sample was contained in an annular aluminum can placed in an Orange cryostat. All data were background corrected and normalized to the incoherent scattering of vanadium using standard routines in the program LAMP. We employed two configurations with incident energies of 3.27 and 7.08 meV, giving resolutions of around 0.1 and 0.35 meV, respectively.

III. RESULTS

A. Physical properties

The magnetic susceptibility of CoV$_2$O$_6$, measured in a 500-Oe field, is shown in Fig. 2(a) and shows a sharp transition to an antiferromagnetically ordered state below $T_N = 7$ K. No divergence between field- and zero-field-cooled measurements was seen. The inverse susceptibility of CoV$_2$O$_6$ is well fitted by the Curie-Weiss law in the range 125–300 K with a fitted moment of 5.22(2)$\mu_B$ and a Weiss temperature of 9.2(2) K. The moment shows a substantial increase due to nearest-neighbor ferromagnetic correlations, as a sizable divergence between field- and zero-field-cooled measurements was seen. The inverse susceptibility of CoV$_2$O$_6$: the black line shows the Curie-Weiss fit to the high-temperature region described in text. Inset shows $\chi T$ as a function of temperature. (b) Magnetic specific heat of CoV$_2$O$_6$: line shows integrated magnetic entropy, inset shows total specific heat and estimated lattice contribution.
heat to a function of the form

where \( a \) and \( b \) are constants. The constant \( CoV \) of the Co 

We estimated the lattice contribution to the specific heat of CoV 

above the metamagnetic field) both suppresses and broadens 

in this temperature range. Application of a 1-T field (which is 

interchain (or plane) exchange. Long-range order is therefore the result of antiferromagnetic 

domains that the ground state of the Co 

isotherms measured for CoV 

were obtained (5.43 J/mol K) is very close to the expected value for 

isotherms shown in Fig. 3(a). These observations corroborate 

the evidence from the susceptibility measurements for nearest-
neighbor ferromagnetic exchange in CoV. Based on the 

isotherms shown in Fig. 3(a), these correlations can be seen 
to extend well above \( T_N \), to \( \sim 35 \) K. Isotherms measured 
in the range \( 2 < T < T_N \) are shown in Fig. 3(b). At 2 K, 
two field-induced transitions are seen. The first transition 
at 3600 Oe corresponds to a plateau at almost exactly 
one third of the saturation magnetization \( (0.95 \mu_B) \), and the 

second transition at 5900 Oe is a metamagnetic transition to a plateau that shows the full saturation magnetization, 

\( 2.9 \mu_B \) at 9 T \( (\mu_{\text{sat}} = 2.8 \mu_B) \). Considerable 

hysteresis was observed around the 1/3 plateau at the lowest temperatures 

measured. \( M(\mathcal{H}) \) isotherms at higher temperatures show that 

the 1/3 plateau becomes nonhysteretic at 4 K and disappears 
 betwen 4.5 and 5 K [Fig. 3(b)], whereas the metamagnetic 

transition persists up to the Néel temperature.

B. Neutron powder diffraction measurements

Our neutron powder diffraction measurements at 2 K 

showed the presence of magnetic order and were also used to 

refine the crystallographic structure. The data were analyzed 
as follows. First, the crystal structure of CoV was refined 

from the short-wavelength (1.7973 Å) data collected on the 

high-resolution diffractometer E9. Due to the low symmetry, 

the lattice parameters and background were first refined using 

a Le Bail parameterless fit, giving results similar to those 

reported at room temperature. The peak shape parameters (a 

pseudo-Voigt function), scale function, and detector zero-point 

shift were then refined before the internal coordinates were 

allowed to vary. In order to reduce the number of variables, 

and because of the low scattering length of vanadium, the 

atomic displacement parameters (ADPs) of the Co and V 
sites were constrained to be equal, as were the oxygen ADPs. 

The possibility of antisite disorder between Co and V was 

investigated but failed to give an improvement in the fit 

residuals and was therefore discounted. The refinement for this 

histogram converged with \( R_{wp} = 0.0664 \) and \( R_p = 0.0512 \) 

gave the results shown in Tables I and II. Notably, the 

refined Co-O-Co bond angles support our suggestion 
of ferromagnetic superexchange interactions along the chain 
direction, as in all cases, these are less than \( \sim 95^\circ \). 

The observed, calculated, and difference plots for the Rietveld fits 

are shown in Figs. 4(a) and 4(b).

At low angles, magnetic reflections which did not index 
on the chemical unit cell were observed [Fig. 4(a)]. Previous 

work on related Mn- and CuV materials \(^{24,28}\) has shown 

that simple collinear ground states consisting of ferromagnetic 
chains coupled antiferromagnetically are found. However, 

neither of these compounds has strong single-ion anisotropy, 

which is expected to complicate the magnetic ordering. In 

the case of CoV, we were able to index the largest 

magnetic reflections on a supercell with \( k = (1/2,0,0) \). 
A simple magnetic structure of ferromagnetic planes coupled 
antiferromagnetically accounted for the majority of the magnetic 
scattering. However, we also detected a large number of extra 
satellite reflections [see inset of Fig. 4(a)]. These resisted all 

attempts at indexing due to the low crystallographic symmetry.

FIG. 3. (Color online) (a) Magnetization isotherms measured for 
CoV above magnetic ordering temperature; (b) magnetization 
isotherms measured for CoV below magnetic ordering temper- 
ature. A constant x-axis offset of 1500 Oe has been applied to the 
results in (b) for clarity. Lines in all plots are guides to the eye.
and probably correspond to a long-wavelength modulation of the magnetic structure as seen in, e.g., Ca₃Co₂O₆. Incommensurate magnetic structures, often with multiple propagation vectors, are common in systems with competing interactions. In this case, interplay between superexchange and single-ion anisotropy on the two crystallographically independent sites is a possible origin. Future single-crystal diffraction studies are necessary to solve this structure.

In order to determine the extent of critical fluctuations in CoV₂O₆, we measured the intensity of several fundamental magnetic reflections as a function of temperature using E₆. We chose the reflections between 30° and 40° marked in Fig. 4(a). A great deal of diffuse scattering was observed around the most intense magnetic reflection (∼11°) near T_N, precluding use of this region of the diffraction patterns. A plot of the resulting normalized magnetic intensity versus reduced temperature is shown in Fig. 5 (assuming a Néel temperature of 6.3 K). A crossover between critical behavior and true long-range order is clearly seen at ∼5.1 K, which matches the region identified by the M(H) isotherms without a 1/3 magnetization plateau. A fit of a power-law function gave a critical exponent, β = 0.22(2), which is at the upper end of the range found for anisotropic layered Ising systems, although strongly reduced from the value of 0.35 found for Mn₃V₂O₆. Further measurements with better temperature resolution are needed to determine a more accurate value.

C. Inelastic neutron scattering measurements

A summary of the measurements performed with E_i = 7.08 meV and T > T_N is shown in Fig. 6. Here the excitations are expected to be representative of the one-dimensional chains. As expected from the single-ion anisotropy, the majority of the inelastic spectral weight is gapped at 7 K. Due to the almost nondispersive nature of the magnetic response, the data are integrated over all momentum transfers and hence approximate to the magnetic density of states. The sharpness of the gapped peaks is significant, as Van Hove singularities are expected in the magnetic density of states in low-dimensional materials. This reinforces our observations from the specific heat measurements which showed that only 35% of the magnetic entropy is recovered at T_N, and we conclude that CoV₂O₆ is highly one-dimensional. Next, by following the temperature dependence of the inelastic response, we confirm the magnetic nature of all these features and show the origin of those above and below 1.5 meV is rather different.

### TABLE I. Refined atomic coordinates for CoV₂O₆ at 2 K from neutron powder diffraction.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(1)</td>
<td>0</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>Co(2)</td>
<td>0.0284(29)</td>
<td>0.1715(25)</td>
<td>0.028(4)</td>
</tr>
<tr>
<td>V(1)</td>
<td>0.704(16)</td>
<td>0.951(16)</td>
<td>0.462(24)</td>
</tr>
<tr>
<td>V(2)</td>
<td>0.719(17)</td>
<td>0.631(15)</td>
<td>0.433(24)</td>
</tr>
<tr>
<td>V(3)</td>
<td>0.498(16)</td>
<td>0.240(14)</td>
<td>0.143(21)</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.1620(14)</td>
<td>0.4970(11)</td>
<td>0.3456(19)</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.8413(15)</td>
<td>0.6399(13)</td>
<td>0.1623(21)</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.1746(13)</td>
<td>0.6964(13)</td>
<td>0.8841(19)</td>
</tr>
<tr>
<td>O(4)</td>
<td>0.1537(13)</td>
<td>0.0250(12)</td>
<td>0.8270(19)</td>
</tr>
<tr>
<td>O(5)</td>
<td>0.1697(14)</td>
<td>0.8925(11)</td>
<td>0.3428(21)</td>
</tr>
<tr>
<td>O(6)</td>
<td>0.7877(12)</td>
<td>0.8019(14)</td>
<td>0.6320(18)</td>
</tr>
<tr>
<td>O(7)</td>
<td>0.4748(14)</td>
<td>0.9122(12)</td>
<td>0.7127(20)</td>
</tr>
<tr>
<td>O(8)</td>
<td>0.4724(14)</td>
<td>0.5803(12)</td>
<td>0.7046(21)</td>
</tr>
<tr>
<td>O(9)</td>
<td>0.5222(13)</td>
<td>0.7539(14)</td>
<td>0.2123(18)</td>
</tr>
</tbody>
</table>

### TABLE II. Selected refined distances and angles for CoV₂O₆ at 1.6 K from neutron powder diffraction.

<table>
<thead>
<tr>
<th>Bond distance or angle (Å or deg)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(1)-O(1) × 2</td>
<td>1.962(9)</td>
</tr>
<tr>
<td>Co(1)-O(2) × 2</td>
<td>2.036(11)</td>
</tr>
<tr>
<td>Co(1)-O(3) × 2</td>
<td>2.024(11)</td>
</tr>
<tr>
<td>Co(2)-O(2)</td>
<td>1.993(25)</td>
</tr>
<tr>
<td>Co(2)-O(3)</td>
<td>2.113(25)</td>
</tr>
<tr>
<td>Co(2)-O(4)</td>
<td>2.005(23)</td>
</tr>
<tr>
<td>Co(2)-O(5)</td>
<td>2.099(25)</td>
</tr>
<tr>
<td>Co(2)-O(6)</td>
<td>2.193(21)</td>
</tr>
<tr>
<td>Co(2)-O(7)</td>
<td>2.009(25)</td>
</tr>
<tr>
<td>Co(1)-O(2)-Co(2)</td>
<td>94.8(8)</td>
</tr>
<tr>
<td>Co(1)-O(3)-Co(2)</td>
<td>91.6(7)</td>
</tr>
<tr>
<td>Co(2)-O(4)-Co(2)</td>
<td>93.5(9)</td>
</tr>
</tbody>
</table>
METAMAGNETISM AND SOLITON EXCITATIONS IN THE
...
temperature, we have employed the fluctuation dissipation theorem to extract the generalized susceptibility $\chi''(Q,\omega)$:

$$S(Q,\omega) \propto \frac{\chi''(Q,\omega)}{1 - \exp(-\hbar\omega/k_B T)}.$$  \hspace{1cm} (3)

The low-energy signal is clearly resolved into two peaks just above $T_N$ as shown by the cuts at $Q = 1.3 \pm 0.1 \text{ Å}^{-1}$ in Fig. 8.

This response reaches a maximum at $\sim 11$ K and collapses with further heating. In this region the data were fitted by the sum of two Lorentzians and a sloping background. The position of the excitations was 0.55(1) and 1.06(1) meV at 11 K. Upon heating, a gradual broadening and convergence of the two peaks was observed. Above 20 K, the data could be equivalently described by a single damped peak. These low-energy features thus approximately match the temperature region where our magnetic susceptibility and specific heat measurements detect low-dimensional ferromagnetic fluctuations (Fig. 2).

The onset of magnetic order, and the associated internal field in CoV$_2$O$_6$, dramatically changes both the low- and high-energy spin excitations. As shown in Fig. 8, the former almost entirely disappears below 5 K. The gapped features are also strongly affected, as shown by the data collected in the higher-energy configuration. Figure 9 shows that, below $T_N$, a more complex structure emerges from the broad bands at 3 and 4.5 meV. The two bands of excitations found above $T_N$ split into at least five distinct modes, whose fitted positions (extracted using Lorentzian functions) are shown in the inset to Fig. 9. Assuming these are bound states, as discussed more fully below, an approximately linear increase in energy with the bound-state level was found (inset, Fig. 9).

IV. DISCUSSION

The above results represent a comprehensive investigation of the structure, magnetic properties, and dynamics of CoV$_2$O$_6$. Our principal conclusion is that CoV$_2$O$_6$ may be regarded as a one-dimensional spin chain with considerable Ising-type anisotropy and ferromagnetic nearest-neighbor exchange. This is supported by both physical property and neutron scattering measurements. Here, we briefly review the former before commenting in detail on the latter and the phase diagram which we derive for CoV$_2$O$_6$. Turning first to the physical property measurements in low magnetic fields, both the magnetic susceptibility [Fig. 2(a)] and the specific heat of CoV$_2$O$_6$ [Fig. 2(b)] show a single antiferromagnetic transition at $T_N = 6.3$ K. However, the positive Weiss temperature of 9.2(2) K and the peak seen in $\chi T$ versus $T$ above $T_N$ imply nearest-neighbor ferromagnetic exchange. Our specific heat...
measurements confirm the presence of magnetic fluctuations up to temperatures of around 40 K. These measurements also provide the first piece of evidence for Ising anisotropy as the integrated magnetic entropy is very similar to that expected for an effective $S = 1/2$ spin. This picture is strongly confirmed by the $M(H)$ isotherms shown in Figs. 3(a) and 3(b) and the critical exponent $\beta = 0.22(2)$ derived from neutron powder diffraction (Fig. 5). These physical property measurements compare well with those previously reported\(^{33,34}\) for Ising FM salts such as CoCl$_2 \cdot 2$H$_2$O, which also show a 1/3 magnetization plateau.

Our results start to differ from those reported for these simple materials as we consider our neutron scattering data. First, our diffraction measurements at 2 K show that the magnetic order is incommensurate, although the majority of the scattering can be modeled assuming FM chains coupling antiferromagnetically (Fig. 4). Second, as we now discuss in more detail, our inelastic neutron scattering results do not coincide with predictions for a linear FM Ising spin chain. Unlike AFM Ising chains, soliton excitations in materials with a FM nearest-neighbor exchange $J_1$ do not deconfine. The excitations are instead isolated flips of blocks of spins,\(^6\) and the results of zero-field inelastic neutron scattering may be modeled using standard spin-wave theory.\(^35\) The degeneracy of these excitations may also be lifted by applying magnetic fields, and the resulting spectrum of spin flips has also been observed using infrared transmission experiments.\(^36\) The observation of sharp, almost dispersionless features in CoV$_2$O$_6$, as well as temperature-induced scattering, is inconsistent with these expectations. This shows that any Hamiltonian proposed for CoV$_2$O$_6$ must include terms which account for the low crystallographic symmetry. Of obvious importance here is the period 3 variation of crystallographically distinct Co sites (Fig. 1). This may result in a variation in the local easy axis on moving along the chain. In a simple model based on band folding, the presence of two sites would also result in two gapped soliton bands as experimentally observed. Furthermore, this may also be consistent with the presence of two low-energy features. The fitted gap function for these shows that they originate in Villain-mode-type scattering in the gapped bands. As both show the same temperature dependence, the doubling may hence be an indication of both intra- and interband scattering.

On cooling below $T_N$, the complex features which emerge from the gapped bands between 2 and 5 meV are similar to what was reported for the related compound CoNb$_2$O$_6$. This is proposed to be a result of the confining effect of the internal field caused by magnetic order on domain walls. Interchain coupling imposes a linearly increasing potential between propagating domain walls, quantizing the continuum into a ladder of bound states\(^{3,5}\) above the energy required to create an isolated spin flip ($2J_1$). The overall picture seen in CoV$_2$O$_6$ (inset, Fig. 9) qualitatively agrees with this picture; however, significant dispersion is not evident from our data. In Ref. 5, an empirical parameter which tuned the dispersion was introduced into the Hamiltonian. This is strongly dependent on the exchange topology in each individual material. In our powder averaged case, the energies of the bound states increase linearly, and from the y intercept we estimate an average intrachain interaction of 0.95(1) meV.

The phase diagram of CoV$_2$O$_6$ that we have determined from our physical property measurements is shown in Fig. 10. Of particular note is the 1/3 magnetization plateau. This feature is not found for all temperatures within the antiferromagnetically ordered region below 6.3 K, instead setting in below $\sim$5 K. Interestingly, the region without a plateau coincides extremely well with the region of critical fluctuations identified by neutron powder diffraction shown in Fig. 5. Examination of Fig. 8 also shows that a small amount of the thermally populated domain wall inelastic scattering also remains down to 5 K. This is in some respects similar to the situation found in the intermediate partially disordered magnetic structure in CsCoCl$_3$. This compound has a coexistence of 2/3 ordered spins and soliton excitations in a low-temperature region before complete order sets in.\(^38\) A plausible explanation of our results for CoV$_2$O$_6$, consistent with the anisotropic coupling between chains, would be a crossover between two-

![FIG. 9. (Color online) Momentum transfer summed inelastic scattering of CoV$_2$O$_6$ at 1.5 K and 7.08 meV incident energy showing the confining effect of the internal field in the magnetically ordered state. Lines are fits to Lorentzian functions. The inset shows the energy of the bound states with a linear fit.](Image 83x586 to 263x739)

![FIG. 10. (Color online) The temperature-magnetic field phase diagram of CoV$_2$O$_6$ established from the physical property measurements in this work. The various phases are labeled as FM (fully polarized ferromagnetic), 1/3 (plateau in magnetization at 1/3 of saturation), and AFM (antiferromagnetic phase). The region of hysteresis found at the lower bound of the 1/3 plateau is shown in magenta (unlabeled dark shading).](Image 346x584 to 526x740)
of confinement caused by the internal field. It is likely that the low symmetry of CoV$_2$O$_6$, especially the presence of two crystallographically independent sites in the edge-sharing chains, strongly influences the magnetic properties.

Significant challenges remain, including resolving the exact magnetic structure adopted below 7 K and a complete modeling of the inelastic neutron spectra. We anticipate that these can be addressed once single crystals of CoV$_2$O$_6$ become available.

**ACKNOWLEDGMENTS**

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