Magnetic Structure and Susceptibility of CoSe$_2$O$_5$: A Low Dimensional Antiferromagnet

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CoSe$_2$O$_5$ has a crystal structure consisting of zig-zag chains of edge shared CoO$_6$ octahedra running along the c axis, with the chains separated by SeO$_{2-}$ units. Magnetic susceptibility measurements indicate a transition at 8.5 K to an ordered state. We investigate here the nature of this magnetic ordering using magnetization and specific heat measurements in addition to powder neutron diffraction. A transition to long-range antiferromagnetic order is found below $T_N = 8.5$ K as identified by magnetic susceptibility measurements and magnetic Bragg reflections, with a propagation vector $\mathbf{k} = 0$. The magnetic structure shows that the moments align perpendicular to the c-axis, but with the spins canting with respect to the a axis by, alternately, $+8^\circ$ and $-8^\circ$. Interestingly, the low-field magnetic susceptibility does not show the anticipated cusp-like behavior expected for a well-ordered antiferromagnet. When the susceptibility is acquired under field-cooling conditions under a 10 kOe field, the usual downturn expected for antiferromagnetic ordering is obtained. Heat capacity measurements at low temperatures indicate the presence of gapped behavior with a gap of 6.5 K.

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I. INTRODUCTION

Recently there has been a significant interest in materials with reduced crystallographic dimensionality because of their strong interplay between charge, lattice, and magnetic degrees of freedom.$^{12}$ From the perspective of magnetism, one-dimensional chains of spins are especially interesting because of the possibility of competing nearest and next-nearest neighbor exchange interactions.$^{13}$ Examples of recently studied compounds with magnetic chains include ones showing geometric frustration, magnetoelectric coupling, and possibly quantum tunneling of the magnetization, as exemplified by Ca$_3$Co$_2$O$_6$,$^{14,15}$ MnWO$_4$,$^{16}$ and LiCu$_2$O$_2$.\textsuperscript{17}

Here we report on CoSe$_2$O$_5$, an orthorhombic compound with the Phen space group, consisting of chains of edge sharing CoO$_6$ octahedra which zig-zag along the the c axis. Each chain is bound together by SeO$_{2-}$ units via shared oxygen at the corners of the octahedra. The diselenide units can be visualized as two trigonal pyramids of SeO$_3$ which share a corner and contain two lone pairs of electrons which point in antiparallel directions. This connectivity packs the chains in hexagonal arrays and isolates them magnetically. This compound and its structure was reported by Harrison et al.$^{18}$ but no reports on the properties have been made. We were particularly interested in this compound because of its low dimensionality, the presence of orbitally degenerate octahedral Co$^{2+}$, and the presence of possibly symmetry reducing lone pairs.

We have used a combination of magnetic susceptibility and magnetization measurements, powder neutron diffraction, and specific heat measurements to characterize the nature of the magnetic ground state below 8.5 K and at low magnetic fields. We also suggest the presence of more complex ground states at high fields, a subject for future study. The compound displays a spin gap, with the size of the gap being 6.5 K.

II. EXPERIMENTAL METHODS

CoSe$_2$O$_5$ was prepared following the reported hydrothermal procedure$^{19}$ SeO$_2$ ($5.0$ g, Cerac, 99.99\%) was dissolved in 15 cm$^3$ of water and combined with CoSO$_4$·xH$_2$O ($2.0$ g, Sigma-Aldrich, 98\%). The mixture was sealed in a 23-mL poly(tetrafluoroethylene)-lined pressure vessel (Parr Instruments) and heated to 200°C for 48 hours. The resulting product consisted of dark purple single crystals averaging 1.5 mm × 1.5 mm × 0.5 mm.

ZnSe$_2$O$_5$, a non-magnetic analogue to the title compound, was also prepared to give an estimate of the lattice contribution to the specific heat. SeO$_2$ ($0.7317$ g, Cerac, 99.99\%) was ground in an agate mortar with ZnO ($0.2683$ g, Sigma-Aldrich, 98\%), sealed in a silica tube, and heated at 350°C for 48 hrs.$^{19}$ The resulting product consisted of an off-white polycrystalline powder.

Neutron diffraction data were collected on a sample of
well-ground single crystals at the D2B powder diffractometer at the Institut Laue-Langevin (ILL), France using a wavelength of 1.5943 Å. The wavelength of the incident neutrons was determined by refining the data obtained at 300 K and fixing the cell parameters to the values determined from a room temperature x-ray diffraction pattern collected on a Philips XPERT MPD diffractometer operated at 45 kV and 40 mA. In order to achieve a better fit to the lowest lying magnetic reflections, a diffraction pattern was also collected at 2 K using a wavelength of 2.399 Å.

Temperature dependence of the DC magnetization were measured on well-ground powder samples using a Quantum Design MPMS 5XL SQUID magnetometer. Powders were preferred since the shape and dimensions of the crystal made it difficult to align a single crystal with respect to the field direction. The specific heat data was collected on a 9.5 mg single crystal using the semi-adiabatic technique as implemented in a Quantum Design Physical Property Measurement System (PPMS), under zero applied field, as well as under a 50 kOe field. The measurement on non-magnetic ZnSe$_2$O$_5$ was made by mixing the compound with equal parts by mass of Ag powder and pressing into a pellet in order to improve thermal coupling. The contribution from Ag was measured separately and subtracted.

III. RESULTS AND DISCUSSION

The nuclear and magnetic structure of CoSe$_2$O$_5$ were refined using the Rietveld method as implemented in the FULLPROF software suite. The peak shape was described using the Thompson-Cox-Hastings pseudo-Voigt function, and the background was fit by interpolation between regions showing no Bragg reflections. The crystal structures were analysed based on the model proposed by Harrison et al., although it should be noted that we use the standard setting of space group number 60 ($Pbcn$) instead of the alternate $Pnab$ description originally used. A summary of key refinement results is shown in table I and in table II. For the magnetic structure, a group theoretical analysis was performed using representational analysis as implemented in the program SARA.[13] was used to determine all of the possible spin configurations which were compatible with the crystal symmetry.

The thermal evolution of the neutron-diffraction patterns collected from 300 K to 2 K are shown in fig. [1]. Three magnetic reflections appear below 10 K at 8°, 17°, and 20°. These three peaks could only be fit simultaneously by using the basis vectors of the irreducible representation $\Gamma_8$. The resulting magnetic structure associated with $\Gamma_8$ and refined from the 2.4 Å data is illustrated in fig. [2]. Each chain of Co moments align antiferromagnetically down the length of the chain and with respect to the neighboring chains. The moments cant in the $ac$ plane, forming, alternately, angles of +8° and −8° with respect to the $a$ axis. The moments have no component along $b$. The magnetic moment on every Co atom refined to a value of 3 $\mu_B$ at 2 K using the $\lambda = 2.399$ Å neutron diffraction data. This corresponds to three unpaired spins per Co atom in the ordered antiferromagnetic structure.

The high temperature region (350 K to 400 K) of the
The behavior is unusual and is not in keeping with the magnetic structure which suggests complete antiferromagnetic ordering of spins. It is proposed that the unusual transition in the susceptibility might be associated with the anisotropic, one-dimensional nature of the magnetic structure, and also perhaps, with the magnetism being centered on octahedral Co$^{2+}$ which is orbitally degenerate. Data acquired after field cooling in the larger field of 10 kOe results in the more usual downturn in the susceptibility expected from an exact cancellation of all moments.

To more carefully probe the dependence of the magnetization on magnetic field in the ordered phase, we measured $M(H)$ curves at $T = 2$ K. The low field behavior can be seen most clearly by plotting the differential magnetization ($dM/dH$), as shown in fig. 3(b), showing a small maximum near $H = 0$, with broad minima near $H = 5$ kOe, with no significant dependence on the direction of the magnetic field sweep. Recall that the canted spin structure observed in the neutron scattering experiment was not subject to any external field. These magnetization measurements suggest that even a small external magnetic field can perturb the spin structure towards a more collinear arrangement. Further neutron scattering studies under a magnetic field are planned to explore the nature of magnetic ordering as a function of both field and temperature.

The temperature dependence of the specific heat $C_p$ of CoSe$_2$O$_5$ shown in Fig. 4 exhibits a lambda-type anomaly around 8.5 K corresponding to the transition to long-range magnetic order observed in the susceptibility and in the neutron diffraction data. Measurements on non-magnetic ZnSe$_2$O$_5$ give an estimate of the lattice contribution using a three term expansion with the best fit yielding a Debye temperature, $\Theta_D$, of 222 K. An estimate of the change in entropy associated with the magnetic transition can be obtained by integrating $C_p$/magnetic $\Delta S = R\ln(2S+1)$, $S = 3/2$). The difference between expected and measured magnetic entropy changes could arise from the canted nature of the antiferromagnetic transition was not subject to any external field. These magnetization measurements suggest that even a small external magnetic field can perturb the spin structure towards a more collinear arrangement. Further neutron scattering studies under a magnetic field are planned to explore the nature of magnetic ordering as a function of both field and temperature.

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TABLE II: Atomic positions and anisotropic thermal parameters of CoSe$_2$O$_5$ at 300 and 2 K

|     | x     | y     | z     | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|-----|-------|-------|-------|--------------|--------------|--------------|--------------|--------------|--------------|
| 300 K |       |       |       |              |              |              |              |              |              |
| Co  | 0     | 0.940 | 0.75  | 0.0024       | 0.0001       | 0.0020       | -0.0020      |              |              |
| Se  | 0.631 | 0.154 | 0.968 | 0.0013       | 0.0007       | 0.0051       | 0.0003       | -0.0007      | 0.0002       |
| O1  | 0.805 | 0.210 | 0.342 | 0.0027       | 0.0012       | 0.0098       | 0.0003       | 0.0004       | -0.0001      |
| O2  | 0.5   | 0.932 | 0.250 | 0.0063       | 0.0010       | 0.0109       | -0.0054      |              |              |
| O3  | 0.840 | 0.933 | 0.452 | 0.0007       | 0.0020       | 0.0067       | -0.0015      | -0.0017      | 0.0004       |

|     |       |       |       |              |              |              |              |              |              |
| 2 K |       |       |       |              |              |              |              |              |              |
| Co  | 0.937 | 0.75  |       | 0.0127      | 0.0042       | 0.0128       | -0.0014      |              |              |
| Se  | 0.630 | 0.154 | 0.969 | 0.0099      | 0.0043       | 0.0148       | 0.0002       | 0.0002       | 0.0000       |
| O1  | 0.807 | 0.211 | 0.342 | 0.0109      | 0.0047       | 0.0168       | 0.0000       | 0.0004       | -0.0004      |
| O2  | 0.5   | 0.931 | 0.250 | 0.0112      | 0.0043       | 0.0167       | -0.0003      |              |              |
| O3  | 0.840 | 0.933 | 0.451 | 0.0099      | 0.0050       | 0.0167       | -0.0004      | 0.0000       | 0.0000       |

FIG. 4: Temperature dependence of the specific heat of CoSe$_2$O$_5$ measured on a 0.5 mg single crystal under zero field, and under a $H = 50$ kOe field. A nonmagnetic analogue, ZnSe$_2$O$_5$, was also measured in order to obtain the lattice contribution to the specific heat. Note the large width of the ordering peak and the release of entropy well above the transition temperature of 8.5 K.

FIG. 5: Magnetic specific heat of CoSe$_2$O$_5$ below the ordering temperature fitted to the formula for a gapped spin system, $C_p \propto T^3 \exp(-\Delta/k_B T)$, with $\Delta = 6.5$ K for data acquired under $H = 0$ kOe as well as $H = 50$ kOe.

would be expected for an antiferromagnet. Instead, the best fit to the data was found when an exponential term was included, using $C_{p,mag} \propto T^3 \exp(-\Delta/k_B T)$. Such an analysis reflects the presence of low-lying magnetic excitations with an energy gap $\Delta = 6.5$ K. The presence of spin gaps in one-dimensional magnetic materials is well known.

### A. Conclusions

We have examined the magnetic properties of CoSe$_2$O$_5$ using neutron diffraction, magnetization and magnetic susceptibility, and specific heat measurements. We show that below the magnetic ordering temperature, the one dimensional magnetic chains arrange their moments antiferromagnetically down the length of the chain and with...
respect to neighboring chains. The magnetic order in small fields is found to exhibit some canting, although the net moment is zero. Under large applied field, the magnetic behavior changes, pointing to a rich $H - T$ phase diagram in this system. We see evidence for low lying magnetic excitations with a spin gap of 6.5 K, that are also possibly implicated in the field-induced phase transition seen in $\mathrm{d}M/\mathrm{d}H$ vs. $H$ at 2 K.

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1. S.-W. Cheong and M. Mostovoy, Nat. Mater. 6, 13 (2007).
2. T. Kimura, Annu. Rev. Mater. Res. 37, 387 (2007).
3. S. Park, Y. J. Choi, C. L. Zhang, and S.-W. Cheong, Phys. Rev. Lett. 98, 057601 (2007).
4. V. Hardy, S. Lambert, M. R. Lees, and D. McK. Paul, Phys. Rev. B 68, 014424 (2003).
5. A. Maignan, V. Hardy, S. Hebert, M. Drillon, M. R. Lees, O. Petrenko, D. M. K. Paul, and D. Khomskii, J. Mater. Chem. 14, 1231 (2004).
6. Y. J. Choi, H. T. Yi, S. Lee, Q. Huang, V. Kiryuikhin, and S.-W. Cheong, Phys. Rev. Lett. 100, 047601 (2008).
7. K. Taniguchi, N. Abe, T. Takenobu, Y. Iwasa, and T. Arima, Phys. Rev. Lett. 97, 097203 (2006).
8. T. Masuda, A. Zheludev, B. Roessli, A. Bush, M. Markina, and A. Vasiliev, Phys. Rev. B 72, 014405 (2005).
9. W. T. A. Harrison, A. V. P. McManus, and A. K. Cheetham, Acta Cryst. C48, 412 (1992).
10. G. Meunier and M. Bertaud, Acta Cryst. B30, 2840 (1974).
11. A. W. Hewat and S. Heathman, Acta Cryst. 40, C364 (1984).
12. J. Rodriguez-Carvajal, Phys. B. 192, 55 (1993).
13. A. S. Wills, Phys. B 276, 680 (2000).
14. J. Skalyo and S. A. Friedberg, Phys. Rev. Lett. 13, 133 (1964).
15. A. Tari, The Specific Heat of Matter at Low Temperatures (Hardcover) (Imperial College Press, 2003).
16. H. J. Mikeska and M. Steiner, Adv. Phys. 40, 191 (1991).