Magnetic studies of monoclinic $Cu_4O(SeO_3)_3$, a copper-oxo-selenite derivative

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Abstract. $Cu_4O(SeO_3)_3$ is a copper-oxo-selenite belonging to the $Cu_xO(SeO_3)_{(x-1)}$ family of the topological chiral magnet Cu_2OSeO_3. We report magnetometry and specific heat data measured in a monoclinic $Cu_4O(SeO_3)_3$ single crystal grown through a Chemical Vapour Transport (CVT) reaction. Our study shows a typical antiferromagnetic behaviour, with a Néel temperature $T_N = 58$ K, similar to that of the Cu_2OSeO_3 and an additional transition at 13 K. The effective magnetic moment per Cu atom is 1.84 μ_B, close to the expected theoretical value for Cu^{2+}. The low-temperature $M(H)$ curves, show a transition starting at $H_{c1} \sim 400$ Oe at 1.8 K shifting to a lower value of ~ 280 Oe at 30 K, likely from a helical into a conical intermediate phase, and a second transition at $H_{c2} \sim 1$ kOe, above which the net moment increases linearly with applied field. The magnetisation moment value in a 90 kOe field is 0.053 μ_B/Cu at 1.8 K and attains a maximum value of 0.061 μ_B at 13 K. Low-temperature specific heat measurements confirm the presence of the magnetic transition at 13 K, slightly shifting to lower temperatures under an applied magnetic field.

1 Introduction

$Cu_4O(SeO_3)_3$ is copper-oxo-selenite derivative belonging to the family of $Cu_xO(SeO_3)_{(x-1)}$, $4 \leq x \leq 2$ compounds that includes the topological chiral magnet Cu_2OSeO_3, a most celebrated compound where a skyrmionic magnetic phase was found [1]. Cu_2OSeO_3 crystallises in the chiral space group $P2_13$, the same as B20 compounds where skyrmions where first observed [2]. A magnetic skyrmion is a swirling magnetic spin texture carrying a topological quantum number that occurs due to the competition between isotropic Heisenberg ferromagnetic exchange and antiferromagnetic Dzyaloshinskii-Moriya (DM) interactions [3]. In the magnetic ground state of Cu_2OSeO_3, the Cu moments order in a long period (~ 65 nm) helical structure ($T_N = 58$ K), but close to T_N and under a small applied magnetic field a new magnetic phase with a skyrmionic magnetic arrangement of the spins was found [1, 4].

$Cu_4O(SeO_3)_3$ is known to crystallise in two different polymorphs, with monoclinic and triclinic structures reported long ago by Effenberger et al. [5], the monoclinic structure being more complex than the triclinic one. Although the selenite anions have the typical tetrahedral geometry, the Cu atoms feature distinct coordination geometries. The compound can

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be obtained by thermal decomposition of $CuSeO_3$ in air at high temperatures [6] or using Cu_2OSeO_3. It has also been found as a contaminant during the synthesis of Cu_2OSeO_3 [7, 8]. In this work, we obtained high-quality monoclinic $Cu_4O(SeO_3)_3$ single crystals when we tried to grow Cu_2OSeO_3 using a CVT reaction. Despite the crystal structures of the two poly-morphs of $Cu_4O(SeO_3)_3$ having been reported in the literature, their physical properties are poorly known. In particular, magnetic studies deserve to be performed to better understand the nature of the magnetic interactions in a compound closely related to the topological chiral magnet Cu_2OSeO_3.

2 Materials and Methods

Cu_2OSeO_3 powder was obtained by reacting CuO and SeO_2 (2:1 molar proportion) in evac-uated sealed quartz tubes heated at 600 °C during 3 days. To avoid the formation of other phases, the tube was quenched in water three times during the synthesis, once each 24 h. An olive-green powder was obtained in the quartz tube that was analysed using powder XRD. The diffractogram confirmed the presence of Cu_2OSeO_3 as a majority phase (90% w/w), un-reacted CuO (10% w/w) and no further extraneous phases. This powder was used for the CVT reaction where single crystals were grown.

   The previously obtained powder was sealed in evacuated quartz tubes with an additional small portion of NH_4Cl (0.5 g/cm^3) to act as transport agent in the CVT reaction. The tube was placed in a dual zone furnace and high quality crystals (sizes 1-3 mm) were obtained in the colder zone after six weeks of growth. The temperatures of source and deposition zones were 640 °C and 530 °C, respectively.

3 Structural characterisation

A small crystal was selected for data-collection in a single crystal X-ray diffractometer (Bruker APEXII) equipped with a CCD detector and a Mo X-ray tube (λ = 0.71073 Å). The crystal was found to be a specimen of the monoclinic polymorph, with cell parame-ters a = 15.990(10), b = 13.518(8), c = 17.745(12) Å, β = 90.49(5)° and space group $P2_1/a$. A powder sample was also examined by XRD to check for the presence of extraneous phases. The observed Bragg peaks are consistent with the sole presence of the monoclinic $Cu_4O(SeO_3)_3$ phase.
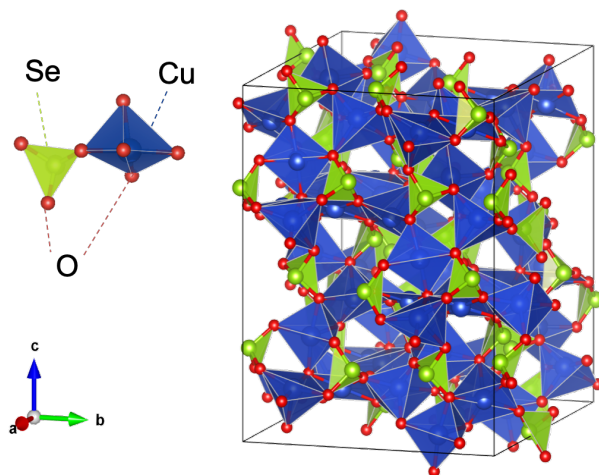
**Figure 1.** Structure of monoclinic $Cu_4O(SeO_3)_3$. Cu and Se atoms and their polyhedra are coloured blue and green, respectively. The O atoms, located at the corners of the coordination polyhedra, are coloured red.

The monoclinic $Cu_4O(SeO_3)_3$ structure is rather complex. The unit cell depicting the main structural units, Se and Cu coordination polyhedra, is shown in Fig. 1 . The asymmetric unit contains 68 independent atoms. The selenite anions have the typical geometry, and the Cu atoms coordinate with the O atoms featuring 3 distinct coordination geometries, 4-, 5- and 6-fold with Cu-O bonds in the range $1.884 - 2.429$ Å that act as magnetic exchange pathways.

## 4 Magnetic and specific heat studies

Magnetometry data were measured on a Quantum Design Dynacool-9T PPMS system equipped with a VSM option. Two samples were analised: a small crystal glued in a quartz sample holder and a powder sample inside a plastic sample holder, obtained by crushing a polycrystalline piece. Zero-field and field cooling (ZFC, FC) thermomagnetic curves were measured in the range $1.8 - 300$ K for applied magnetic fields comprised between 50 Oe and 90 kOe (Fig. 2). A detailed study of the magnetisation process was performed at selected temperatures in the range 1.8 K to 30 K (Fig. 4).
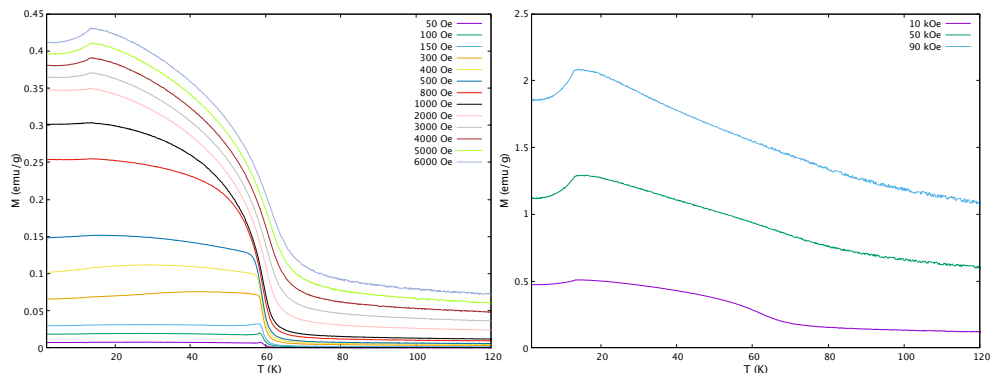
Figure 2. Zero-Field Cooling (ZFC) $M(T)$ curves for a single crystal of $Cu_4O(SeO_3)_3$ for a set of applied magnetic fields (left panel: low fields; right panel: high fields).

The $M(T)$ curves (Fig. 2) show a main magnetic transition at 58 K that gets broader with increasing applied field. In addition, a transition at a lower temperature (13 K) was found, corresponding to an anomaly that is clearly visible above ~ 2 kOe. The anomaly becomes more prominent in increasing applied fields. To better characterise this transition, detailed $M(H)$ curves were measured in the range 1.8–30 K up to the highest available field (90 kOe). Measurements in powder show that in the paramagnetic region the susceptibility follows a modified Curie-Weiss law ($\chi = \chi_0 + C/(T - \Theta)$) with a Curie-Weiss constant corresponding to an effective magnetic moment of 1.84 μ_B/Cu atom, close to that of Cu^{2+} ion, and $\Theta = -81(1)$ K, showing the prevalence of antiferromagnetic interactions (Fig. 3).

The low-temperature $M(H)$ curves (Fig. 4) could be interpreted as a transition occurring at $H_{c1} \sim 400$ Oe at 1.8 K shifting to a lower value of ~ 280 Oe at 30 K, likely from an helical into an intermediate conical phase, and a second transition at $H_{c2} \sim 1$ kOe, above which the net moment increases linearly with applied field. The magnetisation moment value at 90 kOe field and 1.8 K is 0.053 μ_B/Cu, peaking at ~ 0.06 μ_B/Cu at 13 K, far from the full Cu^{2+} moment [4]. Notably, above 13 K and below 30 K a very small remnant is observed in the hysteresis loops.
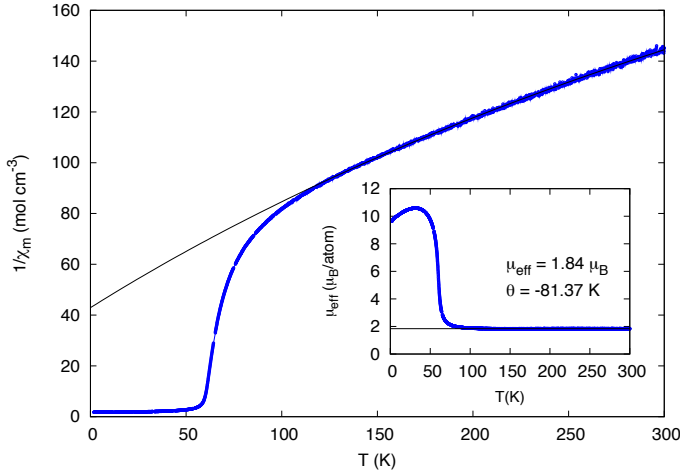
Figure 3. Reciprocal molar susceptibility in a polycrystalline sample measured with an applied field H = 1 kOe, as a function of temperature. The fit of a modified Curie-Weiss law to the data is shown as a solid line. The insert shows the effective magnetic moment as function of temperature.

The obtained results for monoclinic $Cu_4O(SeO_3)_3$ show resemblances to those of the topological chiral magnet Cu_2OSeO_3, with an additional transition at 13 K. However, the curves in Fig. 4 are still far from saturation at 90 kOe, in contrast to the case of Cu_2OSeO_3.
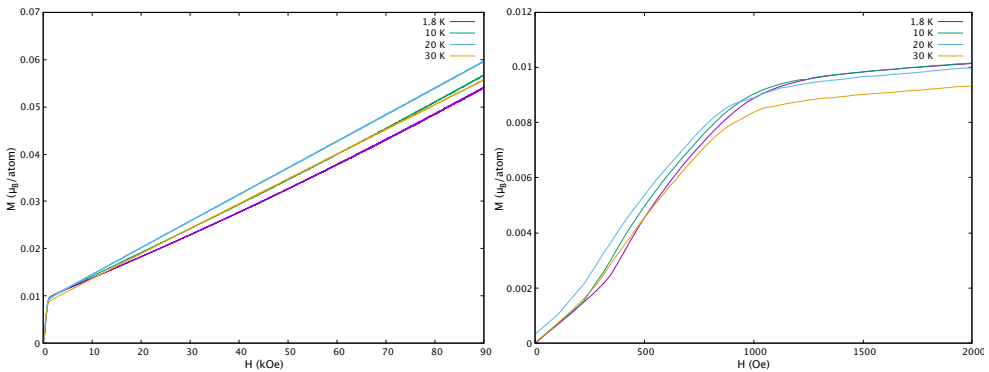

Figure 4. Magnetic-field dependence of the magnetisation ($M(H)$) at low temperature. The right panel shows in detail the low field region.

The same small $Cu_4O(SeO_3)_3$ single crystal used for magnetic measurements was also used for specific heat measurements, under different applied magnetic fields up to 90 kOe, using a semi-adiabatic thermal relaxation method as implemented in the PPMS specific-heat option from Quantum Design. The transition at 13 K found in the magnetometric data was also present in the specific heat data as a clear anomaly found at the same temperature. A plot of $C_p(T)$ is depicted in Fig 5. The transition slightly shifts to lower temperatures as the applied magnetic field is increased. This behaviour is consistent with the main antiferromagnetic character of the magnetic ground state.

5 Conclusions

Monoclinic $Cu_4O(SeO_3)_3$ has a complex structure with a large number of symmetry independent atoms, capable of hosting complex magnetic structures. The magnetic behaviour of
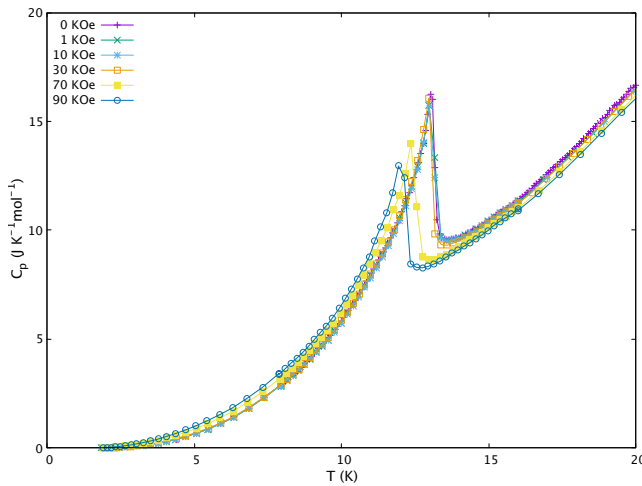
Figure 5. Heat Capacity (C_p) as function of temperature under different applied magnetic fields.

the monoclinic polymorph of $Cu_4O(SeO_3)_3$ shows clear resemblance to that of Cu_2OSeO_3, reported in literature. It is an antiferromagnet with a Néel temperature similar to that of Cu_2OSeO_3 but it shows an additional transition at 13 K, observed both in magnetometric as well as in specific heat measurements. Under an applied magnetic field, the likely helimagnetic antiferromagnetic ground state acquires a small ferromagnetic component.

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