Magnetic studies of monoclinic Cu$_4$O(SeO$_3$)$_3$, a copper-oxo-selenite derivative

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Abstract. Cu$_4$O(SeO$_3$)$_3$ is a copper-oxo-selenite belonging to the family of the topological chiral magnet Cu$_2$OSeO$_3$. We report magnetometry and specific heat data measured in a monoclinic Cu$_4$O(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$_2$OSeO$_3$ and an additional transition at 13 K. The effective magnetic moment per Cu atom is 1.84 $\mu_B$, 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 $\sim 280$ 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 $\mu_B$/Cu at 1.8 K and attains a maximum value of 0.061 $\mu_B$ 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$_4$O(SeO$_3$)$_3$ is copper-oxo-selenite derivative belonging to the family of Cu$_x$O(SeO$_3$)$_{3(x-1)}$, $4 \leq x \leq 2$ compounds that includes the topological chiral magnet Cu$_2$OSeO$_3$, a most celebrated compound where a skyrminionic magnetic phase was found [1]. Cu$_2$OSeO$_3$ 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$_2$OSeO$_3$, the Cu moments order in a long period ($\sim 65$ 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$_4$O(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 CuSeO₃ in air at high temperatures [6] or using Cu₂OSeO₃. It has also been found as a contaminant during the synthesis of Cu₂OSeO₃ [7, 8]. In this work, we obtained high-quality monoclinic Cu₄O(SeO₃)₃ single crystals when we tried to grow Cu₂OSeO₃ using a CVT reaction. Despite the crystal structures of the two polymorphs of Cu₄O(SeO₃)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 Cu₂OSeO₃.

2 Materials and Methods

Cu₂OSeO₃ powder was obtained by reacting CuO and SeO₂ (2:1 molar proportion) in evacuated 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 Cu₂OSeO₃ 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 NH₄Cl (0.5 g/cm³ ) 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 parameters a = 15.990(10), b = 13.518(8), c = 17.745(12) Å, β = 90.49(5)° and space group P2₁/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 Cu₄O(SeO₃)₃ phase.

![Structure of monoclinic Cu₄O(SeO₃)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.](image)
The monoclinic Cu$_4$O(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 analysed: 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$_4$O(SeO$_3$)$_3$ for a set of applied magnetic fields (left panel: low fields; right panel: high fields).](image-url)

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 $\mu_B$/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 $\mu_B$/Cu, peaking at ~ 0.06 $\mu_B$/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.
The obtained results for monoclinic Cu₄O(SeO₃)₃ show resemblances to those of the topological chiral magnet Cu₂OSeO₃, 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 Cu₂OSeO₃.

The same small Cu₄O(SeO₃)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 Cu₄O(SeO₃)₃ has a complex structure with a large number of symmetry independent atoms, capable of hosting complex magnetic structures. The magnetic behaviour of
the monoclinic polymorph of Cu₄O(SeO₃)₃ shows clear resemblance to that of Cu₂OSeO₃, reported in literature. It is an antiferromagnet with a Néel temperature similar to that of Cu₂OSeO₃ 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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References