

## Interplay of magnetic sublattices in langite $\text{Cu}_4(\text{OH})_6\text{SO}_4 \cdot 2\text{H}_2\text{O}$

S. Lebernegg, Alexander A. Tsirlin, O. Janson, G. J. Redhammer, H. Rosner

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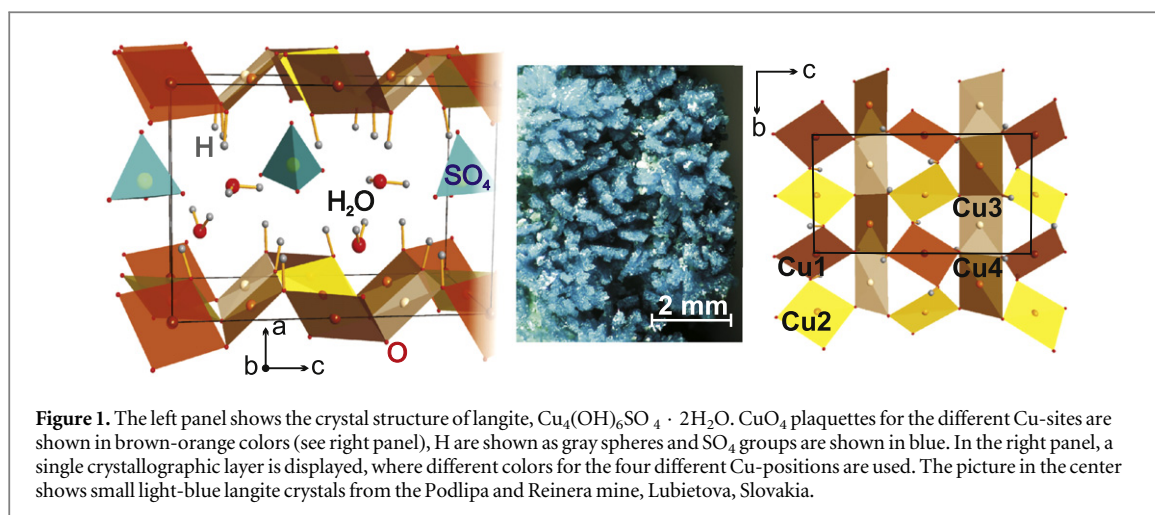
S Lebernegg<sup>1</sup>, A A Tsirlin<sup>2,3</sup>, O Janson<sup>4</sup>, G J Redhammer<sup>5</sup> and H Rosner<sup>1</sup><sup>1</sup> Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Str. 40, D-01187 Dresden, Germany<sup>2</sup> Experimental Physics VI, Center for Electronic Correlations and Magnetism, Institute of Physics, University of Augsburg, D-86135 Augsburg, Germany<sup>3</sup> National Institute of Chemical Physics and Biophysics, 12618 Tallinn, Estonia<sup>4</sup> Institute of Solid State Physics, Technical University Vienna, Wiedner Hauptstr. 8–10/138, A-1040 Vienna, Austria<sup>5</sup> Department of Materials Engineering and Physics, University Salzburg, Hellbrunnerstr. 34, A-5020 Salzburg, AustriaE-mail: [st.lebernegg@gmail.com](mailto:st.lebernegg@gmail.com)**Keywords:** spin-1/2 quantum magnet, frustrated magnet, thermodynamic properties, microscopic magnetic model,  $\text{Cu}^{2+}$ -mineralSupplementary material for this article is available [online](#)**Abstract**

Magnetic and crystallographic properties of the mineral langite  $\text{Cu}_4(\text{OH})_6\text{SO}_4 \cdot 2\text{H}_2\text{O}$  are reported. Thermodynamic measurements combined with a microscopic analysis, based on density-functional bandstructure calculations, identify a quasi-two-dimensional (2D), partially frustrated spin-1/2 lattice resulting in the low Néel temperature of  $T_N \simeq 5.7$  K. This spin lattice splits into two parts with predominant ferro- and antiferromagnetic (AFM) exchange couplings, respectively. The former, ferromagnetic (FM) part is prone to the long-range magnetic order and saturates around 12 T, where the magnetization reaches  $0.5 \mu_B/\text{Cu}$ . The latter, AFM part features a spin-ladder geometry and should evade long-range magnetic order. This representation is corroborated by the peculiar temperature dependence of the specific heat in the magnetically ordered state. We argue that this separation into ferro- and antiferromagnetic sublattices is generic for quantum magnets in  $\text{Cu}^{2+}$  oxides that combine different flavors of structural chains built of  $\text{CuO}_4$  units. To start from reliable structural data, the crystal structure of langite in the 100–280 K temperature range has been determined by single-crystal x-ray diffraction, and the hydrogen positions were refined computationally.

**1. Introduction**

Low-dimensional magnets show unique diversity of crystal structures and associated spin lattices, where a plethora of quantum phenomena can be observed [1–3]. The physics of quantum spin chains has been actively explored in  $\text{Cu}^{2+}$  compounds featuring chains of corner- or edge-sharing  $\text{CuO}_4$  plaquette units. The corner-sharing geometry results in uniform spin chains with a negligibly small second-neighbor coupling, as in  $\text{Sr}_2\text{CuO}_3$  [4, 5],  $\text{AgCuVO}_4$  [6] and  $\text{KCuMoO}_4(\text{OH})$  [7]. The edge-sharing geometry is by far more common. It gives rise to competing nearest-neighbor and next-nearest-neighbor (NNN) couplings, where the former ( $J_1$ ) is typically ferromagnetic (FM), while the latter ( $J_2$ ) is antiferromagnetic (AFM). Such  $J_1 - J_2$  frustrated spin chains develop incommensurate spin correlations and helical magnetic order [8, 9], although few instances of FM intrachain spin order are known as well [10, 11]. The helical spin arrangement observed in simple binary compounds  $\text{CuCl}_2$  [12] and  $\text{CuBr}_2$  [13] and in more complex materials like linarite  $\text{PbCu}(\text{OH})_2\text{SO}_4$  [14], all being frustrated  $J_1 - J_2$  spin chains, may trigger electric polarization induced by the magnetic order, thus leading to multiferroic behavior [15–18]. Additionally, small interactions beyond the isotropic Heisenberg model lead to an intricate magnetic phase diagram, including multipolar (three-magnon) phases, which has been studied recently [19]. However, the complex interplay of frustration and anisotropy needs further investigations on different systems as, e.g.,  $\text{LiCuVO}_4$  [20–23].

One may naturally ask what happens when two types of spin chains, those with edge- and corner-sharing geometries, are placed next to each other within one material. Spin systems comprising several magnetic



sublattices with different dimensionalities and energy scales may have very unusual low-temperature properties. When two sublattices are weakly coupled, they are, to a certain extent, independent, hence two magnetic transitions manifesting the ordering within each of the sublattices could be observed. On the other hand, the ordering within one sublattice will necessarily depend on the other sublattice, because three-dimensional (3D) long-range order typically involves interactions between the sublattices. Unusual manifestations of quantum order-from-disorder have been observed in  $\text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2$  [24–28] featuring interpenetrating square lattices with drastically different exchange couplings. In  $\text{CuP}_2\text{O}_6$ , where spins, arranged on a planar square lattice, coexist with uniform spin chains, very strong spin fluctuations are observed even below the Néel temperature  $T_N$ , and the value of  $T_N$  is unusually low for a quasi-2D antiferromagnet [29]. The coexistence of corner- and edge-sharing  $\text{Cu}^{2+}$  chains could be even more interesting because of the different nature of spin correlations, which are expected to be AFM collinear and helical, for the corner- and edge-sharing chains, respectively.

The respective magnetic ground state of these compounds depends very subtly on the interplay of various exchange integrals, including possible frustration and strong quantum fluctuations. In particular, in edge-sharing geometries (with  $\text{Cu}-\text{O}-\text{Cu}$  bond angles near  $90^\circ$ ) the leading exchange integrals and, thus, the actual magnetic model are often difficult to establish due to a pronounced dependency of the exchange on the structural details: small changes of bond angles or minor changes of the local  $\text{Cu}-\text{O}$  environment, e.g. by attached H-atoms [30, 31], may even swap the ground state qualitatively. Owing to the high complexity of the structure-properties relation in these compounds, the combination of experimental investigations with theoretical methods appeared to be very successful to disentangle the complicated interplay. In particular, in recent years density functional calculations have developed to a valuable tool, establishing accurate magnetic models on microscopic grounds [13, 32, 33], even for involved geometries like coupled edge-sharing chains or various magnetic sublattices in a single compound.

The coexistence of the edge- and corner-sharing geometries is rather common for  $\text{Cu}^{2+}$  minerals. In antlerite [34] and szenicsite [35], one edge-sharing chain is encompassed by two corner-sharing chains that together form a three-leg spin ladder. The edge- and corner-sharing chains can also form infinite layers, as in deloryite  $\text{Cu}_4(\text{UO}_2)(\text{MoO}_4)_2(\text{OH})_6$  [36], derriksite  $\text{Cu}_4(\text{UO}_2)(\text{SeO}_3)_2(\text{OH})_6$  [37], niedermayrite  $\text{Cu}_4\text{Cd}(\text{SO}_4)_2(\text{OH})_6$  [38], and langite  $\text{Cu}_4(\text{OH})_6\text{SO}_4 \cdot 2\text{H}_2\text{O}$ . The crystal structure of the latter mineral is shown in figure 1. Layers of alternating edge- and corner-sharing chains (figure 1, right) are well separated by  $\text{SO}_4$  sulphate groups and water molecules. A somewhat similar structure without water molecules has been reported for the mineral brochantite  $\text{Cu}_4(\text{OH})_6\text{SO}_4$  [39, 40] that, however, features a much smaller interlayer separation, hence substantial interlayer couplings can be expected. In this paper, we focus on the magnetism of langite, where individual structural planes should be very weakly coupled magnetically and sufficiently pure natural samples of this mineral are available.

We show that, in contrast to our expectations, individual structural chains in this material cannot be considered as weakly coupled magnetic chains. On the other hand, two sublattices formed by the structural chains of either type, can be distinguished in the overall very intricate spin lattice. These sublattices reveal drastically different magnetic couplings and facilitate the description of the complex low-temperature magnetism on a qualitative microscopic level.

The paper is organized as follows: applied experimental and theoretical methods are described in section 2. The crystal structure of langite including the single-crystal data collected at low temperatures and hydrogen positions determined computationally is presented in section 3. Section 4 provides experimental results on

thermodynamic properties of langite. The electronic band structure and computed exchange coupling constants are discussed in section 5. Eventually, a detailed discussion and summary are given in sections 6 and 7, respectively.

## 2. Methods

All experiments have been performed on a natural sample of langite (figure 1) from the Podlipa and Reiner mine, Lubietova, Slovakia. The sample quality was first thoroughly controlled by laboratory powder x-ray diffraction (XRD) (Huber G670 Guinier camera,  $\text{CuK}\alpha_1$  radiation, ImagePlate detector,  $2\theta = 3 - 100^\circ$  angle range).

Single-crystal x-ray diffraction between 100 and 280 K was performed on a Bruker SMART APEX CCD-diffractometer equipped with a Cryostream liquid nitrogen low-temperature device. A single crystal, selected on the basis of its optical properties (sharp extinctions, regular shape and homogeneity in color) was glued on top of a glass capillary (0.1 mm). Intensity data were collected with graphite-monochromatized  $\text{MoK}\alpha$  radiation (50 kV, 30 mA). The crystal-to-detector distance was 40 mm and the detector was positioned at  $-28^\circ 2\theta$  using an  $\omega$ -scan mode strategy at four different  $\varphi$ -positions ( $0^\circ$ ,  $90^\circ$ ,  $180^\circ$  and  $270^\circ$ ). 630 frames with  $\Delta\omega = 0.3^\circ$  were acquired for each run. The 3D data were integrated and corrected for Lorentz polarization and background effects using the APEX2 software (Bruker–Nonius, 2004). Structure solution (using Patterson methods) and subsequent weighted full-matrix least-square refinements on  $F^2$  were done with SHELXL-97 [41] as implemented in the program suite WinGX 1.64 [42].

All further experiments were performed on a powder sample since the natural crystals are very small and fragile as well as strongly intergrown, preventing us from collecting a sufficient amount of single crystallites for magnetic and specific heat measurements. Magnetization measurements were done on a Quantum Design (QD) SQUID MPMS in magnetic fields up to 5 T and using the vibrating sample magnetometer setup of QD PPMS up to 14 T in the temperature range of 1.6–300 K. Heat capacity data were acquired with the QD PPMS in fields up to 14 T.

Electronic structure calculations within density functional theory (DFT) were performed with the full-potential local-orbital code FPLO9.07-41 [43] on the 100 K crystal structure in combination with the local density approximation (LDA) [44], generalized gradient approximation (GGA) [45] and the DFT +  $U$  method [46, 47]. A  $4 \times 4 \times 4$   $k$ -mesh was employed for LDA and GGA runs while super cells used for DFT +  $U$  calculations were computed for about 100  $k$ -points in the symmetry-irreducible part of the first Brillouin zone. We also performed auxiliary calculations using the Heyd–Scuseria–Ernzerhof (HSE06) hybrid DFT-functional [48, 49] as implemented in the Vienna *ab initio* Simulation Package (VASP5.2) code [50, 51].

The hydrogen positions, which are essential for the calculation of the exchange couplings [30, 31], have not been determined so far [52] since H is almost invisible in XRD due to its very low scattering power. Alternative experimental techniques such as neutron diffraction require large and, preferably, deuterated samples that are not available in nature. Therefore, we determined the positions of hydrogen by numerical optimization of the atomic parameters with respect to a minimization of the total energy. These calculations were performed within GGA and have proved to be highly efficient and sufficiently accurate for cuprates in recent studies [30, 31, 53].

The exchange coupling constants  $J_{ij}$  were calculated within DFT following two different strategies. One strategy involves the analysis of the half-filled LDA bands at the Fermi level allowing for the determination of leading exchange pathways by an evaluation of the electron hopping integrals  $t_{ij}$ . The  $t_{ij}$  are computed as off-diagonal Hamiltonian matrix elements of Cu-centered Wannier functions (WFs) constructed for the half-filled bands. The spurious metallic state produced for magnetic insulators within LDA can be remedied by inserting LDA-based  $t_{ij}$  into an effective Hubbard model with the effective onsite Coulomb repulsion  $U_{\text{eff}}$ , where in cuprates typically  $U_{\text{eff}} \simeq 4.5$  eV [29, 31, 53]. In the limit of strong correlations,  $t_{ij} \ll U_{\text{eff}}$ , which is perfectly fulfilled in langite (see table 2), AFM contributions to the total exchange constants  $J_{ij}$  can be estimated in second order as  $J_{ij}^{\text{AFM}} = 4t_{ij}^2/U_{\text{eff}}$ . A more detailed description of the procedure can be found, e.g., in [31, 54].

Alternatively, strong electron correlations are added on top of LDA by the LSDA+ $U$  method in a mean-field way and are thus included in the self-consistent procedure. This allows for calculating total exchange constants  $J_{ij} = J_{ij}^{\text{FM}} + J_{ij}^{\text{AFM}}$ , which contain also the FM contributions. A fully localized limit approximation was used for correcting the double counting. The on-site Coulomb repulsion and Hund's exchange were set to  $U_d = 8.5 \pm 1$  eV and  $J_d = 1$  eV, respectively, a choice which has been successfully used for several other cuprates [31, 32, 53]. The total exchange coupling constants  $J_{ij}$  of the spin Hamiltonian

$$\hat{H} = \sum_{\langle ij \rangle} J_{ij} \hat{S}_i \cdot \hat{S}_j \quad (1)$$

are calculated as differences between total energies of various collinear (broken-symmetry) spin states [13, 53, 55].

**Table 1.** Refined atomic positions (in fractions of lattice parameters) and isotropic displacement parameters  $U_{\text{iso}}$  (in  $\times 10^{-2} \text{ \AA}^2$ ) of langite,  $\text{Cu}_4(\text{OH})_6\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , collected at 100 K. Refinement residuals are  $R_1 = 4.64\%$ ,  $wR_2 = 7.6\%$ . All atoms are in the general position  $2a$  of the space group  $P1c1$ . The lattice parameters are as follows:  $a = 7.1231(8) \text{ \AA}$ ,  $b = 6.0305(7) \text{ \AA}$ ,  $c = 11.1935(12) \text{ \AA}$  and  $\beta = 90.1479(14)^\circ$ . OW and HW denote the O and H atoms of the  $\text{H}_2\text{O}$  molecules. The OS atoms belong to the  $\text{SO}_4$  tetrahedra. The H-positions have been obtained by numerical optimization within GGA. For OW, experimental and optimized positions are provided.

Atom	$x/a$	$y/b$	$z/c$	$U_{\text{iso}}$
Cu1	0.99960(13)	0.99762(18)	0.49990(9)	0.46(2)
Cu2	0.99260(13)	0.49213(19)	0.50188(9)	0.43(3)
Cu3	0.00399(14)	0.75566(18)	0.75295(11)	0.40(2)
Cu4	0.00878(15)	0.25490(17)	0.75183(11)	0.38(2)
S	0.5778(4)	0.1854(3)	0.4201(3)	0.46(4)
O1	0.8860(9)	0.0001(10)	0.6634(6)	0.41(12)
O2	0.8882(9)	0.5044(10)	0.6652(6)	0.54(13)
O3	0.1156(9)	0.5098(10)	0.8432(7)	0.43(13)
O4	0.1412(8)	0.2452(11)	0.5604(6)	0.39(13)
O5	0.8600(8)	0.7441(9)	0.4412(6)	0.45(13)
O6	0.1256(9)	0.0054(10)	0.8398(7)	0.56(14)
OS1	0.7845(8)	0.2311(9)	0.4116(5)	0.42(12)
OS2	0.5388(8)	0.0666(9)	0.5344(6)	1.08(13)
OS3	0.4770(8)	0.4015(10)	0.4219(6)	0.94(12)
OS4	0.5165(8)	0.9519(10)	0.8163(6)	0.91(13)
OW1	0.2626(9)	0.7398(10)	0.6008(6)	0.73(13)
OW2	0.5178(9)	0.4283(11)	0.6955(7)	1.16(15)
GGA-optimization				
OW1	0.27422	0.73641	0.59891	
OW2	0.52514	0.43403	0.69849	
H1	0.27170	0.74411	0.03266	
H2	0.35870	0.38187	0.12901	
H3	0.72674	0.74906	0.46285	
H4	0.26599	0.00612	0.33549	
H6	0.74761	0.99558	0.65733	
H7	0.25162	0.46853	0.36133	
H1W1	0.51463	0.54313	0.28622	
H2W1	0.36074	0.85755	0.57697	
H1W2	0.51392	0.27508	0.68068	
H2W2	0.74644	0.49444	0.67040	

### 3. Crystal structure

Using the experimental crystal structure of langite reported in [52], we first routinely performed a DFT-optimization of the atomic parameters of all atoms in the unit cell with the lattice parameters being fixed to their experimental values. Deviations up to  $0.3 \text{ \AA}$  between the experimental and optimized Cu–O bond lengths prompted us to reinvestigate the crystal structure of langite with single-crystal XRD. We also performed low-temperature XRD measurements in order to probe possible temperature-induced structural changes that may be relevant to understanding the magnetism.

Table 1 compiles the results of the structural study at 100 K, which served as input for all DFT calculations. Additional crystallographic data collected at 140, 220, 250, 280 K are provided in the supplementary material<sup>6</sup>. In the temperature range between 100 and 280 K the unit cell volume increases by about 0.9% with increasing  $T$ . The largest change in the lattice parameters was observed not along  $a$  perpendicular to the structural layers (figure 1), as one might intuitively expect, but along the  $c$  direction. With increasing  $T$ , the  $c$  parameter increases

<sup>6</sup> See supplementary material for single-crystal crystallographic data collected at temperatures between 100–280 K, the back ground contributions to  $C_p(T)$  at  $H = 0 \text{ T}$ , powder XRD pattern of Langite and exchange constants  $J_{ij}$  from HSE06 hybrid DFT-calculations, description of the tetramer model provided as an alternative to the model of two magnetic sublattices, band structures and density of states of different structures and optimizations, structural details of the layers (angles and distances), hydrogen bonds and bonding of  $\text{H}_2\text{O}$  and the  $\text{SO}_4$  groups to the Cu–O layers.

by about 0.35% reflecting the flattening of the layers. Changes along the  $a$  and  $b$  axes are similar, about 0.26% each. The monoclinic angle remains almost constant for the investigated temperature range.

In the presently available structural data [52], hydrogen positions have been determined on a semiempirical level, only. One of the hydrogens has been placed on the sulphate group which is quite unexpected. In the related Cu–sulphate brochantite,  $\text{Cu}_4(\text{OH})_6\text{SO}_4$ , H-atoms have been reliably located by neutron diffraction on a deuterated sample, and no hydrogen was found at the  $\text{SO}_4$  groups but at the Cu–O layers [39]. More doubts on the reliability of the tentative H-positions of langite, as provided in [52], arise from the geometry of the water molecules. While one of them shows bond lengths close to a free water molecule, the other one is strongly distorted with O–H distances of 0.919 and 1.032 Å respectively, and a H–O–H angle of only 88.54°. These issues already call for a reinvestigation of the hydrogen positions in langite. Besides gaining new structural information, accurate atomic H-positions are also essential for the computation of exchange coupling constants which are very sensitive to O–H distances and the position of H with respect to the  $\text{CuO}_4$  plaquette planes (figure 1) [30]. New atomic hydrogen positions are given in table 1, which were obtained by GGA-optimization (see section 2) using various tentative positions as starting values to test the stability of the results. When only hydrogen atoms were allowed to relax, the forces on the oxygen atoms of water molecules (OW1 and OW2) turned out to be quite large, while one of the hydrogen atoms moved towards the  $\text{SO}_4$  group. Though, such a situation cannot fully be excluded and may arise for a certain temperature regime due to the spatial proximity of layers and  $\text{SO}_4$  groups it appears unlikely as explained before. In a further step, the positions of all H atoms together with those of OW1 and OW2 have been relaxed. This way, we could stabilize the anticipated langite structure by 2.6 eV/unit cell, while the  $\text{HSO}_4$  configuration became energetically highly unfavorable. A full relaxation of all atomic positions further confirms the stability of the  $\text{Cu}_4(\text{OH})_6\text{SO}_4 \cdot 2\text{H}_2\text{O}$  structure and shows no signatures of the  $\text{HSO}_4$  groups. For the two different water molecules, O–H bond lengths between 0.985–0.997 Å and H–O–H angles of 103.8° and 109.2°, respectively, have been obtained, i.e. there are no asymmetrical distortions as proposed in the previous structural work [52]. A plot showing the hydrogen bonds and the bonding between the  $\text{SO}_4$  groups, water molecules and Cu–O layers can be found in the supplementary material (see footnote 6). LDA band structures and density of states around the Fermi level computed for the different crystal structures, i.e. from [52] and our data collected at 100 K, are provided in the supplementary material (see footnote 6). LDA-calculations on the crystal structures with optimized hydrogen positions and optimized positions of oxygen in the water molecules (OW) are shown as well. Band shifts between 50 and 100 meV and considerable changes in the band dispersion are observed particularly between  $-0.6$  and  $-0.1$  eV. Since the LDA-bands around the Fermi level crucially determine the exchange interactions, these data demonstrate how crucial hydrogen positions and accurate crystal structures are for computing a microscopic magnetic model.

Table 1 summarizes atomic positions in langite, including the OW1 and OW2 positions determined both experimentally and by the GGA-optimization. The difference between the experimental and computational positions of water molecules may reflect temperature-induced structural changes, because DFT yields the crystal structure at zero temperature, whereas experimental structure determination has been performed down to 100 K, only. However, we did not observe any structural phase transitions below 100 K in the thermodynamic properties reported in section 4. It is also possible that the discrepancy between the experimental and computational positions of water molecules is intrinsic and related to marginal disorder, which is a plausible explanation, given the weak (hydrogen) bonding between the water molecules and the rest of the crystal structure. Vibration spectroscopy could provide further insight into the nature of hydrogen bonding and positions of water molecules in langite, but it lies beyond the scope of our study, which is focused on the magnetism of langite. Relevant magnetic interactions run within the Cu–O layers and should not depend on the exact positions of the out-of-plane water molecules. For the sake of consistency and given the fact that magnetic ordering in langite occurs well below 100 K, we used the relaxed positions of OW1 and OW2 in the further microscopic analysis (section 5).

The crystal structure of langite features four different Cu-positions. The basic building units are layers formed by planar chains of edge-sharing  $\text{CuO}_4$  plaquettes (type A chain) as well as buckled chains of corner-sharing  $\text{CuO}_4$  plaquettes (type B chains) (figure 1), where the chains are directly linked to each other. Sulphate groups and water molecules are located between the layers. The Cu–O–Cu bridging angles, which are of crucial importance for the exchange couplings between the Cu-sites, amount to 99.49°/99.11°, 98.64°/97.81° in the type-A chains. Between two edgesharing plaquettes in the type-A chains, the two bridging angles are different, i.e. the bridge is not symmetrical. Both angles are given separated by ‘/’. In the cornersharing type-B chains two different bridging angles of 101.05° and 104.71°, respectively, occur (see table 2). A figure showing Cu–O bonding distances and bridging angles of the two different chain types is provided in the supplementary material (see footnote 6). The bridging angles between the two chain types, A and B, are between 105° and 109°, i.e. the layers are strongly buckled (figure 1). According to Goodenough–Kanamori rules, one expects FM exchange for bridging angles close to 90° and AFM exchange for larger bridging angles. The crossover is at

**Table 2.** The transfer integrals  $t_{ij}$  (meV) and the AFM contributions to the exchange constants  $J_{ij}^{\text{AFM}} = 4t_{ij}^2/U_{\text{eff}}$  (K), where  $U_{\text{eff}} = 4.5$  eV.  $d(\text{Cu-Cu})$  and  $\text{Cu-O-Cu}$  denote Cu-Cu distances (Å) and Cu-O-Cu angles (deg), respectively. The  $J_{ij}$  (K) given in the last column are calculated with the LSDA+ $U$  method and  $U_d = 8.5 \pm 1$  eV and  $J_d = 1$  eV. The different groups of exchange couplings are sorted with respect to Cu-Cu distances. For a detailed explanation of the bridging angles see section 3 as well as the supplementary material (see footnote 6).

	$d(\text{Cu-Cu})$	$\text{Cu-O-Cu}$	$t_{ij}$	$J_{ij}^{\text{AFM}}$	$J_{ij}$
Type A chains (edge-sharing)					
$J'_1$	3.011	97.81/98.64	-144	213	$9 \pm 15$
$J_1$	3.020	99.10/99.49	-155	247	$38 \pm 20$
$J'_2$	6.030		61	39	$36 \pm 6$
$J_2$	6.030		59	36	$35 \pm 6$
Type B chains (corner-sharing)					
$J_s$	2.983	101.05	40	16	$-74 \pm 10$
$J'_s$	3.049	104.706	62	40	$-23 \pm 3$
$J_{s2}$	6.030		31	10	$< 1$
$J'_{s2}$	6.030		30	9	$< 1$
nearest-neighbor interchain couplings					
$J_a$	3.139	103.55	85	74	$-19 \pm 1$
$J_b$	3.144	105.08	-109	123	$5 \pm 5$
$J_c$	3.163	106.64	91	85	$-6 \pm 2$
$J_d$	3.168	105.23	109	121	$8 \pm 5$
$J_e$	3.186	106.65	-91	85	$0 \pm 4$
$J_f$	3.190	106.61	94	91	$-12 \pm 2$
$J_g$	3.219	106.10	-92	87	$-13 \pm 1$
$J_h$	3.229	109.23	-107	119	$31 \pm 7$
Next-nearest-neighbor interchain couplings					
$J_I$	6.309		-51	27	$10 \pm 10$
$J_{II}$	6.407		-61	38	$51 \pm 20$
interlayer coupling					
$J'$	7.874		-5	0.2	

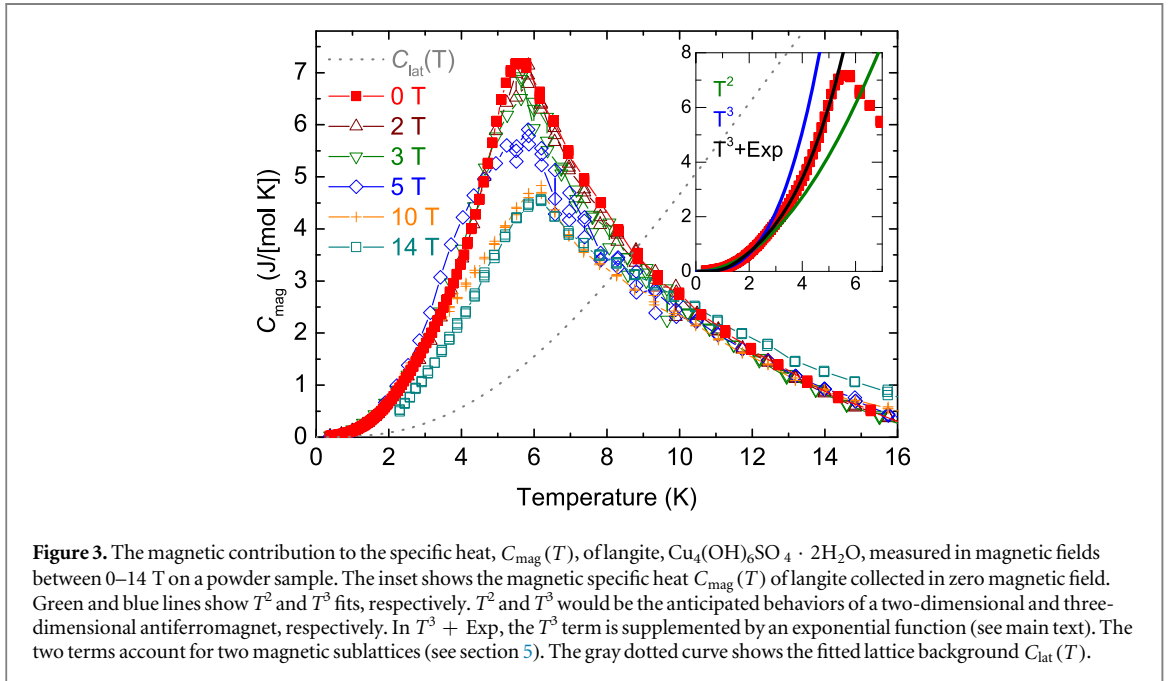
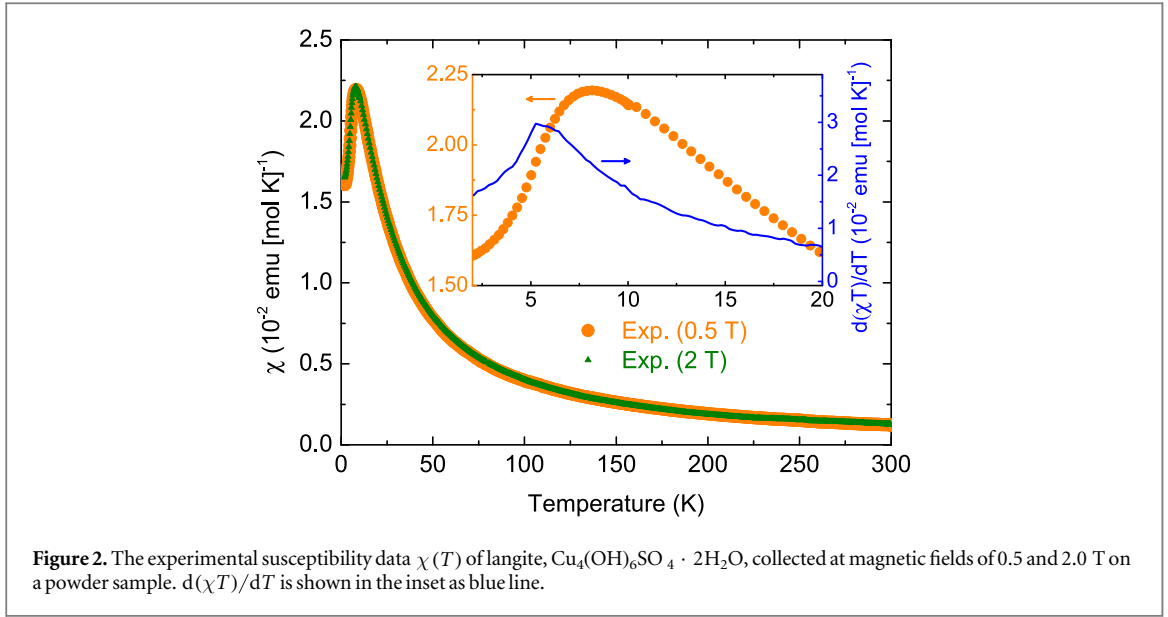
about  $95^\circ$ – $100^\circ$  [54, 56], and the exchange couplings in the edge-sharing chains of langite are difficult to guess in this transition region, even qualitatively (see section 5), while all other couplings would naively be assumed AFM. However, such simple considerations are bound to fail for langite as will be demonstrated in sections 5 and 6 below.

#### 4. Thermodynamic properties

All measurements presented in this section were performed on powder from the same specimen as the one used for the single-crystal XRD. The powder quality has been diligently checked by powder XRD, revealing langite as the only detectable phase (see footnote 6).

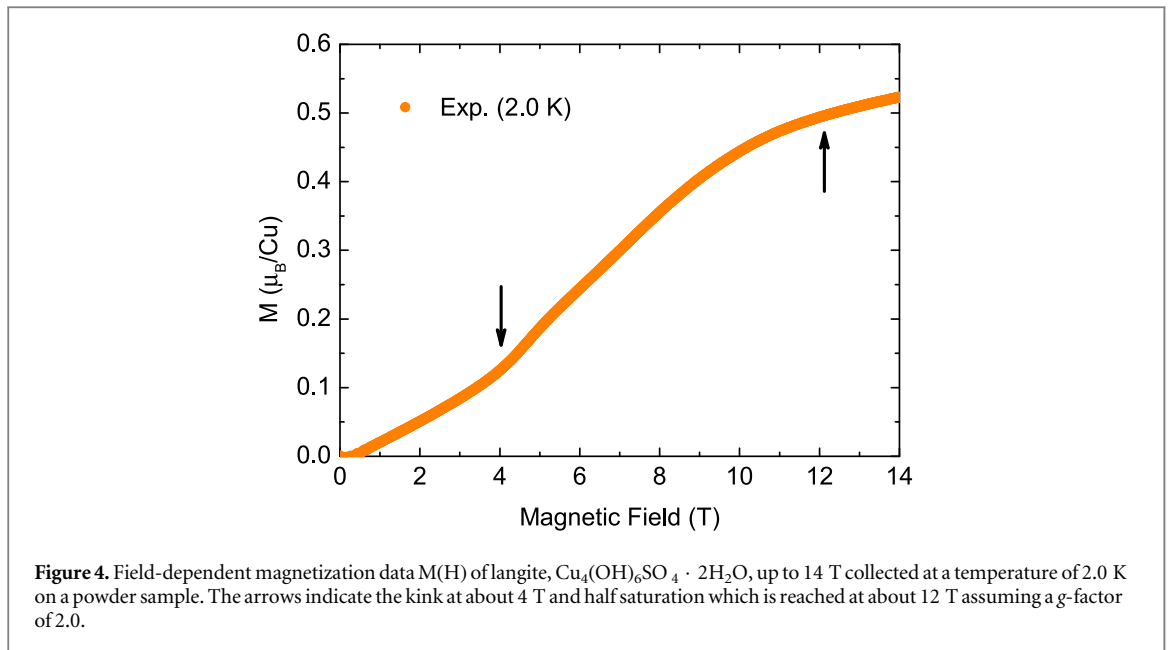
The temperature-dependent magnetic susceptibility  $\chi(T)$  measured in magnetic fields of 0.5 and 2 T is shown in figure 2, where the two curves are almost identical. A Curie-Weiss fit  $\chi(T) = C/(T + \theta)$  of the high-temperature regime (220–290 K) of the 2 T data yields  $\theta = 18.2$  K and  $C = 0.481$  emu K (mol Cu) $^{-1}$ . From the constant  $C$ , we obtain an effective magnetic moment of  $1.96 \mu_B/\text{Cu}$  which is larger than the spin only value of 1.73 and implies the  $g$ -factor of 2.26 lying still in the expected range for  $\text{Cu}^{2+}$  compounds [31, 39, 57]. The positive  $\theta$  indicates predominant AFM couplings, which are, however, quite weak. In the low-temperature regime,  $\chi(T)$  features a rather sharp peak at 7.5 K. This peak is somewhat asymmetric and thus different from the susceptibility maxima in conventional low-dimensional antiferromagnets, where short-range magnetic order is formed well above the Néel temperature  $T_N$  [58, 59]. While no indications of a magnetic transition are seen in the raw susceptibility data, Fisher's heat capacity  $d(\chi T)/dT$  reveals a kink around 5.5 K that can be paralleled to the anomaly in the specific heat and ascribed to the magnetic ordering transition. The absence of a Curie tail at the lowest  $T$ , typically arising from paramagnetic spin-1/2 impurities (see e.g. [31]), demonstrates the high quality of our natural sample.

The 5.7 K anomaly in the specific heat generally resembles a  $\lambda$ -type anomaly, which is expected at a second-order phase transition. The broadening of this anomaly may be driven by effects of magnetic anisotropy. The magnetic nature of the 5.7 K transition is corroborated by its field dependence. Despite the relatively low value of  $T_N$ , the transition is well visible up to at least 14 T, and the transition temperature changes only slightly in the



applied magnetic field. At higher temperatures, the lattice contribution to the specific heat dominates. Below the transition temperature  $T_N$ , the magnetic contribution  $C_{\text{mag}}(T)$  to the specific heat decreases. At low temperatures, one expects the power-law behavior, such as  $T^3$  in a conventional 3D AFM or  $T^2$  in a quasi-2D AFM with a very weak interlayer coupling  $J' \ll T_N$ . In our case, the  $T^3$  behavior could be obtained only at very low temperatures below 2 K (see figure 3). The tentative  $T^2$  fit extends to a slightly higher temperature of 2.5 K but the best description by far could be achieved by using a  $aT^3 + b(\Delta/T)^{3/2} \cdot e^{-\Delta/T}$  function where  $a$  and  $b$  are adjustable parameters. It combines the  $T^3$  term for a long-range-ordered antiferromagnet and the exponential term for a gapped antiferromagnet without long-range ordering. This model arises naturally from our microscopic analysis, where two distinct magnetic sublattices are proposed.  $\Delta$  is the size of the spin gap and is evaluated to 3.5–6.5 K depending on the  $T$ -range used for the fit.

The magnetic contribution  $C_{\text{mag}}$  was obtained by subtracting the lattice contribution  $C_{\text{lat}}$  from the measured  $C_p$  data, where  $C_{\text{lat}}(T)$  was approximated by fitting a polynomial (see footnote 6)  $C_{\text{lat}}(T) = \sum_{n=3}^{n=7} c_n T^n$ , proposed by Johnston *et al* [60], to the  $C_p(T)$  data in the temperature range of 20–39 K. The same polynomial was used to extract the magnetic contributions from specific heat data measured in the various magnetic fields. In zero magnetic field, the magnetic entropy  $S_{\text{mag}}$ , released within the magnetic transition, was estimated to



about 6.8 J/(mol K) by integrating  $C_{\text{mag}}/T$ . Thus, only about 30% of the expected  $S_{\text{mag}} = 4R \ln 2$  for a spin-1/2 system is released within the transition anomaly and right above  $T_N$ , while the rest is spread towards higher temperatures, which is typical for low-dimensional antiferromagnets [59] and corroborates that  $T_N$  is much lower than the energy scale of the exchange couplings given by, e.g.,  $\theta \simeq 18$  K. A similar value for  $S_{\text{mag}}$  has been reported for the related mineral brochantite (see also section 6) releasing 7.9 J/(mol K), which is about 34% of the total magnetic entropy, in the vicinity of the magnetic transition [39].

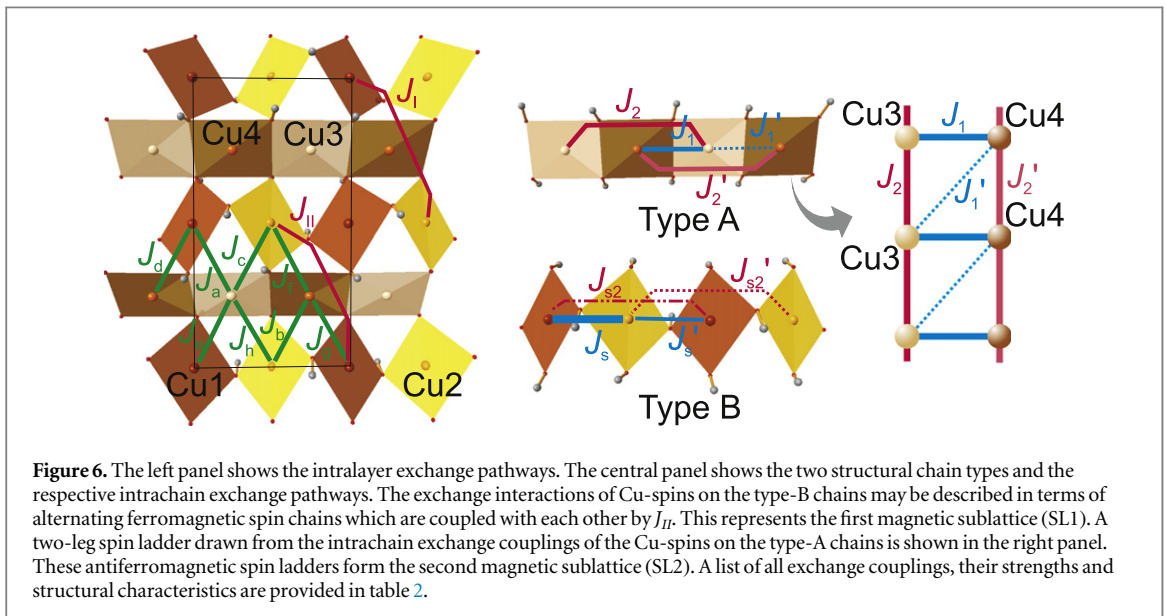
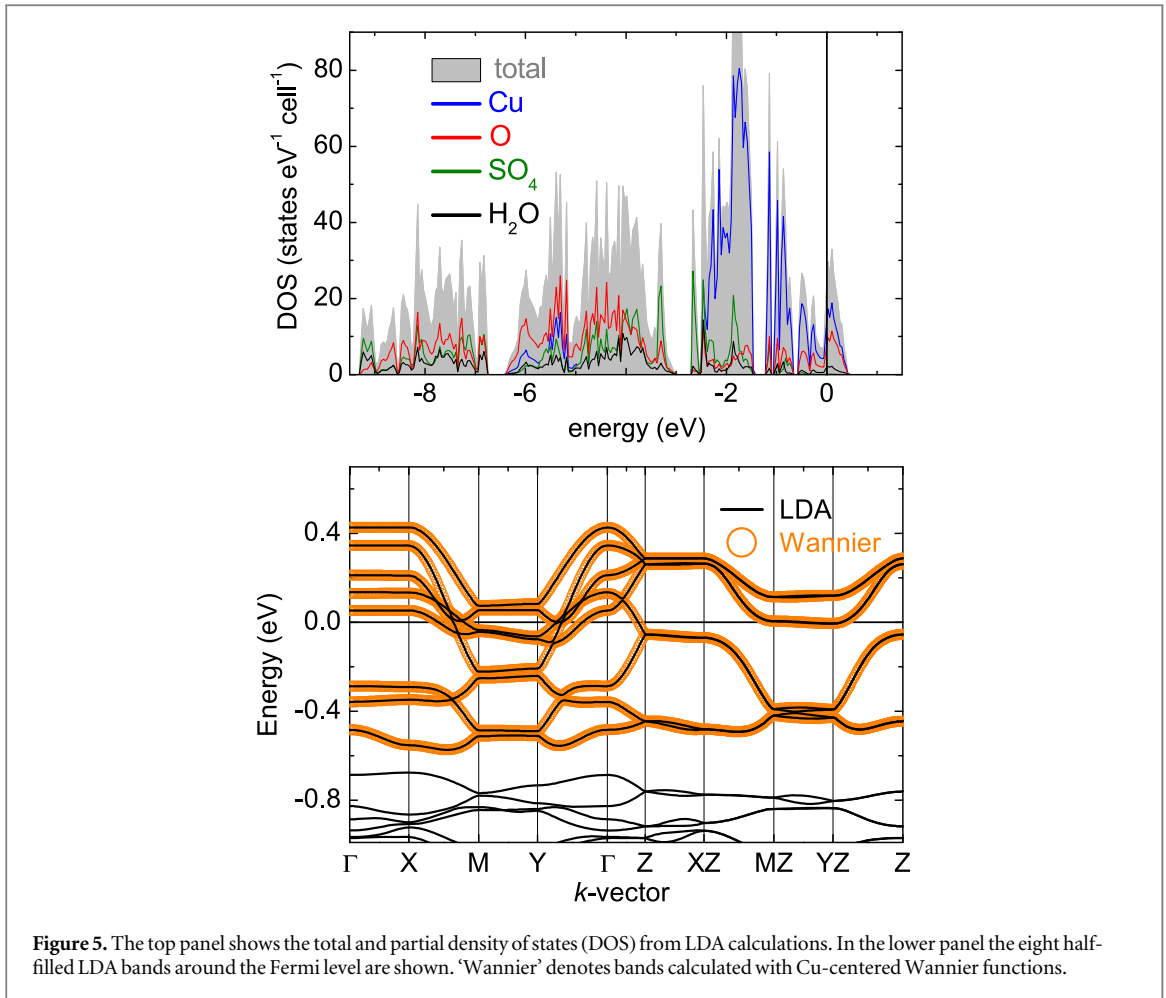
Field-dependent magnetization  $M(H)$  (figure 4) measured in fields up to 14 T features a kink around 4 T, reaches half-saturation around 12 T, and keeps increasing up to at least 14 T. The kink at 4 T is reminiscent of a spin-flop transition that, however, happens at a much higher field than in other  $\text{Cu}^{2+}$  oxides (e.g. [61]). Above 2 K, the features of the magnetization curve are smeared out, so we were not able to map them as a function of temperature and construct a comprehensive  $T$ – $H$  phase diagram.

## 5. Electronic structure and magnetic exchange couplings

In this section, we derive a microscopic magnetic model that could be used to understand the complex behavior of langite. Microscopic models based on empirical considerations are prone to error because superexchange in  $\text{Cu}^{2+}$  compounds depends on tiny structural details and cannot be fully captured by empirical rules. Moreover, the presence of four distinct Cu sites in the crystal structure implies that interactions with similar Cu–Cu distances and superexchange pathways are not related by symmetry and may be unequal. Therefore, an empirical approach for deriving a microscopic magnetic model is bound to fail for langite. Accordingly, we employ numerical electronic structure DFT calculations allowing for a direct computation of individual exchange couplings  $J_{ij}$ . In combination with numerical simulations of the thermodynamical properties, such calculations often provided consistent description of the macroscopic magnetic behavior based on microscopic considerations [13, 29, 33, 62].

With suitably chosen correlation parameters, such as the Coulomb repulsion  $U_d$  in LSDA+ $U$ , one expects that DFT results are accurate within 10% for most insulating spin-1/2 materials and the respective interaction pathways. However, the error bars increase for very weak couplings and for those couplings, where special nature of the superexchange pathway renders ferro- and antiferromagnetic contributions comparable in size. Further information on the computational procedure and the accuracy of computed exchange couplings can be found in [13, 32, 63–66].

As a first step, LDA calculations were performed, yielding a broad valence band complex of about 10 eV (figure 5), which is typical for cuprates [30, 31, 53]. Low-energy magnetic excitations should be largely determined by the band complex of eight half-filled bands around the Fermi level, between  $-0.5$  and  $0.45$  eV. The eight bands arise from the eight  $\text{Cu}^{2+}$ -ions per unit cell and their corresponding eight half-filled 3d-orbitals. Local coordinate systems on the eight Cu-sites (with the local  $z$ -axis chosen perpendicular to the  $\text{CuO}_4$ -planes and the local  $x$ -axis oriented parallel to a Cu–O bond) allow analyzing the orbital character of the half-filled bands. They are essentially of  $\text{Cu}(3d_{x^2-y^2})$  and  $\text{O}(2p_x, 2p_y)$  character while admixtures from  $\text{H}_2\text{O}$  and



particularly  $\text{SO}_4$  groups are small. Accordingly, the latter molecules do not play a direct role for the exchange couplings in langite. This set of eight bands is now projected onto Cu-centered WFs to evaluate the hopping parameters  $t_{ij}$ . Owing to the four different Cu-sites, many different exchange pathways are effective in langite. Table 2 lists all  $|t_{ij}| > 20$  meV as well as the corresponding  $J_{ij}^{\text{AFM}}$ . The largest interlayer hopping  $t'$  is only

about  $-5$  meV rendering the spin lattice of langite nearly 2D. The positions of the respective exchange pathways in the crystal structure are shown in figure 6.

Full exchange constants  $J_{ij} = J_{ij}^{\text{FM}} + J_{ij}^{\text{AFM}}$  computed with the LSDA+ $U$  method are provided in the last column of table 2, where error bars show the effect of changing the Coulomb repulsion parameter  $U_d$  by  $\pm 1$  eV. This parameter affects absolute values of exchange couplings, while their ratios typically change by few percent only. However, for weak couplings error bars can exceed absolute values, and thus the ratios are strongly affected as well.

The two nearest-neighbor (NN) couplings of the Cu-spins on the type-B chains,  $J_s$  and  $J'_s$ , are both FM, with the absolute value of  $J'_s$  being much smaller than that of  $J_s$ . This results in FM spin chains with alternating exchange couplings. These spin chains interact antiferromagnetically via  $J_{II}$  and represent the first magnetic sublattice (SL1). The difference between  $J_s$  and  $J'_s$  can be traced back to the relevant Cu–O–Cu angles (table 2). The smaller angle for  $J_s$  leads to a stronger FM interaction (see also section 6).

The NN coupling  $J_1$  of the Cu-spins on the edge-sharing type-A chains is AFM and about four times stronger than the weak coupling  $J'_1$ . The AFM NNN couplings  $J_2$  and  $J'_2$  are of the same strength as  $J_1$ . The exchange interactions of the spins on the type-A chains may, thus, be described in terms of magnetic two-leg ladders (figure 6), where  $J_2$  and  $J'_2$  build the legs, while  $J_1$  forms the rungs, and  $J'_1$  is a frustrating diagonal interaction. This represents the second magnetic sublattice (SL2). The strengths of  $J_1$  and  $J'_1$  can be again traced back to the Cu–O–Cu angles. The smaller bridging angles render  $J'_1$  weaker than  $J_1$ . However, these AFM couplings are observed for the bridging angles below  $100^\circ$ , while the FM couplings  $J_s$  and  $J'_s$  occur for the bridging angles above  $100^\circ$ . This instructive situation highlights limitations of the Goodenough–Kanamori–Anderson rules and the importance of the mutual arrangement of the  $\text{CuO}_4$  plaquettes, which share edges ( $J_1$  and  $J'_1$ ) or corners ( $J_s$  and  $J'_s$ ), respectively.

Multiple couplings between the two sublattices are mostly weak. The strongest inter-sublattice interaction  $J_h$  is comparable in size to  $J_1$ ,  $J_2$ , and  $J'_2$ . However, it is less abundant than the intra-sublattice couplings, and on average one finds that only half of  $J_h$  contributes to the effective molecular field on the SL2. Therefore, in a first approximation one can consider langite as antiferromagnet built of two sublattices, where the sublattice SL2 is 1D, the sublattice SL1 is 2D, and the inter-sublattice couplings are weaker than the leading couplings within each of the sublattices. The interlayer coupling  $J'$ , which is about 0.2 K, may be responsible for the long-range magnetic order observed in langite because 3D order requires the coupling between the layers (figure 3). We refrained from estimating  $J'$  using LSDA+ $U$ , though, because such small couplings are hard to calculate reliably [53].

The exchange couplings given in table 2 allow estimating a ‘local Curie–Weiss temperature’  $\theta_k$  for each Cu-site  $i$  according to  $\theta_k = S(S + 1)/3 \cdot \sum_i (z_i \cdot J_i)$ , where  $S$  is the electron spin and  $z_i$  shows how often a certain coupling  $J_i$  occurs on a given site.  $\theta_k$  is thereby a measure for the local coupling strengths on the Cu-site  $k$ . Accordingly, we get for the four Cu-sites (figure 6):  $\theta_1 = -15$  K,  $\theta_2 = -3$  K,  $\theta_3 = 31$  K,  $\theta_4 = 27$  K. The overall Curie–Weiss temperature may be approximated by averaging over all sites yielding  $\theta = 10$  K which is in reasonable agreement with the experimental value of 18.2 K (see section 4) regarding the intricate microscopic magnetic model and the large number of exchange couplings. The striking difference between  $\theta_1$  and  $\theta_2$  arises from the nearest-neighbor interchain couplings, where the FM  $J_a$  operates on Cu-site 1 and the AFM  $J_h$  is effective on Cu-site 2. It is worth noting that the single experimental parameter  $\theta$  is usually sufficient for verifying the choice of  $U_d$  in LSDA+ $U$ , because the uncertainty in absolute values of the computed exchange couplings is much higher than in their ratios, and thus only the absolute scale of computed exchange couplings should be cross-checked experimentally. On the other hand, experimental evaluation of individual exchange couplings in langite may be an arduous task, given the overall complexity of the spin lattice. In section 6, we further discuss ramifications of our microscopic magnetic model and its relevant macroscopic features that can be tracked experimentally.

We also performed calculations using a HSE06 hybrid DFT-functional [48, 49], as implemented in VASP 5.2 [50, 51]. These calculations were feasible for short-range couplings only. The long-range couplings would require big supercells that cannot be treated with the computationally expensive HSE06 method with the required accuracy.

In contrast to LSDA+ $U$ , the hybrid-functional approach does not include the effect of local Coulomb repulsion explicitly, thus leading to less accurate estimates of individual exchange couplings and the overestimate of FM terms [53]. On the other hand, this method is free from adjustable parameters and does not involve the ambiguous choice of the Coulomb repulsion  $U_d$ . The HSE06 results can be found in the supplementary material (see footnote 6). They are generally similar to those from LSDA+ $U$  (table 2) and confirm main features of the langite spin lattice: (i) the FM nature of  $J_s$  and  $J'_s$ ; (ii) the AFM nature of  $J_1$  and  $J'_1$ , and (iii) the  $|J_s| > |J'_s|$  and  $J'_1 < J_1$  trends discussed above. The inter-sublattice couplings are mostly FM in HSE06 because of the general tendency of hybrid functionals to overestimate FM contributions to the exchange.

In order to reduce the complexity of the spin lattice in langite, we neglect  $J'_1$  in our discussion. Owing to the sizable error bars in the evaluation of this coupling, it still might be significant. However, it always remains considerably smaller than all other couplings in the type-A chains. This way, we arrive at two magnetic sublattices for langite where each one, taken for itself, is non-frustrated because none of the leading couplings  $J_s$ ,  $J'_s$ , and  $J_{II}$  for the type-A chains and  $J_1$ ,  $J_2$ , and  $J'_2$  for the type-B chains compete with each other. The two leading couplings between the sublattices, FM  $J_a$  and AFM  $J_b$ , are not frustrated either, because they are compatible with the AFM order between the FM type-B chains, as imposed by  $J_{II}$ . However, other inter-sublattice couplings frustrate the spin lattice and render it very complex. Given the large number of non-equivalent exchange couplings and their frustrated nature, we restrict ourselves to a qualitative discussion of the magnetic behavior in section 6 below.

## 6. Discussion

Magnetic properties of the natural  $\text{Cu}^{2+}$ -mineral langite are peculiar, yet complicated. Its crystal structure consists of layers formed by directly connected and alternating ordered edge- and corner-sharing chains of  $\text{CuO}_4$  plaquettes. Such structural motives can be found in several compounds (see section 3) that have same topology of the magnetic layer, but slightly different Cu–O–Cu angles and, thus, potentially different exchange scenarios. Magnetic properties of only one of these materials, brochantite, have been reported. Therefore, it is still an open question which magnetic properties arise when edge- and corner-sharing  $\text{Cu}^{2+}$  chains are joined into layers, and how these properties are affected by structural details.

Our study shows that such layers cannot be viewed as a simple combination of weakly coupled magnetic chains. Unanticipated interchain couplings, such as  $J_{II}$  that features an unusually long superexchange pathway, render the spin lattice much more complex. Remarkably, though, we can still split this lattice into two sublattices composed of type-A and type-B chains, respectively. The difference between these sublattices and individual chains pertains to the fact that all type-B chains form a single 2D sublattice SL1, whereas sublattice SL2 comprises weakly coupled type-A chains and thus remains effectively 1D. We should also emphasize that the inter-sublattice couplings are clearly non-negligible. A quantitative description of langite will, therefore, require the consideration of the full spin lattice that is partially frustrated. This problem must be tackled with advanced simulation techniques and lies beyond the scope of our present study, where we restrict ourselves to the qualitative analysis and demonstrate that the model of two different sublattices can be used to rationalize main features of the experimental data.

First, the abrupt increase of the magnetization in low fields and the fact that half-saturation is reached already at 10–12 T is consistent with the presence of sublattice SL1, which is largely FM. This sublattice should saturate as soon as the magnetic field overcomes the effect of the AFM coupling  $J_{II}$ . There is only one  $J_{II}$  coupling per Cu site, so the half-saturation should be reached at  $H_{s1} = k_B J_{II} / (g\mu_B) \simeq 38$  T, which is much higher than 12 T observed experimentally. The origin of this discrepancy is not entirely clear. The presence of the second magnetic sublattice SL2 (comprising the spins on the type-A chains) and the frustrated interactions between the sublattices may overcome the effect of  $J_{II}$  and facilitate the saturation of the SL1 (consisting of spins on the type-B chain) already in low field, although a detailed investigation of this behavior requires numerical simulations for the full spin lattice of langite. The SL2 is AFM and its saturation is expected at  $H_{s2} = k_B / (g\mu_B) (J_1 + J_2 + J'_2) \simeq 81$  T which would be interesting to probe experimentally. We thus expect that above 14 T the magnetization of langite increases much slower than in low fields, and that full saturation is reached around 80 T reflecting the presence of sizable AFM couplings in this system.

Magnetic susceptibility of langite lacks a broad maximum that would be expected in a quasi-2D antiferromagnet. This observation is also consistent with the presence of the mostly FM sublattice SL1 (figure 6) which lacks any susceptibility maximum down to  $T_N$  and, thus, masks the susceptibility maximum related to the AFM sublattice SL2. A similar behavior has been observed in  $\text{CuP}_2\text{O}_6$  [29], where none of the sublattices is FM, but very weak couplings in one of the sublattices render half of the spins paramagnetic down to low temperatures, and no susceptibility maximum is observed down to  $T_N$ . It is worth noting that the asymmetric maximum in the susceptibility of langite around 8 K cannot be taken as a typical signature of short-range order in a quasi-2D system, because about half of the magnetic entropy is released above 8 K. Moreover, this maximum is observed at temperatures well below the Curie–Weiss temperature  $\theta \simeq 18$  K, whereas in a 2D system, e.g., in a square-lattice antiferromagnet,  $T^{\text{max}} \simeq \theta$  is expected.

The temperature of the AFM ordering in langite,  $T_N \simeq 5.7$  K, is quite low compared to leading exchange couplings  $|J_s|$ ,  $J_1$ ,  $J_{II}$ ,  $J_2$ , and  $J'_2$  that are at least 35–40 K each. We tentatively find  $T_N/J < 0.2$ , which is very low for a quasi-2D antiferromagnet [67]. A frustration ratio of  $\theta/T_N \simeq 3$  is less impressive, but one has to acknowledge that the macroscopic  $\theta$  is a sum of FM and AFM couplings (table 2) and thus underestimates the overall energy scale of exchange couplings in langite.

The magnetic ground state of langite may be peculiar. In sublattice SL1, one expects FM order along  $b$  and AFM order along  $a$  and  $c$ , arising from the interchain interaction  $J_{II}$  and the weak interlayer coupling  $J'$ . The sublattice SL2 is a two-leg spin ladder and, when taken on its own, features a spin-singlet ground state without long-range magnetic order. Although interchain couplings and the couplings to SL1 will trigger the formation of ordered moments even in SL2, these moments are expected to be much smaller than in SL1. This difference in the ordered magnetic moments is one of the fingerprints of the two-sublattice model and can be probed experimentally by nuclear magnetic resonance or neutron scattering.

The drastic difference between the ordered magnetic moments on different Cu-sites has been previously seen in other  $\text{Cu}^{2+}$  minerals. In antlerite  $\text{Cu}_3(\text{OH})_4\text{SO}_4$  [34, 68], two side chains of the B-type encompass the central chain of the A-type that together form a ribbon, which is sometimes considered as a three-leg spin ladder. Neutron scattering revealed ordered magnetic moment of  $0.88 \mu_B$  on the terminal (type-B) chains and zero magnetic moment on the central (type-A) chains [34]. A similar type of magnetic order is expected in langite, where spins in the type-B chains will form long-range magnetic order, whereas spins in the type-A chains should develop a gapped ground state with zero ordered moment, as typical for two-leg spin ladders. This unusual, partial magnetic order may be reflected in magnetic excitations and macroscopic properties such as specific heat below  $T_N$ . In section 4 we indeed demonstrated that the specific heat below  $T_N$  clearly deviates from the standard  $T^2$  or  $T^3$  behaviors. However, it could be well fitted with a function accounting for an ordered sublattice following a  $T^3$  law and a spin ladder in the gapped state which supports our scenario of two magnetic sublattices in langite. The respective size of the spin gap is 3.5–6.5 K. Regarding to the very similar energy scales, one might expect that the kink at 4 T in the field dependent magnetization arises from a closing of this spin gap.

Another  $\text{Cu}^{2+}$  mineral, brochantite  $\text{Cu}_4(\text{OH})_6\text{SO}_4$ , is remarkably different from both langite and antlerite. From the chemistry perspective, it is a dehydrated version of langite featuring same type of magnetic layers. However, details of their geometry are somewhat different because water molecules are missing, and the separation between the layers is about twice shorter than in langite. Neutron diffraction reports very small magnetic moments within the corner-sharing type-B chains ( $0.22 \mu_B$ ) and much larger ordered moments within the type-A chains ( $0.74 \mu_B$ ) [39]. This is very different from the ground state of antlerite (and, presumably, of langite) and may indicate a different exchange topology. Indeed, the Curie–Weiss temperature of brochantite ( $\theta \simeq 90$  K) [39] is much higher than 18 and 4 K in langite and antlerite [69], respectively. Moreover, brochantite features a broad susceptibility maximum around 60 K, far above  $T_N$ , while neither langite nor antlerite show such broad maxima. These features suggest that magnetic interactions in brochantite are predominantly AFM, whereas langite and antlerite reveal a subtle interplay of FM and AFM exchange couplings. Further microscopic insight into these differences is clearly needed and requires a systematic computational study of the aforementioned  $\text{Cu}^{2+}$  minerals.

Naively, the AFM nature of brochantite can be ascribed to the larger Cu–O–Cu angles in the range  $105.6^\circ$ – $122.5^\circ$ , while the Cu–O–Cu angles in langite are, generally, smaller ( $103.5^\circ$ – $109.2^\circ$ ). However, this simple analysis in the spirit of Goodenough–Kanamori–Anderson rules may often be misleading.

We have mentioned that the values of the Cu–O–Cu bridging angles account for  $|J_s| > |J'_s|$  and  $J_1 > J'_1$ , but they do not explain why  $J_s$  and  $J'_s$  are FM, while  $J_1$  and  $J'_1$  with the smaller bridging angles are AFM. Other effects are obviously important in this case. In particular, hydrogen atoms bonding to the bridging oxygen have strong influence on the superexchange [30]. Hydrogen atoms located out of the  $\text{CuO}_4$  planes, favor FM exchange. This is definitely relevant for  $J_s$  and  $J'_s$  in langite where the O–H bond on the bridging oxygen and the  $\text{CuO}_4$  plaquettes enclose angles up to  $60^\circ$ . For the Cu-mineral clinoclase,  $\text{Cu}_3(\text{AsO}_4)(\text{OH})_3$  it was recently demonstrated [30] that such a large out-of-plane angle can drive the exchange coupling even from a strongly AFM to the FM coupling regime. Quite similar results for the intrachain physics of the type-B chains have been reported in recent studies on antlerite,  $\text{Cu}_3(\text{OH})_4\text{SO}_4$  [34, 68]. The crystal structure of this compound features triple chains consisting of a central type-A chain and type-B chains bonded to it on each side. For the Cu-spins on the type-B chains an alternating FM coupling has been reported from neutron experiments with an antiparallel order between the chains [34, 68]. For brochantite,  $\text{Cu}_4(\text{OH})_6\text{SO}_4$ , featuring structural layers similar to those in langite, neutron data also revealed a FM coupling of the Cu-spins within the type-B chains [39]. Eventually, in a joint experimental and theoretical study [35] on the rare Cu-mineral szenicsite,  $\text{Cu}_3\text{MoO}_4(\text{OH})_4$ , an alternating FM coupling on the type-B chains has been reported. This compound features triple chains similar to those in antlerite.

## 7. Summary

In summary, structural and magnetic properties of the  $\text{Cu}^{2+}$  mineral langite have been investigated in a joint experimental and theoretical study. Crystal structure of langite was refined in the 100–280 K temperature range using single-crystal XRD, and the H-positions were subsequently determined for the 100 K structure using

theoretical DFT-approach. The crystal structure consists of two types of directly connected Cu-chains, edge- and corner-sharing, which form layers separated from each other by about 7.5 Å. These layers are a common structural motive in cuprate minerals, but their relevant magnetic interactions and resulting magnetic properties have been only scarcely investigated. Along with the fact that both chain-types taken on their own have revealed fascinating magnetic properties, it intrigued us what kind of physics may arise from their combination into layers.

Our density-functional calculations show that such layers can not be viewed as a stack of weakly coupled magnetic chains. While different chains form different magnetic sublattices, interactions between the chains are non-negligible, and even the two-sublattice model describes the magnetic behavior only qualitatively. It does, however, capture the crucial feature that the sublattice SL1 is predominantly FM and prone to the formation of the long-range order, whereas the sublattice SL2 is entirely AFM and gapped because of its two-leg-ladder geometry. Therefore, we expect a peculiar magnetic ground state with drastically different ordered moments in the two sublattices. This ground state can be paralleled to that of antlerite, where the ‘idle-spin’ behavior (no detectable ordered moment) on type-A chains has been observed.

Experimentally, langite undergoes long-range magnetic ordering, but at the Néel temperature  $T_N \simeq 5.7$  K that is well below the Curie–Weiss temperature  $\theta \simeq 18$  K. An effective ‘frustration ratio’  $\theta/T_N \simeq 3$  demonstrates that the magnetic order in langite is impeded. However, the Curie–Weiss temperature is a sum of FM and AFM couplings and thus underestimates the energy scale of magnetic exchange. Taking computed  $J$ 's from table 2, one finds that the Néel temperature of langite is remarkably low for a quasi-2D antiferromagnet. This reduced value of  $T_N$  is a signature of strong quantum fluctuations that have three concurrent origins: (i) spin-1/2 nature of  $\text{Cu}^{2+}$  and magnetic low-dimensionality; (ii) in-plane frustration; (iii) proximity of sublattice A to the spin-singlet state without long-range magnetic order.

Altogether, langite is a frustrated quasi-2D antiferromagnet where frustration arises from the coupling between the two different magnetic sublattices. The Neel temperature  $T_N \approx 6$  K is well below the Curie–Weiss temperature  $\theta \approx 18$  K and well below the individual intralayer exchange couplings. Moreover, only about 30% of the magnetic entropy is released below  $T_N$ , thus, indicating the suppression of the long-range magnetic order in langite. Low-dimensionality and suppressed long-range ordering together, render langite an interesting quantum magnet, featuring a peculiar two-sublattice structure of the spin lattice. Its ground state is of particular interest for future studies, given the anticipated difference between the ordering processes in two magnetic sublattices. Specific heat of langite measured in the ordered state does not follow conventional  $T^2$  or  $T^3$  behavior, thus providing first evidence for the unconventional nature of the magnetic ground state and calling for further investigation of this interesting material.

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