Experimental report

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Proposal: **5-41-1083** **Council:** 4/2020

Title: The magnetic structure of the S = 1/2 distorted kagome system clinoatacamite, $Cu_2Cl(OH)_3$

Research area: Physics

This proposal is a new proposal

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Samples: Clinoatacamite / $Cu_2Cl(OH)_3$

Instrument	Requested days	Allocated days	From	To
D10	7	5	09/03/2021	14/03/2021

Abstract:

The natural mineral clinoatacamite, $Cu_2Cl(OH)_3$, has been discussed in the literature as a frustrated quantum spin system. Electronic structure calculations have shown that its monoclinic crystal structure can be read as antiferromagnetic kagome layers, which are coupled ferromagnetically. Studies on clinoatacamite polycrystals have shown that this material undergoes magnetic transitions at 18.1 and 6.4 K. A previous neutron diffraction study on deuterated clinoatacamite powder had revealed magnetic reflections with a propagation vector q = (0, 0, 0).

In the past, however, the determination of the magnetic structure of clinoatacamite had led to some difficulties due to the weakness of the Cu magnetic moments and the incoherent scattering from the hydrogen. A magnetic structure was proposed in the literature but without determining the magnetic moment values. Here, a high number of magnetic reflections is required in order to determine precisely the magnitudes of the individual magnetic moments, as there are three Wyckoff positions in clinoatacamite. We therefore propose to carry out a neutron diffraction study using the instrument D10 with three-axis energy analysis.

Experimental report

Title of the experiment: The magnetic structure of the $S = 1/2$ distorted kagome system clinoatacamite, $Cu_2Cl(OH)_3$ (09/03/2021 – 14/03/2021)
Proposal No.: 5-41-1083
Experimental team (online): Leonie Heinze (TU Braunschweig, Germany), Manfred Reehuis (Helmholtz-Zentrum Berlin, Germany)
Instrument: D10
Local contacts: Bachir Ouladdiaf, Ketty Beauvois

Summary

We have carried out a neutron diffraction experiment on the natural mineral clinoatacamite using the four-circle diffractometer D10. Clinoatacamite, $Cu_2Cl(OH)_3$ [1,2], has been studied intensively within the field of frustrated quantum magnets in the past [3–9]. Its magnetic coupling scheme has either been discussed as corner-sharing tetrahedra of Cu ions or as a distorted kagome system. Studies on polycrystals have shown that this material undergoes magnetic transitions at $T_N = 18.1$ K and ~ 6.4 K [3,4]. In a neutron diffraction study on deuterated clinoatacamite powder, magnetic reflections with a propagation vector $\mathbf{q} = \mathbf{0}$ were observed below 6.5 K [6]. No magnetic reflections were observed above this temperature. A zero-field μSR study revealed a complex temperature evolution of the magnetic state below [4], which, in combination with the neutron diffraction measurements, left an incomplete picture of clinoatacamite. Recently, bandstructure calculations were carried out for clinoatacamite [10]. By means of DFT and GGA+U it was shown that its magnetic coupling scheme can be understood as anisotropic antiferromagnetic kagome layers with weak ferromagnetic coupling to the interlayer Cu sites. From this starting point, we have investigated the magnetic properties of single-crystalline clinoatacamite. We have carried out thermodynamic measurements revealing that the lower magnetic phase transition is in fact a double transition at 6.2 K / 6.4 K in zero field and that the temperature region between 6.2 K and 18 K hosts a complex in-field behavior with various magnetic phases/regimes.
During the present single-crystal neutron diffraction experiment at D10, we have measured a data set of magnetic reflections at 2 K in order to determine the magnetic structure of clinoatacamite below 6.2 K. Further, we have studied the temperature dependence of selected magnetic reflections.

Experimental procedure and results

The single-crystal neutron diffraction experiments were carried out at the instrument D10 which uses a PG monochromator selecting the neutron wavelength $\lambda = 2.36$ Å. For the experiments, the instrument was equipped with a closed-cycle ^{4}He cryostat. In order to determine the magnitude of the magnetic moments the overall scale factor has been determined from a data set collected in the paramagnetic range at 30 K (109 reflections, 43 unique). The positional and thermal parameters were taken from the refinements of the data set collected at room temperature in a previous experiment at the instrument E5 of HZB and were not allowed to vary.
For the determination of the magnetic structure of clinoatacamite we have used the representation analysis applied earlier by Bertaut [11]. In the present study, the basis vectors of the irreducible representations (*irreps*) were generated for the Cu atoms with the program *BasIreps* implemented in the *FullProf* suite [12] using the propagation vector $\mathbf{q} = (0, 0, 0)$ and the space group $P\,2_1/n$ (No. 14, standard $P\,2_1/c$). The unit cell contains three magnetic Cu atoms [labeled as Cu(1), Cu(2) and Cu(3)] located at the following Wyckoff positions: $2d$ (Cu(1)) [Cu(11) $(1/2, 0, 0)$, Cu(12) $(0, 1/2, 1/2)$], $2a$ (Cu(2)) [Cu(21) $(0, 0, 0)$, Cu(22) $(1/2, 1/2, 1/2)$] and $4e$ (Cu(3)) [Cu(31) (x, y, z), Cu(32) $(-x + 1/2, y + 1/2, -z + 1/2)$, Cu(33) $(-x, -y, -z)$, Cu(34) $(x + 1/2, -y + 1/2, z + 1/2)$].
In Table 1, the vectors $\mathbf{S}_k(j)$ (the Fourier components of the magnetic moments) of the different *irreps* are listed. It can be seen that Cu(1) and Cu(2) have the same site symmetry $\overline{1}$, where one obtains for both atoms the same *irreps* Γ_1 and Γ_3. Here, the spin sequences are either $+\,-$ along x, $+\,+$ along y, $+\,-$ along z (Γ_1) or $+\,+$ along x, $+\,-$ along y, $+\,+$ along z (Γ_3). Further, it can be assumed the moment values of both atoms are the same and they form one sublattice [Cu(11) (1/2, 0, 0), Cu(12) (0, 1/2, 1/2), Cu(21) (0, 0, 0), Cu(22) (1/2, 1/2, 1/2)].
The magnetic intensities were generated for all possible spin sequences. From the first four magnetic reflections the strongest magnetic intensities are observed for reflections $(0\,0\,1)_M$, $(0\,1\,0)_M$ and $(1\,1\,\overline{1})_M$. At these positions magnetic intensity is generated if the spin sequences are: $+\;-\;+\;-$ along x and z [$\Gamma_1(2d, 2a)$] and $+\;-\;+\;-$ along y [$\Gamma_3(2d, 2a)$]. Accordingly, magnetic intensity is generated for Cu(3)

irrep	$\mathbf{S}_k(1)$	$\mathbf{S}_k(2)$		
$\Gamma_1(2d)$	(u, v, w)	$(-u, v, -w)$		
$\Gamma_3(2d)$	(u, v, w)	$(u, -v, w)$		
irrep	$\mathbf{S}_k(1)$	$\mathbf{S}_k(2)$		
$\Gamma_1(2a)$	(u, v, w)	$(-u, v, -w)$		
$\Gamma_3(2a)$	(u, v, w)	$(u, -v, w)$		
irrep	$\mathbf{S}_k(1)$	$\mathbf{S}_k(2)$	$\mathbf{S}_k(3)$	$\mathbf{S}_k(4)$
$\Gamma_1(4e)$	(u, v, w)	$(-u, v, -w)$	(u, v, w)	$(-u, v, -w)$
$\Gamma_2(4e)$	(u, v, w)	$(-u, v, -w)$	$(-u, -v, -w)$	$(u, -v, w)$
$\Gamma_3(4e)$	(u, v, w)	$(u, -v, w)$	(u, v, w)	$(u, -v, w)$
$\Gamma_4(4e)$	(u, v, w)	$(u, -v, w)$	$(-u, -v, -w)$	$(-u, v, -w)$

Table 1: General expressions of the Fourier coefficients $\mathbf{S}_k(j)$ obtained from the basis functions calculated from the different representations of the three Cu sites at the Wyckoff positions $2d$ (Cu(1)) [Cu(11) $(1/2, 0, 0)$, Cu(12) $(0, 1/2, 1/2)$], $2a$ (Cu(2)) [Cu(21) $(0, 0, 0)$, Cu(22) $(1/2, 1/2, 1/2)$] and $4e$ (Cu(3)) [Cu(31) $(x,\ y,\ z)$, Cu(32) $(-x + 1/2,\ y + 1/2,\ -z + 1/2)$, Cu(33) $(-x,\ -y,\ -z)$, Cu(34) $(x + 1/2,\ -y + 1/2,\ z + 1/2)$].

if the sequences are $+\ -\ -\ +$ (along x) $+\ +\ -\ -$ (along y) and $+\ -\ -\ +$ (along z) all belonging to $\Gamma_2(4e)$. Taking into account these spin sequences a total of six magnetic components were allowed to vary. The magnetic moment components μ_x(Cu1,Cu2) and μ_z(Cu1,Cu2) resulted in small moment values $< 0.2\,\mu_\mathrm{B}$ with a standard deviation of $\pm 0.2\,\mu_\mathrm{B}$ and they are not well defined.
For a preliminary refinement, we used the first eight magnetic reflections. The moment components μ_y(Cu1,Cu2), μ_x(Cu3), μ_y(Cu3) and μ_z(Cu3) were allowed to vary resulting in $R_\mathrm{M} = 0.108$ (in F).

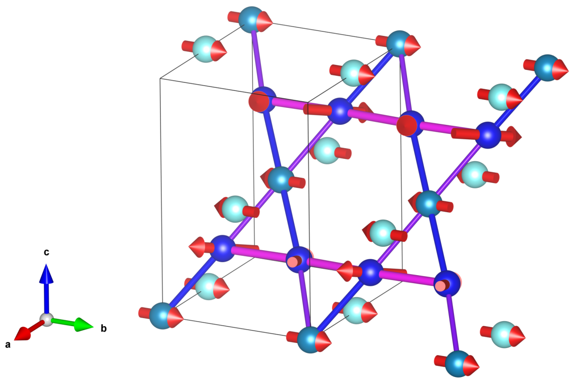

Figure 1: Drawing of the magnetic structure of clinoatacamite at $T = 2\,\mathrm{K}$ derived from a preliminary refinement of the single-crystal neutron diffraction data together with a kagome unit. The black solid lines indicate the unit cell of clinoatacamite. There are three inequivalent Cu sites in clinoatacamite: Cu(1) (light blue), Cu(2) (teal), Cu(3) (dark blue). The preliminary magnetic moments are μ_ord(Cu(1),Cu(2)) $= [0, 0.44(6), 0]\,\mu_\mathrm{B}$ and μ_ord(Cu(3)) $= [0.63(5), 0.30(5), 0.27(10)]\,\mu_\mathrm{B}$.

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