

Competing Ordering Modes in the Distorted Quantum Kagome Material Clinoatacamite $\text{Cu}_2\text{Cl}(\text{OH})_3$

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 (Received 26 January 2026; revised 19 June 2026; accepted 21 July 2026; published 8 September 2026)

We have studied the magnetic properties of clinoatacamite $\text{Cu}_2\text{Cl}(\text{OH})_3$, the parent compound of the quantum spin liquid candidate herbertsmithite and a long-standing puzzle among frustrated quantum magnets. As we reveal using density-functional theory, clinoatacamite belongs to the class of distorted kagome antiferromagnets with the kagome plane being embedded into a low-symmetry crystal structure. By means of thermodynamic measurements, muon spin rotation and relaxation, as well as neutron diffraction on single crystals, we find in zero magnetic field complex behavior below $T_1 = 18.1$ K which unfolds in three temperature regions I–III. We propose this complexity in multicritical clinoatacamite to arise from the competition of antiferromagnetic ordering modes from the underconstrained manifold of modes, which can lead to a metamagnetic texture in zero field.

DOI: [10.1103/xmh8-68vk](https://doi.org/10.1103/xmh8-68vk)

For decades, experimental research on antiferromagnetic (AFM) quantum kagome materials has been primarily driven by the hunt for the quantum spin liquid (QSL) ground state [1,2]. Yet, despite immense efforts, this highly entangled quantum spin state turned out to be hard to observe in real materials. Notably, the mineral herbertsmithite $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ stands out from this research on kagome magnetic insulators as a promising QSL candidate with the absence of magnetic order or spin freezing down to mK temperatures [3–5]. This experimental observation

motivated the research on an entire family of kagome materials as well as the synthesis of several new kagome compounds [6–14]. In effect, the years have shown that the sought-after QSL state is extremely unstable: Most $S = 1/2$ kagome materials adopt static order instead of QSL behavior, and, to date, it has remained unclear what defines in detail the boundary between static order and highly correlated disorder.

More recently, another direction of kagome research has formed, which explicitly turns towards *distorted* quantum kagome materials featuring a nonuniform motif of exchange couplings. It has been demonstrated that such a nonuniformity of the kagome lattice can lead to non-QSL but still exotic (quantum) behavior as, for instance, patterned valence bond solid states [15,16], coplanar order [13,17], trimer networks [18], and unusual applied-field properties such as magnetization plateaus [19]. Some of these properties have no counterpart in the uniform, ideal AFM kagome lattice described by the Hamiltonian

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$$\mathcal{H} = J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j. \quad (1)$$

Here, J denotes the exchange interaction between nearest-neighbor (NN) spins on the corner-sharing spin triangles and $\mathbf{S}_{i,j}$ are the spin operators at sites i, j .

Distortions of a spin lattice impair the equivalence of magnetic sites. At first sight, this should lift the under-constrained nature of a kagome antiferromagnet and select distinct ordering modes. However, the manifold of ordering modes may decompose into a system of modes pertaining to different symmetries. Their competition can reestablish magnetic frustration at a higher level, resulting in complex magnetic behavior. In the present Letter, we address the unusual magnetic properties of one such system, clinoatacamite $\text{Cu}_2\text{Cl}(\text{OH})_3$, a distorted kagome material and a long-standing puzzle [20] in frustrated quantum magnetism. As parent compound of the paratacamite family $\text{Zn}_x\text{Cu}_{4-x}\text{Cl}_2(\text{OH})_6$, clinoatacamite ($x = 0$) is closely related to herbertsmithite ($x = 1$), but its kagome motif of Cu sites is embedded into a low-symmetry crystal structure with different symmetries for the kagome sites. Further, unlike the QSL candidate herbertsmithite, clinoatacamite undergoes a magnetic transition at 18.1 K [20].

Although actively discussed in the context of kagome physics in the past [21–27], the ground states of clinoatacamite have remained inconclusive [28], in part because of the lack of single-crystal studies. In this Letter, employing density-functional theory (DFT) we will first demonstrate that clinoatacamite can be understood as a nonuniform kagome antiferromagnet with weak ferromagnetic (FM) couplings to the interlayer Cu sites. Hence, it clearly distinguishes itself from other kagome materials in the atacamite family [8] leading to a weak network of kagome planes and interlayer sites. We will further

demonstrate using thermodynamic as well as microscopic measurement techniques and single-crystalline samples that clinoatacamite exhibits a complex zero-field sequence of magnetic states below $T_1 = 18.1$ K. Zero-field muon spin rotation and relaxation (μSR) and neutron diffraction reveal different types of long-range order which separate the temperature range below T_1 into three regions I–III. We further find that the multicritical nature of the distorted kagome compound clinoatacamite manifests itself in the $\mathbf{q}_m = (0, 0, 0)$ state at lowest temperatures. It consists of simultaneous odd-even AFM ordering modes implying a metamagnetic texture [31]. With this, clinoatacamite serves as an example of a frustrated spin-1/2 antiferromagnet with complex magnetic behavior in zero field. To account for this, we combine complementary measurement techniques, microscopic details as well as phenomenology for multicritical systems.

Clinoatacamite crystallizes in a monoclinic structure of space group $P2_1/n$ (No. 14) [32] and with lattice parameters $a = 6.1675(7)$ Å, $b = 6.8327(8)$ Å, $c = 9.1517(4)$ Å and $\beta = 99.492(2)^\circ$ [33] [Fig. 1(a)]. Three inequivalent copper sites Cu(1)–Cu(3) are present. As depicted in Fig. 1(a), Cu(1)(OH)₆ and Cu(2)(OH)₄Cl₂ octahedra alternate along the a axis. Cu(3)(OH)₄Cl₂ octahedra form chains along the b axis. The Cu(2) and Cu(3) sites form a slightly distorted kagome motif, spanned by the $[010]$ and $[10\bar{1}]$ crystal directions. Cu(1) sites are interlayer sites. There are three inequivalent NN Cu–Cu exchange paths (J_4 – J_6) within the kagome layers and three inequivalent NN Cu–Cu exchange paths (J_1 – J_3) between kagome and interlayer sites [Fig. 1(b)].

We show that the kagome motif is formed by the dominant exchange couplings by employing DFT with full potential local orbital basis [45] and generalized gradient approximation (GGA) functional [46]. Electronic correlations on the

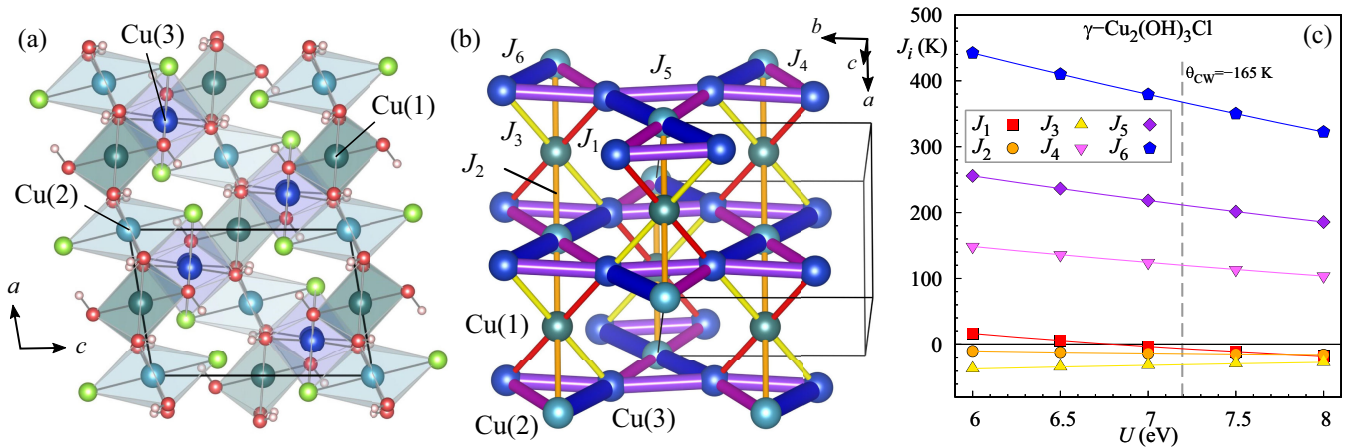


FIG. 1. (a) Crystal structure of clinoatacamite [33] viewed along the b axis [Cu(1): teal, Cu(2): light blue, Cu(3): dark blue, Cl: green, O: red, H: white]. (b) Motif of NN Cu–Cu exchange interactions J_1 – J_6 and (c) their strength derived by means of DFT and GGA + U , plotted as function of the on-site Coulomb repulsion U . At $U = 7.19$ eV, the mean-field Curie-Weiss temperature agrees with the experimental value $\Theta_{\text{CW}} = -165(1)$ K with $J_1 = -6.8$ K, $J_2 = -14.5$ K, $J_3 = -30.3$ K, $J_4 = 120.1$ K, $J_5 = 211.6$ K, and $J_6 = 367.7$ K (details in Ref. [34]). In panels (a) and (b), the unit cells are indicated.

Cu^{2+} ions were accounted for by GGA + U [47]. As the strength of the exchange couplings is well known to sensitively depend on Cu–O–Cu bond angles, we have first studied the crystal structure of clinoatacamite using single-crystal neutron diffraction. We collected the data using the Four-Circle Diffractometer E5 at the BER II reactor of the Helmholtz-Zentrum Berlin für Materialien und Energie (HZB), Germany [34,48–51]. Subsequently, we used the obtained positional parameters as input for the DFT-based analysis together with lattice parameters from Ref. [33]. Figure 1(c) visualizes the U dependence of J_1 – J_6 . Next-nearest neighbor exchanges J_7 – J_{29} were found to be $|J_i| < 10$ K [34]. We calculated the J_i at $U = 7.19$ eV, where the mean-field Curie-Weiss temperature agrees with the experimental value $\Theta_{\text{CW}} = -165(1)$ K extracted from a fit of the inverse magnetic susceptibility [34].

The dominant exchange couplings, $J_4 = 120.1$ K, $J_5 = 211.6$ K, and $J_6 = 367.7$ K, form the nonuniform AFM kagome layers. Here, J_6 couples units of three Cu sites into trimers, similar to the motif deduced in Ref. [22] for in-plane exchange only [52,53]. The couplings $J_1 = -6.8$ K, $J_2 = -14.5$ K and $J_3 = -30.3$ K are FM, as suggested in Ref. [54]. These couplings between kagome sites and interlayer sites $|J_i| \lesssim 0.082 J_6$ are somewhat stronger than the interlayer couplings in herbertsmithite [55] where nonmagnetic Zn occupies the interlayer sites. In clinoatacamite, this leads to a weak ferromagnetic network between kagome and interlayer sites which stabilizes long-range order. Still, the FM couplings to the interlayer Cu sites are significantly smaller than in the mineral barlowite $\text{Cu}_4(\text{OH})_6\text{FBr}$ with uniform AFM kagome planes [56]. In a classical Monte Carlo approach for the ordered magnetic ground state resulting from the Hamiltonian of clinoatacamite we find that the interlayer Cu(1) spins adopt a spiral order reflecting the weak coupling to the kagome spins with up-up-down order ($T_N^{\text{MC}} = 13$ K; details in Ref. [34]).

Experimentally, the use of natural single-crystalline samples (details in Ref. [34]) allows us to resolve a complex sequence of magnetic transitions in zero and weak magnetic fields ($\mathbf{H} \parallel b$ axis). As shown in Fig. 2(a), the magnetic specific heat c_{mag} [34] features an anomaly at 18.1 K in zero field, in full agreement with earlier results [20,29]. Additionally, we observe two transition anomalies at 6.2 and 6.4 K [inset Fig. 2(a)], not resolved as distinct maxima in previous polycrystal studies [29]. At 4.6 K, we detect a weak kink in the specific heat not reported before. The magnetic entropy S_{mag} at 18.1 K, obtained via an integration of c_{mag}/T [34], is only $\sim 1/3$ of $2R \ln(2)$, the entropy expected for two spin-1/2 per formula unit. The entropy change at 18.1 K is very small. The very sharp and intense 6.2 K-anomaly resembles that of a first-order phase transition.

Magnetometry in weak dc magnetic fields $\mathbf{H} \parallel b$ axis reveals different behavior below 6.2 K for field-cooled (FC) and zero-field cooled (ZFC) samples up to ~ 0.1 T

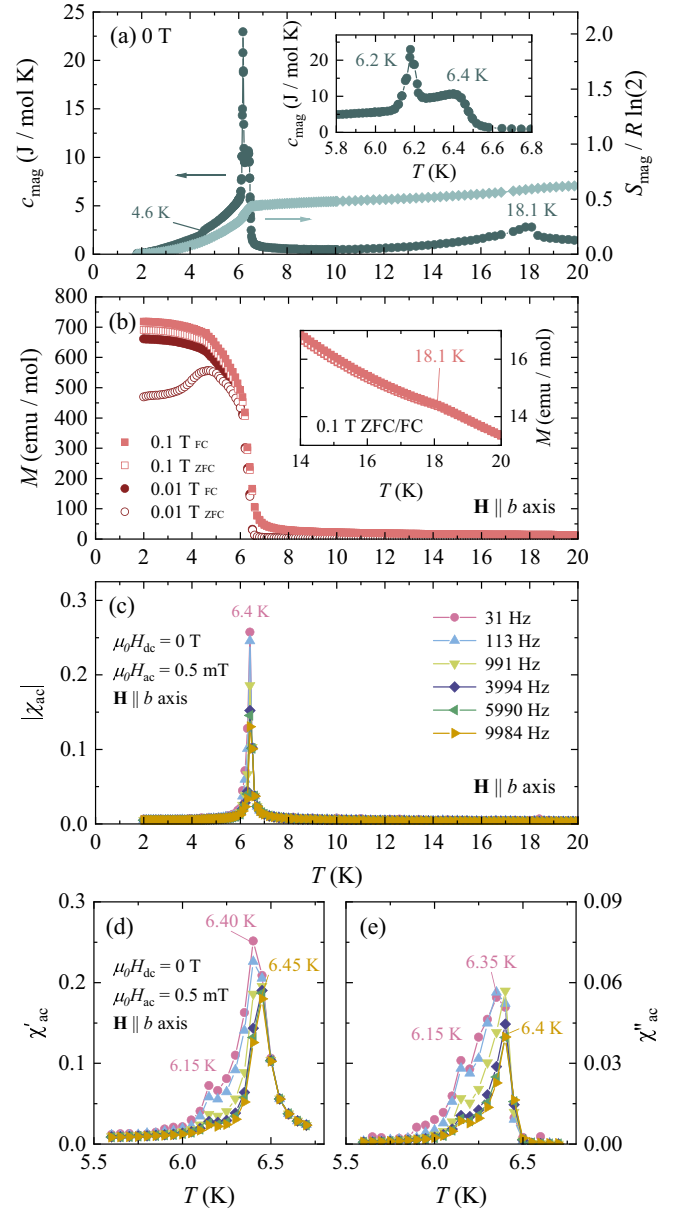


FIG. 2. (a) Magnetic specific heat c_{mag} and entropy S_{mag} in zero field and as function of temperature. The inset enlarges the region of the maxima at 6.2 and 6.4 K. (b) Temperature dependence of the magnetization in weak dc magnetic fields (0.01, 0.1 T) for FC and ZFC samples ($\mathbf{H} \parallel b$ axis). The inset shows the subtle kink at 18.1 K in 0.1 T. (c) Temperature dependence of the magnitude of the ac magnetic susceptibility $|\chi_{\text{ac}}| = \sqrt{\chi_{\text{ac}}'^2 + \chi_{\text{ac}}''^2}$ with $\mu_0 H_{\text{dc}} = 0$ T and $\mu_0 H_{\text{ac}} = 0.5$ mT ($\mathbf{H} \parallel b$ axis) for various frequencies up to 9984 Hz. (d),(e) In-phase and out-of-phase components of the ac susceptibility, χ_{ac}' and χ_{ac}'' , in the region of the 6.2 and 6.4 K anomalies.

[Fig. 2(b)] in accordance with earlier results for polycrystals [29]. At 4.7 K, slightly shifted from the temperature of the weak anomaly in the specific heat [Fig. 2(a)], the $M(T)$ data feature a kink (maximum) at 0.01 T FC (ZFC). The magnetization anomaly at 18.1 K is very weak and is visible on a reduced scale only [inset Fig. 2(b)]. The ac

magnetic susceptibility χ_{ac} [Fig. 2(c)] features an intense anomaly at 6.4 K for all frequencies studied ($\mu_0 H_{dc} = 0$ T, $\mu_0 H_{ac} = 0.5$ mT). A frequency-dependent behavior of $|\chi_{ac}|$ sets in at 6.4 K and persists down to ~ 4.5 K, where a weak kinklike anomaly is present, not visible on the scale of Fig. 2(c). No anomaly can be resolved at 18.1 K. In Figs. 2(d) and 2(e), in-phase and out-of-phase components of the ac susceptibility, χ'_{ac} and χ''_{ac} , are plotted in the temperature region of the 6.2 and 6.4 K transitions where the frequency dependence is most pronounced. Our observations are at variance with the behavior presented in the past for synthetic, polycrystalline clinoatacamite, where χ'_{ac} was found to be clearly frequency dependent and χ''_{ac} to be nonzero even below 5 K [29]. Based on those earlier results, a spin-glass-like ground state was stated. Our results rule out spin glassiness at low temperatures.

We complement the view on the zero-field sequence of phases by carrying out single-crystal μ SR as well as neutron diffraction experiments. Zero-field (ZF) and weak transverse field (wTF) μ SR measurements were carried out using the General Purpose Surface-Muon Instrument [57] of the Swiss Muon Source at the Paul Scherrer Institut, Switzerland. μ SR clearly senses long-range magnetic order below 18.1 K. In wTF (30 G) at temperatures $T > 18.1$ K, in the paramagnetic phase, the whole asymmetry oscillates as the muon spins precess with the frequency of the external field [34]. Below 18.1 K the asymmetry in wTF is lost indicating that long-range order is present. Exemplary ZF asymmetry spectra as function of time taken at 1.73, 5.3, and 10.8 K are presented in Fig. 3(a). They are typical for the temperature regions below 4.6 K, above 6.4 K, and the region between these two thermodynamic transitions, and they indicate different types of long-range magnetic order. While above 6.4 K and below 4.6 K the experimental data can be well fitted to three distinct precession frequencies due to internal fields [Figs. 3(a) and 3(b)], the situation in the intermediate range is more complex with indications for enhanced spin dynamics similar to the findings on polycrystalline material reported in Ref. [20]. An extensive analysis of our μ SR data with detailed discussion will be given elsewhere.

In agreement with previous results for deuterated clinoatacamite powder [21–23], our single-crystal neutron diffraction study reveals magnetic reflections below 6.4 K which are compatible with the magnetic propagation vector $\mathbf{q}_m = (0, 0, 0)$ [34]. Neutron diffraction experiments [58–60] were carried out using the Four-Circle Diffractometer D10, and subsequently D10+, of the Institut Laue-Langevin (ILL), France, as well as the Flat-Cone Diffractometer E2 [61] at HZB, Germany. As displayed in Fig. 3(c), the integrated intensity of the purely magnetic (00 1) reflection decreases upon an increase of temperature and vanishes at 6.4(1) K, signaling the suppression of the $\mathbf{q}_m = \mathbf{0}$ state.

In the temperature region directly below $T_1 = 18.1$ K, we observe on D10+ magnetic reflections which can be

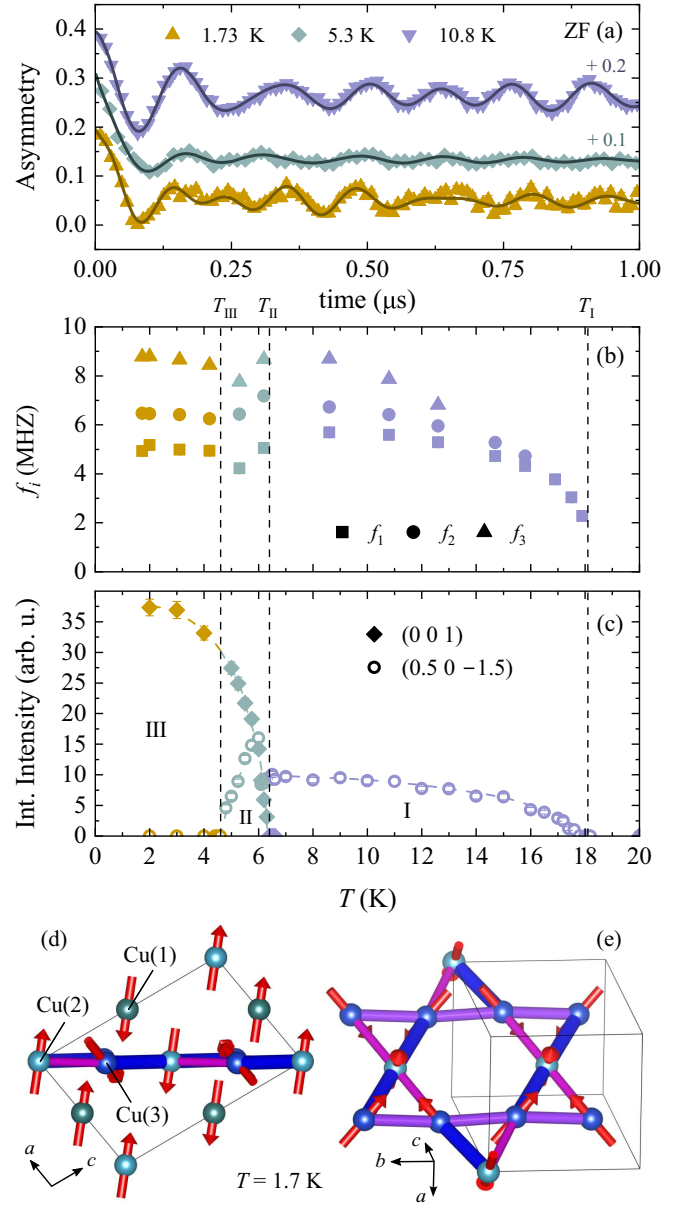


FIG. 3. (a) Zero-field μ SR asymmetry of single-crystalline clinoatacamite as function of time measured at 1.73, 5.3, and 10.8 K. The data at 5.3 and 10.8 K are shifted vertically for clarity. Solid curves are fits to the data. (b) Temperature dependence of the muon spin precession frequencies f_i determined from the fits; for details see Ref. [34]. (c) Temperature dependence of the integrated intensities of the purely magnetic (00 1) and (0.5 0 -1.5) reflections from neutron diffraction in zero field. (d), (e) Magnetic structure at 1.7 K [$R_M = 0.0545$ (in F)] together with the kagome motif viewed along the b axis and (e) displaying a single distorted kagome unit formed by Cu(2) and Cu(3) sites.

described by the magnetic propagation vector $\mathbf{q}_m = (-0.5, 0, 0.5)$ which also was observed at 7 K during a recent neutron diffraction study on deuterated powder [62]. In Fig. 3(c) we present the temperature dependence of the integrated intensity of the magnetic (0.5 0 -1.5) reflection. It goes through an intensity maximum at 6.0 K and persists

down to 4.6(1) K. As a result, the magnetic states with propagation vectors $\mathbf{q}_m = (0, 0, 0)$ and $\mathbf{q}_m = (-0.5, 0, 0.5)$ coexist between $T_{\text{III}} = 4.6$ K and $T_{\text{II}} = 6.4$ K, which is where the μSR fits reflected a more complex behavior. We label the regions I (6.4–18.1 K), II (4.6–6.4 K), and III (below 4.6 K) as indicated in Figs. 3(b) and 3(c). Our findings fully resolve the apparent inconsistency between neutron diffraction and μSR data which has persisted for decades [28]. While the determination of the magnetic structure in region I will be given elsewhere, we reveal that the competition of ordering modes already manifests itself in the $\mathbf{q}_m = (0, 0, 0)$ order in region III. Our findings further rule out the scenario of clinoatacamite as valence bond solid from Ref. [21].

Key to the determination of the magnetic structure in region III was to measure the intensity of magnetic reflections, weak ones in particular, with good accuracy. This was limited in earlier powder studies [21–23], whereas single-crystal neutron diffraction allows to record the integrated intensities of individual Bragg peaks. Based on a corresponding experiment on D10 [58], we have carried out a refinement of the magnetic structure employing representation analysis [63–65] (details in Ref. [34]). We found that the data are best described [$R_M = 0.0545$ (in F)] using different irreducible representations for Cu(1) and Cu(2) on Wyckoff sites $2d$ and $2a$ as well as for Cu(3) on $4e$. The resulting magnetic structure is displayed in Figs. 3(d) and 3(e). The magnetic moments of Cu(1) and Cu(2) [66] lie in the ac plane with components of $\mu_{\text{ord,Cu(1)}}(x) = \mu_{\text{ord,Cu(2)}}(x) = 0.30(2)\mu_B$ and $\mu_{\text{ord,Cu(1)}}(z) = \mu_{\text{ord,Cu(2)}}(z) = 0.29(3)\mu_B$, resulting in a total moment of $\mu_{\text{ord,Cu(1)}} = \mu_{\text{ord,Cu(2)}} = 0.38(2)\mu_B$. The magnetic moments of Cu(3) lie in the ab plane with $\mu_{\text{ord,Cu(3)}}(x) = 0.29(2)\mu_B$ and $\mu_{\text{ord,Cu(3)}}(y) = 0.25(2)\mu_B$ resulting in a total moment of $\mu_{\text{ord,Cu(3)}} = 0.38(2)\mu_B$. The refinement yields collinear Cu(1) and Cu(2) moments, almost normal to the kagome plane, produced by an even-parity ordering mode (inversion-symmetric). The noncollinear Cu(3) moments are produced by an odd-parity ordering mode (broken inversion symmetry).

As the frustration of clinoatacamite is strong, below 18.1 K, these symmetry-different modes are expected to be close to multicriticality. This can be understood by considering the deformation of the underconstrained undistorted kagome antiferromagnet which supports many degenerate modes. Some of these modes must be connected with the distinct selected modes dominating magnetic ordering along the distortion path. From phenomenological Landau theory for multicritical systems, one of the two competing modes should yield long-range order by a conventional continuous phase transition upon lowering temperature from the paramagnetic state. Eventually, a transition to a state of coexisting modes, or a domain state involving other modes, could be seen in a bi- or tetracritical phase diagram [67].

From phenomenology of the multicritical system of modes, the behavior of clinoatacamite can be rationalized.

Owing to the even and odd parity of the ordering modes, the magnetic free energy contains so-called *Lifshitz-type* invariants (LTIs), bilinear terms with one gradient [34]. These coupling terms allow the coexistence of symmetry-different modes in a common texture, a spatially modulated state in the order-parameter space as a homogeneous long-range order of one mode is destabilized against a spatially varying admixture of the other mode. The mechanism is similar to the rotation of the magnetization vector in a chiral helimagnet [68]. Such modulated mixtures of symmetry-different modes have been observed so far only in non-centrosymmetric magnetic crystals: as *metamagnetic texture*, a field-driven mixture of an AFM configuration with a FM state [31], while in a highly frustrated magnetic system similar textures have been invoked to explain the observation of quasistatic lumps of noncollinear spin structures in absence of any long-range order [69]. The spin configuration below $T_{\text{II}} = 6.4$ K is a mixture of competing symmetry-different modes. This confirms the multicritical nature of magnetic ordering in clinoatacamite. Hence, the transition at $T_1 = 18.1$ K could signal the formation of a textured state dominated by a primary mode frustrated by the closeness of another mode. The formation of such a partial order can explain the weak thermodynamic signature of this transition from the paramagnetic state. Consequently, the complex transition at T_{II} appears to be triggered when the second ordering mode becomes thermodynamically stable upon lowering temperature. This process should reorganize the textured high-temperature state into a long-range ordered phase, which may explain the observation of a sequence of narrow intermediate or mesophase states at this transition.

In conclusion, clinoatacamite exemplifies a geometrically frustrated antiferromagnet where the existence of an underconstrained manifold of modes allows for a mechanism where competing modes can coexist and create textured magnetic states of mixed symmetry. The even or odd parity of the ordering modes is instrumental for such states. Such systems become exceedingly complex because of the multicriticality and the higher-level, i.e., nonlocal, frustration through the chiral Lifshitz invariants. In addition, in a low-symmetry crystal like clinoatacamite, many anisotropic coupling terms will influence its magnetic phase diagram.

Acknowledgments—We thank the Helmholtz-Zentrum Berlin für Materialien und Energie as well as the Institut Laue-Langevin for allocation of neutron radiation beamtime and thankfully acknowledge the financial support from HZB and ILL. This work is further based on experiments performed at the Swiss Muon Source μS , Paul Scherrer Institute, Villigen, Switzerland. We thankfully acknowledge technical support from B. Veltel using the Physics Laboratory of MLZ. We thank T. Lampe and A. Kriele for their support during the sample preparation at the TU Braunschweig and at the Materials Science

Lab operated by Helmholtz-Zentrum Hereon at the Heinz Maier Leibnitz Zentrum (MLZ), Germany. We further thank J. L. Winter, K. Koschel, and J. Willwater for their support in the early stages of this project. This work has partially been supported by the DFG under Contract No. SU229/9-2, through SFB 1143 (Project No. 247310070) and Project No. 390858490 (Würzburg-Dresden Cluster of Excellence on Complexity, Topology and Dynamics in Quantum Matter—ctd.qmat, EXC 2147). H. O. J. acknowledges support through JSPS KAKENHI Grants No. 24H01668 and No. 25K08460. F. B. acknowledges support from the Agence Nationale de la Recherche (ANR), Project No. ANR-25-CE30-2010-01. U. K. R. thanks U. Nitzsche for assistance with computational resources. Crystal and magnetic structures were drawn using VESTA 3 [70].

Data availability—Some of the data that support the findings of this article are openly available [58–60]. All other data are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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