Direct visualization and control of antiferromagnetic domains and spin reorientation in a parent cuprate

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We report magnetic optical second-harmonic generation (SHG) polarimetry and imaging on Sr$_2$Cu$_3$O$_4$Cl$_2$, which allows direct visualization of the mesoscopic antiferromagnetic (AFM) structure of a parent cuprate. Temperature- and magnetic-field-dependent SHG reveals large domains with 90° relative orientations that are stabilized by a combination of uniaxial magnetic anisotropy and the Earth’s magnetic field. Below a temperature $T_R \sim 97$ K, we observe an unusual 90° spin reorientation transition, possibly driven by competing magnetic anisotropies of the two copper sublattices, which swaps the AFM domain states while preserving the domain structure. This allows deterministic switching of the AFM states by thermal or laser heating. Near $T_R$, the domain walls become exceptionally responsive to an applied magnetic field, with the Earth’s field sufficient to completely expel them from the crystal. Our findings unlock opportunities to study the mesoscopic AFM behavior of parent cuprates and explore their potential for AFM technologies.

Antiferromagnetic (AFM) materials host a rich variety of magnetic phenomena and are appealing for robust high-speed spin-based technologies [1–4]. Cuprate Mott insulators, the parent compounds of high-$T_c$ superconductors, are particularly intriguing AFM materials owing to their model Heisenberg behavior, record-high exchange interactions, and tunability with doping [5, 6]. However, there is limited understanding of their mesoscopic magnetic properties due to the difficulty of achieving local readout of AFM order and spatial mapping of AFM domain wall distributions [7, 8]. Here we directly visualize AFM domains in the parent cuprate Sr$_2$Cu$_3$O$_4$Cl$_2$ using optical second-harmonic generation (SHG) polarimetry and imaging. We uncover a spin-reorientation transition that enables thermally controlled deterministic 90° switching of AFM states and complete expulsion of AFM domain walls with Oersted-level magnetic fields.

Magnetic crystals that break time-reversal symmetry permit time-noninvariant (c-type) SHG processes that directly couple to the magnetic order parameter [9, 10], making SHG a potentially powerful probe of AFM domains [9, 11] and dynamics [12]. Although c-type SHG is most widely reported in the electric-dipole channel from noncentrosymmetric AFM materials [13–19], it has also been detected in weaker magnetic-dipole (MD) channels from centrosymmetric materials [17, 18]. However, ideal AFM-ordered parent cuprates preserve time-reversal symmetry because even though time-reversal is locally broken at each Cu site, it is restored upon translation by a primitive lattice vector. This leads to perfect cancellation of c-type SHG radiation from the two magnetic sublattices. Therefore, cuprate antiferromagnetism is expected to be SHG inactive, as was recently confirmed in the prototypical compound Sr$_2$CuO$_2$Cl$_2$ [11, 20].

The centrosymmetric tetragonal structure (point group, 4/mmm) of Sr$_2$Cu$_3$O$_4$Cl$_2$ is nearly identical to Sr$_2$CuO$_2$Cl$_2$ except for an additional set of Cu$^{2+}$ ions (Cu$_{II}$) located in every other plaquette of the conventional CuO$_2$ lattice (Cu$_I$, Fig. 1b) [21]. The Cu$_I$ spins interact via strong intralayer AFM exchange ($J_I = 130$ meV) and order below $T_{N,I} \approx 380$ K, well above the AFM ordering temperature of the Cu$_{II}$ sublattice ($T_{N,II} \approx 40$ K) [22]. However, because Cu$_{II}$ breaks the equivalence of neighboring Cu$_I$ sites, the AFM ordered Cu$_{II}$ sublattice becomes SHG active below $T_{N,II}$. The AFM ordered Cu$_{II}$ sublattice generates a net field at the Cu$_{II}$ sites via a weak pseudodipolar interaction [23, 24]. This induces a polarization of Cu$_I$ spins and slight canting of Cu$_I$ spins, resulting in a centrosymmetric AFM structure (point group $mm'm'n'$) with a small net in-plane ferromagnetic moment $M$ [23, 24] (Fig. 1). Four degenerate 90°-rotated AFM domain configurations correspond to $M$ along [110], [110], [110] or [110], which can in principle be distinguished via MD SHG. A previous study used bulk magnetometry to infer the existence of stable AFM domains with 90° relative orientations and a domain wall phase transition near 100 K [1], where it was proposed that domains are stabilized by entropic [17] or magnetoelastic [25] effects. However, direct observation of AFM domains has remained elusive.

To establish the existence of an SHG response that directly couples to the magnetic order parameter, which can be represented by $M$, we performed rotational anisotropy (RA) measurements on (001)-cleaved single
FIG. 1. Local AFM readout in Sr$_2$Cu$_3$O$_4$Cl$_2$. (a) Crystal and magnetic structure of single Cu-O layer in Sr$_2$Cu$_3$O$_4$Cl$_2$. Only the moment induced by internal pseudodipolar field is depicted. Thick arrow indicates M. (b) Schematic of RA-SHG experimental geometry, where angle of incidence (θ), scattering plane angle (φ), in-plane magnetic field (H) direction, and input and output electric field polarizations (P or S) are varied. (c) Temperature dependence of normal incidence (θ = 0°) SHG intensity. Solid line is a least-squares fit to $I(θ) ∝ (T − T_N,1)^β$, where $β = 0.32(3)$ and $T_N,1 = 380(1)$ K. Fit is performed near $T_N,1$ (360 K ≤ T ≤ 380 K) with uncertainties given as 1 standard deviation. Inset: normal incidence RA-SHG for co-linearly polarized excitation and detection beams measured at $T = 295$ K and fit by $χ_i^{MD(′)}(mm′m′)$ process (solid line). (d) Oblique-incidence (θ = 10°) $P_{in}$-$P_{out}$ RA-SHG pattern at 400 K fit by $χ_{ij}^{EQ(′)}(4/mmm)$ process (solid line). (e) $P_{in}$-$P_{out}$ RA-SHG pattern (θ = 10°) at 295 K fit to a coherent superposition of $χ_{ij}^{EQ(′)}(4/mmm)$ and $χ_{ij}^{MD(′)}(mm′m′)$ processes. EQ and MD processes are illustrated on the right, where patterns represent the $P_{in}$-light-induced nonlinear polarization projected along $P_{out}$. Filled and white lobes indicate opposite phase. (f) Dark-field optical micrograph of cleaved (001) Sr$_2$Cu$_3$O$_4$Cl$_2$. Bright and dark lines correspond to surface terrace steps. (g) Wide-field SHG image under horizontal excitation polarization (along x axis) at 295 K. Domains A and B are labeled with arrow corresponding to M. (h) $P_{in}$-$P_{out}$ RA-SHG patterns at 295 K for domains A and B.

crystals of Sr$_2$Cu$_3$O$_4$Cl$_2$ using a fast-rotating scattering-plane-based technique (Fig. 1h) [20]. Under normal incidence (θ = 0°), a nonzero SHG signal appears below $T_N,1$ and shows no thermal hysteresis (Fig. 1i), consistent with a continuous AFM transition. The dumbbell-shaped RA patterns are well described by a magnetization-a continuous AFM transition. The dumbbell-shaped RA pattern (Fig. 1h) shows no thermal hysteresis (Fig. 1i), consistent with a continuous AFM transition. The dumbbell-shaped RA patterns are well described by a magnetization- 

and domains is achieved using wide-field polarized SHG imaging at normal incidence. Under horizontal excitation polarization [27], regions with M along the ±y (±x) direction appear bright (dark). An SHG image captured over the same field of view at $T = 295$ K shows clear bright and dark regions spanning hundreds of microns (Fig. 1k). By collecting oblique incidence RA patterns at different locations throughout the imaged area (Fig. 1l), we find that the entire bright (dark) region corresponds to a single AFM domain with M oriented along $−y$ ($+x$). The realization of only two out of four possible domain orientations is observed across multiple crystals. By repeating these measurements following multiple thermal cycles across $T_N,1$ and under different orientations of the crystal in the laboratory frame, we report two main phenomena [27]. First, the location of 90° domain walls is largely reproducible, suggesting pinning to structural features. Second, the direction of M within the bright (dark) domain is fixed along either the $+y$ ($+x$) direction or the $−y$ ($−x$) direction, depending on the orientation of the crystal relative to the Earth’s magnetic field.
Anti-phase domains with 180° walls are removed even by the weak field of Earth upon cooling below $T_{N,1}$. These observations suggest that a particular AFM configuration is selected through an interplay of the Earth’s field with an underlying uniaxial magnetic anisotropy along the $y$ ($x$) axis in the bright (dark) domain.

The presence of uniaxial anisotropy can be probed using anisotropic magneto-SHG (AM-SHG), where RA patterns are measured under different applied in-plane magnetic field ($H$) directions ($\alpha$) [33]. Figure 2 shows $S_{\text{in}}$-$S_{\text{out}}$ RA patterns from two 90° domains for different $\alpha$ with $H = 1$ kOe. The AM-SHG patterns, obtained by summing RA patterns over $\alpha$, exhibit a clear two-fold rotational symmetry ($C_2$) characteristic of uniaxial anisotropy (Fig. 2a), with the axis differing by 90° for the two domains. These data confirm the presence of a domain-dependent in-plane uniaxial magnetic anisotropy. A low field was necessary for this measurement because for $H > 3$ kOe, a spin rotation transition occurs for $H$ along (100) [23, 24], which obscures the $C_2$ contribution to the AM-SHG patterns (Fig. 2b). Field-dependent SHG imaging shows that a domain can be reoriented by 90° at sufficiently high $H$ (Fig. 2c), which appears to occur through the growth and merger of smaller domains [27]. Combined with the thermal cycling results, the data suggest that the structural symmetry is lower than tetragonal above $T_{N,1}$. Structural domains may arise from previously unresolved high-temperature orthorhombic distortions, which impose spatially nonuniform uniaxial anisotropy below $T_{N,1}$. The system may also be subject to extrinsic stresses from crystallographic defects as well as intrinsic stresses that are expected to accompany AFM order in finite crystals [25, 27].

The AFM domain distribution is dictated primarily by competition between the uniaxial anisotropy and Cu$_4$-Cu$_4$ spin exchange energies. Although anisotropy is much weaker than exchange [27], a 90° AFM domain wall can nevertheless form along structural domain boundaries because the exchange energy cost scales with the wall area, whereas the anisotropy energy saved scales with the domain volume. Just below $T_{N,1}$, we observe fragmentary AFM domains with rough edges (Fig. 2d), likely conforming to an underlying distribution of structural domains. Upon further cooling, fragments merge to form larger AFM domains with smoother walls, indicating an increasing exchange contribution relative to the anisotropy that is possibly driven by changes in the ordered moment magnitude and temperature-dependent anisotropy. From 160 K down to 100 K, the domain boundaries remain largely stable. This general trend is consistent across multiple samples [27].

Figure 3 shows the evolution of a typical 90° AFM domain upon further cooling below 100 K. Remarkably, within 1 K around $T_R = 97$ K, the domain wall is rapidly expelled from the sample—realizing a global single-domain state—and then reappears and snaps back into its original position with swapped bright and dark regions. This behavior is completely reversible upon reheating through $T_R$ with slight thermal hysteresis. Local RA measurements confirm that $M$ reorients by 90° within each domain across $T_R$, with the two domains effectively swapping $M$. While a previous study observed magnetization anomalies and inferred changes in relative domain sizes in this temperature regime [7], the domain reorientation at $T_R$ has remained hidden until this work. This reorientation transition enables repeated determin-
FIG. 3. Thermally driven domain reorientation transition. (a) SHG images acquired at select temperatures upon warming (top) and cooling (bottom). Arrows indicate \( M \). Excitation was vertically polarized. Similar behavior was confirmed in a second sample \[27\]. (b) MD SHG intensity on domain A under repeated thermal switching through heating to 120 K (red) and cooling to 80 K (blue). Corresponding \( P_{\text{in}}-P_{\text{out}} \) patterns shown on right. (c) SHG images acquired at three different excitation intensities for 95.5 K. (d) AM-SHG patterns acquired at \( T_R - 10 \text{ K} \), \( T_R \), and \( T_R + 5 \text{ K} \) with \( H = 1180 \text{ Oe} \) from a single domain. (e) Schematic of competing magnetic anisotropies model. The graph depicts how \( \text{Cu}_I \) and \( \text{Cu}_{II} \) in-plane spin anisotropies, labelled as \( K_I \) and \( K_{II} \) respectively, may vary around \( T_R \). The factor of two in front of \( K_I \) arises because there are twice as many \( \text{Cu}_I \) as \( \text{Cu}_{II} \) per unit cell. In the crystal schematics, blue (green) lobe sizes and orientations depict the direction and strength of \( \text{Cu}_I \) (\( \text{Cu}_{II} \)) spin anisotropy above and below \( T_R \) for domain A. Domain B is similar but rotated by 90°.

istic 90° switching of the local AFM order parameter simply by cycling the cryostat temperature through \( T_R \) (Fig. 3b), or by fixing the cryostat temperature below \( T_R \) and changing the optical power (Fig. 3c).

The AM-SHG pattern from a single AFM domain has \( C_2 \) symmetry just above \( T_R \), becomes \( C_4 \) at \( T_R \), and then recovers a \( C_2 \) form below \( T_R \) that is 90° rotated from the high-temperature pattern (Fig. 3d). This strongly suggests that the reorientation transition is driven by a change in sign of the uniaxial magnetic anisotropy at \( T_R \). In Fig. 3b, we propose a simple microscopic picture in which \( \text{Cu}_I \) and \( \text{Cu}_{II} \) spins exhibit temperature-dependent in-plane uniaxial magnetic anisotropies (\( K_I \) and \( K_{II} \)). An expression for the anisotropy energy of a single domain is:

\[
E(T) = E_0 + [2K_I(T) - K_{II}(T)] \sin^2 \psi - K_4 \cos(4\psi),
\]

where \( \psi \) is the angle between \( M \) and the +\( x \) direction, and \( K_4 \) is a biaxial anisotropy term \[23, 24, 34\]. The \( \text{Cu}_I \) and \( \text{Cu}_{II} \) spins prefer a relative orientation of 90°. If \( K_I \) and \( K_{II} \) have the same sign but different strength (depicted by blue and green lobes in Fig. 3c), the two terms compete, with the larger of 2\( K_I \) and 2\( K_{II} \) determining the sign of the net uniaxial anisotropy and resulting orientation of \( M \). We hypothesize that \( K_I \) and \( K_{II} \) exhibit different temperature dependencies and cross at \( T_R \), driving the 90° AFM reorientation. Since \( \text{Cu}_I \) and \( \text{Cu}_{II} \) lie at nonequivalent lattice sites, it is reasonable that a distortion-dependent single-ion anisotropy \[35\] will differ for each ion in both its strength and temperature dependence. The uniaxial anisotropy may also microscopically involve two-ion terms such as anisotropic exchange and magnetic dipole-dipole coupling, which is beyond the scope of this work to disentangle. We further note that spin correlations within the \( \text{Cu}_{II} \) sublattice have been shown to onset near \( T = 100 \text{ K} \) \[32\], potentially inducing magnetoelastic deformations.

This phenomenon is reminiscent of the transition across the isotropic point of \( \text{Fe}_3\text{O}_4 \) \[36, 37\] and the Morin transition of \( \alpha\text{-Fe}_2\text{O}_3 \) \[38\]. In these cases, spin reorientation occurs when temperature-dependent anisotropy contributions, originating from different magnetic ions or anisotropy mechanisms \[39, 40\], compensate one another to drive an anisotropy term across zero \[41\]. Our observations in \( \text{Sr}_2\text{Cu}_2\text{O}_2\text{Cl}_2 \) are distinguished from other temperature-dependent spin reorientation transitions in that the domain distribution is preserved, with the underlying distortions holding a memory of the domain structure while the anisotropy sets the spin orientation. Moreover, in \( \text{Sr}_2\text{Cu}_2\text{O}_2\text{Cl}_2 \), the transition has been difficult to discern using bulk-averaged probes because it involves domain-dependent spin reorientation as opposed to a global change in easy axis.
Near $T_R$, the AFM domain walls become exceptionally responsive to small $H$. Figure 1 illustrates the change in position ($\Delta y$) of the 90° domain wall when $H$ is varied from 0.5 Oe to 5.5 Oe along the $x$ direction. As the temperature varies from 90 K to 96 K, $\Delta H$ has an increasingly large effect on domain wall motion. Since wall motion along $y$ is nearly uniform, the change in magnetization along $x$ is proportional to $\Delta y$, hence $\Delta y/\Delta H$ measures domain wall susceptibility. By repeating this experiment at many temperatures, we identify a striking divergence in the domain wall susceptibility at $T_R$, consistent with conclusions drawn from low-field magnetometry [7, 27]. As the net uniaxial anisotropy crosses zero, 90° domain walls become energetically unfavorable and are easily expelled by small $H$. High domain wall tunability near $T_R$ may be leveraged to prepare large AFM domains of a desired orientation [27, 42].

Our approach to locally readout AFM states, globally image AFM domain walls, and deterministically switch 90° domains in a cuprate Mott insulator augments existing AFM detection and manipulation schemes in other material classes, such as magnetoelectric oxides, rare-earth orthoferrites, and metallic alloys [43]. Temperature-tunable anisotropy may be valuable for domain wall engineering, spin-superfluidity experiments [44], and studies of intrinsic domain wall mobility [15, 47]. Because Sr$_2$Cu$_3$O$_4$Cl$_2$ is sensitive to small changes in the microscopic parameters, especially around $T_R$, it may be amenable to AFM manipulation with various other techniques, including strain tuning and nonthermal optical control [48].

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[1] T. Jungwirth, X. Marti, P. Wadley, and J. Wunderlich, Antiferromagnetic spintronics, Nat. Nanotechnol. 11, 231 (2016).
[2] V. Baltz, A. Manchon, M. Tsoi, T. Moriyama, T. Ono, and Y. Tserkovnyak, Antiferromagnetic spintronics, Rev. Mod. Phys. 90, 015005 (2018).
[3] P. Nemec, M. Fiebig, T. Kampfrath, and A. V. Kimel, Antiferromagnetic opto-spintronics, Nat. Phys. 14, 229 (2018).
[4] O. Gomonay, V. Baltz, A. Brataas, and Y. Tserkovnyak, Antiferromagnetic spin textures and dynamics, Nat. Phys. 14, 213 (2018).
[5] E. Manousakis, The spin-1/2 heisenberg antiferromagnet on a square lattice and its application to the cuprous oxides, Rev. Mod. Phys. 63, 1 (1991).
[6] P. A. Lee, N. Nagaosa, and X.-G. Wen, Doping a mott insulator: Physics of high-temperature superconductivity, Rev. Mod. Phys. 78, 17 (2006).
[7] B. Parks, M. A. Rastner, Y. J. Kim, A. B. Harris, F. C. Chou, O. Entin-Wohlman, and A. Aharony, Magnetization measurements of antiferromagnetic domains in Sr$_2$Cu$_3$O$_4$Cl$_2$, Phys. Rev. B 63, 134433 (2001).
[8] B. Náfrádi, T. Keller, F. Hardy, C. Meingast, A. Erb, and B. Keimer, Magnetostriction and magnetostructural domains in antiferromagnetic YBa$_2$Cu$_3$O$_6$, Phys. Rev. Lett. 116, 047001 (2016).
[9] M. Fiebig, V. P. Pavlov, and R. V. Pisarev, Second-harmonic generation as a tool for studying electronic and magnetic structures of crystals, J. Opt. Soc. Am. B 22, 96 (2005).
[10] A. Kirilyuk and T. Rasing, Magnetization-induced second-harmonic generation from surfaces and interfaces, J. Opt. Soc. Am. B 22, 148 (2005).
[11] S.-W. Cheong, M. Fiebig, W. Wu, L. Chapon, and V. Kiryukhin, Seeing is believing: visualization of antiferromagnetic domains, npj Quantum Materials 5, 1 (2020).
[12] M. Fiebig, N. P. Duong, T. Satoh, B. B. Van Aken, K. Miyano, Y. Tomioka, and Y. Tokura, Ultrafast magnetization dynamics of antiferromagnetic compounds, Phys. D Appl. Phys. 41, 164005 (2008).
[13] J.-Y. Chauleau, E. Haltz, C. Carréféré, S. Fusil, and...
M. Viret, Multi-stimuli manipulation of antiferromagnetic domains assessed by second-harmonic imaging. [Nat. Mater. 16, 803 (2017)]

14. C. Tschaschel, T. Satoh, and M. Fiebig, Tracking the ultrafast motion of an antiferromagnetic order parameter, [Nat. Commun. 10, 3995 (2019)]

15. Z. Sun, Y. Yi, T. Song, G. Clark, B. Huang, Y. Shan, S. Wu, D. Huang, C. Gao, Z. Chen, M. McGuire, T. Cao, D. Xiao, W.-T. Liu, W. Yao, X. Xu, and S. Wu, Giant nonreciprocal second-harmonic generation from antiferromagnetic bilayer CrI₃, [Nature 572, 497 (2019)]

16. H. Chu, C. J. Roh, J. O. Island, C. Li, S. Lee, J. Chen, J.-G. Park, A. F. Young, J. S. Lee, and D. Hsieh, Linear magnetoelastic phase in ultrathin MnPS₃ probed by optical second harmonic generation, [Phys. Rev. Lett. 124, 027601 (2020)]

17. B. Kaminski, M. Lafrentz, R. V. Piaserev, D. R. Yakovlev, V. V. Pavlov, V. A. Lukoshkin, A. B. Henriques, G. Springholz, G. Bauer, E. Abramof, P. H. O. Rappl, and M. Bayer, Spin-induced optical second harmonic generation in the centrosymmetric magnetic semiconductors EuTe and EuSe, [Phys. Rev. Lett. 103, 037203 (2009)]

18. M. Matsubara, A. Schmehl, J. Mannhart, D. G. Schlom, and M. Fiebig, Large nonlinear magneto-optical effect in the centrosymmetric ferromagnetic semiconductor EuO, [Phys. Rev. B 81, 214447 (2010)]

19. A. de la Torre, K. L. Seyler, L. Zhao, S. D. Matteo, M. S. Scheurer, Y. Li, B. Yu, M. Greven, S. Sachdev, M. R. Norman, and D. Hsieh, Mirror symmetry breaking in a model insulating cuprate, [Nat. Phys. 17, 777 (2021)]

20. A. de la Torre, S. Di Matteo, D. Hsieh, and M. R. Norman, Implications of second harmonic generation for hidden order in Sr₂Cu₃O₄Cl₂, [Phys. Rev. B 104 (2021)]

21. B. Grande and H. Müller-Buschbaum, Über oxocuprate, XIV zur kristallchemie von Sr₂Cu₃O₄Cl₂, Zeitschrift für Naturforschung B 31, 405 (1976)

22. K. Yamada, N. Suzuki, and J. Akimitsu, Magnetic properties of (Sr,Ba)₂Cu₃O₄Cl₂: Two-dimensional antiferromagnetic cuprates containing two types of Cu-site, [Physica B Condens. Matter 213-214, 191 (1995)]

23. F. C. Chou, A. Aharony, R. J. Birgeneau, O. Entin-Wohlman, M. Greven, A. B. Harris, M. A. Kastner, Y. J. Kim, D. S. Kleinberg, Y. S. Lee, and Q. Zhu, Ferromagnetic moment and spin rotation transitions in tetragonal antiferromagnetic Sr₂Cu₃O₄Cl₂, [Phys. Rev. Lett. 78, 535 (1997)]

24. M. A. Kastner, A. Aharony, R. J. Birgeneau, F. C. Chou, O. Entin-Wohlman, M. Greven, A. B. Harris, M. A. Kastner, Y. J. Kim, Y. S. Lee, M. E. Parks, and Q. Zhu, Field-dependent antiferromagnetism and ferromagnetism of the two copper sublattices in Sr₂Cu₃O₄Cl₂, [Phys. Rev. B 59, 14702 (1999)]

25. H. V. Gomonay, I. G. Kornienko, and V. M. Loktev, Theory of magnetization in multiferroics: Competition between ferromagnetic and antiferromagnetic domains, [Phys. Rev. B 83, 054424 (2011)]

26. J. W. Harter, L. Niu, A. J. Woss, and D. Hsieh, High-speed measurement of rotational anisotropy nonlinear optical harmonic generation using position-sensitive detection, [Opt. Lett. 40, 4671 (2015)]

27. See Supplemental Material for further details of the experimental methods and supporting data, which includes Refs. [28-31].
and T. Ono, Fast domain wall motion in the vicinity of the angular momentum compensation temperature of ferrimagnets, Nat. Mater. 16, 1187 (2017).

[47] L. Caretta, M. Mann, F. Büttner, K. Ueda, B. Pfau, C. M. Günther, P. Hessing, A. Churikova, C. Klose, M. Schneider, D. Engel, C. Marcus, D. Bono, K. Bagschik, S. Eisebitt, and G. S. D. Beach, Fast current-driven domain walls and small skyrmions in a compensated ferrimagnet, Nat. Nanotechnol. 13, 1154 (2018).

[48] A. de la Torre, D. M. Kennes, M. Claassen, S. Gerber, J. W. McIver, and M. A. Sentef, Colloquium: Nonthermal pathways to ultrafast control in quantum materials, Rev. Mod. Phys. 93, 041002 (2021).
Supplementary Information:
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1. Experimental methods

Sr$_2$Cu$_3$O$_4$Cl$_2$ crystals were grown by an optimized method of slow cooling from the melt [1]. Quantities of SrO, SrCl$_2$, and CuO powders were mixed in a 1:1:3 stoichiometric ratio and placed in a large high form alumina crucible. The mix was gradually heated in air $1030^\circ$C, dwelled for 5h, then cooled to $900^\circ$C at a rate of $2^\circ$C h$^{-1}$. Placing the crucible in a slight temperature gradient (off-center of the hot chamber of the box furnace) resulted in a cm-sized plate-like single crystal. Samples are stable in air. High quality of the samples was attested by X-ray diffraction, Laue X-ray, and low-temperature magnetization measurements. The samples were affixed to an oxygen-free high thermal conductivity copper mount using a small amount of epoxy and then cleaved before measurement to leave clean surfaces parallel to the Cu$_3$O$_4$ (001) planes.

RA-SHG measurements were carried out using a rotating scattering plane based technique [2] with laser pulses at a fundamental wavelength of 800 nm delivered by a Ti:sapphire amplifier ($\sim$80 fs pulse duration, 100 kHz repetition rate). The experimental geometry is depicted in Fig. 1b. The beam diameter was $\sim$40 $\mu$m with a fluence $\sim$3 mJ/cm$^2$. For oblique incidence data, the angle of incidence was $\theta$ = 10°.

Wide-field imaging was performed with linear polarized excitation at $\theta$ $\approx$ 0° with a fluence of $\sim$1 mJ/cm$^2$ unless otherwise specified. The excitation spot size was $\sim$200 $\mu$m for Fig. 1g and $\sim$500 $\mu$m for all other figures. The direction of the linear polarization for each dataset, which determines whether a particular domain is bright or dark, is indicated in the respective figure captions. The intensity fall-off near the edges of the image is an artefact due to the intensity profile of the excitation beam; M does not vary appreciably within a single domain at a given temperature. Additional bright or dark lines in the SHG image arise from scattering off the terrace edges. Significantly higher average power was required for SHG imaging (typically $\sim$100 mW) compared to RA-SHG ($\sim$3 mW) due to the larger illumination area, which causes additional sample heating. The temperature values reported in Fig. 3a and Fig. 4 are corrected for this laser heating by comparing low-power (0.5 mW) RA-SHG data on domain B to the SHG images.

The magnetic-field-dependent measurements (AM-SHG and field-dependent SHG imaging) were performed using home-built permanent magnet setups (neodymium for room-temperature or SmCo for low-temperature studies). The magnetic field direction and magnitude were controlled by adjusting the permanent magnet positions with translation and rotation stages, and the setup was calibrated with a gauss meter.

To determine the domain wall positions for Fig. 4, a linecut was performed along the y direction in each SHG image after averaging 16 $x$ pixels. The position was then determined from the derivative of the linecut after applying a Savitzky-Golay filter. The spatial resolution was limited by the pixel size ($\sim$4.2 $\mu$m), which was used as the uncertainty of the domain wall position.
2. Analysis of the SHG processes

In this section, we provide a mathematical description of the SHG response. Above $T_{N,1}$, Sr$_2$Cu$_3$O$_4$Cl$_2$ possesses a centrosymmetric tetragonal structure (point group 4/mmm), so the bulk electric dipole (ED) response vanishes. Surface ED (point group 4mm) as well as bulk magnetic dipole (MD) $i$-type processes are allowed, but these terms are $\varphi$-independent in the $P_{\text{out}}$ channels and zero in the $S_{\text{out}}$ channels [3]. This is incompatible with our experiments (Fig. S1), so we exclude such contributions. SHG can also arise from an electric quadrupole (EQ) process ($\chi^{\text{EQ}(i)}$) from 4/mmm, similar to what occurs in Sr$_2$CuO$_2$Cl$_2$ [3]. This process has the form $P_{2\omega} = \chi^{\text{EQ}(i)}_{ijkl} E_{\omega}^{i} \partial_{k} E_{\omega}^{j} + \partial_{k} E_{\omega}^{i} E_{\omega}^{j}$, where $P_{2\omega}$ is the second-harmonic polarization at frequency $2\omega$, $E_{\omega}$ is the electric field at the fundamental frequency $\omega$, and the indices $i,j,k,l$ run over the coordinates $x,y,z$. The bulk EQ SHG intensity has $|a + b \cos 4\varphi|^2$ dependence (where $a$ and $b$ are constants) for $P_{\text{out}}$ channels and $|\sin 4\varphi|^2$ dependence for $S_{\text{out}}$ channels, consistent with our observations. In fact, the Sr$_2$Cu$_3$O$_4$Cl$_2$ SHG is similar to Sr$_2$CuO$_2$Cl$_2$ in not only symmetry but also intensity, which suggests that they share a common SHG origin. For Sr$_2$CuO$_2$Cl$_2$, it was proposed that the EQ SHG is enhanced by an EQ $d$-$d$ transition at the fundamental energy (1.5 eV) [3, 4], so the same resonant SHG process likely also occurs in Sr$_2$Cu$_3$O$_4$Cl$_2$. The full $i$-type (time invariant) rank-4 polar susceptibility tensor $\chi^{\text{EQ}(i)}$ and the EQ SHG expressions for 4/mmm are detailed thoroughly in Ref. [3].

Below $T_{N,1}$, where the Cu$^\text{II}$ spins antiferromagnetically order and the Cu$I$ spins become polarized due to the pseudodipolar interaction, Sr$_2$Cu$_3$O$_4$Cl$_2$ possesses the magnetic point group mm$m'$. The two lowest order processes that become allowed below $T_{N,1}$ are $c$-type (time-noninvariant) bulk MD SHG ($\chi^{\text{MD}(c)}$) and $c$-type surface ED SHG ($\chi_\text{ED}(c)$). We first describe the MD case, and then we will discuss the surface ED process and why it is likely weak relative to the MD process. The MD process may be written as $P_{2\omega} = \chi^{\text{MD}(c)}_{ijkl} E_{\omega}^{i} H_{\omega}^{j}$, where $H_{\omega}$ is the fundamental-frequency magnetic field and $\chi^{\text{MD}(c)}$ is the $c$-type rank-3 axial susceptibility tensor that that respects mm$m'$. The data show the onset of a magnetic SHG process that is linearly related to the ferromagnetic moment $M$. We therefore expand the susceptibility as $\chi^{\text{MD}(c)}(M) = \chi^{\text{MD}}_{0,ijkl} + \chi^{\text{ijkl}} M_{i}$. The first term (H3 in Birss [5]) represents a crystallographic contribution (independent of magnetic order) that gives $\varphi$-independent SHG response [3] contrary to our observations and can therefore be neglected. $\chi^{\text{ijkl}}$ is an $i$-type rank-4 polar tensor that respects the crystallographic point group of the paramagnetic phase. Under tetragonal symmetry, $\chi^{\text{ijkl}}$ possesses the following form (H4 in Birss [5])

$$\chi^{\text{ijkl}} = \begin{pmatrix}
\chi_{xxxx} & 0 & 0 & 0 \\
0 & \chi_{xyyx} & 0 & 0 \\
0 & 0 & \chi_{zzzz} & 0 \\
0 & \chi_{zyzx} & 0 & \chi_{zzzz} \\
\chi_{zyzx} & 0 & 0 & \chi_{zzzz} \\
0 & 0 & \chi_{zzzz} & 0 \\
0 & 0 & 0 & \chi_{zzzz} \\
\chi_{zzzz} & 0 & 0 & \chi_{zzzz}
\end{pmatrix}. \tag{1}
$$

In general, these tensor elements are complex. Using the in-plane ferromagnetic moment, $M = (M_x, M_y, 0)$, we may
write the following susceptibility tensor for the MD SHG process

\[
\chi^{\text{MD}(c)}_{ijkl}(\mathbf{M}) = \chi_{ijkl} \mathbf{M}_l ... \text{are very similar but the additional independent elements allow for a different magnetic response along the } x \text{ and } y \text{ axes.}
\]

The total SHG intensity below \( T_{N,1} \) is given by

\[
I(2\omega, \phi) = |A\hat{e}_{\text{out}}^{\text{EQ}(i)} \chi_{ijkl}^{\text{in}} \hat{q}_k \hat{e}_{\text{in}}^i + A\hat{e}_{\text{out}}^{\text{MD}(c)}(\mathbf{M}) \hat{e}_{klm}^j \epsilon_{klm} \hat{q}_l \hat{e}_{\text{in}}^i|^2 I(\omega)^2,
\]

where \( \hat{q} \) is the wavevector of incident light, \( \hat{e} \) is the polarization of incoming fundamental or outgoing second-harmonic light, \( I(\omega) \) is the intensity of the fundamental beam, \( A \) is a constant that depends on the polarization geometry, and \( \epsilon_{klm} \) is the Levi-Civita symbol. The MD contributions to the second-harmonic electric fields for the four polarization geometries are then given by

\[
E_{P1P1}^\omega \propto \sin^2 \theta (-M_y \cos \varphi - M_x \sin \varphi) \chi_{xxxx} \\
+ \cos^2 \theta \left(-M_y \chi_{xyxy} \cos^3 \varphi + M_x (-\chi_{xxxx} + \chi_{xyxy}) \cos^2 \varphi \sin \varphi \right) \\
+ M_y (-\chi_{xxxx} + \chi_{xyxy}) \cos \varphi \sin^2 \varphi - M_x \chi_{xyxy} \sin^3 \varphi
\]

(4)

\[
E_{S1P1}^\omega \propto \sin^2 \theta (M_y \cos \varphi + M_x \sin \varphi) \chi_{xxxx} \\
+ \cos^2 \theta \left(M_y \chi_{xyxy} \cos^3 \varphi + M_x (-\chi_{xxxx} - \chi_{xyxy}) \cos^2 \varphi \sin \varphi \right) \\
+ M_y (\chi_{xxxx} - \chi_{xyxy}) \cos \varphi \sin^2 \varphi + M_x \chi_{xyxy} \sin^3 \varphi
\]

(5)

\[
E_{P1S1}^\omega \propto \cos \theta \left(-M_x \chi_{xxxy} \cos^3 \varphi + M_y (-\chi_{xxxx} + \chi_{xyxy}) \cos^2 \varphi \sin \varphi \right) \\
+ M_x (-\chi_{xxxx} + \chi_{xyxy}) \cos \varphi \sin^2 \varphi + M_y \chi_{xxxy} \sin^3 \varphi
\]

(6)

\[
E_{S1S1}^\omega \propto \cos \theta \left(M_x \chi_{xxxy} \cos^3 \varphi + M_y (-\chi_{xxxx} + \chi_{xyxy}) \cos^2 \varphi \sin \varphi \right) \\
+ M_x (\chi_{xxxx} - \chi_{xyxy}) \cos \varphi \sin^2 \varphi - M_y \chi_{xxxy} \sin^3 \varphi
\]

(7)

In the case of normal incidence (\( \theta = 0^\circ \)), the EQ contribution goes to zero, leaving MD SHG with \( C_2 \) symmetry in the RA intensity pattern, consistent with Fig. 1c. At oblique incidence, the nonzero EQ SHG will interfere with the MD SHG, leading to RA patterns with \( C_1 \) symmetry, consistent with our observations (Fig. S1). We note that to achieve good fits to the magnetic-field-dependent RA patterns in Fig. 2a, we must assume that \( \chi_{ijkl} \) respects orthorhombic symmetry. In this case, \( \chi_{ijkl} \) possesses the same basic form as with the tetragonal case (Eq. 1) but more elements are independent of one another (D4 in Birss [5]). Therefore, the resulting SHG expressions are very similar but the additional independent elements allow for a different magnetic response along the \( x \) and \( y \) axes.
Below \( T_{N,I} \), a c-type electric dipole (ED) process, \( P^2_2 = \chi^{\text{ED}(c)}_{\text{s},ijk} E^\omega_j E^\omega_k \), from the surface magnetic point group \( m'm2' \) also becomes allowed. In this case, we proceed similar to the MD case, but \( \chi_{ijkl} \) becomes an axial tensor for the surface crystallographic structure (I4 in Birss [5]). The surface ED contributions to the second-harmonic electric fields for the four polarization geometries are given by

\[
E_{s,PP}^{2\omega} \propto \cos \theta \sin^2 \theta (M_y \cos \varphi + M_x \sin \varphi) (\chi_{zzzz} + 2\chi_{zzzy}) \\
+ \cos^3 \theta (M_y \chi_{xxxx} \cos^3 \varphi + M_x (-2\chi_{xxxy} - \chi_{yyxx}) \cos^2 \varphi \sin \varphi \\
+ M_y (-2\chi_{xxxy} - \chi_{yxxx}) \cos \varphi \sin^2 \varphi + M_x \chi_{xxxx} \sin^3 \varphi)
\]

(8)

\[
E_{s,SP}^{2\omega} \propto \cos \theta (-M_y \chi_{yyyy} \cos^3 \varphi + M_x (\chi_{xxxx} + 2\chi_{xxxy}) \cos^2 \varphi \sin \varphi \\
+ M_y (\chi_{xxxx} + 2\chi_{xxxy}) \cos \varphi \sin^2 \varphi - M_x \chi_{yyyy} \sin^3 \varphi)
\]

(9)

\[
E_{s,PS}^{2\omega} \propto \sin^2 \theta (-M_x \cos \varphi + M_y \sin \varphi) \chi_{zzzy} \\
+ \cos^2 \theta (M_x \chi_{yyyy} \cos^3 \varphi + M_y (\chi_{xxxx} + 2\chi_{xxxy}) \cos^2 \varphi \sin \varphi \\
+ M_x (-\chi_{xxxx} - 2\chi_{xxxy}) \cos \varphi \sin^2 \varphi - M_y \chi_{yyyy} \sin^3 \varphi)
\]

(10)

\[
E_{s,SS}^{2\omega} \propto -M_x \chi_{yyyy} \cos^3 \varphi - M_y (\chi_{yyyy} + 2\chi_{xxxy}) \cos^2 \varphi \sin \varphi \\
+ M_x (\chi_{yyyy} + 2\chi_{xxxy}) \cos \varphi \sin^2 \varphi + M_y \chi_{yyyy} \sin^3 \varphi
\]

(11)

By comparing Eq. (4)–(7) and Eq. (8)–(11), we see that the \( \varphi \)-dependence is similar. It is therefore not surprising that bulk MD and surface ED achieve comparable fits to the data. However, prior work has shown that the susceptibility for surface-magnetization-induced ED SHG is an order of magnitude weaker than that of crystallographic surface ED in 3d transition metal systems [6, 7]. In addition, for \( \text{Sr}_2\text{IrO}_4 \), which has much stronger spin-orbit coupling and magnetic moment (\( \sim 0.1 \mu_B/\text{Ir} \)), the magnetic surface ED term is still much weaker than the bulk MD term [8]. While we cannot rule out the presence of a magnetic surface ED process, this strongly suggests that the bulk magnetic MD term should dominate in \( \text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2 \).
3. RA-SHG above and below \( T_{N,1} \)

Figure S1 shows RA-SHG patterns for \( P_{in}-P_{out} \), \( S_{in}-P_{out} \), \( P_{in}-S_{out} \), and \( S_{in}-S_{out} \) channels on domain A and B above and below \( T_{N,1} \). Above \( T_{N,1} \), the patterns are consistent with an EQ process, \( \chi^{EQ(i)} \), from the reported bulk 4/\( mmm \) crystal structure. Below \( T_{N,1} \), all patterns are reduced to \( C_1 \) symmetry and fit well to a coherent superposition of a \( \chi^{EQ(i)} \) process from the bulk 4/\( mmm \) crystal structure and a magnetization-induced \( \chi^{MD(c)} \) process from the reported magnetic structure \( mm'm' \). Fitting expressions are provided in Section S2.

FIG. S1. RA-SHG patterns for all four polarization geometries taken above \( T_{N,1} \) at 400 K and below \( T_{N,1} \) at 295 K. The top (bottom) panel shows data for domain A (B). Solid curves are fits to the data using a \( \chi^{EQ(i)} \) (4/\( mmm \)) process for above \( T_{N,1} \) and coherent superposition of \( \chi^{EQ(i)} \) (4/\( mmm \)) and \( \chi^{MD(c)} \) (\( mm'm' \)) processes for below \( T_{N,1} \). The direction of the ferromagnetic moment \( \mathbf{M} \) is indicated on the right.
4. Thermal cycling studies and magnetic domains in free-standing sample

Figure S2 explores the origin of the magnetic domains with relative order parameter orientations of 90°. By tracking \( M \) at 295 K after thermal cycling through \( T_{N,1} \), we determine that the Earth’s magnetic field can train the moment direction in each domain (Fig. S2a). This may explain why we do not observe 180° domain walls, since they are likely very sensitive to small magnetic fields. We also observe that domains always prefer to orient along a fixed axis; changing the direction of Earth’s field can flip each domain by 180° but never by 90°. The data imply the existence of a uniaxial magnetic easy axis for each domain.

Thermal cycling measurements in Fig. S2b reveal pinned domain states and domain walls after thermal cycling through \( T_{N,1} \), though the particular configuration depends on the temperature as well as whether the sample has been cooled (from 400 K) or heated (from 80 K). One possibility is that the pinning effects arise from extrinsic factors, such as the stress from the sample mounting procedure. However, we also observe similar 90° domains in nearly free-standing samples (Fig. S2c), so it is likely that the pinning originates from characteristics of the samples themselves.

FIG. S2. a, Effect of thermal cycling above \( T_{N,1} \) on the direction of \( M \) for different Earth magnetic field directions. Each circle depicts \( M \) of domain A (red arrow) and B (blue arrow) at 295 K after thermal cycling to 400 K using a particular direction of the \( \sim 0.5 \) Oe Earth’s magnetic field (dashed green arrow and labeled angle). b, Domain pinning after thermal cycling. Each of the four panels show SHG images at the specified temperature after cooling (left column) from 400 K or after heating from 80 K (right column) for seven different thermal cycles (rows). Images acquired with vertical excitation polarization. c, SHG image from a different “free-standing” \( \text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2 \) sample showing large magnetic domains at 295 K with relative magnetization directions of 90°. The sample was loosely attached to double-sided tape at 295 K to minimize stress on it.
5. Magnetic field dependence of domains at room temperature

Figure S3 shows how the domain structure evolves under increasing in-plane magnetic fields at 295 K. The evolution from a 90° to 0° domain appears to take place through nucleation of small domains that grow and merge. We note that the 90° domain wall position does not show appreciable motion at low fields, which indicates a larger uniaxial anisotropy and a smaller domain wall susceptibility at room temperature compared to near $T_R$.

To obtain a rough estimate of the uniaxial anisotropy energy, one can calculate the energy needed to magnetize a domain in a direction perpendicular to its easy axis. Figure S3 shows that this occurs for $H_u \approx 500$ Oe, which corresponds to an energy of $mH_u \approx 2\text{neV}$, where $m$ is the magnetic moment per unit cell [9]. We note that this simple estimate ignores the effect of the fourfold anisotropy ($\sim 1\text{neV}$ [9]). Nevertheless, it gives an approximate upper bound for the uniaxial anisotropy energy scale near 295 K.

FIG. S3. SHG images at select magnetic fields applied along the magnetization direction of the dark domain. Images acquired with horizontal excitation polarization.
Comparison to conclusions drawn from prior magnetization experiments

It was originally proposed that the domain wall stability and dynamics in Sr$_2$Cu$_3$O$_4$Cl$_2$ may originate from entropy considerations [10], which can energetically favor the creation of domain walls. However, this explanation relies on there being interactions between many domain walls. Our SHG imaging experiments clearly show that the samples contain very few domain walls, so entropic terms cannot play a central role in the domain wall stability or magnetic field dependence. Instead, we have shown that the domain formation is controlled by a spatially dependent uniaxial anisotropy.

Subsequent theoretical work proposed that domain wall stability may be controlled by magnetoelastic effects that cause intrinsic internal stresses in antiferromagnets [11]. The stresses can then give rise to an in-plane uniaxial magnetic anisotropy, consistent with our observations. However, this intrinsic “de-stressing” effect should depend on the sample shape, and it is expected that samples with a square or rectangular shape possess a domain morphology that is regular and periodic in order to minimize the de-stressing energy [12]. The antiferromagnetic domains we observe do not show this regularity (Fig. S2). Furthermore, while de-stressing effects can give rise to a divergent domain wall susceptibility, it is not clear how they can produce domain-dependent spin reorientation. Therefore, intrinsic crystallographic distortions or inhomogeneous stresses from defects likely play a more important role in stabilizing the antiferromagnetic domains in Sr$_2$Cu$_3$O$_4$Cl$_2$. Based on the thermal cycling data in Section 4, these structural inhomogeneities should exist even above $T_{N,1}$. Further work is needed to better understand their microscopic nature.

In ref. [10], a Landau theory was used to explain the low-field magnetization behavior of Sr$_2$Cu$_3$O$_4$Cl$_2$. They found that the divergent magnetic susceptibility arises when the parameter $a \to 0$. However, the magnetization data show very similar behavior above and below $T_R$, which does not agree with the theory if it is assumed that $a$ crosses through zero (i.e., $a > 0$ for $T > T_R$ and $a < 0$ for $T < T_R$). Our temperature-dependent SHG imaging data (Fig. 3a) show that the domains A and B effectively swap their magnetic moments across $T_R$. This symmetry in the domain structure above and below $T_R$ implies that the potential energy landscape should be very similar above and below $T_R$, so $a$ should reach a minimum at $T = T_R$ instead of changing sign. Our work therefore further constrains the theory of ref. [10]. Moreover, our finding that the spin reorientation controls the divergent susceptibility suggests that $a$ must be related to the in-plane uniaxial anisotropy.
7. Full temperature dependence of magnetic domains

Figure S4 shows the magnetic domain structure temperature dependence. At intermediate temperatures, there is significant thermal hysteresis. In general, at lower temperatures, the crystal prefers a domain structure with smooth walls and a few large domains, which is consistent with exchange dominating relative to the anisotropy.

**FIG. S4.** Temperature-dependent SHG imaging starting from 385 K (top left), cooling (1st and 3rd rows, blue shading) to 80 K (bottom right), and then heating (4th and 2nd rows) back to 385 K. Significant thermal hysteresis is seen between approximately 130 K and 270 K. Images are acquired with vertical excitation polarization, so bright (dark) regions correspond to horizontal (vertical) magnetization direction. All images are plotted on the same color scale except for the 80 K image intensity, which was scaled down by 25%.
8. Observation of domain reorientation transition in an additional sample

Figure S5 explores SHG imaging on an additional sample, which shows the same essential features as the main sample. In particular, there exist magnetic domains with a relative orientation of 90°. The 90° domain wall becomes smoother at low temperatures. And when heating or cooling through \( \sim 100 \text{K} \), the sample becomes a single magnetic domain followed by a 90° domain reorientation with the domain wall position unchanged.

![Micrograph](image)

**FIG. S5.** a, Bright-field optical micrograph. b, SHG images at different temperatures showing the evolution of the 90° domain wall. Images acquired with horizontal excitation polarization. The bright and dark lines are due to the variation in scattering off terrace steps. c, Temperature dependence of the magnetic domains heating from 80 K to 140 K (top row) and cooling back to 80 K (bottom row). Red and blue arrows show the magnetization directions given by local RA-SHG measurements.
9. Field-direction dependence of single-domain magnetization near $T_R$

Figure S6 shows SHG images taken while thermally cycling through $T_R$ in the presence of a weak applied magnetic field. The magnetization direction of the single-domain state at $T_R$ is determined by the orientation of the applied field. This allows the preparation of a large-area (sample-sized, $\sim 1 \text{ mm}^2$ in this case) single-domain antiferromagnet.

![SHG images](image)

FIG. S6. Temperature dependence of magnetic domains at selected temperatures across the $T_R$ transition with an applied magnetic field of 2 Oe in the downward, (a), or rightward, (b), directions. The single-domain state close to $T_R$ possesses magnetization in the downward (rightward) directions for (a) (b), as confirmed by local RA-SHG measurements. Images acquired with horizontal excitation polarization.
[1] S. Noro, T. Kouchi, H. Harada, T. Yamadaya, M. Tadokoro, and H. Suzuki, Magnetic properties of Ba$_2$Cu$_3$O$_4$Cl$_2$ single crystals, Mater. Sci. Eng. B 25, 167 (1994).

[2] J. W. Harter, L. Niu, A. J. Woss, and D. Hsieh, High-speed measurement of rotational anisotropy nonlinear optical harmonic generation using position-sensitive detection, Opt. Lett. 40, 4671 (2015).

[3] A. de la Torre, K. L. Seyler, L. Zhao, S. D. Matteo, M. S. Scheurer, Y. Li, B. Yu, M. Greven, S. Sachdev, M. R. Norman, and D. Hsieh, Mirror symmetry breaking in a model insulating cuprate, Nat. Phys. 17, 777 (2021).

[4] A. de la Torre, S. Di Matteo, D. Hsieh, and M. R. Norman, Implications of second harmonic generation for hidden order in Sr$_2$CuO$_4$Cl$_2$, Phys. Rev. B 104 (2021).

[5] R. R. Birss, Symmetry and magnetism (North-Holland Pub. Co., 1964).

[6] J. Reif, J. C. Zink, C. Schneider, and J. Kirschner, Effects of surface magnetism on optical second harmonic generation, Phys. Rev. Lett. 67, 2878 (1991).

[7] A. Kirilyuk and T. Rasing, Magnetization-induced-second-harmonic generation from surfaces and interfaces, J. Opt. Soc. Am. B, JOSAB 22, 148 (2005).

[8] K. L. Seyler, A. de la Torre, Z. Porter, E. Zoghlin, R. Polski, M. Nguyen, S. Nadj-Perge, S. D. Wilson, and D. Hsieh, Spin-orbit-enhanced magnetic surface second-harmonic generation in Sr$_2$IrO$_4$, Phys. Rev. B 102, 201113 (2020).

[9] F. C. Chou, A. Aharony, R. J. Birgeneau, O. Entin-Wohlman, M. Greven, A. B. Harris, M. A. Kastner, Y. J. Kim, D. S. Kleinberg, Y. S. Lee, and Q. Zhu, Ferromagnetic moment and spin rotation transitions in tetragonal antiferromagnetic Sr$_2$Cu$_3$O$_4$Cl$_2$, Phys. Rev. Lett. 78, 535 (1997).

[10] B. Parks, M. A. Kastner, Y. J. Kim, A. B. Harris, F. C. Chou, O. Entin-Wohlman, and A. Aharony, Magnetization measurements of antiferromagnetic domains in Sr$_2$Cu$_3$O$_4$Cl$_2$, Phys. Rev. B 63, 134433 (2001).

[11] H. V. Gomonay, I. G. Korniienko, and V. M. Loktev, Theory of magnetization in multiferroics: Competition between ferromagnetic and antiferromagnetic domains, Phys. Rev. B 83, 054424 (2011).

[12] H. V. Gomonay and V. M. Loktev, Shape-induced phenomena in finite-size antiferromagnets, Phys. Rev. B 75, 174439 (2007).