Giant magnetic in-plane anisotropy and competing instabilities in Na$_3$Co$_2$SbO$_6$

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(Dated: October 18, 2022)

We report magnetometry data obtained on twin-free single crystals of Na$_3$Co$_2$SbO$_6$, which is considered a candidate material for realizing the Kitaev honeycomb model for quantum spin liquids. Contrary to a common belief that such materials can be modeled with the symmetries of an ideal honeycomb lattice, our data reveal a pronounced two-fold symmetry and in-plane anisotropy of over 200%, despite the honeycomb layer’s tiny orthorhombic distortion of less than 0.2%. We further use magnetic neutron diffraction to elucidate a rich variety of field-induced phases observed in the magnetometry. These phases manifest themselves in the paramagnetic state as diffuse scattering signals associated with competing ferro- and antiferromagnetic instabilities, consistent with a theory that also predicts a quantum spin liquid phase nearby. Our results call for theoretical understanding of the observed in-plane anisotropy, and render Na$_3$Co$_2$SbO$_6$ a promising ground for finding exotic quantum phases by targeted external tuning.

Frustrated magnetic systems have the potential to realize exotic quantum spin liquids (QSLs) [1–3]. The exactly solvable Kitaev model [4], which features bond-dependent Ising interactions between effective spin-1/2 neighbors on a honeycomb lattice, has motivated intensive QSL research in recent years. As a guiding principle, it is believed that such interactions can be realized in spin-orbit coupled Mott insulators [5–8]. Solid-state platforms for realizing the Kitaev model have evolved over the years from 5d iridium [9] to 4d ruthenium [10] compounds, and most recently to 3d cobaltates [11–15]. Despite a potential drawback of weaker spin-orbit coupling, the cobaltates are believed to have relatively weak non-Kitaev and further-neighbor interactions compared to their 4d and 5d counterparts [11,12,15].

As a reality of nature, essentially all candidate Kitaev magnets have long-range order at low temperatures [6,10,20]. This has been attributed to the presence of interactions beyond the Kitaev model [9,21,22], such that additional tuning is needed to overcome the ordering tendency, e.g., by using thermal disorder and external fields [13,81,37], in order to recover QSL behaviors. To this end, it is important to know how close the microscopic model of a given system is to an anticipated QSL phase. The cobaltate Na$_3$Co$_2$SbO$_6$ is promising in this regard, as its model is inferred to situate near boundaries between ferromagnetic (FM), antiferromagnetic (AFM), and QSL phases [14]. This understanding is supported by the relatively low Néel temperature ($T_N$) and small saturation fields of the system compared to its sister compound Na$_3$Co$_2$TeO$_6$ [16,38,40].

Notably, while non-Kitaev and further-neighbor terms are widely considered in theoretical constructions [21,23,30,11,15], the low, monoclinic symmetry of many candidate materials, including Na$_2$IrO$_3$ [17,18], α-RuCl$_3$ [19,36], and Na$_3$Co$_2$SbO$_6$ [16], is often neglected. Even though originating from inter-layer stacking, the monoclinicity also means lack of $C_3$ rotational symmetry of the crystal field and a transition-metal ion’s interactions with its neighbors in the same layer. Approximating the interactions with their bond-averaged values [30] is an assumption commonly taken but rarely checked. Two cobaltates, Na$_2$Co$_2$TeO$_6$ [16] and BaCo$_2$(AsO$_4$)$_2$ [29], have the $C_3$ symmetry, but their zero-field ground states are reported to be dissimilar to the monoclinic systems [20,47,48], and no consensus has been reached concerning the microscopic models [49,50]. The lack of $C_3$ symmetry should result in magnetic in-plane anisotropy, as has been observed in α-RuCl$_3$ [55]. However, the anisotropy is found to vary considerably [55,57], possibly due to sample-dependent monoclinic domain population.

Here, we report a systematic study of Na$_3$Co$_2$SbO$_6$ aided by the use of twin-free crystals. Magnetometry reveals at low temperatures a strong $C_2$ in-plane anisotropy, in both the low-field susceptibility and the critical fields for switching toward a series of field-induced
They have a well-defined T and C X and ultimately verified with screening with Raman spectroscopy (Fig. S7 in [58]), which closely compete and produce distinct diffuse states. They signify a series of AFM and FM instabilities, which completely compete and produce distinct diffuse scattering above T_N in zero field. These results render Na_3Co_2SbO_6 a highly intriguing system with the potential to realize exotic phases under targeted tuning.

**MAGNETOMETRY ON TWIN-FREE CRYSTALS**

Figure 1(a-b) presents the crystal and reciprocal-space structure of Na_3Co_2SbO_6, which has the same space group (C2/m) as α-RuCl_3 [19, 10]. A peculiarity common to both structures is in the stacking: adjacent honeycomb layers are offset from each other by a/3, hence we have a/c ≈ −3 cos β, with [a, b, c] = [5.371, 9.289, 5.653] Å and β = 108.6° in Na_3Co_2SbO_6 [39]. Similar to α-RuCl_3 [10], the orthorhombic distortion in the honeycomb layer of Na_3Co_2SbO_6 is tiny: the distortion is measured as √3a/b − 1 < 0.002 [39, 10]. Yet, we find that such a small distortion removes the overall S_6 and C_3 symmetries. We will next show the far-reaching consequences on the magnetism using a rare growth product: twin-free single crystals. Such crystals can be found by screening with Raman spectroscopy (Fig. S7 in [58]), and ultimately verified with X-ray diffraction (Fig. 1(c)). They have a well-defined T_N of about 6.6 K (Fig. S8 in [58]) with sample-dependent variation of no more than 1 K possibly caused by structural imperfections. The variation is considerably smaller than in the literature [10, 55, 56]. This is in line with the facts that our best crystals have very few stacking faults [Fig. 1(c)] compared to a previous report [39], and that the observed Bragg intensities agree well with calculation based on the ideal crystal structure [Fig. 1(d)]. Our further refinement attempts suggest that the agreement cannot be improved by introducing anti-site disorder between Co and Sb [39]. While the data do not allow us to rule out disorder in the Na layers [39], we consider its role to be minor because such disorder is expected to cause stacking faults which are rare in our crystals.

Figure 2(a) shows how a pronounced a-b anisotropy develops in the magnetic susceptibility upon cooling. Far above T_N, we observe a ~10% anisotropy consistent with the anisotropy of the g-factor, g_y > g_x (Figs. S9, S10 in Table S1 in [58]), as is also seen from high-field magnetization where moments are nearly polarized [Fig. 2(b)]. The anisotropy drastically increases to over 200% near T_N (see Fig. S9 in [58] for out-of-plane anisotropy), which signifies the role of the fluctuations – the moments respond much more strongly in the easy direction nearly parallel to the developing order parameter [59]. This understanding also explains why the anisotropy is reversed below T_N. The reversal is no longer observed in B = 2 T (Fig. S9 in [58]) which is large enough to overcome the AFM order. We make two remarks here to relate to previous works: (1) The a-axis response clearly drops below T_N.
FIG. 2. (a) DC magnetic susceptibility measured in fields of 0.1 T along the a and b axes. Inset displays the susceptibility versus in-plane angle at 2 K and 10 K (dashed lines in the main panel), showing highly pronounced $C_2$ profiles which reverse the long and short axes across $T_N$. (b) Magnetization versus field data (solid lines) reveal two transitions along both a and b at 2 K. The critical fields ($B_{c1}$, $B_{c2}$) are determined from the derivative (dashed lines) as (0.82 T, 1.76 T) for a and (0.52 T, 1.37 T) for b, with an uncertainty of ±0.02 T. Data are displayed for both field-up and -down sweeping directions, which are nearly identical except near $B_{c1}$, indicating a hysteretic nature of the transition. (c) In-plane angle dependence of magnetization versus field (left) and the field-derivative (right) at 2 K. Measurement at each angle is performed over a field-up sweep, and the field is decreased to zero before moving to the next angle. It is seen that $B_{c1}$ splits away from a and b. (d) Summary of the result in (c) after 180° symmetrization. Empty arrows are a reference for the field directions in Fig. 4.

The competition between anisotropic interactions and the applied field is more clearly seen in the magnetization at 2 K [Fig. 2(b-d)], where our twin-free sample reveals a wealth of remarkable features unnoticed in previous works [16, 38–40, 55]. Two well-separated transitions are observed along both a and b, at critical fields [$B_{c1}$ and $B_{c2}$, Fig. 2(b)] that again differ strongly between the two directions. The lower-field transition is clearly hysteretic, as indicated by the magnetization’s dependence on the field-sweeping direction. It further splits into two hysteretic transitions, the critical fields of which we refer to as $B_{c1,low}$ and $B_{c1,high}$, when the field is applied in-plane but away from the high-symmetry a and b axes [Fig. 2(c-d)]. The lowest $B_{c1,low}$ value is found at about 15° away from b. The highest $B_{c1,high}$ can approach $B_{c2}$ and become no longer visible from the data, over a range of field directions between 10° and 30° away from a. Hence, very unexpectedly, there is nearly no 6-fold symmetry in the results, including in the nearly field-polarized state at 2 T (Fig. S9 of [58]). The large magnitude of a-b anisotropy sharply contrasts with the $C_3$-symmetric sister compound Na$_3$Co$_2$TeO$_6$, where the magnetic responses along a and a$^*$ are reasonably similar [37, 50]. We note that quenched disorders may play a role in the experimentally observable anisotropy in Na$_3$Co$_2$SbO$_6$. By heating up a twin-free crystal to 600 °C at 20 °C/min, staying for 1 hour, and quenching the crystal in liquid nitrogen, we found the susceptibility anisotropy ratio [$\chi_b/\chi_a$, see Fig. 2(a)] to change from 1.81 to 1.78 at 10 K, and from 0.53 to 0.75 at 2 K. The two field-induced transitions [Fig. 2(b)] at 2 K also became considerably smeared out. According to X-ray diffraction, the crystal remained twin-free after the quenching.
FIG. 3. (a) $Q_\perp$-integrated diffraction data measured at 6K and in zero field. Gray hexagons indicate 2D Brillouin zones. Color-coded crosses and arrows indicate locations of line cuts in (b-d). Dashed box indicates the restricted data coverage in Fig. 4. (b) Line cuts along $Q_\perp$ through nuclear and magnetic Bragg peaks. The nuclear peaks at $Q_\perp = 0$ and $\pm 1/3$ are contributed by physical reflections $(0, 2b^*, 0)$ of Sa and $(a^*, b^*, 0)$ of S60, respectively. The magnetic peaks at $Q_\perp = \pm 1/6$ are contributed by reflections $(\pm a^*/2, \pm b^*/2, 0)$ of both domains. (c-d) Line cuts along $Q_a$ and $Q_b$ through the magnetic reflections. The map in (a) has been symmetrized, whereas the line cuts in (b-d) are not symmetrized.

MAGNETIC NEUTRON DIFFRACTION

We next turn to the intermediate state(s) between $B_{c1}$ and $B_{c2}$. While the step-like and hysteretic (near $B_{c1}$) behaviors hinted at a spin-flop origin [16, 38–40], our observation of the transitions along both a and b (and everywhere in between) defies such an interpretation. The result in Fig. 2(c) is furthermore independent of field or temperature history, precluding the relevance of magnetic domain repopulation [34, 59]. Motivated by the fact that the magnetization above $B_{c1}$ resembles “plateau” phases found in low-dimensional frustrated magnets [60][63], i.e., it reaches about 1/3 and 1/2 of saturation [Fig. 2(b)] for $B_\parallel b$ and $B_\parallel a$, respectively, we have performed neutron diffraction in magnetic fields to explore this possibility. The experiment was done on a co-aligned but twinned array of crystals with their $c^*$ axis horizontal, such that the vertical field was along a for 1/3 of the sample (Sa), and at 60° from a for the rest (S60), see illustrations in the upper-left corner of Fig. 4. In spite of the twinning, there is no ambiguity in the domain origin (Sa or S60) of the field-evolving signals, under the assumption that magnetization and diffraction see the same transitions (Fig. S1 in [58]). According to magnetization [Fig. 2(d)], all transitions occur below (above) 1 Tesla for S60 (Sa). The difference is illustrated by the thick horizontal arrow diagrams in the upper half of Fig. 4.

We use here a “hybrid” orthogonal coordinate system for the reciprocal space, illustrated in Fig. 1(b). Wave vectors are denoted as $(Q_a, Q_b, Q_\perp)$, with $Q_b$ and $Q_\perp$ in units of $b^*$ and $c^*$, respectively. $Q_a$ is in units of $a^*$ projected onto the real-space a-axis, and it is parallel to the vertical field. This coordinate system is convenient for describing a twinned sample, because the twinning features $C_6$ rotations within the ab-plane, and mixes up $Q_a$ and $Q_b$ while leaving $Q_\perp$ intact. We will write $a^*$, $b^*$, and $c^*$ explicitly when we refer to the (physical) monoclinic indices. A table reference for transforming between the two indexing systems can be found in Table S3 [58]. To give some examples, nuclear Bragg peaks at $(0, 2, \pm 1/3)$ in the hybrid notation [Fig. 3(a-b)] are associated with physical indices $(\pm a^*, \pm b^*, 0)$ of S60. In zero field, the AFM wave vectors $(\pm a^*/2, \pm b^*/2, 0)$ [39] of S6 transform into $(\pm 0.5, \pm 0.5, \pm 1/6)$ in the hybrid notation [Fig. 3(b-d)], producing diffractions at four $(Q_a, Q_b)$ locations, whereas the same diffractions from the two copies of S60 (Fig. 4) are expected at six $(Q_a, Q_b)$ locations. All of these AFM wave vectors have $|Q_\perp| = 1/6$ as indicated by empty symbols in Fig. 4 While the data
FIG. 4. The upper half illustrates the behavior of two sample parts \( S_a \) or \( S_{60} \), see legends on the left and text) as the field passes through their respective phase boundaries [Fig. 2(d)]. \( S_a \) is uniquely defined as per the in-plane orientation, and it contributes diffractions indicated by blue circles. \( S_{60} \) further contains two parts that are related by 180° rotation about the field, which contribute diffractions indicated by left- and right-pointing orange triangles. Empty and filled symbols indicate AFM\(_{1/2}\) and AFM\(_{1/3}\) wave vectors (see text), respectively, which are measured by restricting \( Q_{\perp} \) to \([-0.2, 0.2]\) and \([0.3, 0.7]\), respectively. Miniatures of diffraction data (measured at \( T = 0.25 \) K) are displayed in the bottom row of the illustration in a left-right split fashion, where the observed diffraction peaks (encircled by dashed ellipses centered at their expected locations, some of which fall beyond the data coverage) are fully consistent with the “\( S_a + S_{60} \)” combination of the cartoons. Solid and dashed hexagons are the first Brillouin zone and the 2/3 of it, respectively. In the lower half, we display diffraction data measured at three selected fields, where the solid and dashed hexagons have the same meaning as in the upper-half illustration. Note that the vertical (\( || Q_a \)) data coverage is limited compared to that in Fig. 3, magnetic diffractions above and below the \( Q_a = 0 \) (horizontal) plane are partly observed. This is enabled by vertical focusing optics [58], which relaxes the momentum resolution and elongates diffraction features in the \( Q_a \) direction.

The results in Fig. 4 can be summarized as follows: the AFM wave vectors switch from \((\pm a^*/2, \pm b^*/2, 0)\) at \( B = 0 \), to \((\pm a^*/3, \pm b^*/3, \pm c^*/3)\) above \( B_{c1} \), and eventually no AFM is left above 2.2 T (see Methods and Figs. S1-S13 in [58] for additional evidence for the peak indexing). We therefore refer to the zero-field and the
intermediate states as AFM$^1_2$ and AFM$^1_3$, respectively. The AFM$^1_2$ wave vectors all have $Q_L = 4/9$ or $5/9$ [58], which allows the diffraction peaks to be observed separately from the AFM$^1_3$ ones by restricting $Q_L$ in the experiment (Fig. 4). Notably, due to the low-symmetry field direction for $S_{60}$, the wave vectors in this part of the sample do not switch together. Instead, the switching occurs in two steps for the diffraction peaks situated on the sample do not switch together. Instead, the switching in external in-plane fields, $N_a$, as expected for a field-polarized state. The wave-vector switch supports the idea that AFM$^1_2$ is a ferrimagnetic phase with an enlarged 2D cell compared to AFM$^1_3$, such as “↑↑↓” compared to “↑↓”. With the understanding that AFM$^1_2$ features zigzag order [39], which consists of alternating FM chains running along zigzag lines of the honeycomb lattice, AFM$^1_3$ could feature alternating wide and narrow FM ribbons and chains. An illustration of such FM chains without the alternating correlation can be found in Fig. 6(a). The two-step transitions of $B_{c1}$ and the single-step transition of $B_{c2}$ introduce some restrictions on the magnetic structure, which we discuss in [58]. We further note that $B_{c2}$ does not necessarily mark entrance into a field-polarized state, certainly not for $S_{60}$, since the AFM$^1_2$ diffraction peaks persist above $B_{c2}$ (Fig. 4). The nature of $B_{c2}$ will be reported elsewhere. Further above $B_{c2}$, all magnetic diffraction eventually coincide with nuclear Bragg peaks, as expected for a field-polarized state.

Taken together, the results show that at very low $T$ and in external in-plane fields, $Na_3CoSbO_6$ sequentially goes through magnetic states characterized by the M-point, the “$\frac{2}{3}M$”-point, and eventually the zone-center Γ-point, forming an evolution along the Γ-M lines [Fig. 1(b)]. The direction of the field affects only when, but not whether, the transitions would occur. It is therefore tempting to think that the system possesses competing AFM-FM instabilities with wave vectors lined up along Γ-M. In Fig. 5 we use variable-$T$ neutron diffraction to show that this is indeed the case. The experiment was performed on a twinned sample, in zero magnetic field. The most remarkable observation is found at 10 K [Fig. 5(c)]: we see distinct hexagonal-star-shaped diffuse scattering, which “flows” into the long-range magnetic Bragg peaks at the M-points upon further cooling [Fig. 5(b)]. The observed star consists of six narrow streaks which precisely cover the Γ-M lines. In a twin-free sample, the number of streaks would likely be four [Fig. 5(b)], which would help explain the giant in-plane magnetic anisotropy, and it warrants further experimental confirmation. The streaks are, in fact, quasi-2D objects in reciprocal space with only weak dependence on $Q_L$ (Fig. S14 in [58]). They correspond to quasi-1D correlations in real space (Fig. 6 further discussed below), and can be viewed as a counterpart of rod-like diffuse scattering in Yb$_2$Ti$_2$O$_7$ [64, 65], which has been attributed to coexisting FM and AFM correlations [66, 67]. Below $T_N$, the body of the star is depleted, including the FM-like diffuse scattering near Γ [Fig. 5(a)]. Such a temperature-evolution, together with the field-evolution at low $T$ (Fig. 4), signifies a close competition between a variety of AFM and FM instabilities, with or without thermal disorder. Indeed, the M-point AFM order might be energetically favored in zero field by only a small margin. We have further found evidence for a weak field-trainable net moment in a twin-free sample (Fig. S15 in [58]), which supports an incipience of the ferromagnetism.
FIG. 6. (a) A random placement of ferromagnetic zigzag chain segments on a honeycomb lattice. Blue, red, and black circles indicate spin-up, spin-down, and spin-less sites, respectively, which contribute positive, negative, and zero neutron-scattering amplitudes in the simulation. (b) Fourier component squared of the scattering amplitudes in the field of view in (a), computed on a fine 2D momentum grid. (c) Neutron diffraction intensities at 10 K, similar to those in Fig. 5(c) but acquired with a higher incident energy (Table S8 in [58]). Data are $Q_{\perp}$-integrated, and have been $C_6$-symmetrized for better comparison with (b). Black hexagons indicate 2D Brillouin zones. Sharp diffraction spots are nuclear Bragg peaks. Halo-like diffuse intensities in the first and part of the second zones are $T$-independent scattering from the sample holder and glue (Cytop).

DISCUSSION

Our results motivate further exploration of exotic quantum phases in Na$_3$Co$_2$SbO$_6$, as well as in extended Kitaev and related theoretical models. Magnetic field-induced phases in candidate Kitaev materials have been under intense research in recent years [20, 34, 37, 50, 56, 68–76], and the magnetization’s step-like transitions into and out of the intermediate states in Fig. 2 resemble some of the reports [20, 37, 56], even though the wave-vector switching behavior might not be the same [20, 56]. These results suggest that the candidate materials commonly possess multiple magnetic instabilities – a hallmark of frustration. Our findings are consistent with the view that Na$_3$Co$_2$SbO$_6$ is close to a trisecting point of FM, AFM, and QSL phases [13], yet the pronounced in-plane anisotropy clearly adds complexity and novelty to the previous understanding. Specifically, given the anisotropy, uniaxial strains both perpendicular [13] and parallel to the honeycomb layers might help promote QSL physics.

Meanwhile, the $\Gamma$-$M$ characteristics of the ordering wave vectors and diffuse scattering imply a particular combination of competing instabilities, which are not commonly seen in model systems [42]. In Fig. 6, we show that the star-shaped diffuse scattering pattern can be well-simulated by FM zigzag chains randomly placed on a honeycomb lattice. Each star streak in $Q$ space is contributed by chains in real space that run perpendicular to the streak. Because neutron scattering probes magnetic moments perpendicular to $Q$, we infer that the magnetic moments in the FM chains point largely parallel to the chains – similar to those in a typical zigzag magnetic structure [15, 17]. Given that the AFM order below $T_N$ is preceded by the short-range FM chains above $T_N$, a plausible scenario is that the system’s leading magnetic interactions are strongly in favor of individual FM-chain formation, yet at the same time, they are weakly in favor of an alternating side-by-side arrangement of the chains, i.e., against the formation of 2D FM order. Together with our inference of the moment direction above, the scenario echoes with the idea of bond-dependent anisotropic interactions, which is at the core of the Kitaev and related models.

We further notice that, among three types of parameters that are commonly considered for explaining the zigzag order [42], our result appears to be consistent with the expected behaviors of models with a leading nearest-neighbor symmetric off-diagonal interaction term, $\Gamma_1 > 0$. This is because for a given nearest-neighbor pair, the $\Gamma_1 > 0$ term favors FM alignment of the spin component parallel to the bond, but AFM alignment of the component parallel to the bond and the Ising axis of the Kitaev term. Together with the geometry of the honeycomb lattice, the $\Gamma_1 > 0$ term can thus explain both the FM chains’ formation tendency and their resistance to form 2D FM order. Indeed, in the Appendix of Ref. [42] we find a discussion of such models’ several similar behaviors compared to our observations, including the formation of AFM$_1^2$ order and competing instabilities at a star-shaped set of wave vectors. Another major feature of such models is their demonstrated ability to produce large magnetic-response anisotropy without a highly anisotropic $g$ tensor [42]. We thus expect our results to motivate further theoretical research of frustrated magnetism in the off-diagonal models [77, 79], some of which may have a QSL ground state [79].

To conclude, we have elucidated the field-induced
phases and competing instabilities in the quantum magnet Na$_2$Co$_8$SbO$_6$, and uncovered an unexpectedly large magnetic anisotropy. The results indicate exotic magnetic phases and render this system highly promising for further explorations using targeted external tuning. The results also stimulate future theoretical research of spin-orbit-coupled quantum magnets.

We are grateful for technical support by Qizhi Li and Jianping Sun, and for discussions with Wenjie Chen, Ji Feng, L. Janssen, G. Khalilluin, V. Kocsis, Huimei Liu, Qiang Luo, A. U. B. Wolter, and Shilong Zhang. The work at Peking University was supported by the National Basic Research Program of China (Grant Nos. 2021YFA1401900 and 2018YFA0305602) and the NSF of China (Grant Nos. 12061131004, 11874069, and 11888101). The work at Brookhaven National Laboratory was supported by Office of Basic Energy Sciences (BES), Division of Materials Sciences and Engineering, U.S. Department of Energy (DOE), under contract DE-SC0012704. X. L. further acknowledges support from China Postdoctoral Science Foundation (Grant No. 2020M680179). A portion of this research used resources at Spallation Neutron Source, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory. One of the neutron scattering experiments was performed at the MLF, J-PARC, Japan, under a user program (No. 2020B0148).

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Supplemental Material for
“Giant magnetic in-plane anisotropy and competing instabilities in Na$_3$Co$_2$SbO$_6$”

METHODS

Single crystal growth. Single crystals of Na$_3$Co$_2$SbO$_6$ were synthesized with a flux method similar to the method for growing Na$_2$Co$_2$TeO$_6$ [87]. Highest-quality crystals were of a dark purple color and a flaky hexagonal shape [Fig. S7(a)]. The correspondence between sample shape and the cobalt honeycomb sub-lattice is shown in Fig. S7.

Single-crystal X-ray diffraction. The measurements were performed with a custom-designed instrument equipped with a Xenocs Genix3D Mo K$_\alpha$ (17.48 keV) X-ray source, which produced a beam-spot diameter of 150 $\mu$m at the sample position with 2.5 $\times$ 10$^7$ photons/sec. The samples were mounted on a Huber four-circle diffractometer. A highly sensitive PILATUS3 R 1M solid-state pixel array detector (with 980 $\times$ 1042 pixels, 172 $\mu$m $\times$172$\mu$m per pixel) was used to collect the diffraction signals. Three-dimensional mapping of the reciprocal space was achieved by taking diffraction images in 0.1$^\circ$ sample-rotation increments. Due to a small non-monochromaticity of the X-rays, each observed Bragg peak consisted of closely-spaced $K_a1$ and $K_a2$ components, and was further accompanied by a weak $K_b$ peak and a radial tail [red dashed lines in Fig. 1(c)].

Raman spectroscopy screening for twin-free samples. The measurements were performed under a microscope in a confocal backscattering geometry, using a Horiba Jobin Yvon LabRAM HR Evolution spectrometer equipped with 1800 gr/mm gratings and a liquid-nitrogen-cooled CCD detector. A He-Ne laser with $\lambda = 632.8$ nm was used for excitation (with 1.2 mW laser power). The measurements were performed at room temperature, in air, and on crystal surfaces parallel to the $ab$-plane. Linear polarizations of both incident and scattered photons were set parallel to each other and along twelve in-plane directions, as illustrated in Fig. S7(a).

Specific-heat measurement and magnetometry. Specific-heat measurements were performed with a Quantum Design PPMS, using a relaxation method. DC magnetometry was performed with a Quantum Design MPMS equipped with a sample rotator. The angle dependence of magnetization in Fig. 2(c) was measured in a sweep-field mode (+3 Oe/sec) after initially cooling the sample in zero field. The field was reset to zero between adjacent orientations without thermal cycling. The systematic results in Fig. 2(c) indicate a lack of dependence on the field history.

Neutron diffraction on a twin-free sample. The experiment was performed on the SIKA cold neutron triple-axis spectrometer at the Australian Nuclear Science and Technology Organization (ANSTO) [83]. A twin-free crystal was mounted with reciprocal vectors $[K\alpha^*, K\beta^*, Lc^*]$ in the horizontal scattering plane, and the measurement was performed with $k_i = k_f = 1.97$ Å$^{-1}$ neutrons and a beryllium filter. In this experiment, only diffractions in the horizontal scattering plane could be accessed, due to the use of a cryomagnet which did not allow for sample tilting. The applied vertical fields were at 60$^\circ$ (anticlockwise) from the $a$-axis [Fig. S11(c)]. This geometry made the studied sample equivalent to S$_{60}$ discussed in main text, and allowed us to access the $[1/2a^*, 1/2b^*, 0]$ reflection in the AFM$_1^4$ state, as well as the $[2/3a^*, 2/3b^*, -1/3c^*]$ reflection in the AFM$_2^4$ state.

Neutron diffraction on twinned samples. The neutron diffraction experiments displayed in Figs. 3-6 of main text were performed with twinned crystal arrays, which were co-aligned in the $ab$-plane on aluminum plates with a hydrogen-free adhesive (Cytop). 1/3 of the sample mass belonged to S$_6$ (see text), for which the vertical direction was parallel to the $a$-axis, and the corresponding horizontal scattering plane was [0, $K\beta^*$, $Lc^*$]. The other 2/3 of the sample belonged to S$_{60}$, for which the vertical direction was at 60$^\circ$ from the $a$-axis and the horizontal plane was $[K\alpha^*, K\beta^*, Lc^*]$ (or symmetry equivalent). As explained in main text and below, we use $(Q_a, Q_b, Q_\perp)$ to denote wave vectors. $Q_a$ is along the vertical direction, and the horizontal plane is $(Q_b, Q_\perp)$. $(Q_a, Q_6)$ in Fig. 3(a), Fig. 4 and Fig. 5(c) of main text denotes 2D wave vectors in the vertical (real-space) $ab$-plane.

The diffraction experiment in magnetic fields (Fig. 4 of main text) was performed on the HYSPEC time-of-flight spectrometer at the SNS, Oak Ridge National Laboratory [81], using a helium-3 insert and a 14 T vertical-field cryomagnet as sample environment. Equipped with the incident beam-focusing optics, the narrow vertical opening
angle of ±7° of the cryomagnet allowed us to detect the magnetic diffractions out of the horizontal scattering plane. We used a relatively high incident neutron energy $E_i = 35$ meV to have the full out-of-plane access for acquiring the data in Figs. 4 and S10 and a relatively low incident neutron energy $E_i = 15$ meV for accurate peak indexing Fig. S13. The sample was 0.5 gram in total mass, and had a full mosaic spread of about 2.3°. Diffraction data were acquired by rotating the sample over a 78° range in 0.5° steps, resulting in a three-dimensional data set, which we further symmetrize with $Q_b$ and $Q_\perp$ mirror operations for plotting.

The diffraction experiment at variable temperatures without magnetic field. (Figs. 3, 5, 6 of main text) was performed on the 4SEASONS time-of-flight spectrometer at the MLF, J-PARC, Japan [82]. The sample was 0.7 gram in total mass with a full mosaic spread of about 2.7°. The data in Figs. 3(a), 5(c) 6(c) and S12 were collected at fixed temperatures by rotating the sample over an 85° range in 1° steps. The data in Fig. 5(a-b) were acquired with a “sit-and-count” method, i.e., the sample was rotated to fixed orientations, and counting was continuously performed during a slow warm-up of the sample at a rate of about 0.022 K/min. Data were reduced and analyzed with the Utusemi [83] and Horace [84] software packages.

The time-of-flight scattering experiments generated high-dimensional data sets, which were sliced into lower dimensions for plotting. Detailed measurement conditions and slicing restrictions can be found in Table S2.

**Conversion between coordinate systems for the reciprocal space.** A fully-twinned sample contains all $C_6$-related counterparts of any chosen monoclinic domain, where the $C_6$ rotation is about the normal direction of the $ab$-plane, or $c^*$. It is straightforward to show that, if a monoclinic domain has a physical wave vector of $[Ha^*, Kb^*, Lc^*]$, the wave vector will be observed at a total of six positions in the $(Q_a, Q_b, Q_\perp)$ coordinate system: $(H, K, L+H/3)$, $(H/2+K/2, -3H/2+K/2, L+H/3)$, $(-H/2+K/2, -3H/2-K/2, L+H/3)$, $(-H, -K, L+H/3)$, $(-H/2-K/2, 3H/2+K/2, L+H/3)$, $(H/2-K/2, 3H/2-K/2, L+H/3)$. Note that they share the same $Q_\perp$. It is straightforward to verify that all magnetic peaks in Fig. S12 in zero field are consistent with $Q = [\frac{1}{2}a^*, \frac{1}{2}b^*, 0] + G$ and symmetry equivalent, and that all magnetic peaks in Fig. S13 above $B_{c1}$ are consistent with $Q = [\frac{1}{2}a^*, \frac{1}{2}b^*, \frac{1}{2}c^*] + G$ and symmetry equivalent, where $G$ is a reciprocal lattice vector. A reference table for the conversion between the coordinate systems can be found in Table S3.

**Discussion of magnetic structure.** Recent indications of triple-$q$ order [47, 48] in the sister compound Na$_2$Co$_2$TeO$_6$ motivate us to consider a multi-$q$ possibility here as well. In this regard, the two-step transitions of $B_{c1}$ (e.g., in Na$_6$O) are intriguing. In zero field, the magnetic Hamiltonian has $C_2$ symmetry around the $b$-axis. In the single-$q$ zigzag scenario, the symmetry of magnetic ground state is spontaneously lowered to $C_1$, and $C_2$-symmetry-related magnetic domains are formed, featuring FM zigzag chains running in directions related to each other by $C_2$ rotation around the $b$-axis. However, in an external magnetic field applied not along the $b$-axis (or the $a$-axis), as is the case for Na$_6$O, the magnetization energy of the $C_2$-related magnetic domains will no longer be degenerate. In other words, considering the combination of the crystallographic structure and the field direction, the Hamiltonian’s symmetry is lowered to none ($C_1$) from the first place. This low symmetry is at the origin of the split between $B_{c1,low}$ and $B_{c1,high}$ for essentially all field directions between the $a$ and $b$-axes.

At $B_{c1,low}$ and $B_{c1,high}$, since the wave vectors switch only along the same $\Gamma$-$M$ line, the resultant AFM$_{1/2}$ order would continue to have their FM ribbons/chains running in inequivalent directions, i.e., same as in the original zigzag domains. Then, by the same symmetry argument, it is natural to expect the two types of AFM$_{1/2}$ domains to have their next transitions occur at somewhat different $B_{c2}$. However, only a single transition is experimentally observed. Under the zigzag scenario, this empirical “simplicity” can only be attributed to a coincidence not required by symmetry, yet it holds over a wide angular range – magnetometry always sees a single $B_{c2}$ transition [Fig. 2(c-d)]. Moreover, the two-step transitions between AFM$_{1/2}$ and AFM$_{1/2}$ are consistently observed independent of field history [Fig. 2(c)], which means that the above two types of domains always reappear after the symmetry-lowering field is removed. Such lack of domain repopulation by the fields is somewhat difficult to understand if the zero-field magnetic ground state’s symmetry is indeed spontaneously lowered to $C_1$ (as for zigzag). Alternatively, these remaining puzzles for the zigzag scenario could imply that the “domains” are not macroscopically separated, but instead, the two sets of wave vectors arise from the same part of the sample, hinting at a multi-$q$ scenario for at least some of the magnetic orders. We therefore believe that the precise nature of the AFM phases in Na$_3$Co$_2$SbO$_6$ is still open for further research.
FIG. S7. **Finding twin-free samples with Raman spectroscopy.** (a) Photograph of a twin-free single crystal. The a and b-axis are indicated by solid arrows, whereas dashed lines indicate directions at 60° from the a and b-axis. (b) The corresponding Co honeycomb sub-lattice. (c) Raman spectra obtained with different parallel polarization directions color-coded with (a). Given the space group $C2/m$ of $Na_3Co_2SbO_6$, there are 15 Raman-active optical phonons, which can be labeled as irreducible representations of the $C_{2h}$ point group: 7 $A_g$ and 8 $B_g$ modes. The spectra in (c) reveal intensity variations of two $A_g$ modes at 207 cm$^{-1}$ and 218 cm$^{-1}$. This empirical knowledge can be used to identify twin-free crystals by scanning the laser spot over the top and bottom surfaces of the entire crystal.

FIG. S8. **A twin-free crystal’s signatures of $T_N$.** (a) Specific heat in zero field. (b) Derivatives of DC magnetic susceptibility measured with fields of 0.1 T along the a and b-axes. The measurements were performed on a temperature ramp (+1 K/min). (c) AFM reflection at $[0.5a^*, 0.5b^*, 0]$ measured as a function of temperature. Inset: the derivatives of DC susceptibility with fields of 0.1 T along 60° from a, which is in the same direction as in Fig. S11. All three measurements in the figure were performed on the same twin-free crystal of 6.2 mg in mass, and $T_N = 6.6$ K is indicated by grey dashed lines in each panel.
FIG. S9. **Magnetic anisotropy at high temperature and high field.** (a) Susceptibility from 2 K to 300 K measured with $B = 0.1$ T applied along four different directions. Inset shows ratio between the directions. (b) In-plane angle-dependent susceptibility plotted in polar coordinates measured at different temperatures and fields. The outermost ring represents $M/B = 1$ emu/mol Co/Oe. It is noteworthy that in a relatively large magnetic field of 2 T, the thermally disordered state at 10 K ($> T_N$) has stronger anisotropy (by the $a/b$ ratio) than at 2 K. This indicates that fluctuations under anisotropic interactions contribute significantly to the observed anisotropy.

FIG. S10. **Inverse magnetic susceptibility and Curie-Weiss fitting.** Same data as in Fig. S9(a). A small background constant has been subtracted from the susceptibility (to account for contribution from the sample mount) before taking the inverse. The inverse susceptibility is found to be well approximated by linear functions of temperature over the 20 K $< T < 120$ K low-$T$ range and the 200 K $< T < 300$ K high-$T$ range, but not as well in between. The associated Curie-Weiss fit parameters of the two temperature ranges are somewhat different, as summarized in Table S1. This difference may arise from thermal activation to the $J_{eff} = 3/2$ electronic states in the high-$T$ range. Hence, results extracted from the low-$T$ range may better reflect the physics of the $J_{eff} = 1/2$ states.
FIG. S11. AFM\textsuperscript{1/2} to AFM\textsuperscript{1/3} wave vector switch in a twin-free crystal. (a) Magnetization versus field (solid, field-up) and its derivative (dashed) at $T = 2$ K with field along 60\degree from $a$-axis. In this direction, the phase transition from AFM\textsuperscript{1/2} to AFM\textsuperscript{1/3} occurs in two steps, at $B_{c1,\text{low}} = 0.53$ T and $B_{c1,\text{high}} = 0.73$ T. Above $B_{c2} = 0.91$ T, the system enters into a field-saturated state. (b) Field-evolution of magnetic diffraction at $[1/2a^*, 1/2b^*, 0]$ (light) and $[2/3a^*, 2/3b^*, -1/3c^*]$ (dark, which is $[1/3a^*, 1/3b^*, 1/3c^*]$ subtracting $[0, 0, c^*]$). (c) Schematic of magnetic wave-vector switching according to (b). The indicated wave vectors are in the monoclinic notation.

FIG. S12. Peak indexing in zero field for a twinned sample. (a) Symmetrized $(Q_a, Q_b)$ plane of neutron diffraction results with $Q_z$ integrated within 1 r.l.u. around zero. All observed peaks on the Brillouin zone boundaries (dashed-dotted lines) are due to the AFM\textsuperscript{1/2} order. The measurement was performed in zero field, at a temperature of about 6 K (below $T_N$), using a twinned sample. Dashed arrows indicate $Q_a = 0$ and $Q_b = 0.5$ and are reference for (b) and (c). (b-c) Viewing the same data as in (a), but with $Q_z$ displayed as vertical axis. (d-e) Cuts through magnetic and structural peaks, respectively.
FIG. S13. Peak indexing in vertical fields for a twinned sample. (a-b) Magnetic peaks in the \((Q_a, Q_b)\) plane in a vertical field of 0.7 T and at \(T = 250 \text{mK}\), together with their \(Q_{\perp}\) locations to be checked against the attributions in Fig. 4 of main text. (c) Line-cut through the data in (b). (d-e) Magnetic peaks in the \((Q_a, Q_b)\) plane in a vertical field of 1.6 T, together with their \(Q_{\perp}\) locations to be checked against the attributions in Fig. 4 of main text. (f) Line-cut through the data in (e). The integrated energy window is ±0.2 meV.

FIG. S14. Momentum structure of the diffuse scattering above \(T_N\). (a) \(Q_{\perp}\)-integrated data obtained at \(T = 10K\), same as in main text Fig. 5. (b) Viewing the same data as in (a), but for the chosen \(Q_b\) and with \(Q_{\perp}\) displayed as horizontal axis. (c) Line-cuts at selected \(Q_a\) positions in (b) after subtracting 45 K data as background. The magnetic diffuse scattering is seen to be only weakly structured along \(Q_{\perp}\), where the intensity decrease with increasing \(Q_{\perp}\) is due to the magnetic form factor.
FIG. S15. **Incipient ferromagnetism.** A weak moment in a twin-free sample, measured upon warm-up in zero field, after preparing the sample with $B_{\parallel b} = 0.02$ T field-cooling to 2 K. Inset shows the angle dependence at 10 K after 0.4 T field-cooling, revealing a clear $C_2$ symmetry that is consistent with a frozen-in net ferromagnetic moment. The field 0.4 T is almost enough to “saturate” the moment, whereas the field of 0.02 T is not enough but it ensures that the apparatus has no remnant magnetic field. The weak ferromagnetism might originate from a small amount of disorder in the crystal (such as stacking faults) which stabilizes the ferromagnetic fluctuations discussed in main text.
TABLE S1. $g$-factor anisotropy revealed by magnetic susceptibility [Figs. S9(a) and S10] along four different directions. The effective moments $\mu_{\text{eff}}$ and Weiss temperature $\theta$ are obtained from Curie-Weiss fitting $\chi = \chi_0 + C/(T - \theta)$ in two temperature ranges: 20 K $< T < 120$ K (low-$T$), and 200 K $< T < 300$ K (high-$T$). $\chi_0$ accounts for a small background from the holder and glue, and $C = N\mu_0\mu_{\text{eff}}^2/(3k_B)$. The Landé $g$-factor is related to $\mu_{\text{eff}}$ as $\mu_{\text{eff}} = g\sqrt{J(J+1)}\mu_B$ with $J = 1/2$.

|       | $\mu_{\text{eff}}$ ($\mu_B$/Co$^{2+}$) | $\theta$ (K) | $g$ |
|-------|---------------------------------|-------------|-----|
| low-$T$ | $B \parallel a$ | $B \parallel 60^\circ$ | $B \parallel b$ | $B \parallel a$ | $B \parallel 60^\circ$ | $B \parallel b$ | $B \perp ab$
| $\mu_{\text{eff}}$ ($\mu_B$/Co$^{2+}$) | 5.9 | 6.1 | 6.3 | 5.4 | 5.8 | 5.8 | 6.2 |
| $\theta$ (K) | 1.0 | 5.7 | 6.8 | 26.2 | 22.4 | 27.6 | -220 |
| $g$ | 6.8 | 7.1 | 7.3 | 6.3 | 6.7 | 6.7 | 7.2 |

TABLE S2. Detailed measurement and time-of-flight data-reduction conditions used in figures.

| Data | $Q_a$ range (r.l.u.) | $Q_b$ range (r.l.u.) | $Q_\perp$ range (r.l.u.) | $E_i$ (meV) | chopper frequency (Hz) | $\Delta E$ range (meV) |
|------|-----------------|-----------------|-----------------|-----------|-----------------|-----------------|
| Fig. 3(a) | - | - | [-1, 1] | 16.8 | 150 | [-0.1, 0.1] |
| Fig. 3(b) blue | [-0.1, 0.1] | [1.9, 2.1] | - | 16.8 | 150 | [-0.1, 0.1] |
| Fig. 3(b) orange | [0.4, 0.6] | [0.4, 0.6] | - | 16.8 | 150 | [-0.1, 0.1] |
| Fig. 3(c) | - | [0.4, 0.6] | [-5, 5] | 5.6 | 150 | [-0.1, 0.1] |
| Fig. 3(d) | [0.4, 0.6] | - | [-5, 5] | 5.6 | 150 | [-0.1, 0.1] |
| Fig. 4 left | - | - | [-0.2, 0.2] | 35 | 120 | [-0.2, 0.2] |
| Fig. 4 right | - | - | [0.3, 0.7] | 35 | 120 | [-0.2, 0.2] |
| Fig. 5(a) | - | [-0.2, 0.2] | [-2.2, 2.2] | 5.6 | 150 | [-0.2, 0.2] |
| Fig. 5(b) | [-0.2, 0.2] | - | [-2.2, 2.2] | 5.6 | 150 | [-0.2, 0.2] |
| Fig. 5(c) | - | - | [-2.2, 2.2] | 5.6 | 150 | [-0.2, 0.2] |
| Fig. 5(c) | - | - | [-2.2, 2.2] | 16.8 | 150 | [-0.1, 0.1] |
| Fig. 6(c) | - | - | [-1, 1] | 16.8 | 150 | [-0.1, 0.1] |
| Fig. S12 a) | - | - | [-1, 1] | 16.8 | 150 | [-0.1, 0.1] |
| Fig. S12 b) | [-0.1, 0.1] | - | - | 16.8 | 150 | [-0.1, 0.1] |
| Fig. S12 c) | [0.4, 0.6] | - | - | 16.8 | 150 | [-0.1, 0.1] |
| Fig. S12 d) | [-0.1, 0.1] | [0.9, 1.1] | - | 16.8 | 150 | [-0.1, 0.1] |
| Fig. S12 e) | [-0.1, 0.1] | [1.9, 2.1] | - | 16.8 | 150 | [-0.1, 0.1] |
| Fig. S13 b) | [-0.1, 0.1] | - | - | 5 | 360 | [-0.2, 0.2] |
| Fig. S13 c) | [-0.1, 0.1] | [0.567, 0.767] | - | 5 | 360 | [-0.2, 0.2] |
| Fig. S13 e) | [0.2, 0.285] | - | - | 15 | 360 | [-0.2, 0.2] |
| Fig. S13 f) | [0.2, 0.285] | [0.233, 0.433] | - | 15 | 360 | [-0.2, 0.2] |
| Fig. S14 a) | - | - | [-2.2, 2.2] | 5.6 | 150 | [-0.2, 0.2] |
| Fig. S14 b) | - | [0.6, 0.8] | - | 5.6 | 150 | [-0.2, 0.2] |
| Fig. S14 c) | - | [0.6, 0.8] | - | 5.6 | 150 | [-0.2, 0.2] |

a Incident neutron energy.
b Neutron energy transfer.
| B || | \(Q_a\) \(\otimes Q_{\perp}\) | \(B\parallel a\) | 60° from \(a\) | 120° from \(a\) | 180° from \(a\) | 240° from \(a\) | 300° from \(a\) |
|---|---|---|---|---|---|---|---|
| **AFM** \(\tfrac{1}{2}\) \((H, K, L)\) index | \(\pm(\tfrac{1}{2}, \tfrac{1}{2}, 0)\) | \(\pm(\tfrac{1}{2}, -\tfrac{1}{2}, 0)\) | \(\pm(0, 1, \tfrac{1}{2})\) | \(\pm(1, 0, 0)\) | \(\pm(0, 0, 1)\) | \(\pm(\tfrac{1}{2}, 0, \tfrac{1}{2})\) | |
| \((Q_a, Q_b, Q_{\perp})\) | \((\tfrac{1}{2}, \tfrac{1}{2}, \frac{1}{8})\) | \((\frac{1}{2}, 0, \frac{5}{8})\) | \((0, 1, \frac{1}{8})\) | \((\frac{1}{2}, \frac{5}{8}, \frac{1}{8})\) | \((0, -1, \frac{1}{8})\) | \((\frac{1}{2}, -\frac{5}{8}, \frac{1}{8})\) | |
| **AFM** \(\tfrac{\pi}{2}\) \((H, K, L)\) index | \(\pm(\tfrac{1}{2}, \tfrac{1}{2}, \frac{1}{2})\) | \(\pm(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\) | \(\pm(0, 1, \frac{1}{2})\) | \(\pm(\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})\) | \(\pm(0, -1, \frac{1}{2})\) | \(\pm(\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})\) | |
| \((Q_a, Q_b, Q_{\perp})\) | \((\tfrac{1}{4}, \tfrac{1}{4}, \frac{1}{8})\) | \((\frac{1}{4}, 0, \frac{5}{8})\) | \((0, 1, \frac{1}{8})\) | \((\frac{1}{4}, \frac{5}{8}, \frac{1}{8})\) | \((0, -1, \frac{1}{8})\) | \((\frac{1}{4}, -\frac{5}{8}, \frac{1}{8})\) | |

**TABLE S3.** Index conversion between the physical coordinate system, \((H, K, L)\), and the hybrid coordinate system, \((Q_a, Q_b, Q_{\perp})\), for different crystallographic orientations with respect to the vertical magnetic field \(B\). Magnetic diffraction wave vectors in the first 2D Brillouin zone in the two AFM phases are illustrated by circles color-coded with their indices in the table. Solid and faded-out halves of the illustrations indicate negative and positive \(Q_{\perp}\) components, respectively.
FIG. S16. **Full data behind Fig. 4 of main text.** (Animated) Symmetrized diffraction maps measured as a function of vertical field, presented in three constant-$Q_\perp$ slices with $Q_\perp$ integrated over the ranges indicated in the panel titles. Figure 3 of main text presents an overview of these data. $Q_a = 0$ corresponds to the horizontal scattering plane.