

Supplementary Information for
**Cascade of magnetic-field-induced quantum spin states in a spin-1
honeycomb magnet**

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I. FIRST-ORDER FIELD-INDUCED PHASE TRANSITIONS

We elucidate that all the field-induced magnetic transitions in $\text{Na}_3\text{Ni}_2\text{BiO}_6$ are first-order in nature. Judging from $M(H)$, it is evident that a first-order transition occurs at H_{c1} , as corroborated by the remarkable hysteresis between the up and down field sweeps (main text Fig. 2b and Supplementary Fig. 4d). The transitions at $H_{c2} - H_{c5}$ behave differently: above 1.5 K, the positions of H_{c3} and H_{c4} appear to be dependent on the direction of H sweeps, whereas signatures at H_{c2} and H_{c5} are roughly reversible (Supplementary Figs. 4a and b); at 0.15 K, clear hysteresis is observed in $\tau(H)$ near H_{c2} but appears to be less distinct at H_{c5} (Supplementary Fig. 2d). Despite this, we suggest that the transition at H_{c5} is likely to be of first order, yet with weaker hysteresis (due to small energy barrier between the two phases involved at this transition [1]). Evidence is mainly provided by the strong feature in the imaginary magnetoelectric (ME) coefficient α_y at H_{c5} , as mentioned in Methods.

Now we turn to the two characteristic fields within the 1/3 magnetization plateau, H_1^* and H_2^* . They are almost identical for up and down sweeps of H (main text Figs. 2a and b), whereas the hysteretic changes in M (main text Fig. 2b) and distinguishable features in α_y (Supplementary Fig. 8d) again point towards transitions with first-order character. It should be stressed that whilst the hysteretic behaviour of the steplike features in $M(H)$ (main text Fig. 2) can potentially originate from either first-order phase transitions or domain formation (e.g., domain boundary pinning), the two processes can be explicitly distinguished in practice. In the present case, if the characteristic fields H_1^* and H_2^* mark the occurrence of H -induced phase transitions inside the 1/3 magnetization plateau, their positions should be intrinsic properties of the material $\text{Na}_3\text{Ni}_2\text{BiO}_6$; alternatively, if the corresponding features stem from multiple-step domain flip or domain-wall motion, H_1^* and H_2^* ought to show variations among data collected in different samples, by different experimental methods and from repeated cycles of field sweeps. In the main text, we show the data from totally four pieces of $\text{Na}_3\text{Ni}_2\text{BiO}_6$ single crystals: Samples #1 and #2 were used in ac magnetostriction measurements (Supplementary Fig. 8); Sample #3, on which the specific heat and magnetization data were taken; Sample #4, a smaller crystal cut from #3, was used in the study of torque magnetometry. We remark that:

- (i) The results of ac magnetostriction measurement (Supplementary Fig. 8c) reveal identical positions of peak features (at H_1^* and H_2^*) in Samples #1 and #2;

(ii) As shown in main text Fig. 2a, H_1^* and H_2^* determined from the signatures in $\alpha_x(H)$ (Sample #1), $\tau(H)$ (Sample #4) and $M(H)$ (Sample #3) are generally consistent with each other: $\mu_0 H_1^* \approx 5.7$ T, $\mu_0 H_2^* \approx 6.3$ T at $T = 1.5$ -2 K; the discrepancies of ~ 0.1 T are most likely attributed to sample misalignments.

(iii) To further verify this point, we measured low- T magnetization $M(H)$ in a new Sample #5. The result, displayed in Supplementary Fig. 9, is in full accordance with that measured in Sample #3 (main text Fig. 2b) which yields $\mu_0 H_1^* \approx 5.6$ -5.7 T and $\mu_0 H_2^* \approx 6.3$ -6.4 T at $T = 0.4$ K. These characteristic fields also stay unchanged upon repeated cycles of field sweeps.

We summarized these results of H_1^* and H_2^* in Supplementary Table 1. It unambiguously demonstrates that the two characteristic fields are intrinsic properties of $\text{Na}_3\text{Ni}_2\text{BiO}_6$; their sample dependence, as well as variances among different thermal cycles and field sweeps, are quite small. In other words, they lack all the hallmarks of disorder-dependent domain alignment or dynamical domain-wall motions. Hence, we conclude that they represent H -induced phase transitions with weak first-order character, instead of being caused by domain formation and domain-wall dynamics. This again reinforce our key point that the 1/3-plateau phase in $\text{Na}_3\text{Ni}_2\text{BiO}_6$ is segmented into multiple spin states, a novel phenomenon unobserved in other quantum magnets.

Sample	technique	T (K)	$\mu_0 H_1^*$ (T)	$\mu_0 H_2^*$ (T)
#1	magnetostriction, α_x	2	5.6(8)	6.3(0)
#2	magnetostriction, α_x	2	5.6(5)	6.2(8)
#3	magnetization, $M(H)$	0.4	5.6(2)	6.3(9)
	dM/dH	2	5.6(8)	6.3(0)
#4	torque, $\tau(H)$	0.2	5.6(2)	6.5(8)
	$d(\tau/H)/dH$	1.5	5.8(8)	6.3(6)
#5	magnetization, $M(H)$	0.4	5.6(8)	6.3(4)

Supplementary Table 1: Characteristic fields H_1^* and H_2^* determined for five $\text{Na}_3\text{Ni}_2\text{BiO}_6$ samples (#1 – #5) from varying experimental methods. The values are presented with an uncertainty of approximately 0.04 T. Note that the torque data measured in Sample #4 were collected with a small angle (unknown, presumably a few degrees) between H and the c^* axis, whereas for all the other measurements we have $H \parallel c^*$. The consistency among these datasets is remarkable.

As for the first-order nature of these transitions, a few additional points can be put forward. First, the absence of features at H_1^* and H_2^* in specific heat $C_p(H)$ is in agreement with the expectation for weak first-order phase transitions (in contrast, second-order

transitions are usually manifested as peak anomalies in $C_p(H)$ due to entropy maxima [2]. Second, the multi-peak profiles of the anomalies developed at H_1^* and H_2^* in the real part of the ME coefficient α_x probably reflect domain formations in the vicinity of these first-order transitions. (We also point out that the salient peak features in α_x clearly demonstrate the occurrence of changes in the microscopic magnetic order, instead of domain alignments/flips, since in the latter case only the domain boundaries are affected and they occupy a relatively small percentage of the sample's volume [3]). Third, the remarkable negative peak features at H_1^* and H_2^* in the imaginary part of the ME coefficient, α_y (Supplementary Fig. 8d), also corroborate first-order characteristics of the corresponding phase transitions, as we explained in Methods. The analysis and discussion presented above can also be applied to the characteristic fields $H_{c3} - H_{c5}$ (see Supplementary Figs. 4a-c), suggesting that these are also H -induced first-order phase transitions.

A recent study of the triangular lattice magnet $\text{K}_2\text{Co}(\text{SeO}_3)_2$ [4] has revealed an interesting phenomenon that a low concentration of disorder (e.g., vacancies of magnetic ions) can give rise to multiple sub-plateaus in the field region where a $1/3$ - M_s plateau is expected for a clean system. This result, however, lacks direct relevance with our observations in $\text{Na}_3\text{Ni}_2\text{BiO}_6$. Most notably, such additional plateaus caused by sequential spin flips near vacancy sites exhibit relatively smooth evolution of $M(H)$ profiles from one to another, in contrast to the distinct magnetization steps and sharp features in magnetostriction reported in this work. The remarkable specific heat anomalies between sub-plateaus observed in $\text{K}_2\text{Co}(\text{SeO}_3)_2$ [4] add to the difference. Nevertheless, although we identify H_1^* and H_2^* as field-induced first-order transitions, we cannot fully preclude that these transitions are related to certain types of disorder in our samples; future spectroscopic investigations (for instance, Raman scattering or infrared spectroscopy) may shed light on this topic.

II. EXPLORING THE METASTABLE CHARACTERS OF THE $1/3$ -PLATEAU PHASES

In a spin-chain Ising magnet $\text{Ca}_3\text{Co}_2\text{O}_6$, the low- T magnetic properties are profoundly influenced by slow spin dynamics [5]; consequently, the $1/3$ magnetization plateau developed above $T \sim 10$ K evolves into several incommensurate magnetization steps at lower T [6], the amplitudes of which are highly dependent on the field-sweep history and long-time relaxation

[3, 6, 7]. It has been pointed out that these low- T magnetization steps represent nonequilibrium, metastable spin states that are subjected to slow spin dynamics with a time scale of 10^4 s [6, 7]. The equilibrium ground state, i.e., the $1/3$ -plateau phase, can be stabilized after a field-cooling (FC) process at the lowest T [3]. To further examine whether the $1/3$ -plateau phases I, II and III in $\text{Na}_3\text{Ni}_2\text{BiO}_6$ possess similar nonequilibrium signatures, we conducted additional low- T magnetization measurements. The results are shown in Supplementary Figs. 10 and 11.

First, the history of field application appears to have a much weaker impact on the magnetic properties of $\text{Na}_3\text{Ni}_2\text{BiO}_6$. In $\text{Ca}_3\text{Co}_2\text{O}_6$, the nonequilibrium spin states manifest themselves as multiple steps in low- T $M(H)$ that deviate drastically from the $1/3$ - M_s plateau; such steps emerge with much larger amplitudes on the down-sweep branch of $M(H)$ [6]. In $\text{Na}_3\text{Ni}_2\text{BiO}_6$, on the contrary, the up and down sweeps of H lead to a narrow hysteresis loop over the field range of $1/3$ magnetization plateau, yet the values of M are not far from $M_s/3$ for either branches (main text Fig. 2b); the congruence between the down-sweep $M(H)$ and the FC data (inset of Supplementary Fig. 10b) is also remarkably different from $\text{Ca}_3\text{Co}_2\text{O}_6$ (wherein FC erases the steps and stabilizes the $1/3$ -plateau phase [3]). Moreover, the exact $1/3$ - M_s plateau cannot be realized by either field cooling (Supplementary Fig. 10b) or long-time relaxation (Supplementary Fig. 11) in our samples. Therefore, there is no evidence showing that the exact $1/3$ magnetization plateau serves as the equilibrium ground state in $\text{Na}_3\text{Ni}_2\text{BiO}_6$, which contradicts the case of $\text{Ca}_3\text{Co}_2\text{O}_6$.

Second, in stark contrast to the remarkable slow spin dynamics reported in $\text{Ca}_3\text{Co}_2\text{O}_6$, the $1/3$ -plateau phases $\text{Na}_3\text{Ni}_2\text{BiO}_6$ show less pronounced time evolution. The zero-field-cooled (ZFC) $M(T)$ curves measured after a 1-hour relaxation at the lowest T (solid circles in Supplementary Fig. 10b) appear to be only slightly changed compared to the data without relaxation (Supplementary Fig. 10a, same data as in main text Fig. 2d). We also performed measurements of time-dependent magnetization $M(t)$ at 0.4 K under three different magnetic fields: 5.5 T (phase I), 6.2 T (phase II) and 6.8 T (phase III); as shown in Supplementary Fig. 11, all the relaxation curves were measured after a ZFC process. For all three magnetic fields, the $M(t)$ data show some small jumps ($< 3\%$ in amplitude) within the initial 30 minutes of relaxation, then reach a relatively stable value and barely change in the remaining relaxation procedure up to $t = 10000$ s. Such behaviour tells that (i) the $1/3$ -plateau phase I, II and III may possess weak metastable signatures, as their magnetization appears to be

stabilized by a short period of relaxation; (ii) the change of M during relaxation is marginal, suggesting the absence of profound nonequilibrium character; (iii) the slow spin dynamics (continuous evolution of M over several hours) highlighted in $\text{Ca}_3\text{Co}_2\text{O}_6$ [5, 6] is completely missing here; (iv) all three plateau phases I, II and III can reach its individual equilibrium state after the short relaxation, which implies that these states and the phase transitions between them (H_1^* and H_2^*) are not caused by non-equilibrium spin dynamics.

According to all these experimental facts, we elucidate that:

1. The two magnets are distinct in essence: $\text{Na}_3\text{Ni}_2\text{BiO}_6$ is a quasi-2D honeycomb magnet with strong exchange frustration, whereas $\text{Ca}_3\text{Co}_2\text{O}_6$ is a quasi-1D spin-chain compound characterized by predominant geometric frustration. They harbor very different forms of magnetic interactions: $\text{Ca}_3\text{Co}_2\text{O}_6$ is an Ising spin system, $\text{Na}_3\text{Ni}_2\text{BiO}_6$ is not — Heisenberg exchange is instead dominant herein, with Kitaev interaction likely also involved.
2. The magnetization steps in $\text{Ca}_3\text{Co}_2\text{O}_6$ correspond to specific metastable spin phases that are totally different from the $1/3\text{-}M_s$ plateau — the latter is a classical ferrimagnetic state engendered by the order-by-disorder mechanism [8]. By contrast, the $1/3\text{-}M_s$ plateau in $\text{Na}_3\text{Ni}_2\text{BiO}_6$ is *composed of* spin phases I, II and III and the order-by-disorder mechanism is completely irrelevant as we emphasized in the main text; the intermediate spin states (beyond the plateau) in these two materials are also different in nature with contrasting signatures.
3. Whilst the well-established models for $\text{Ca}_3\text{Co}_2\text{O}_6$ cannot be applied to the case of $\text{Na}_3\text{Ni}_2\text{BiO}_6$ (since it lacks the 1D Ising chains in its spin configuration), they may still provide some insights into the formation of multiple $1/3$ -plateau phases. It has been proposed [8, 9] that the multiple steps in $\text{Ca}_3\text{Co}_2\text{O}_6$ are related to spin-density-wave-type microphases with small, incommensurate wave vectors varying continuously upon cooling; their formation is attributed to a particular form of frustrated inter-chain interactions which effectively emulates the axial next-nearest-neighbor Ising (ANNNI) model. Here, we postulate that the occurrence of $1/3$ -plateau phases I, II and III may stem from the weak, frustrated interlayer interaction in $\text{Na}_3\text{Ni}_2\text{BiO}_6$, which leads to the phenomenology mimicking a modified ANNNI model. Despite the exact form of such interlayer interaction requires to be revealed by future theoretical efforts, the

phenomenological similarities between $\text{Na}_3\text{Ni}_2\text{BiO}_6$ and $\text{Ca}_3\text{Co}_2\text{O}_6$ (i.e., the emergence of multiple magnetization steps) strengthens our conjecture that peculiar spin physics akin to the ANNNI model may be at play in $\text{Na}_3\text{Ni}_2\text{BiO}_6$.

We note that one additional transition appears on the magnetic torque $\tau(H)$ between H_1^* and H_2^* at $T \leq 0.2\text{K}$ (down triangles in main text Fig. 2c). Whether this transition is more non-equilibrium in nature is unclear, because such ultra-low temperatures cannot be reached in our measurement of longitudinal magnetization M with the available facilities. Unfortunately, torque measurement using a piezoresistive cantilever is not a reliable method for studying relaxation of magnetization (because during a long-time relaxation, small jumps occasionally occur due to the extrinsic response of the cantilever itself rather than the sample). This additional transition is not among the key results of our work and we leave further explorations of it to the future.

III. ANALYSIS OF THE SPECIFIC HEAT

1. Analysis of the magnon contribution

We analyzed the low- T specific heat data (between 0.1 and 3.8 K) with two components taken into account: the magnetic specific heat C_m and the phonon contribution C_{ph} . In a spin system possessing bosonic excitations (magnons), $C_m(T)$ can be described as [10]:

$$C_m = \int_0^\infty E g(E) \frac{df(E)}{dT} dE. \quad (\text{S1})$$

Here, $f(E) = 1/[\exp(\frac{E}{k_B T}) - 1]$ is the Bose-Einstein distribution function. The density of state (DOS) of spin excitations $g(E)$ can be written as $g(E) = (V_m/2\pi^2 \beta \alpha^{\frac{3}{\beta}})(E - \Delta_{\text{mag}})^{\frac{3}{\beta}-1}$ if the excitation spectrum taking the form of $E = \Delta_{\text{mag}} + \alpha k^\beta$, where Δ_{mag} represents the energy gap in magnon dispersion (here we only consider the isotropic model for simplicity). Thereby, following a thermal activation model of gapped magnetic excitations, the specific heat is given by [10, 11]:

$$C_m = AT^{-n} \exp(-\Delta_{\text{mag}}/k_B T), \quad (\text{S2})$$

where $n = 3/\beta - 2$. We applied this model to the measured $C_p(T)$ with $n = 0$ ($\beta = 3/2$),

which yields the best fits. The phonon background $C_{\text{ph}} = BT^3$ (inset of Supplementary Fig. 6a) was obtained by fitting the 14 T data to $C_{\text{p}}(T) = A \exp(-\Delta_{\text{mag}}/k_{\text{B}}T) + BT^3$. We assumed that C_{ph} is independent of H . C_{ph} is confirmed to be insignificant (contributing to less than 1% of C_{p}) below 3.8 K.

In Supplementary Fig. 6, fitting of specific heat for the zigzag, 1/3-plateau and polarized states using the above-mentioned model reveal a nonmonotonic H dependence of the spin excitation gap Δ_{mag} (Supplementary Fig. 6d). In the 1/3 plateau phases, the magnetic excitations are gapped as expected [12] and Δ_{mag} decreases with increasing H . In the fully polarized state above 11 T, the obtained Δ_{mag} (with an amplitude of 6.5-10 K) increases upon increasing field, qualitatively consistent with recent NMR results [13] (the gap size is smaller in this work, probably due to the different temperature ranges of fitting). Though Ref. [13] reports a gap closing at 8.3 T (corresponding to H_{c5}), we cannot verify this claim because of the low- T upturn behaviour of $C_{\text{p}}(T)$ (main text Fig. 3). At this stage, it is unknown whether the “hidden” ground state in the intermediate field region between H_{c2} and H_{P} is gapped or gapless.

2. Nuclear Schottky anomaly in the specific heat of $\text{Na}_3\text{Ni}_2\text{BiO}_6$

A system with discrete energy levels gives rise to a Schottky term C_{Sch} in specific heat [14], with the common characteristic of a broad peak at which $k_{\text{B}}T$ is comparable to the energy differences $\Delta\epsilon_i$ ($i = 1, 2, \dots$) between discrete levels. When $k_{\text{B}}T \gg \Delta\epsilon_i$, the Schottky anomaly manifests itself as an inverse-power-law upturn [14], for the simplest two-level case:

$$C_{\text{Sch}} \propto \left(\frac{\Delta\epsilon}{T}\right)^2 \frac{\exp(\frac{\Delta\epsilon}{T})}{[1 + \exp(\frac{\Delta\epsilon}{T})]^2} \propto T^{-2}. \quad (\text{S3})$$

In the case that the Schottky anomaly arises from the nuclear spin levels, such T^{-2} behaviour is prominent because their hyperfine splitting yields very small $\Delta\epsilon_i$ (usually on the order of 10 mK) and the high- T condition is easily realized in practice. In $\text{Na}_3\text{Ni}_2\text{BiO}_6$, we expect that the nuclear Schottky contribution predominantly comes from the ^{209}Bi nuclei (nuclear spin number $I = 9/2$), whose 10-fold degeneracy of spin levels can be lifted by the Zeeman effect of an effective field H_{eff} (the sum of external H_{ex} and the internal hyperfine field stemming from electron spins) and the quadrupole interactions. Nonetheless, we point out that the low- T divergence of specific heat in $\text{Na}_3\text{Ni}_2\text{BiO}_6$ (Fig. 3) cannot be simply attributed

to such nuclear Schottky term: even with the presence of multiple energy levels, the heat capacity for ^{209}Bi nuclei still takes the form [15]:

$$C_{\text{Sch}} = \frac{1}{3}I(I+1)\frac{1}{k_{\text{B}}T^2}[A_{\text{quad}}(e^2qQ)^2 + (\hbar\gamma_n\mu_0H_{\text{eff}})^2], \quad (\text{S4})$$

$$H_{\text{eff}} = H_{\text{ex}} + K_z\mu_B S_z + K_{ab}\mu_B \langle S_{ab} \rangle,$$

to the leading term in the high- T limit. Here, the first and second terms are caused by the quadrupolar splitting and effective (hyperfine) field H_{eff} , respectively; Q is the nuclear quadrupole moment, eq the electric field gradient, γ_n the gyromagnetic ratio and $K_z(K_{ab})$ the constant calibrating the strength of hyperfine interaction with out-of-plane (in-plane) electron spins. Such T^{-2} behaviour is in contrast to our observation of $C_{\text{p}}(T) \propto T^{-\alpha+1}$ ($\alpha \sim 2.4\text{--}2.7$), which is clearly displayed in main text Fig. 3d and Supplementary Fig. 12. In addition, we attempted to fit the low- T anomaly in $C_{\text{p}}(T)$ using a two-level Schottky model with magnon contributions taken into account; as shown in Supplementary Fig. 13, the fitting results prove that neither the low- T divergence for 7.5-10.5 T nor the hump anomaly at above 10.5 T can be satisfyingly reproduced by such model. Moreover, the low- T anomaly of C_{p} only occurs in a finite field range (7.5-11.0 T, inset of main text Fig. 3b); such phenomenon has never been reported for nuclear specific heat in any real materials; the typical field evolution of C_{Sch} is that the T^{-2} rise gradually shifts to higher T upon an increase of H , as $\Delta\epsilon_i$ is enlarged by the Zeeman term [14]. Since all these hallmarks of conventional nuclear Schottky contribution are missing in our data, the diverging $C_{\text{p}}(T)$ in $\text{Na}_3\text{Ni}_2\text{BiO}_6$ must have a different origin. Nonetheless, at this stage we cannot completely rule out the possibility that the nuclear spins participate in the formation of such specific heat anomaly; further explorations down to lower T are demanded to draw an unambiguous conclusion on this point.

It can also be noticed that the $C_{\text{p}}(T)$ curve taken at 7.5 T (immediately above $H_{\text{c}2}$) shows an approximate T^{-2} rise below $\simeq 0.35$ K (Fig. 3d and Supplementary Fig. 12a), resembling the Schottky-type response in Eq. S3 (Supplementary Fig. 13a). Considering the appreciable hysteresis of $C_{\text{p}}(H)$ in the vicinity of this field with multiple steps on the downsweep curve (Supplementary Fig. 4e), we point out a possible scenario that in a narrow range of H above $H_{\text{c}2}$, the low- T specific heat anomaly incorporates the contribution from proliferation of states (e.g., domain walls with random interactions) possessing close energies [16],

which gives rise to a two-level/multi-level Schottky-like term in $C_p(T)$. Spatial domains of coexisting phases are naturally expected for the first-order transitions H_{c2} - H_{c5} . Above H_{c5} , however, the reversible rise of $C_p(T)$ (Supplementary Fig. 4e) cannot be associated with domain wall physics in any sense.

3. Possible influence of the Schottky anomaly stemming from impurities

To investigate the potential contribution of magnetic impurities, we first performed composition characterization on two $\text{Na}_3\text{Ni}_2\text{BiO}_6$ single crystals using the technique of electron probe microanalysis (EPMA). Since $\text{Na}_3\text{Ni}_2\text{BiO}_6$ is insulating, a very thin layer of carbon was coated on its surface before measurement. The EPMA results, as shown in Table S1, verify that apart from Na, Ni, Bi, and O, no other elements can be detected in our sample; measurements taken at different positions on the sample confirm that the chemical composition is uniform. The level of impurity concentration or chemical inhomogeneity does not exceed 2%.

Sample 1					
MEAS position \ element(mol%)	Na (K α)	O (K α)	Bi (M α)	Ni (K α)	Total
1	20.900	55.434	7.319	16.347	100
2	22.224	53.826	7.547	16.404	100
3	20.938	55.404	7.581	16.077	100
4	20.538	55.419	7.402	16.641	100
Average	21.150 ± 0.738	55.021 ± 0.797	7.462 ± 0.123	16.367 ± 0.231	
Sample 2					
MEAS position \ element(mol%)	Na (K α)	O (K α)	Bi (M α)	Ni (K α)	Total
1	21.707	54.032	7.486	16.775	100
2	21.535	54.246	7.505	16.713	100
3	21.676	54.086	7.686	16.552	100
4	22.085	53.390	7.603	16.921	100
Average	21.751 ± 0.235	53.939 ± 0.377	7.570 ± 0.093	16.740 ± 0.153	

Supplementary Table 2: The chemical composition and atomic ratio of different elements measured in two $\text{Na}_3\text{Ni}_2\text{BiO}_6$ samples by the EPMA method. No additional elements can be resolved besides Na, Bi, Ni and O.

Now we examine the possibility that a small amount of unknown magnetic impurities (with concentration $n/N \sim 1\%$, N is the number of unit cells in the sample) yield the

observed specific heat anomaly. For a multilevel system, the Schottky term of specific heat can be written as [17, 18]:

$$C_{\text{Sch}} = nk_B \left\{ \frac{x^2 e^x}{(e^x - 1)^2} - (2J + 1)^2 \frac{x^2 e^{(2J+1)x}}{[e^{(2J+1)x} - 1]^2} \right\} \quad (\text{S5})$$

where J is the total angular momentum, $x = g\mu_B\mu_0 H_{\text{eff}}/k_B T$ (g is the Landé g -factor, μ_B is the Bohr magneton and H_{eff} is the effective magnetic field). We applied this model to the fitting of $C_p(T)$ data with and without the limitation of n/N . The results are shown in Supplementary Fig. 14. The model fails to satisfyingly trace the $C_p(T)$ data even with the optimized fitting parameters shown in Supplementary Fig. 14a: This fit deviates from the data when T rises to only $\simeq 0.3$ K, akin to the results displayed in Supplementary Fig. 12. We point out that:

- (i) For most reasonable values of J ($J = 1/2, 1, 3/2$), the impurity-level C_{sch} given by Eq. S5 tends to manifest a broad peak (Supplementary Fig. 14b), instead of an upturn at the lowest T which is more typical for nuclear spin levels (Supplementary Fig. 12);
- (ii) The optimized fitting curve shown in Supplementary Fig. 14a requires a very high impurity concentration, $n/N \approx 0.35$, which is evidently unphysical;
- (iii) The fits to experimental data tend to yield a small $g\mu_0 H_{\text{eff}} < 0.1$ T, whereas the data were measured under $\mu_0 H > 8$ T (increase of $g\mu_0 H_{\text{eff}}$ leads to a shift of the maximum of C_{Sch} towards higher T , see dashed lines in Supplementary Fig. 14b).

With all these disagreements, we conclude that the low- T specific heat anomaly cannot be assigned to a Schottky term originates from impurities. This anomaly, reaching $\approx 8 \text{ J mol}^{-1} \text{ K}^{-2}$ at 100 mK and $\mu_0 H = 8.5$ T (main text Fig. 3b), is indeed two orders of magnitude larger than the typical Schottky contributions from magnetic impurities at similar temperatures [18].

We further emphasize that three aspects of the low- T upturn signature in our $C_p(T)$ data cannot be reconciled with any Schottky contribution from multilevel systems, regardless of the nature of the system (nuclear spin levels or local moments of paramagnetic impurities). First, the T dependence of our observation (main text Fig. 3d) remarkably contradicts the expectation for a Schottky anomaly (which is $C_p/T \propto T^{-2}$); this has been clearly demonstrated in Supplementary Figs. 12 and 13. Second, the abnormal upturn is only observed in a limited field range, i.e, between H_{c2} (the characteristic magnetic field marking the ter-

mination of the $1/3-M_s$ plateau) and the full spin polarization H_P . Despite that impurities with a small number of non-degenerate levels may indeed give rise to nonmonotonic evolution of specific heat under H , it is very unlikely that the nonmonotonic feature can be so severe — suddenly emerges at a certain H and becomes fully suppressed at a field just $\simeq 3$ T higher (Supplementary Fig. 4e). Third, the low- T upturn of C_p is absent under an in-plane H ($H \perp c^*$) in the field range where it is remarkable under $H \parallel c^*$ (Supplementary Fig. 12f); on the contrary, the Schottky anomaly is usually expected to depend weakly on the direction of H . Among all known materials, a Schottky anomaly in the specific heat that fulfills the above-mentioned three phenomena is unheard of.

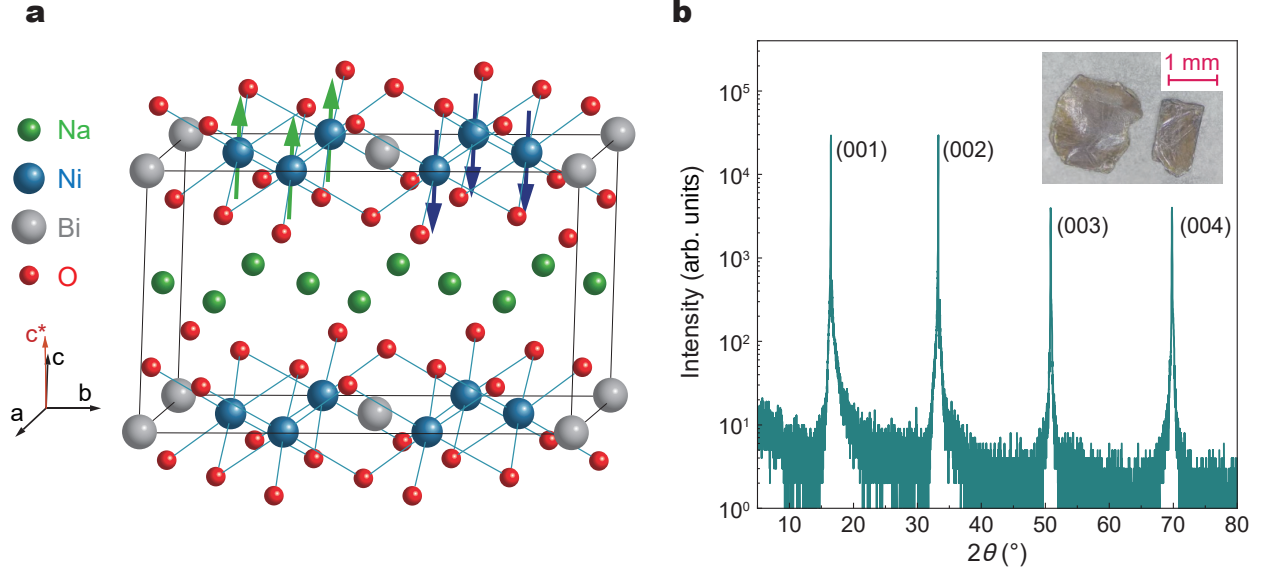
IV. CONNECTION BETWEEN SPECIFIC HEAT DIVERGENCE AND FIELD-INDUCED SPIN PHASE

1. Determination of the true saturation field

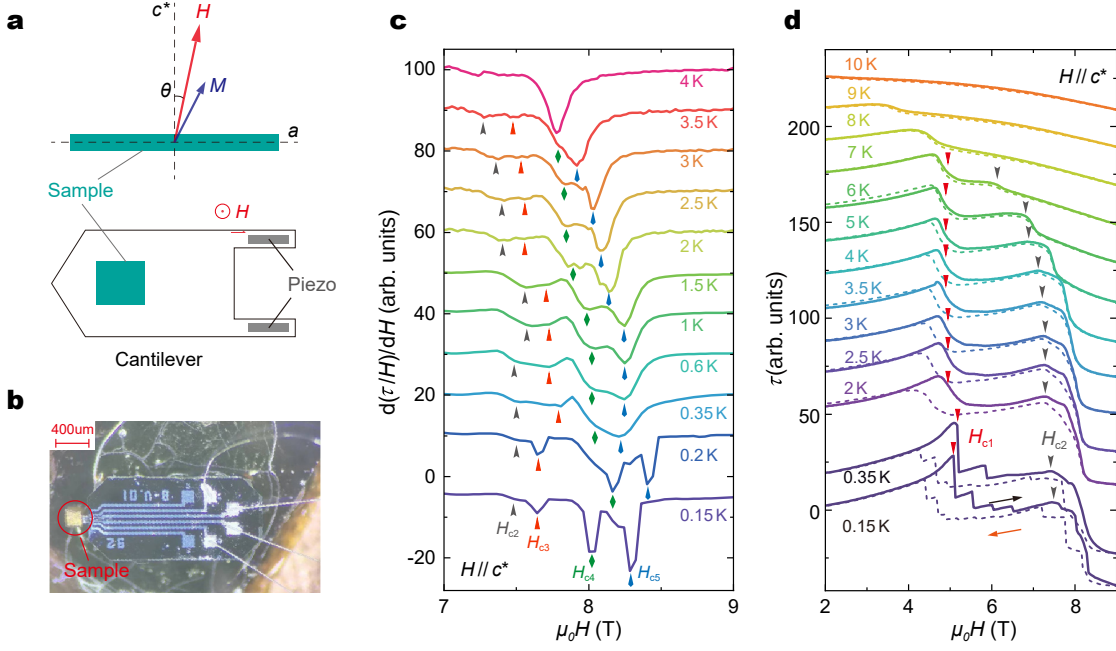
The magnetic torque can be defined as the vector product: $\tau = \mu_0 \mathbf{M} \times \mathbf{H}$; its amplitude is thus $\tau = \mu_0 M_\perp H$. Here, M is the sample magnetization vector and $M_\perp = \tau/\mu_0 H$ is the transverse magnetization (the component of $\mathbf{M}$ perpendicular to $\mathbf{H}$). Note that in practice, the applied H -field always has a small misalignment with respect to the perpendicular direction c^* of the sample, thus $\tau(H)$ remains nonzero in the polarized state (the polarization is only induced by the out-of-plane component of H along the c^* axis [19]). Therefore, as the spin system enters the polarized state, $M_\perp$ becomes a constant given that the direction of $\mathbf{M}$ stays unchanged; as a result, $\tau(H)$ should increase linearly with H . Such a linear $\tau - H$ relation is indeed observed in $\text{Na}_3\text{Ni}_2\text{BiO}_6$ at high H (main text Fig. 4b); we define the onset field of this behaviour as H_P . The fact that $\mu_0 H_P \simeq 10.5$ T at 0.15 K indicates a gradual crossover into the full polarization above H_{c5} , i.e., the nominally “polarized” state above H_{c5} (main text Fig. 4a) may possess finite in-plane spin component in a wide field region up to H_P , at which the Ni spins are eventually fully aligned along c^* . On the other hand, an apparent deviation from linear $\tau - H$ occurs above 12.8 T (main text Figs. 4b and c); the reason for such deviation is likely to be extrinsic, as the increasing τ under high H can bring the sensor out of its linear response regime, or make the sample position unstable.

2. The imminent transition towards an emergent “hidden” spin phase

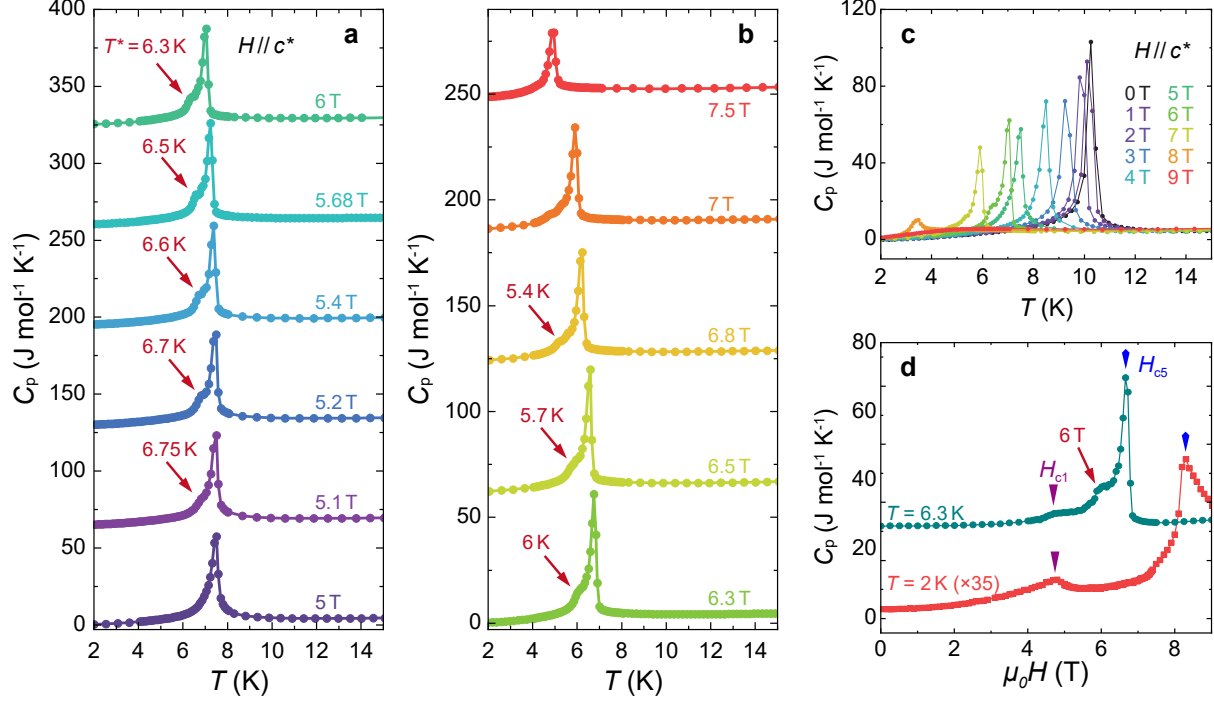
Here we elucidate that inverse-power-law divergence of $C_p(T)$ (main text Fig. 3 and Supplementary Fig. 7) is most reasonably interpreted as incipient manifestation of an imminent transition towards an emergent spin order developing at ultralow temperatures. Since C_p/T represents the second derivative of free energy F with respect to T , the observed remarkable singularity in $C_p(T)$ likely signals the occurrence of a magnetic phase transition at $T_{\text{em}} < 100$ mK (which marks the upper boundary of the putative emergent low- T spin order in the $H - T$ phase diagram). We mention that a single field-induced phase transition, for instance the one at H_{c5} , is insufficient to give rise to the observation that a divergent $C_p(T)$ occurring in an extended range of H (from $\mu_0 H_{c2} \approx 7.4$ T to $\mu_0 H_P \approx 10.5$ T, main text Fig. 4a). Several comments can be put forward regarding to the low- T emergent order: (1) Its spin configuration can be distinct from all phases displayed in main text Figs. 1e and 4a, including the “intermediate” spin phases between H_{c2} and H_{c5} ; this is guaranteed by the presence of a transition line at T_{em} which separate it from those phases. (2) This ordered phase probably persists up to $H \simeq H_P$ at the lowest T , i.e., it survives to $H > H_{c5}$ where the antiferromagnetic order depicted in main text Fig. 1e terminates. (3) As the formation of this order is constrained to a field range between the end of the 1/3-plateau phase and the full spin polarization, we propose that it likely involves the in-plane spin components of Ni^{2+} ; in particular, we may tentatively ascribe it to a superfluid phase arising from the condensation of dilute hard-core bosons that depict the excitation of the in-plane components. (4) Considering that an emergent low- T order must have its onset and offset boundaries on the H axis at zero T , we postulate that a thermodynamic measurement at very low T can promisingly reveal two transitions (entering and exiting this order) during a field-sweep process. Such an attempt may serve as a stringent test of our proposed scenario. (5) It relies on future investigations exploiting spectroscopic methods to determine the nature of this order, including its spin structure and whether it is gapped or gapless.



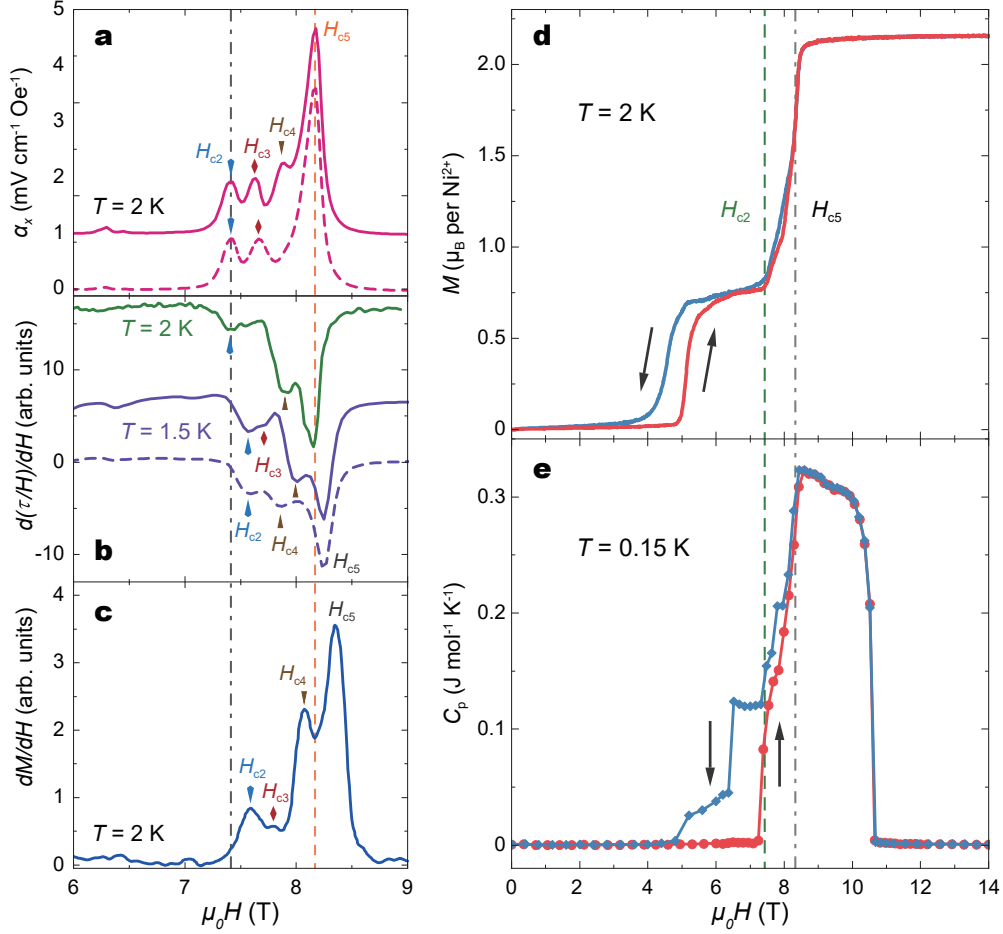
Supplementary Fig. 1: Crystal structure of $\text{Na}_3\text{Ni}_2\text{BiO}_6$. **a**, Crystal structure of $\text{Na}_3\text{Ni}_2\text{BiO}_6$. Spins of Ni^{2+} are shown in green and blue arrows, constructing a zigzag magnetic configuration in the zero-field ground state. **b**, Room temperature X-ray diffraction (XRD) pattern for a $\text{Na}_3\text{Ni}_2\text{BiO}_6$ single crystal, measured using $\text{Cu K}\alpha_1$ radiation. The XRD pattern shows only the $(00l)$ ($l = 1, 2, 3, \dots$) reflections, indicates that the top surface of the plate-shaped samples (inset) corresponds to the crystalline (001) plane, i.e., the ab plane in the main text.



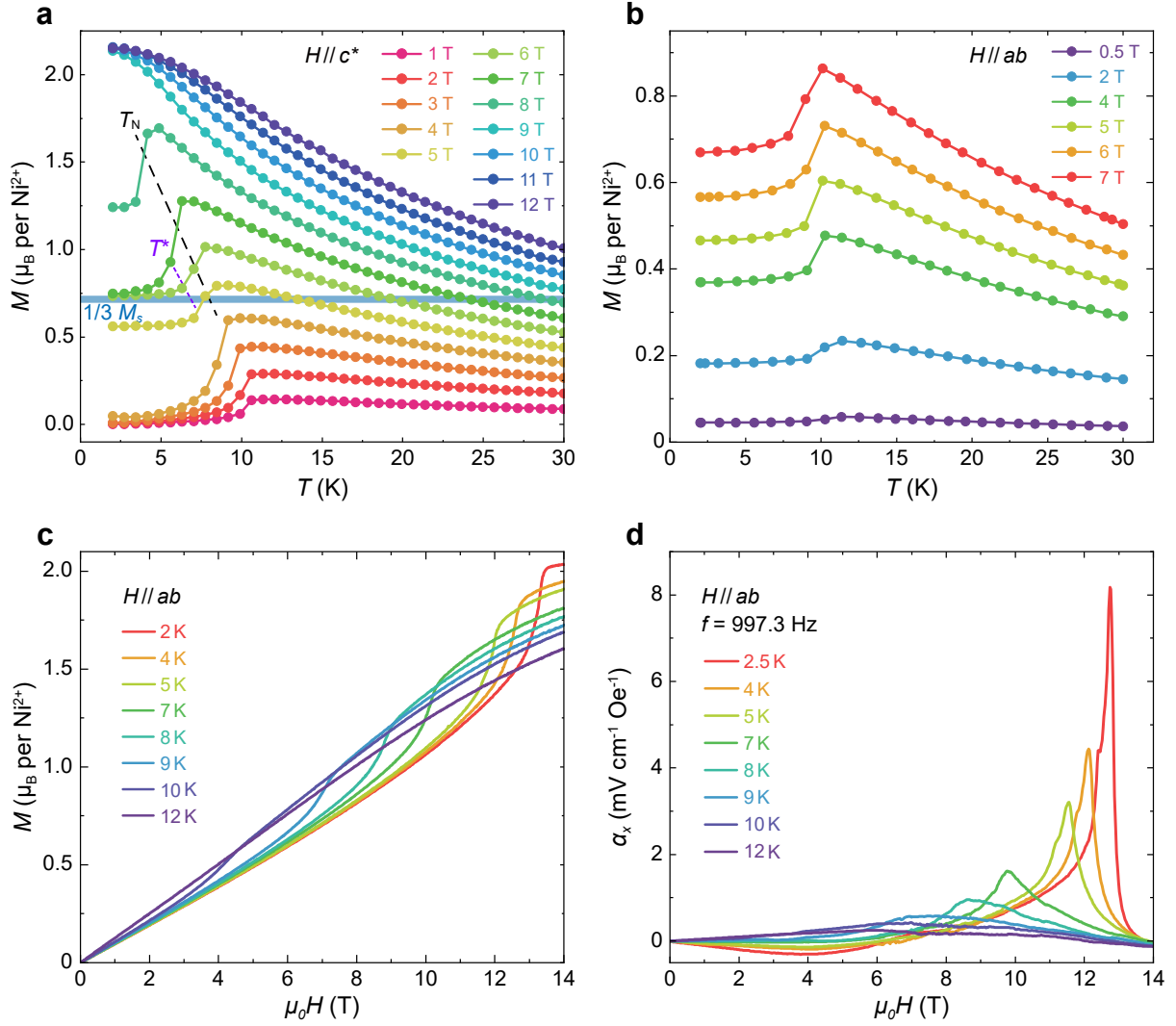
Supplementary Fig. 2: Torque magnetometry in $\text{Na}_3\text{Ni}_2\text{BiO}_6$. **a**, Schematic of torque magnetometry measurement setup using a piezoresistive cantilever. θ is the tilt angle between H and crystalline high-symmetrical axis. **b**, Optimal image of a SCL piezoresistive sensor used in this work. A small $\text{Na}_3\text{Ni}_2\text{BiO}_6$ single crystal ($\sim 200 \times 200 \times 50 \mu\text{m}^3$) is attached to the tip of the cantilever. **c**, Field derivatives of magnetic torque $d(\tau/H)/dH$ for various temperatures. Successive magnetic transitions in the intermediate region (H_{c2} - H_{c5}) are indicated by solid symbols. **d**, H -dependent magnetic torque measured between 0.15 and 10 K, Data are shifted vertically for clarity. Both up (solid lines) and down (dashed lines) field sweeps of $\tau(H)$ are shown for $T = 0.15$ K; the remarkable hysteresis loops developed at low T between these two curves demonstrate that all the field-induced transitions are of first order. For other T , only upsweeps are displayed.



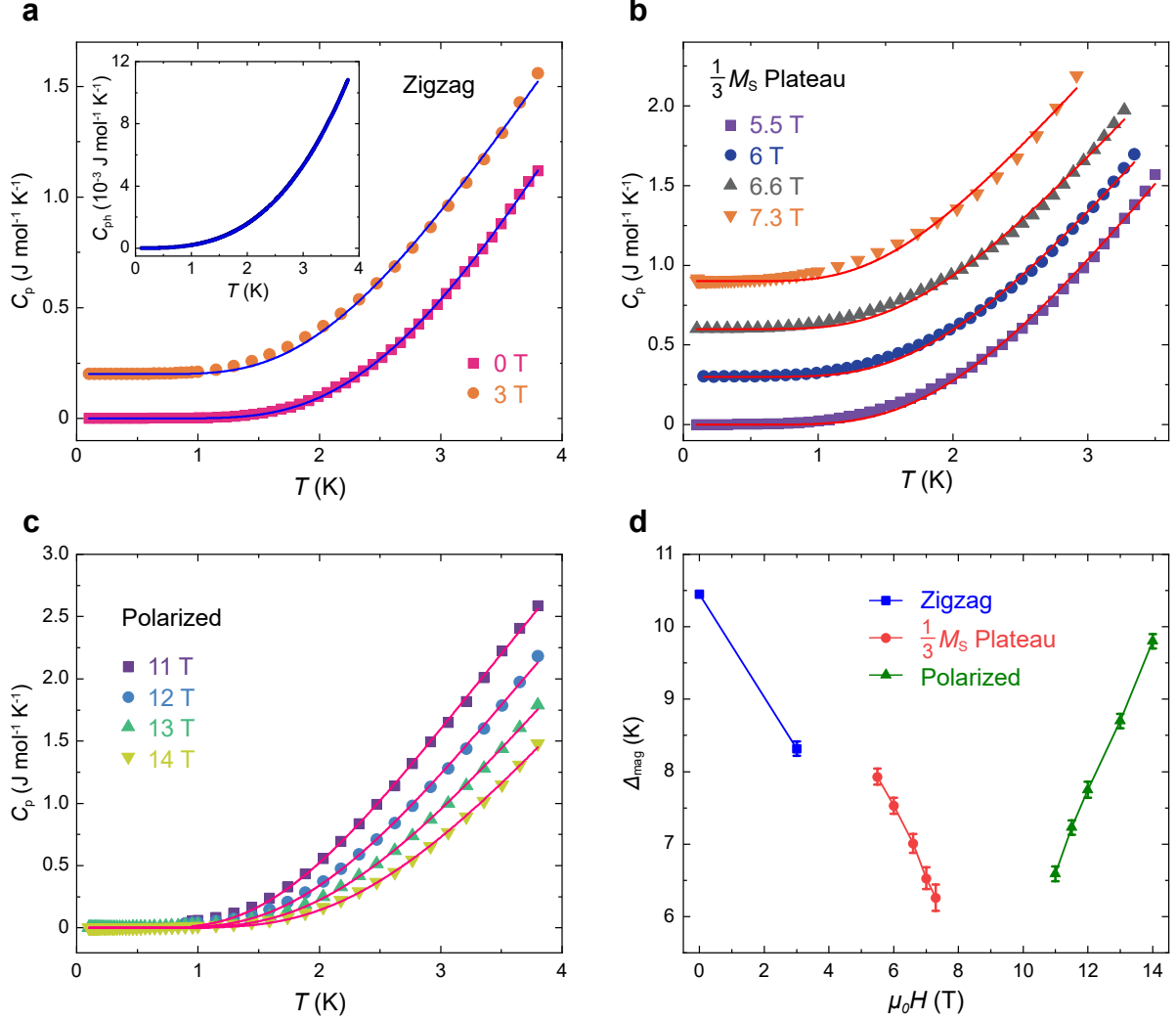
Supplementary Fig. 3: Additional magnetic transition below T_N implied by specific heat. **a-c**, Specific heat $C_p(T)$ of $\text{Na}_3\text{Ni}_2\text{BiO}_6$ measured with varying H applied parallel to c^* . A “shoulder”-like anomaly (indicated by red arrows) emerges on the lower side of T_N , in the field range of 5.1-6.8 T. Data in **a** and **b** are displayed in a vertical stack for the field range of 5.0-6.0 T and 6.3-7.5 T, respectively. **d**, Field-dependent specific heat $C_p(H)$ taken at 6.3 K (olive) and 2 K (red) in upsweeps of H . The step-like feature occurring at $\mu_0 H = 6$ T for $T = 6.3$ K is in accordance with the putative magnetic transition revealed by $C_p(T)$.



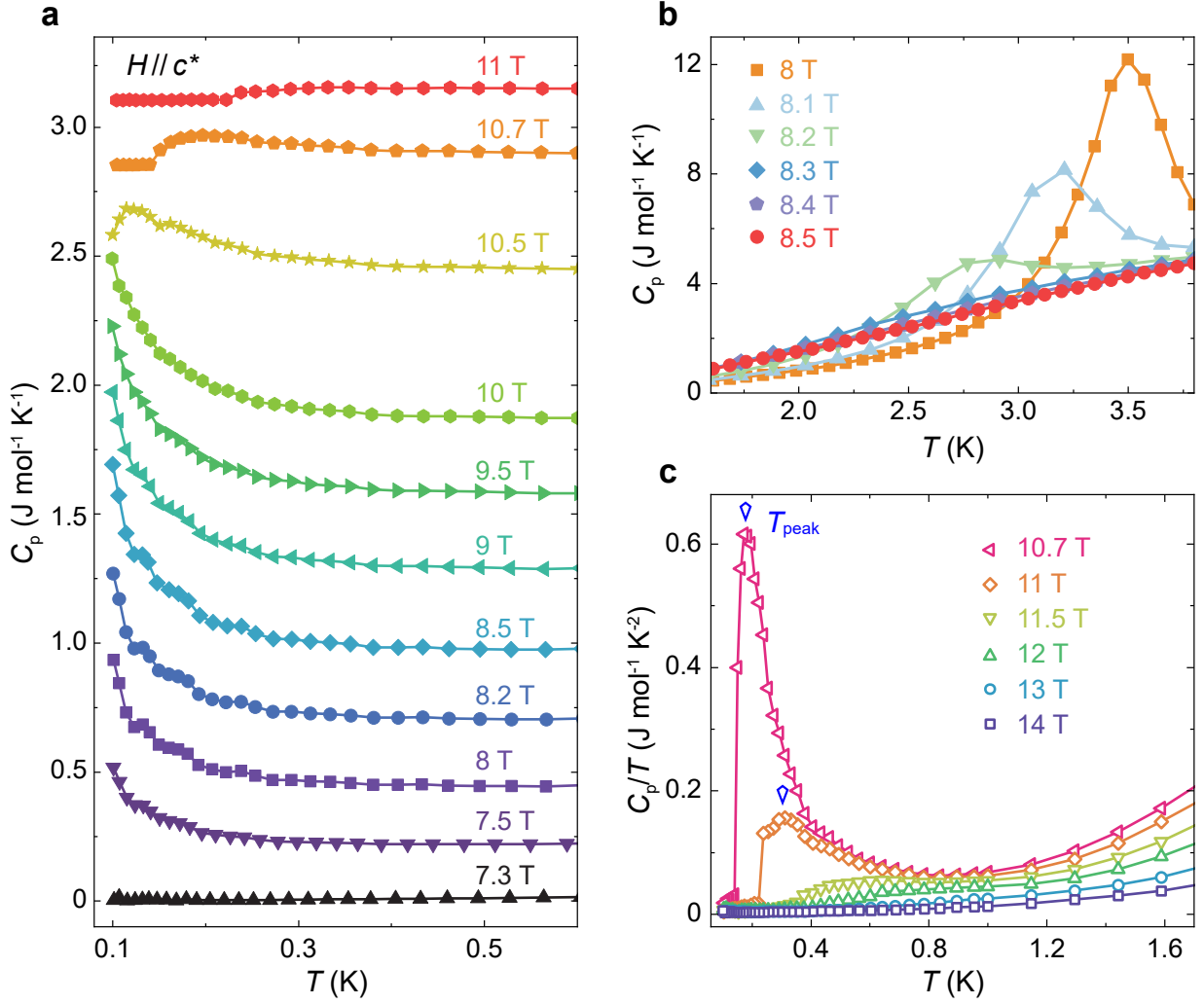
Supplementary Fig. 4: Consistency and reversibility of thermodynamic parameters of $\text{Na}_3\text{Ni}_2\text{BiO}_6$. **a-c**, Comparison of H -dependent ME coefficient $\alpha_x(H)$ (Methods) (**a**), $d(\tau/H)/dH$ (**b**) and field derivative of magnetization dM/dH (**c**) between 6 and 9 T, all measured at 2 K. $d(\tau/H)/dH$ data for $T = 1.5$ K is also shown in **b** (purple). The critical fields $H_{c2} - H_{c5}$ determined from $\alpha_x(H)$ and $d(\tau/H)/dH$ are generally consistent, whereas the small disagreements with those in dM/dH (**c**) are probably due to different sample misalignments with respect to H . Solid and dashed lines are up and down sweeps of H , respectively. Positions of H_{c2} and H_{c5} appear to be almost reversible at these temperatures, but show dependence on field-sweep direction at lower T (Supplementary Fig. 2d). **d**, Magnetization isotherms $M(H)$ measured at $T = 2$ K with $H \parallel c^*$, showing the H -upsweep (red) and downsweep (blue) data. Arrows indicate field-sweep directions. **e**, Specific heat $C_p(H)$ measured at 0.15 K during up (red) and down (blue) sweeps of H . A pronounced anomaly appears at a field roughly coincides with H_{c2} (green vertical dashed line) and persists into the nominally “polarized” state above H_{c5} (grey dash-dotted line). The hysteretic behaviour of such anomaly, however, only shows up below H_{c5} , above which the upsweep and downsweep curves develop an overlap.



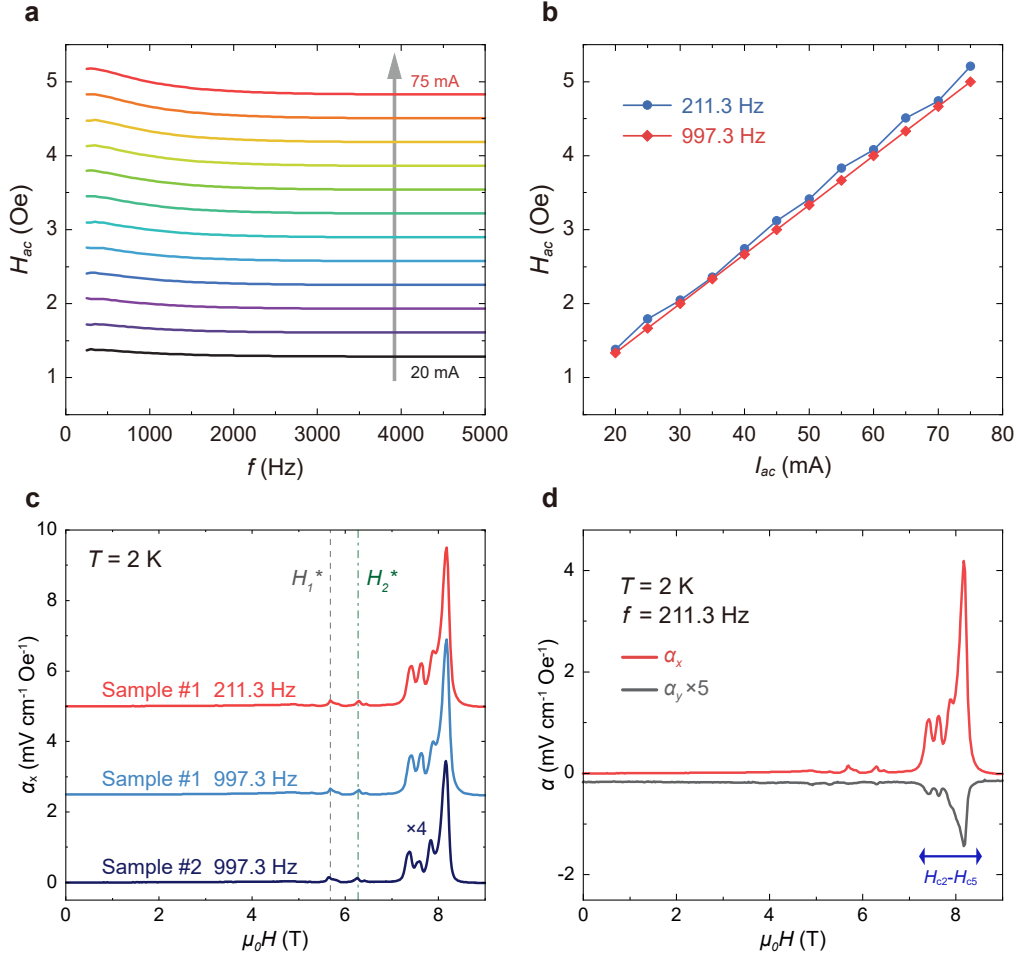
Supplementary Fig. 5: Additional magnetization and ac magnetostriction data. **a, b,** T -dependent magnetization $M(T)$ measured with $H \parallel c^*$ (**a**) and $H \perp c^*$ (i.e., in the ab plane) (**b**), respectively. For $H \parallel c^*$, the low- T parts of $M(T)$ for $\mu_0 H = 6$ and 7 T are indicative of the development of $1/3$ magnetization plateau ($\sim 0.72 \mu_B$ per Ni , denoted by the horizontal blue ribbon). The Néel temperature T_N (black dashed line, determined from the position of peak in dM/dT) and the second magnetic transition T^* implied by the “shoulder-like” feature in $C_p(T)$ (purple dashed line) are marked on the curves. **c,** $M(H)$ measured with $H \parallel ab$ at various T from 2 to 12 K . The step-like feature corresponds to a spin-flop transition. **d,** The ac ME coefficient $\alpha_x(H)$ collected under an in-plane H ; the peak is consistent with the spin-flop transition determined from $M(H)$ (**c**).



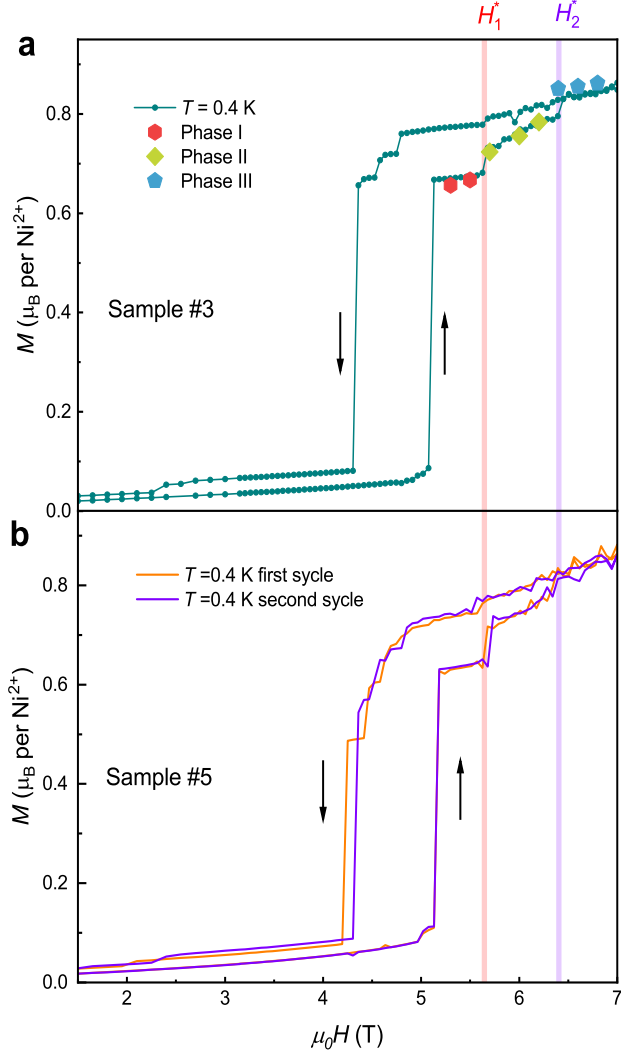
Supplementary Fig. 6: Magnon gap determined from specific heat $C_p(T)$. **a-c**, $C_p(T)$ data measured in the zigzag AFM phase (**a**), $1/3$ -plateau phases (**b**) and the high- H polarized state (**c**). Solid lines are fits to the model incorporating the contributions from phonons and gapped magnons, $C_p(T) = C_{ph}(T) + C_m(T)$ (Supplementary Sec.III). The phononic specific heat $C_{ph} = BT^3$ (inset of panel **a**, obtained by fitting the 14 T data) is almost negligible below 1 K. The satisfactory fitting of above-mentioned model corroborates the gapped magnon spectrum in all three phase regimes. **d**, Evolution of magnon gap under H in the zigzag AFM phase (blue squares), $1/3$ -plateau phases (red circles) and polarized state (olive triangles). Errors represent the standard deviation.



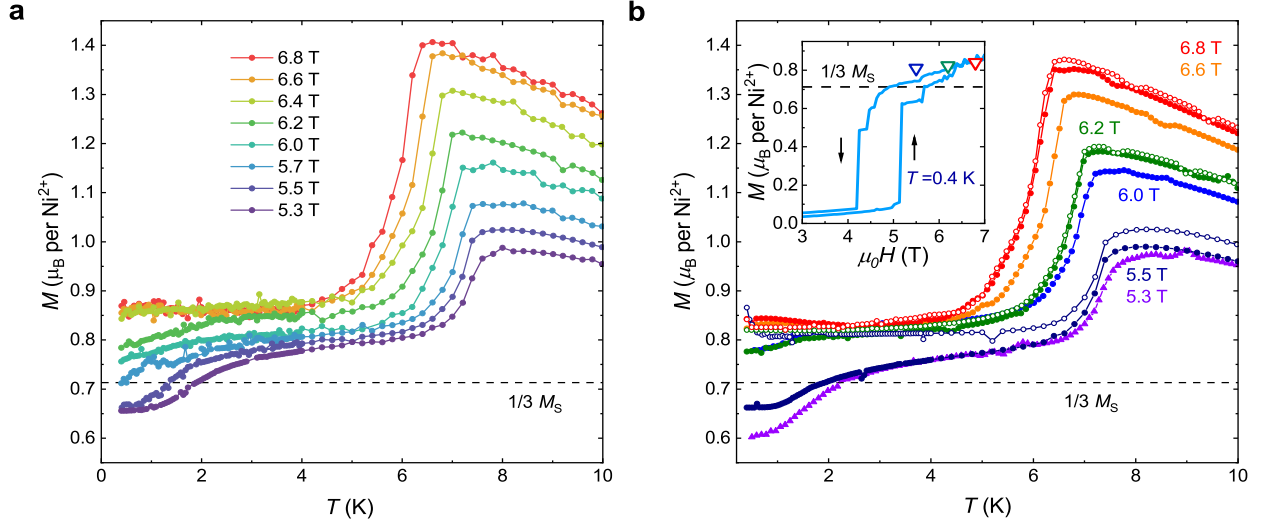
Supplementary Fig. 7: Additional data of low- T specific heat. **a**, $C_p(T)$ between 0.1 and 0.35 K measured under various $H \parallel c^*$ from 7.3 to 11 T. **b**, Evolution of the peak in $C_p(T)/T$ at T_N up to its full suppression. The AFM transition is suppressed to $T_N = 2.75$ K at $\mu_0 H = 8.2$ T before becoming almost indistinguishable at 8.3 T. **c**, An expanded view of the hump-like anomaly of C_p/T appearing above 10.5 T, where the divergent behaviour is weakened. Blue open symbols indicate the position of maximum in C_p/T , T_{peak} (summarized in main text Fig. 4a). An abrupt drop occurs below this maximum, suggesting the crossover to a gapped ground state.



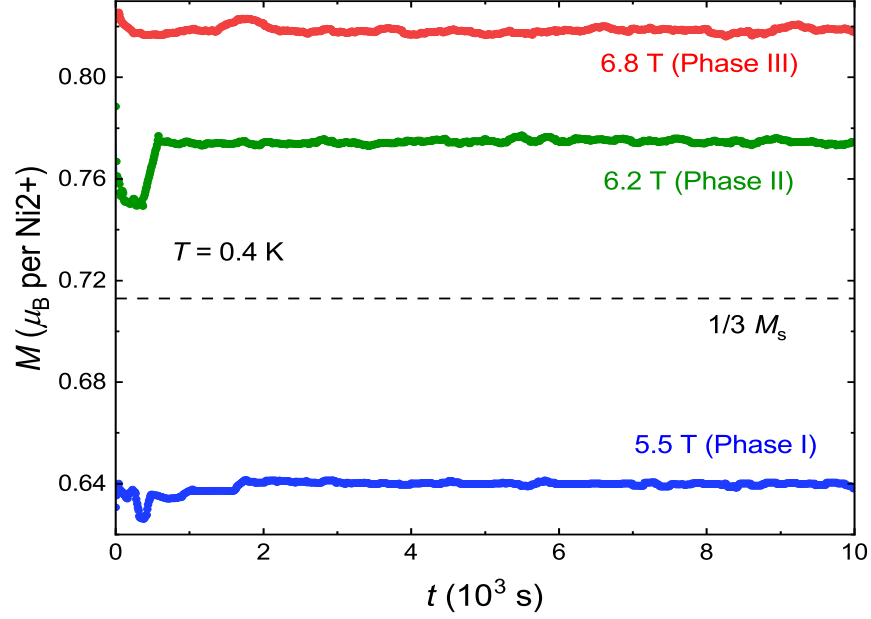
Supplementary Fig. 8: The AC magnetoelectric technique for a direct probing of the linear magnetostriction coefficient. **a**, The ac magnetic field (H_{ac}) generated by the Helmholtz coil in the ac magnetoelectric (ME) probe plotted against the excitation frequency f with application of various excitation current amplitudes from 20 mA to 75 mA. **b**, H_{ac} as a function of excitation currents for fixed $f = 211.3$ Hz (blue) and 997.3 Hz (red). The linear relationship is independent of f . **c**, The real ME coefficient α_x (see Methods) measured with $f = 211.3$ and 997.3 Hz in two samples (#1 and #2). The spectrum is almost f -independent and shows no sample dependence, thus representing the intrinsic behaviour of $\text{Na}_3\text{Ni}_2\text{BiO}_6$. **d**, H -dependent real (α_x) and imaginary (α_y) components of the ME coefficient measured with $f = 211.3$ Hz and $H \parallel c^*$. The magnetic phase transitions are consistently manifested as salient features in $\alpha_x(H)$ and $\alpha_y(H)$, yet with opposite signs (evidence for first-order transitions, see Methods). Data in panels **c**, **d** are offset vertically for clarity.



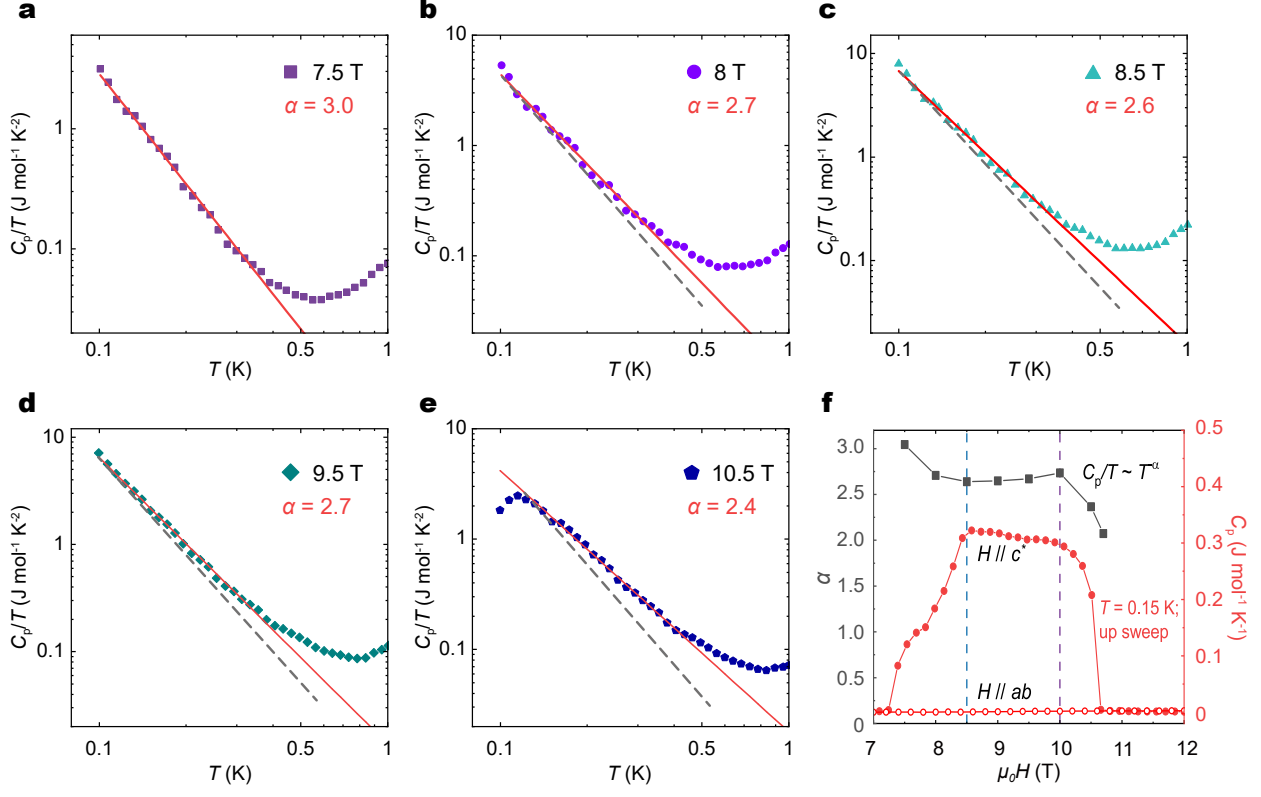
Supplementary Fig. 9: Comparison of the $M - H$ hysteresis loops measured in two $\text{Na}_3\text{Ni}_2\text{BiO}_6$ samples. **a**, $M(H)$ measured at $T = 0.4$ K in Sample #3 (the same data as shown in main text Fig. 2b). **b**, $M(H)$ measured in Sample #5, also at $T = 0.4$ K. In this test, we performed two cycles of field sweeps (orange and purple, respectively). Directions of field sweeps are indicated by the black arrows. Locations of the two steps at H_1^* and H_2^* are highly consistent between the two samples and stay unchanged in different field-sweeping cycles, implying that these signatures correspond to intrinsic field-induced phase transitions.



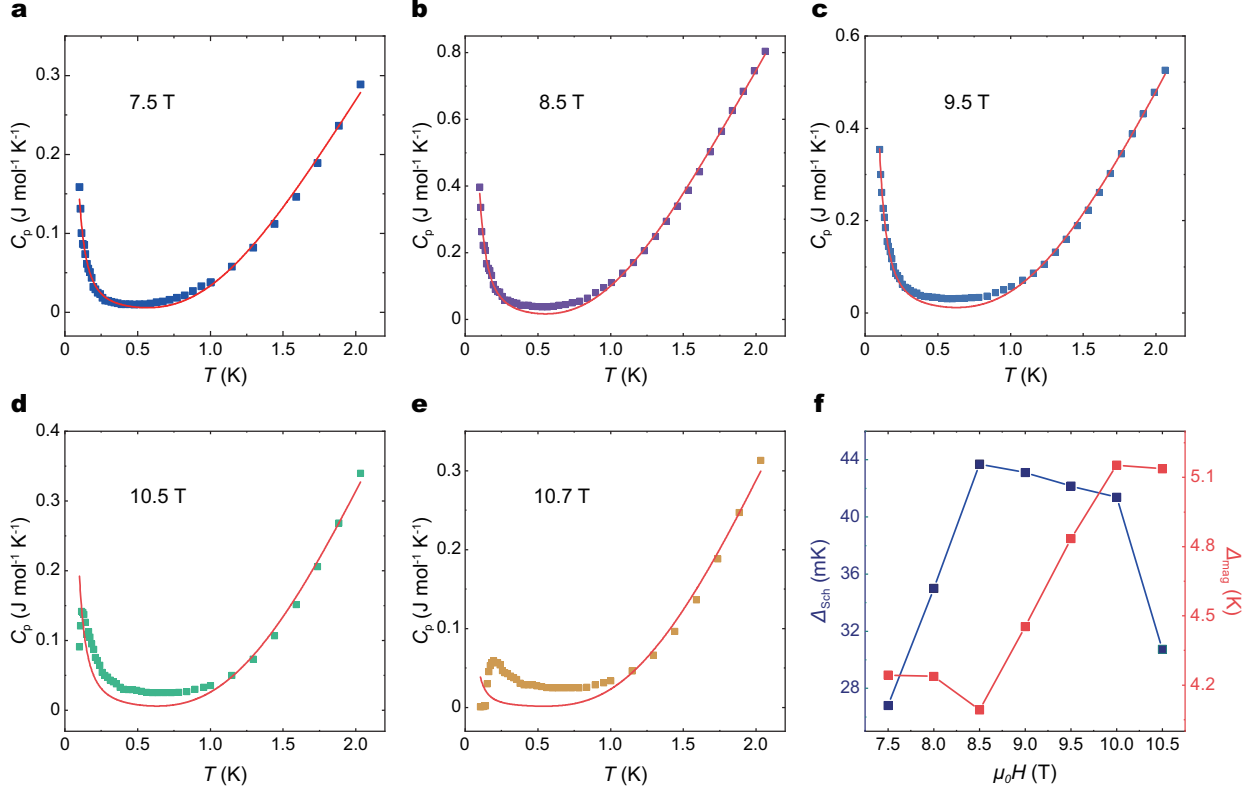
Supplementary Fig. 10: Zero-field-cooled (ZFC) and field-cooled (FC) magnetization $M(T)$ measured under varying magnetic fields. **a**, Data measured in Sample #3, which are the same as those shown in main text Fig. 2d but displayed in unit of magnetic moments per Ni ion. All these curves were measured after a ZFC process. **b**, $M(T)$ data measured in Sample #3. Solid and open symbols are ZFC and field-cooled (FC) data, respectively. Except for the 5.3 T ZFC data (triangles), other ZFC curves (circles) were measured after a one-hour relaxation under the corresponding fields at the lowest T . Inset shows the $M(H)$ hysteresis loop measured in the same sample; arrows indicate the directions of field sweeps. Down triangles represent the values of M extracted from the FC curves measured at 5.5 T (navy), 6.2 T (olive) and 6.8 T (red), respectively.



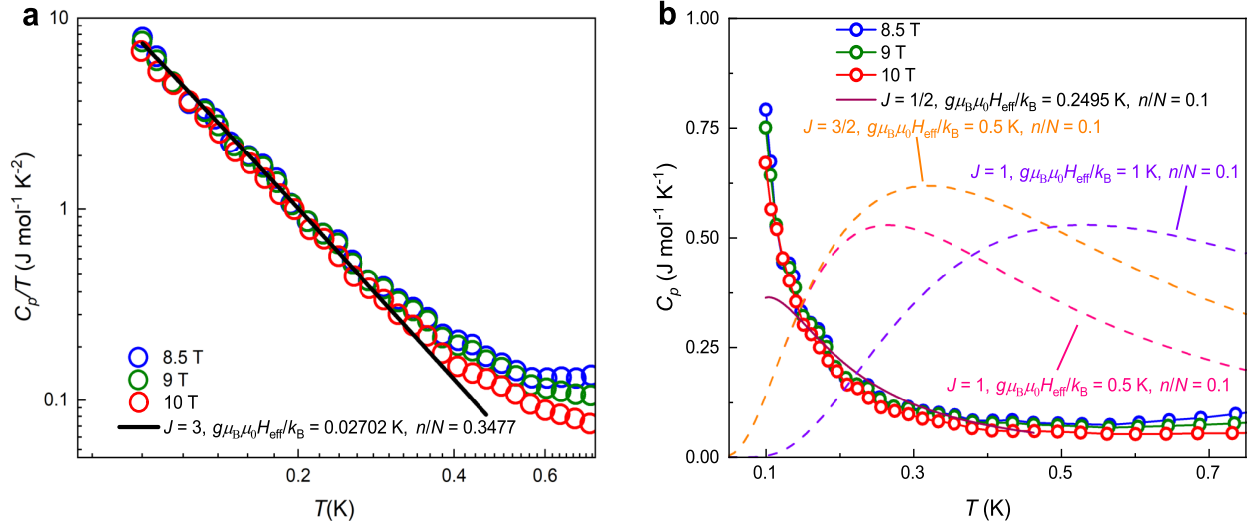
Supplementary Fig. 11: Time evolution of the ZFC magnetization of $\text{Na}_3\text{Ni}_2\text{BiO}_6$. $M(H)$ measured at $T = 0.4$ K under different magnetic fields: $\mu_0 H = 5.5$ T (blue), 6.2 T (olive) and 6.8 T (red). Data were recorded after the ramping of H to the set point and over a relaxation time of 10000 s (~ 2.78 hours). In this experiment we used a vibrating sample magnetometer (VSM) equipped with a He-3 insert; under the specific experimental conditions (close to its base temperature and fields higher than 5 T), it generally yields a noise level of 1.5% of the sample signal during the measurements of $M(H)$. We note that the small jiggling of the curve occurring at $t > 2000$ s is likely to be caused by experimental error of the VSM.



Supplementary Fig. 12: Inverse-power-law fitting for the divergent low- T anomaly of C_p . **a-e**, Log-log plots of C_p versus T under various fields: $\mu_0 H = 7.5$ T (**a**), 8 T (**b**), 8.5 T (**c**), 9.5 T (**d**) and 10.5 T (**e**), respectively. Solid lines verify the validity of inverse-power-law fits $C_p/T \propto T^{-\alpha}$ ($\alpha \simeq 2.4 - 3.0$) in this intermediate phase region. In panels **b-e**, the dark grey dashed lines denote expectation for a high- T limit of the nuclear Schottky contribution, $\alpha = 3$, which obviously deviates from the experimental data. **f**, H dependence of the fitting parameter α (the exponent), compared with the profile of $C_p(H)$. Vertical dashed lines denote the field range in which the low- T anomaly is the strongest. Solid and hollow circles are data of $C_p(H)$ measured at 0.15 K with $H \parallel c^*$ and $H \perp c^*$, respectively (both were taken during upsweeps).



Supplementary Fig. 13: Exclusion of nuclear Schottky specific heat as the origin of low- T C_p anomaly. **a-e**, $C_p(T)$ under various fields [$\mu_0 H = 7.5$ T (**a**), 8.5 T (**b**), 9.5 T (**c**), 10.5 T (**d**) and 10.7 T (**e**), respectively] were fitted to a two-level Schottky model considering also the contribution of gapped magnons: $C_p = C_{\text{Sch}} + C_{\text{m}} = R \left(\frac{\Delta_{\text{Sch}}}{k_B T} \right)^2 \frac{\exp(\Delta_{\text{Sch}}/k_B T)}{[1 + \exp(\Delta_{\text{Sch}}/k_B T)]^2} + A \exp(-\Delta_{\text{mag}}/k_B T)$. Here, $R = k_B N_A$ is the ideal gas constant (N_A the Avogadro constant), Δ_{Sch} and Δ_{mag} are the Schottky gap (energy separation between two levels of nuclear spins) and magnon gap, respectively. Fitting results prove that neither the low- T divergence (**a-c**, note the deviation from data above $\simeq 0.2$ K in **b** and **c**) nor the hump-like anomaly (**d**, **e**) in $C_p(T)$ can be reproduced by the nuclear Schottky model. **f**, Summary of fitting parameters, Schottky gap Δ_{Sch} (blue squares) and magnon gap Δ_{mag} (red squares), plotted against H . The nonmonotonic H dependence of Δ_{Sch} challenges the conventional understanding of nuclear spin level splitting.



Supplementary Fig. 14: Fits and simulations of $C_p(T)$ based on the impurity-induced Schottky contribution. **a**, Best fit of low- T C_p/T anomaly with free parameters J , $xk_B T$ and n/N (black solid line). See Eq. S5 and the contexts for the details of modeling. Blue, green and red symbols are data taken under $\mu_0 H = 8.5, 9$ and 10 T, respectively. **b**, A best fit with J fixed to $1/2$ (the two-level case) and constraint $n/N < 0.1$ (wine solid line). Dashed lines are simulations with specific parameters of J , $xk_B T$ and n/N noted besides the curves. Data points are the same as in **a**.

Spin configurations	ΔE (meV per Ni^{2+})
“ $\circ \uparrow \circ \downarrow \uparrow \uparrow$ ”	0
“ $\uparrow \circ \downarrow \circ \uparrow \uparrow$ ”	-0.78
“ $\circ \uparrow \downarrow \circ \uparrow \uparrow$ ”	0.10
“ $\uparrow \circ \circ \downarrow \uparrow \uparrow$ ”	-0.51

Supplementary Table 3: DFT-calculated energy difference (ΔE) for spin systems with hypothetical partial spin-flop configurations having degenerate net magnetization of $1/3 M_s$ [19]. Here, the magnetic unit is a 6-site spin chain; four spin configurations with spin-flop take place on different sites are depicted as “ $\circ \uparrow \circ \downarrow \uparrow \uparrow$ ”, “ $\uparrow \circ \downarrow \circ \uparrow \uparrow$ ”, “ $\circ \uparrow \downarrow \circ \uparrow \uparrow$ ” and “ $\uparrow \circ \circ \downarrow \uparrow \uparrow$ ”, where symbols “ $\uparrow$ ”, “ $\downarrow$ ” and “ $\circ$ ” represent up, down and flopped (in-plane) spins, respectively. The calculated result suggests that these postulated spin configurations are actually nearly-degenerate states with small energy differences (ΔE less than 1 meV per Ni^{2+}).

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