Supplementary Materials for

Magnetic structure of layered $Co_2B_2O_5$ and the role of the bridging B_2O_5 anions in three-dimensional magnetic ordering

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SM1. Structural information

Table S1 Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $Co_2B_2O_5$.

Atom	Wyck.	*x*	*y*	*z*	U_{iso}*/U_{eq} (Å^2)
Co1	2*i*	0.73014(13)	0.21238(8)	0.35890(5)	0.0081(2)
Co2	2*i*	0.23455(13)	0.37164(8)	0.10170(5)	0.0074(2)
B1	2*i*	0.6984(11)	0.6811(7)	0.3555(4)	0.0075(7)
B2	2*i*	0.3331(11)	0.8810(6)	0.1692(4)	0.0072(7)
O1	2*i*	0.2608(8)	0.6962(5)	0.0542(3)	0.0092(5)
O2	2*i*	0.2175(8)	0.0929(5)	0.1811(3)	0.0099(5)
O3	2*i*	0.7386(8)	0.4765(4)	0.2580(3)	0.0086(5)
O4	2*i*	0.5594(8)	0.8604(4)	0.2986(3)	0.0101(5)
O5	2*i*	0.7713(8)	0.7247(5)	0.5030(3)	0.0104(5)

Table S2 Anisotropic atomic displacement parameters (Å^2) of $Co_2B_2O_5$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co1	0.0080(3)	0.0094(3)	0.0072(3)	0.0026(2)	0.00013(19)	-0.00059(19)
Co2	0.0075(3)	0.0085(3)	0.0065(3)	0.0027(2)	0.00046(18)	-0.00019(18)
B1	0.0055(15)	0.0094(17)	0.0077(17)	0.0024(13)	0.0004(12)	0.0016(12)
B2	0.0075(14)	0.0091(18)	0.0053(16)	0.0024(14)	0.0021(12)	-0.0007(12)
O1	0.0088(11)	0.0102(12)	0.0082(12)	0.0014(10)	-0.0009(9)	-0.0007(9)
O2	0.0127(12)	0.0075(12)	0.0097(12)	0.0023(9)	0.0007(9)	0.0021(9)
O3	0.0107(12)	0.0079(12)	0.0068(11)	0.0011(9)	0.0013(9)	-0.0001(9)
O4	0.0132(11)	0.0085(12)	0.0077(11)	0.0003(9)	-0.0029(9)	0.0010(9)
O5	0.0092(11)	0.0155(13)	0.0063(12)	0.0018(9)	0.0009(9)	0.0012(9)

Table S3. Bond valence (v.u.) analysis for $Co_2B_2O_5$ [1]. The calculations were carried out for cobalt and boron ions with R_{Co} = 1.692, R_B = 1.371, and parameter R = 0.37. The *C.N.* denotes coordination number.

	Co1	Co2	B1	B2	Σ	Σ/*C.N.*
O1		0.294 0.300 0.359		1.038	1.991	0.498
O2	0.216 0.209	0.416		1.076	1.917	0.479
O3	0.375	0.287 0.326	1.031		2.019	0.505
O4	0.300		0.890	0.880	2.070	0.690
O5	0.461 0.392		1.101		1.954	0.651
Σ	1.953	1.982	3.022	2.994		

SM2. Sample characterization

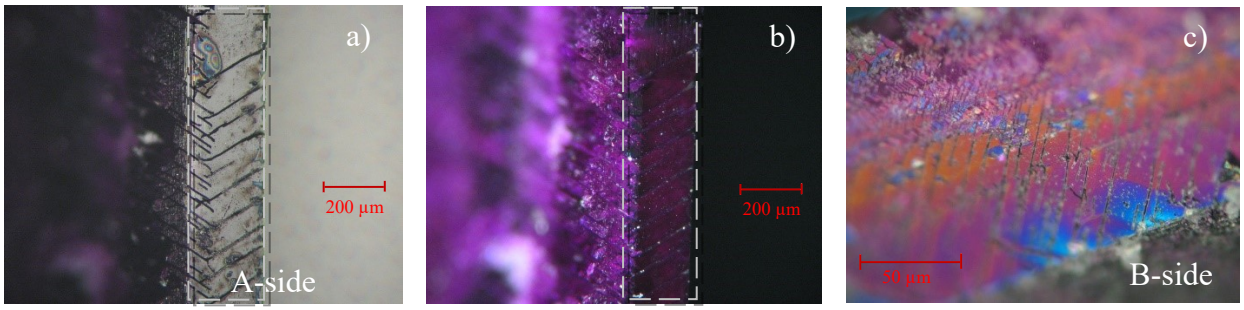

Fig. S1 Micrographs of the $Co_2B_2O_5$ single crystal in a brightfield (a) and darkfield polarized (b,c) reflected light. The A-side has a mirror surface.

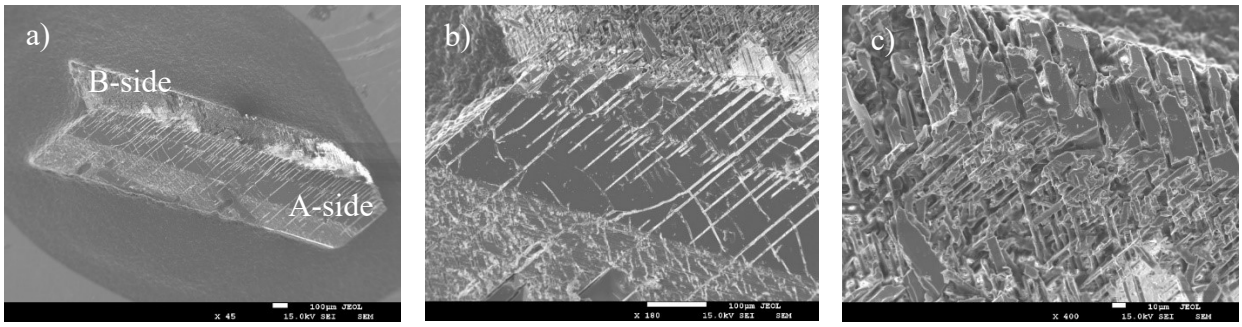

Fig. S2. (a) SEM images of $Co_2B_2O_5$ single crystal. Magnified views of the surfaces of A-side (b) and B-side (c).

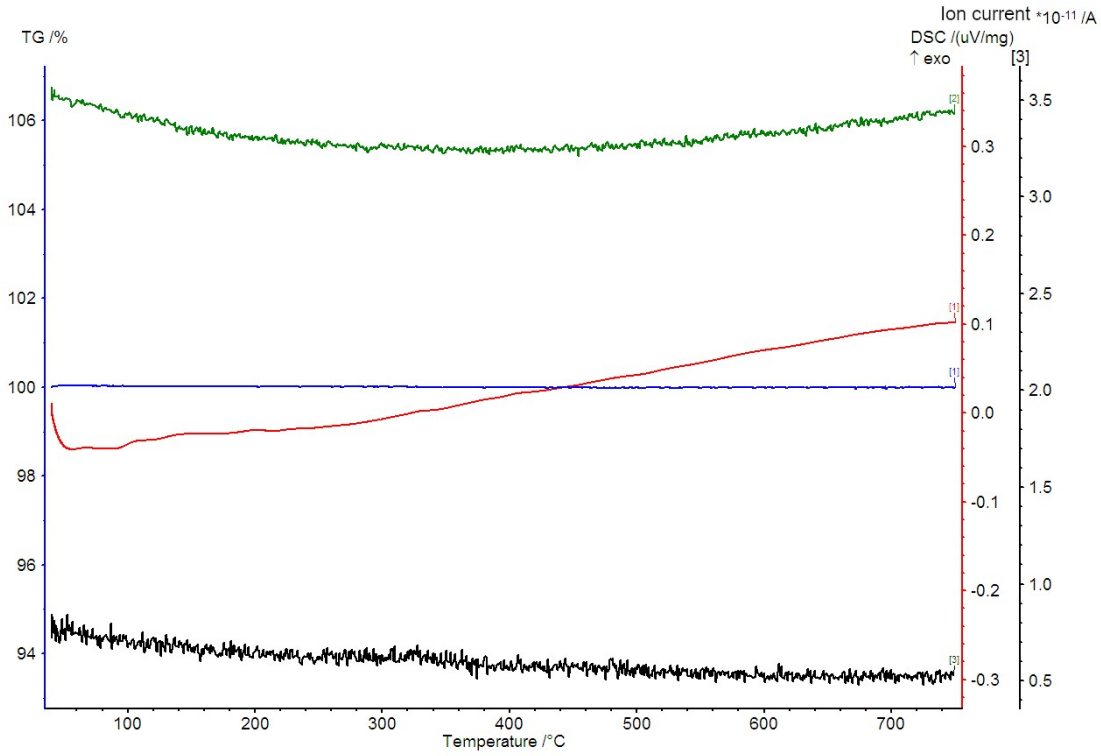

Fig. S3 TG (blue), DSC (red) and intensity of ion current (olive, m/z=18; black m/z=44) curves for the crashed single crystal $Co_2B_2O_5$.

SM3. DFT+U calculations

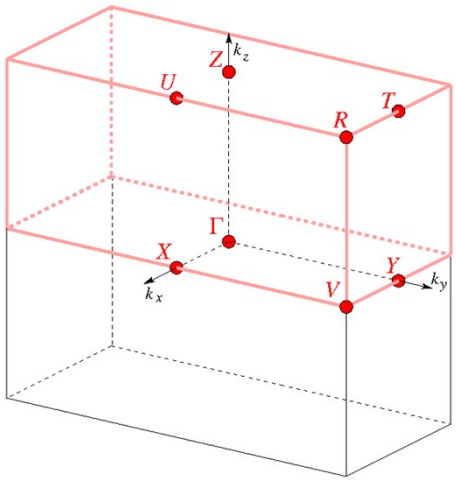

Fig. S4. Brillouin zone of $Co_2B_2O_5$ with the high symmetry **k**-points marked as used in calculations (retrieved from Bilbao Crystallographic server [2]).

Table S4. Variation of band gap, magnetic moments, and lattice parameters of $Co_2B_2O_5$ with Hubbard parameter *U*.

U (eV)	Band gap (eV)	Moment per atom (μ_B)		Lattice parameters					
		Co1	Co2	*a* (Å)	*b* (Å)	*c* (Å)	α (grad)	β (grad)	γ (grad)
0	0.23	2.58	2.59	3.1875	6.2104	9.3264	104.28	90.85	91.95
1	1.22	2.65	2.66	3.1890	6.2137	9.3292	104.28	90.85	91.96
2	2.13	2.69	2.70	3.1900	6.2155	9.3316	104.29	90.84	91.96
2.5	2.62	2.71	2.72	3.1905	6.2168	9.3334	104.29	90.84	91.96
3	3.14	2.73	2.74	3.1910	6.2179	9.3351	104.29	90.84	91.97
3.5	3.55	2.75	2.76	3.1914	6.2187	9.3365	104.29	90.84	91.97
4	4.17	2.77	2.78	3.1916	6.2193	9.3373	104.30	90.83	91.97
5	4.78	2.80	2.81	3.1920	6.2207	9.3393	104.30	90.83	91.98
6	5.11	2.82	2.83	3.1921	6.2217	9.3401	104.31	90.82	91.99

The effect of the Hubbard parameter *U* on the band gap, magnetic moments, and lattice parameters is summarizes in Table S4. With increasing *U*, the band gap increases and at $U = 4$ eV approaches the value close to the experimental optical band gap of 4.20 eV. The magnetic moments on Co atoms are noticeably changed up to $U = 4$ eV, followed by the small change. The *a*, *b*, and *c* lattice parameters increase significantly up to $U = 4$ eV, after which the increase is not steep. For $U = 4$ eV the lattice parameters approach the values close to our experimental and reported in Ref. [3].

Table S5. Maximal magnetic space groups for the parent space group $P\bar{1}$ and the propagation vectors k = (0, 0, 0), (½, 0, 0), and (0, ½, ½). The type of ordering permitted in the sublattice (ferro- or antiferromagnetic) determine the net magnetic moment. The MAXMAGN program [4] on the Bilbao Crystallographic Server was used to prepare this table.

Group (BNS)		Magnetic moment			
		Per atom	Net	Per atom	Net
		2*i* position (Co1)		2*i* position (Co2)	
k = (0, 0, 0)					
P-1' (#2.6)	mGM_1^-	±Mx, ±My, ±Mz	0, 0, 0	±Mx, ±My, ±Mz	0, 0, 0
P-1 (#2.4)	mGM_1^+	Mx, My, Mz	Mx, My, Mz	Mx, My, Mz	Mx, My, Mz
k = (½, 0, 0)					
P_S-*1* (#2.4.7)	mX_1^-	±Mx, ±My, ±Mz	0, 0, 0	±Mx, ±My, ±Mz	0, 0, 0
P_S-*1* (#2.4.7)	mX_1^+	Mx, My, Mz	0, 0, 0	Mx, My, Mz	0, 0, 0
k = (0, ½, ½)					
P_S-*1* (#2.4.7)	mT_1^-	±Mx, ±My, ±Mz	0, 0, 0	±Mx, ±My, ±Mz	0, 0, 0
P_S-*1* (#2.4.7)	mT_1^+	Mx, My, Mz	0, 0, 0	Mx, My, Mz	0, 0, 0

Table S6. The selective collinear (C) magnetic orderings constructed in accordance with basis vectors of the irreducible representations (IRs). The reference energies ΔE (meV/f.u.) are given relative to the energy of the ground magnetic ordering ($C\text{-}AFM_{T\#1}$). The A and B ribbons consist of the rows Co1-Co2-Co2′-Co1′ (see text, Fig. 3). The rows are ferromagnetically coupled along [100] direction for **k** = (0, 0, 0) and (0, ½, ½) and antiferromagnetic for **k** = (½, 0, 0). The cobalt magnetic moments are directed along [101] for all propagation vectors. The arrows indicate the mutual direction of the magnetic moments within each row. The *M* is total magnetic moment per formula unit (μ_B).

IRs	Magnetic ordering	ΔE	A (Co1-Co2-Co2′-Co1′)	B (Co1-Co2-Co2′-Co1′)	*M*
			k = (0, 0, 0)		
mGM_1^-	$C\text{-}AFM_{GM\#1}$	4.12	↑ – ↑ – ↓ – ↓	↑ – ↑ – ↓ – ↓	0
mGM_1^-	$C\text{-}AFM_{GM\#2}$	7.98	↑ –↓ – ↑ – ↓	↑ –↓ – ↑ – ↓	0
mGM_1^+(Co1) ⊕ mGM_1^-(Co2)	$C\text{-}AFM_{GM\#3}$	18.65	↑ – ↓ – ↑ – ↑	↑ –↓ – ↑ – ↑	3.45
mGM_1^-(Co1) ⊕ mGM_1^+(Co2)	$C\text{-}AFM_{GM\#4}$	35.90	↑ – ↑ – ↓ – ↑	↑ – ↑ – ↓ – ↑	3.53
mGM_1^+	$C\text{-}FM_{GM\#5}$	37.50	↑ – ↑ – ↑ – ↑	↑ –↑ –↑ –↑	6.9
			k = (0, ½, ½)		
mT_1^-	$C\text{-}AFM_{T\#1}$	0	↑ –↑ – ↑ – ↑	↓ – ↓ – ↓ –↓	0
mT_1^-	$C\text{-}AFM_{T\#2}$	12.57	↑ –↓ – ↓ – ↑	↓ – ↑ – ↑ – ↓	0
mT_1^+	$C\text{-}AFM_{T\#3}$	27.76	↑ –↑ – ↓ – ↓	↓ –↓ – ↑ – ↑	0
			k = (½, 0, 0)		
mX_1^-	$C\text{-}AFM_{X\#1}$	29.53	↑ –↑ – ↑ – ↑	↓ – ↓ – ↓ –↓	0
mX_1^+	$C\text{-}AFM_{X\#2}$	39.84	↑ –↑ – ↓ – ↓	↑ –↑ – ↓ – ↓	0

Table S7. The selective non-collinear (NC) magnetic orderings constructed in accordance with basis vectors of the irreducible representations (IRs). The reference energies ΔE (meV/f.u.) are given relative to the energy of the ground magnetic ordering (C-AFM$_{T\#1}$). The A and B ribbons consist of the rows Co1-Co2-Co2′-Co1′ (Fig. S6). The rows are ferromagnetically coupled along [100] direction. The directions of the cobalt magnetic moments are shown in the 2nd column for Co1 – Co1′ and Co2 – Co2′. The arrows indicate the mutual direction of the magnetic moments within each row. The *M* is total magnetic moment per formula unit (μ_B).

IRs	Magnetic moments directions	Magnetic ordering	ΔE	A (Co1-Co2-Co2′-Co1′)	B (Co1-Co2-Co2′-Co1′)	*M*
			k = (0, 0, 0)			
mGM_1^+	[100] - [010]	NC-FM$_{GM\#1}$	9.31	↑ – ↑ – → – →	↑ – ↑ – → – →	3.25
mGM_1^+	[010] - [001]	NC-FM$_{GM\#2}$	9.35	↑ – ↑ – → – →	↑ – ↑ – → – →	3.15
mGM_1^+	[100] - [001]	NC-FM$_{GM\#3}$	9.52	↑ – ↑ – → – →	↑ – ↑ – → – →	3.26
mGM_1^+	[010] - [001]	NC-AFM$_{GM\#4}$	35.9	↑ – ↑ – → – →	↓ – ↓ – ← – ←	0.12
mGM_1^+	[100] - [010]	NC-AFM$_{GM\#5}$	37.1	↑ – ↑ – → – →	↓ – ↓ – ← – ←	0.17
mGM_1^+	[100] - [001]	NC-AFM$_{GM\#6}$	39.1	↑ – ↑ – → – →	↓ – ↓ – ← – ←	0.21
			k = (0, ½, ½)			
mT_1^+	[100] - [010]	NC-FM$_{T\#1}$	4.8	↑ – ↑ – ← – ←	↓ – ↓ – → – →	0.86
mT_1^+	[010] - [001]	NC-FM$_{T\#2}$	5.0	↑ – → – ← – ↓	↓ – ← – → – ↑	0.90
mT_1^+	[100] - [001]	NC-FM$_{T\#3}$	6.6	↑ – ↑ – ← – ←	↓ – ↓ – → – →	0.91
mT_1^-	[010] - [001]	NC-AFM$_{T\#4}$	48.3	↑ – ↑ – ← – ←	↓ – ↓ – → – →	0.37
mT_1^-	[100] - [010]	NC-AFM$_{T\#5}$	51.8	↑ – ↑ – ← – ←	↓ – ↓ – → – →	0.41
mT_1^-	[100] - [001]	NC-AFM$_{T\#6}$	56.2	↑ – ↑ – ← – ←	↓ – ↓ – → – →	0.45

Table S8. Atomic coordinates of the triclinic and monoclinic structures of $Co_2B_2O_5$ obtained from DFT+U calculations. All sites are of 2*i* and 4*e* Wyckoff positions for triclinic and monoclinic strictures, respectively.

	Triclinic, space group $P\bar{1}$(2), Z = 4			Monoclinic, space group $P2_1/c$(14), Z = 4		
Atoms	*x*	*y*	*z*	*x*	*y*	*z*
Co1	0.1358	0.7873	0.6411	0.8979	0.7119	0.3134
Co2	0.6358	0.7873	0.6411	0.1021	0.2881	0.6865
Co3	0.3643	0.2128	0.3589	0.1021	0.2118	0.1866
Co4	0.8643	0.2128	0.3589	0.8979	0.7881	0.8134
Co5	0.3818	0.6276	0.8981	0.3581	0.7954	0.6067
Co6	0.8818	0.6276	0.8981	0.6420	0.2049	0.3932
Co7	0.1182	0.3725	0.1020	0.6419	0.2953	0.8933
Co8	0.6182	0.3725	0.1020	0.3580	0.7048	0.1068
B1	0.1510	0.3183	0.6451	0.7012	0.0726	0.5708
B2	0.6510	0.3183	0.6451	0.2987	0.9273	0.4293

B3	0.3490	0.6817	0.3549	0.2988	0.5727	0.9292
B4	0.8490	0.6817	0.3549	0.7012	0.4273	0.0707
B5	0.3329	0.1110	0.8307	0.8192	0.7226	0.4544
B6	0.8329	0.1110	0.8307	0.1808	0.2777	0.5458
B7	0.1671	0.8800	0.1693	0.1808	0.2226	0.0456
B8	0.6671	0.8800	0.1693	0.8191	0.7776	0.9542
O1	0.3692	0.3035	0.9460	0.9455	0.7867	0.6516
O2	0.8692	0.3035	0.9460	0.0547	0.2131	0.3485
O3	0.1309	0.6964	0.0539	0.0545	0.2867	0.8484
O4	0.6309	0.6964	0.0539	0.9453	0.7133	0.1515
O5	0.3913	0.9077	0.8188	0.4972	0.3024	0.6379
O6	0.8913	0.9077	0.8188	0.5028	0.6976	0.3621
O7	0.1087	0.0923	0.1813	0.5028	0.8024	0.8621
O8	0.6087	0.0923	0.1813	0.4971	0.1976	0.1379
O9	0.1306	0.5238	0.7418	0.7414	0.2727	0.7616
O10	0.6306	0.523835	0.7418	0.2587	0.7274	0.2385
O11	0.3694	0.4762	0.2582	0.2586	0.7726	0.7384
O12	0.8694	0.4762	0.2582	0.7413	0.2274	0.2615
O13	0.2201	0.1405	0.7017	0.6449	0.2243	0.6589
O14	0.7201	0.1405	0.7017	0.3553	0.7755	0.3411
O15	0.2799	0.8594	0.2983	0.3552	0.7244	0.8411
O16	0.7799	0.8594	0.2983	0.6449	0.2755	0.1590
O17	0.1142	0.2761	0.4973	0.83034	0.8492	0.5604
O18	0.6142	0.2761	0.4973	0.1694	0.1506	0.4392
O19	0.3858	0.7239	0.5027	0.1696	0.3492	0.9396
O20	0.8858	0.7239	0.5027	0.8306	0.6507	0.0607

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