Magnetization plateaux cascade in the frustrated quantum antiferromagnet Cs$_2$CoBr$_4$

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We have found an unusual competition of two frustration mechanisms in the 2D quantum antiferromagnet Cs$_2$CoBr$_4$. The key actors are the alternation of single ion planar anisotropy direction of individual magnetic Co$^{2+}$ ions, and their arrangement in a distorted triangular lattice structure. In particular, uniquely oriented Ising-type anisotropy emerges from competition of easy plane ones, and for a magnetic field applied along this axis one finds a cascade of five ordered phases at low temperatures. Two of these phases feature magnetization plateaux. The low field one is supposed to be a consequence of collinear ground state stabilized by the anisotropy, while the other plateau bears characteristics of an “up-up-down” state endemic for lattices with triangular exchange patterns.

A conventional picture of frustrated quantum magnet implies a competition between the Heisenberg terms in $S = 1/2$ Hamiltonian. A Heisenberg magnet on a generic triangular lattice is an archetype example [1]. Anisotropy, if present, is usually just a weak perturbation stemming from the spin-orbit interactions. Alternatively, like in triangular lattice XXZ model, it acts in the same way on every bond and this situation is not drastically different from the Heisenberg case [2]. However, recently emerging topics of quantum spin ice [3, 4] or Kitaev magnets [5, 6] teach us a very different approach. In those emerging topics of quantum spin ice [3, 4] or Kitaev magnets, but is also possible in 3d magnets, for instance cobalt-based ones [17]. In fact, in low symmetry Co$^{2+}$ magnets ($S = 3/2$ and quenched orbital momentum) the single ion anisotropy that splits the $|\pm 1/2\rangle$ and $|\pm 3/2\rangle$ spin states may not be uniform between the sites. If no unique anisotropy axis is present, the interactions between the spins become frustrated automatically. If the spins are at the same time residing on a non-bipartite lattice such as a triangular one, geometrical frustration is also there. Two frustration mechanisms are present simultaneously and this results in a complicated interplay. This possibility is relatively well explored for a perfect triangular lattice [5], but much less so for less symmetric cases.

The subject material of the present Letter, Cs$_2$CoBr$_4$, possesses an interesting combination of geometric frustration and anisotropy very much in line with the above discussion. It is the last unexplored member of otherwise well known family of quantum magnets with the distorted triangular lattice Cs$_2$MX$_4$, where $M$ is copper or cobalt and $X$ is chlorine or bromine. The other three materials, essentially chain-like magnets Cs$_2$CuCl$_4$ [9, 10], Cs$_2$CoCl$_4$ [11, 12] and more two-dimensional Cs$_2$CuBr$_4$ [14, 15] demonstrate very rich phase diagrams in applied magnetic fields. Although the existence of the last material in this quartet, Cs$_2$CoBr$_4$, was documented a long time ago [16], it was never investigated in a context of quantum magnetism. In this Letter we report the highly unusual magnetic phase diagram of Cs$_2$CoBr$_4$, that is very anisotropic and features a cascade of magnetization plateaux for one particular direction of the magnetic field. One of these plateaux is found at zero magnetization, while the other corresponds to a field induced “up-up-down” phase that is characteristic for the triangular lattice systems. The plateaux are well compatible with the effective Hamiltonian, which at the same time creates a lot of uncertainty for the nature of the remaining phases due to the unusual interplay of different frustration mechanisms.

Transparent, cerulean-coloured single crystals of Cs$_2$CoBr$_4$ were grown using the Bridgman method [16]. Its structure is isomorphic to that of the other Cs$_2$MX$_4$ materials, orthorhombic $P_{nma}$ (space group 62) with $a = 10.181$, $b = 7.723$, $c = 13.492$ Å. The unit cell shown in Fig. 1(a) contains four Co$^{2+}$ $S = 3/2$ ions within four CoBr$_4$ distorted tetrahedra, related to each other by mirror reflections in $ab$ and $bc$ planes. Mirror $ac$ plane is the only symmetry of an individual distorted tetrahedron. As local symmetry at Co$^{2+}$ site is lower than cubic, the single ion anisotropy $D(n \cdot S)^2$ should be present. The anisotropy axis is $n = (\pm \cos \beta, 0, \sin \beta)$ on different tetrahedra, as the symmetry dictates. The angle $\beta$ and sign of anisotropy constant $D$ are not known a priori (in a sister material Cs$_2$CoCl$_4$ they are estimated as $\beta \simeq 51^\circ$ and $D \simeq 7$ K [11]). Further idea about interactions between the cobalt spins can be derived from comparison with Cs$_2$CoCl$_4$, Cs$_2$CuCl$_4$ and Cs$_2$CuBr$_4$. All of them have dominant interaction $J$ within the chains running along $b$ direction, while the weaker zig-zag exchange $J'$ connects the chains into distorted triangular lattice in the $bc$ plane, see Fig. 1(c). The exchange along the $a$ direction is negligibly small. Value of $J'/J$ may vary from almost zero (Cs$_2$CoCl$_4$ case) to $0.3 - 0.5$ in copper based members of the family.

The key parameters of the Hamiltonian, such as $D$, $\beta$ and mean field exchange coupling $J_0 = 2J + 4J'$ can be straightforwardly extracted from the magnetic susceptibility data for fields, applied along the three principal directions of the crystal. Magnetic susceptibility $\chi = M/H$ of an $m = 8.9$ mg Cs$_2$CoBr$_4$ single crystal...
was measured with an MPMS SQUID magnetometer in a field of 0.1 T. This data is shown in Fig. 1(b). The $H \parallel b$ (perpendicular to $n$) susceptibility is quite different from $H \parallel a, c$ directions that look rather similar (angles $\beta$ and $\pi/2 - \beta$ between the field and $n$). All of them show typical “Curie tail” behavior at high temperatures, that becomes suppressed at low temperatures as antiferromagnetic correlations take over. Susceptibility along $b$ shows a rounded maximum close to 4 K — a picture, typical for low-dimensional magnets with suppressed magnetic order. No signs of ordering are found down to 0.8 K. The simultaneous fitting of the data for all three directions, based on a single ion model with mean field interactions (see the Supplemental Material for details) yields $D = 14(1)$ K, $\beta = 44(1)^\circ$ and $J_0 = 5.5(2)$ K, with $g$-factors being 2.42(1), 2.47(2) and 2.37(1) along $a, b$ and $c$ directions. This means that i) single ion anisotropy is of easy plane type, so at low temperature only pseudospin-1/2 degrees of freedom are active, and ii) easy planes, while being uniform within the chains, have alternating orientation between the chains and the neighboring ones are nearly orthogonal to each other. We can consider $\beta = \pi/4$ for practical purposes. Then, utilizing the “rotated” $xyz$ coordinate system [Fig. 1(d)], the approximate Hamiltonian for the $S = 3/2$ cobalt spins can be written as:

$$
\hat{H}_{3/2} = \sum_{i,j} D \left[ \left( \hat{S}_{2i,j}^z \right)^2 + \left( \hat{S}_{2i+1,j}^z \right)^2 \right] + J \langle \hat{S}_{i,j} \cdot \hat{S}_{i,j+1} \rangle \\
+ J' \langle \hat{S}_{i,j} \cdot \hat{S}_{i+1,j} \rangle + J'' \langle \hat{S}_{i,j} \cdot \hat{S}_{i+1,j+1} \rangle
$$

To construct the effective low-energy Hamiltonian, one needs to project out the high-spin states that are inaccessible at low temperatures due to large $D$. This is achieved by SchriefferWolff transformation [12, 18], where to the zeroth order we can simply replace spin-3/2 operators with spin-1/2 ones as $\hat{S}_{x\gamma} \rightarrow 2\hat{S}_{x\gamma}^z$ and $\hat{S}_{z} \rightarrow \hat{S}_{z}$ in even chains; $\hat{S}_{x\gamma} \rightarrow 2\hat{S}_{x\gamma}^z$ and $\hat{S}_{x} \rightarrow \hat{S}_{x}$ in odd chains. The resulting Hamiltonian is:
The low temperature specific heat in A- and C-phases is vanishingly small. This suggests their gapped nature (see the Supplemental Material for some details [17]). While for small magnetic fields the gap seems a natural consequence of Ising-like anisotropy, its presence in the magnetized C-state is not so trivial. A candidate gapped state in a system featuring triangular bond pattern is the famous “up-up-down” (abbreviated as und) collinear spin arrangement. This is further confirmed by a direct measurement of Cs$_2$CoBr$_4$ magnetization curve at 100 mK. This measurement is performed on the same sample as the specific heat with the help of miniature home-built Faraday balance magnetometer with a twist-resistant cantilever [21]. The resulting curves are demonstrated in Fig. 3 together with the reference data from SQUID magnetometer at 1.8 K that was also used for calibration. While for the transverse $\mathbf{H} \parallel \mathbf{a}$ direction the measured magnetization curve is relatively smooth and shows only weak kinks at the two phase transitions, the situation is very different for longitudinal $\mathbf{H} \parallel \mathbf{b}$ magnetization. Most of the transitions are marked with discontinuities. Moreover, the slope of the magnetization curve is clearly reduced in A- and C-phases. But are these the real magnetization plateaux? We argue that they are. The extra slope $dM/dH$ is originating from admixing of single ion high energy $|\pm 3/2⟩$ states to the ground state by a non-commuting magnetic field, and it is also pronounced at high fields when the pseudospin degrees of freedom are fully polarized. The slope of magnetization curve slightly above 6 T [22] should provide a reasonable estimate of the effect. The corrected data representing the relative magnetization of the pure pseudospin-1/2 is shown in the inset of Fig. 3(b). The plateau character of the A- and C-phases is much more pronounced in this representation.

For the low field A-phase a suitable candidate structure might be a collinear antiferromagnetic “stripe” state (as it was observed in a sister material Cs$_2$CoCl$_4$ [13], see Fig. 4). This state automatically satisfies the anisotropic exchange interactions within both even and odd chains. On the mean field level the chains remain decoupled for any strength of $J'$, and the overall collinear structure must be fixed by some kind of “order from disorder”
importance of collinear structure. This is again pointing to the saturated value for the pseudospin, validating it as a proposal for extremely exotic physics is too preliminary at the moment, Hamiltonian (2) taken together with the phase diagram in Fig. 2(b) is suggestive of some nontrivial spin textures that may be present among the many magnetic phases. We would also like to stress that the proposed Hamiltonian (2) is the most basic one, and does not include further symmetry-allowed terms such as second single-ion anisotropy constant $E$ and multiple Dzyaloshinskii–Moriya interactions (that are very important in Cs$_2$CuCl$_4$, for instance [10, 32, 33]).

To summarize, $S = 3/2$ quantum antiferromagnet Cs$_2$CoBr$_4$ is found to feature an unusual type of frustration that stems from both the geometry of exchange bonds and geometry of the strong single-ion anisotropies. The “spin space” component of frustration creates an effective $S = 1/2$ Hamiltonian with an emergent special direction. Application of the field along this direction results in a cascade of phase transitions, with two phases being $M \approx 0$ and $M \approx 1/3$ magnetization plateaux. While the plateau states can be preliminarily identified as collinear antiferromagnetic and uud structures naturally compatible with the effective Hamiltonian, the situation is much less certain for the magnetizable phases. Both $J - J'$ character of exchange interactions and frustrated anisotropies are equally important here. This makes the scenarios derived from both XXZ-like triangular lattice or XY-like chain equally problematic for the description of the possible states. To the best of our knowledge, frustrated Hamiltonians of this type were not considered before in the literature. At the same time, the prototype material is already there and the corresponding parameters can easily be tuned by chemical composition or pressure. We believe that further experimental and theoretical effort aimed at exploring this specific frustration mechanism may yield some novel exotic magnetic states.

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[1] O. A. Starykh, “Unusual ordered phases of highly frus-

FIG. 4. Sketches of the plausible collinear magnetic phases (stripe, uud and saturated) in Cs$_2$CoBr$_4$ for $H \parallel b$ field direction. Intervening phases “B”, “D” and “E” remain to be clarified.
trated magnets: a review,” Rep. Prog. Phys. 78, 052502 (2015).

[2] D. Yamamoto, G. Marmorini, and I. Danzhu, “Quantum Phase Diagram of the Triangular-Lattice XXZ Model in a Magnetic Field,” Phys. Rev. Lett. 112, 127203 (2014). D. Sellmann, X.-F. Zhang, and S. Egger, “Phase diagram of the antiferromagnetic XXZ model on the triangular lattice,” Phys. Rev. B 91, 081104 (2015).

[3] K. A. Ross, L. Savary, B. D. Gaulin, and L. Balents, “Quantum Excitations in Quantum Spin Ice,” Phys. Rev. X 1, 021002 (2011). M. Taillefer, O. Benton, H. Yan, L. D. C. Jaubert, and N. Shannon, “Competing Spin Liquids and Hidden Spin-Nematic Order in Spin Ice with Frustrated Transverse Exchange,” Phys. Rev. X 7, 041057 (2017).

[4] M. J. P. Gingras and P. A. McClarty, “Quantum spin ice: a search for gapless quantum spin liquids in pyrochlore magnets,” Rep. Prog. Phys. 77, 056501 (2014).

[5] A. Kitaev, “Anyons in an exactly solved model and beyond,” Ann. Phys. 321, 2 (2006).

[6] Winter S. M., A. A. Tsirlin, M. Daghofer, J. van den Brink, Y. Singh, P. Gegenwart, and R. Valentí, “Models and materials for generalized Kitaev magnetism,” J. Phys.: Cond. Mat. 29, 493002 (2017). H. Takagi, T. Takayama, G. Jackeli, G. Khaliullin, and S. E. Nagler, “Concept and realization of Kitaev quantum spin liquids,” Nat. Rev. Phys. 1, 264 (2019).

[7] H. Liu, J. Chaloupka, and G. Khaliullin, “Kitaev Spin Liquid in 3d Transition Metal Compounds,” (2020), arXiv:2002.05441 [cond-mat.str-el].

[8] Z. Zhu, P. A. Maksimov, S. R. White, and A. L. Chernyshev, “Topography of Spin Liquids on a Triangular Lattice,” Phys. Rev. Lett. 120, 207203 (2018). P. A. Maksimov, Z. Zhu, S. R. White, and A. L. Chernyshev, “Anisotropic-Exchange Magnets on a Triangular Lattice: Spin Waves, Accidental Degeneracies, and Dual Spin Liquids,” Phys. Rev. X 9, 021017 (2019).

[9] R. Coldea, D. A. Tennant, A. M. Tsvelik, and Z. Tylczynski, “Experimental Realization of a 2D Fractional Quantum Spin Liquid,” Phys. Rev. Lett. 86, 1335 (2001). Y. Tokiwa, T. Radu, R. Coldea, H. Wilhelm, Z. Tylczynski, and F. Steglich, “Magnetic phase transitions in the two-dimensional frustrated quantum antiferromagnet Cs$_2$CuCl$_4$,” Phys. Rev. B 73, 134414 (2006).

[10] A. I. Smirnov, K. Yu Povarov, S. V. Petrov, and A. Ya Shapiro, “Magnetic resonance in the ordered phases of the two-dimensional frustrated quantum magnet Cs$_2$CuCl$_4$,” Phys. Rev. B 85, 184423 (2012).

[11] E. Schulze, S. Arsenijev, L. Opherden, A. N. Ponomaryov, J. Wosnitza, T. Ono, H. Tanaka, and S. A. Zvyagin, “Evidence of one-dimensional magnetic heat transport in the triangular-lattice antiferromagnet Cs$_2$CuCl$_4$,” Phys. Rev. Research 1, 032022 (2019).

[12] O. A. Starykh, H. Katsura, and L. Balents, “Extreme sensitivity of a frustrated quantum magnet: Cs$_2$CuCl$_4$,” Phys. Rev. B 82, 014421 (2010).

[13] M. Kenzelmann, R. Coldea, D. A. Tennant, D. Visser, M. Hofmann, P. Smeibidl, and Z. Tylczynski, “Order-to-disorder transition in the XY-like quantum magnet Cs$_2$CoCl$_4$ induced by noncommuting applied fields,” Phys. Rev. B 65, 144432 (2002).

[14] O. Breunig, M. Garst, E. Sela, B. Buldman, P. Becker, L. Bohatý, R. Müller, and T. Lorenz, “Spin-$\frac{1}{2}$ XXZ Chain System Cs$_2$CoCl$_4$ in a Transverse Magnetic Field,” Phys. Rev. Lett. 111, 187202 (2013).

[15] O. Breunig, M. Garst, A. Rosch, E. Sela, B. Buldman, P. Becker, L. Bohatý, R. Müller, and T. Lorenz, “Low-temperature ordered phases of the spin-$\frac{1}{2}$ XXZ chain system Cs$_2$CoCl$_4$,” Phys. Rev. B 91, 024423 (2015).

[16] T. Ono, H. Tanaka, H. Aruga K., F. Ishikawa, H. Mitamura, and T. Goto, “Magnetization plateau in the frustrated quantum spin system Cs$_2$CuBr$_4$,” Phys. Rev. B 67, 104431 (2003). H. Tsuji, C. R. Rotundu, T. Ono, H. Tanaka, B. Andráka, K. Ingersent, and Y. Takano, “Thermodynamics of the up-up-down phase of the $S = \frac{1}{2}$ triangular-lattice antiferromagnet Cs$_2$CuBr$_4$,” Phys. Rev. B 76, 060406 (2007).

[17] N. A. Fortune, S. T. Hannahs, Y. Yoshida, T. E. Sherline, T. Ono, H. Tanaka, and Y. Takano, “Cascade of Magnetic-Field-Induced Quantum Phase Transitions in a Spin-$\frac{1}{2}$ Triangular-Lattice Antiferromagnet,” Phys. Rev. Lett. 102, 257201 (2009).

[18] H. J. Seifert and I. Al-Khudair, “¨Uber die systeme alkalimetallbromid/kobalt(II)-bromid,” J. Inorg. Nucl. Chem. 37, 1625 (1975). H.-J. Seifert, “Investigation of phase diagrams by DTA and X-ray methods: The systems $AX/CoX_2 (A = Na-Cs, Tl/X = Cl, Br, I)$,” Thermochim. Acta 20, 31 (1977).

[19] See the Supplemental Material for more details.

[20] J. R. Schrieffer and P. A. Wolff, “Relation between the Anderson and Kondo Hamiltonians,” Phys. Rev. 149, 491 (1966). S. Bravyi, D. P. DiVincenzo, and D. Loss, “Schrieffer-Wolf transformation for quantum many-body systems,” Ann. Phys. 326, 2793 (2011).

[21] A. Scheie, “LongHCPulse: Long-Pulse Heat Capacity on a Quantum Design PPM,” J. Low Temp. Phys. 193, 60 (2018).

[22] Y. Feng, K. Yu Povarov, and A. Zhleudev, “Magnetic phase diagram of the strongly frustrated quantum spin chain system PbCuSO$_4$(OH)$_2$ in tilted magnetic fields,” Phys. Rev. B 98, 054419 (2018).

[23] D. Bloßer, L. Facheris, and A. Zhleudev, “Miniature capacitive Faraday force magnetometer for magnetization measurements at low temperatures and high magnetic fields,” (2020), arXiv:2002.10168 [cond-mat.mtrl-sci].

[24] At high magnetic field this effect is reduced, as the magnetization curve flattens in general.

[25] C. L. Henley, “Ordering due to disorder in a frustrated vector antiferromagnet,” Phys. Rev. Lett. 62, 2056–2059 (1989).

[26] A. V. Chubukov and D. I. Golosov, “Quantum theory of an antiferromagnet on a triangular lattice in a magnetic field,” J. Phys.: Cond. Mat. 3, 69–82 (1991).

[27] M. M. Bordelon, E. Kenney, C. Liu, T. Butch, C. Brown, M. J. Graf, L. Balents, and S. D. Wilson, “Field-tunable quantum disordered ground state in the triangular-lattice antiferromagnet NaYbO$_2$,” Nat. Phys. 15, 1058 (2019).

[28] K. M. Ranjith, S. Luther, T. Reimann, B. Schmidt, Ph. Schlender, J. Schichelsmidt, H. Yasnouka, A. M. Strydom, Y. Skourski, J. Wosnitza, K. Kühne, Th. Doert, and M. Baenitz, “Anisotropic field-induced ordering in the triangular-lattice quantum spin liquid NaYbSe$_2$,” Phys. Rev. B 100, 224417 (2019).

[29] J. Ma, J. Li, Y. H. Gao, C. Liu, Q. Ren, Z. Zhang, W. Shen, J. Embes, E. Feng, F. Zhu, Huang...
Q., Z. Xiang, L. Chen, E. S. Choi, Z. Qu, L. Li, J. Wang, H. Zhou, Y. Su, X. Wang, Q. Zhang, and G. Chen, “Spin-orbit-coupled triangular-lattice spin liquid in rare-earth chalcogenides,” (2020), arXiv:2002.09224 [cond-mat.str-el].

[28] R. Chen, H. Ju, H.-C. Jiang, O. A. Starykh, and L. Balents, “Ground states of spin-$\frac{1}{2}$ triangular antiferromagnets in a magnetic field,” Phys. Rev. B 87, 165123 (2013).

[29] C. Griset, S. Head, J. Alicea, and O. A. Starykh, “Deformed triangular lattice antiferromagnets in a magnetic field: Role of spatial anisotropy and Dzyaloshinskii-Moriya interactions,” Phys. Rev. B 84, 245108 (2011).

[30] S. P. Gosuly, Neutron Scattering Studies of Low-Dimensional Quantum Spin Systems (PhD thesis, University College London, 2016).

[31] M. Becker, M. Hermanns, B. Bauer, M. Garst, and S. Trebst, “Spin-orbit physics of $j = \frac{1}{2}$ Mott insulators on the triangular lattice,” Phys. Rev. B 91, 155135 (2015).

[32] R. Coldea, D. A. Tennant, K. Habicht, P. Smeibidl, C. Wolters, and Z. Tylczynski, “Direct Measurement of the Spin Hamiltonian and Observation of Condensation of Magnons in the 2D Frustrated Quantum Magnet Cs$_2$CuCl$_4$,” Phys. Rev. Lett. 88, 137203 (2002).

[33] K. Yu Povarov, A. I. Smirnov, O. A. Starykh, S. V. Petrov, and A. Ya Shapiro, “Modes of Magnetic Resonance in the Spin-Liquid Phase of Cs$_2$CuCl$_4$,” Phys. Rev. Lett. 107, 037204 (2011).