Observation of valence bond fluctuations in the spin-1/2 honeycomb lattice

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Quantum spin liquids are materials that feature quantum entangled spin correlations and avoid magnetic long-range order at T = 0 K. Particularly interesting are two-dimensional honeycomb spin lattices where a plethora of exotic quantum spin liquids have been predicted. Here, we experimentally study an effective S=1/2 Heisenberg honeycomb lattice with competing nearest and next-nearest neighbor interactions. We demonstrate that YbBr₃ avoids order down to at least T=100 mK and features a dynamic spin-spin correlation function with broad continuum scattering typical of quantum spin liquids near a quantum critical point. The continuum in the spin spectrum is consistent with plaquette type fluctuations predicted by theory. Our study is the experimental demonstration that strong quantum fluctuations can exist on the honeycomb lattice even in the absence of Kitaev-type interactions, and opens a new perspective on quantum spin liquids.
Introduction

Magnetism arises because of the quantum mechanical nature of the electron spin, yet for the understanding of many materials, particularly those used in today’s applications, a classical approach is sufficient. Materials with strong quantum fluctuations are rare, but attract significant research attention since they hold enormous potential for future technologies (1) that make use of the long-range entanglement for quantum communication (2, 3). Fault-tolerant quantum computers are proposed to operate with anyon quasi-particles (2) which exist in a class of quantum spin liquids (4, 5).

Quantum spin liquids (QSL) are caused by quantum fluctuations which reduce the size of the ordered magnetic moment of static magnetic structures and can affect the dynamics of the spin excitations. This happens in the $S = 1/2$ antiferromagnetic square lattice, where the zone boundary spin-waves develop a dispersion due to the presence of quantum dimer-type fluctuations between nearest neighbors (6). These fluctuations are similar to the resonant valence bond fluctuations predicted in the frustrated triangular lattice (7), which are believed to be relevant for high-temperature superconductors (8). Frustration can also be induced by competing interactions and depending on their relative strength, incommensurate magnetic phases, valence bond solids with periodic ordering of local quantum states, or QSLs with different symmetry are theoretically predicted (4, 9–15).

It has been a challenge to identify and understand appropriate model systems to study QSLs. In general lowering the dimension will increase quantum fluctuations. In one-dimension QSLs have been identified in antiferromagnetic (AF) spin chains. Case in point are KCuF$_3$ (16) and Cu(C$_6$D$_5$COO)$_2$·3D$_2$O (17). In two- and three-dimensions, quantum fluctuations can be enhanced by frustration, and there are several routes to achieve this: The inherent geometrical frustration of Kagomé (18), triangular (19), spinel (20) and pyrochlore (21) lattices may pro-
hibit long-range ordering at low temperatures. Another promising candidate is the honeycomb lattice which has received relatively little attention until Kitaev’s work when it was realized that bond-dependent anisotropic interactions can stabilize a new form of QSL whose properties are known exactly. Representatives materials are $\alpha$-RuCl$_3$ (22), Li$_2$IrO$_3$ (23) and $\text{H}_3\text{LiIr}_2\text{O}_6$ (24) which show signatures of quantum spin entangled correlations.

Quantum fluctuations are stronger in the honeycomb lattice compared to the square lattice since the number of neighbors of each spin is lower, thus placing it closer to the quantum limit. When next-nearest neighbour frustrating exchange interactions are sufficiently larger than the nearest neighbour exchange, theories predict a quantum phase transition from a Néel state into a quantum entangled state. However, there is no consensus on this state as theories predict either a QSL (11, 12) or a plaquette valence bond crystal (pVBC) (13–15) with different magnetic excitations which include spinons (11), or rotons and plaquette fluctuations (15).

Here, we study the static and dynamic properties of the trihalide two-dimensional compound YbBr$_3$ that forms a realization of the undistorted S=1/2 honeycomb lattice with frustrated interactions. Short-range magnetic correlations between the Yb moments develop below $T \approx 3$ K, but the correlation length is only of the order of an elementary honeycomb plaquette at $T = 100$ mK consistent with a quantum disordered ground-state. Inelastic neutron measurements reveal well defined dispersive low energy magnetic excitations close to the Brillouin zone center. At high energies, a continuum of excitations is observed that provides direct evidence for quantum plaquette fluctuations.

**Results**

**Crystal structure, magnetic susceptibility, and crystal electric field**

YbBr$_3$ crystallizes with the BiI$_3$ layer structure in the rhombohedral space group $R\bar{3}$ (148), where the Yb ions form perfect two-dimensional (2D) honeycomb lattices perpendicular to the
$c$-axis, as shown in Fig. 1. The magnetic susceptibility displays Curie-Weiss behavior at higher temperatures, $\chi^{a,c}(T) = C/(T - \theta_{CW})$, with $\theta_{CW} = -44$ K. The temperature dependence of the magnetic susceptibility has a broad maximum around $T = 3$ K, showing no evidence for long-range magnetic order. In fact, we will later demonstrate that YbBr$_3$ avoids magnetic order down to at least 100 mK. In addition, in the low temperature range we observe $\chi^a \approx 1.25 \chi^c$ which reflects a small easy-plane anisotropy.

Yb$^{3+}$ features a $J = 7/2$ ground-state multiplet that is split by the crystal-electric field (CEF), giving rise to three CEF excitations that are observable using neutron scattering. The first excited level is observed at 15 meV and the (Kramers-) ground-state is an effective $S = 1/2$ state. We calculated an easy-plane anisotropy in the magnetic moments to be $g_a |\langle J_\perp \rangle| = 2.2$ and $g_c |\langle J^z \rangle| = 0.4$ (see Supplement).

**Magnetic ground state**

Fig. 2a shows a measurement of the equal-time spin-spin correlation function at $T = 100$ mK, that exhibits broad diffuse scattering, but no magnetic Bragg peaks are visible. Therefore YbBr$_3$ avoids magnetic order down to at least this temperature. The broad scattering peaks are centered at (1, 0, 0) and equivalent wave-vectors, which means that the short-range correlations are described by a propagation vector $\mathbf{Q}_0 = (0,0,0)$. We used group theory analysis to classify the possible symmetry of the spin correlations (see Supplement). Symmetry restricts the spins to ferro- or collinear antiferromagnetic alignments. Our experiment excludes 3D order since we find scattering only in the [h,k,0] plane. 3D antiferromagnetic order would instead lead to scattering in planes [h,k,l] with $l = 1, 2$. Summarized, we find a 2D magnetic ground-state with strong antiferromagnetic nearest-neighbor spin correlations and an in-plane magnetic moment of $\mu = 2.5 \mu_B$.

Fig. 2b shows a cut along the $\mathbf{Q} = (q,0,0)$ direction which reveals diffuse scattering with a
Lorentzian shape that is reminiscent of short-range magnetic order (25). From a fit to the neutron intensity with \( I(Q) \propto \kappa^2/(q^2 + \kappa^2) \), we determine an in-plane correlation length between the Yb moments of \( \xi = 1/\kappa \approx 10 \, \text{Å} \) at \( T = 100 \, \text{mK} \), comparable to the fourth nearest-neighbour distance with \( d_f = 10.66 \, \text{Å} \). This also corresponds to \( \sim 1.25 \) times the diameter of an Yb\(_6\) hexagon plaquette.

**Magnetic excitations**

We found well-defined magnetic excitations at \( T = 250 \, \text{mK} \) along three reciprocal lattice directions. Within experimental resolution we observed a single excitation branch and no spin gap at the zone center. As shown in the constant energy-scan in Fig. 2c and in Fig. 3, the magnetic excitations are sharp and long-lived close to the Brillouin zone center. One of the key results of this study is the observation of a broadening of the spectrum when the dispersion approaches the zone boundary, as shown in Fig. 3. In fact, the inelastic neutron spectrum close to the zone boundary exhibits a continuum which extends to over twice the energy of the magnetic excitation. In contrast to the low-lying sharp excitations, the broad excitations are only observed at higher energies.

The well-defined excitations can be described by a Heisenberg Hamiltonian including nearest and next-nearest neighbor coupling, and dipolar interactions,

\[
H = -\frac{1}{2} \sum_{i,j} \sum_{\alpha,\beta} \left[ g^2_\alpha \delta_{\alpha\beta} J(i, j) + g_\alpha g_\beta D_{\alpha,\beta}(i, j) \right] S^\alpha_i S^\beta_j,
\]

where \( \alpha, \beta = x, y, z \). Here \( J(i, j) \), denote the Heisenberg interactions, \( D(i, j) \) the dipolar interactions between sites \( i \) and \( j \), \( (i \neq j) \), and \( g_\alpha \) are the anisotropic \( g \)-factors which reflect the CEF-anisotropy. For the calculation of the spin wave dispersion, we took the Néel state with spins in the hexagonal plane and \( S = 1/2 \). Our measurements allow the determination of these microscopic parameters, and we find good agreement between measured and calculated...
spin-wave dispersions. The nearest- and next-nearest-neighbour exchange interactions $J_1$, $J_2$ are obtained from a least-square fit to the data. We obtained $g^2 J_1 = -0.69(8) \text{ meV}$ and $g^2 J_2 = -0.09(2) \text{ meV}$ (see Supplementary for details).

While it may appear surprising that we observe well defined excitations as the correlation length is of the order of $10\text{Å}$, this agrees with Schwinger-Boson (26) and modified spin-wave theories (27) which predict that spin-waves can propagate in low-dimensional systems with short-range Néel order. However, our spin wave theory does not describe all aspects of our experimental results: It predicts an optical branch for values of the easy-plane anisotropy that corresponds to the measured susceptibility (cf. Fig. 1), while we do not find evidence for such a second branch.

**Continuum of excitations**

As shown in Fig. 3, the magnetic excitation spectrum also features weaker broad scattering at energies where the optical branch is expected. This is particularly evident near the M-points at $(0.5, 0.5, 0)$ and $(0.5, -1, 0)$, where the excitations extend to $0.8 - 1 \text{ meV}$ and are reminiscent of scattering observed in other low-dimensional antiferromagnets (28,29). In most materials, spin-waves are long-lived excitations that are resolution-limited as a function of energy. When the spin-waves are damped or interact with other spin-waves they have a finite life-time and the line-shape of the dynamical structure factor $S(Q, \omega)$ broadens (see Methods). We have simulated the line-shape of $S(Q, \omega)$ derived from our model and convoluted it with the resolution of the spectrometer obtained from the Takin software (30). While the spin-wave model adequately explains the dispersion and intensity distribution close to the Brillouin zone centers, it fails to describe the inelastic neutron line-shape close to the maximum of the dispersion of the spin-wave branch. With increasing values of $Q$, the line-shape of the magnetic excitations broadens and becomes non-Lorentzian, as shown in Fig. 4.
Discussion

The spin wave dispersion in YbBr$_3$ can be well described by a spin-1/2 Heisenberg Hamiltonian including nearest and next-nearest interactions with $J_2/J_1 \approx 0.13$. This is close to the value $J_2/J_1 \approx 0.16$ (9), where classical theories predict instability of the Néel state, and also close to $J_2/J_1 \approx 0.1$ (10, 27), where quantum fluctuation in linear spin wave theory destroy long-range Néel order. We note that other theoretical approaches find that quantum fluctuations may stabilize the Néel phase up to somewhat higher ratios of $J_2/J_1$. These approaches include Schwinger boson approach (11), variational wave functions (15, 31) and exact diagonalization (13) which all yield a critical ratio $J_2/J_1 \approx 0.2$. Since we do not find any evidence for static magnetism, we thus conclude that YbBr$_3$ must be in close proximity of such a quantum phase transition.

In YbBr$_3$ the Yb-ion has a large magnetic moment of the order of 2 $\mu_B$ and the dipolar interactions cannot be neglected. At the classical level, one can show that these interactions favor antiferromagnetic Néel order with the spins along the $c$-axis (32) enabled by a spin gap at the zone center of $\sim 200 \mu$eV. This spin gap is reduced by the CEF easy-plane anisotropy which contributes to a destabilization of the Néel state at finite temperature (Supplement Fig. S1). At $g_c \approx g_z/g_x \equiv 0.985$ the spin gap closes and quantum fluctuations will be enhanced. Below that value the spins rotate into the basal plane. An increase in anisotropy in the new phase entails a lifting of the degeneracy of the two spin-wave branches at the zone center. The splitting increases with increasing easy-plane anisotropy. A large anisotropy would be visible since the branch separation becomes large enough to be resolved. A computation of $S(Q, \omega)$ at $g_c$ is shown in Fig.3. Experimentally, we have observed neither a splitting of spin waves nor a spin gap with the available energy resolution. This suggests that the absence of the long-range order in YbBr$_3$ at $T = 100 \text{ mK} \ll |\theta_W|$ is caused by the competition between easy-plane anisotropy and dipolar interactions that accentuates quantum fluctuations and places YbBr$_3$ close to the
quantum critical point towards a spin-liquid phase of the spin-1/2 Heisenberg Hamiltonian on the honeycomb lattice.

Our experiment provides clear evidence for the presence of a continuum of excitations at high energies in YbBr₃. We can exclude the possibility of the line-shape broadening being caused by two-magnon decay. The necessary cubic anharmonicities are absent for collinear magnets such as YbBr₃. We observe that the intensity of the continuum is stronger at the M’ points along (h,-1,0) and (h,h,0) directions whereas it is weaker along (0,k,0) and at the Γ and Γ’ points. We found, as shown in Fig. 5, that this modulation of neutron intensity can be reproduced by a random-phase approximation (RPA) calculation for a hexameric plaquette with the exchange parameters obtained from the spin-wave calculations (cf. Methods). This picture of local excitations in YbBr₃ is supported by a calculation of the magnetic susceptibility which shows a broad maximum at T ≃ 4 K (see Supplement). Our measurements are in agreement with recent Monte-Carlo calculations of the dynamical structure factor for the frustrated honeycomb lattice that show a continuum corresponding to plaquette excitations (15). Such excitations associated with small spin clusters were also observed in the spinel lattice (34).

In summary, we have shown that the magnetic ground-state of YbBr₃ remains partially disordered well below the maximum in the static susceptibility. Analysis of the dispersion of the magnetic excitations reveals competition between the nearest-neighbour and next-nearest-neighbour exchange interactions while no roton minimum is observed at the K-point (15). We have observed a continuum of excitations, where the spectrum of excitations extends to approximately twice the energy of the position of the maximum in S(Q, ω). The neutron inelastic intensity due to the continuum follows the modulation expected for the fluctuations of a honeycomb spin plaquette. Our results demonstrate that YbBr₃ is a two-dimensional S = 1/2 system on the honeycomb lattice with spin-liquid properties without Kitaev-type interactions. The observation of the continuum of excitations supports the view of a deconfined quantum
critical point (35) in the frustrated honeycomb lattice, in agreement with results from coupled
cluster methods, density matrix renormalization group calculations and Monte-Carlo simula-
tions (14, 15, 36). Our measurements set a quantitative benchmark for future theoretical work.
Methods

Experimental methods

The neutron experiments were performed at the Swiss Spallation Neutron Source (SINQ) utilizing different instruments. On all instruments filters were used to reduce contamination of the beam by higher-order neutron wavelengths.

Crystal growth and sample preparation

An YbBr$_3$ single crystal of cylindrical shape (15 mm diameter, 18 mm height) was grown from the melt in a sealed silica ampoule by the Bridgman method, as previously described for ErBr$_3$ (37). YbBr$_3$ was prepared from Yb$_2$O$_3$ (6N, Metall Rare Earth Ltd.) by the NH$_4$Br method (38) and sublimed for purification. All handling of the hygroscopic material was done under dry and O-free conditions in glove boxes or closed containers.

Crystal-field excitations

The crystal-field splitting of the Yb$^{3+}$ ions was determined on the thermal three-axis spectrometer EIGER operated in the constant final-energy mode with $k_f = 2.662$ Å$^{-1}$ at $T = 1.5$ K. With that configuration the energy resolution is $\Delta E = 0.8$ meV.

Magnetic Susceptibility

The magnetic susceptibility was determined with a MPMS SQUID system (Quantum Design).

Powder diffraction and chemical structure

The crystal structure of YbBr$_3$ was refined using diffraction data collected with the high-resolution powder diffractometer HRPT at the wavelength of $\lambda = 1.494$ Å at room temperature. The crystal structure and lattice parameters were refined with Fullprof.
Diffuse scattering

The magnetic ground-state was investigated with the multi-counter diffractometer DMC at the wavelength $\lambda = 2.4576 \text{ Å}$.

Magnetic excitations

The dispersion of the magnon excitations is bound by $\hbar \omega(q) < 1 \text{ meV}$ in YbBr$_3$ which required the use of cold neutrons that provide an improved energy resolution. Therefore the measurements of the spin-waves were performed with the TASP three-axis spectrometer using $k_f = 1.3 \text{ Å}^{-1}$ which resulted in an energy-resolution of $\Delta E = 80 \mu\text{eV}$. To maximize the intensity, the measurements were performed without collimators in the beam and the analyzer was horizontally focusing.

Theoretical methods

Crystal electric field and single-ion anisotropy

We used the program multiX (39) to determine the single-ion anisotropy resulting from the CEF.

Magnetic ground-state

The symmetry-allowed magnetic structures of YbBr$_3$ were derived via group theory, as explained e.g. in Ref. (40).

Magnetic excitations

We analyzed the dispersion of the magnetic excitations with a Heisenberg Hamiltonian,

$$H_h = -\frac{1}{2} \sum_{i,j} J(i,j) \sum_{\alpha} g_{\alpha}^{i} S_{i}^{\alpha} S_{j}^{\alpha}. \quad (2)$$
$J(i, j)$ are the exchange constants between sites $i$ and $j$, to be determined experimentally and the anisotropic $g$-factors reflect the crystal-field anisotropy where $\alpha = x, y, z$ denotes Cartesian coordinates. For Heisenberg interactions $g_x = g_y = g_z \equiv g$. Because the magnetic moment of Yb$^{3+}$ is large, we also consider the dipolar interactions,

$$H_{\text{dip}} = -\frac{\mu_0\mu_B^2}{4\pi} \frac{1}{2} \sum_{i,j} \sum_{\alpha,\beta} g_\alpha g_\beta D_{\alpha,\beta}(ij) S_i^\alpha S_j^\beta,$$

with

$$D_{\alpha,\beta}(ij) = \frac{3(R_{ij})_\alpha(R_{ij})_\beta}{R_{ij}^3} - \frac{1}{R_{ij}^3} \delta_{\alpha,\beta},$$

where $R_{ij} \equiv R_j - R_i$ is the relative position vector between the $j$'th and $i$'th ion. The dispersion of magnetic excitations was calculated within the random-phase approximation where the spin-waves appear as poles in the dynamical tensor $\overline{\chi}(q, \omega)$,

$$\overline{\chi}(q, \omega) = \left[1 - \chi_0(\omega) \overline{M}(q)\right]^{-1} \chi_0(\omega)$$

with $\overline{M}(q)$ the Fourier transform of the exchange and dipolar interactions and $\chi_0(\omega)$ the single-ion susceptibility. The neutron cross-section is proportional to the imaginary part of the dynamical susceptibility (41),

$$\frac{d^2 \sigma}{d\Omega dE} \propto \sum_{\alpha,\beta} \left( \delta_{\alpha,\beta} - \frac{Q_\alpha Q_\beta}{|Q|^2} \right) S^{\alpha,\beta}(Q, \omega),$$

where we defined the dynamical structure factor,

$$S^{\alpha,\beta}(Q, \omega) = \frac{1}{\pi} \frac{1}{1 - \exp(-\hbar\omega/k_B T)} \sum_{u,v} \Im \chi^{\alpha,\beta}_{u,v}(Q, \omega).$$

Here $Q$ denotes the scattering vector, and $u, v$ labels the Yb-ions in the magnetic cell. To analyse the data, the scattering cross-section was convoluted with the resolution of the spectrometer using Popovici method implemented in Takin (30).
References

1. J. P. Dowling & G. J. Milburn, Quantum technology: the second quantum revolution. Phil. Trans. R. Soc. Lond. A 361, 1655-1674 (2003).

2. A. Kitaev, Fault-tolerant quantum computation by anyons. Ann. Phys. 303, 2-30 (2003).

3. C. Nayak, S.H. Simon, A. Stern, M. Freedman & S. Das Sarma, Non-Abelian anyons and topological quantum computation, Rev. Mod. Phys. 80, 1083 - 1159 (2008).

4. A. Kitaev, Anyons in an exactly solved model and beyond. Ann. Phys. 321, 2-111 (2006).

5. L. Savary & L. Balents, Quantum spin liquids: a review, Rep. Prog. Phys. 80, 016502-016568 (2016).

6. N. Tsyrulin, T. Pardini, R.R.P. Singh, F. Xiao, P. Link, A. Schneidewind, A. Hiess, C.P. Landee, M.M. Turnbull & M. Kenzelmann, Quantum Effects in a Weakly Frustrated S = 1/2 Two-Dimensional Heisenberg Antiferromagnet in an applied magnetic field. Phys. Rev. Lett. 102, 197201 (2009).

7. P.W. Anderson, Resonating valence bonds: A new kind of insulator? Mat. Res. Bull. 8, 153-160 (1973).

8. P.W. Anderson, P. A. Lee, M. Randeria, T.M. Rice, N. Trivedi & F.C. Zhang, The physics behind high-temperature superconducting cuprates: the plain vanilla version of RVB. J. Phys.: Condens. Matter 16, R755R769 (2004).

9. A. Mulder, R. Ganesh, L. Capriotti & A. Paramekanti, Spiral order by disorder and lattice nematic order in a frustrated Heisenberg antiferromagnet on the honeycomb lattice. Phys. Rev. B 81, 214419 (2010).
10. J.B. Fouet, P. Sindzingre & C. Lhuillier, An investigation of the quantum $J_1 - J_2 - J_3$ model on the honeycomb lattice. Eur. Phys. J. B **20**, 241-254 (2001).

11. J. Merino & A. Ralko, Role of quantum fluctuations on spin liquids and ordered phases in the Heisenberg model on the honeycomb lattice. Phys. Rev. B **97**, 205112 (2018).

12. F. Wang, Schwinger boson mean field theories of spin liquid states on a honeycomb lattice: Projective symmetry group analysis and critical field theory. Phys. Rev. B. **82**, 024419 1-13 (2010).

13. A.F. Albuquerque, D. Schwandt, B. Hetényi, S. Capponi, M. Mambrini & A.M. Läuchli, Phase diagram of a frustrated quantum antiferromagnet on the honeycomb lattice: Magnetic order versus valence-bond crystal formation. Phys. Rev. B **84**, 024406 (2011).

14. R. Ganesh, J. van den Brink & S. Nishimoto, Deconfined criticality in the frustrated Heisenberg Hamiltonian honeycomb antiferromagnet. Phys. Rev. Lett. **110**, 127203 (2013).

15. F. Ferrari & F. Becca, Dynamical properties of Néel and valence-bond phases in the $J_1$-$J_2$ model on the honeycomb lattice. [arXiv:1912.09310](https://arxiv.org/abs/1912.09310) [cond-mat.str-el] (2019).

16. D.A. Tennant, T.G. Perring, R.A. Cowley & S.E. Nagler, Unbound spinons in the $S = 1/2$ antiferromagnetic chain KCuF$_3$. Phys. Rev. Lett. **70**, 4003-4006 (1993).

17. D.C. Dender, P.R. Hammar, D.H. Reich, C. Broholm, & G. Aeppli, Direct observation of field-induced incommensurate fluctuations in a one-dimensional $S = 1/2$ antiferromagnet. Phys. Rev. Lett. **79**, 1750-1753 (1997).

18. P. Mendels & F. Bert, Quantum kagome frustrated antiferromagnets: One route to quantum spin liquids. C. R. Physique **17**, 455-470 (2016).
19. Y. Shimizu, K. Miyagawa, K. Kanoda, M. Maesato, & G. Saito, Spin Liquid State in an organic Mott insulator with a triangular lattice. Phys. Rev. Lett. 91, 107001 (2003).

20. J. Villain, Insulating Spin Glasses. Z. Physik B 33, 33-42 (1979).

21. B. Canals & C. Lacroix, Pyrochlore Antiferromagnet: A Three-Dimensional Spin Liquid. Phys. Rev. Lett. 80, 2933-2936 (1998).

22. A. Banerjee, C.A. Bridges, J.-Q. Yan, A.A. Aczel, L. Li, M.B. Stone, G.E. Granroth, M.D. Lumsden, Y. Yiu, J. Knolle, S. Bhattacharjee, D.L. Kovrizhin, R. Moessner, D.A. Tennant, D.G. Mandrus & S.E. Nagler, Proximate Kitaev quantum spin liquid behaviour in a honeycomb magnet. Nature Materials 15, 733-741 (2016).

23. Y. Singh, S. Manni, J. Reuther, T. Berlijn, R. Thomale, W. Ku, S. Trebst & P. Gegenwart, Relevance of the Heisenberg-Kitaev model for the Honeycomb Lattice Iridates A3IrO3. Phys. Rev. Lett. 108, 127203 (2012).

24. K. Kitagawa, T. Takayama, Y. Matsumoto, A. Kato, R. Takano, Y. Kishimoto, S. Bette, R. Dinnebier, G. Jackeli & H. Takagi, A spinorbital-entangled quantum liquid on a honeycomb lattice. Nature 554, 341-345 (2018).

25. M.R. Collins, Magnetic Critical Scattering (Oxford University Press, 1989).

26. A. Mattsson, P. Fröjdh & T. Einarsson, Frustrated honeycomb Heisenberg antiferromagnet: A Schwinger-boson approach. Phys. Rev. B 49, 3997-4002 (1994).

27. E. Ghorbani, F. Shahbazi & H. Mosadeq, Quantum phase diagram of distorted J1-J2 Heisenberg S = 1/2 antiferromagnet in honeycomb lattice: a modified spin wave study. J. Phys.: Cond. Mat. 28, 406001 (2016).
28. M. Mourigal, M. Enderle, A. Klpperpieper, J.S. Caux, A. Stunault & H.M. Rønnow, Fractional spinon excitations in the quantum Heisenberg antiferromagnetic chain, Nat. Phys. 9, 435-441 (2013).

29. T.-H. Han, J.S. Helton, S. Chu, D.G. Nocera, J.A. Rodriguez-Rivera, C. Broholm & Y.S. Lee, Fractionalized excitations in the spin-liquid state of a kagome-lattice antiferromagnet. Nature 492, 406-410 (2012).

30. T. Weber, R. Georgii & P. Böni, Takin: An open-source software for experiment planning, visualization, and data analysis. SoftwareX 5, 121-126 (2016).

31. F. Ferrari, S. Bieri & F. Becca, Competition between spin liquids and valence-bond order in the frustrated spin-1/2 Heisenberg model on the honeycomb lattice. Phys. Rev. B 96, 104401 (2017).

32. C. Pich & F. Schwabl, Order of two-dimensional isotropic dipolar antiferromagnets. Phys. Rev. B 47, 7957-7960 (1993).

33. M.E. Zhitomirsky & A.L. Chernyshev, Colloquium: Spontaneous magnon decays. Rev. Mod. Phys. 85, 219-243 (2013).

34. S.-H. Lee, C. Broholm, W. Ratcliff, G. Gasparovic, Q. Huang, T.H. Kim & S.-W. Cheong, Emergent excitations in a geometrically frustrated magnet. Nature 418, 856-858 (2002).

35. T. Senthil, L. Balents, S. Sachdev, A. Vishwanath & M.P.A Fisher, Quantum criticality beyond the Landau-Ginzburg-Wilson paradigm. Phys. Rev. B. 70, 144407 (2004).

36. R.F. Bishop, P.H.Y. Li & C.E. Campbell, Valence-bond crystalline order in the s = 1/2 J_1-J_2 model on the honeycomb lattice. J. Phys.: Condens. Matter 25, 306002 (2013).
37. K.W. Krämer, H.U. Güdel, B. Roessli, P. Fischer, A. Dönni, N. Wada, F. Fauth, M.T. Fernandez-Diaz & T. Hauss, Noncollinear two- and three-dimensional magnetic ordering on the honeycomb lattices of $\text{Er}X_3$ ($X=\text{Cl},\text{Br},\text{I}$). Phys. Rev. B 60, R3724-R3727 (1999).

38. G. Meyer, Advances in the Synthesis and Reactivity of Solids, 2, 1-26 (Elsevier science & technology, Oxford, 1994).

39. A. Uldry, F. Vernay & B. Delley, Systematic computation of crystal-field multiplets for x-ray core spectroscopies. Phys. Rev. B 85, 125133 (2012).

40. A.S. Wills, Symmetry and magnetic structure determination: developments in refinement techniques and examples. Appl. Phys. A, 74, s856-s858 (2002).

41. J. Jensen & A.R. Macintosh, Rare Earth Magnetism (Clarendon Press, Oxford, 1991).
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Figure 1: **Magnetic susceptibility, crystal electric field and crystal structure.** (a) View along [210] on the unit cell of YbBr$_3$. (b) Yb$^{3+}$ honeycomb layer. (c) Temperature dependence of the inverse magnetic susceptibility $1/\chi$ of YbBr$_3$ for field orientations along the a- and c-axes. Curie-Weiss fits are shown as black lines. The susceptibility $\chi(T)$ for low temperatures is depicted in the inset.
Figure 2: **Magnetic diffuse scattering and correlation length.** (a) Magnetic diffuse scattering in YbBr$_3$ in the [h,k,0] plane at $T = 100$ mK, after subtraction of the nuclear Bragg contribution. $a^*$, $b^*$ indicate the reciprocal lattice directions. (b) Cut through the diffuse scattering along the (h,0,0) direction. The line is a fit to the data with a Lorentzian function. (c) Constant-energy scan for $\hbar \omega = 0.4$ meV in YbBr$_3$ at $T = 250$ mK showing well-defined low energy excitations. The solid line represents the computed inelastic neutron scattering cross-section. Neutron intensity not included in the calculation is due to accidental scattering.
Figure 3: **Magnetic excitations along high symmetry directions.** False color plot of the observed (top) and calculated (bottom) inelastic neutron cross section of the magnetic excitations in YbBr$_3$ at $T = 0.25$ K. The intensity is shown on a logarithmic scale. Note that the continuum of excitations extends to about twice the energy at maximum intensity close to the Brillouin zone boundary.
Figure 4: **Excitation continuum near the Brillouin zone boundary.** a)-f) Observed and simulated magnon spectra based on the spin-wave model explained in the text. The lines are fits to the data with a Lorentzian function. An intrinsic line-width $\epsilon = 0.1$ meV was used for the simulation. The shaded area indicates the continuum of excitations.
Figure 5: **Calculated neutron form factor for a plaquette.** The neutron form factor of an Yb$_6$ hexagon calculated within the random-phase approximation and assuming short range Néel order. The directions of the neutron measurement are indicated by white arrows: cut I corresponds to $(h, h, 0)$, cut II is $(0, -k, 0)$ and cut III is $(h, -1, 0)$. High-symmetry points are labeled similar to Fig. 3.
Supplementary materials

The supplementary materials include

1. Section S1: Crystal structure
2. Section S2: Magnetic susceptibility
3. Section S3: Crystal electric field
4. Section S4: Magnetic ground-state
5. Section S5: Magnetic excitations
6. Fig. S1: Dependence of the energy gap as a function of easy-plane anisotropy
7.References

Section S1: Crystal structure

YbBr₃ crystallizes with the BiI₃ layer structure in the rhombohedral space group $R\bar{3}$ (148) with lattices parameters of $a = 6.97179(18)$ Å and $c = 19.1037(7)$ Å at room temperature. The lattice parameters are in good agreement with powder (1) and crystal (2) diffraction data found in literature. The unit cell contains six Yb³⁺ ions on site (6c) at (0, 0, z), (0, 0, z) + (2/3, 1/3, 1/3) and (0, 0, z) + (1/3, 2/3, 2/3) with $z = 0.1670(2)$. The Yb ions have $C_3$ point symmetry and form two-dimensional (2D) honeycomb lattices perpendicular to the $c$-axis, see Fig. 1. Yb³⁺ has a distorted octahedral coordination by Br⁻ ions which are located on site (18f) at (x, y, z) with x=0.3331(5), y=0.3131(5), and z=0.08336(15). Surprisingly, the distance between Yb³⁺-Br⁻ varies by less than $10^{-2}$ Å, however the Br⁻-Yb³⁺-Br⁻ bond angles differ significantly between 87.3° and 91.1°. The crystallographic parameters determined on HRPT are are summarized in Table 1.
Section S2: Magnetic Susceptibility

The temperature dependence of the inverse static susceptibility $1/\chi$ is shown in Fig. 1c for magnetic field orientations in-plane ($a$-axis) and out-of-plane ($c$-axis). At higher temperatures the curves are close to linear. Fits to the Curie-Weiss law

$$\chi^{a,c}(T) = \frac{C}{T - \theta_{CW}}$$

between $200 \text{ K} < T < 300 \text{ K}$ result in $\theta_{CW} = -44 \text{ K}$ and indicate antiferromagnetic correlations in YbBr$_3$. $\chi T$ values (not shown) increase with temperature and do not saturate up to 300 K. The values at 300 K are 2.282 and 2.687 cm$^3$K/mol along the a- and c-axes, respectively. The average of 2.417 cm$^3$K/mol is slightly below the expectation value of 2.572 cm$^3$K/mol for the $^2F_{7/2}$ ground-state of Yb$^{3+}$. At lower temperatures a maximum in the $\chi$ versus $T$ curves is observed at $T = 2.75 \text{ K}$, see the inset in Fig. 1c. The ratio $f = -\theta_{CW}/T_N = 44 \text{ K}/2.75 \text{ K} = 16$ indicates frustration between nearest and next-nearest exchange interactions in YbBr$_3$. We have calculated the temperature dependence of the static susceptibility for an Yb$_6$ honeycomb with the exchange parameters determined from the spin-wave analysis and easy-plane anisotropy parameters $g_a/g_c = 1.25$. We find that the susceptibility has a broad maximum around $T \simeq 4 \text{ K}$ and reproduces the experimental $\chi(T)$ above 5 K well, as shown in Fig. S2.

Section S3: Crystal electric field (CEF)

We find three excitations in our measurements of the CEF at $\hbar \omega = 15 \text{ meV, } 22 \text{ meV and } 33 \text{ meV. We used the program multiX (39) to determine the single-ion anisotropy caused by the CEF. In agreement with the susceptibility measurements, calculations show that at high temperatures anisotropy is small in YbBr$_3$ with easy-plane anisotropy developing below $T=50 \text{ K. At } T=4 \text{ K, we have } \chi_a \approx 1.25 \chi_c$. The magnetic moment of Yb is calculated from the ground-state wave-function $g_a \langle J^+ \rangle = 2.2$ and $g_c \langle J^z \rangle = 0.4$, a value that is close to the magnetic moment of
Yb$^{3+}$ obtained by refining the diffraction data at T=100 mK.

**Section S4: Magnetic ground-state**

Fig. 2a. shows the elastic magnetic scattering of YbBr$_3$ that was obtained by calculating the difference between diffraction patterns taken at $T=100$ mK and $T=10$ K in order to eliminate the nuclear scattering. As the magnetic scattering is observed around the $\Gamma$-points, the magnetic and nuclear cells coincide. The symmetry-allowed magnetic structures of YbBr$_3$ can be derived via group theory as explained, e.g., in Ref. (40). For the propagation vector $Q_0 = (0,0,0)$ there are six one-dimensional irreducible representations of space group $R\bar{3}$ and each one appears once in the decomposition of the magnetic representation. The symmetry allowed basis vectors describe either a collinear ferromagnetic or antiferromagnetic alignment of the Yb-ions located at Yb$_1$=(0,0,+z) and Yb$_2$=(0,0,-z), $z = 1/3$ (see Section “Crystal structure”). The basis functions of the Yb-ions related by a translation $t$ of the $R\bar{3}$ space group acquire a phase $\exp(-iQ_0 \cdot t) = 1$ as the propagation vector is zero. Symmetry analysis allows the magnetic moments to be aligned either along the $c$-axis or in the hexagonal plane. Calculation of the neutron structure factors indicates that the absence of magnetic scattering around $Q = (1,1,0)$ excludes a ferromagnetic ground-state of YbBr$_3$. A 3D antiferromagnetically ordered structure would produce magnetic scattering at [h,k,l] Bragg positions with $l = 1$ or 2. As the magnetic scattering appears in the [h,k,0] plane, there are no magnetic correlations along the $c$-axis which demonstrates the two-dimensional character of the magnetic properties of YbBr$_3$.

The classical ground-state is given by the eigenvectors of the largest eigenvalue $\lambda (\mathbf{q})$ of the Fourier transform of the interaction matrix $\overline{M}(\mathbf{q})$ (4–6). $\lambda (\mathbf{q})$ has a maximum at $Q_0 = (0,0,0)$ in YbBr$_3$ and the ground-state is a collinear antiferromagnet. We find that the dipolar energy becomes independent of the distance between the Yb-planes for a lattice parameter $c > 20$ Å, which shows that the 2D limit is reached in YbBr$_3$ and inter-layer interactions can be neglected.
Neutron magnetic intensities are consistent with a 2D magnetic ground-state with Yb$^{3+}$ spins aligned antiferromagnetically with a magnetic moment $\mu = 2.5 \mu_B$. However, the presence of magnetic domains when the spins are in the hexagonal plane did not allow us to determine the spin direction unambiguously. Fig. 2a. indicates that the magnetic scattering does not consist of sharp Bragg peaks but is broad in reciprocal space. Fig. 2b. shows a cut along the $Q = (q, 0, 0)$ direction which reveals diffuse scattering with a Lorentzian shape that is reminiscent of short-range magnetic order (25). From a fit to the neutron intensity $I(Q)$ with

$$I(Q) \propto \frac{\kappa^2}{q^2 + \kappa^2}$$

we determine an in-plane correlation length between the Yb moments of $\xi = 1/\kappa \sim 10 \text{ Å}$ at $T = 100$ mK.

**Section S5: Magnetic excitations**

Because of the large separation between the ground-state and the first CEF doublet, the magnetic properties of YbBr$_3$ can be approximated by a spin $S = 1/2$. In that case the non-zero elements of the single-ion susceptibility matrix are $\chi_{0}^{xx}(\omega) = \chi_{0}^{yy}(\omega)$ and $\chi_{0}^{xy}(\omega) = -\chi_{0}^{yx}(\omega)$ which correspond to excitations transverse to the (local) spin direction $\hat{z}$. In the mean-field approximation

$$\chi_{0}^{xx}(\omega) = \frac{1}{2} \frac{\Delta}{\Delta^2 - (\omega + i\epsilon)^2}$$
$$\chi_{0}^{xy}(\omega) = \frac{i}{2} \frac{\omega + i\epsilon}{\Delta^2 - (\omega + i\epsilon)^2},$$

with $\Delta \equiv \Delta_i = -\sum_j J(i, j) \langle S \rangle$ the local field acting on the Yb moment and $\epsilon$ the finite line width of the excitations.

Good agreement between measured and calculated spin-wave dispersions was obtained with $g^2 J_1 = -0.69(8)$ meV and $g^2 J_2 = -0.09(2)$ meV. Within linear spin-wave theory, the dipole-dipole interactions induce a gap in the spin-wave dispersion (7, 32). Using a Yb magnetic

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moment of 2 \( \mu_B \), the dipolar interactions produce a spin gap at the zone center \( \simeq 200 \, \mu\text{eV} \).

The easy-plane anisotropy favors alignment of the spins in the hexagonal plane. The spin gap opened by \( H_{\text{dip}} \) is reduced by the easy-plane anisotropy. At \( g_c \sim g_{zz}/g_{xx} = 0.985 \) the spin gap is minimal and below that value the spins rotate into the basal plane, see Fig. S1. The easy-plane anisotropy lifts the degeneracy of the spin wave branches at the zone center and the splitting increases with increasing anisotropy. Calculations of the neutron cross section at \( g_c \) are shown in Fig. 3.
## Supp. Tables

**Table 1: Structural parameters of YbBr$_3$ determined on HRPT at room temperature**

| Name | x     | y    | z           | occ. |
|------|-------|------|-------------|------|
| Yb1  | 0     | 0    | 0.33289(21) | 0.317(3) |
| Yb2  | 0     | 0    | 0           | 0.009(0) |
| Br   | 0.35362(57) | 0.00022(60) | 0.08325(15) | 1    |
Supp. Figures

S1: Dependence of the energy gap as a function of easy-plane anisotropy.

Fig. S1: Dependence of the energy gap as a function of easy-plane anisotropy. Above $g_{zz}/g_{xx} = 0.985 = g_c$, the calculated branches $\omega_1(q)$ and $\omega_2(q)$ are degenerate while for $g_{zz}/g_{xx} < g_c$ the two spin-wave branches split. All points are calculated with a precision of $\sim 0.005$ meV. The magnetic configurations shown in the figure correspond to a Néel antiferromagnet with spins aligned along the c-axis for $g_{zz}/g_{xx} > 0.985$ and in the hexagonal plane for $g_{zz}/g_{xx} < 0.985$. 

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S2: Calculated susceptibility for a Yb$_6$ hexamer.

Fig. S2: Calculated susceptibility for a Yb$_6$ hexamer. The measured low-temperature magnetic susceptibility is shown together with the calculation (solid lines) for a single plaquette with $S = 1/2$, $g_a = 3.5$, $g_c = 2.8$, and $J_1 = -0.69$ meV, $J_2 = -0.09$ meV.
References

1. G. Meyer, Private communication to powder diffraction data base (PDF2), no. [42-0968] (1990).

2. M. Brenner, Kinetische Studien zu Phasenumwandlungen zwischen polymorphen Formen von YbBr$_2$ sowie die Bestimmung der Kristallstruktur von YbBr$_3$. Dissertation Universit"at Karlsruhe (1997).

3. A.P. Ramirez, Strongly geometrically frustrated magnets. Annu. Rev. Mater. Sci 24, 453-480 (1994).

4. J.N. Reimers, Diffuse-magnetic-scattering calculations for frustrated antiferromagnets. Phys. Rev. B 46, 193-202 (1992).

5. H. Kadowaki, Y. Ishii, K. Matsuhira & Y. Hinatsu, Neutron scattering study of dipolar spin ice Ho$_2$Sn$_2$O$_7$: Frustrated pyrochlore magnet. Phys. Rev. B 65, 144421 (2002).

6. M. Enjalran & M.J.P. Gingras, Theory of paramagnetic scattering in highly frustrated magnets with long-range dipole-dipole interactions: The case of the Tb$_2$Ti$_2$O$_7$ pyrochlore antiferromagnet. Phys. Rev. B 70, 174426 (2004).

7. C. Pich, & F. Schwabl, Spin-wave dynamics of two-dimensional isotropic dipolar Honeycomb antiferromagnets. JMMM 148, 30-31 (1995).