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We present high-field electron spin resonance (ESR) studies of the honeycomb-lattice material α-RuCl$_3$, a prime candidate to exhibit Kitaev physics. Two modes of antiferromagnetic resonance were detected in the zigzag ordered phase, with magnetic field applied in the ab plane. A very rich excitation spectrum was observed in the field-induced quantum paramagnetic phase. The obtained data are compared with results of recent numerical calculations, strongly suggesting a very unconventional multiparticle character of the spin dynamics in α-RuCl$_3$. The frequency-field diagram of the lowest-energy ESR mode is found consistent with the behavior of the field-induced energy gap, revealed by thermodynamic measurements.

Spin systems with honeycomb structures have recently attracted a great deal of attention, both theoretically and experimentally. It was proposed that some of such systems can be experimental realizations of the Kitaev-Heisenberg model [1], which encompasses a variety of possible magnetic ground states (from a conventional Néel order to a quantum spin liquid) and emergent fractional excitations (e.g., Majorana fermions and gauge fluxes) [2–8]. An essential peculiarity of this model is the presence of anisotropic bond-dependent interactions, defined in the Hamiltonian (Eq. 1) by the Kitaev parameter K:

$$\mathcal{H} = J \sum_{\langle i,j \rangle} \boldsymbol{S}_i \cdot \boldsymbol{S}_j + K \sum_{\langle i,j \rangle_m} \boldsymbol{S}_i^m \cdot \boldsymbol{S}_{j'}^m - \boldsymbol{h} \sum_i \boldsymbol{S}_i, \quad (1)$$

where S_i and S_j are spin-1/2 operators at sites i and j, respectively, J is the Heisenberg exchange interaction, $m = x$, y, z label the three different links of the lattice, and h is the uniform magnetic field. The Kitaev physics is thought to be realized in Ir-based magnets (such as A_2IrO$_3$, A = Na or Li [2, 9–11]), where, due to a strong spin-orbit interaction, the multiorbital $5d$ t_{2g} state can be mapped into a single orbital state with a pseudospin $j_{eff} = 1/2$.

Recently, the honeycomb-lattice material α-RuCl$_3$ [Fig. 1(a)] has been proposed as another promising candidate to exhibit Kitaev physics. The local cubic symmetry of α-RuCl$_3$ is almost perfect, in contrast to the iri-

dates. As revealed experimentally [12, 13], the magnetic susceptibility and magnetization of α-RuCl$_3$ are very anisotropic, evident of the low-spin state of Ru^{3+}. Low-temperature neutron scattering measurements [14, 15] suggested a collinear zigzag-ordered magnetic structure, which is one of the magnetic states predicted by the Kitaev-Heisenberg model. Magnetic field applied in the ab plane suppresses the long-range magnetic order, so that above the critical field $H_c \approx 7$ T the system is in a quantum paramagnetic phase [12, 13, 16]. At about 23 T the system undergoes the transition into the magnetically saturated phase [13, 17]. One exciting property of the quantum paramagnetic phase is the presence of a field-induced energy gap, revealed experimentally by means of nuclear magnetic resonance and heat-transport measurements [18–21].

In this work, we present results of systematic high-frequency electron spin resonance (ESR) studies of α-RuCl$_3$ in magnetic fields up to 16 T, allowing us to gain a deeper insight into the nature and peculiarities of the spin dynamics in this material across different phases of its phase diagram.

Single-crystal α-RuCl$_3$ samples with typical sizes of 3x3x0.5 mm^3 were prepared using a vapor transport technique starting from pure RuCl$_3$ powder [14]. The samples were characterized using standard thermodynamic techniques; the obtained specific-heat data are consistent with published results [12], exhibiting a sharp peak at $T_N \simeq 7.5$ K and the onset of a broad anomaly near

14 K (the latter is attributed to the presence of stacking faults [13]). The ESR measurements were performed employing a 16 T transmission-type ESR spectrometer, similar to that described in Ref. [22]. In our experiments, a set of backward-wave oscillators, Gunn diodes, and VDI microwave sources were used, allowing us to probe magnetic excitations in this material in the very broad quasi-continuously covered frequency range from ca 50 GHz to 1.2 THz. The experiments were done in the Voigt configuration with magnetic field applied in the *ab* plane at temperatures down to 1.4 K.
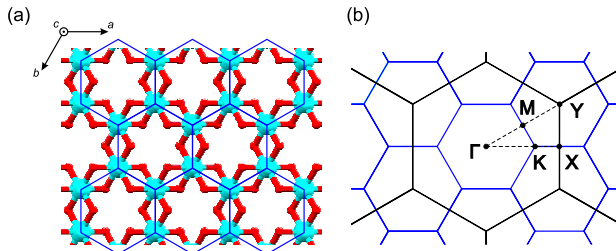

FIG. 1: (*a*) Schematic view of the α-RuCl$_3$ crystal structure in the trigonal setting (*ab* view). The Ru^{3+} ions are shown in cyan, while the Cl$^-$ ions are shown in red. (*b*) The reciprocal lattice of the honeycomb lattice (first and second Brillouin zones are shown).
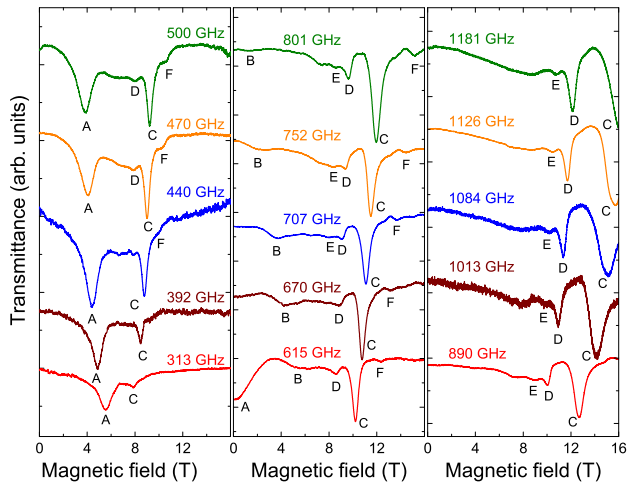

FIG. 2: Examples of ESR spectra taken at different frequencies ($H \parallel [110]$, $T = 1.4$ K). The spectra are offset for clarity.

A very rich excitation spectrum was observed at a temperature of 1.4 K (Fig. 2), revealing the presence of six absorption lines: modes A and B were detected in the low-field zigzag-ordered phase, while modes C, D, E, and F in the field-induced quantum paramagnetic phase.

Angular dependences of resonance fields for modes C, D, and E (measured at a frequency of 1119 GHz, $T = 1.4$ K) are shown in Fig. 3. The experiment reveals the 60° periodicity of ESR fields, as expected for a honeycomb

structure. The angles 0° and 30° correspond to [110] and [100] direction, respectively. We would like to stress the importance of these measurements, allowing us to confirm the very high, twin-free, quality of the single-crystalline samples we used.
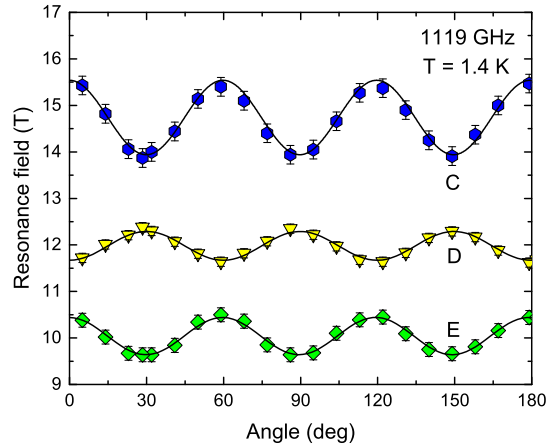

FIG. 3: Angular dependence of the ESR modes C, D, and E, taken at a frequency of 1119 GHz, $T = 1.4$ K. The angles 0° and 30° correspond to [110] and [100] direction, respectively. Lines are guides to the eye.

The frequency-field diagrams of ESR excitations for $H \parallel [110]$ are shown in Fig. 4. As mentioned, two gapped ESR modes, A and B, were observed below H_c, where the system is in the zigzag-ordered state. The intensities of both modes decrease with increasing temperature, and at about $T_N \simeq 7.5$ K both resonance lines vanish (Fig. 5), evidenced that the detected ESR modes are indeed the modes of antiferromagnetic resonance (AFMR) in the long-range magnetically ordered zigzgag phase. The extrapolation of the frequency-field dependences of modes A and B to zero field [23] revealed gaps $\Delta_A = 620$ GHz (which corresponds to 2.56 meV) and $\Delta_B = 790$ GHz (3.27 meV), respectively [Fig. 4]. The gap $\Delta_A = 620$ GHz is consistent with results of inelastic neutron scattering at the Γ point [24], time-domain THz spectroscopy [25] measurements (shown in Fig. 4 by a gray circle) and calculations [26], providing clear evidence of magnetic excitations at the center of the Brillouin zone. It is important to mention that due to absence of the inversion symmetry on the second-nearest-neighbour bonds, the Dzyaloshinskii-Moria (DM) term in α-RuCl$_3$ is allowed, allowing in its turn, ESR transitions at the K point (Fig. 1). Such excitations at the Brillouin-zone boundaries were observed in a number of multisublattice antiferromagnets (see, e.g., [27–29]) and known as *exchange* modes. Thus, mode B can be interpreted as exchange AFMR mode. Both AFMR branches demonstrate pronounced softening with increasing field. It is
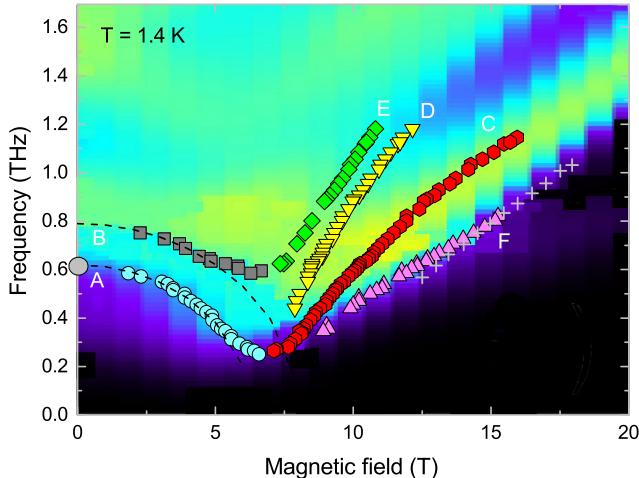
FIG. 4: Frequency-field diagrams of ESR excitations in α-RuCl$_3$ for $H \parallel [110]$, $T = 1.4$ K (symbols). The experimental data are shown together with the ESR response at the Γ point for $H \parallel a$, $h_\omega \perp H$ (color scale), obtained numerically by means of ED for clusters up to 24 spins [31]. Zero-field excitations observed at the Γ point by means of neutron scattering [24] and THz spectroscopy [25] measurements are shown by a gray circle. Dash lines correspond to the fit results as described in [23]. The field-induced gap revealed in the high-field phase by means of heat-transport measurements [20] is denoted by crosses.
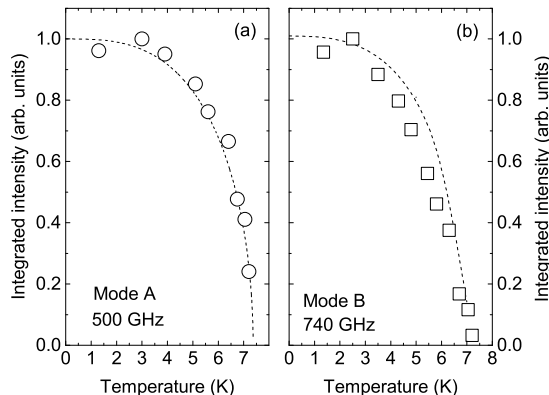

FIG. 5: Temperature dependence of integrated ESR intensities for modes A (a) and B (b), taken at frequencies 500 and 740 GHz, respectively ($H \parallel [100]$).

noticeable, that the lowest-energy observed AFMR gap, corresponding to magnetic excitations at the Γ point, remains open at H_c. The presence of additional anisotropic terms (such as, e.g., the staggered DM interaction) can be a reason of the observed phenomenon [30].

Now we would like to focus on the high-field spin dynamics in α-RuCl$_3$. Above $H_c \approx 7$ T, the long-range

zigzag order is suppressed, and the system is in the magnetically disordered but strongly correlated quantum paramagnetic phase. There, four modes were observed. The corresponding frequency-field diagrams of magnetic excitations for $H \parallel [110]$ are shown in Fig. 4. In our experiments, the most intensive mode C can be detected at temperatures up to ~ 20 K (Fig. 2). Mode D is less intensive and was observed at temperatures up to ~ 15 K. Modes E and F are relatively week, but still can be detected at lowest available temperature, 1.4 K.

Using exact diagonalization (ED) calculations on a 22-spin cluster for an extended Kitaev-Heisenberg model, Yadav *et al.* [3] predicted the presence of a field-induced gapped quantum spin liquid state. In addition to the Kitaev coupling $K = -5.6$ meV, in-plane g factor $g_{ab} = 2.51$, and isotropic Heisenberg exchange interactions between nearest-, second-nearest-, and third-nearest-neighbor sites, $J_1 = 1.2$ meV, $J_2 = J_3 = 0.25$ meV, the model includes nearest-neighbor symmetric anisotropic exchange constants $\Gamma_{xy} = -1.2$ meV and $\Gamma_{zx} = -\Gamma_{yz} = -0.7$ meV. For the given set of parameters, a spin liquid state was predicted to exist in α-RuCl$_3$ between approximately 11.5 and 14 T [3]. Notably, the crossover from the spin-liquid to a spin-polarized phase should be accompanied by a pronounced dip in the excitation energy at about 15 T [3]. No indication of such a dip in magnetic fields up to 16 T (at least for the chosen direction of the applied magnetic field) has been reveled in our experiments.

Baek et al. [18] performed ED calculations for the regular Kitaev-Heisenberg model on a 24-spin cluster, without symmetric anisotropic coupling and assuming $K = -10.0$ meV, $g_{ab} = 2.4$, $J_1 = 2.0$ meV, $J_2 = J_3 = 0.5$ meV. The calculations were done for intensities integrated over a broad momentum range and revealed a very rich excitation spectrum.

Recently, Winter *et al.* [31] have reported another ED study of α-RuCl$_3$ for magnetic excitations at the Γ point (which is the most common case for ESR) and including symmetric anisotropic coupling. They considered a simplified C_3-symmetric four-parameter model, assuming $J_1 = -0.5$ meV, $K_1 = -5.0$ meV, $\Gamma_1 = 2.5$ meV, $J_3 = 0.5$ meV. For fields $H > H_c$ the calculations showed a large redistribution of spectral weight, which can be attributed to the anisotropic frustration of the considered model. Comparison of the calculation results for magnetic field H applied along the a axis (which corresponds to the [110] axis in our experiments) with the ESR data revealed a very good qualitative agreement. The calculation results are shown as color scale together with the experimental data in Fig. 4. A particular good agreement was obtained for the most intensive ESR mode C, suggesting that this mode corresponds to excitations at the Γ point. The observation of a number of ESR modes, not accounted by the calculations [31] for magnetic excitations at the Γ point, potentially suggests the presence

of exchange ESR modes (see the discussion above). The corresponding calculations are in progress [32].

Numerical calculations [18, 31] above H_c predicted a rather complex excitation spectrum, consisting of a number of modes, whose activation energy increases with increasing field. A noticeable high-field property of the detected modes C and F is their unusually large slope $g_{ab}\mu_B\Delta S \approx 0.27$ meV/T (it is interesting, that the field dependence of mode F, the lowest mode observed in our ESR study in the $H > H_c$ region, matches that of the gap, extracted from the heat-transport experiments [20]). The remarkably large slope might imply the presence of ESR transitions with $\Delta S \approx 2$ (contrary to $\Delta S = 1$, expected for elementary one-particle excitations in simple $S = 1/2$ systems). This observation (together with results of the ED calculations, evident of a number of excitation modes, split off from the higher-energy continuum), suggests that the spin dynamics of α-RuCl$_3$ has an emergent multiparticle nature. To the best of our knowledge, such unconventional discrete (bound-state-like) multiparticle excitation spectrum has never been previously observed in magnetic systems with a honeycomb lattice. One can speculate that strong ferromagnetic Kitaev's coupling K may facilitate the formation of two-magnon bound states that are strongly split down from the two-magnon continuum. However, at present stage, it is unclear whether observed multiparticle excitations correspond to bound magnons or to bound Majorana spinons (and, in the latter case, whether the spinons are confined or simply bound). We hope that our data will stimulate further theoretical studies of the unusual spin dynamics in α-RuCl$_3$, in particular, in its high-field phase.

In conclusion, we performed comprehensive high-field ESR studies of α-RuCl$_3$, an anisotropic spin system with a honeycomb structure that is considered a top candidate for exhibiting Kitaev's spin-liquid physics. Our experiments revealed the presence of two soft AFMR modes in the zigzag-ordered phase and uncovered the rather complex spin dynamics in the field-induced quantum paramagnetic state, characterized by emergent multiparticle excitations. Our observations can have a broader impact, suggesting that honeycomb-lattice magnets might serve as an excellent playground to study unconventional many-body quantum processes in condensed matter, including, e.g., field-induced condensation of bound states (with a potential realization of the spin-nematic order), Efimov effect, etc.

*N*ote: Upon finalizing this manuscript, we became aware of two other high-field spectroscopy studies of α-RuCl$_3$, by Wang et al. [33] and Wellm [34]. Apart from the low-frequency AFMR mode and a number of excitations in the field-induced disordered phase (partially similar to that observed by us), a signature of a broad excitation continuum, an indication of the unconventional multiparticle spin dynamics in α-RuCl$_3$, was revealed.

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