Anisotropic Ru$^{3+}$ $4d^5$ magnetism in the $\alpha$-RuCl$_3$ honeycomb system: susceptibility, specific heat and Zero field NMR

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Hexagonal $\alpha$-Ru trichloride single crystals exhibit a strong magnetic anisotropy and we show that upon applying fields up to 14 T in the honeycomb plane the successive magnetic order at $T_1 = 14$ K and $T_2 = 8$ K could be completely suppressed whereas in the perpendicular direction the magnetic order is robust. Furthermore the field dependence of $\chi(T)$ implies coexisting ferro- and antiferromagnetic exchange between in-plane components of Ru$^{3+}$-spins, whereas for out-of-plane components a strong antiferromagnetic exchange becomes evident. $^{105}$Ru zero-field nuclear magnetic resonance evidence a complex (probably chiral) long-range magnetic order below 14 K. The large orbital moment on Ru$^{3+}$ is found in density-functional calculations.

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Low dimensional $4d$- and $5d$-magnets show a wide variety of magnetic ground states due to crystal electric field (CEF) splitting in combination with a strong spin-orbit coupling (SOC). Especially the $5d^5$- iridate compounds earned great attention because of the predicted topological Mott insulating state due to the strong SOC and the Coulomb correlation[1]. Furthermore the strong SOC favors the asymmetric Dzyaloshinskii-Moriya interaction that often results in chiral spin arrangements in the ordered phases[2, 3]. In addition, for spin-1/2 systems geometrical frustration of the magnetic exchange interactions frequently leads to a quantum spin-liquid ground state[4]. Among $4d$- and $5d$- systems, the Heisenberg-Kitaev model was established to describe the competing bond-dependent magnetic exchange interactions in the honeycomb type of lattice structures[5]. Prominent examples are the 2-1-3 iridates ($\text{Li}_2\text{IrO}_3$, $\text{Na}_2\text{IrO}_3$) where the magnetism is associated to the $5d^5$ electrons on the Ir$^{3+}$ ions. According to the Heisenberg-Kitaev model, the phase diagram provides a transition from a conventional Néel-type of antiferromagnetic (AFM) order to a AFM stripey- (or zigzag-) type of order towards a pure antiferromagnetic (AFM) order to a $\alpha$-RuCl$_3$ honeycomb system: susceptibility, specific heat and Zero field NMR (QSL) phase as a function of control parameter[6]. Indeed $\text{Na}_2\text{IrO}_3$ shows an AFM order of zigzag-type at $T = 15$ K, whereas the $\text{Li}_2\text{IrO}_3$ system is more close to the QSL regime and the anomaly observed at 15 K might be a partial freezing of some spins out of the QSL state[7].

Unfortunately, these 2-1-3 iridates are not easy to synthesize and sizable single crystals are a rare occurrence. Therefore, there is a need for search for new $4d$- or $5d$- model system with the honeycomb lattice arrangement. $\alpha$-RuCl$_3$ turns out to be an excellent candidate because the $3^+$ state of Ru ($4d^5$) is isoelectronic to the $4^+$ state of Ir ($5d^5$). However, low-temperature magnetic properties of $\alpha$-RuCl$_3$ were not studied in detail and, so far, on powders only. Recently, Plumb and co-workers have shown in a spectroscopic experiment that $\alpha$-RuCl$_3$ is a magnetic insulator due to sizable Coulomb correlations accompanied by the spin-orbit coupling[8].

In this Rapid Communication, we report detailed studies on the magnetic anisotropy by magnetization and specific heat on single crystals over a wide temperature and field range. Furthermore, we applied $^{99,101}$Ru zero-field nuclear magnetic resonance as a local and "on-site" probe for the ordered ground state. The system has a strong magnetic anisotropy and reveals an overall ferromagnetic exchange when field is applied in the plane ($H \parallel c$) and an AFM one when the field is applied perpendicular to the plane ($H \perp c$). Moreover, two phase transitions at $T_1 = 14$ K and $T_2 = 8$ K have been detected. We show further that upon applying fields up to 14 T in the plane, the complex magnetic order could be completely suppressed, whereas in the perpendicular direction the magnetic order is robust up to 14 Tesla.

Single crystals of $\alpha$-RuCl$_3$ were grown by chemical transport reaction, starting from a microcrystalline powders of pre-reacted materials, which were obtained by the reaction of the elements. The transport experiment was carried out from microcrystalline sample of $\alpha$-RuCl$_3$ in an evacuated quartz tube in a temperature gradient from 730°C (source) to 660°C (sink). Chlorine (2 mg/ml) was used as transport agent. Selected crystals were analyzed by EDXS (which provides a typical stoichiometry of $\text{Ru:Cl} = 1:3.09$), chemical and thermal analysis, and X-ray diffraction. $\alpha$-Ru trichloride forms a hexagonal structure (P$3_1\overline{12}$) with $a=5.97$ Å and $c=17.2$ Å[9]. The structure hosts two different Ru sites. The crystals have lateral dimensions of a few mm, whereas their thickness is less than 0.1 mm. Magnetization measurements were performed with a commercial SQUID VSM (vibrating sample magnetometer) from Quantum Design (QD). Specific heat measurements are conducted at a commercial PPMS (Physical Property Measurement System) from Quantum Design by use of a modified sample holder for "vertical" (field in-plane) specific heat measurements.
Magnetization measurements in pulsed fields up to 50 T are performed on powder samples at the high field research center (HLD) at Helmholtz-Zentrum Dresden-Rossendorf. All magnetic measurements are performed in the ZFC (zero field cooled) modes. Between field cycles the sample was always heated to 200 K and then the field was ramped to zero. Magnetization and specific heat measurements are performed on a single crystal (~1 mg), whereas zero field NMR was done on a stack of single crystals (~90 mg). NMR measurements are carried out by applying conventional pulsed NMR. The zero-field NMR spectra have been obtained by sum of the spin echo time FFT (Fast Fourier Transform) spectra measured typically 0.2 MHz step. In general, the zero field spectra originate from the anisotropic hyperfine field transferred from the Ru-$4d^{5}$ moments.

FIG. 1: (Color online) (a): Temperature dependence of the magnetic susceptibility ($\chi_{\parallel}$ and $\chi_{\perp}$) of $\alpha$-RuCl$_3$ measured in H=100 Oe, (b): Inverse susceptibilities and Curie Weiss fit (straight lines).

Figure 1(a) shows the susceptibility as a function of temperature for the two directions (in-plane and perpendicular to the plane) in $\alpha$-RuCl$_3$. For $H \parallel c$ there are clear signatures of two phase transitions at 14 and 8 K, whereas for $H \perp c$ between 14 and 8 K a plateau-like behavior is found, followed by a sharp decrease of the susceptibility. This decrease points towards a sort of spin compensation (eg., an antiferromagnetic transition or an effective dimerization in the ab plane). Below 300 K, the in-plane susceptibility $\chi_{\parallel}$ is larger than the out-of-plane component $\chi_{\perp}$ ($\chi_{\perp}/\chi_{\parallel} \approx 2.5$ at 60 K). The inverse susceptibility is shown in figure 1(b). The Curie Weiss fit of the inverse susceptibility clearly yields dissimilar effective coupling constants for the two field directions: i) for $H \parallel c$ a Curie Weiss temperature of $+37$ K evidences an effective ferromagnetic exchange ($J/K_B=37$ K) and an effective moment of $2.14 \mu_B$/Ru and ii) for $H \parallel c$ a Curie Weiss temperature of $-150$ K which evidences a strong antiferromagnetic effective exchange and an effective moment of $2.7 \mu_B$. So far no single crystal data for magnetization were available in the literature. From powder results a positive Curie Weiss temperature $\theta = 23-40$ K was determined and the moments calculated are around $2.3 \mu_B$. This is approximately what we found for the in-plane contribution in our single crystal and it is most likely that the powder average is dominated by this in-plane contribution. Nonetheless, our single crystal studies clearly reveal the anisotropic nature of the magnetic exchange and give clear evidence for an effective antiferromagnetic exchange interaction with a larger effective moment of $2.7 \mu_B$ when field is applied along the $c$ direction. This is well above the spin-only value for the $S = 1/2$ low spin configuration of Ru (1.73 $\mu_B$) which points towards a prominent SOC. This is supported by our field-dependent susceptibility studies shown in figure 2(a). In the $c$ direction, the susceptibility and the step-like transitions at 14 K and 8 K remain unaffected in fields up to 7 T. In contrast to that, the in-plane susceptibility is strongly affected by magnetic fields for $T<50$ K. Upon applying fields the phase transitions are shifted towards lower temperatures and the susceptibility is enhanced. This is not expected because of the effective ferromagnetic coupling evidence from the Curie Weiss fit. The reduction of $\chi_{\perp}$ with field evidences admixed antiferromagnetic correlations which supports the scenario of dissimilar exchange interaction (Heisenberg type versus Kitaev type) being present in the honeycomb layer.

FIG. 2: (Color online) $\chi$ for $H \perp c$ and $H \parallel c$ at different magnetic fields, $(C/T)$ versus $T^2$ at different magnetic fields for $H \perp c$ and $H \parallel c$.

To study the complex phase transitions and the effect of the magnetic field for both directions, we conducted specific heat measurements (figure 2). In figure 2(b), the quotient of specific heat and temperature is plotted as a function of $T^2$ between 2K and 20 K in fields up to 14 T and for the $H \perp c$ configuration. At zero field, the
two phase transitions at 14 K and 8 K could be clearly identified. The high temperature transition is somewhat broader than the low-temperature transition. Upon applying magnetic fields up to 14 T, the complex transition is monotonously suppressed which is consistent with our findings in the susceptibility. At highest fields of 14 T, the onset of the low-T transition is at about 3 K. Above this transition, the $C/T$ curve remains smooth and shows a nice $C \sim T^2$ (inset of Figure 2(b)) power law between 5 K and 14 K, which might indicate a spin-liquid-like behavior. In contrast to that, there is no such strong field dependence for the $H||c$ configuration. Here, both phase transitions at 14 K and 8 K remain unaffected by the field. Assuming a negligible phonon contribution, we find an entropy of $S \approx 0.5R\ln 2$ below 20 K for $H = 0$ T. So far we do not have a proper phonon reference to do a more quantitative specific heat analysis.

As a microscopic probe of the anisotropic magnetic order, we performed $^{99,101}$Ru zero-field NMR on the α-RuCl₃ single crystal. Due to the presence of two isotopes with the higher (>1/2) spin (3/2 for $^{99}$Ru and 5/2 for $^{101}$Ru) a complex zero-field NMR spectrum is expected. Early $^{99}$Ru Moessbauer measurement on the α-RuCl₃ powder show the absence of sizable quadrupolar interaction and provide the powder-averaged hyperfine field at the Ru-site of about 20.9 T [10]. The value of the hyperfine field is in good agreement with the prediction of Watson and Freeman of about 20 T per unpaired 4$d$ electron (and 11 T per unpaired 3$d$ electron) [11]. For the Ru$^{3+}$ 4$d^5$ state in the low-spin configuration (LSC) a hyperfine field of 20 T is expected whereas for the Ru$^{4+}$ 4$d^4$ state in LSC in the perovskite-type SrRuO₃ a hyperfine field of about 40 T is expected and experimentally confirmed [12,13].

From the hyperfine field of $H_{hf} = 20.9$ T we could calculate the NMR frequency by the gyromagnetic ratio $^{101}\gamma = 2.193$ MHz/T which leads to an average NMR frequency of about 45.83 MHz. Figure 3(c) shows the $^{101}$Ru zero-field NMR frequency spectra at 4.3 K, 8 K and 10 K. The 4.3 K spectra is located somewhat lower in frequency than expected and, moreover, the line exhibits a pronounced broadening of about 10 MHz which corresponds to 4.56 T. This unexpected broad line (absence of quadrupolar interaction) implies a strongly anisotropic and a more complex non-collinear (probably helical) spin structure in the ordered state in analogy to the structural homologue FeCl₃. The latter compound orders at about $T_N = 15$ K. The Fe$^{3+}$ ions are in the high-spin state and carry a large moment of about 5 $\mu_B$ [14]. For α-RuCl₃ there are two different Ru sites in the lattice, and these sites may be strongly anisotropic because of the strong SOC. For the FeCl₃ this anisotropy is absent because of the weak SOC. The spectra at 8 K and 10 K might promote this speculation because here two separated $^{101}$Ru lines are clearly resolvable. These lines quickly vanish when approaching temperatures above 14 K.

To probe the ordered moments, we performed magnetization measurement in pulse field ($H \leq 60$ T) on a powder specimen. To calibrate the high-field data, dc magnetization measurement performed in static fields up to 14T (Figure 3(a)) were used. The powder-averaged results suggest an in-plane critical field of about 15 T (in good agreement with the heat capacity), whereas the critical field of the out-of-plane component is above 60 T because a clear saturation is not reached yet. Studies up to much higher fields are required for an exact determination of the saturation moment.

Finally, we briefly discuss microscopic features of α-RuCl₃. Plumb et al. [8] have shown that ruthenium ions are in the 3+ state, and the formation of the insulating state is driven by both spin-orbit coupling (SO) and on-site electronic correlations ($U$). To explore the electronic structure of α-RuCl₃, we performed full-relativistic density-functional calculations using the FPLO code [15] with the basis set of local orbitals and Perdew-Wang exchange-correlation potential (LDA) [17].

The LDA+SO band structure is shown in Fig. 2 top right. It is very similar to the scalar-relativistic band structure obtained in LDA (without SO, not shown). The band structure is metallic, with states at the Fermi level dominated by Ru 4$d$ orbitals. The fraction of Cl 3p states is about 34% (27% in the $t_{2g}$ bands and 44% in the $e_g$ bands), which is comparable to 35% of oxygen 2p states in honeycomb iridates. Therefore, α-RuCl₃ and Ir$^{4+}$ com-
pounds feature same degree of metal-ligand covalency. Two well-separated band complexes centered at around −0.5 eV and 2.0 eV belong to the $t_{2g}$ and $e_g$ states of Ru, respectively, but no further splitting of the $t_{2g}$ levels can be observed. In contrast to iridates, neither crystal-field effects nor the spin-orbit coupling split the broad $t_{2g}$ complex into narrow bands that would be then easily split by even weak electronic correlations. We quantified orbital energies by fitting the LDA+SO band structure with Wannier functions and found $\varepsilon_{x^2} = -0.33$ eV, $\varepsilon_{yz} = -0.34$ eV, $\varepsilon_{xz} = -0.36$ eV, $\varepsilon_{3z^2-r^2} = 2.00$ eV, and $\varepsilon_{x^2-y^2} = 1.89$ eV, where $x$, $y$, and $z$ axes are directed along the Ru–Cl bonds within the RuCl$_6$ octahedra, and the $LS$-basis is used. Similar energies of the $xy$-, $yz$-, and $xz$-orbitals reflect marginal distortion of the octahedra and suggest minor importance of crystal-field effects.

In order to reproduce the effect of electronic correlations, we performed LSDA+U+SO calculations assuming the ferromagnetic spin arrangement in α-RuCl$_3$. This simplest possible spin configuration enables us to focus not only numerically different for different field directions, but also differ in sign being positive for the field in-plane and negative for the field out-of-plane. This strongly suggests that the physics of the Heisenberg-Kitaev model (HKM) can be observed in α-RuCl$_3$. Details of this physics require further investigation, though, and a careful evaluation of individual exchange parameters that is, unfortunately, complicated by the structural complexity (two nonequivalent Ru$^{3+}$ sites) and possible stacking disorder. From a phenomenological viewpoint, α-RuCl$_3$ reveals very peculiar physics with two transitions at 14 K and 8 K that are also strongly anisotropic. First $^{105}$Ru zero-field NMR results point towards a complex long-range magnetic order below 14 K. Single-crystal neutron diffraction studies are required to obtain the magnetic structure in the ordered phase.

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FIG. 4: (Color online) Left panel: crystal structure of α-RuCl$_3$ built of honeycomb Ru–Cl layers that are held together by weak van-der-Waals forces. Right panel: electronic density of states (DOS) for α-RuCl$_3$ calculated within LDA+SO (top) and LSDA+U+SO (bottom, total DOS for both spin directions is shown). The Fermi level is at zero energy. Note that the spin-orbit coupling does not split the broad complex of $t_{2g}$ bands crossing the Fermi level. The gap is formed only in LSDA+U+SO, where correlation effects are accounted for in a mean-field fashion.

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Here, we report results for the fully relaxed crystal structure with one RuCl$_3$ layer per unit cell. Given the fact that α-RuCl$_3$ features large amount of stacking disorder, the consideration of different stacking sequences may be important and even vital for understanding the overall magnetic order, especially in the direction perpendicular to the layers. This problem will be addressed in future studies.

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