Towards the quantum spin liquid ground state: ……. complex magnetic interaction networks meet spin orbit entangled spins

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The physics of S = ½ quantum magnets (QMs) is extremely rich, owing to the variety of magnetic exchange interaction networks in different systems, as determined by the lattice geometry and the orbital hybridization [1-3]. Systems studied so far include quasi-one-dimensional (1D) linear chains, planar 2D systems (ladders, kagome layers, planar triangular- or square-lattices), and more complex 3D structures such as hyperkagome and pyrochlore lattices. Recently, the field of S = ½ quantum magnetism has been extended away from 3d ions (such as those containing Cu^{2+}- or V^{4+}-ions) towards 4d-, 5d- and even 4f-systems [1]. In these materials an effective J_{eff} = ½ moment can be realized due to strong spin-orbit coupling (SOC), and in certain compounds (e.g. planar honeycomb lattices or triangular lattices) the presence of strong spin orbit assisted frustration leads to quantum spin-liquid (QSL) ground states with non-trivial-band-topology [1].

In general, having the energy of the SOC, the Coulomb interaction (parametrized by U) and the crystal electric-field splitting of the same order of magnitude leads to highly degenerate magnetic states and complex excitations for many 4d- and 5d-QMs. These excitations can be gapless or gapped, but their nature is complicated by the presence of disorder and anisotropic interactions, and their understanding is hindered by the scarcity of model materials [1-3].

4d- and 5d- planar honeycomb quantum magnets: proximate spin liquids

Among the 4d- and 5d-systems, the Heisenberg-Kitaev model (HKM) was established to describe the competing bond dependent magnetic exchange interactions in the honeycomb type of lattice structures [4]. Prominent examples are the 2-1-3 iridates Li_2IrO_3, Na_2IrO_3, and the rhodate Li_2RhO_3 where the magnetism is associated with the $5d^5$ electrons on the Ir^{4+} ions and the $4d^5$ electrons on the Rh^{4+} ions. While Na_2IrO_3 displays zigzag magnetic ordering and α-Li_2IrO_3 exhibits incommensurate spiral ordering the 4d homologue Li_2RhO_3 exhibits no sign of long-range magnetic ordering [5]. In order to search for new 4d- or 5d-model systems with the honeycomb lattice arrangement as a platform of HKM, α-$RuCl_3$ turns out to be an excellent candidate because the low spin 3+ state of Ru ($4d^5$) is equivalent to the 4+ state of Ir or Rh. Density functional electronic structure calculations indicate that the low spin state in α-$RuCl_3$ is indeed formed through the subtle interplay of the crystal field, a sizeable SOC for the Ru 4d-states and a Coulomb repulsion U, which is rather moderate compared to related, but much stronger correlated 3d systems. Furthermore, we were able to grow sizable flake-like single crystals (Fig. 1) by chemical transport methods at the CPFS and used these to study the magnetic anisotropy of that material for the first time [6].

Our single crystal study reveals that α-$RuCl_3$ exhibits a complex magnetic ordered state with a strong magnetic anisotropy (Fig. 2). Applying fields up to 14 T in the honeycomb plane the magnetic order is completely suppressed, whereas in the perpendicular direction the magnetic order is rather robust. Interestingly the specific heat in the plane shows a T^{-2} behaviour at the highest fields, which is indicative for a quantum spin liquid [6]. By analogy to honeycomb graphene, 2D honeycomb QSLs, with linear dispersive fermionic

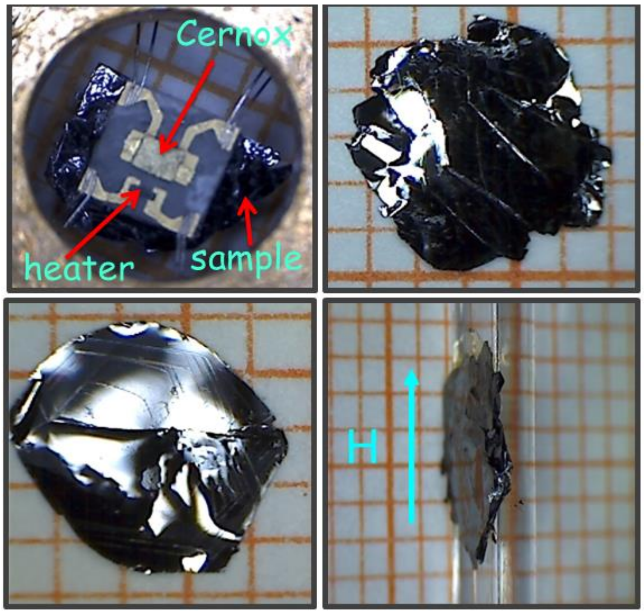

Fig.-1: Examples of flake like α-$RuCl_3$ single crystals used for our studies. (top left picture) Single crystal on the heat capacity platform. (bottom right picture) Single crystal glued on a quartz rod for susceptibility measurements.

spinon bands and low-energy gapless magnetic excitations (spinons or Majorana fermions), are expected to exhibit T^2 behavior of the magnetic specific heat and also power-law spin-lattice relaxation in the nuclear magnetic resonance NMR: $1/T_1 \sim T^n$ [7].

The nuclear magnetic resonance is a microscopic probe for static (local susceptibility) and dynamic (magnetic excitations) magnetism which simultaneously provides information about possible structural distortions (e.g. buckling of layers) or disorder (site mixing) in the lattice. We performed NMR on the Li- and the Na-nuclei in the 2-1-3 iridates and rhodates (joined project with University Augsburg) as well as Ru-NMR on the trichlorid α-$RuCl_3$.

The magnetization of Li_2RhO_3 in small magnetic fields provides evidence of the partial spin-freezing of a small fraction of Rh^{4+} moments at 6 K, whereas the Curie-Weiss behavior above 100 K suggests a pseudo-spin-1/2 paramagnet with a moment of about 2.2μ_B. The magnetic specific heat (C_m) exhibits no field dependence and demonstrates the absence of long-range magnetic order down to 0.35 K (Fig. 3) [8].

C_m/T passes through a broad maximum at about 10 K and $C_m \propto T^2$ at low temperatures. The Li – NMR spin-lattice relaxation rate ($1/T_1$) reveal a gapless slowing-down of spin fluctuations upon cooling with $1/T_1 \sim T^{2.2}$ (Fig. 4). A scenario in which a minority of Rh^{4+} moments in a short-range correlated frozen state coexisting with a majority of moments in a liquid-like state that continue to fluctuate at low temperatures seems to be plausible from NMR and µSR. The $C_m \sim T^2$

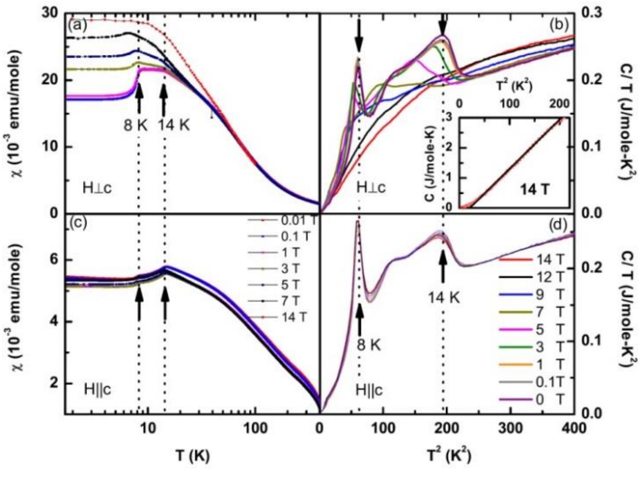

Fig.-2: (left) Susceptibility of α-$RuCl_3$ parallel (top) and perpendicular (bottom) to the honeycomb plane. Specific heat divided by T parallel (top) and perpendicular (bottom) to the honeycomb plane. The inset shows the T^2 behaviour of the specific heat in the plane at 14 T [6].

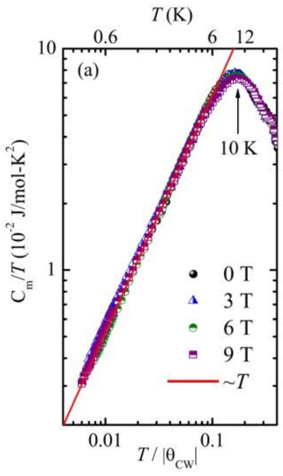

Fig.-3: Magnetic heat capacity coefficient (C_m/T) of Li_2RhO_3 in various fields as a function of $T/|\theta_{CW}|$. The upper axis shows the absolute T dependence and the solid line represents $C_m \sim T^2$ [8].

and the $1/T_1 \sim T^{2.2}$ behavior at low T might therefore be assigned to the emerging Kitaev spin-liquid state in Li_2RhO_3 [8].

Beside local probes (like NMR or µSR) and bulk probes, miniaturized torque magnetometry was performed to study the magnetic anisotropy of honeycomb iridates and Ru-trichlorid in high magnetic field [9, 10]. This was a joined project with the MPG research group "Physics of Microstructured Quantum Matter" and the National High Field Laboratories in Los Alamos and Tallahassee. Resonant torsion magnetometry is a new development that directly measures the derivative of torque in small crystals. As such, it is highly sensitive and provides additional thermodynamic information at

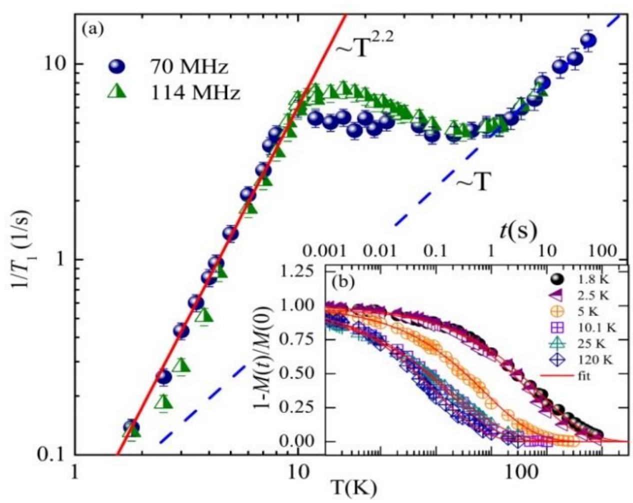

Fig.-4: Spin lattice relaxation of Li_2RhO_3 as function of temperature. The inset shows the longitudinal magnetization recovery curves M(t) at various temperatures [8].

continuous phase boundaries, similar to specific heat. [10].

Three dimensional quantum spin liquids

Another approach in searching for QSL systems was to study Tellurium oxide based materials. Whereas Ba_2CuTeO_6 was identified as a S = ½ quantum critical spin ladder system with orbital ordering [11] the related system $PbCuTe_2O_6$ was identified as a rare example of a spin liquid candidate featuring a three-dimensional magnetic lattice [12].

In $PbCuTe_2O_6$, strong geometric frustration arises from the dominant antiferromagnetic interaction that generates a hyperkagome network of Cu^{2+} ions. Through a combination of bulk magnetization and local probe investigations by NMR and muon spin relaxation down to 20 mK, robust evidence for the absence of spin freezing in the ground state is provided (Fig. 5). Furthermore it was shown that $PbCuTe_2O_6$ remains in a fluctuating spin liquid state down to the lowest temperature [12].

Planar triangular d- and 4f-quantum magnets: effect of lattice distortions and spin orbit coupling on the QSL ground state

Planar spin ½ triangular lattice quantum magnets (TQMs) with antiferromagnetic exchange interaction are ideal QSL candidates as proposed by P.W. Anderson in his outstanding contribution from 1973. Prominent examples are found among the organic materials (K-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, Et$_n$Me$_{4-n}$Sb[Pd(DMIT)$_2$]$_2$) whereas QSL model systems among inorganic compounds are very rare ($Ba_3CuSb_2O_9$) [3]. We extended our work towards TQMs with 5d- or even 4f-ions because here the spin orbit interaction becomes a new and rather important ingredient to QSL physics [1]. Beside highly degenerated fermionic band like spinon excitations the spin orbit entanglement is believed to lead to highly anisotropic interactions among the moments which should strongly enhance the quantum fluctuations and promote the QSL ground state.

The 3d-TQM $Sc_2Ga_2CuO_7$ was studied by bulk methods [13] and the local NMR probe [14] and strong evidence was found for a quantum spin liquid near the percolation threshold. Work on the 5d-Iridate TQM $Ba_3IrTi_2O_9$ [15, 16] and the diluted system $Ba_3M_xTi_{3-x}O_9$ (M = Ir, Rh) [17] is proceeding along the same line. Here the effect of vacancies on the magnetic ion site on the spin liquid like ground state was investigated by bulk and local probes [17, 18].

As site-mixing, lattice distortions and in particular vacancies are present in many of the systems, the search for the ideal TQM with strong spin orbit interaction is still ongoing, both in our group and worldwide. Trigged by the huge interest on the 4f-triangular magnet QSL candidate $YbMgGaO_4$ [19] we focused our efforts on new Yb-quantum magnets within the same space group (R-3m). For these Yb-TQMs the spin orbit coupling of the 4f-electrons and the crystal electric field creates a ground state doublet which at low temperatures could be described with an effective spin ½ at the Yb-site.

As most of the $A^{1+}B^{3+}O_2$ delafossites share the same space group and a planar triangular spin arrangement we concentrated our efforts on Yb-based delafossites. Among the delafossites there are some reports on $AYbO_2$ (A = Ag, Na) but the emergence of a pure pseudo spin S=1/2 state is in question and so far no single crystals are available. It might be possible to tune the lattice further towards a pseudo spin S=1/2 state by replacing the oxygen with another chalcogenide. The sulphur delafossites $NaYbS_2$ and $LiYbS_2$ as well as the oxide $NaYbO_2$ could be synthesized in poly crystalline form ($NaYbS_2$ also as single crystals) at the CPFS and in collaboration with the Technical University of Dresden and characterized by bulk methods like magnetization and specific heat, but also by local probes like NMR, ESR and µSR. Our studies clearly evidence a strongly anisotropic pseudo spin S=1/2 state of Yb in $NaYbS_2$ single crystals towards low temperatures and an absence of long range magnetic order (down to 300 mK) which identify Yb-based delafossites as new putative quantum spin liquids [18].

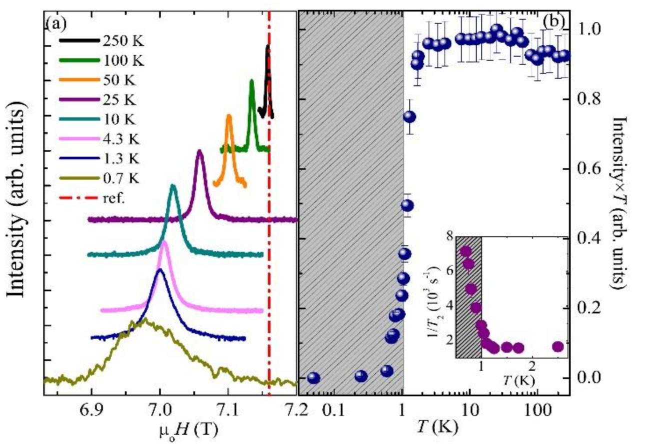

Fig.-5: Field sweep Pb NMR spectra in $PbCuTe_2O_6$ at various temperatures (a) and NMR intensity (b) together with the spin-spin relaxation time (inset) [12].

Kagome – layer minerals: QSLs by nature?

The two-dimensional kagome lattice quantum magnet Herbertsmithite $ZnCu_3(OH)_6Cl_2$ is a natural mineral and it is one of the prototype QSL system [3]. New polymorphs of the Herbertsmithite mineral could be synthesized in rather pure form by hydrothermal preparation at the University of Frankfurt. Our joined research has two directions: i) Doping of Herbertsmithite (replacing Zn^{2+} by Ga^{3+} or Y^{3+} [21]) and ii) search for new polymorphs (e.g. Barlowite [22]). NMR is proven to be a superb tool because it could probe the local magnetism and possible lattice distortions simultaneously.

External Cooperation Partners

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