Recipe for a spin-orbital liquid

N. Tang, Y. Gritsenko, Kenta Kimura, S. Bhattacharjee, A. Sakai, M. Fu, H. Takeda, H. Man, K. Sugawara, Y. Matsumoto, Y. Shimura, J.-J. Wen, C. Broholm, H. Sawa, M. Takigawa, T. Sakakibara, S. Zherlitsyn, J. Wosnitza, R. Moessner, S. Nakatsuji

Contact

Dr. Nan Tang[1,2]; Prof. Roderich Moessner[3]; Prof. Satoru Nakatsuji[2]

nan.tang@uni-a.de; moessner@pks.mpg.de; satoru@phys.s.u-tokyo.ac.jp

University of Augsburg[1]; University of Tokyo[2]; MPI for the Physics of Complex Systems[3]

An international team of scientists has observed an exotic quantum state of matter: a spin-orbital liquid formed on the pyrochlore oxide $Pr_2Zr_2O_7$. Here, both spin and orbital degrees of freedom remain dynamic down to extremely low temperature. It is known from the long history of condensed matter physics that suppressing orbital order down to low temperatures is extremely difficult, a precondition for the next tricky step of obtaining a spin-orbital liquid state. $Pr_2Zr_2O_7$ serves as a rare counterexample in which spins and orbitals are interlocked, so that fluctuation of one necessitates fluctuation of the other.

The work of a group assembled by physicists at the University of Tokyo, including scientists from the MPI for the Physics of Complex Systems in Dresden and for Solid State Research in Stuttgart, the Helmhotz Zentrum Dresden-Rossendorf, ICTS-TIFR in Bangalore and Johns Hopkins University in Baltimore, is published in the current issue of Nature Physics.

Introduction

We know that people act differently in a group than when they are alone. Interestingly, this applies to atoms as well. The Nobel-prize winning physicist P. W. Anderson once put “More is different”, which explains unpredictable phenomena in a complex system that cannot be simply understood by the sum of its microscopic constituents. This idea lies at the heart of modern many-body physics, perhaps most famously in the case of superconductivity where pairs of electrons enter a cooperative state which carries electrical currents without resistance – as used in superconducting maglev nowadays.

Recently, macroscopic quantum entanglement which appears in quantum many-body systems, is receiving much attention because the manipulation of such entanglement effect should lead to realization of a series of next-generation technologies, ranging from quantum computing to quantum cryptography. The international research team focused on an exotic many-body state called "spin-orbital liquid" to advance the search for long-range entanglement effects.

Pursuing "liquid" in solids

In nature, matter mainly exists in the forms of solid, liquid, and gas. In solids, all the atoms are periodically arranged and remain immovable from their own sites, while particles in liquid and gas are not that "well-behaved" but move rather randomly. The notion of states of matter can be applied to wider topics as well, such as magnetism. At low temperatures, spins, the most basic building block of magnets, tend to order parallel or antiparallel to each other, forming a neatly aligned "solid" state. Interestingly, spins are like humans, that they also feel comfortable to behave like everybody else. However, in the past decades, "quantum spin orbital liquid" is proposed as a counterexample to the conventional form of magnetism, in which spins and orbitals refuse to form any patterns and remain "liquid" at low temperatures inside solids.

Such a spin-orbital liquid is hard to realize because spins and orbitals like to go their own way. Spins are driven by low energy spin-exchange interactions, while orbitals are "pulled" by surrounding crystal lattice which has much higher energy scales, into ordered state. In this way, it is considered almost impossible to have high-energy orbitals and low-energy spins fluctuate simultaneously.

Bringing down the energy scale of "orbitals"

The research team proposed a new route to realize spin-orbital liquid in a Praseodymium based mineral, $Pr_2Zr_2O_7$ (Figure 1), also known as a quantum spin ice candidate (Figure 2, bottom). Pr ions form a pyrochlore lattice structure, which is a corner-sharing network of tetrahedra, and realizes an oxidation state of Pr^{3+}, which has two $4f$ electrons. "The fact of possessing even number electrons, which we call 'non-Kramers' system, is actually the key to realize this spin-orbital liquid.", said Dr. Nan Tang from University of Tokyo. The lowest-energy state of $Pr_2Zr_2O_7$ is a non-Kramers doublet, which can be described by electric quadrupolar moments (orbitals) [S_x, S_y components] as well as a magnetic dipolar moment (spin) [S_z component] (Figure 3). Now the energy scales of orbitals and spins meet! When one of them fluctuates, the other fluctuates as well, which means a spin-orbital liquid can be brought to life on this setting. Unfortunately, as a drawback of all non-Kramers systems, the requirements of crystal quality becomes extremely strict. Since non-Kramers ion Pr^{3+}, unlike its

Kramers counterpart (possessing odd number electrons), is not protected by a particular symmetry called “time reversal symmetry”, slight amount of disorder can affect the crystal environment and alter its physical properties. Therefore, a normal high-quality sample used for conventional Kramers system would not be good enough.

This time, the research team succeeded in growing an extremely high-quality $Pr_2Zr_2O_7$ single crystal. It is obtained by the floating-zone method, in which a polycrystalline rod is melted at temperatures higher than 2000℃ and then the melted ingredient crystallizes into a single crystal via cooling. The team of Prof. Satoru Nakatsuji came up with the strategy of making the polycrystalline rod much thinner than previous, which, in principle, should result in a more homogenous single crystal. However, such a thin rod is easily broken and requires more precision when being set inside the synthesis apparatus. “We have overcome such technical difficulties, with an optimized recipe and improved synthesis conditions over time, which finally leads to an extremely pure $Pr_2Zr_2O_7$ single crystal”, said Dr. Kenta Kimura from University of Tokyo. Its top quality is confirmed by both crystallographic analysis from synchrotron X-ray and physical property measurements including magnetization, nuclear quadrupole resonance, and specific heat.

Spin ice physics adds some more flavour

Furthermore, the authors have performed thermal expansion and magnetostriction measurements which measure the length change of samples with respect to temperature and magnetic field, respectively (Figure 4, left), along with ultrasound and dielectric constant measurements. They found no evidence for long-range order (i.e., spins form a static pattern throughout the crystal) of $Pr_2Zr_2O_7$ down to extremely low temperatures in all the measurements, which, along with other experimental data, points to a dynamic state. To be noted, the length change of insulating materials at low temperature are extremely small and its measurement requires a resolution equivalent to a ping-pong ball on the background of Mount Fuji. Moreover, the generation of extreme low temperature (near -273℃) requires dilution refrigerator which is necessary for the research of quantum phenomena, including quantum computing (Figure 4, right).

By applying magnetic fields, they observed evident increase at the same magnetic fields in all measurements, which is called metamagnetic anomaly. Metamagnetic anomaly, a characteristic feature of spin ice, serves as a boundary line to separate a “gas” phase and a “liquid” phase in $Pr_2Zr_2O_7$. In this sense, the observation of metamagnetic anomaly serves as an example of the manipulation of macroscopic quantum entanglement by magnetic field. The theorists team, Prof. Roderich Moessner from MPI and Prof. Subhro Bhattacharjee from Tata Institute of Fundamental research, also discover that the lattice can actually enhance spin-orbital dynamics (Figure 2) and stabilize such a topological quantum spin ice state, since orbitals couple with crystal lattice directly (Figure 3).

Beauty of many-body physics

$Pr_2Zr_2O_7$ is a quantum material with a complex interplay among spins, orbitals and lattice degrees of freedom. Any of the interactions or electronic correlations become too strong and overwhelm one another, the system would suddenly fall into a state of magnetic, electrical, or structural order. The team's extremely pure $Pr_2Zr_2O_7$ has a fine balance of various interactions and thus succeeded in observing spin-orbital dynamics.

Quantum many-body phenomena, in which various degrees of freedom are intricately intertwined, are a treasure trove of new discoveries, and their quantum entanglement effects are an attractive research topic for next-generation quantum technologies. “The spin-orbital liquid is an important concept that embodies quantum many-body physics and could turn into a building block for future quantum technology.” said Dr. Nan Tang. “This research is expected to serve as a guideline for the design of materials to realize spin-orbit liquids in the future and provides insights for the manipulation of quantum entanglement.” added Prof. Satoru Nakatsuji.

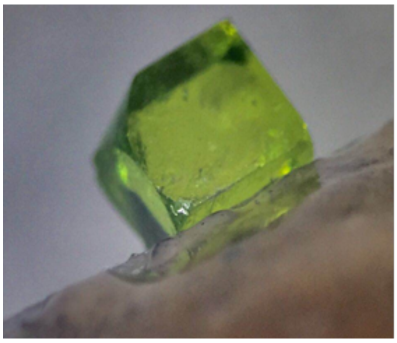

Figure 1. A piece of ultra-high quality crystal sample of the pyrochlore oxide $Pr_2Zr_2O_7$ grown in the laboratory of Prof. Nakatsuji. The sample shows green transparent color and are free from cracks.

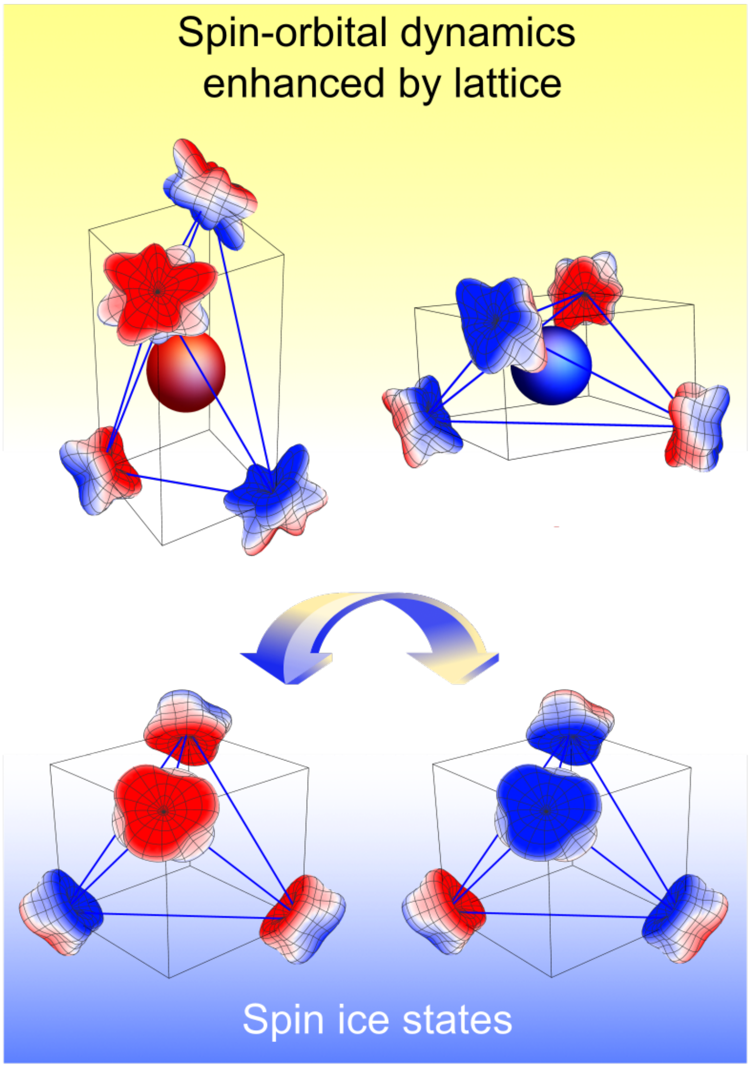

Figure 2：A schematic of spin-orbital dynamics enhanced by the lattice structure of $Pr_2Zr_2O_7$. The bottom objects show two different configurations of spin ice states, where the red-to-blue gradient objects are the orbitals and spin components of Pr ions in the lowest energy state, located on the vertex of tetrahedrons. The top two objects are excited states that are distorted by lattice.

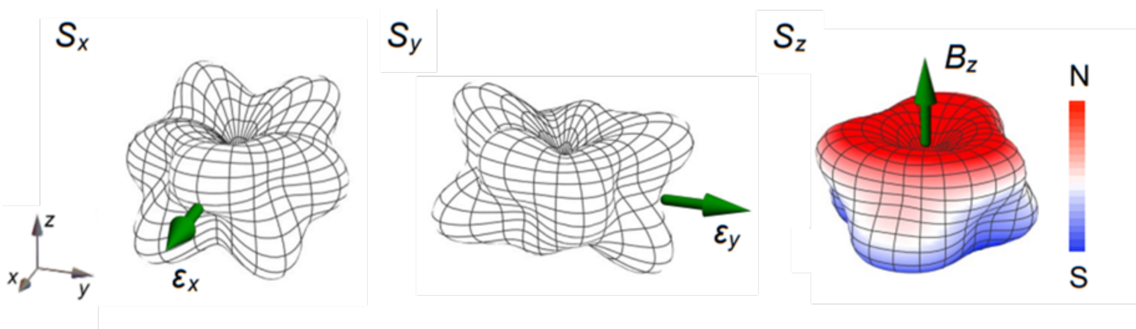

Figure 3：A schematics of spin-orbital entanglement in $Pr_2Zr_2O_7$. S_x, S_y is electric quadrupoles (orbital components) and S_z is a magnetic dipole (spin component). Electric quadrupoles couple with lattice distortion（ε_x, ε_y）directly, and magnetic dipoles couple with magnetic field（B_z）. N and S represents the direction of spins, north or south pole of a magnet.　In this setting, orbitals and spins have to fluctuate together because they are now described by a unified framework of spin S. In a conventional spin ice, S_x and S_y component (the source of fluctuation) is absent, hence a static state is realized. In quantum spin ice, S_x, S_y component acts as transverse fields (the origin of quantum fluctuation) and hence, leads to a dynamic state.

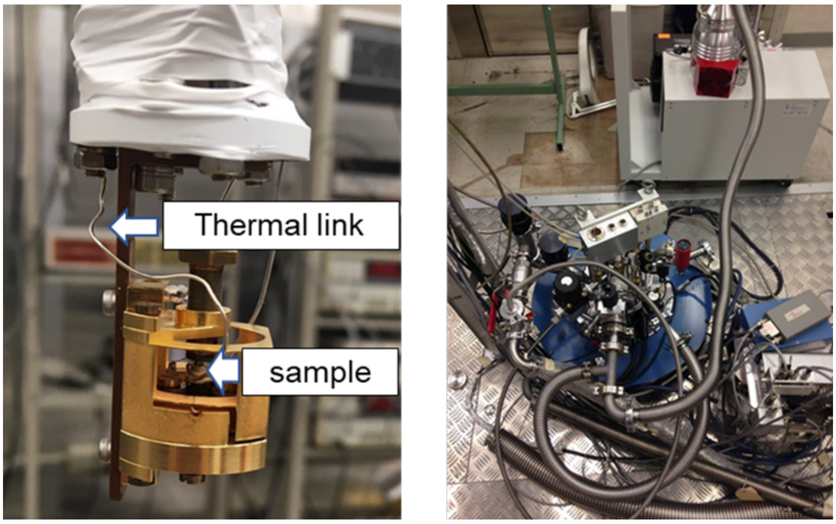

Figure 4: Photos of low-temperature experimental apparatus. (Left) The scientists placed the $Pr_2Zr_2O_7$ sample inside a high-precision instrument called dilatometer for measuring thermal expansion and magnetostriction (change in the shape of magnetic material under an external magnetic field). The sample is connected to the coldest part of the dilution refrigerator by a thermal link made of silver. (Right) A dilution refrigerator is being prepared to cool down to eventually around -273 ℃, by pumping it to high vacuum.

Glossary

A topological magnetic state: quantum spin ice

At ambient pressure, ice (H_2O) has a pyrochlore lattice structure and satisfies the constraints where one O^{2-} ion has two of the four neighboring hydrogen ions H^+ nearby and the other two far away. A similar situation of such "2-near, 2-far" occurs in a magnetic material called spin ice, in which the displacement of the H^+ ions is replaced by Ising spin, which can orient in only two directions, up and down. In spin ice, the Ising spins are located at the vertices of a tetrahedron, and two of the four Ising spins point inward and the other two point outward the tetrahedron (a structure called "2-in, 2-out").

Quantum spin ice is a state in which quantum mechanical effects (transverse fluctuations S_x and S_y components) are present (Figure 3), resulting in dynamic quantum tunneling among different "2-in, 2-out" structures (Figure 2, bottom). This is different from conventional classical spin ice, where a particular "2-in, 2-out" state is selected and then stabilized statically. In addition, quantum spin ice has a topological order rather than a long-range order as in conventional magnetic materials, which differentiates itself from a completely disordered state. This topological nature supports new type of excitations, which might be utilized in low-energy consumption devices or quantum computers.