

## Competition between spin-orbit coupling and molecular orbital crystal in pyrochlore ruthenate $\text{In}_2\text{Ru}_2\text{O}_7$

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Transition metal oxides are a platform for a plethora of exotic electronic phases where multiple degrees of freedom of correlated  $d$ electrons, together with an underlying lattice topology, are at play. The ground states of these systems are governed by a subtle balance of relevant electronic parameters such as Coulomb repulsion, bandwidth, and crystal fields.  $4d$  ruthenium compounds have been playing a significant role in providing novel electronic states such as unconventional superconductivity, metal-insulator transition, and quantum magnetism.

Besides metallic or Mott insulating ground states, some ruthenium compounds exhibit a nonmagnetic ground state, which is accompanied by the formation of molecular orbitals generated by direct hopping between spatially extended  $4d$  orbitals. A prominent example is the honeycomb ruthenate  $\text{Li}_2\text{RuO}_3$ , which undergoes dimerization of Ru atoms below  $\sim 550$  K and forms a "molecular orbital crystal", where the  $4d$  electrons are accommodated into the bonding and antibonding molecular orbitals localized on the dimers.

In heavy-transition-metal compounds such as ruthenates, another key ingredient for their exotic electronic states is spin-orbit coupling (SOC) which produces spin-orbit entangled  $J_{\text{eff}}$  pseudospins. Probably the most striking impact on magnetism is realised in  $\text{Ru}^{4+}$  ruthenates with a  $d^4$  configuration. While SOC produces a nominally non-magnetic  $J_{\text{eff}} = 0$  singlet, "excitonic" magnetism can arise via the interaction between excited states, and spin-orbit excitons may condense into an exotic long-range magnetic order. Up to date, excitonic magnetism has been only established in a layered perovskite  $\text{Ca}_2\text{RuO}_4$  and remains unexplored in other ruthenates.

The competition between electronic phases including molecular orbital crystal and spin-orbit magnetism is expected to be more pronounced in ruthenates with a frustrated lattice, such as pyrochlore ruthenates  $A_2\text{Ru}_2\text{O}_7$  ( $A$ : trivalent cation). The pyrochlore ruthenates have been regarded as  $S = 1$  Mott insulators due to the presence of a trigonal distortion which may lift the degeneracy of the  $t_{2g}$  orbitals and thus competes with SOC. While most of them order magnetically at low temperatures,  $\text{Tl}_2\text{Ru}_2\text{O}_7$  exhibits a metal to non-magnetic insulator transition at  $\sim 120$  K. The origin of the nonmagnetic ground state has been attributed to the formation of a Haldane gap in the one-dimensional zigzag chains of Ru atoms on top of the pyrochlore lattice. The distinct behaviour of  $\text{Tl}_2\text{Ru}_2\text{O}_7$  may be related to the covalency of Tl-O bonds, which has been discussed as playing a key role in the metal-insulator transition. The covalent character of  $A$ -O bonds thus may be an important parameter for the ground state of pyrochlore oxides. On the other hand, the role of spin-orbit coupling has not been fully investigated in pyrochlore ruthenates.

In an attempt to explore the novel phase competition in pyrochlore ruthenates, we discovered a new compound  $\text{In}_2\text{Ru}_2\text{O}_7$  using high pressure synthesis. At high temperatures above  $\sim 450$  K,  $\text{In}_2\text{Ru}_2\text{O}_7$  crystallizes in a cubic pyrochlore structure, but adopts a weakly distorted tetragonal structure at room temperature as elucidated with single crystal x-ray and powder neutron diffraction. From the spectroscopic measurements,  $\text{In}_2\text{Ru}_2\text{O}_7$  was found to host a spin-orbit-entangled  $J_{\text{eff}} = 0$  -like state at room temperature, despite presenting the largest trigonal distortion among the family of pyrochlore ruthenates. The spin-orbit entangled singlet state is expected to display excitonic magnetism. Strikingly, through successive structural transitions likely associated with the covalent In-O bonds, the singlet state collapses and  $\text{In}_2\text{Ru}_2\text{O}_7$  forms a non-magnetic state below  $\sim 220$  K as evidenced by muon spin rotation. The nonmagnetic ground state was found to originate from a molecular orbital formation in the semi-isolated  $\text{Ru}_2\text{O}$  trimer molecules decorating the pyrochlore lattice. Such molecular orbital formation, which involves not only the  $\text{Ru}^{4+}$  ions but the  $\text{O}^{2-}$  anions as well, has not been reported in other pyrochlore oxides.

In this talk we discuss the subtle competition between spin-orbit coupling and molecular orbital crystal formation in pyrochlore ruthenate  $\text{In}_2\text{Ru}_2\text{O}_7$ . We present the structural details of the  $\text{Ru}_2\text{O}$  trimer formation and its impact on the magnetism and electronic structure of  $\text{In}_2\text{Ru}_2\text{O}_7$ . We argue that the unique molecular orbital formation involving an oxygen atom, distinct from dimers with direct overlap of  $d$ -orbitals commonly found in other transition metal oxides, is assisted by the distortion of the In-O network. Our result demonstrates that bond covalency of constituent ions can be an additional key parameter in understanding phase competitions in complex transitionmetal oxides.

**Keywords:** correlated materials, ruthenate, structural phase transition, spin-orbit coupling, molecular orbital crystal