

TRANSITION METAL OXIDES

Travels in one dimension

The discovery that electrons in $Tl_2Ru_2O_7$ lose their three-dimensional nature at low temperatures and arrange in chains, opens up a new direction in research into transition metal oxides.

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The world of transition metal oxides is full of surprises and intriguing effects, ranging from large changes of resistance in the presence of a magnetic field (the colossal magnetoresistance), to high-temperature superconductivity. In this issue, Seongsu Lee and co-workers uncover yet another revelation¹. A detailed investigation of the crystallographic, magnetic and electronic properties of the ruthenium oxide $Tl_2Ru_2O_7$ indicates that at temperatures below 120 K the electrons reorganize and effectively change their dimensionality — they go one-dimensional.

At elevated temperatures, $Tl_2Ru_2O_7$ seems to be an unassuming three-dimensional conductor, much like, for instance, iron. But there are startling changes in electronic and magnetic properties when $Tl_2Ru_2O_7$ is cooled down. Below the critical temperature, the electrical resistivity suddenly increases by two orders of magnitude: the metal freezes into an insulator. By combining neutron scattering experiments with electronic structure calculations, Lee and co-workers are able to predict that in the insulating phase the electrons form one-dimensional chains, whereas the crystal itself retains a three-dimensional structure. If this happens, theory says that in $Tl_2Ru_2O_7$ these chains should display a most peculiar magnetic phase, the so-called Haldane state. This state is known to exist exclusively in one-dimensional magnets.

The experimental observation of this Haldane state by Lee *et al.*, using neutron scattering experiments, is a telltale sign of the effectively one-dimensional world that the cold electrons are living in. Such a distinct temperature-induced change in dimensionality from a three-dimensional conductor to a one-dimensional Haldane-magnet is unprecedented in any material.

What makes it possible for electrons in $Tl_2Ru_2O_7$ to change dimensionality so easily? It turns out that this ruthenium oxide contains a subtle ingredient: degenerate electronic orbitals. Electronic orbitals

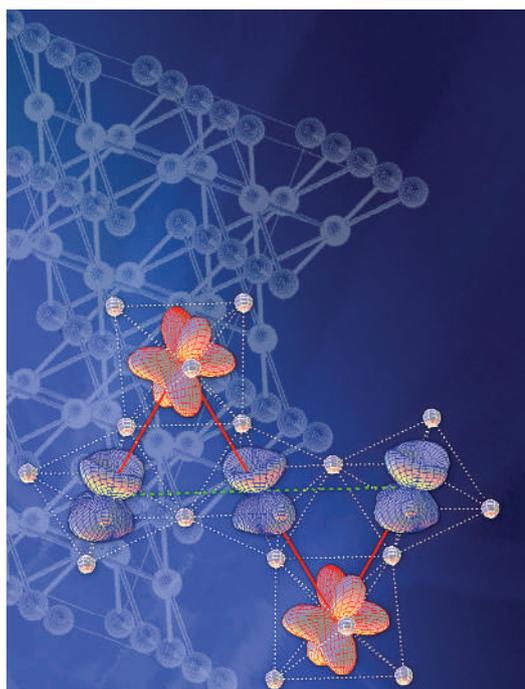


Figure 1 Orbital ordering in $Tl_2Ru_2O_7$. Driven by orbital degrees of freedom, electrons in the three-dimensional crystal (background) self-organize into one-dimensional chains (foreground).

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— the ‘clouds’ formed by the electrons around the atomic nucleus— are well known from textbook chemistry and physics. In most common cases, it is straightforward for electrons to choose which orbitals to occupy. They simply fill up all the available orbitals at the lower energy levels, leaving the high-energy orbitals empty and inert. But in oxides of transition metals (such as Ru) the situation can be very different: their electrons encounter orbital configurations that are energetically equivalent (termed degenerate). Because of the strong Coulomb interactions between electrons, only a single electron can be in one of the degenerate orbitals at any one time. The possibility for electrons to occupy one orbital or another therefore constitutes a new degree of freedom.

Whether or not such an orbital degree of freedom actually occurs in a material, depends on details of the atomic ions and the surrounding crystallographic

lattice. Famous examples of ions that can have an orbital degree of freedom are Mn^{3+} and Cu^{2+} . These are present in many important transition metal oxides, such as LaMnO_3 and La_2CuO_4 , the mother compounds of the colossal magnetoresistance manganites and the high-temperature superconductors, respectively. In $\text{Tl}_2\text{Ru}_2\text{O}_7$, the Ru^{4+} ion has degenerate orbitals.

Compared with other degrees of freedom in a solid, there is a feature that is unique to orbitals: their shape is anisotropic, that is, every orbital is oriented in a specific direction. Each of the degenerate orbitals corresponds to a different direction. When electrons in a solid are travelling around and hopping from atom to atom, from orbital to orbital, the spatial orientation of the orbitals will determine the priority of the hopping direction for the travelling electrons. The orbitals act as a kind of signpost.

It turns out that in $\text{Tl}_2\text{Ru}_2\text{O}_7$, at low temperatures, the orbitals order in such a way that they direct electrons almost exclusively along zigzag chains. This explains the transition from a metal to an insulator, the subtle lattice deformation, and the one-dimensional magnetism that Lee *et al.* observe.

This spectacular orbital-related dimensional reduction in $\text{Tl}_2\text{Ru}_2\text{O}_7$ was unanticipated. Can we expect more surprises from the orbitals in complex oxides? Nothing is sure, of course, but it is likely that in the near future we will find many more orbital orderings, in particular in crystallographic lattices with complex structures, such as spinels. The extraordinary arrangement of charges in hexagonal rings in the spinel CuIr_2S_4 is one example².

But there are also many open fundamental questions related to orbital physics. For instance, what role do orbitals play at metal–insulator transitions in complex oxides? The interesting observation is that in many complex oxides below the metal–insulator transition, a relatively large gap in the electronic states opens up. For instance, in the iron oxide Fe_3O_4 , an energy gap of about 1,600 K opens at a temperature of 119 K — the famous Verwey metal–insulator transition³. In $\text{Tl}_2\text{Ru}_2\text{O}_7$, the critical temperature is similar and the gap is about 900 K. How such large gaps at relatively low temperatures can come about is a fascinating problem. An idea suggested recently is that, at least in some materials, the anomalously large gaps are related to a rearrangement of orbital degrees of freedom, and are related to an effective lowering of dimensionality at the metal–insulator phase-transition.

It is remarkable that such a role of orbitals at metal–insulator transitions in complex oxides is relatively little investigated, with VO_2 as the only other exception^{4,5}. Further investigations are likely to uncover more surprises. Maybe we will even gain new insights into some of the classical problems in complex oxides such as the mysterious Verwey metal–insulator transition. The work by Lee *et al.* shows that for such discoveries, orbital degrees of freedom can certainly lead the way.

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