The causes and consequences of high conductivity in delafossite oxides

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As soon as delafossite metals were discovered in the late seventies, their high conductivity was remarked upon. However, neither its causes nor its consequences were investigated until recently. In the last few years we have shown that the high conductivity originates from extraordinary chemical purity of these materials. Furthermore, we demonstrated that the combination of purity, metallicity and hexagonal symmetry of the electronic structure gives us access to a previously uninvestigated regime of non-local transport, which we explore in several ways, yielding novel physical insights. Finally, careful experiments on these pure materials uncovered new quantum coherent effects, motivating future theoretical and experimental study.

Understanding the electronic properties of delafossite metals [1], a family of two-dimensional transition metal oxides, is one of the goals of the Physics of Quantum Materials (PQM) Department. Delafossites have proven to provide a versatile playground for investigating surface and bulk electronic structure, and allowed us to research a range of different phenomena, such as maximal Rashba spin-splitting and itinerant ferromagnetic states [2, 3]. Despite this richness, our original motivation to study delafossites was the deceptively simple experimental observation of extremely high electrical conductivity. In the last several years we have concentrated on understanding the underlying causes and remarkable consequences of this property, reaching conclusions whose relevance surpasses understanding the behavior of one material class, and offers new insights into physics of electronic transport.

To contextualize this line of research it is useful to illustrate what is meant by 'extremely high conductivity.' At room temperature the electron mean free path of $PdCoO_2$ and $PtCoO_2$ is higher than that of copper, silver, gold and aluminum. Low temperature mean free paths are typically on the order of several microns, reaching as much as 20μm in the purest $PdCoO_2$, a truly remarkable value to be observed in a multicomponent oxide [4]. Broadly speaking, there are two different scenarios that could account for this behavior: either these materials exhibit an unprecedented level of chemical purity, or disorder is present at the usual levels but specific features of the electronic structure result in scattering protection, similar to that observed in some Dirac and Weyl systems.

A first step towards distinguishing these scenarios was gaining a detailed understanding of the electronic structure in the vicinity of the Fermi level, which was achieved in collaboration with the groups of Kazuhiko Kuroki (Osaka University) and Takashi Oka (University of Tokyo, at the time a joint group leader between MPI CPfS and MPI PKS) [5]. We discovered that the momentum dependence of the orbital content of the wave function at the Fermi level indeed leads to a scattering suppression of a factor of 2-4 compared to the expectation with no orbital-momentum locking. Combined with the high Fermi velocities measured by angle resolved photoemission (ARPES) [6], this suppression is sufficient to account for the observed room temperature conductivity, but it does not help explain the long low-temperature mean free paths - a mean free path that is 2-4 times shorter than the observed one would still be remarkable!

The analysis of the previous section motivates a careful study of the defect concentration in delafossite metals [7]. Firstly, we attempted to visualize the defects using transmission electron microscopy (TEM), in collaboration with the group of David Muller (Cornell University). Remarkably, no defects were observed even when atomic contrast was achieved, indicating that their concentration is lower than the TEM resolution. We therefore decided to use high-energy electron irradiation (at the SIRIUS facility at Ecole Polytechnique in Paris, in collaboration with Marcin Konczykowski) to deliberately and controllably introduce known concentrations of point defects, in order to study their effects on electrical transport. We found that once defects are introduced, they create resistivity at exactly the rate expected for two-dimensional materials, called the unitary scattering rate (Fig. 1). We have therefore conclusively proven that unusual chemical purity is the the dominant cause for the remarkably long mean free paths in these materials.

In parallel with the investigation of the causes of high conductivity described above, we have explored its consequences. In particular, the long mean free paths in delafossites, combined with advanced microstructuring techniques based on focused ion beam sculpting of single crystals, allowed us to reach

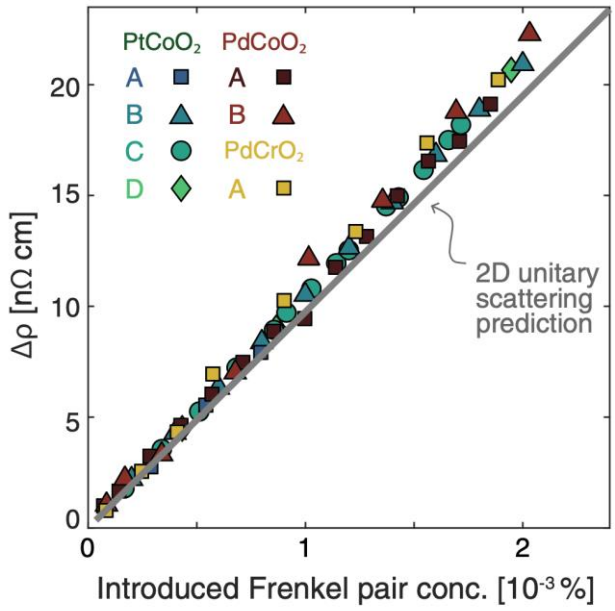

Fig. 1: Resistivity increment of four $PtCoO_2$ samples, two $PdCoO_2$ samples and a $PdCrO_2$ sample as a function of introduced Frenkel pair concentration compared to the unitary scattering prediction.

the limit in which the electronic mean free path is comparable to, or larger than, sample dimensions. This results in a change of transport regime, from the usual Ohmic to 'ballistic', an unconventional regime of non-local electrical transport. Although ballistic effects as such are not novel, they are dominantly studied in semiconducting heterostructures and graphene, primarily because the electronic mean free path in quasi-two-dimensional metals is typically less than 100 nm. The discovery of the long mean free paths in delafossites therefore opens an entirely new field of study of non-local transport in metals, and in particular in metals with faceted hexagonal Fermi surfaces. Exploration of this newly accessible transport regime led to us several exciting discoveries. Firstly, we were able to study the interplay of the point group symmetry of the material with the symmetry of the device made out of the said material. In particular, although the delafossite point group symmetry requires the in-plane transport to be isotropic, we have shown that this need not be the case in the ballistic regime, and that the resistivity can strongly depend on the measurement direction. We call this effect 'directional ballistics.' [8]. We furthermore investigated directional ballistic effects in several 'classical' mesoscopic geometries previously used in studies of low carrier density systems with circular Fermi surfaces, such as the square devices shown in Fig 2. The fact that this experiment was done in a metal allowed us to test whether the Landauer-Büttiker quantum transport formalism, typically used in low-carrier density systems, remains valid at high carrier densities; it does. Furthermore, the directionality of the ballistic effects in delafossites, compared to the isotropic diffusive transport, has proven to provide a sensitive detection method for the presence of ballistic effects. It allowed us to identify ballistic effects in devices as large as ~15 times the mean free path, well beyond the regime in which they would be intuitively expected [9]. Another feature of ballistic transport is that geometric electron-beam optics should be achievable in solid-state devices, and essential elements of electron optics have indeed been demonstrated in translationally invariant systems with circular Fermi surfaces. Achieving such effects in systems of varying Fermi surface shape and anisotropy provides a level of tunability accessible to neither free-space electron optics, nor to solid state devices based on circular Fermi surfaces. Delafossites, with their faceted Fermi surfaces, proved to be an ideal test ground to investigate the influence of the Fermi surface shape on electron trajectories in a magnetic focusing experiment, and again demonstrated how the purity combined with anisotropy can lead to novel transport effects [10].

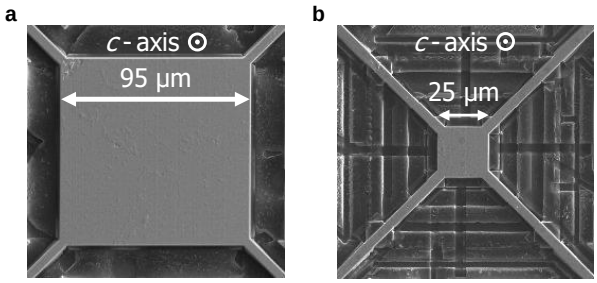

Fig. 2: Scanning electron microscope images, at the same scale, of a $PtCoO_2$ square structured using a focused ion beam (FIB) with (a) side length 95 μm and (b) with the edge size reduced to 25 μm using the FIB.

We pursued the research of the novel effects described above because we understood that the combination of purity and directionality results in a previously unexplored transport regime. Perhaps even more remarkable was a discovery of an effect which was entirely unexpected, but also requires the combination of extreme purity and metallicity. It was revealed in an experiment where electrical resistivity was measured along the direction perpendicular to the two-dimensional layers, while a magnetic field was applied in the layers. The resistivity was found to be periodic as a function of the magnetic field, with a period corresponding to that expected for an integer number

of flux quanta threading a plaquette defined by the whole sample width and the spacing between layers (Fig. 3). Although this phenomenon is reminiscent of the Aharonov-Bohm effect, which would entail the electron travelling along the entire sample width before tunneling to the next layer at the sample edges, this explanation proves to be inconsistent with the experimental observations. Instead, the basic understanding, achieved in a close collaboration between experimental (PQM and the group of Philip Moll) and theoretical (Takashi Oka, Roderich Moessner, Ady Stern) groups, relies on transmitting a coherent electron plane wave between adjacent layers. This observation demonstrates quantum transport of coherent electron waves spanning the width of the entire sample. Remarkably, this essentially quantum effect persists up to temperatures of more than 50K, over lengths longer than 10µm. While the mean free path influences the signal size and the maximum device dimensions in which the effect can be observed, it does not influence the high onset temperature. This puzzling fact motivates further theoretical work [11].

All of the work described so far was done on non-magnetic delafossites, $PdCoO_2$ and $PtCoO_2$. Their sister compound, $PdCrO_2$, hosts conductive Pd layers very similar to those in $PdCoO_2$, but the CrO_2 layer is Mott insulating and antiferromagnetic, in contrast to the band-insulating non-magnetic CoO_2 layer in $PdCoO_2$ and $PtCoO_2$. Repeating the mesoscopic experiments on $PdCrO_2$, and comparing the results to those on $PdCoO_2$, will therefore offer a unique opportunity to isolate the influence of the coupling between highly itinerant and Mott insulating antiferromagnetic layers on non-local transport. In fact, our recent ARPES work on $PdCrO_2$ allowed us to understand that this coupling is Kondo-like, to identify the effective Hamiltonian describing it, and to experimentally constrain the parameters of that Hamiltonian [12]. This level of understanding of the microscopic interactions will be valuable in understanding future unconventional transport experiments.

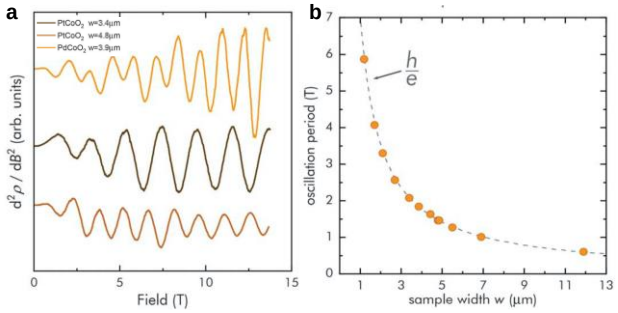

Fig. 3: (a) The second derivative of the resistivity highlights the oscillatory part of the magnetoresistance for three different delafossite samples. (b) The oscillation period is shown for different sample widths. The sample width dependence shows extraordinary agreement with the oscillation period expected for a single-particle magnetic flux quantum, h/e, per area enclosed by the sample width and the spacing between layers.

To summarize, over the last few years we made significant progress in understanding the origins of the long mean free paths in delafossites, as well as in exploring their consequences for unconventional transport. Our work emphasizes the importance of performing careful experiments on high purity materials for discovery and understanding of novel physical phenomena.

External Cooperation Partners

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