Surface and bulk spin structure in delafossite metals

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Although our main motivation for studying layered metals in the delafossite crystal structure was their remarkably high electrical conductivity, they have proved to be a rich playground for the study of surface and bulk spin textures. Here we report on our research to date, stressing the opportunities provided by layer-by-layer variation between nearly free electrons and strongly correlated states, and between different types of magnetism. In particular, our research on the delafossites has revealed a new route to achieving giant Rashba-like spin splittings from states based on transition metal oxide atoms.

One focus of the research in the Physics of Quantum Materials department over recent years has been the properties of delafossite metals of general formula ABO_2, in which triangular co-ordinated A site layers of Pd or Pt are sandwiched between transition metal oxide layers in a stacking sequence named in honour of the crystallographer Gabriel Delafosse. Our interest in these materials was first stimulated by their bulk properties, and specifically their remarkably high electrical conductivity, which sees them have longer mean free paths at room temperature than Ag, Au, Al or Cu, and low temperature mean free paths of tens of microns [1-3]. The huge conductivity results from extremely broad conduction bands based on the 4*d*-5*s* electrons of Pd and the 5*d*-6*s* electrons of Pt, whose character is nearly free electron like. Seen from this perspective, the delafossites might seem unlikely candidates for the study of magnetism, but in reality their properties are controlled by a subtle interplay between this nearly free electron physics and the physics of strong correlations that exists in the transition metal layers. In fact, in an era in which there is so much interest in the construction of layer-by-layer heterostructures to combine metallicity and strong correlations, the delafossites give the opportunity to study essentially perfect heterostructures of this kind in naturally growing crystals.

So far, we have concentrated our studies on $PdCoO_2$, $PtCoO_2$, $PdRhO_2$ and $PdCrO_2$ [1-6]. Of these, only $PdCrO_2$ shows bulk magnetism, as we will discuss below, but we have discovered intriguing surface magnetism in the others, as part of a programme to characterize their electronic structure using angle resolved photoemission spectroscopy (ARPES). In this project, a collaboration with the group of Phil King at the University of St Andrews set up through a joint studentship held by Veronika Sunko, we noticed that photoemission spectra from $PtCoO_2$ depend on which surface is uppermost following the high vacuum cleave that is always performed at the beginning of an ARPES experiment. Especially striking were observations such as those shown in Fig. 1. Thanks to detailed electronic structure calculations we can unambiguously identify the bulk bands of $PtCoO_2$ so it was clear that the broader states seen near the Fermi level in Fig. 1 resulted from surface states, and we established through experimental investigations that slab calculations that they originated from the Co-O layer. Plotted in *k*-space as shown in Fig. 2, the surface states showed concentric, *k*-split shape reminiscent of Rashba-like splitting that occurs in the presence of spin-orbit coupling and inversion symmetry breaking. We verified the existence of Rashba-like spin textures in spin-resolved photoemission experiments, but the surprise was the scale of the split. In previously studied

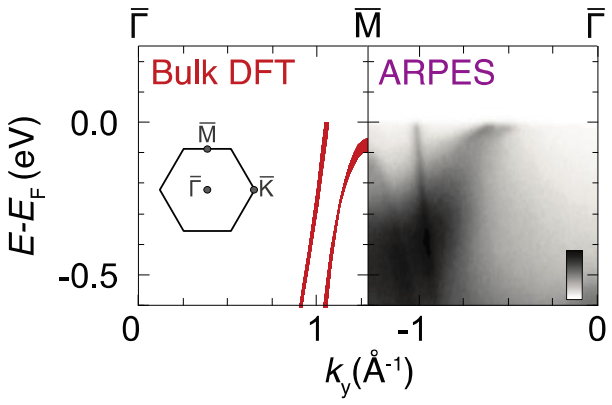

Fig.-1: ARPES spectra from near the Fermi level of $PtCoO_2$ when cleaved such that the terminating plane is that of the Co-O octahedra. The predicted bulk bands are seen as sharp features in this nearly two-dimensional material, but there is further spectral weight at the Fermi level closer to the zone centre. Although this is a surface state and therefore perfectly two-dimensional, it is much broader because it comes from the strongly correlated Co derived states. Very similar spectra are seen in $PdCoO_2$ and $PdRhO_2$ for Co-O and Rh-O surface terminations respectively.

examples of Rashba splitting, large splits were always observed in states based on heavy atoms with giant atomic spin-orbit coupling scales, such that the split observed in the actual bands was a small fraction of the bare atomic scale. The puzzle in our observations was that we believed them to come from Co-based states, and to be split by essentially the entire Co spin-orbit coupling energy.

After puzzling over this for some time, we realized that not just the existence of inversion symmetry breaking and spin-orbit coupling are important; the relative energy scales of the two effects also plays a key role. In most situations in which Rashba splitting is observed, the inversion breaking scale is weaker than the spin-orbit one, and limits the scale of the Rashba split. In the delafossites, the unusual orientation of the Co-O octahedral relative to the cleaved surface means that this might not be the case. By tight-binding electronic structure modeling, we showed that the inversion-breaking scale at a Co-O terminated surface is not only large, but controlled by the Co-O-Co hopping bandwidth. This model not only accounted for the fact that the full Co spin-orbit scale contributes to the Rashba splitting, but also predicted that if Co could be exchanged for Rh, the Rashba split would scale up by the ratio of the Rh/Co spin orbit scales. Single crystals of $PdRhO_2$ large enough for ARPES experiments never been successfully grown, but

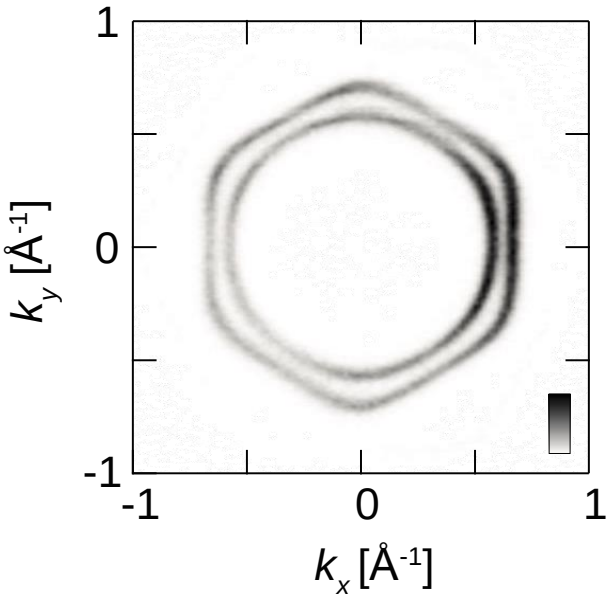

Fig.-2: The Fermi surfaces traced out by the Co-O derived surface states in $PdCoO_2$. Similar observations were made for the Co-O and Rh-O surface states in $PtCoO_2$ and $PdRhO_2$. The observed splitting is accompanied by Rashba-like spin texturing.

Seunghyun Khim succeeded in doing so, helped by advice from chemistry colleagues the Institute. The ARPES experiments were tried, and showed the predicted effect [7]. We believe that this work will prove to have broad significance, because it points to essentially crystal-chemistry routes to engineering the large Rashba splits that will be of importance to the development of electronic technologies based on electron spins (see for example Z.-X. Shen & J. Sobota, *Nature* **549**, 464 (2017), a commentary article on our Sunko et al. paper).

If one of the Pd-based delafossite crystals cleaves with a Pd layer at the surface instead of the transition metal layer, a different form of surface magnetism results. The polar surface charge results in the formation of flat bands whose density of states is large enough that the Stoner criterion for ferromagnetism is fulfilled. Demonstrating that this physics is at play required the combination of detailed measurements with careful surface electronic structure calculations, but we believe that the evidence that we have acquired is convincing [8]. This surface ferromagnetism is of particular interest in $PdCrO_2$, because its Cr-O layers are Mott insulators with antiferromagnetic spin texture. The opportunity to put ferromagnetic surface states in angstrom proximity to antiferromagnetic layers is rare and may also open the way to future exploitation.

The layered bulk magnetism of $PdCrO_2$ is also likely to be of considerable interest in terms of the coupling of the Mott physics that underlies the magnetism with the nearly free electron physics of the bulk Pd-derived states. Coupling between the highly delocalized carriers in one layer with the localized states in the adjacent layer may be expected to lead to hybrid many-body states with dual character. Understanding the formation and consequences of such states will be a feature of our future research on the fascinating and rich physics of the delafossites.

External Cooperation Partners

This work was done in close collaboration with P.D.C. King and F. Mazzola of the University of St Andrews, Scotland, as part of the collaborative programme between the Physics of Quantum Materials Department and St Andrews School of Physics and Astronomy. St Andrews group members L. Bawden, O.J. Clark and J.M. Riley contributed to the ARPES measurements, as did beam line scientists T.K. Kim and M. Hoesch from the Diamond Light Source in the UK and J. Fujii and I. Vobornik from the Elettra synchrotron in Italy.

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