Coulomb-enhanced spin-orbit splitting: The missing piece in the Sr_2RhO_4 puzzle

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Since the discoveries of high-temperature superconductivity and colossal magnetoresistance in Mott insulators made metallic by hole-doping, 3*d* transition metal oxides have remained at the forefront of research. Their many lattice and electronic (orbital, charge, and spin) degrees of freedom are coupled by effective interactions (electron-phonon, hopping, t, Coulomb repulsion, U, and Hunds rule coupling, J), and when some of these are of similar magnitude, competing phases may exist in the region of controllable compositions, fields, and temperatures. The interactions tend to remove low-energy degrees of freedom, e.g., to reduce the metallicity. This rarely happens by merely shifting spectral weight from a quasiparticle band into incoherent Hubbard bands, as in the U/t-driven metal-insulator transition for the single-band Hubbard model, but is usually assisted by lattice distortions which break the degeneracy of low-energy orbitals and split the corresponding quasiparticle – or partly incoherent – bands away from the chemical potential.

When going from 3*d* to 4*d* transition metal oxides, the larger extent of the 4*d* orbitals cause the hopping, t, and the coupling to the lattice to increase, and U and J to decrease. It was therefore hardly surprising that the Fermi surface (FS) of Sr_2RuO_4 measured by various techniques like dHvA and ARPES was in good agreement with LDA calculations, in which strong electronic correlations are only moderately represented. It was, however, surprising that substituting Rh for Ru, e.g. adding one electron and one nuclear charge and roughly keeping the crystal structure, lead to strong disagreement between experiments and LDA theory [1].

In both the ruthenates and the rhodenates the Fermi level crosses the t_{2g} manifold, but in the latter, the interaction between the *xy* and the x^2-y^2 orbitals due to the rotation of the RhO_6 octahedra around the *z*-axes is such as to gap those two bands at the Fermi level. As a consequence, only the equivalent 1D *xz*- and *yz*-bands, which hardly hybridize with the other *d*-bands nor with each other, remain at the Fermi level, with the single t_{2g} hole distributed equally between them. However, also the LDA FS calculated for the proper structure deviates substantially from the experimental FS [1,2]. This discrepancy clearly seen in Fig. 1 (LDA) is disturbing because there is no experimental indication of any further distortion. Hence, Coulomb-enhanced crystal-field splitting can not be the solution to this puzzle.

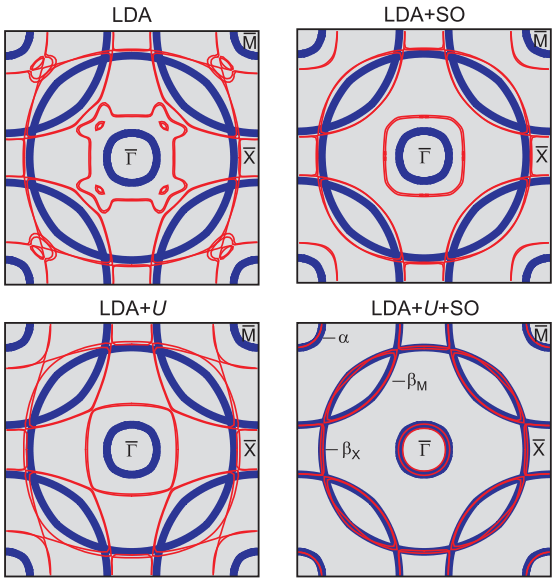

Figure 1: Comparison of Sr_2RhO_4 FS for DFT and ARPES experiment. Blue: ARPES [1,2]. Red: DFT using different approximations.

In order to resolve this puzzle we first fitted the Fermi surface to a tight binding model consisting of the *xz*- and *yz*-orbitals on a 2D square lattice, e.g., neglecting the rotation of the RhO_6 octahedra and the hopping in the *z*-direction [3]. The resulting bands and Fermi surfaces with and without spin-orbit (SO) coupling are shown in Figs. 2 and 3 respectively. The perfect fit was obtained with the parameters in the figure caption.

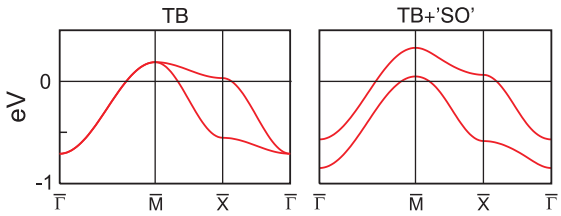

Figure 2: The unfolded 2D tight-binding band structure of Sr_2RhO_4. The tight-binding parameters are $\varepsilon_F = 0.26$ eV, $t_\pi = 0.185$ eV and $t_\delta = 0.039$ eV. The SO coupling constant ζ used in the (TB+′SO′) calculation is 0.28 eV.

We then performed *ab initio* LDA calculations including the SO coupling [3,4] and later also the on-site Coulomb effects in the LDA+U approximation. The results are shown in Fig. 1. As may be seen in Fig. 1 (LDA+SO), the agreement with ARPES is less good for the *ab initio* relativistic LDA FS: the SO splitting along $\overline{\Gamma M}$ is too small. In fact, fitting the LDA+SO FS to our tight-binding model, yields essentially the same values for t_π/ε_F and t_δ/ε_F, but the SO-parameter ζ/ε_F is smaller than $\zeta_{ARPES}/\varepsilon_F$ by the *large factor* of 2.15. The LDA+SO calculation yields: $\zeta = 0.13$ eV, a value which is smaller than the 0.16 eV obtained for elemental fcc Rh due to the O p_z tails of the rhodate Wannier orbitals. The TB results in Figs. 2 and 3 are obtained with $\zeta = 0$.

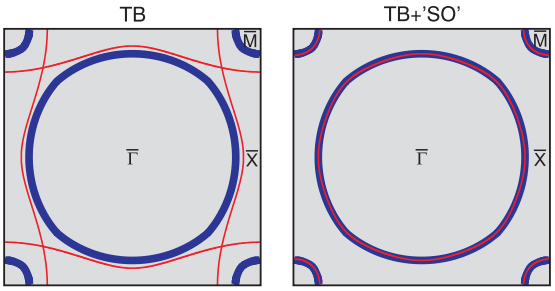

Figure 3: Comparison of the FS for the tight- binding model in the unfolded BZ using the parameters in Fig. 2 with ARPES experiment for Sr_2RhO_4. Blue: ARPES [1,2]. Red: tight-binding.

In order to enhance the SO splitting we performed relativistic LDA+U calculations with $U-J$ adjusted such as to give the best agreement with the ARPES FS. As is obvious from Fig. 1 (LDA+U+SO), this agreement is even more perfect than for TB+′SO′.

The LDA+U+SO bands in Fig. 4 are well reproduced in the range from 0.15 eV below to 0.5 eV above the Fermi level by the TB+′SO′ bands folded into the BZ/2 with corners at $\overline{X}$. Features not reproduced are the tiny splittings due to in-plane *xz*-*xy* hopping and out-of-plane hoppings neglected in our TB model. The agreement between the TB and the LDA calculation is less satisfactory, first of all because without SO-quenching the in-plane *xz*-*xy* hopping produces a splitting along $\overline{\Gamma}\overline{M}$, and secondly because the rotation-induced xy-(x^2-y^2) gapping is not complete without SO coupling. In fact, it takes the LDA+U+SO to push the lower edges of the xy-(x^2-y^2) gap to –0.16 eV along $\overline{\Gamma}\overline{M}$, and even deeper along $\overline{\Gamma}\overline{X}$, locations close to those observed with ARPES [2]. Note finally, that the LDA+U alone, without SO coupling, brings little improvement compared with the LDA.

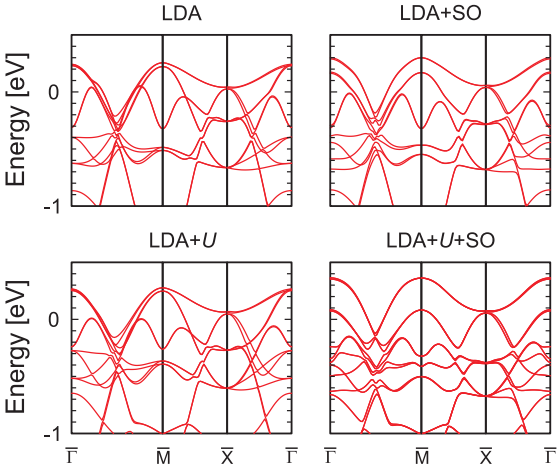

Figure 4: Band structure of Sr_2RhO_4 by DFT using different approximations.

In conclusion, resolution of the Sr_2RhO_4 puzzle has taught us that although usually neglected in 4*d*-oxides, the spin-orbit coupling belongs to the list of competing interactions which cause the rich physics of these materials.

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[2] *Perry, R.S., F. Baumberger, L. Balicas, N. Kikugawa, N.J.C. Ingle, A. Rost, J.F. Mercure, Y. Maeno, Z.X. Shen and A.P. Mackenzie.* New Journal of Physics **8**, 175 (2006).

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