From Copper Oxide to the Mixed Valence Cuprates – a Spectroscopic Journey –

Simon Moser

Advanced Light Source (ALS)
Lawrence Berkeley National Laboratory
Berkeley, California 94720, USA

The two principal oxides of copper – cuprous oxide Cu_2O and cupric oxide CuO – differ widely in their physical and spectroscopic properties (*1*). Cu_2O contains monovalent Cu(I) ions with a completely filled Cu $3d$ shell and is a non-magnetic band insulator, well described by density functional theory (DFT). CuO on the other hand contains divalent Cu(II) ions with an open Cu $3d^9$ shell, and is an antiferromagnetic charge-transfer insulator (*2*). Its lowest energy hole excitations are commonly referred to as Zhang-Rice Singlets (*3, 4*), and are a matter of longstanding debate (*5, 6*).

Coupling a divalent copper Cu(II) system to monovalent Cu(I) through common oxygen ligands adds additional complexity and leads to the emergence of novel electronic phenomena. This is exemplified by our angle resolved photoemission (ARPES) experiments on $LiCu_2O_2$, a mixed-valence compound where one-dimensional edge-sharing chains of $Cu(II)O_4$ are coupled to two-dimensional (2D) square lattices of Cu(I) ions through hybridization with common oxygen atoms (*7*). Even though these individual structural subunits retain their own electronic character, the electronic structure was found to be highly non-trivial, with an experimental bandwidth of the Cu(I)-derived valence band 250 % *broader* than predicted by density functional theory (DFT). This is at odds with two widely accepted tenets of many-body theory, namely that correlation effects are weak in filled bands, and that they generally yield narrower bands and larger electron masses.

Even more intriguing effects are observed in mixed valence systems hosting two-dimensional networks of Cu(II)O. Such a system is embodied in $LiCu_3O_3$, the least studied member in the lithium copper oxide family (*8*). $LiCu_3O_3$ possesses both the 2D Cu(I) square lattice of $LiCu_2O_2$ as well as the 2D CuO planes of the cuprates, but a stochastic distribution of lithium introduces significant disorder. Transport reveals a 2D Coulomb glass behavior induced by this disorder. Yet ARPES still finds Zhang-Rice Singlet quasi-particles dispersing on the Cu(II)O subsystem. $LiCu_3O_3$ thus presents a unique model cuprate where Zhang-Rice Singlets stabilize in a highly disordered mixed valence Coulomb glass.

References

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