Electronic Properties of Cupric and Ferrous Monoxides

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Transition metal monoxides (TMOs), from MnO through NiO, share an uniquely common structural and electronic property. All four compounds possess a cubic rocksalt structure whose edge bonding is between two divalent cations from the 3d row separated by an intervening a divalent oxygen anion, and are experimentally found by transport and optical measurements to be antiferromagnetic insulators. This observation was originally quite mysterious given that single particle electronic formalism based on empirical exchange approximations to Hartree-Fock self-consistent-field theory, today known as density-functional-theory (DFT), an enormously successful framework describing the electronic properties of the majority of insulators, semiconductors and metals, predicted the TMOs to be metals arising from delocalization of the partially filled (5 – 8 electrons) transition metal oxides.

This enigma was resolved with the emergence of the Mott-Hubbard model which took into account on-site coulomb repulsion of simultaneous, Pauli-allowed, opposite spin occupation of a given orbital state which is neglected in the usual DFT formalism. This interaction separated otherwise spin-degenerate orbitals sufficiently far apart to create a charge-transfer gap between bonding and antibonding s-p-d states and an insulating ground state. Today this interaction is accounted for within an "ab initio" formalism known as "LDA+U," local-density-approximation plus an on-site coulomb repulsion Hubbard potential, U. It would be expected that cubic rocksalt cupric monoxide, the uppermost complex in the TMO series, should exhibit similar properties to the rest of the series and, in fact, have a substantially higher Neel temperature than its next lowest neighbor, NiO. Actually, cubic rocksalt CuO has, to date, not been successfully synthesized, and stoichiometric cupric monoxide only exists in the highly asymmetric monoclinic mineral tenorite, which is, indeed, an antiferromagnetic material with four CuO molecules per unit cell, and a Neel temperature about half that of NiO.

We have performed plane-wave pseudopotential (PWPP) LDA+U calculations on surrogate rocksalt cubic CuO in the lattice constant range 3.9 – 4.2 Angstroms and for U up to 10 eV. As expected, we obtain a metallic ground state for U = 0, but quite unexpectedly for all values of U tested as well. These results are not influenced by choice of initial spin distribution when starting the SCF iteration, each round ending with a converged nearly uniform occupation averaging roughly 0.97 per spin state, very suggestive of Cu+, and not Cu2+. There is some indication that extra positive charge is localized on oxygen states which we are investigating further.

On the other hand, on imposing a tetragonal distortion of order c/a ~ 1.4, approximately that observed for 4 ML films grown by forced-epitaxy on strontium ruthenate , we obtain a metallic ground state for U = 0, which is gapped by about 0.4 eV when a U of 5 eV is inserted. Thus, the intrinsic metallic ground state for Cu2+ in highly symmetric coordination appears unstable to the simultaneous imposition of Hubbard coulomb repulsion and uniaxial distortion, reminiscent of the original Jahn-Teller and mixed valency arguments proposed for the origin of high temperature superconductivity.

Recently another class of transition metal compounds, the ferrous oxypnictides, with Group V elements playing the role of oxygen, have been discovered to high temperature superconductors hosted by a doped antiferromagnetic layered structure. Cubic rocksalt ferrous monoxide, the mineral wuestite FeO, may play a proxy role similar to CuO in the attempt to understand superconductivity in these new materials. Although PWPP LDA+U calculations indeed yield an AF ground state for a finite U, this result strongly depends on the particular spin occupation chosen

to launch the SCF calculation, unlike the case for cubic CuO. There are several nearby metastable AF metallic states for U = 5 eV, and we will report our most recent calculations on how these states behave under tetragonal distortion. Fe2+ and Cu2+ can be viewed as electronic duals of each other, the former one electron in excess of a fully occupied Hund's Rule majority spin band, and the latter as one hole less than a fully occupied 3d shell. The occurrence of high temperature superconductivity in each manifold may not just be a fortuitous event.