

Title: "Direct Observation of d-orbital holes and Cu-Cu bonding in Cu₂O"

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Summary: In order to explain the superconductive properties of copper oxides at the atomic level, the authors explored the possibility that some transition metals with intact (full) d orbitals funnel electrons into available s or p orbitals to create a hole in the d orbital. To prove this, they "imaged" a copper d_{z²} orbital of Cu₂O. This orbital, shown with difference mapping, looks amazingly like textbook theoretical drawings.

Discussion: Crystal studies have shown the copper-oxygen lattice of Cu₂O to consist of two interconnected networks (as shown in Figure 1), which would be predicted to repel each other due to the proximity of identically-charged atoms (copper-copper and oxygen-oxygen). The fact that the lattices are stable indicates that an attractive force must be present instead of the expected electrostatic repulsion. The authors predicted that copper does not exist as an ion in the crystal but rather participates in covalent bonding.

The electron configuration of copper is [Ar]3d¹⁰4s¹. Because the d-orbital is filled, its shape is spherical, and the only "available" reactive electron would be the 4s. This however cannot explain the Cu-Cu interaction that must occur in order to have the observed lattice. Other researchers have postulated that one of the d-electrons gets bumped to fill out the 4s level, to give a configuration of [Ar]3d⁹4s². As the d-orbital has 5 degenerate states (d_{xy}, d_{xz}, d_{yz}, d_{x²-y²}, d_{z²}), this would leave an absence, or hole, in one of the orbitals. The paper states that the d_{z²} is only possible d-orbital that could be vacated, due to symmetry constraints.

The reason no one has experimentally seen this before is largely a matter of technique. In theory, x-rays are perfectly elastic and are reflected with coherence (there is a fixed relationship between the phases of the incident wave and the exit wave). Although x-ray crystallography does show the areas of electron density within a crystal, there are often unwanted systematic "extinctions", or absences in the reflection pattern, that cause errors when trying to exactly pinpoint the electron distribution around specific atoms. (This is different than the useful systematic absences that arise from symmetry that are used to deduce the space group). The type of error described in the paper is called "secondary extinction", and arises when, due to mosaic spread in the crystal, surface unit cells reflect more than the deeper ones. This secondary extinction is proportional to $[\sin \theta / \lambda]$ - this is a term that shows up in the temperature factor correction, which is important when assigning anisotropic electron distributions that result from atomic vibrations. The authors got around this problem by supplementing x-ray results with electron diffraction results, which do not have extinction problems. The keys to their success were the importance given to the anharmonicity in the temperature factor for copper, and the improved accuracy of electron position determination due to their methods.

The authors obtained optimal electron densities when they included large *non*-spherical terms in the refinement algorithm. If the copper had been ionic (spherical), the electron difference in the crystal would have been zero. Because it was non-zero, the copper must not be ionic, and therefore must be experiencing covalent effects. This was

not seen for the oxygen atoms, indicating that oxygen does exist as an anion in the crystal.

Comments: I liked this article because it was easy to interpret and the relevance was readily apparent (not only for theoreticians interested in quantum mechanical descriptions of atomic orbitals, but also for experimentalists interested in superconductivity). I would have liked more information on their X-ray and electron diffraction methods, and I wish I knew more about the refinement methods and the assumptions made. I also didn't understand where the energy comes from to kick a d-electron into a higher-energy unoccupied s orbital (I assume the strength of the covalent bond compensates for it).