Direct observation of d holes and Cu-Cu bonding in Cu_2O

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A striking feature of metal oxide chemistry is the unusual behavior of Cu(I) and Ag(1). As a detailed understanding of Cu-O bonding is essential to the, so-far elusive, theory of high T_C copper oxide superconductors, it is of considerable importance that this be understood. Particularly in the case of Cu(I), a linear 2-coordination to oxygen is the usual configuration; even more striking is the observation[1] that in very many compounds the Cu(I) or Ag(I) cations adopt close-packed and related configurations with short metal-metal distances strongly suggestive of the occurrence of metal-metal bonding despite the formal nd^{10} closed-shell configuration. Such observations have been explained[2,3] by suggesting that for these atoms there is significant participation of orbitals of higher principal quantum number, i.e. (n+1)s and (n+1)p, with concomitant creation of d holes on the metal atom. Here we report direct experimental evidence for this hypothesis and for Cu-Cu bonding, using the recently developed[4] method of quantitative convergent-beam electron diffraction (CBED) and X-ray for charge-density mapping. The experimental results are compared with calculations using the full-potential linearized augmented plane-wave (FLAPW) method, using the local density approximation (LDA).

Cu_2O has a cubic structure with no free internal parameters (only Ag_2O is isostructural). The copper atoms are at the points of a f.c.c. lattice with oxygen atoms in tetrahedral sites at (1/4,1/4,1/4) and (3/4,3/4,3/4) of the cubic cell. The resulting arrangement of Cu-O links is made up of two interpenetrating networks (Fig. 1). The simplest description of Cu_2O using an ionic model with closed-shell Cu^+ and O^{2-} ions is known to be inadequate. Not only does it fail to explain the observed linear 2-coordination of Cu but it also is not in accord with the observation that the two sublattices repel each other electrostatically, so that to account for their interpenetration some short range Cu-Cu attractive interaction must be invoked[5]. Note that the

closest approach of atoms of the two networks is a Cu-Cu distance of 3.02 Å — the shortest O-O distances are 3.70 Å.

Considerable progress has been made in mapping the charge density of light-element molecular crystals by x-ray diffraction[6], especially, using a synchrotron source[7]. The extension of this method to inorganic solids of interest to material science is complicated by the well-known X-ray extinction effect, which masks the much smaller bonding effect at low scattering angle, especially for heavy elements[8]. The electron diffraction method used here allows the extinction-free measurement of low-order crystal structure factors, which are most sensitive to valence electrons. Here we combine these with x-ray diffraction results for weak and high-order reflections. Electron diffraction was also used to assess the error due to extinction in x-ray diffraction data, and to replace strongly affected reflections with electron diffraction data. The result clearly shows that ambiguities in previous X-ray studies[9,10] of the charge density of cuprite are due to large extinction effects on the strong low order reflections.

Accurate measurements of the low order structure factors were made with a versatile quantitative CBED technique[4] that we have developed recently. The method takes advantage of the small probe of nanometer dimensions available in our electron microscope. Using this probe, one can almost always find a region of perfect crystal, for which the perfect-crystal theory of dynamical diffraction can be applied. The measurements are made by comparing experimental intensity profiles across CBED disks (rocking curves) with calculations, using a goodness of fit (GOF) criterion, as illustrated in fig. 2. The intensity is calculated using the Bloch wave method, with structure factors, absorption coefficients, the beam direction and thickness treated as refinable parameters. Structure factors for the (531) and higher-order reflections out to (14,4,2) were taken from X-ray measurements[9]. Weak (ooe) (with o for odd and e for even) and very weak (eeo) reflections [except (110)] were also taken from X-ray work.

Direct Fourier transform of experimental structure factors was not useful due to the missing reflections in the collected data set[9], so a multipole refinement[11, 6] was used to map the charge density from the measured structure factors. In the multipole method, the crystal charge density is expanded as a sum of non-spherical pseudo-atomic densities. These consist of a spherical-atom (or ion) charge density obtained from multi-configuration Dirac-Fock (MCDF) calculations[12] with variable orbital occupation factors to allow for charge transfer, and a small non-spherical part in which local symmetry–adapted spherical harmonic functions were used. In addition atomic vibrations were accounted for using the Charlier-Gram expansion[6] for the temperature factor; since the electron and x-ray measurements were done at different temperatures, the combined refinement used the almost linear dependence of temperature factors between 100K and RT[10]. Refinements with and without anharmonic terms in temperature factor clearly show the importance of an anharmonic term for Cu, especially for high order reflections

with $s = \sin\theta / \lambda > 1.0$ (Å^{-1}). In either case the charge transfer from Cu to O refined to 1.01(5) (i.e. Cu^{+} and O^{2-}). The multipole refinement results are listed in table 1.

Compared to previous results[9,10], we obtain much better estimates for the non-spherical distortion of oxygen and Cu. This improvement is due to the absence of extinction effects in our electron diffraction measurements. X-ray diffraction has a particularly strong extinction effect for strong reflections with small s values. For example, for Cu_2O (200), $F^x \approx 78.8$ e/cell, and the measured x-ray SF is about 90% of the actual value, with a difference of ~7.9 e/cell. For this reflection, the difference between the ionic and the neutral-atom models is about 0.07 e/cell. To detect this very small difference, the extinction correction used has to have better than 1% accuracy. By comparison, the electron diffraction measurement has an accuracy of 0.04 e/cell. The electron measurements allow us to evaluate the extinction effect in the x-ray data and exclude those with a large extinction factor.

The large non-spherical contributions in the multipole fitting point to an appropriate description of the charge density in terms of distorted ions, the effect of bonding interactions (other than the electrostatic interaction between spherical ions) can be seen by comparing the measured electron density with that resulting from a model consisting of superposition of spherical ions. Fig. 3a shows a three-dimensional plot of the difference between the static crystal charge density obtained from the multipole fitting to experiment, and superimposed spherical O^{2-} and Cu^{+} ions calculated by the MCDF method. The O^{2-} ion was calculated using a Watson sphere of 1.2 Å radius. Fig. 3b shows a contour map of the difference charge density for the (110) plane. Fig. 3b was synthesized by introducing random noise to the Fourier coefficients for each pixel, to illustrate the uncertainty in the mapped charge density. The noise introduced reflects the uncertainty in the estimated multipole parameters. For comparison, in Fig.3c, we also plot the theoretical difference charge density map obtained from the FLAPW method, using the local density approximation (LDA) for exchange and correlation and the WIEN95 program[13]. This calculation improves upon the previous muffin-tin calculation[14] by using the full potential. For the theoretical map O^{2-} and Cu^{+} ($3d^{10}$) ions were calculated using the same LDA as the FLAPW calculation.

The electron density difference shown in Fig. 3a would be zero everywhere if cuprite were purely ionic (i.e. consisted of spherical ions). The difference, here seen unambiguously for the first time, confirms earlier theoretical speculation[2, 1, 3] that a covalent contribution exists. The correspondence between our *experimental* map and the classical diagrams of d_z^2 orbitals sketched in textbooks is striking. All our difference maps show strong non-spherical charge distortion around the copper atoms, with the characteristic shape of d-orbitals, and excess charge in the interstitial region. There is little variation around oxygen in both the experimental and the theoretical results, which suggests that an O^{2-} anion description is valid. The most significant difference between experiment and theory is around Cu, and the charge in the interstitial region.

The charge modification around Cu in the experiment is broader and larger than the theory. The experimental map also shows a large (~0.2e/Å^3) positive peak in the unoccupied tetrahedral interstitial region of the 4 neighboring Cu atoms, which suggests a strong Cu^+-Cu^+ covalent bonding. For comparison, the Si-Si covalent bond peak is about 0.21 e/Å^3 [15]. We note that these differences between experiment and theory are experimentally significant. In fig. 4, we compare experimental and theoretical structure factors. The experimental SF clearly shows a larger deviation from that of superimposed neutral atoms. The difference between theory and experiment is generally larger than the experimental error.

The non-spherical charge density around Cu^+ can be interpreted as due the hybridization of d electrons with higher-energy unoccupied s and p states, according to [14,2,3]. Among these states, hybridization is only allowed for d_z^2 and 4s by symmetry, and when this happens part of the d_z^2 state becomes unoccupied ("d hole"). These states are responsible for the spatial distribution of the deficiency in the map shown in fig. 3a. The complementary empty states are important for spectroscopies which probe empty states, such as electron energy-loss spectroscopy and X-ray absorption spectroscopy[16]. The experimental studies reveal that the unoccupied states are predominately Cu-d character for the Cu $L_{2,3}$ edge; theory shows that they originate from hybridized d_z^2 orbitals. This theoretical interpretation, based on the calculated partial DOS of the one-electron band structure, is supported by the generally good agreement with experimental spectroscopy of both occupied and unoccupied states[16]. From the characteristic and localized distortion around Cu, we can estimate the population of the outer valence shells from the multipole model coefficients[6,9]. From the data in table 1, we estimate the hybridization coefficient between d_z^2 and 4s, $|x| \sim 0.36$, so that about 0.22 electrons are removed from d_z^2 states. This is in good agreement with the calculated DOS, which gives a similar number for x.

In conclusion, an experimental sub-Å-resolution charge density map of cuprite (Cu_2O) has been mapped to reveal the nature of the occupied valence orbitals. We find direct evidence of d-s hybridization for Cu(I) with production of d holes, and an accumulation of charge between Cu(I) ions associated with Cu-Cu bonding.

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Table 1 : Cu2O multipole model refinement results. In the multipole model, crystal charge density is a sum of aspherical 'atoms'[6]: $\rho^a(\mathbf{r}) = \rho^s(\mathbf{r}) + \sum_{lm} P_{lm\pm} N_{lm\pm} R_l(r) y_{lm\pm}(\theta,\varphi)$.

Here ρ^s is the spherical charge with $\rho^s_{cu} = \rho^s_{Cu^+} + (1-q)(\rho^s_{Cu} - \rho^s_{Cu^+})$ and $\rho^s_O = \rho^s_O + q(\rho^s_{O^{2-}} - \rho^s_O)$ with q as the charge transfer from Cu to O; $R_l(r) = r^{n_l}\exp(-\alpha r)$ (n_3=3; n_4=4) is the radial function with population coefficient $P_{lm\pm}$; $N_{lm\pm}$ is the density-normalization coefficient. Numbers in parentheses are esd's.

O			Cu				q	R
α Å^{-1}	P_{oct}	P_{hex}	α Å^{-1}	P_{20}	P_{40}	P_{43+}	(e)	(%)
2.24 (10)	-1.65 (14)	3.28 (10)	15.7(10)	-0.195 (30)	-0.219 (38)	-0.043 (20)	1.01 (5)	0.71

Figure Captions

Fig. 1. The structure of Cu_2O. Left, as a ball and stick model with O atoms blue, Cu atoms red and bonds green. One network is coloured darker than the other. Notice that there are no bonds joining the two nets. Right, as corner connected OCu_4 tetrahedra. Dark and light tetrahedra are on independent networks. In both sketches, dotted white lines outline a unit cell.

Fig 2. An example of electron diffraction structure factor measurement for Cu_2O (200) and (400); a) experimentally recorded and processed CBED pattern b) best fit for intensities along lines indicated in a. The experiment was performed using the LEO-912 Ω energy-filtering electron microscope with the Gatan liquid nitrogen cooled sample holder. The specimen used is a natural mineral cooled to about 130K. A 15eV energy-filtering slit was placed around the zero-loss peak to remove the contribution from inelastically scattered electrons, which form a background due to plasmon and other loss processes. Off-zone-axis systematic diffraction conditions were used to collect diffraction intensities for reflections up to (400). The CBED patterns were recorded on both a slow-scan CCD camera and on the new Fuji Imaging Plates, which were then processed for the fitting[4]. The refinement was carried out using the EXTAL program[4].

Fig 3. The experimental and theoretical difference maps between the static crystal charge density and superimposed spherical O^{2-} and Cu^{+} ions. A) a 3-D rendering of the experimental difference map from the multipole model fitting with anharmonic temperature factors. The map was made using the T3D program[FS] using a color scheme of blue ($\Delta\rho<0$), white ($\Delta\rho=0$) and red ($\Delta\rho>0$). A translucency factor was used to remove the mostly white background. B) Contour map of the difference charge density for the (110) plane with a contour increment of 0.2 e/Å^3 and colored using the same color scheme for A). The dashed line is for contours with $\Delta\rho \leq 0$. C) The difference charge density map obtained from the FLAPW (LDA) calculations, plotted in the same way as B).

Fig 4. Comparsion between experimental and theoretical structure factors. The structure factor shown is the difference between the crystal and the neutral atoms model.