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Final Comment on the Discussions of "The Case of Cuprite"[**]

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Introduction

During recent years (1) closed-shell interactions, (2) polar covalences, (3) d-shell holes, and (4) direct images of orbitals[1] have been the subject of many investigations. The discussions in the literature had culminated in the "direct observation of d-orbital holes and Cu–Cu bonding in Cu_2O",[2] accompanied by "electrons seen in orbit", in *Nature*.[3] Since this journal declined further discussion of questionable statements, comments had to be published elsewhere (see Refs. [1, 4–6]; see also Refs. [7, 8] and Refs. [6a–h] in [1]). Focussing on topics (1) to (4) listed above, our Essay[1] touched a dozen specific points. About one half of them (concerning the other points, see, for instance: Refs. [4–6]) became the subject of the preceding letter of Zuo et al.,[9] namely:

1) the correct values of the *experimental structure factors* of defectless cuprite (Cu_2O) crystals;
2) the validity of the *derived electron density distributions* around oxygen and around copper, and the existence or nonexistence of a local electronic charge accumulation in the center of the "empty" Cu_4 tetrahedra of the cuprite structure;
3) the *effective partial charges* on O and on Cu; and
4) the *differences* between, and the reliability and accuracy of, the different diffraction experiments and quantum calculations.

The aim of our Essay,[1] and especially of the four respective sections of the present Correspondence, is to formulate some open scientific questions as clearly as possible. Possible answers, and suggestions of how to corroborate them by scientific procedures, shall be given. In the concluding Section 5 we will address the following more general issues: a) What are the forces that hold cuprite together; b) how strongly deformed are the copper and oxygen units in cuprite; and c) how ionic is this transition metal oxide?

1. Experimental Structure Factors

The most accurate experimental structure factors of Cu_2O are, most probably, those from the Arizona (Zuo et al.[2, 9]) and Hamburg groups (Lippmann and Schneider: Refs. [11a, b] in Ref. [1]; and Ref. [10]). The latter works, however, were not considered by Zuo et al. The statement by Zuo et al.[9] that the differences in the published electron density maps are "due to observed differences in low order structure factors" has still to be substantiated. We suggest here once more that the two experimental groups perform a cross-analysis of their multipole refinement procedures for the other group's data sets. So far it is an open question whether, and how much, the experimental structure factors really differ.

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2. Electron Density Distributions Derived Therefrom

The different densities, derived from data obtained by different experimental procedures on different specimens by different mathematical procedures differ, without doubt. The densities were determined by fitting *single* zeta multipole basis functions to the measured structure factors, assuming the vibrating rigid atom model. The single zeta restriction, for instance, can result in unphysical correlations of the calculated "experimental" densities at different positions in the crystal.

1) A most stirring proposition is that of an electron difference density maximum of 0.2 e Å^{-3} in the center of the otherwise *empty Cu$_4$ tetrahedra* (note that $D(\mathrm{Cu}\cdots\mathrm{Cu}) = 3$Å, while the effective radius of Cu$^+$ is 0.5 Å). That is a position of high potential energy,[1] because it is surrounded by six O^{2-} ions at distances of 2.1 and 3.0 Å, where the tails of the oxygen single zeta model functions[2] overlay significantly. We suggest to add a Gaussian function at the center of Cu$_4$ and to refine it in order to generate a less biased "experimental" density at that position. Anyhow there are needed more arguments than just the statement[9] that this density is not an artifact of the applied multipole model. Zuo's reference to Figure 3 of Ref. [9] is not relevant, because the increment of the contour lines is large, namely 0.2 e Å^{-3}, and because this figure just does not show any maximum at the position of the center of Cu$_4$. We reiterate that no "bond density" between the copper ions is needed for van der Waals attraction between them.
2) Concerning the *oxygen region*, there is quite good agreement between the densities of Zuo et al. and our's. We cannot explain why Zuo et al.[9] insist on the respective opposite statement. There is *no* "large surplus electron density around oxygen" in our calculated map (see Figure 4 of Ref. [1]) "which is [also] absent in [Zuo et al.'s][2] experiment and calculations".
3) Concerning *copper*, we find, by density functional theory (DFT), as well as by ab initio MP2 cluster-calculations, just as Zuo et al. do in their experimental and DFT crystal electron density maps (Figure 3 of Ref. [9]), very localized charge accumulations in the not fully occupied 3d shell near the Cu nucleus. Furthermore, we find a belt of weak 3d–4s hybrid density at distances ≥ 1 Å in the equatorial plane around Cu, which is absent in the maps of Zuo et al. (compare Figures 5a, b in Ref. [1]). Note, however, that our two lowest contour lines correspond to 0.025 and 0.05 e Å^{-3}, while Zuo et al.'s lines correspond to 0.2 and 0.4 e Å^{-3}. We suggest to refer to contour lines of comparable order of magnitude when comparing contour maps.

3. Effective Atomic Charges

Despite the inherent basic problems with the definitions of atomic effective charges in compounds,[11] those charges have a meaning to the practicing chemist. The sense of communicating charges is to transfer that chemically useful information. The formulas $\mathrm{A}^{1.0+}\mathrm{B}^{1.0-}$ or $\mathrm{Cu}_2^{1.0+}\mathrm{O}^{2.0-}$ (Zuo et al.[2]) mean to the chemist that these compounds are highly ionic compounds like NaCl or K$_2$O. We, however, find only a polar, partially ionic bond in Cu$_2$O, in addition to some covalent overlap population.[1] We suggest to investigate what the "chemical" meaning of the charge values calculated by Zuo et al.[2] might be.

4. Agreement and Differences

4.1. Experiments

One of the problems with density determinations, mentioned by Zuo et al.[9], is the zero-point and thermal motion of the atoms in the crystal. One tries to eliminate this motion by different recipes in the experimental and theoretical static density maps. Ample experiences, with experimental X-ray scattering[12] as well as with theoretical investigations (for example, Ref. [13]), demonstrate that liquid nitrogen temperatures, not to speak of room temperatures, often principally rule out the extraction of the more subtle details of the bond densities from X-ray or from electron-scattering experiments or from vibrationally smeared calculations. When discussing bond densities, low-temperature experiments are recommended ("He temperatures" of the order of 10 to 20 K). In addition we suggest to the experimentalists to include higher order anharmonic terms in the atomic Debye–Waller factors of the multipole refinement.

4.2. Calculations

In principle there are also specific problems with the quantum chemical calculations. Zuo et al. note problems of DFT with open-shell transition metal systems. They mention that the Cu units carry a fractional hole in the 3d shell and interpret this as an intermediate state of Cu in cuprite between Cu$^+$ and Cu^{2+}. This is faulty, the "3d shell" of Cu is closed, but polarized, that is, 3d–4sp hybridized. Zuo also mentions possible differences between a crystal and a cluster embedded in the crystal field. However, Zuo et al.'s[2, 9] self consistent field (SCF) DFT calculations of the crystal, our SCF-DFT calculation of an embedded cluster, and our respective non-DFT ab initio correlated MP2 calculation, all agree very well; they are, for instance, within only 0.02 e Å^{-3} (!) at the saddle point of the difference density in the center of the heavily discussed Cu$_4$ units. The same density value, within this small error range, was experimentally found by the Lippmann and Schneider group.[10] Only Zuo et al.'s "experimental" map[2] shows really more electron density (0.2 instead of 0.05 e Å^{-3} difference density) in this very region.

5. Conclusions

The Madelung energy of a point charge lattice of cuprite is weakly repulsive in the sense of $[\mathrm{Cu}_4\mathrm{O}_2] \rightarrow 2\,[\mathrm{Cu}_2\mathrm{O}]$.[14] The multipole interaction contributions, the polarization contributions, and the dispersion contributions to the energy seem sufficient to explain the stability.[1] Experimental and theoretical investigations on Cu–O cluster molecules and similar systems (see, for example, Refs. [15, 16]) are consistent with our picture of cuprite. The isolated evidence[2] of a localized charge accumulation at a high potential energy saddle point[1] in the middle between Cu^+ ions at 3 Å distance, interpreted as covalent Cu^+–Cu^+ bonding, is so unexpected and unusual that it deserves further investigation and checking. Above we have given some suggestions.

There *is* astonishingly good agreement between different experiments and different calculations concerning the following points: (1) the oxygen anions are only weakly deformed, and (2) the copper cations are closed-shell subunits with a deficit of 3d population along the O–Cu–O z axis and in the xy plane (mainly due to d–s hybridization, which leads to slight density increase in the xy plane at larger distances), and localized deformation density maxima between those d–s orbital holes (density minima) near the Cu nucleus. This density difference looks topologically similar to an f atomic orbital. Furthermore it is to be stressed that the Cu–O covalent interaction corresponds to electron deficit on the bond line, with respect to Cu^+ and O^{2-}.

There exists disagreement concerning the following points: (1) the electron density inside the "empty" Cu_4 tetrahedra—most investigations show very little density; and (2) how strongly ionic Cu_2O is—we find covalent back-donation of electronic charge from oxygen, which is only a formally charged O^{2-}, into the (only partially positively charged) copper 4sp shell.

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