Über die Wechselwirkung zwischen abgeschlossenen Schalen, polare Kovalenz, Löcher in d-Schalen und die direkte Abbildung von Orbitalen: der Fall Cuprit

Response to the Essay by S. G. Wang and W. H. E. Schwarz

J. M. Zuo,* M. O'Keeffe, M. Kim, and J. C. H. Spence

In their critical Essay on the charge distribution in cuprite,[1] Wang and Schwarz concluded that there is no proof of significant Cu^{+}–Cu^{+} closed shell binding and disagreed with our interpretation of the nature of the Cu^{I}–O bonds. These conclusions are drawn from their approximate theoretical calculations and their purported agreement with the previous X-ray measurements, rather than from a careful reexamination of the experimental and theoretical evidence presented in our original report.[2]

Much of the criticism of Wang and Schwarz is directed to statements made in the interpretation of our report.[1] By quoting sentences which were not in the original text and commenting on them together with our original report, the authors confuse the scientific content of our original report with media chatter for which we can not be held responsible. Putting these aspects aside, there are two main points worthy of serious discussion. Before we look into these in detail, it is helpful to recall the basic approximations in all electronic structure calculations: 1) the use of an approximate treatment for the exchange and correlation energy,[3] and 2) the assumption of a static crystal that ignores the thermal motion of atoms. The limitation of the first approximation is well-known, a highly relevant example is its failure in predicting the correct antiferromagnetic ground states of Cu-based high-temperature superconductors.[4] In addition to these two approximations, the calculations of Wang and Schwarz used a 25-atom cluster to approximate the three-dimensional infinite crystal.

[*] Prof. J. M. Zuo,[+] M. Kim, J. C. H. Spence
Department of Physics and Astronomy
Arizona State University
Tempe, AZ 85287 (USA)
E-mail: jianzuo@uiuc.edu
M. O'Keeffe
Department of Chemistry
Arizona State University
Tempe, AZ 85287 (USA)
[+] Present address:
Department of Materials Science and Engineering
University of Illinois at Urbana-Champaign
1304 West Green Street, Urbana, IL 61801 (USA)
Fax: (+1) 217-333-2736

Most crystals contain defects. The treatment of X-ray diffraction in a real crystal with defects is based on the mosaic model, first introduced by Darwin in 1922.[5] In this model, an ideal imperfect crystal is defined as one comprised of very small mosaic blocks with slightly different orientations. This is opposite to the ideal perfect crystal free of defects. Real crystals are often in between the ideally perfect and ideally imperfect models, and the measured X-ray integrated intensity is often less than predicted by the theory for ideally imperfect crystals (extinction) but larger than predicted by the theory for an ideal perfect crystal. An improved treatment of real crystals introduces a statistical distribution for the mosaic block orientations and also the size of mosaic blocks, and derives a formula for the averaged integrated intensities of diffracted beams.[6, 7] The accuracy of such an averaged treatment ultimately depends on the defect distribution in the crystal, and is fundamentally limited in accuracy by the statistical fluctuations in the distribution of defects and by the oversimplification of the complex strain field introduced by defects with mosaic blocks.

By comparison, our electron diffraction measurements use the convergent beam electron diffraction (CBED) technique with a focused probe a few nanometers in diameter on a crystal of thickness from 100 to 200 nanometers. The crystal under the probe is selected free from defects by using electron imaging. Thus, electron diffraction within the probed volume can be described by the perfect crystal theory. The refinement procedure that we used for measuring electron structure factors compares experimental intensities with the Bloch wave theory of electron diffraction which takes the full account of primary extinction (multiple scattering) and absorption.[8] As a result, the measured electron structure factors are free from extinction and absorption, and can be used directly in charge density analysis without corrections. It also allows us to assess the errors due to extinction in conventional X-ray data. The method has proved its accuracy, as demonstrated, for example, in Ref. [9].

Figure 1 shows the ratio R ($R = F_x/F_{fit}$) of as-measured X-ray data by Restori and Schwarzenbach[10] and the structure factors obtained from our best multipole model fit as a

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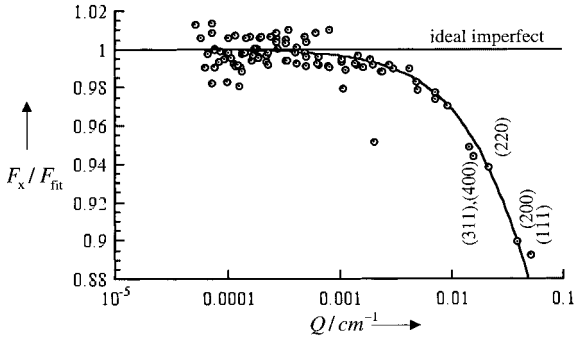

Figure 1. The ratio of as-measured X-ray data (F_x)[10] and the structure factors obtained from our best multipole model fit (F_{fit}) as a function of the scattering strength Q. The curved solid line is the best fit using the Zachariasen extinction model. The standard deviation from Zachariasen's model is about 0.8%, which is generally larger than the measurement error. The error comes from the random distribution of crystalline defects and the limitation of an averaging model such as Zachariasen's model, and it is the main source of error in charge densities determined by X-ray.

function of Q [Eq. (1)]. For ideal imperfect crystals, the ratio should be a constant one. For strong low order reflections with a large Q, the ratios are much lower than one, as we expected from the extinction effect. Using the Zachariasen's two-beam

$$Q = \left|\frac{e^2 F}{m_e c^2 V}\right|^2 \frac{\lambda^3}{\sin 2\theta} \qquad (1)$$

model for correcting extinction effects, we have obtained a best fit to extinction with this data. For strong reflections with $Q > 0.001$, we estimated the standard deviation of R from Zachariasen's model to be about 0.008 and the associated error in the structure factor of strong reflections to be $0.008*F(h,k,l)/R$. This amounts to about 1% for the (111) and (200) reflections. The error is larger than the measurement error, which is about 0.4%. In comparison, the error in the extinction-free electron diffraction measurements is less than 0.3% for the same reflections.

The error due to extinction significantly reduces the amount of information about the charge distribution that we can obtain from the measured X-ray data. Figure 2a and b plot the contributions to the total structure factor from each term in the multipole model for O and Cu, respectively. For O, contributions significantly above the experimental error are limited to three reflections: (110), (111), and (200). Individually, the charge transfer term dominates (110) and the octopole of charge deformation only affects (111). For Cu, the charge transfer term is too small to be detected. Conversely, the effect of the nonspherical modulation of Cu extends to many reflections over a wide scattering angle, with the largest contribution from the quadrupole ($l = 2$, $m = 0$). As a result, the determination of charge transfer and bond charge distribution depends critically on the first three low-order reflections. Among these, both the (111) and (200) are strong and have large extinction errors in the X-ray measurement. The estimated X-ray structure factor errors for the (111) and (200) reflections are approximately twice the expected changes from bonding. This is the reason for the observed extreme model dependence of the charge transfer and the

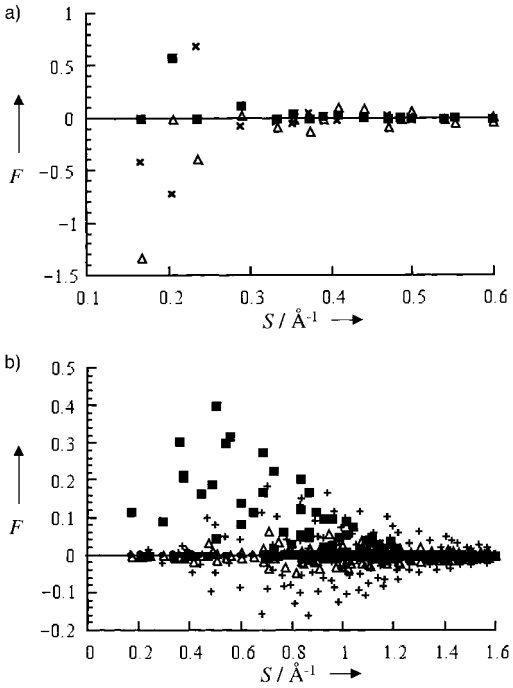

Figure 2. Contributions to the total structure factor (in units of e/cell) from each term in the multipole model for: a) oxygen with charge (triangles), octopole charge transfer (black squares), and hexapole charge transfer (crosses); and b) copper for each of three nonspherical terms with $(lm) = \{20, 40, 43\}$ (represented as black squares, crosses, and triangles, respectively). The charge transfer term (black circles) is significant only for oxygen.

oxygen charge deformation in the previous X-ray refinements.[10, 11]

The definition of partial charges of ions in crystals, while it is often found to be useful as a simple number in chemistry, is problematic in practice. Fundamentally, it is impossible to define a unique partial charge based on a single charge density measurement or calculation.[12] The partial charges obtained by different definitions often differ significantly in scale (sometimes by a factor of 10, according to Ref. [13]). In their calculations, Wang and Schwarz used the wave function based Mulliken partial charges, which give $Cu^{0.5+}O^{1-}$. Our definition of charge transfer is based on the multipole model for the experimental deformation density, from which we obtain $Cu^{1+}O^{2-}$. When we apply the same multipole model to the theoretical charge density calculated with the full potential linearized augmented plane wave (LAPW) method which uses the same density functional theory (DFT) approximation, we obtain $q = 0.9$, which compares favorably with our "experimental" value of 1.0. Given the widely different definitions for the partial charges used, the disagreement between the Mulliken charges of Wang and Schwarz and our multipole model charge transfer is not surprising. What is surprising is the purported agreement between previous experiments and the calculation of Wang and Schwarz. In fact, the charge transfer term in the quoted refinement of Restori and Schwarzenbach depends so much on the model and the treatment of experimental data, it was deemed experimentally meaningless by the original authors.[10] The synchrotron measurement[11] improves upon the data set of

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Restori and Schwarzenbach by an additional measurement of 21 very weak reflections, which are dominated by the anisotropic thermal vibration of Cu, and thus does not fundamentally alter the conclusions reached by Restori and Schwarzenbach. Their reported difference charge density map (Figure 8a of ref. [11]) differs from theoretical calculations in basic features around Cu.

Our experimental map shows a significant amount of charge between Cu^+ ions. This is due to the observed differences in low-order structure factors between experiment and theory, not because of the model deficiency as suggested by Wang and Schwarz. We have applied the same charge density reconstruction procedure to the theoretical map we obtained from LAPW calculations to test the flexibility of our model and check for possible systematic errors. Figure 3 shows the reconstructed theoretical map using the same set of reflections as the experiment. Compared to the original theoretical map, the model recovers most of the features.

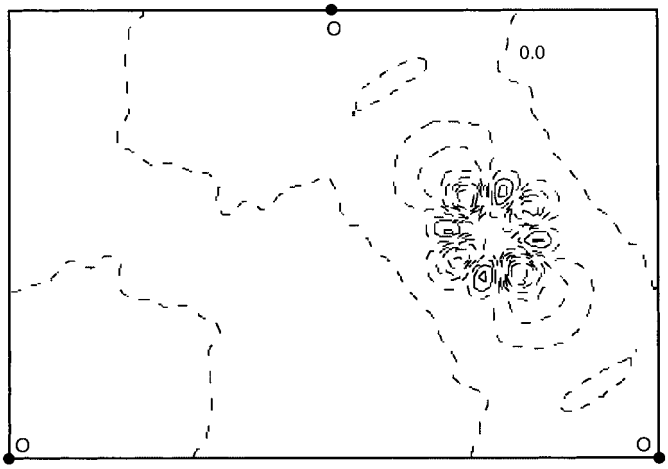

Figure 3. Theoretical difference map in a (110) plane with a contour increment of 0.2 e Å^{-3} obtained by fitting the same multipole model used in our experiment to the theoretical structure factors obtained from the LAPW calculation. This map recovers most features of the original theoretical map and demonstrates the flexibility of the model for charge density analysis.

The calculation of Wang and Schwarz differs significantly from our LAPW calculations and our experimental map in the oxygen charge distribution. Their difference map (Figure 4 in ref. [1]) between the crystal charge density and the superimposed spherical Cu^+ and O^{2-} ions shows a large surplus electron density around oxygen, which is absent in our experiment and the LAPW calculations.[2, 14] The calculation of Wang and Schwarz also differs significantly from our LAPW calculations regarding the charge distribution between Cu ions. The LAPW calculations show a broad surplus charge distribution of 0.17 e Å^{-3} near Cu slowly reducing to about 0.06 e Å^{-3} at the center of the empty tetrahedral site, this is in contrary to the saddle of 0.045 e Å^{-3} estimated by Wang and Schwarz for this region.

It is also important to recall that the reference atoms used in the difference map, that is, the charges of spherical O^{2-} and Cu^+ ions, are different in theory and in the experiment. The experimental map uses the atomic charge density obtained by multiconfigurational Dirac–Fock calculations. Our theoretical map uses the atomic charge density calculated with the same DFT approximations used in the LAPW calculations. The references used by Wang and Schwarz are presumably different too.

We wish also to comment on the question of whether the Cu–Cu distance precludes any bonding in cuprite as suggested by Wang and Schwarz. It has been known for many years that bond lengths vary significantly with bond strength, and chemists often use the interatomic distance as a guide to the strength of a bond. Many years ago Pauling suggested[17] an exponential dependence of bond strength or valence (v) on length (d): $d = R + b \ln v$ where R is the single bond length ($v = 1$). It follows that for a given pair of atoms, the difference in bond length for a difference in bond valence is as shown in Equation (2). Brown and Altermatt[18] proposed that $b =$ 0.37 Å could be taken as a universal parameter, and it was subsequently shown[19] that this applied to a wide range of materials including covalent molecules, ionic crystals, and metals.

$$d_1\text{-}d_2 = b \ln\left(\frac{v_1}{v_2}\right) \qquad (2)$$

It is well documented[20] that in the case of compounds of metals, one cannot always use metal–metal distances as diagnostic of bonding; but the question at hand is whether the Cu–Cu distance (3.02 Å) in Cu_2O precludes significant bonding. Our benchmark is elemental copper which has the same Cu atom arrangement, and in which the Cu–Cu distance is 2.55 Å. Equation (2) shows that this difference in interatomic distance would correspond to $(v_1/v_2) = 0.28$; so that if the Cu–Cu distance in Cu_2O were determined just by Cu–Cu bonding, there would be very considerable bonding. Actually the Cu–Cu distance in that material is determined very largely by the Cu–O bond length, but the important conclusion remains that the Cu–Cu distance does not preclude significant Cu–Cu bonding.

In questioning experiments based on the findings of approximate theoretical calculations, Wang and Schwarz raise an interesting question about the relative accuracy of experimental and theoretical charge densities. In the case of silicon, where both accurate experimental and theoretical structure factors are available, we have shown that the difference between experiment and theory is due to the approximate treatment of core electrons in the density functional approximation.[21] Theoretically, the remarkable agreement between experiment and the DFT-based calculations reported in our paper is due to the nearly closed-shell configuration of Cu^+ ions. In the case of Cu^{2+} with an open-shell configuration, the current DFT approximations are known to be insufficient due to the neglect of strong electron–electron interactions. In cuprite, both experiment and theory reveal that a d hole exists and that the Cu configuration is in between Cu^+ and Cu^{2+}. Thus, it is an open question as to how well current theories agree with the experiment. Understanding this will go a long way toward our understanding of high-temperature superconductivity.

In conclusion, we would like to emphasize that our results were built upon the accumulated experience of past decades

about experimental measurements of charge density.[15, 16] Significant results about charge states and bonding in various crystals have been obtained by X-ray diffraction, especially, for organic crystals with light elements where the proportion of bonding electrons is much higher and thus much easier to measure. For inorganic crystals with a relatively small unit cell, experimental measurement of charge density requires very great accuracy for the few low order reflections that contain critical bonding information. This is where electron diffraction can play an important role.

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Abschließender Kommentar zur Diskussion um den „Fall Cuprit“**

Shu Guang Wang und W. H. Eugen Schwarz*

Einleitung

In der jüngeren Vergangenheit sind 1) Wechselwirkungen zwischen abgeschlossenen Schalen, 2) polare Kovalenzen, 3) Löcher in d-Schalen und 4) die direkte Abbildung von Orbitalen[1] Gegenstand intensiver Untersuchungen gewesen. Die Diskussionen erreichten ihren Höhepunkt mit der „direkten Beobachtung von d-Orbital-Löchern und einer Cu-Cu-Bindung in Cu_2O“[2] und dem „Sehen von Elektronen auf ihren Bahnen“ in *Nature*[3]. Da dort keine weiteren Diskussionen über diskussionswürdige Aussagen erwünscht waren, mussten Kommentare anderenorts erscheinen[1, 4–6] (siehe auch Lit. [7, 8] und insbesondere die Zitate [6a–h] in Lit. [1]). In unserem Essay[1] hatten wir uns auf die oben genannten vier Themenkreise konzentriert und über ein Dutzend Punkte berührt. Auf etwa die Hälfte von ihnen gehen Zuo et al. in ihrem vorstehend abgedruckten Brief[9] ein (bezüglich der anderen Punkte siehe etwa Lit. [4–6]), darunter die folgenden:

1) die korrekten Werte der *experimentellen Strukturfaktoren* von idealen Cuprit(Cu_2O)-Kristallen;
2) die Zuverlässigkeit der daraus *abgeleiteten Elektronendichteverteilungen* im Bereich des Sauerstoffatoms wie in dem der Kupferatome sowie die Existenz oder Nichtexistenz einer lokalen Elektronendichteansammlung im Zentrum der ansonsten „leeren“ Cu_4-Tetraeder der Cuprit-Struktur;
3) die *effektiven Ladungen* der O- und Cu-Atome;
4) die Genauigkeiten und Diskrepanzen zwischen den diversen Beugungs- und quantenmechanischen Daten.

Der Zweck unseres Essays[1] und insbesondere der vier diesbezüglichen Abschnitte dieser Korrespondenz ist es, die offenen wissenschaftlichen Detailfragen so klar wie möglich zu formulieren. Mögliche Antworten sowie Vorschläge, sie auf wissenschaftliche Art zu stützen, werden ebenfalls gegeben. Im abschließenden Abschnitt 5 sollen folgende allgemeinere Probleme angesprochen werden: a) Welche Kräfte halten Cuprit zusammen; b) wie stark deformiert sind die Kupfer- und Sauerstoff-Einheiten in Cuprit; c) wie ionisch ist dieses Übergangsmetalloxid.

1. Die experimentellen Strukturfaktoren

Die verlässlichsten experimentellen Strukturfaktoren für Cu_2O stammen höchstwahrscheinlich aus Arizona (Zuo et al.[2, 9]) und Hamburg (Lippmann und Schneider[10] sowie Zitate [11a, b] in Lit. [1]). Letztere Arbeiten wurden allerdings von Zuo et al. nicht berücksichtigt. Deren Aussage,[9] die Unterschiede in den publizierten Elektronendichtekarten beruhten auf Unterschieden in den Strukturfaktoren niedri-

[*] Prof. Dr. W. H. E. Schwarz, Prof. Dr. S. G. Wang[+]
Theoretische Chemie der Universität Siegen
57068 Siegen (Deutschland)
Fax: (49) 271-740-2851
E-mail: schwarz@chemie.uni-siegen.de
[+] Heimatadresse: School of Chemistry, Jiao Tong University Shanghai (China)

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