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Charge distribution and chemical bonding in Cu_2O

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We have applied the augmented plane-wave plus local-orbitals method to investigate the charge density of Cu_2O by means of Bader's topological analysis and electric-field gradients (EFGs). It is rather clear that a simple Cu^+-O^{2-} model is inadequate for the explanation of bonding properties of Cu_2O. Appearance of s-d hybridization in this system has been pointed out already in the literature. However, the amount of charge transferred from d to s Cu orbitals is overestimated by both the local-density approximation (LDA) and the generalized gradient approximation. As a result, the calculated EFG is underestimated by about 50% compared to experiment. Also the topological analysis of calculated densities suggests that density-functional theory overestimates the covalency of the Cu-O bond. In order to demonstrate the role of s-d hybridization as the main reason for the mentioned discrepancies, we have utilized artificially modified basis sets. Removing part of the $4s$ Cu character from the wave function increases the absolute EFGs and decreases the calculated bulk modulus, both resulting in better agreement with experiment. This is a result of an increased Cu d occupation and consequently a decreased asphericity of the d charge distribution. A more physical description of the localized nature of the $3d$ orbitals should be given by the LDA$+U$ correction. We find that LDA$+U$ "self-interaction corrected" (SIC) by Anisimov *et al.* [V.I. Anisimov, I.V. Solovyev, M.A. Korotin, M.T. Czyżyk, and G.A. Sawatzky, Phys. Rev. B **48**, 16 929 (1993)] leads to EFGs in good agreement with experiment while LDA$+U$ "around mean field" Cyżyk and Sawatzky [Phys. Rev. B **49**, 14 211 (1994)] even worsens the results. This is to be expected according to the analysis given above, which indicates that the on-site correlations are important but are implemented only in the LDA$+U$ (SIC) method.

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I. INTRODUCTION

A detailed understanding of Cu-O bonding is essential for explaining copper oxide high-temperature superconductors or even, more generally, the properties of transition-metal compounds. The compound cuprite Cu_2O, has a simple structure and thus is almost ideally suited for this task. Cu_2O has a simple cubic structure with space group $Pn\overline{3}m$ and its unit cell contains six atoms. The four copper atoms are at the positions of a face-centered-cubic (fcc) sublattice, and the two oxygens are in tetrahedral sites at positions (1/4, 1/4, 1/4) and (3/4, 3/4, 3/4) forming a body-centered-cubic sublattice. As a result the structure contains oxygen atoms fourfold coordinated by copper atoms whereas Cu is linearly coordinated by two oxygens, a rare occurrence. Alternatively the structure can be described as an arrangement of Cu-O links composing two interpenetrating networks.

A simple closed-shell model of the interaction between Cu^+ and O^{2-} is inadequate in this case. First, it cannot explain the linear coordination of Cu by O. Second, the two interpenetrating networks would repel each other due to small Cu^+-Cu^+ and O^{2-}-O^{2-} distances and the structure would be unstable. The need for attractive interactions to stabilize the network could suggest copper-copper bonding, despite their formal $3d^{10}$ configuration.[3] Such a bond can be understood as a result of hybridization of the $3d$ states with the $4s$ or $4p$ states.[4] This hybridization depletes the d shell and consequently leads to an asphericity of the d charge distribution.

A lot of theoretical work has been devoted to the study of Cu_2O properties, beginning with early Hartree-Fock studies by Kleinman and Mednick,[5] the non-self-consistent augmented plane-wave (APW) calculations by Dahl and Switendick,[6] and Robertson's tight-binding approach.[7] Marksteiner, Blaha, and Schwarz performed[8] linearized augmented plane-wave (LAPW) calculations within the muffin-tin (MT) approximation, mainly discussing bonding. Ching, Xu, and Wong[9] reported studies by means of the orthogonalized linear combination of atomic orbitals method, focusing on ground-state and optical properties. In a recent paper Ruiz *et al.*[10] performed electronic structure calculations using the Hartree-Fock method including the interaction energy of the two interpenetrating frameworks.

Recently, Zuo *et al.*[11] published results of combined electron-diffraction and x-ray data and reported the existence of a local maximum in the difference charge density (i.e., the difference between the crystalline density and a superposition of Cu^+ and O^{2-} densities) at the empty Cu_4 tetrahedral site. This paper was highly questioned in the charge-density community. For a critical analysis of the chemical bonding see, e.g., Wang and Schwarz.[12] The existence of this maximum is, for example, in contradiction to Lippman and Schneider's results,[13,14] who have published a charge density that was refined from high-energy synchrotron data. They provided a topological analysis, which gives us the possibility to compare their data with our calculations.

Our main goal is to report an augmented plane-wave plus local-orbitals (APW+lo) calculation of the Cu_2O charge density, which shall be characterized by Bader's topological analysis and electric-field gradients (EFGs). The calculated values of the Cu EFGs, both by local-density approximation (LDA) or generalized gradient approximation (GGA), turns out to be about 50% smaller than the experimental values.[15]

Thus the situation is very similar to the high-T_c superconductors,[16] where such a small EFG is also found, namely, for Cu(2) in the CuO_2 plane. An analysis of the contributions to the EFG originating from different *l* characters of the wave functions allows us to draw some conclusions concerning the asphericity of the *d* charge distribution and the origin of this failure. We will show that it is mainly due to an improper description of the *s*-*d* hybridization by density-functional theory. The role of *s*-*d* hybridization in the bonding properties of Cu_2O is investigated utilizing modified basis sets, which restrict the Cu 4*s* admixture. We show that this modification improves the calculated EFGs and the charge density.

Since electron correlation effects seem to be important for the electronic properties of Cu_2O we focus our attention on comparing results produced by the LDA, the GGA, and two different Hubbard *U* corrections to the LDA functional (LDA+*U*) proposed by Cyżyk and Sawatzky[2] and Anisimov *et al.*[1] The LDA+*U* corrections have already been applied to many electronic structure calculations of transition-metal compounds.[17] These LDA+*U* calculations are known to improve LDA results for magnetic[18] but also nonmagnetic[19] systems in cases where the standard LDA is not sufficient.

II. METHODOLOGY

The calculations reported in this work were performed using the WIEN2K package,[20] which is an implementation of the density-functional[21] APW+lo method. The APW+lo method expands the Kohn-Sham orbitals[22] in atomiclike orbitals inside the atomic (MT) spheres and plane waves in the interstitial region. The details of the method have been described in the literature.[23–27] The basis set inside each MT sphere is split into core and valence subsets. For oxygen only 1*s*, and for Cu 1*s*, 2*s*, and 2*p*, are in the core subset. The core states are treated within the spherical part of the potential only and are assumed to have a spherically symmetric charge density totally confined inside the muffin-tin spheres. Sphere radii of 1.8 and 1.55 bohr were used for copper and oxygen, respectively. The valence part is treated within a potential expanded into spherical harmonics up to $l=4$. The valence wave functions inside the spheres are expanded up to $l=10$. Since Bader's topological analysis needs a smooth charge density ρ across the atomic sphere boundary, an expansion of ρ up to $l=10$ turns out to be necessary. In all cases we use an APW+lo-type basis[24] with additional local orbitals (LOs) for the Cu 3*s* and 3*p* semicore states. The linearization energies for these LOs were set at the center of the Cu 3*s* and 3*p* bands. A plane-wave expansion with $R_{MT}\,K_{MAX}$ equal to 7, and *k* sampling with a $5\times5\times5$ *k*-points mesh in the full Brillouin zone turns out to be satisfactory.

The calculations have been performed utilizing the LDA in the form given by Perdew and Wang[28] and the GGA with the potential by Perdew, Burke, and Ernzerhof.[29] Electron correlation effects are important for the electronic structure of transition-metal compounds, thus we also tested two LDA+*U* corrections. LDA+*U* is a method going beyond the LDA by special treatment of a chosen set of states, which in our case are the 3*d* states of Cu. The corrected density functional can be written as

$$F^{LDA+U}=F^{LDA}+E^{ee}(\hat{n})-F^{dc}(\hat{n}),$$

where F^{LDA} is the standard LDA functional, $\hat{n}$ is the occupation number matrix, E^{ee} is the electron-electron interaction among 3*d* orbitals in Cu in accordance with a multiband Hubbard model,[30,31] and F^{dc} is the so-called double-counting term. In the original scheme of Anisimov *et al.*[32] F^{dc} was chosen to reduce F^{LDA+U} to F^{LDA} in the case of equal occupation of all *d* orbitals. For a nonmagnetic case this scheme is equivalent to the model introduced later by Czyżyk and Sawatzky[2] [in the literature, referred to as an "around mean field" (AMF) correction]. A slightly different form of the correction has been introduced by Anisimov *et al.*[1] The double-counting term has been chosen to ensure an atomiclike limit of the LDA, which approximately removes the electron self-interaction, hence it is usually referred to as the self-interaction corrected (SIC) LDA+*U* method. This latter scheme is usually more appropriate for fully localized electrons while the former might be better for weakly correlated systems. The difference between AMF and SIC models can be easily seen if one considers only the diagonal elements of the density matrix and neglects the exchange interaction. The orbital-dependent corrections to the LDA potential have then the following form:

$$\Delta V^{AMF}=U(\langle n_{\sigma}\rangle-n_{m,\sigma}), \tag{1}$$

$$\Delta V^{SIC}=U\left(\frac{1}{2}-n_{m,\sigma}\right). \tag{2}$$

Assuming a positive *U*, the AMF correction to the potential is attractive for orbitals occupied with more than the average and repulsive for states occupied with less than the average occupancy. The SIC potential does the same for states occupied by more or less than one-half. In order to define the LDA+*U* functional and potential, one has to specify *U* and *J* parameters, which are average Coulomb and exchange interactions in the considered shell. In our calculations we adopt the standard *U* and *J* values for Cu oxides, namely, 0.59 Ry and 0.07 Ry, respectively.

In order to investigate the role of the Cu 4*s* state and the *s*-*d* hybridization we performed LDA calculations with three different basis sets. The motivation for this is the weakness of LDA-based methods to properly treat the *s*-*d* hybridization in Cu_2O. The basis set modifications concern only the Cu *s* functions. In the standard setup [we will refer to it as the (S)-type basis], the Cu 3*s* states are described by LOs with a linearization energy around -7.81 Ry, while the *s* part of the APW contains a 4*s* radial function at a linearization energy of 0.3 Ry. In this case, both Cu 3*s* and 4*s* states have full variational flexibility. In the next setup the linearization energy of the Cu 4*s* orbital is set to $+30$ Ry, which practically removes the variational freedom to describe the 4*s* character of the wave function. Only the Cu 3*s* state can be fully described by the 3*s* LO. This restricted basis will be

TABLE I. Partial charges (e^-) for one spin direction calculated inside the atomic spheres in various approximations. (S) represents standard basis, (R) 4*s* completely removed, and (P) 4*s* partially removed (see text).

	Cu *s*	Cu *p*	Cu *d*	d_{z^2}	$d_{x^2y^2}+d_{xy}$	$d_{xz}+d_{yz}$	O *s*	O *p*
LDA (S)	1.092	3.033	4.303	0.755	1.752	1.797	0.757	1.731
GGA (S)	1.091	3.033	4.305	0.752	1.753	1.800	0.763	1.741
AMF (S)	1.093	3.034	4.299	0.744	1.753	1.802	0.757	1.733
SIC (S)	1.084	3.029	4.373	0.787	1.774	1.812	0.757	1.728
LDA (R)	0.997	3.058	4.377	0.836	1.751	1.790	0.792	1.755
LDA (P)	1.016	3.043	4.349	0.798	1.750	1.800	0.759	1.764

referred to as (R). In the last case the linearization energy of the Cu *s* APW is set to -7.8 Ry but the Cu 3*s* local orbital is removed from the basis [setup is (P)—partially restricted]. Here the 4*s* character of the wave function must be described by the 3*s* radial function and its energy derivative $\dot{u}$. As a result, the 3*s* character is properly described, but the variational freedom for the 4*s* character is strongly reduced [but less than in basis (R)].

III. RESULTS

A. Partial charges

Due to the type of the basis used in the APW+lo method the wave functions and the charge density can be decomposed into local (inside each atomic sphere) and partial (l character) contributions.[33] These quantities enable us to conclude some information concerning the atomic nature of the calculated wave functions and densities inside the atomic spheres. The changes of the partial charges with the basis setup and LDA+U correction allow us to understand the behavior of the EFGs described in the next paragraph.

Table I contains partial charges calculated inside the Cu and O spheres for all types of calculations. Comparing LDA and GGA results one can see that the differences are rather small for the Cu sphere, while for the O sphere the GGA increases the occupancy since the respective wave functions are slightly more spatially localized than in the LDA. While both AMF and SIC corrections have also negligible effects on the Cu *s* and Cu *p* partial charges, they have a large effect on the Cu *d* states (up to a few hundreds of an electron). As expected, the AMF correction does not change the average Cu *d* occupancy, but lowers the occupation of the d_{z^2} orbital and slightly increases the occupations of the rest of the Cu *d* shell. On the other hand, the SIC correction significantly increases the occupation of the whole Cu *d* shell with the strongest effect on the d_{z^2} orbital. This behavior can be explained by analyzing Eqs. (1) and (2). The occupation of all Cu *d* orbitals is much higher than one-half. This causes the SIC correction to shift all *d* states down in energy, leading to an increased occupation. One can see that only the d_{z^2} occupation differs significantly from the average value n_0. This causes the AMF correction to shift this state up in energy, leading to decreasing occupation.

The dependence of the partial charges in the Cu sphere on the basis setup is even more significant. The Cu *s* partial charge is obviously the lowest for the (R) setup (where the 4*s* character has been completely removed from the basis) and highest for the standard (S) basis set. The Cu *p* and *d* characters in the case of (R) and (P) gain some charge in comparison to the (S) case. As we will see the changes in the *p* character, although small, result in a change of the difference charge density (difference between the crystalline and the superposition of Cu^+ and O^{2-} ionic charge densities) near the empty tetrahedral site. The variation of the Cu *d* shell occupation concerns of course mainly the d_{z^2} orbital. Both (R) and (P) setups enhance the d_{z^2} occupation, with the (R) basis leading to the highest occupation.

It is clear from Table I that LDA+U corrections do not significantly influence the *s* and *p* partial charges of oxygen. However, the change in the basis set affects these occupations. The amount of the O *s* partial charge increases from the (S) to (R) setups. For the O *p* partial charge the (P) setup produces the highest occupation, and the (S) setup the lowest. Thus most of the Cu 4*s* character that is present in a standard calculation is transferred [after switching to the (R) or (P) setups] to the oxygen atom and the rest to the Cu *d* (mainly d_{z^2}) and Cu *p* orbitals. This redistribution leads to an increased ionicity of the bonding between Cu and O atoms. Filling up the *d* shell also affects the Cu-Cu bond and the values of the Cu EFGs as described next.

B. Electric-field gradients (EFGs)

The EFG tensor serves as a critical test for the quality of the calculated electron density. In $\mathrm{Cu_2O}$ the copper atoms are located on the threefold axes which means that the Cu-EFG tensor is diagonal and thus fully described by its principal component V_{zz}, whereas the O atom has no EFG due to its tetrahedral coordination. The EFG is sensitive to the anisotropy of the charge distribution close to the nucleus and can be calculated within the APW method[34,35] by $V_{zz} \propto \int [\rho(r) Y_{20}/r^3] dr$. For further analysis the charge density $\rho(r)$ can be decomposed into different angular momentum contributions in order to trace back which orbitals contribute to the EFG. Most important are the *p*-*p* and *d*-*d* contributions[16] which are proportional to the respective partial charges as $V_{zz}^{p\text{-}p} \propto \langle 1/r^3 \rangle_p [1/2(p_x+p_y)-p_z]$ and $V_{zz}^{d\text{-}d} \propto \langle 1/r^3 \rangle_d [(d_{xy}+d_{x^2-y^2})-1/2(d_{xz}+d_{yz})-d_{z^2}]$.

The total EFG and its partial contributions from wave functions inside the Cu sphere are presented in Table II. The absolute value of the Cu EFG measured by means of nuclear

TABLE II. Cu EFG in units (10^{21} V/m^2). All columns except the last one, which gives the total EFG, contain partial EFG contributions from inside the Cu sphere. The experimental value (Ref. 15) (only the magnitude is known) is 9.8×10^{21} V/m^2, using $Q(^{63}\mathrm{Cu})=0.22$ (Ref. 36) (for labels see Table I).

	p-p	d-d	s-d	"Sphere"	Total
LDA (S)	−15.9	10.6	0.18	−5.1	−5.1
GGA (S)	−16.4	10.7	0.17	−5.5	−5.5
AMF (S)	−15.9	11.6	0.18	−4.2	−4.1
SIC (S)	−16.2	8.7	0.15	−7.4	−7.3
LDA (R)	−14.2	1.1	0.02	−13.1	−13.1
LDA (P)	−16.7	5.0	−0.06	−11.6	−11.8

quadrupole resonance (NQR) is 9.8×10^{21} V/m^2 using for the conversion the most recent value of the nuclear quadrupole moment $Q(^{63}\mathrm{Cu})=0.22$.[15,36] The LDA calculation with the standard basis set gives an EFG of about half the experimental value. The calculated EFG is negative and originates mainly from the large negative p-p contribution (since the p_z occupation is larger than p_x, p_y) that is partially canceled by the smaller but positive d-d contribution caused by the reduced d_{z^2} occupation. The GGA produces about a 7% bigger EFG than the LDA, thus going in the right direction, but the effect is by far too small. This increase originates mainly from an increased p-p contribution.

We speculate that an overestimation of the s-d hybridization may be responsible for this discrepancy with experiment. In order to demonstrate this, we performed model calculations with restricted Cu 4s basis sets with more (P) or less (R) flexibility.

As discussed in the previous paragraph the (R) and (P) basis sets mainly affect the occupation of the d_{z^2} orbital and enhance the sphericity of the d charge distribution. For the (R) setup (where the 4s character is completely removed) the d-d contribution to the EFG almost vanishes since the d shell becomes completely filled (spherical) leading to a total EFG even larger than experiment. For the (P) setup, where the 4s character is only partially removed, $V_{zz}^{d\text{-}d}$ is decreased to about one-half its value leading to an EFG in fair agreement with experiment.

It is therefore very interesting to see whether or not LDA+U can correct for these shortcomings. The results for the two LDA+U corrections are rather surprising: The SIC correction seems to improve the results slightly, while the AMF makes it even worse. The SIC correction increases the d_{z^2} occupation, and the charge distribution of the d shell becomes more spherical leading to decreasing $V_{zz}^{d\text{-}d}$. In the case of the AMF correction one observes the expected depletion of the d_{z^2} orbital. Thus the asphericity of the d shell increases together with the d-d contribution. This results in a larger cancellation of the leading p-p contribution, and a smaller absolute value of the EFG. Of course, one could play around with the value of U. For instance, one can increase the EFG to about -10.7×10^{21} V/m^2 using the SIC version but with the unscreened (atomic) $U=1.29$ Ry. Therefore some intermediate value would reproduce the experimental EFG. One could also argue that the way LDA+U is applied within the LAPW method is not really consistent with the LDA+U (SIC) scheme, in which the occupation is one-half plays an important role. In the LAPW method the density matrix is calculated only inside the atomic spheres and this implies that, for example, a half occupied state does not have occupation 0.5, since only $0.43e^-$–$0.45e^-$ reside within the sphere. Thus one could rescale the density matrix by a factor of 1.1–1.15 which would increase the Cu EFG to -8.1 -8.5×10^{21} V/m^2 and thus only a marginally larger U would be necessary. In any case, it is worth noting that the two versions of LDA+U have opposite effects on the EFG and only the SIC method gives changes consistent with experiment, whereas in the (undoped) high-T_c cuprates all LDA+U schemes work well and give similar results.[37]

It should be noted that the EFG values for $\mathrm{Cu_2O}$ quoted by Petrilli *et al.*[38] are in better agreement with experiment although their result is based on a GGA calculation. This good result, however, is fortuitous and mainly comes from an insufficient treatment of the Cu 3p semicore states.

In contrast to our work, positive EFG values have been reported, which were based on x-ray-diffraction results.[14,39] However, these experimentally estimated values are two to five times larger than the NQR results. According to our analysis the leading contribution originates from the p character of the wave function which is a rather diffuse function. As we have shown previously[16] the p-p EFG mostly results (due to the $1/r^3$ factor) from contributions up to the first node of the wave function, i.e., from a region of 0.2 bohr around the nucleus. In this region it is not possible to experimentally obtain a sufficiently accurate charge distribution by x-ray diffraction. Thus the EFG determined from an x-ray charge-density refinement is rather unreliable and the reported positive values probably reflect only the positive d-d contribution, but not the total EFG.

C. Topological analysis and critical points

A topological analysis[40] following Bader's "atoms in molecules" theory is considered to be a useful tool for a quantitative description of the charge-density distribution ρ. This method gives a unique definition of partitioning space into atomic basins by simply knowing the total electron density. It results in atomic charges and ionicities, and allows to characterize the density by a well-defined set of so-called critical points (CPs).

The atomic basin is defined as a region of space traversed by trajectories of the density gradient terminating at a given nucleus (attractor) and enclosed inside a zero charge-density flux surface ($\vec{\nabla}\rho\cdot\vec{n}=0$). Table III contains total charges of Cu and O defined as the integrated densities inside the atomic basins. In all calculations with the standard basis set the total charges of O and Cu are nearly equal -1 and 0.5, respectively. We have already noticed, when analyzing the partial charges inside the atomic spheres, that the calculations with the restricted (P) and (R) basis sets enhance the ionicity of the system. This is also reflected in the Bader charges, where the ionicity increases to about -1.3 and $+0.65$ for O and Cu, respectively. The corresponding data

TABLE III. Atomic charges (e^-) within the atomic basins of O and Cu calculated according to Bader's topological analysis (for labels see Table I).

	O	Cu
LDA (S)	-1.03	0.51
GGA (S)	-1.07	0.53
AMF (S)	-1.03	0.52
SIC (S)	-1.00	0.50
LDA (R)	-1.32	0.66
LDA (P)	-1.28	0.64

reported by Lippmann and Schneider[14] (LS) are in the range of -1.68–-1.14 for O and from 0.84 to 0.57 for Cu. Here we compare only LS data, which have the largest goodness of fit. For comparison we generated reference charge densities by a superposition of neutral atoms and of pure ionic Cu^+ and O^{2-} densities (O^{2-} was calculated with a Watson sphere radius equal to 1.2 Å, see the next paragraph). We found Bader charges of 0.33 to 0.73 for Cu representing somehow the limiting cases of neutral and fully ionized Cu^+, while neutral oxygen and O^{2-} yielded charges of -0.66 to -1.46. Our crystalline Bader charges are between these limits and one can estimate the actual ionicity from this comparison.

According to the definition, a CP is a point in space where the gradient of a charge density $\nabla\rho(r)$ vanishes. Calculating the Hessian of the density, defined as a matrix of second derivatives $(\partial^2\rho/\partial x_i \partial x_j)$, one can characterize each critical point by the principal curvatures of the charge density (eigenvalues of the Hessian). A CP where all curvatures are negative is a local maximum, and is usually referred to as $(3,-3)$ CP. A $(3,-1)$ CP has one positive eigenvalue, is called a bond CP, and corresponds to a saddle point of ρ. A $(3,+1)$ CP with two positive eigenvalues is a ring CP, and a $(3,+3)$ CP for which all eigenvalues are positive is a local minimum (cage CP). For a bond CP, where two curvatures calculated in the directions perpendicular to the bond are equal (h_1 and h_2), the ratio of principal curvatures $|h_1|/h_3$ together with the Laplacian provide information for a classification of chemical bonding. A small value $|h_1|/h_3 \ll 1$ is typical for closed-shell (ionic) interactions, while for covalent bonding this ratio increases with bond strength. Accordingly, the Laplacian is positive and large for ionic bonding, but small or negative for covalent bonds.

From five detected (symmetry unique) critical points two are bond CPs, one is a ring CP, and two are local minima. The first bonding point described in Table IV corresponds to the bond between Cu and O. All parameters are rather insensitive to the type of exchange-correlation potential or the choice of U correction. Only the basis set restrictions have some influence on eigenvalues of the Hessian and the charge density. Compared to a standard calculation, the (R) (P) basis produces 8% (3%) lower densities and 63% (48%) larger Laplacians. This confirms our previous conclusions, that the manipulation of the Cu s basis function enhances the ionicity of Cu-O bonding. The LS data have a large dependence on the details of their analysis. However, they agree quite well with our results, in particular in their most favorable refinement, where they find an almost identical position and only slightly larger densities, Laplacians and h_3 values. Clearly their parameters are closer to our standard calculation than to those with restricted basis sets, where much larger Laplacians have been found.

The second bonding CP described in Table IV has been found middistance between two Cu atoms belonging to one Cu_4 tetrahedra. This bond fixes two interpenetrating Cu-O networks. The density is seven times smaller than at CP1 and also the Laplacian is more than an order-of-magnitude smaller. The basis set restrictions have a much larger influence than the choice of the exchange and correlation functional except for the LDA+U (SIC) method. Both the (R) basis and LDA+U (SIC) yield a 10% smaller ρ, but while the former has a 20% smaller Laplacian, the latter gives a 2% larger value. As one can see in Table IV the theoretical Laplacian is lower and the density is slightly larger than given by LS. The other CPs are of less importance, but for the sake of completeness the LDA values are given in Table V: one ring point in the middle of the triangular faces of the empty Cu tetrahedra, and two minima, one in the center of the empty Cu tetrahedra, and the second in the center of the Cu octahedra.

D. Charge-density distributions and Cu-Cu bonding

The results of our calculations are presented in Fig. 1, where the difference density (ρ_d, difference between the total charge density and a superposition of Cu^+ and O^{2-} densities) in the (110) plane for LDA, LDA+U (SIC), and the (R) basis set calculations are displayed. We can clearly identify the partially unoccupied Cu d_{z^2} orbital in good agreement with Zuo *et al.*,[11] but we do not confirm the hexadecapole term found in the experiment of LS.[13] This latter distortion, although allowed by symmetry, could only occur due to a very strange and most likely unphysical hybridization of some Cu d orbitals.

TABLE IV. Position, curvatures, Laplacian, and charge density at the $(3,-1)$ critical points from LDA calculations and experiment (LS) (Ref. 14).

	x	y	z	h_1 (Å^{-5})	h_2 (Å^{-5})	h_3 (Å^{-5})	$\nabla^2\rho$ (10^2 Å^{-5})	ρ (Å^{-3})
LDA	0.1231	0.1231	0.1231	-3.8	-3.8	20.6	13.0	0.794
LS	0.1227	0.1227	0.1227	-4.1	-4.1	23.1	14.9	0.816
LDA	$\frac{3}{4}$	$\frac{1}{4}$	0	-0.22	-0.17	0.87	0.47	0.116
LS	$\frac{3}{4}$	$\frac{1}{4}$	0	-0.12	-0.11	0.84	0.61	0.092

TABLE V. Position, curvatures, Laplacian, and charge density at critical points others than $(3,{}^{-}1)$ from LDA calculations.

Type	x	y	z	h_1 (Å^{-5})	h_2 (Å^{-5})	h_3 (Å^{-5})	$\nabla^2\rho$ (10^2 Å^{-5})	ρ (Å^{-3})
(3,1)	0.6795	0.1784	0.1784	−0.10	0.29	0.33	0.52	0.083
(3,3)	0.75	0.25	0.25	0.16	0.16	0.18	0.51	0.077
(3,3)	0.5	0	0	0.09	0.09	0.25	0.42	0.043

Recently Zuo *et al.*[11] published results of combined electron-diffraction and x-ray data, where they reported the existence of a local maximum in the difference charge density at the center of the empty Cu_4 tetrahedron. This maximum was interpreted as evidence of direct Cu-Cu bonding, but was not verified by LS.[13] We find an excess ρ_d in the Cu_4 tetrahedron region and a depletion of ρ_d around both Cu^+ and O^{2-} ions indicating a large delocalization with respect to the free ions. However flat maxima at the center of the empty Cu_4 tetrahedron exist only for the calculations with a modified basis setup [see Fig. 1(c)]. The height of the difference density is between 0.05 and 0.06 e Å^{-3}, which is about four times smaller than the value calculated by Zuo *et al.* For the standard setups we have maxima in ρ_d shifted towards Cu, and a minimum at the tetrahedral site. The charge densities of Cu^+ and O^{2-} ions have been calculated using the GGA.[29] Since O^{2-} is unstable as a free ion, a Watson sphere model[41] with a sphere radius (R_w) of 1.2 Å was used to stabilize it. It mimics the stabilizing effect of the surrounding ions of a crystal. Since the choice of R_w affects the O^{2-} density,[42] we determined the resulting ρ_d at the tetrahedral site using O^{2-} calculated with R_w from 1.1 to 1.3 Å but found no strong dependence.

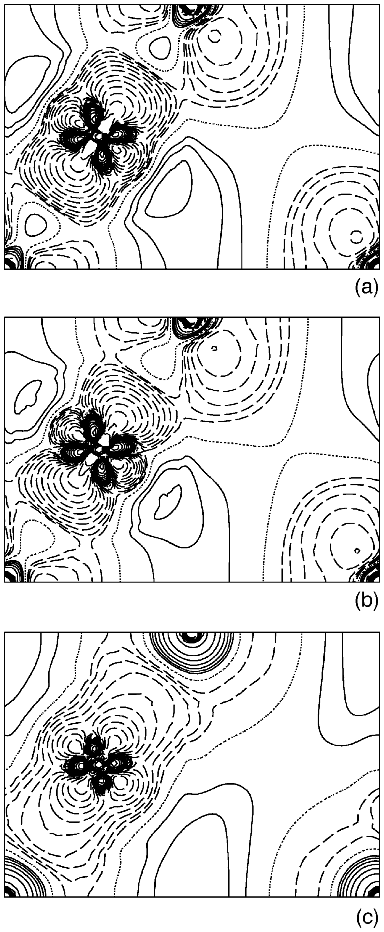

FIG. 1. Difference densities calculated within the LDA (a), LDA+U (SIC) (b), and the restricted (R) basis set (c). Positive values are shown as full, negative as dashed and zero as dotted lines. The scale is logarithmic, and consecutive lines differ by $\sqrt{2}$, starting at ±0.03 e Å^{-3}.

Two questions arise: what is the origin of these maxima and are they real evidence of direct Cu-Cu bonding? The first question can be answered by considering how localized/delocalized the valence Cu $4s$, $4p$, or $3d$ wave functions are. This suggests that only Cu $4p$ states can participate in the creation of these maxima far away from the Cu nucleus. Both Cu p and d partial charges increase when Cu $4s$ basis functions are removed. But the Cu $3d$ wave functions are rather confined in space and thus cannot create such a maximum.

In order to check the relation between the presence of the maxima and bonding properties we have calculated the equilibrium volumes and bulk moduli for all basis sets and LDA+U corrections. As can be seen from Table VI the LDA underestimates the equilibrium volume and overestimates the bulk modulus as expected. Since d-d correlation seems less important in Cu_2O, both LDA+U methods do not change the results significantly. The GGA calculation gives very good volume (+2.8%) and almost perfect bulk modulus. If we remove the $4s$ basis partly [(P) basis] the equilibrium volume is already strongly overestimated and the corresponding bulk modulus clearly underestimated. For the (R) setup (with the completely removed $4s$ basis) the lattice appears to be unstable. No minimum of the total energy has been found up to 30% volume expansion. This allows us to conclude that the presence of difference density maxima is *not evidence* of a direct Cu-Cu bond. On the other hand removing the Cu $4s$ basis leads to a weakening of the Cu_2O

TABLE VI. Deviations of calculated values from the experimental equilibrium volume and bulk modulus of 77.8 Å^3 and 112 GPa (Ref. 43), respectively (for labels see Table I).

	ΔV (%)	ΔB (%)
LDA (S)	−6.2	35.2
GGA (S)	2.8	0.2
LDA+AMF (S)	−6.4	36.5
LDA+SIC (S)	−5.0	24.5
LDA (R)	unstable	
LDA (P)	11.8	−12.6

bonds and a destabilization of the whole structure. Important for the bonding, besides the obvious ionic character, is the *s*-*d* hybridization at the Cu site, which seems to be overestimated in the LDA, but definitely cannot be completely neglected.

IV. CONCLUSIONS

We have applied the APW+lo method to investigate the charge density of Cu_2O using Bader's topological analysis, EFGs, and difference density maps. It is rather clear that a simple Cu^+-O^{2-} model is insufficient to explain the bonding properties of Cu_2O. The importance of *s*-*d* hybridization in this system has been pointed out previously.[8] However, a comparison between calculated and experimental EFGs suggests that the amount of *s*-*d* hybridization is overestimated by both the LDA and GGA. This conclusion is also supported by the topological analysis. By comparing our results with a similar analysis performed on charge densities refined from high-energy synchrotron experiments[14] we find that the LDA calculations overestimate the covalency and strength of the Cu-O and Cu-Cu bonds causing too large values of the calculated bulk moduli and too small equilibrium volumes.

We have artificially manipulated the magnitude of the *s*-*d* hybridization by modifing the Cu 4*s* basis sets. As shown above, decreasing the *s*-*d* hybridization increases the calculated absolute values of the EFG, and decreases the calculated bulk modulus, bringing both in better agreement with the experimental data. This improvement is a consequence of an increased Cu *d* shell occupation and the corresponding decrease of the asphericity of the Cu *d* charge distribution. As an accompanying effect we have observed some charge transfer to the O atom and an increased Cu 4*p* occupancy, which leads to flat maxima in the difference charge density at the empty tetrahedral Cu_4 sites, as measured by Zuo *et al.* However Zuo *et al.* found maxima that are four times larger than ours, which they interpreted as evidence for direct Cu-Cu bonding. This is in contrast to what we found, namely, that this effect is accompanied by a weakening of the bonds in Cu_2O.

A physically more appealing method of correcting the *s*-*d* hybridization would be an improved description of the electron-electron interactions, and for this purpose we have applied two different versions of the LDA+U to solve this problem. However, the available LDA+U corrections behave quite differently depending on the form of the double-counting correction. We noticed that LDA+U (AMF) leads to even poorer agreement, whereas the SIC method improves the situation, but would require an unexpectedly large U value. By analyzing the underlying equations, one can easily understand these results. It is important to properly include the self-interaction energy of the *d* electrons, and this is approximately done by the SIC-method. The SIC calculation shifts the center of the Cu *d* bands down in energy, and thus indirectly reduces the *s*-*d* hybridization, whereas the AMF correction does not change the center of the *d* bands.

Therefore we can conclude that characterization of the chemical bonding in Cu_2O requires a good description of the localized nature of the Cu 3*d* orbitals which must go beyond the LDA or GGA. An improved description using the LDA +U (SIC) method affects the *s*-*d* hybridization which is inadequately described in the LDA or GGA and is the main source of the discrepancy between theory and experiment.

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