Doping induced charge redistribution in the high temperature superconductor \( \text{HgBa}_2\text{CuO}_{4+\delta} \)

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To understand the link between doping and electronic properties in high temperature superconductors, we report first-principles calculations on the oxygen doping effect for the single layer cuprate \( \text{HgBa}_2\text{CuO}_{4+\delta} \). The doping effect is studied both by supercell and single cell virtual crystal type approaches. We find ionic behavior of the dopant atom up to an optimal doping concentration of \( \delta = 0.22 \). The excess oxygen attracts electrons from the \( \text{CuO}_2 \) plane leading to an increase of the hole concentration in this building block. The maximum amount of holes is reached when the oxygen \( p \)-shell is nearly completely filled. As a consequence the density of states at the Fermi level exhibits a pronounced maximum at the optimal oxygen content. The calculated hole content as a function of doping is in accordance with experimental findings.

It is commonly believed that the charge carriers responsible for the superconducting pairing of high \( T_c \) cuprates are holes mainly confined to the \( \text{CuO}_2 \) layers. Similar correlations between \( T_c \) and and \( n_s/m^* \), with \( n_s \) and \( m^* \) being the charge carrier density and the effective mass, respectively, do not only include high \( T_c \) materials, but also other families of superconductors. A universal relationship between \( T_c/T_c^{\text{max}} \) and the hole content \( p \), exhibiting a common feature among the \( p \)-type high-\( T_c \) superconductors, was presented by Zhang et al. This dependence is characterized by a plateau, where the variation of \( T_c/T_c^{\text{max}} \) is independent of the compound considered.

In all these materials of interest the actual amount of holes is driven by doping. However, for most of the theoretical models describing the superconducting phase transition the hole content rather than the doping level is the crucial input parameter. Above all, hardly anything is known about the relationship between these two physical quantities. Without a detailed knowledge of how doping influences the number of carriers in the normal state, also the superconducting properties will lack a profound understanding. In view of being able to tune the amount of carriers and thereby the superconducting transition temperature a full clarification of how doping affects the electronic structure is not only highly interesting, but even inevitable. In this context the following questions are raised: (i) Where does the excess charge go upon doping? (ii) How does doping influence the carrier concentration in the copper-oxygen planes? (iii) What limits the amount of holes in these building blocks? (iv) How does the density of states (DOS) behave as a function of doping?

In order to address these topics, we have carried out electronic structure calculations based on density functional theory (DFT). For that purpose we have chosen the simplest representative of the Hg-based high \( T_c \) compounds, the \( \text{CuO}_2 \) single-layer \( \text{HgBa}_2\text{CuO}_{4+\delta} \) (Hg1201).

This family of layered structures with the formula unit of \( \text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta} \) represents the class of superconducting materials with the highest transition temperature so far. It reaches a value of 136 K for \( n = 3 \) which can be even enhanced by applying pressure. Upon adding some excess oxygen, \( T_c \) can be dramatically increased. For Hg1201, a systematic study over a wider range of doping (\( 0.03 \leq \delta \leq 0.4 \)) revealed a parabolic-like \( T_c \) dependence on the oxygen content \( \delta \) exhibiting a maximum at \( \delta_{\text{opt}} \approx 0.22 \). At this optimal doping concentration \( T_c \) is 97 K for ambient pressure, and climbs up to 118 K at 24 GPa, which is the highest \( T_c \) of any single-layer cuprate. Although the mercury based high \( T_c \) compounds are not explicitly included in the experimental analysis described above, one can expect them to fit into this framework.

Theoretically, doping effects in this class of materials have been studied for a high doping level of \( \delta = 1/2 \) only revealing strong covalent bonding in the basal plane with large overlap of the Hg and the dopant oxygen orbitals. This oxygen concentration, however, has never been achieved experimentally. Therefore a detailed study of the much more important low doping regime is highly desirable. In our investigations special emphasis is put to the doping induced redistribution of the hole concentration in the \( \text{CuO}_2 \) layer. In addition, the doping effect on the crystal structure is studied. In order to make arbitrary doping levels feasible we treat an excess oxygen concentration \( \delta \) by adding the appropriate amount of valence electrons \( 6 \times \delta \) (6 electrons for the fully doped cell) to the crystal in a single-cell calculation. To guarantee charge neutrality the corresponding positive charge was placed in a sphere at the doping oxygen site, i.e. in the middle of the Hg squares in the basal plane. As we will see below, this virtual crystal approach is justified by the ionic behavior of the dopant oxygen. We have cross-checked our results by supercell calculations for doping levels of \( \delta = 1/6 \) and \( \delta = 1/4 \), and in addition for \( \delta = 1/2 \). For the systematic study of the doping-dependent electronic structure, the crystalline data as a function of doping were taken from Ref. In a next
step, we also investigate the effect of doping on the lattice parameters and atomic positions by total-energy and atomic-force calculations.

All calculations are carried out within the full-potential linearized augmented plane-wave (LAPW) method \cite{9} utilizing the WIEN97 code \cite{10}. Exchange and correlation effects are treated within the local density approximation (LDA). The Brillouin zone integrations are carried out on a $20 \times 20 \times 8$ $k$-point mesh (consisting of 220 points in the irreducible wedge) applying a Gaussian smearing of 0.002 mRy. Our basis set includes approximately 1500 LAPW’s supplemented by local orbitals for the low-lying semicore-states Hg–5$p$, Cu–3$p$ and O–2$s$. We used atomic sphere radii of 2.0, 2.2, 1.9, and 1.55 a.u. for Hg, Ba, Cu and O, respectively. The atomic-like basis functions used within the LAPW method allow an analysis and the orbital symmetry decomposition of the electronic charge within the atomic spheres. For the labelling of the oxygen atoms see Fig. ??

As already found by previous calculations carried out for the undoped material \cite{6,11}, the Fermi level intersects a single free-electron-like two-dimensional half-filled $d_{p^*}$ band, with its states being of Cu($d_{x^2-\gamma^2}$) and O($p_{2}$) character. Upon doping the effect on the electronic structure is twofold. First, the dopant adds states at the Fermi level, where these new charge carriers cause a shift of $E_F$. Second, the shift of the Fermi level changes the carrier concentration in the CuO$_2$ plane. This can be seen in Fig. \ref{fig1} where the corresponding losses in the partial charges with respect to the undoped system are displayed. The occupation number for the copper $d_{x^2-y^2}$ orbital $Q(d_{x^2-y^2})$ is decreased by 0.09 $e$ (from 1.443 $e$ for the undoped case to 1.353 $e$ for $\delta_{opt}$), and similarly the O1($p_{2}$) charge $Q(p_{2})$ drops by 0.030 $e$ (from 0.982 to 0.952). Both orbitals clearly exhibit their minimum occupation number (maximum amount of holes) as a plateau around the experimentally observed optimal doping content. The hole concentration within the copper-oxygen planes with respect to the undoped case is obtained by $Q(d_{x^2-y^2})(0) + 2 \times Q(p_{2})(0) - [Q(d_{x^2-y^2})(\delta) + 2 \times Q(p_{2})(\delta)]$ also displayed in Fig. \ref{fig1}. In excellent agreement with experiment \cite{5} its optimal value is found to be 0.16 $e$.

The increase of the hole content can be generally understood in an ionic picture: The excess oxygen attracts electrons from the copper-oxygen plane thereby increasing the hole concentration in this region. In fact, the O3 states do not show strong overlap with the neighboring Hg states in the entire doping regime up to optimal doping. This picture is confirmed by supercell calculations for doping concentrations of \( \delta = 1/6 \) and \( \delta = 1/4 \) (with one excess oxygen O3 per six and four single cells, respectively). It shows a nearly flat oxygen band at $E_F$ with vanishing Hg–$d$ admixture, whereas the Hg–$d$ states are found somewhat below. The total and partial densities of states for \( \delta = 1/4 \) are shown in Figure \ref{fig2}. It exhibits covalent bonding of Cu and O1 with peaks at -0.35 eV and a small feature right below $E_F$. Covalent bonds are also formed by Hg and the apical oxygen O2, whereas the dopant atom O3 has the highest contribution to the DOS at the Fermi level with hardly any common feature with mercury. This fact is supported by the partial charges in the Hg sphere which are not affected by doping. Only in the overdoped region, investigated for $\delta = 1$, and for $\delta = 1/2$ by a supercell calculation, stronger bonds between oxygen and mercury atoms are formed as was also found in the three-layer compound for the heavily oxygenated material \cite{6}.

Let us turn now to the question what the limiting factor for the creation of holes in the CuO$_2$ plane is. We propose that the hole concentration reaches its maximum when the dopant band is nearly completely occupied, i.e. for a closed $O^2$ shell. Since the excess oxygen attracts electrons from the CuO$_2$ plane, its orbitals will be systematically filled up not only by the electrons provided by the oxygen atom itself, but also by those coming from the CuO$_2$ unit. In order to quantitatively prove our hypothesis, we have repeated our calculations with a muffin tin radius of 2.5 a.u. for the artificial O3 atoms with nuclear charge of $Z = 65$. This sphere is big enough to include the doping charge and therefore allows the interpretation of the charges inside this sphere as absolute occupation numbers. We indeed find a nearly closed shell at the experimentally observed optimal doping concentration $\delta_{opt} = 0.22$ \cite{5} which limits the amount of holes in the CuO$_2$ plane an therefore most probably the superconducting transition temperature. Furthermore, the occupation of the $2p_{2}$ shell of the doping O atom (full oxygen atom here) is found by 4cell calculation. We used a muffin tin sphere pf 3.0 a.u. in this calculation and an O anion is found with the negative charge of 1.4 $e$. Further increase of the muffin tin sphere was not possible due to computational difficulties. Therefore, at this moment it is not easy to estimate whether a $O^{2-}$ anion is formed or an anion with less then 2.0 $e$ negative charge. Nevertheless, the presence of anion dopant state at the doping site can be clearly seen on the basis of LDA calculations. In the overdoped region covalent bonds between O3 and Hg are formed. By this change the pure ionic character of the dopant oxygen gets lost and therefore no more carriers are attracted from the CuO$_2$ plane which results in the broad plateau on Fig. \ref{fig2} in accordance with the experimental findings \cite{5}.

These findings also show up in the density of states which in the optimal doping regime exhibits an almost filled band right below $E_F$. The calculated DOS at the Fermi level $N(E_F)$ as displayed in Fig. \ref{fig2} has a pronounced maximum at $\delta_0 = 0.22$. It contains large contributions from the CuO$_2$ plane, but also a considerable amount of apical oxygen and some O3. All the contributions peak at the optimal doping content. From the density of states at $E_F$ the electronic specific heat coefficient can be determined. Assuming a similar behavior for other high-$T_c$ materials like the Bi-based compounds, the measured specific heat coefficient $\gamma$ of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ as a function of doping \cite{5} can be understood by the
pronounced increase of the DOS around optimal doping. Moreover, the calculated maximum value of $\gamma = 4.4$ mJ/(mol K$^2$) is in excellent accordance with experimental values for other high $T_c$ materials at optimal doping [10].

As already mentioned, we crosschecked our results with supercell calculations for $\delta = 1/6$ and $\delta = 1/4$ in order to ensure that no artifacts may arise due to our single-cell approach for the treatment of doping. The partial charges in all the atomic spheres agree very well with the corresponding single-cell calculation (within one hundredth of an e). E.g. for $\delta = 1/4$ the copper $Q_{z(x^2-y^2)}$ partial charge is 1.364 compared to 1.353 in the single-cell approach, the oxygen $Q_{p_x}$ charges are 0.949 and 0.952, respectively. For $\delta = 1/6$ the deviations are also below 1%. Excellent agreement is also found for the density of states at the Fermi level, as can be seen for both cases in Fig. 3.

Not only the electronic properties, but also the crystal structure is influenced by doping. The redistribution of bond lengths can again be explained within the ionic picture. Since doping does not change the symmetry of the crystal, it only leads to displacements of Ba and the apical oxygen in $z$-direction. With increasing oxygen content at the doping site, the positive Ba ions are expected to be attracted by the oxygen, whereas the negatively charged O2 ions should be repelled. Indeed a shift of the Ba position towards the basal plane is observed together with a displacement of the O2 ions away from this plane. In Fig. 4 the corresponding z-coordinates of both atoms are shown which were calculated by fully optimizing the crystalline data for selected doping concentrations: For $\delta = 0.08, 0.17, and 0.23$ the unit cell volumes, $c/a$ ratios, and atomic positions were obtained by total-energy and atomic-force calculations using a similar procedure like in Ref. [4]. The results are displayed in Table 1. All trends are in agreement with experimental observations [5]. These are a shrinkage of the unit cell upon doping, a shortening of the lattice parameter $a$, an increase of $c$ for small doping levels followed by a nearly linear decrease, an increasing distance between the basal plane and the Ba layer, as well as a reduction of the distance between the layers of Ba and O2. In agreement with measured data, the latter two quantities show a less pronounced dependence up to $\delta = 0.08$ and a stronger one for higher oxygen contents.

In summary, we have investigated the relationship between doping and electronic and structural properties in the high temperature superconductor HgBa$_2$CuO$_4+\delta$. We find that for doping concentrations up to optimum the dopant does not form covalent bonds with the neighboring Hg atoms, but shows purely ionic behavior. The doping oxygen adds states close to the Fermi level showing nearly pure O3 character. Due to its high electronegativity the excess oxygen attracts electrons from the CuO$_2$ plane resulting in a redistribution of charge carriers and an increase of the number of holes in this plane. At optimal doping the DOS at the Fermi level exhibits a pronounced maximum in accordance with experimental specific heat data of other cuprates. The doping-induced charge redistribution is accompanied by a shrinkage of the unit cell and displacements of Ba and the apical oxygen O2 towards and from the basal plane, respectively. The amount of holes created in the CuO$_2$ plane is limited by the fact that at optimal doping a closed oxygen shell is reached. We conclude that this behavior is a general feature among different families of high $T_c$ compounds.

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TABLE I. Crystalline data as a function of doping obtained from total-energy and atomic-force calculations.

| δ   | a [Å]       | c [Å]       | Ω [Å³]       | z(Ba) [c] | z(O2) [c] |
|-----|-------------|-------------|--------------|-----------|-----------|
| 0.00| 3.8574      | 9.7228      | 144.6676     | 0.3003    | 0.2014    |
| 0.08| 3.8192      | 9.8191      | 143.2211     | 0.2965    | 0.2023    |
| 0.17| 3.8058      | 9.6887      | 140.3283     | 0.2851    | 0.2055    |
| 0.23| 3.8312      | 9.5604      | 140.3280     | 0.2808    | 0.2074    |

FIG. 1. Doping induced changes in the partial charges within the atomic spheres of Cu (half filled circles) and O1 (open circles) and total amount of holes (filled circles) in the CuO₂ plane as a function of the doping concentration δ.

FIG. 2. Total and site-projected densities of states in states per eV and unit cell volume Ω for δ = 0.25 obtained by a supercell calculation containing one O3 atom per four formula units. (The Fermi level is set to zero.)

FIG. 3. Total density of states at $E_F$ per eV and formula unit for HgBa₂CuO₄⁺δ as a function of doping. The right axis indicates the electronic linear specific-heat coefficient γ in mJ per mol and K². The maximum value is found exactly at the experimentally observed optimum doping concentration. The results for the supercell calculations are indicated by stars.

FIG. 4. Doping induced changes in the atomic positions of Ba and O2 in units of the lattice parameter c as function of doping.
doping induced holes \([e]\) vs. doping concentration \(\delta\)

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\text{CuO}_2\text{ layer}
\]

\[
\text{Cu-d}^\text{-}x^2-y^2
\]

\[
\text{O-p}_x
\]
