On the Stereochemistry of the Cations in the Doping Block of Superconducting Copper-Oxides

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Metal-oxygen complexes containing Cu, Tl, Hg, Bi, and Pb cations are electronically active in superconducting copper-oxides by stabilizing single phases with enhanced $T_c$, whereas other metal-oxygen complexes deteriorate copper-oxide superconductivity. Cu, Tl, Hg, Bi, Pb in their actual oxidation states are closed shell $d^{10}$ or inert $s^2$ pair ions. Their electronic configurations have a strong tendency to polarize the oxygen environment. The closed shell $d$ ions with low lying $nd^{10} \leftrightarrow nd^{10}(n+1)s$ excitations form linear complexes through $d_{z^2} - s$ hybridization polarizing the apical oxygens. Comparatively low $nd^{10}(n+1)s$ excitation energies distinguish Cu$^{1+}$, Tl$^{3+}$, Hg$^{2+}$ from other closed shell $d^{10}$ ions deteriorating copper-oxide superconductivity, e.g. Zn$^{2+}$.

I. INTRODUCTION

Electronic inhomogeneities are an important feature of the superconducting copper-oxides. Upon doping the CuO$_2$ planes are separated into hole rich and hole poor regions on a mesoscopic lengthscale [8]. Phase separation in the doped CuO$_2$ planes renders the microscopic mechanisms of normal electric conductivity and of superconductivity unconventional. To reduce the complexity of the problem many approaches to the phase separation problem neglect the details of the atomic and electronic structure of the so-called doping block. Its function is thus reduced to an efficient charge transfer pump.

On the other hand the phenomenology of the atomic structures of the superconducting copper-oxides shows specific properties of the doping-blocks beyond their function as charge reservoirs to be relevant for superconductivity in the CuO$_2$ planes. For example, inelastic neutron scattering experiments on RBa$_2$Cu$_3$O$_{7-\delta}$ ($\delta = 1-0$) compounds yielded strong evidence for relationships between phase separation in the planes and ordering of the oxygen dopants in the chains [4].

Due to the large variety of doping blocks, various types of non-stoichiometries, locally distorted clusters, disorder-order phenomena, variable valence states, and anomalous lattice dynamics, it seems to be a hopeless undertaking to generalize other electronic properties than their well established charge transfer capability. Therefore the observed relationship between phase separation in the planes and oxygen ordering in the doping block of RBa$_2$Cu$_3$O$_{7-\delta}$ might be interpreted as an exceptional case arising from the chain structure in this particular compound. However, recent neutron scattering experiments on superoxygenated La$_2$Cu$_4$$\delta$O$_{4+\delta}$ show additional evidence for a possible relationship between phase separation and ordering in the doping block. The dopants in La$_2$Cu$_4$$\delta$O$_{4+\delta}$ are excess oxygens which occupy an interstitial site between the La-O layers. The interstitial excess oxygens turn out to order in intercalating layers [1] instead to distribute themselves randomly, as assumed so far.

Not at least these recent findings on relationships between phase separation in the planes and ordering phenomena in the doping block strengthen the need for a more detailed understanding of the physics and chemistry of the doping blocks [8]. In this short note we adress the specific role of the metal-oxygen complexes present in the doping blocks of the superconducting Cu, Tl, Hg, Bi, Pb copper-oxides.

II. ATOMIC SITES OF THE DOPANTS

The crystal structures of the superconducting oxides are characterized by superconducting CuO$_2$ sheets embedded in a dielectric medium, which consists of structurally and electronically different block layers. The CuO$_2$ layers are structurally nearly perfect, whereas the block layers exhibit many structural imperfections, which are also a source of electronic inhomogeneities. The dopants reside in atomic sites adjacent to the CuO$_2$ planes [2]. However, it is difficult to localize these sites precisely. Anions (mostly oxygen) and a few species of cations act as dopants, independently of each other, or in combination, e.g. in complexes with variable oxidation states of the metals. Table I lists a compilation of superconducting copper-oxides, using a recently proposed four number naming scheme [8]. This scheme allows for an immediate identification and comparisons of the different structures and sub-structures. It is advantageous over the popular naming scheme delineating the cation stoichiometries and rather helpful in localizing the dopants and their sites. For example the "123" system writes in the number four (ijkl) naming scheme 1212, where the first entry labels $i = 1$ 'insulating' layer (copper-oxygen chains), the second entry $j = 2$ 'spacing' layers (barium-
apical oxygen), the third entry \( k = 1 \) 'separating' layer (rare earth), and the fourth entry \( k = 2 \) 'conducting' CuO\(_2\) layers \([1]\).

In the sub-group lacking an 'insulating' layer (first entry: \( i = 0 \)) the dopants are located in or close to the two 'spacing' layers with commonly barium, strontium and lanthanum as metal atoms. For example in La\(_2\)Ba\(_3\)CuO\(_4\) the cation Ba\(^{2+}\) acts as dopant replacing La\(^{3+}\) in the 'spacing' layer. In superoxygented La\(_2\)CuO\(_{4+\delta}\) extra oxygens between the two adjacent La\(^{3+}\)-O 'spacing' layers dope the system. The so-called infinite layer compounds are reported to exhibit in the \( i = 0 \) sub-group the highest \( T_c \sim 90 - 130 \) K. From the structural phenomenology they appear as rather exceptional cases with \( i, \) two divalent metals in the 'spacing' layer, \( ii, \) no apical oxygen in the 'spacing' layer, and \( iii, \) an ill defined oxygen stoichiometry. Indeed, recent structural investigations analyze the infinite-layer systems as phase mixtures, and find the superconductivity in the (Sr,Ca)CuO\(_2\) system to come from the tetragonal phases Sr\(_{n+1}\)Cu\(_n\)O\(_{2n+1+\delta}\) (\( n = 2, 3, 4 \)) not from the infinite-layer phase \([1]\). The 'spacing' layers of Sr\(_{n+1}\)Cu\(_n\)O\(_{2n+1+\delta}\) (\( n = 2, 3, 4 \)) comprise the apical oxygens but surprisingly no cations, since the strontium site is assigned to the 'separating' layers. The lack of single phase compounds Sr\(_{n+1}\)Cu\(_n\)O\(_{2n+1+\delta}\) prevents so far more detailed characterizations of the dopant and its site. Sr\(_{n+1}\)Cu\(_n\)O\(_{2n+1+\delta}\) is an interesting system, which possibly exhibits a doping mechanism in the 'spacing' layer by excess oxygens similar to superoxygented La\(_2\)CuO\(_{4+\delta}\), but with enhanced \( T_c \).

The solution of the infinite-layer enigma \([1]\) supports strongly the role of the apical oxygen as a necessary and a crucial atomic constituent of the superconducting copper-oxides \([1]\).

Superconductivity in the \( i = 0 \) system Sr\(_{n+1}\)Cu\(_n\)-O\(_{2n+1+\delta}\) also evidences that the 'insulating layers' are not the decisive atomic constituents for superconducting copper-oxides with enhanced \( T_c \). But 'insulating layers' are able to stabilize single phases with enhanced \( T_c \), which is a problem interesting in itself.

III. THE CATIONS IN THE 'INSULATING' LAYER

Only a few species of metal atoms are found in the 'insulating' layers: Cu\(^{3+}\), \( Ti^{3+}, Hg^{2+}, Bi^{3+}, Pb^{2+} \). In inorganic chemistry these metal ions are classified as 'soft', in other words as highly polarizable. High polarizability may be related to various properties as large ionic radii, electronegativity, ionization potentials.

But high polarizability has less to do with these properties than with the electronic configurations in the actual ionization state. Ions with a high density of low-lying electronic states exhibit a strong tendency to enhanced polarizabilities, due to hybridization. Hybridization as a source of high polarizabilities is well known in ferroelectric oxides \([5]\), where \( \alpha_{\text{polar}} \) is enhanced by hybridization of the transition metal \( d \) states with the oxygen \( p \) states. The metal ions in the 'insulating' layers have in common either closed shell \( d^{10} \), or inert pair \( s^2 \) configurations.

\( \mathrm{Ti}^{3+}, Hg^{2+} \) exhibit closed \( d^{10} \) shells as well as \( Cu^{1+} \). The electronic configuration of \( Cu^{3+} \) is usually believed to be \( 3d^6 \), but the \( 2p \) core-level spectra of excited 'trivalent' \( d \) states exhibit the typical signatures of \( Cu^{1+} \) and \( Cu^{2+} \) ions. This finding is not surprising from the typical monovalent- and divalent-like bondlengths in the distorted 'trivalent' CuO\(_3\) plaquettes. We therefore assume \( Cu^{3+} \) has to have at least partially closed shell \( d^{10} \) properties.

\( Bi^{3+} \) and \( Pb^{2+} \) exhibit so-called inert pair \( s^2 \) configurations \([6]\).

Both configurations, closed shell \( d^{10} \) and inert pair \( s^2 \), exhibit a strong tendency to polarize the oxygen environment. Their stereochemistry is rather unusual inducing in the metal-oxygen complexes anisotropic polarizabilities. For the interesting anorganic chemistry of these metallic ions see e.g. Ref. \([8]\) and references therein.

A. Closed shell \( d^{10} \) ions

Closed shell \( d^{10} \) ions are known to form compounds with a low coordination number, and in particular linear complexes \([2, 4]\). The capability of \( d^{10} \) ions to form linear complexes is strongly correlated with excitations from the \( (n-1)d^{10} \) ground state to low lying \( (n-1)d^9ns \) and \( (n-1)d^9np \) states.

\( d_z^2 \) and \( s \) orbitals can be hybridized to give new orbitals of the type \( \alpha \psi(d_z^2) + \beta \psi(s) \). If the two electrons, which occupy the \( d_z \) orbital of the free ion are put into the hybridized \( 1/\sqrt{2}(d_z + s) \) orbital, the atom develops a strong electronegativity in the \( x \)- and \( y \)-directions, while if the hybridized \( 1/\sqrt{2}(d_z - s) \) orbital is occupied, a strong electronegativity in \( z \)-direction is developed. Hence two arrangements can occur: \( i, \) two electrons in the \( 1/\sqrt{2}(d_z - s) \) orbital and two short bonds in \( z \)-direction, and \( ii, \) two electrons in the \( 1/\sqrt{2}(d_z + s) \) orbital with four bonds in the \( x \)- and \( y \)-directions. Most of the closed shell \( d^{10} \) insulating Cu compounds, e.g. Cu\(_2\)O, LaCuO\(_2\), MCuO\(_3\) (\( M = Na, Rb, K \)), exhibit the arrangement \( i, \) with two short Cu-O bonds of about 1.84 Å in \( z \)-direction. The same occurs in the 'insulating' layer of RBa\(_2\)Cu\(_3\)O\(_{7-\delta}\) with two short bonds (1.85 Å) along the \( c \)-axis to the apical oxygen, and longer bonds (1.95 Å) in the \( y(b) \) direction (chains). Also the short bonds of the Ti-, Hg-complexes point in the \( z \)-direction \([13]\), whereas the long bonds form diagonals in the \( x(a) - y(b) \) plane.
Due to the hybridized $1/\sqrt{2}(d_{z^2} - s)$ orbital $d^{10}$ ions destabilize octahedral and stabilize linear environments. Preferentially the $d^{10}$ ions with the lowest $nd^9(n + 1)s$ excitation energy form linear complexes, because the energy required for $d - s$ mixing is proportional to the $d - s$ separation [12]. But large $d - s$ separations are expected to favour tetrahedral or octahedral environments through $s - p$ hybridization. Table 1 compiles the energies of lowest $d^8s$ and $d^8p$ states above the $d^{10}$ state of closed shell $d^{10}$ ions. $\text{Zn}^{2+}$ and $\text{Cd}^{2+}$ exhibit the largest $d - s$ separations, which may explain their tendency to form tetrahedral or octahedral environments in nonsuperconducting oxides. Well known $\text{Zn}$ inserted in RBA$_2$Cu$_3$O$_7$-$\delta$ does not adapt to the linear complex in the ‘insulating’ layer, substitutes preferentially for Cu in the ‘conducting’ layer, and suppresses efficiently $T_c$. Also Cd-oxygen complexes were found to deteriorate superconductivity in copper-oxides. Cu$^{1+}$, Hg$^{2+}$, Tl$^{3+}$ have smaller $d - s$ separations, form linear complexes and stabilize superconductivity. From the small $d - s$ separations Au$^{1+}$- and Ag$^{1+}$-ions might be be regarded as a particularly well suited metallic species for the formation of linear oxygen complexes. Au was found to substitute for Cu in the chains of YBa$_2$Cu$_3$O$_{7-\delta}$ up $\sim 0.1$, enhancing slightly $T_c$ [14]. At higher concentration Au-ions tend to form metallic clusters due to $d^{10}$-$d^{10}$ interactions [3]. Silver-oxides decompose already at moderate temperatures far below the formation of the copper-oxide. Hence high-pressure synthesis might be be a possible route for synthesis [14].

B. Inert pair $s^2$ ions

Chemical bonding in complexes with inert pair $s^2$ ions is largely determined by $s - p$ mixing [3,9]. In Bi$^{3+}$ (and Pb$^{2+}$) $6s - 6p$ hybridization results in a pair of electrons (lone-pair or inert pair) being pushed off to one side of Bi so that the strong bonds are on the other side. Thus the unshared $s^2$ electron pair causes a tendency to instability to antisymmetric distortions in the cubically co-ordinated ion. The corresponding anisotropic polarizability tends to remove the center of inversion from the system. Even if the cubic complex is stable it is particularly susceptible to electrical polarization. $s - p$ hybridization of the inert pair $s^2$ ion Bi$^{3+}$ may be therefore responsible for the large dielectric properties of the ‘insulating’ layer in the superconducting Bi copper-oxides.

$\text{Pb}$ form the most complicated metal-oxygen complexes with sometimes more than one metal sites. For instance the ‘insulating’ layer in e.g. Pb$_2$Sr$_2$YCu$_3$O$_{8}$ comprises Pb$^{2+}$ and Cu$^{1+}$, see Ref. [3] and references therein. The discussion of these metal-oxygen complexes is beyond the scope of this paper.

IV. CONCLUSION

‘Insulating’ layers and their metal-oxygen complexes stabilize single phase copper-oxide superconductors with enhanced $T_c$. The stabilizing mechanism may be related to the specific electronic structure of the few ‘successful’ metals, which in their actual oxidation states turn out to be either closed shell $d^{10}$, or inert pair $s^2$ ions. Both species have a strong tendency to polarize the oxygen environment due to $d - s$ or $s - p$ hybridization. In particular $d^{10}$ ions form linearly coordinated oxygen environments strongly polarizing the apical oxygens.

Our study on the possible specific role of the cations Cu, Tl, Hg, Bi, and Pb in the doping block strengthens statements [3] on the very importance of strongly polarized apical oxygens for superconductivity in copper oxides. $d - s$ hybridization implies essentially an ionic bond in which Cu$^{1+}$ forms a $d^8$ plus doubly occupied $(3d_{z^2} - 4s)^2$ hybrid state instead of the spherically symmetric $d^{10}$ state. $d - s$ hybridization has been experimentally [7] and theoretically [13] confirmed to give rise to the linear Cu-O complexes in semiconducting Cu$_2$O (cuprite). Hence Cu$_2$O may be considered as the archetypal closed $d^{10}$ shell copper-oxide allowing for ‘clean’ low temperature studies of the copper-oxide $3d_{z^2} - 4s$ hybrid. Interestingly the electrical conductivity of Cu$_2$O exhibits so far unexplored anomalies at about 280, 200, 160, 130, 110 and 90 K [13].

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[7] Definitions of the crucial material properties were recently proposed by K.A. Müller [3] listing seven (or eight) properties as the ingredients to be used in a cooking recipe for other transition-metal chalcogenide superconductors with a high $T_c$. Three of these ingredients deal explicitly with the properties of the doping block: i. The charge upon doping is coming from atomically defined sites in structural layers adjacent to the CuO$_2$ planes.
For holes present on the planar oxygen \( p \)-orbitals, \( \Delta < U \), where \( \Delta \) is the charge transfer energy, and \( U \) the Coulomb correlation energy of the \( d \)-electrons. \( \Delta \) is in the order of 2.5 eV but depends sensitively on the Madelung energies and screening terms. iii. The high polarizability of the oxygen (\( \alpha = 2-3 \text{Å}^{-3} \)), which in combination with the layered perovskite structure leads to very high dielectric constant and may reduce \( U \) to the order of 1 to tenths eV.

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TABLE I. Structure types of some typical superconducting copper-oxides. The first column lists the generic assignment in the four number naming scheme (see text). The second column indicates common assignments. Column i lists the possible doping ions in the 'insulating' layer. Column j lists the possible doping ions in the 'spacing' layer.

| ijk| Common | Chemical Formula | $T_c$ [K] | i | j |
|----|--------|-----------------|-----------|---|---|
| 0201 | T | (LaBa)$_2$CuO$_4$ | 38 |  |  |
| 0201 | T | La$_2$CuO$_{4+\delta}$ | 44 |  |  |
| 0201 | T | (Nd, Ce)$_2$CuO$_{4-\delta}$ | 24 |  |  |
| 0201 | T | (Nd, Sr, Ce)$_2$CuO$_4$ | 35 |  |  |
| 0212 | (La, Sr, Ca)$_3$Cu$_2$O$_6$ | 58 |  |  |
| 0223 | (PbBa)(YSr)Cu$_3$O$_8$ | 50 |  |  |
| 0223 | (Sr, Ca)$_3$Cu$_4$O$_{10}$ | 70 |  |  |
| 02$^a$∞-1$^a$∞ | (Ca, Sr)Cu$_2$O$_2$ | - |  |  |
| 0223 | Sr$_2$Cu$_3$O$_{7+\delta}$ | 90-110 |  |  |
| 1201 | HgBa$_2$CuO$_{4+\delta}$ | 98 | Hg$^{2+}$, O$^2$ |
| 1212 | YBa$_2$Cu$_3$O$_{7-\delta}$ | 92 | Cu$^{3+, 4+}$, O$^2$ |
| 1223 | TlBa$_2$Cu$_3$O$_{9+\delta}$ | 123 | Tl$^{3+}$, O$^2$ |
| 2201 | Tl$_2$Ba$_2$CuO$_6$ | 95 | Tl$^{3+}$, O$^2$ |
| 2212 | YBa$_2$Cu$_4$O$_8$ | 80 | Cu$^{1+, 3+}$, O$^2$ |
| 2223 | Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{12}$ | 112 | Tl$^{3+}$, O$^2$ |
| 2223 | Hg$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$ | 133 | Hg$^{2+}$, O$^2$ |
| 3201 | Pb$_2$(Sr, La)$_2$Cu$_2$O$_6$ | 32 | Pb$^{2+}$, Cu$^{4+}$ | Sr$^{2+}$, La$^{3+}$, O$^2$ |
| 3212 | Pb$_2$Sr$_2$YCu$_3$O$_8$ | 70 | Pb$^{2+}$, Cu$^{4+}$ |  |

$^a$For references of the structural data see e.g. Ref. [9]. $^b$see text.

TABLE II. Energies of lowest $d^9s$ and $d^9p$ states above the $d^{10}$ states (in cm$^{-1}$)

| | Cu$^{1+}$ | Zn$^{2+}$ | Ag$^{1+}$ | Cd$^{2+}$ | Au$^{1+}$ | Hg$^{2+}$ | Tl$^{3+}$ |
|-----|--------|--------|--------|--------|--------|--------|--------|
| $nd^9(n+1)s$ | 21928  | 76105  | 39164  | 80463  | 15039  | 42862  | 75052  |
| $nd^9(n+1)p$ | 66418  | 137876 | 80173  | 139042 | 63052  | 118616 | 147635 |

$^a$from Ref. [13]