Nonhomogeneous Charge Distribution in Layered High-T_c Superconductors

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We consider the problem of the charge distribution of holes among the various CuO_2 layers in the unit cell for compounds of type $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$. In analogy with graphite intercalation compounds, the charge distribution is strongly nonhomogeneous (for $n \gtrsim 3$) with a depletion in the central layers. This result points to a special importance of the bounding layers and it provides a way to understand the observed maximum T_c as a function of n.

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Among the many compounds synthesized since the discovery of high-temperature superconductivity,[1] particular attention has been focused on the layered compounds of the type $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ and related structures.[2,3] The peculiarity of these systems is that they can be prepared with a variable number (n) of CuO_2 layers per unit cell. A remarkable feature is that the maximum critical temperature observed for each type of compound is $T_c \simeq 90$ K for $n=1$, to $T_c \simeq 110$ K for $n=2$, and up to $T_c = 125$ K for $n=3$.[4] This gave rise to the expectation, based also on various theoretical arguments,[5,6] that T_c may increase monotonically with n up to a saturation value.

Very recently, however, it was shown[7] that $T_c \simeq 110$ K for $n=4$, and there is preliminary evidence for a similar decrease also for the other compounds[8] shown in Fig. 1. Therefore, there is an optimal value of n that maximizes T_c for a given class of compounds. The existence of a maximum actually appears quite reasonable if one considers the analogy[9] between these systems and graphite intercalation compounds (GIC).[10] A key feature of these compounds that governs various properties ranging from transport to in-plane bond length[11] is the strongly nonhomogeneous charge distribution among the various layers in the unit cell.[12]

In this Letter we consider the problem of the charge distribution for the layered superconductors. The relevant charge distribution consists in the number of holes induced in the half-filled Cu-O bands corresponding to the various CuO_2 layers. For $n \gtrsim 3$ this distribution is highly nonhomogeneous in analogy with GIC. The degree of nonhomogeneity depends on various material parameters. A natural consequence of this distribution is that the density of states available for superconductivity can have a maximum as a function of n, as observed experimentally for T_c. Since in our model the value of n corresponding to the maximum T_c becomes larger if the charge distribution is made more homogeneous, we can also provide some criteria for the optimization of the properties of these compounds.

Consider, for example, the structure of $Tl_2Ba_2Ca_2Cu_3O_{10}$ as schematically shown in Fig. 2 (note that the real unit cell is actually twice as large as the one shown in view of a geometric shift of planes that is irrelevant to our discussion). In the language of intercalation compounds this would be defined as a structure of stage 3 because it contains three CuO_2 layers per unit cell. A change of state would imply the addition or the elimination of one plane $(CuO_2)^{-2}$ and one plane Ca^{+2} in order to preserve charge neutrality. In Fig. 2 we also show nominal charges for the various layers. This assignment corresponds to the assumption that each (TlO) plane has a net charge $+1$. Assuming O^{-2}, this implies Tl^{+3}. In such a situation each of the three CuO_2 layers has a net charge of -2 that corresponds exactly to the case of CuO_2 layers in the undoped compounds La-Cu-O and Y-Ba-Cu-O.[2] This gives rise to the half filling of a

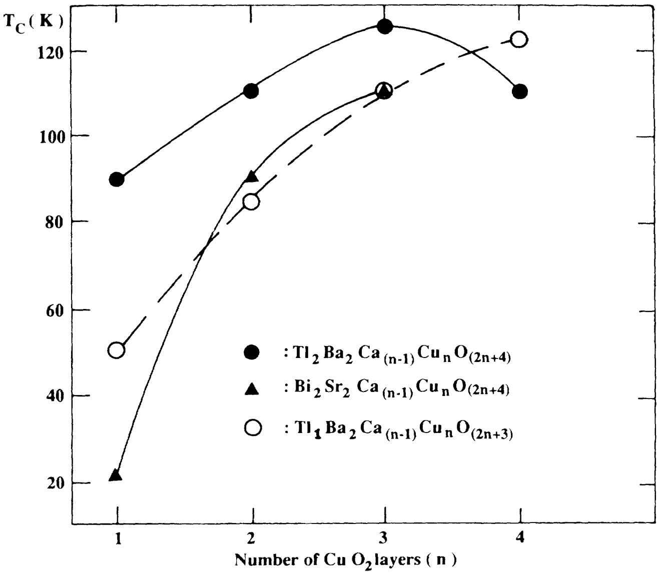

FIG. 1. Dependence of the critical temperature for superconductivity T_c as a function of the number of CuO_2 layers per unit cell (n) for various Tl and Bi compounds. The values reported are the maxima among the various samples measured.

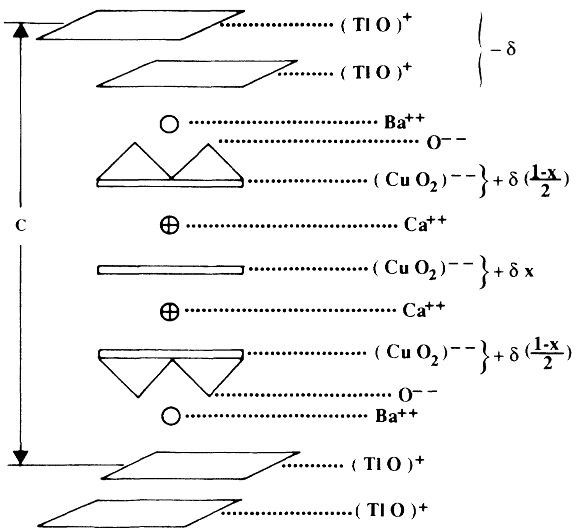

FIG. 2. Schematic picture of the layer structure of the stage-3 compound $Tl_2Ba_2Ca_2Cu_3O_{10}$ that corresponds to the present highest value of $T_c = 125$ K. The nominal charges would correspond to half filling of the Cu-O bands analogous to the undoped La and Y compounds. The TlO bands actually cross the Fermi level and acquire an extra charge density $-\delta$. This induces a density δ of holes to be shared (nonhomogeneously) among the three CuO_2 layers. Since holes are induced in the Cu-O bands in the stoichiometric compound, such a system may be considered as self-doped.

band arising from the hybridization of the d orbitals of copper and the p orbitals of oxygen.[13] It is known, however, that correlation effects led to an antiferromagnetic insulator for exactly half filling.[2,14,15]

The problem of charge transfer is actually more complex because the ionization of thallium is actually less than $+3$. From the point of view of band structure this implies that one of the TlO bands crosses the Fermi surface, as shown by various calculations.[5,16,17] This means that with respect to the nominal charges shown in Fig. 2 there is an extra amount of electrons in the TlO planes and a corresponding amount of holes induced in the CuO_2 layers. In this respect, these structures can be considered as self-doped, in the sense that holes are intrinsically generated in the half-filled Cu-O bands even in the stoichiometric compounds. This situation is different from the La-Cu-O or Y-Ba-Cu-O structures in which these holes can only be generated by doping the system by either metal (M^{+2}) ions or oxygen stoichiometry.

We also define the total charge of these extra electrons per pair of TlO planes as $-\delta$. This gives a density δ of holes to be shared among all the CuO_2 planes (Fig. 2). Up to stage 2 the CuO_2 layers in the system are equivalent and they will have the same amount of holes. For stage 3 (Fig. 2) and above, the problem of the charge distribution among the different CuO_2 layers becomes nontrivial exactly in the same sense as in intercalation compounds.[11] At first sight the structure in Fig. 2 may appear more complex than GIC due to the presence of several charge-compensating layers. These layers are, however, inert (in the sense that their charge is assumed to be fixed) and the only relevant geometric parameter is the distance d_0 between two consecutive CuO_2 layers.

The shape of the charge distribution is determined by two competing effects. The band energy would favor a homogeneous distribution while the electrostatic energy tends to induce the accumulation of charge in the CuO_2 layers that are near the TlO layers, depleting, therefore, the CuO_2 internal layers.

Assuming the charge to be distributed on two-dimensional sheets one can write the band energy $E_B(i)$ for the ith layer with charge δ_i (number density) as

$$E_B(i) = (\pi\hbar^2/2m^*)\delta_i^2 . \tag{1}$$

This expression corresponds to the assumption of parabolic bands with effective mass m^* for the holes induced in the half-filled bands. Note that it is not possible to relate m^* to band-structure calculations because the half-filled band is supposed to develop a gap due to correlation effects and the details of the band structure in this situation are unknown. It would be easy, however, to generalize Eq. (1) also to the case of more realistic (nonparabolic) bands.

Let us first consider the case $n \to \infty$ for which a continuum limit can be taken for the charge distribution $\rho(z) \simeq \delta(z_i)/\delta$ $(z_i = d_0 i)$ along the z axis. In this limit the band energy density is

$$E_B(z) = \frac{\pi\hbar^2\delta^2}{2m^* d_0}\int_0^z dz'[\rho(z')]^2 . \tag{2}$$

The electric field is

$$E(z) = -\frac{4\pi}{\epsilon}\delta + \frac{4\pi\delta}{\epsilon d_0}\int_0^z \rho(z')dz' , \tag{3}$$

where ϵ is the background dielectric constant. The relevant electrostatic energy density is then

$$U_e(z) = \frac{e^2\epsilon}{8\pi}\int_0^z [E(z')]^2 dz' . \tag{4}$$

The minimization of the total energy functional with respect to $\rho(z)$ leads to the equilibrium charge distribution

$$\rho(z) = \sqrt{A}\exp[-(\sqrt{A}/d_0)z] , \tag{5}$$

where

$$A = 4e^2 d_0 m^*/\epsilon\hbar^2 \tag{6}$$

is a dimensionless number. The characteristic length for the decay of the charge distribution is therefore $\lambda = d_0/\sqrt{A}$. Using the values $d_0 = 3.1$ Å,[3] $m^* \approx 4m_e$,[18] and $\epsilon \approx 12$ (notice that this is the background dielectric constant and it should refer to the polarization properties without the band that is explicitly considered in the calculation; we estimate for this a value of about half the experimental value), one obtains $A \approx 8$ that leads to $\lambda \approx d_0/3$. This shows that the charge distribution is strongly nonhomogeneous even on the scale of very few layers.

Let us now consider in detail the case $n=3$ as shown in Fig. 2. We define as δx the charge on the central layer; this gives $\delta(1-x)/2$ for the charge on the two bounding layers.

In this case the total band energy is

$$E_B(x) = (\pi\hbar^2/2m^*)\delta^2(\tfrac{3}{2}x^2 - x + \tfrac{1}{2}) \tag{7}$$

and the total electrostatic energy is (apart from constant terms)

$$U_e(x) = (\pi d_0 e^2/\epsilon)\delta^2 x^2 . \tag{8}$$

Minimizing the total energy with respect to x leads to

$$x = 1/(3+A) \quad (n=3) . \tag{9}$$

Using again $A \approx 8$, one obtains $x \simeq 0.1$ for the fraction of charge in the central layer while the fraction on each of the bounding layers is $(1-x)/2 \simeq 0.45$, showing again a strong nonhomogeneity of the charge distribution.

The same calculation can be easily done also for $n=4$ in which there are now two central layers with charge δx and two bounding layers each with charge $\delta(1-2x)/2$. The result is $x=1/(4+2A)$. For $A \approx 4$ the fraction of charge in each of the two central layers is $x \simeq 0.05$ while it is $(1-2x)/2 \simeq 0.45$ on the bounding layers.

These results therefore point to a special role of the bounding layers that contain most of the holes, and are close to the apex oxygens relevant for charge transfer.[19] We can now speculate about the consequence of this nonhomogeneous charge distribution in relation to the density of states that are involved in the superconductivity, and eventually about the transition temperature. In order to do so we have to make various assumptions that are difficult to test, especially in view of the absence of a microscopic theory for superconductivity. However, some general features are only weakly dependent on these assumptions and it is in this sense that the following discussion should be considered. In any case it would also be easy to consider the consequences of different assumptions. For example, here we assume that superconductivity can be related to the three-dimensional density of states while for a layered system with extremely small couplings between all the layers different pictures may be more appropriate.[20]

Let us focus on the density of states corresponding to the holes induced in the CuO_2 planes as a function of the stage n. Since for a parabolic band in two dimensions the density of states is constant, say, D_0, the three-dimensional density of states is given by

$$D(n) = nD_0/[d_1 + (n-1)d_0] , \tag{10}$$

where $d_1 = 11.62$ Å is the c-axis lattice constant for stage 1 and $d_0 = 3.1$ Å is the change of lattice constant corresponding to the addition of a CuO_2 and a Ca layer. These data refer to the Tl_2 compound as shown in Fig. 2.[3] The dependence given by Eq. (10) gives a monotonic increase of $D(n)$ with n as shown by curve C in Fig. 3. Strictly speaking, therefore the density of states is independent of the charge distribution.

The situation is, however, more complex because it is known from the studies on doped La-Cu-O and Y-Ba-Cu-O (Ref. 2) that superconductivity occurs only if the amount of holes induced in a CuO_2 layer exceeds a minimal value δ_0. Therefore one should consider the density of states only for those CuO_2 layers in which this condition is satisfied. In this respect Eq. (10) should be replaced by

$$D(n) = \frac{\sum_{i=1}^{n} D(\mu_i)\theta(\mu_i - \mu_0)}{d_1 + (n-1)d_0} , \tag{11}$$

where $\theta(\mu)$ is the step function, μ_i is the chemical potential defined from the bottom of each band for the ith layer corresponding to the charge distribution we have pre-

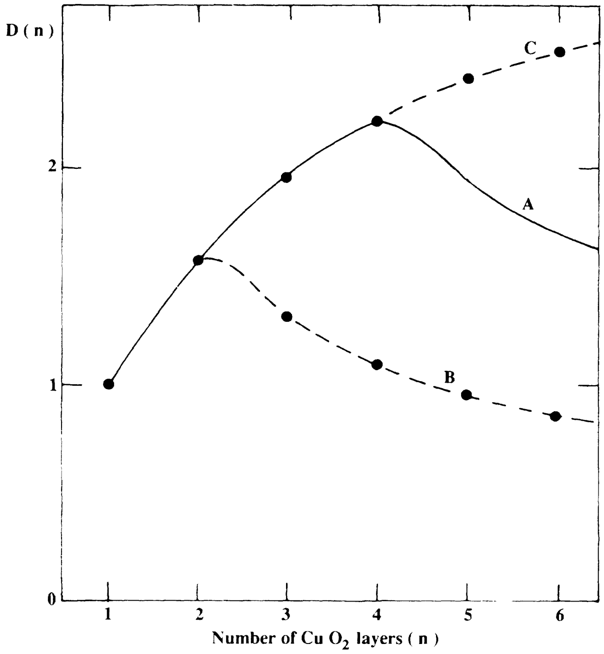

FIG. 3. Density of states $D(n)$ relevant to superconductivity (corresponding to the holes induced in the CuO_2 layers) as a function of the number of CuO_2 layers per unit cell (n). Curve C corresponds to the case in which all CuO_2 layers contribute to the density of states. Curve B corresponds to the situations in which already at stage 3 the hole density in the central layer is too small to contribute to superconductivity. Curve A shows instead the case in which the depletion of holes in the central layer makes it inactive only from stage 5 on. Assuming a monotonic dependence of T_c on $D(n)$ these results may provide an understanding of the $T_c(n)$ data of Fig. 1.

viously computed, and μ_0 is the chemical potential corresponding to δ_0.

Assuming for simplicity that the charge $-\delta$ induced in the pair of TlO layers is independent of the stage n of the compound, as is the case in graphite intercalation compounds,[11] we have that for $n=1$ the holes in the CuO_2 layer are δ. For $n=2$ we have $\delta_1=\delta_2-\delta/2$ and there is evidence that this value is well within the range of doping that gives rise to superconductivity in the La and Y compounds.[2,16] For $n=3$, however, we have a substantial decrease of hole density in the central layer as given by Eq. (11). If this density is less than δ_0, this gives rise to a deviation from the monotonic dependence of $D(n)$ on n as shown by curve B in Fig. 3. Curve A corresponds instead to the case in which the inactive layers only begin to appear from stage 5 on.

Assuming a monotonic relation between density of states and critical temperature T_c (as is the case in BCS theory), we can finally interpret the decrease of T_c at large stages (n) as due to the depletion of the hole density in the central layers. This leads to some interesting consequences. In fact, it should be possible to achieve higher values of T_c by designing compounds in which the maximum of T_c as a function of n is shifted as much as possible towards higher values of n. Finally, it should be remarked that the nonhomogeneity of the charge distribution among the various CuO_2 layers gives rise to specific predictions for various other properties. For example, the core-level spectroscopy should manifest a doubling or broadening of certain peaks for $n\geq 3$. Also, the transport properties of the normal (nonsuperconducting) state should show features that reflect this distribution in analogy with GIC.[10]

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