

Charge distribution in $Tl_2Ba_2Ca_2Cu_3O_{10}$

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We have calculated the distribution of holes among the CuO_2 layers in the unit cell of $Tl_2Ba_2Ca_2Cu_3O_{10}$. We find that, when the distribution of charge within the layers is taken into account, the distribution of holes among the layers is approximately uniform, in agreement with experimental indications.

It is well established that T_c in cuprate superconductors depends on the hole density on the CuO_2 planes, with T_c being maximum at a hole density of about 0.2 holes per Cu in the CuO_2 plane.¹⁻⁵ Consequently, the distribution of charge among the CuO_2 layers must be understood in order to describe adequately the variation of T_c with the number of CuO_2 layers per unit cell in layered cuprates with three or more CuO_2 planes.

There are experimental indications that there is a significant hole density on the inner layer. For example, T_c for the entire range of superconducting cuprates correlates closely with the bond valence sum $V_+ = 6 - V_{Cu(2)} - V_{O(2)} - V_{O(3)}$, where V_{Cu} and V_O are the copper- and oxygen-bond valence sums.^{6,7} However, for three-layer compounds V_+ must be calculated for the central CuO_2 layer; the correlation breaks down if V_+ is calculated for the outer layers as shown in Fig. 1, suggesting that there are a significant number of holes on the central layer. Also, the $n=3$ Bi and Tl cuprates lie on the underdoped side of $T_c(\text{max})$ while the $n=2$ and $n=1$ compounds lie on the overdoped side.⁴ If very little charge is transferred to the central layer the $n=3$ compounds should lie on the

overdoped side along with the $n=2$ compounds. Moreover, the change in doped hole concentration for $n=3$ is approximately $\frac{2}{3}$ that for $n=2$ when the two are subjected to the same change in annealing conditions.⁴ All this suggests that the distribution of charge among the three layers is approximately uniform.

In addition, in a recent ^{17}O NMR study in $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{19}$, Trokner *et al.*⁸ deduced temperature-dependent Knight shifts comparable to those in $YBa_2Cu_3O_{6.96}$ and $YBa_2Cu_3O_{6.60}$ for the outer and inner layers. This implies a hole density of 0.18 for the outer layer and 0.12 for the inner layer.⁶

Recently DiStasio, Müller, and Pietronero⁹ used a simple model in which the holes on the CuO_2 planes are assumed to form homogeneous sheets of charge. They found the distribution of holes among the CuO_2 planes in the $n=3$ Tl compound to be highly nonuniform with about 10% of the holes on the central layer and the remainder on the outer layers. We have modified their model to allow for the distribution of the charge *within* the planes and we find that, for physically reasonable values of the parameters, the distribution of holes *among* the planes is approximately uniform.

In the sheet charge model of DiStasio, Müller, and Pietronero⁹ the total energy per formula unit is given by the sum of a band term and an electrostatic term, which is calculated from the energy density of the electric field between two uniformly charged sheets:

$$U_T = \frac{\pi \hbar^2}{2m^* a^2} \delta^2 \left(\frac{3x^2}{2} - x + \frac{1}{2} \right) + \frac{\pi d_0 e^2}{\epsilon a^2} \delta^2 x^2, \quad (1)$$

where x is the fraction of the holes on the central CuO_2 layer, δ is the total charge per formula unit transferred from TlO layers to CuO_2 layers, m^* is the effective mass of holes in a two-dimensional CuO_2 band, d_0 is the separation between planes, and ϵ is the dielectric constant due to the electrons not included in the band term. To take account of the charge distribution within the planes, we replace the sheet charge electrostatic term by the Madelung energy per formula unit, as in purely ionic models,¹⁰⁻¹²

$$U_{es} = \frac{e^2}{2} \sum_R \sum_{q,q'} \frac{Z_q Z_{q'}}{|\mathbf{R} + \mathbf{q} - \mathbf{q}'|} = \frac{e^2}{2S} \sum_{q,q'} Z_q Z_{q'} S_{qq'}, \quad (2)$$

where Z_q is the charge at site q and the Madelung sums

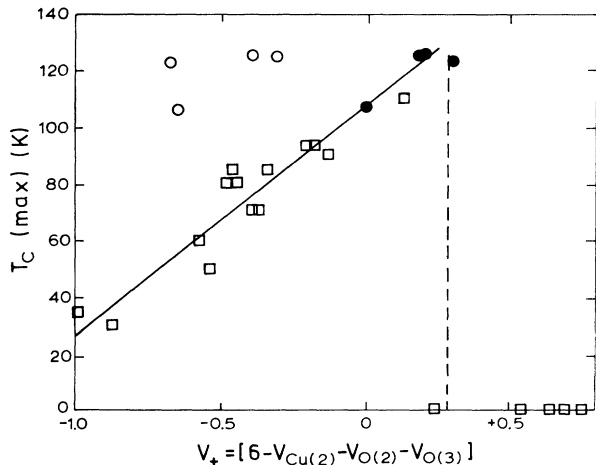


FIG. 1. Plot of $T_c(\text{max})$ vs the bond valence sum V_+ showing the breakdown of the correlation of $T_c(\text{max})$ with V_+ when V_+ is calculated using the outer layers. ●, V_+ calculated using the inner layers in Tl and Bi $n=3$ compounds; ○, V_+ calculated using the outer layers in Tl and Bi $n=3$ compounds; □, V_+ for other cuprate compounds (from Refs. 6 and 7).

$S_{qq'} = \sum_R S / |\mathbf{R} + \mathbf{q} - \mathbf{q}'|$ where S is the average Wigner-Seitz radius, can be calculated by standard techniques.¹³ We used the atomic positions quoted by Kasowski, Hsu, and Herman¹⁴ which are based on the measurements of Torardi *et al.*¹⁵ to calculate the Madelung sums. We assume the charge distribution shown in Table I, where f is the fraction of holes on Cu sites in a particular plane. Equation (2) can be written as a function of f and x :

$$U_{es} = \frac{e^2\delta}{2S} (a_1f + a_2x + a_3fx + a_4f^2 + a_5x^2 + a_6f^2x + a_7fx^2 + a_8f^2x^2), \quad (3)$$

ignoring terms independent of f and x , where the a_i depend on δ and the Madelung sums $S_{qq'}$. Or, for fixed f , U_{es} can be written as a function of δ and x :

$$U_{es} = \frac{e^2\delta}{2S} [b_0 + b_1\delta + (b_2 + b_3\delta)x + b_4\delta x^2], \quad (4)$$

where the b_i depend on f and the Madelung sums $S_{qq'}$. (Note that each $S_{qq'}$ is actually infinite, however, in the combinations that give the a_i and b_i the infinities cancel due to charge neutrality in the unit cell.) The total energy per formula unit becomes

$$U_T = \frac{\pi\hbar^2}{2m^*a^2} \delta^2 \left(\frac{3x^2}{2} - x + \frac{1}{2} \right) + \frac{e^2\delta}{3\epsilon S} [b_0 + b_1\delta + (b_2 + b_3\delta)x + b_4\delta x^2], \quad (5)$$

where a^2 is the area of the unit cell in the CuO_2 plane. The coefficients b_i for $f=0$ (all holes on O sites) and $f=1$ (all holes on Cu sites) are shown in Table II. The energies predicted by the sheet charge and point-charge models are shown in Fig. 2 for $m^*/m_e=4$, $\epsilon=12$ (DiStasio, Müller, and Pietronero⁹), and $\delta=0.45$ (this is close to the value calculated by Kondo¹¹ and consistent with that inferred from measurements of T_c). It is clear that with these values of the parameters the sheet charge model considerably overestimates the contribution of the electrostatic energy.

Equation (1) is minimized by

$$x_{\min} = \frac{1}{3 + 2A_s}, \quad (6a)$$

$$A_s = \frac{2m_e e^2 d_0}{\hbar^2} \left(\frac{m^*/m_e}{\epsilon} \right) = 2 \left(\frac{d_0}{a_B} \right) \left(\frac{m^*/m_e}{\epsilon} \right), \quad (6b)$$

TABLE I. The assumed charge on each atom.

Layer	Atom	Charge
	Tl	$3 - \delta/2$
	O 4	-2
	Ba	+2
	O 3	-2
	Ca	+2
Inner	Cu 1	$2 + fx\delta$
Inner	O 1	$-2 + \frac{1}{2}(1-f)x\delta$
Outer	Cu 2	$2 + \frac{1}{2}f(1-x)\delta$
Outer	O 2	$-2 + \frac{1}{4}(1-f)(1-x)\delta$

TABLE II. The coefficients b_i in Eq. (5).

	$f=0$	$f=1$
b_0	0.0000	-9.7757
b_1	0.0000	-0.2701
b_2	-0.6748	-0.5742
b_3	1.0725	1.5329
b_4	0.3817	-0.2522

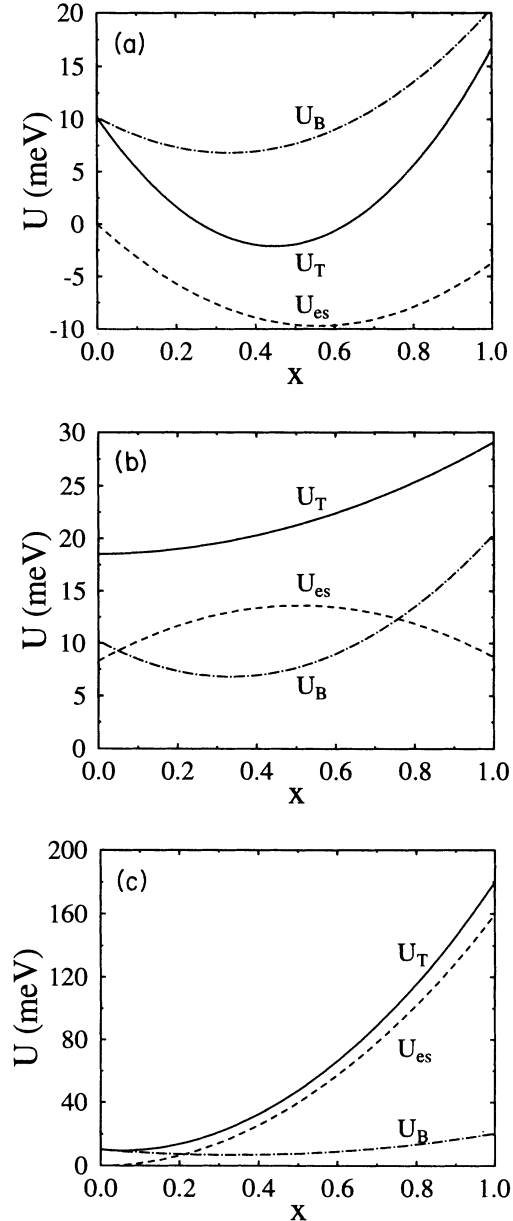


FIG. 2. The total (U_T), band (U_B), and electrostatic (U_{es}) energies as functions of x , the fraction of holes on the inner layer, for (a) the point-charge model with $f=0.0$ (all holes on O sites), (b) the point-charge model with $f=1.0$ (all holes on Cu sites) (note that 1.795 eV has been added to U_{es} and U_T so that they can be plotted on the same scale as U_B), and (c) the sheet charge model, taking $m^*=4m_e$, $\epsilon=12$, and $\delta=0.45$.

where a_B is the Bohr radius. So, in the sheet charge model the optimum fraction of holes in the central plane, x_{\min} , may lie between 0 ($A \rightarrow \infty$, i.e., $m^*/m_e \rightarrow \infty$) and $\frac{1}{3}$ ($A=0$, i.e., $\epsilon \rightarrow \infty$), independent of δ . For the point- or ionic-charge model Eq. (5) has a turning point at

$$x_{\min} = \frac{1 - A_p(b_2/\delta + b_3)}{3 + 2A_p b_4}, \tag{7a}$$

$$A_p = \left(\frac{m_e e^2}{\hbar^2} \right) \left(\frac{a^2}{\pi S} \right) \left(\frac{m^*/m_e}{\epsilon} \right) = \frac{1}{a_B} \left(\frac{a^2}{\pi S} \right) \left(\frac{m^*/m_e}{\epsilon} \right). \tag{7b}$$

If $b_4 < 0$ then if $A_p > \frac{3}{2} |b_4|$ then the turning point is a maximum and the minimum energy subject to the constraint $0 \leq x \leq 1$ is either at $x=0.0$ or $x=1.0$. If x_{\min} given by (7) lies outside $0 \leq x \leq 1$ then the energy minimum lies either at $x=0$ or at $x=1$. Figure 3 shows x_{\min} as a function of δ for a range of values of $(m^*/m_e)/\epsilon$ for $f=0$ (holes on O sites) and $f=1$ (holes on Cu sites). Note that to predict whether the holes are on O sites or Cu sites we would need to include a term allowing for the energy required to remove an electron from Cu^{2+} and the energy required to add an electron to O^- as in the ionic

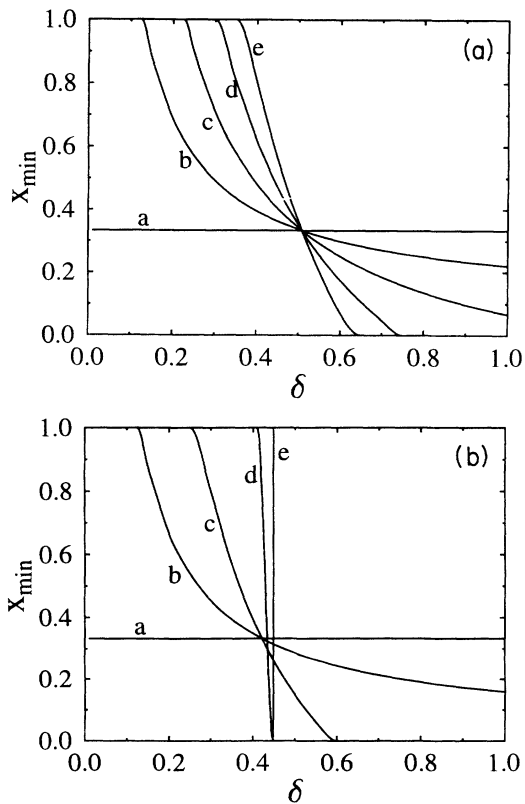


FIG. 3. The fraction of holes on the inner layer, x_{\min} , which minimizes the total energy as a function of the total number of holes transferred per formula unit, δ , in the point-charge model for (a) $f=0.0$ (all holes on O sites) and (b) $f=1.0$ (all holes on Cu sites), for $(m^*/m_e)/\epsilon=0.0$ (curve a), 0.1 (curve b), 0.3 (curve c), 1.0 (curve d), and ∞ (curve e).

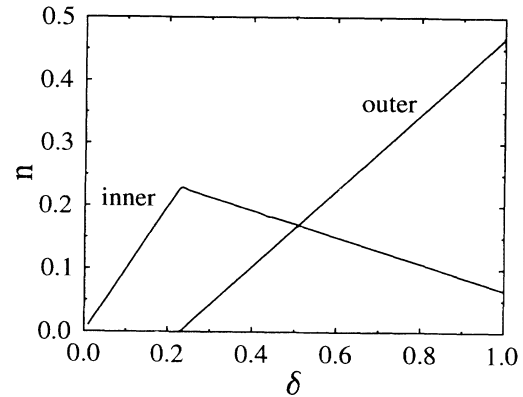


FIG. 4. The number of holes on the inner and outer layers in $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ as a function of the total number of holes transferred from the TlO layers per formula unit in the point-charge model with $m^*=4m_e$, and $\epsilon=12$. This corresponds to curve c of Fig. 3(a).

models of Kondo, Asai, and Nagai¹¹ and Torrance and Metzger.¹² However, so long as f is the same on all the CuO_2 layers such a term does not affect the distribution of charge among the layers. The results shown in Fig. 3 demonstrate that the optimum distribution of charge may vary between $x=1$ and $x=0$ depending on the amount of charge transferred from the TlO planes. Figure 4 shows the hole density on the inner and outer layers as a function of the amount of charge transferred from the Tl layer for plausible values of m^* and ϵ and for $f=0.0$ which implies the holes are on O sites as has been shown by photoemission.¹⁶ Since the charge transfer is expected to be around 0.4–0.6 holes per formula unit, Fig. 4 shows that the charge distribution will be nearly uniform. It also shows that as the charge transfer δ is increased the hole density on the inner plane approaches the optimum for superconductivity from above, while that on the outer plane approaches the optimum from below which raises the question as to whether the inner and outer layers can be separately optimized.

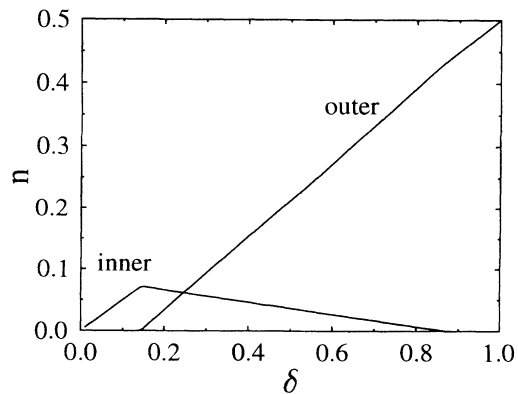


FIG. 5. The number of holes on the inner and outer layers in $\text{Tl}_2\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{12}$ as a function of the total number of holes transferred from the TlO layers per formula unit in the point-charge model with $m^*=4m_e$, and $\epsilon=12$.

A similar calculation can be carried out for the $n=4$ compound $Tl_2Ba_2Ca_3Cu_4O_{12}$ and the results for $f=0.0$ and the same values of m^* and ϵ as in the $n=3$ compound, are shown in Fig. 5. Unlike the $n=3$ compound, the $n=4$ compound has an inhomogeneous charge distribution with 10%–20% of the holes on the inner layers when the charge transfer from the TlO layers is around 0.4–0.6 holes per formula unit. The dependence of the number of holes on the inner and outer planes on the charge transfer δ is qualitatively the same as for $n=3$. However, in $n=3$ the value of δ for which the charge distribution among the planes is homogeneous is given by

$$x_{\min} = \frac{1}{3} \rightarrow \delta = -b_2/(b_3 + \frac{2}{3}b_4) = 0.51,$$

using the values quoted in Table II for $f=0$, which is within the range of the expected actual charge transfer so we expect the charge distribution to be close to homogeneous in the $n=3$ compound. In $n=4$ the homogeneous distribution among the planes occurs when

$$\delta = -b_2/(b_3 + b_4) = 0.25,$$

with $b_2 = -0.4889$, $b_3 = 1.0592$, and $b_4 = 0.9243$ for $f=0$, which is outside the range of the expected actual charge transfer so we expect the actual charge distribution to be inhomogeneous. The b_i depend on the assumed ionic charges (Table I) and the crystal structure. In particular,

b_4 (the coefficient of $x^2\delta^2$) depends on the interactions within and between the CuO_2 planes so it is not surprising that it changes markedly when the number of planes increases.

Since the sheet charge and point-charge models represent two extreme approximations to the actual charge distribution within the CuO_2 layers, which should be intermediate between these extremes, we expect that the actual charge distribution among the CuO_2 layers is intermediate between the predictions of these extreme models. We note, however, that the predictions of the point-charge model are not very sensitive to reducing the assumed ionicity of the CuO_2 planes.

Using our simple model we conclude that, in contrast to the results of the sheet charge model and in agreement with experimental indications, the holes in the $n=3$ layered cuprate superconductors are likely to be more or less evenly distributed among the CuO_2 layers. In $n=4$ materials the holes are likely to be concentrated in the outer layers, as predicted by the sheet charge model.

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