The Structure and a Bond-Valence-Sum Study of the 1-2-3 Superconductors \((\text{Ca}_x\text{La}_{1-x})(\text{Ba}_{1.75-x}\text{La}_{0.25+x})\text{Cu}_3\text{O}_y\) and \(\text{YBa}_2\text{Cu}_3\text{O}_y\)

O. Chmaissem\(^a\), Y. Eckstein\(^b\), and C.G. Kuper\(^b\)

\(^a\)Material Sciences Division, Argonne National Laboratory, Argonne, IL 60439, U.S.A, and
Department of Physics, Northern Illinois University, DeKalb, IL 60115, U.S.A.

\(^b\)Department of Physics and Crown Center for Superconductivity, Technion — Israel Institute of Technology, 32000 Haifa, Israel

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Abstract

We present a study of the crystal structure of the 1-2-3 superconductor \((\text{Ca}_x\text{La}_{1-x})(\text{Ba}_{1.75-x}\text{La}_{0.25+x})\text{Cu}_3\text{O}_y\) (“CLBLCO”). Because of the presence of both La and Ba ions in the “Ba” layer, the local symmetry of \(\text{YBa}_2\text{Cu}_3\text{O}_y\) (“YBCO”) is lost. One can no longer assume that an “apical” oxygen atom always lies strictly on the line joining CuI and CuII ions, and a Pauling bond-valence calculation is very useful as an adjunct to the Rietveld refinement of the positions of the La and Ba ions. When a Rietveld analysis is performed allowing for the possibility that the apical oxygen atoms may be slightly displaced along the \(a\) or \(b\) direction, the bond valence sums for both La and Ba are close to the natural oxidation states of these ions.

We have also used the bond-valence-sum method to study the mean oxidation states of the CuI and CuII ions in both CLBLCO and YBCO. Our results for YBCO differ from some previously published results. Our main conclusion is that, while the method may be useful in finding the charge con-
centration on the CuII plane, it definitely does not yield the concentration of mobile holes, nor the concentration of superconducting charge carriers.

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I. INTRODUCTION

Soon after the discovery [1] of YBa$_2$Cu$_3$O$_y$ ("YBCO") — the first of the “1-2-3” high-temperature superconductors — its structure (Fig. 1) was reported [2]. Various substituents have also been studied, but under the assumption that no substantial changes in the structure occur. Besides illustrating the well-known 1-2-3 structure, Fig. 1 also defines our labelling convention for the distinct copper and oxygen sites.

The critical temperature $T_c$ of cuprate superconductors can be varied by changing the “doping” level (i.e. by varying the oxygen content $y$ or by replacing a cation with another of different valency). There is an “optimum” doping level, for which $T_c$ is a maximum. However, in the 1-2-3 series, overdoping by only varying the oxygen content is usually limited to a very small decline in $T_c$.

This paper reports a study of an intriguing family [3] of 1-2-3 materials $(Ca_xLa_{(1-x)})(Ba_{(c-x)}La_{(2-c+x)})Cu_3O_y$ (“CLBLCO”). An attractive feature of CLBLCO is that, regardless of the values of $x$ and $y$, it always crystallizes in the tetragonal space group $P4/mmm$. As indicated by the way in which we have written the chemical formula, the lanthanum ions occupy two independent crystallographic sites: the “yttrium” $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and the “barium” $(\frac{1}{2}, \frac{1}{2}, z)$ sites of YBCO. (But note that in CLBLCO, the $z$ of La differs slightly from that of Ba.) These two La ionic positions will be denoted La$_{(Y)}$ and La$_{(Ba)}$ respectively. The tetragonality of the material implies that there are no extended “chains” (such as exist in YBCO); the oxygen atoms in the CuI layer are distributed randomly with respect to the $a$ and $b$ directions, and therefore the notation $O_b$ is inappropriate. We will call
these oxygen atoms $O_{\alpha}$, and similarly we will not distinguish between $O_{pa}$ and $O_{pb}$ sites; we label them $O_p$. We note that, for a given set of parameters, our recipe for preparing samples always yields the same $T_c$; this implies that the different types of unit cells (e.g. cells containing Ca and Ba, La and Ba, etc.) are randomly distributed. This fact, together with the tetragonality of the crystal, gives us confidence that the distribution of $O_{\alpha}$ atoms is uniform (although there is no direct evidence). Because the ionic radii of Ba ($R_{(Ba^{+2})} = 1.34\,\text{Å}$) and La ($R_{(La^{+3})} = 1.016\,\text{Å}$) are so very different, we might expect that there will be some distortion of the lattice, and in particular that the $O_c$ and $O_{\alpha}$ atoms will suffer some lateral displacement. A study of this distortion will be one of the main topics of the present paper.

The second attractive feature of CLBLCO is that it is possible to cover the entire range from complete underdoping to complete overdoping by varying only the oxygen content $y$ (in contrast to YBCO, which can be significantly overdoped only by introducing some foreign cations).

The source for our analysis will be the neutron-diffraction data of Chmaissem et al.\cite{4} The method will be a “symbiotic” one, using the techniques of Rietveld refinement\cite{5,ref3} and Pauling bond-valence summation\cite{6,7,8} (BVS). We shall also use the BVS technique to determine separately the average oxidation states (“valence”) of the CuI and CuII ions (since from the stoichiometry it is only possible to compute the global average). We have made BVS calculations for YBCO, and disagree with previously published results which purported to find the concentration of mobile holes on the CuO$_2$ planes. We shall demonstrate that while this procedure probably gives a reasonable approximation to the correct oxidation states of the CuI and CuII layers, it does not give the concentration of mobile charge carriers.

\section*{II. PAULING’S BOND VALENCE SUM TECHNIQUE}

Pauling\cite{6,9} introduced the concept of fractional valences, which he ascribed to the interionic bonds in an ionic crystal, such that the sum of the bond valences (BVS) on an ion
shall be equal to its oxidation state. The bond valence between a cation and a neighboring anion is usually well represented by \( \exp\{ (r_0 - r)/B \} \), where \( B \) is a universal constant having the value 0.37 Å, where \( r_0 \) has a characteristic value for a given cation–anion pair and where \( r \) is the interionic distance. Where an ion can exist with several different oxidation states, the value of \( r_0 \) will depend on the oxidation state. Table I shows all the relevant \( r_0 \) values (taken from Brown and Altermatt [10]). The idea is that the sum of these empirical bond valences about a given ion should agree with that ion’s oxidation state. Any significant discrepancy (say over 30%) between the BVS and the true oxidation state represents strain in the crystal, and may even indicate that the assumed structure is incorrect. The BVS technique has sometimes proved a useful tool in checking crystal structures.

In §3, we first report the positions of the Ba and La\(_{(Ba)}\) ions, as found by a preliminary Rietveld refinement of the neutron-diffraction data of Chmaissem et al. [4]. We find two indications that the resulting picture cannot be exact:

(a) When we calculate BVS’s for these ions, we find BVS’s for La\(_{(Ba)}\) below 2; these are manifestly unacceptable, since the oxidation state of lanthanum is known unambiguously to be La\(^{+3}\). This discrepancy is an indication that this layer is indeed significantly distorted.

(b) The presence of anomalously large atomic displacement parameters (“adp’s”) \( U_{CuI} \), \( U_{O_a} \), and \( U_{O_c} \), for the CuI, O\(_a\), and O\(_c\) ions respectively, tend to confirm the above indication.

In §4, guided by the anomalous BVS values, we repeat the Rietveld analysis, without the constraint that the O\(_a\) and O\(_c\) atoms occupy their “ideal” positions (we continue to rely on the fact that the La and Ba ions in the “Ba” layer are distributed randomly). The new Rietveld-refined structure is then tested by recalculating the BVS’s for the La and Ba ions. We show that the new structure is fairly satisfactory.

We have previously reported [11] BVS calculations for the CuI and CuII ions and the O\(_a\) and O\(_c\) ions, both in YBCO and in CLBLCO. The motivation for these calculations was to determine the separate average oxidation states of the two types of Cu sites. However, the global average of the BVS’s of the CuI and CuII layers does not agree with the global average oxidation state as determined by the stoichiometry. This discrepancy arises because the
interatomic distances (and therefore also the BVS’s) are constrained by the lattice structure; these internal strains must somehow be taken into account.

We will describe the methods proposed by Brown [12] and Tallon [13] to correct for the discrepancy. In particular, Brown calculates the average oxidation state $2 + p$ of the CuII ions, and asserts that this $p$ is the concentration of Cu$^{+3}$ ions in the CuO$_2$ plane (after making a correction for the strain), i.e. $p$ is the number of holes in this plane. In Tallon’s approach, the concentration of Cu$^{+3}$ ions is not assumed to be the number of holes in the CuO$_2$ plane; he includes a contribution from the BVS’s of the oxygens to estimate the number $p$ of holes in the plane. The two approaches do not agree; we describe both of them, and discuss our preference. We also challenge the widely-held conjecture that $p$ represents the concentration of mobile holes.

III. NAÏVE BOND VALENCE SUMS FOR CALCIUM, LANTHANUM, AND BARIUM

Table 2 is a specimen table [14], for calcium concentration $x = 0.4$ and oxygen concentration $y = 6.898$ giving the positions and adp’s of all the ions, as calculated by rietveld refinement from the neutron-diffraction data of Chmaissem et al. [4], assuming that the structure is undistorted. The lattice constants and the distances are in Angstrom units, in all the tables, and the adp’s in Tables 2 and 5 are in units of Å$^2$. Table 3 is the full table of the relevant interionic distances, calculated from the ionic coordinates. Using these distances as a first approximation, the BVS’s of Ca, La, Ba, and O were calculated, and are shown in Table 4, as $\text{BVS}^0_{\text{Ca}}$, etc. The results clearly show that distortion is present.

An example of the calculation is given, for $x = 0.4$ and $y = 6.898$:

$$
\text{BVS}^0_{\text{La(Ba)}} = \sum \exp((r_0 - r)/B)
$$

$$
= 4 \exp\{r_0(\text{La})-r(\text{La(Ba)} \text{ to } O_p))/B\]
$$

$$
+ 4 \exp\{r_0(\text{La})-r(\text{La(Ba)} \text{ to } O_c))/B\]
$$
\[+2(y - 6)\exp\{r_0(\text{La}) - r(\text{La}_{(\text{Ba})} \text{ to O}_\alpha)\}/B\]

\[= 4 \exp\{(2.172 - 2.721)/0.37\} + 4 \exp\{(2.172 - 2.797)/0.37\}\]

\[+ 0.852 \exp\{(2.172 - 3.055)/0.37\}\]

\[= 1.811\] (2)

We see that the BVS of La_{(Ba)} is quite unacceptable, although the BVS’s of La_{(Y)} and Ca are reasonable. We attribute this anomaly for La_{(Ba)} to the distortion induced by the great discrepancy between the La and Ba ionic radii. A further indication that the lattice is distorted is the fact that the adp’s found by Chmaissem et al. for some of the oxygen atoms are anomalously large. They can be improved significantly by assuming that they are not isotropic, but have elliptical symmetry. However, we do not believe that these adp’s are thermal in origin, but rather reflect the possibility that the positions of the O_\alpha and O_c ions depend on the nature of their neighbors, and may suffer static displacements.

IV. IMPROVED BOND VALENCE SUMS FOR CALCIUM, LANTHANUM, AND BARIUM

We should expect the displacements of O_c and O_\alpha ions to depend on their environment. Each O_c has four closest neighbors, which may be La^{3+} or Ba^{2+}. These ions have very different radii \(R_{(\text{La}^{3+})} = 1.016 \text{ Å}; R_{(\text{Ba}^{2+})} = 1.34 \text{ Å}\). We shall assume that the La and Ba are distributed randomly. There are six possible environments for an O_c, as illustrated in Fig. 2. In cases A, B, and C, the symmetry implies that the O_c oxygen atom will not suffer any sideways displacement (but it can be displaced longitudinally to achieve favorable bond lengths). However, because the ionic radius of La is so much smaller than that of Ba, the O_c in cases D, E, and F will clearly be displaced away from Ba ions and towards La ions. We also note that cases A and B are nondegenerate, that case C is doubly degenerate, and that cases D, E, and F are each fourfold degenerate. Let the number of Ba ions per
formula unit be \(2b\), and the number of \(\text{La}_b\) ions be \(2l\), (where, from the chemical formula, \(l + b = 1\)). Because the distribution is assumed to be random, the percentage of displaced \(O_c\) ions in each of the six configurations can be calculated. Thus the total probability \(q_1\) of the \(O_c\) not being displaced is

\[q_1 = l^4 + b^4 + 2b^2l^2,\]

the probability \(q_2\) that \(O_c\) is displaced diagonally is

\[q_2 = 4(l^3b + lb^3),\]

and the probability \(q_3\) of displacement along the \(a\) or \(b\) crystallographic directions is

\[q_3 = 4b^2l^2.\]

Note that \(q_1 + q_2 + q_3 = 1\), i.e. we have taken all possible configurations into account.

The Rietveld refinement was repeated, allowing the \(O_c\) ions to occupy slightly different positions \(r(O_c(1)), r(O_c(2)), r(O_c(3))\), where \(r(O_c(1))\) lies along the \(c\)-axis, but \(r(O_c(2))\) is displaced diagonally from the \(c\)-axis, and \(r(O_c(3))\) is displaced along an \(a\) or \(b\) direction from the \(c\)-axis (Table 3). The relative occupancy of the three sites are given by the configuration-dependent probabilities \(q_1, q_2\) and \(q_3\).

Analogously, the \(O_\alpha\) ions can also suffer displacements depending on their environments. The calculation here is somewhat simpler, since there appears to be a tendency for the \(\text{La}_b\) ions to dimerize, i.e. if there is an \(\text{La}\) ion at position \((\frac{1}{2}, \frac{1}{2}, \zeta)\), it is probable that there is another one at \((\frac{1}{2}, \frac{1}{2}, -\zeta)\). This tendency is indirectly confirmed by the Rietveld neutron refinements. The presence of a lanthanum dimer should leave the \(O_\alpha\) ion in the basal plane. Indeed the \(z\) coordinates of the \(O_\alpha\)'s refined to zero, confirming that there is no displacement along the \(z\) direction and supporting our view that the \(\text{La}\) ions indeed form dimers. However, when the \(O_\alpha\)'s are allowed to occupy the two sites \((\frac{1}{2}, 0, 0)\) and \((\frac{1}{2}, \eta, 0)\) — but are constrained to be confined to the basal plane — the adp is greatly reduced. Allowing only \((\frac{1}{2}, 0, 0)\) sites yields adp's in the range from \(U_{O_\alpha} = 4\) to \(7\), but allowing the additional
site ($\frac{1}{2}, \eta, 0$) reduces them to the reasonable range from $U_{O_{\alpha}} = 1.5$ to 2. Some correlation was seen between the position, the site occupancy, and the adp’s for the two sites, and a final refinement was made keeping this adp fixed at its average value, $U_{O_{\alpha}} = 1.8$. This refinement is the source [4] for new positions and occupancies — see the specimen Table 5, which replaces Table 2. Table 6 is the full table of the interatomic distances, calculated from the revised coordinates; these new distances are used in the subsequent calculations.

The BVS calculations for Ca and La$_{(Y)}$ are straightforward, and proceed exactly as in §3. However, the calculations for Ba and La$_{(Ba)}$, require some care. The main new feature in calculating the Ba and La$_{(Ba)}$ sums is that the $O_c$ environment of a given cation will depend on the three other cation neighbors of that $O_c$. Thus, if we focus our attention on a given La ion, with its four $O_c$ neighbors, the probability $Q(1, \text{La}_{(Ba)})$ that one of its $O_c$ neighbors is undisplaced is (from cases B and C, Fig. 2)

$$Q(1, \text{La}_{(Ba)}) = b^3 + l^3,$$

where $b$ and $l$ are the concentrations of Ba and La respectively.

Cases C and D yield a total probability of $3bl^2 + b^3$, which we split into the two parts

$$Q(2, \text{La}_{(Ba)}) = bl^2 + b^3,$$

corresponding to the case where the $O_c$ is “pushed towards” the given La, and

$$Q(3, \text{La}_{(Ba)}) = 2bl^2,$$

where the displacement of $O_c$ is orthogonal to the undistorted La—$O_c$ bond direction. Finally, the probability $Q(4, \text{La}_{(Ba)})$ of displacement along an $a$ or $b$ direction is:

$$Q(4, \text{La}_{(Ba)}) = 2bl^2.$$

The $Q’s$ for Ba are obtained similarly, by interchanging $l$ and $b$.

As an example, we show the recalculated BVS for La$_{(Ba)}$ for $x = 0.4$ and $y = 6.926$, (which supersedes Eq. (2)):

$$BVS_{\text{La}_{(Ba)}} = \sum \exp\{(r_0 - r)/B\}$$

$$= 4 \exp\{\{r_0(\text{La}) - r(\text{La}_{(Ba)} \text{ to } O_p)\}/B\}$$
\[
+4 \sum_{s=1}^{4} Q_s(s, \text{La}) \exp\{r_0(\text{La}) - r(\text{La}_{(\text{Ba})} \text{ to } O_{c(s)})\}/B \\
+2 \sum_{t=1}^{2} n_t \exp\{r_0(\text{La}) - r(\text{La}_{(\text{Ba})} \text{ to } O_{\alpha(t)})\}/B \\
= 4 \left[ \exp\{-(2.172 - 2.937)/0.37\} + 0.182 \exp\{-(2.172 - 2.754)/0.37\} + 0.379 \exp\{-(2.172 - 2.380)/0.37\} \right. \\
+ 0.143 \exp\{-(2.172 - 2.779)/0.37\} + 0.296 \exp\{-(2.172 - 2.457)/0.37\} \right] \\
+2[0.516 \exp\{-(2.172 - 2.831)/0.37\} + 0.408 \exp\{-(2.172 - 2.378)/0.37\}] \\
= 2.821
g.
\]

This example illustrates the improvement which the revised Rietveld refinement has made in the valence of La.

V. AVERAGE VALENCE OF COPPER IN THE COPPER-I AND COPPER-II LAYERS

All the non-copper ions have well-defined oxidation states; only that of the copper is variable, taking values ranging from +1 to +3 depending on the oxygen content \(y\). (Although, by its definition, the oxidation state of an atom can take only integer values, the average oxidation state of Cu on the CuI or CuII layer will, in general, not be an integer.)

The difficulty in assigning oxidation states to the Cu ions in 1-2-3 materials is that the stoichiometry can only give a global average oxidation state. Pauling’s empirical BVS method was first applied by de Leeuw et al. [13], and Cava et al. [16], and it has become popular [13] to rely on this method, in order to assign separate average oxidation states to the “chain” and “plane” copper layers (CuI and CuII layers respectively).

The motivation for using BVS’s is the belief that they yield good approximations to the actual oxidation states. Following Brown [12], we calculate BVS’s for copper in both the CuI and CuII layers; our expectation is that the appropriately weighted average of the CuI
and CuII BVS’s should yield the true average oxidation state. Let us assume that a fraction \( \xi \) of the Cu ions in one of the layers are Cu\(^{+3} \), so that \((1 - \xi)\) are Cu\(^{+2} \). The average charge (oxidation state) per Cu ion in this layer is thus

\[
V_{\text{Avg}} = 3\xi + 2(1 - \xi) = 2 + \xi.
\]

This should be equal to \( \xi V^{(+3)} + (1 - \xi)V^{(+2)} \), where \( V^{(+3)} = (\text{BVS}_{\text{Cu}^{+3}}) \), i.e. the BVS, calculated using \( r_0(\text{Cu}^{+3}) = 1.73 \, \text{Å} \), and \( V^{(+2)} = (\text{BVS}_{\text{Cu}^{+2}}) \). Hence, solving for \( \xi \), we have (cf. Brown [12]):

\[
\xi = (V^{(+2)} - 2)/(V^{(+2)} + 1 - V^{(+3)}). \tag{4}
\]

Our procedure is thus: (a) calculate \( V^{(+2)} \) and \( V^{(+3)} \), for the CuI layer, and find \( \xi_I \) (i.e. the concentration of Cu\(^{+3} \) ions in this layer); (b) similarly calculate \( V^{(+2)} \) and \( V^{(+3)} \) for the CuII layer, and find \( \xi_{II} \); (c) find the global average (remembering that there are two CuII layers and only one CuI layer in the unit cell):

\[
V_{\text{Avg}}^{\text{Global}} = (V_{\text{Avg}}^{\text{CuI}} + 2V_{\text{Avg}}^{\text{CuII}})/3 = (6 + \xi_I + 2\xi_{II})/3. \tag{5}
\]

As an example, we describe the detailed calculation of \( V^{(+2)}_{\text{CuII}} \) for CuII, with \( x = 0.4 \) and \( y = 6.926 \):

\[
V_{\text{CuII}}^{(+2)} = 4 \exp\{r_0(\text{Cu}^{+2}) - r(\text{CuII to } \text{O}_p)/B\}
+ \sum_{u=1}^{3} q_u \exp\{r_0(\text{Cu}^{+2}) - r(\text{CuII to } \text{O}_{c(u)})/B\}
= 4 \exp\{(1.679 - 1.946)/0.37\} + 0.315 \exp\{(1.679 - 2.292)/0.37\}
+ 0.492 \exp\{(1.679 - 2.322)/0.37\} + 0.193 \exp\{(1.679 - 2.336)/0.37\}
= 2.123 \tag{6}
\]

The calculation of \( V_{\text{CuII}}^{(+3)} \) proceeds similarly, merely replacing \( r_0(\text{Cu}^{+2}) = 1.679 \) by \( r_0(\text{Cu}^{+3}) = 1.730 \), giving \( V_{\text{CuII}}^{(+3)} = 2.437 \), whence \( \xi = 0.180 \), and the average BVS of CuII is \( V_{\text{CuII}}^{\text{Avg}} = 2.180 \).
The calculations for CuI are similar, using the distances \( r(\text{CuI to O}_{\alpha(1)}) \), \( r(\text{CuI to O}_{\alpha(2)}) \), \( r(\text{CuI to O}_{c(1)}) \), \( r(\text{CuI to O}_{c(2)}) \), and \( r(\text{CuI to O}_{c(3)}) \), and the appropriate weight factors \( n(\text{O}_{\alpha(u)}) \) and \( q_u \). The result is that \( V_{\text{AvgCuI}} = 2.079 \).

The global average BVS is

\[
V_{\text{Global}}^{\text{Avg}} = \left( V_{\text{AvgCuI}} + 2V_{\text{AvgCuII}} \right) / 3 = 2.146. \quad (8)
\]

The full results are given in Table 8. Note that these averages do not agree with the average oxidation states, as calculated from the stoichiometry of the material. (For the example above, the global average from stoichiometry is 2.201.) This discrepancy — which we interpret as an indication that bond lengths are constrained by the crystal structure — will be discussed in §8.

VI. BOND VALENCE SUMS FOR THE OXYGEN IONS

The calculations for oxygen are not completely straightforward. The principal complication arises from the fact that the Cu ions may be in either of the states Cu\(^{+2}\) and Cu\(^{+3}\), and therefore we must use the mixing ratios \( \xi_I \) and \( \xi_{II} \) as weights in finding the contributions from the Cu ions. Many previously published papers \[13\] \[16\] \[17\] \[18\] did not make use of the \( \xi' \)s, but made the assumption, de facto, that both \( \xi_I \) and \( \xi_{II} \) were zero.

We illustrate the calculation by the example of \( \text{O}_{c(2)} \) for \( x = 0.4 \) and \( y = 6.926 \):

\[
(BVS)_{\text{O}_{c(2)}} = \xi_I \text{exp}\left[-\{r(\text{CuI to O}_{c(2)}) - r_0(\text{Cu}^{3+})\}/B\right]
+ \xi_{II} \text{exp}\left[-\{r(\text{CuII to O}_{c(2)}) - r_0(\text{Cu}^{3+})\}/B\right]
+ (1 - \xi_I) \text{exp}\left[-\{r(\text{CuI to O}_{c(2)}) - r_0(\text{Cu}^{2+})\}/B\right]
+ (1 - \xi_{II}) \text{exp}\left[-\{r(\text{CuII to O}_{c(2)}) - r_0(\text{Cu}^{2+})\}/B\right]
+ \left\{ b^2 l / (b^2 l + b^2 \ell) \right\} \text{exp}\left[-\{r(\text{Ba to O}_{c(2)}) - r_0(\text{Ba})\}/B\right]
+ \left\{ b l^2 / (b^2 l + b l^2) \right\} \text{exp}\left[-\{r(\text{La}_{(Ba)} to O_{c(2)}) - r_0(\text{La})\}/B\right]
= 1.929 \quad (9)
\]
The full results for the oxygen BVS’s are shown in Table 9.

VII. YBCO

Cava et al. [16] have found the locations of the atoms in YBCO by neutron diffraction, and have used their data to calculate the BVS’s of all the ions present. In some respects the situation is much simpler here than for CLBLCO. The O\textsubscript{c} and O\textsubscript{α} ions are never displaced, so that we do not have O\textsubscript{c(2)}, O\textsubscript{c(3)} or O\textsubscript{α(2)} present. However, there is a complication with respect to the copper ions. When \( y \) is close to 6, the average oxidation state in the CuI layer (chain layer) can be less than 2, \( i.e. \) we may think of the layer as containing a mixture of Cu\textsuperscript{+} and Cu\textsuperscript{+2}. But for rather larger \( y \), the average oxidation state will be greater than 2, and the layer will be a mixture of Cu\textsuperscript{+3} and Cu\textsuperscript{+2}. (The assumption is made that Cu\textsuperscript{+} and Cu\textsuperscript{+3} cannot coexist in any one Cu layer.) To allow for the possibility that a mixture of Cu\textsuperscript{+2} and Cu\textsuperscript{+} is present in a layer, we introduce a new mixing ratio \( \xi^{(1)} \), which is easily shown (by analogy to the calculation of \( \xi \), see Eq. (4) ) to be:

\[
\xi^{(1)} = \frac{V^{(+2)} - 2}{V^{(+2)} - 1 - V^{(+1)}},
\]

where \( V^{(+1)} \) is the BVS for Cu\textsuperscript{+} \( (i.e. \) the BVS calculated with \( r_0 = 1.60) \). If Cu\textsuperscript{+} is present, and not Cu\textsuperscript{+3}, we will find that \( \xi^{(1)} \) is positive, and \( \xi \) is negative, while when Cu\textsuperscript{+3} is present, \( \xi \) is positive and \( \xi^{(1)} \) negative. We therefore always use whichever of the \( \xi \)'s is positive. This complication never arises in CLBLCO, since there \( y \) is never less than about 6.4, and no Cu\textsuperscript{+} will be present; both the CuI and CuII layers will be mixtures only of Cu\textsuperscript{+2} and Cu\textsuperscript{+3}.

There are two reasons for repeating the BVS calculations for YBCO: Firstly, many of the published calculations [13] [16] [17] [18] contain a conceptual error, which we wish to correct. In calculating oxygen BVS’s, these papers make the tacit assumption that only Cu\textsuperscript{+2} is present, \( i.e. \) that \( \xi = \xi^{(1)} = 0 \). And secondly, we hope to show that the comparison between YBCO and CLBLCO can help to clarify the question of the charge on the CuII
plane. Moreover, we discuss the question as to what fraction of that charge is mobile; and we test whether there is a universal relation between the maximum value of $T_c$ and the concentration of holes for all high-$T_c$ materials (as proposed by Tallon [13]). We have recalculated the BVS’s from the data of Cava et al., and were able to confirm their results for copper, barium, and yttrium. However, we could reproduce their results for oxygen only under the assumption that for this calculation $\xi = \xi^{(1)} = 0$, (i.e. that all the copper ions in the CuO$_2$ plane are Cu$^{+2}$).

**VIII. THE CONCENTRATION OF CHARGES IN THE COPPER-I AND COPPER-II LAYERS**

Historically, the BVS technique was introduced as an aid to determining crystal structures [7]. It is clear from our analysis that it is indeed valuable in clarifying details of the structure of CLBLCO. However, it has also become popular recently to use the BVS method in an attempt to find the distribution of electric charge in the high-$T_c$ cuprate materials. It is almost universally agreed that the superconductivity of the cuprates resides on their CuO$_2$ planes. Can BVS calculations really throw any light on the question of the charge distribution on these planes?

As the prescription is empirical, it is not obvious how to interpret the BVS results. Two attempted interpretations have been discussed. In one approach, Tallon [13] interprets the BVS of a given ion as giving directly the actual charge on the ion. He calculates both the average BVS of the CuII ions and the BVS of the O$_p$'s and defines:

$$V_- = (2 + \text{BVS}_{\text{CuII}} - \text{BVS}_{O_{pa}} - \text{BVS}_{O_{pb}}),$$

which, according to his interpretation, should be the concentration of holes in the CuII plane.

The second approach, by Brown [12], uses only $\text{BVS}_{\text{CuII}}$, after making a correction for the internal strain. Brown considers that the $\xi$'s are supposed to give directly the excess
over 2 of the average copper valence, and hence they should describe the concentration of holes in the various Cu layers. The discrepancy between the global average BVS of copper and the stoichiometric average copper valence is a consequence of the strain in the lattice. It is not \textit{a priori} obvious that the strain correction to the Cu I and CuII layers are equal, but in the absence of any better criterion we assume their equality. Thus the corrections which we make to the CuI and CuII oxidation states are just \((V_{\text{Stoich.}}^{\text{Global}} - V_{\text{Avg}}^{\text{Global}})\). In the example of eqs. (6,7), \((y = 6.926, \ x = 0.4)\), we found (see Table 8b) that \(V_{\text{Avg}}^{\text{Global}} = 2.146\), while \(V_{\text{Stoich.}}^{\text{Global}} = 2.201\). Following Brown’s prescription, we add the difference to each Cu layer, giving the corrected average valences

\[
V_{\text{Avg}}^{\text{CuI}} = 2.079 + 0.054 = 2.133, \\
V_{\text{Avg}}^{\text{CuII}} = 2.180 + 0.054 = 2.234,
\]

and hence the net charge on the CuO\(_2\) plane is 0.234. (Note that the value in Table 9 — namely 0.231 — differs slightly from this number because in the Table we made a linear least-square fit of the correction as a function of \(y\).

Of course, if we knew how to correct exactly for the strain, the two methods should agree (since, by definition, the oxidation state of oxygen is exactly 2). Since the method is largely empirical, it is impossible to say, \textit{a priori}, which approach is to be preferred. In the next section, we give reasons why, in our opinion, Brown’s approach is preferable.

\section*{IX. DISCUSSION}

One of the main reasons for the wide interest in BVS studies of the cuprates was the hope that the results would be a help in understanding their superconductivity. In particular, it is important for our understanding of high-\(T_c\) superconductivity to estimate the concentration of mobile holes. In \(\text{La}_{2-x}\text{Sr}_x\text{CuO}_4\), which does not have a “chain” layer, the average oxidation state of copper is determined by the stoichiometry, to be \(2+x\), since the oxidation states of La and Sr and oxygen are unambiguously known (+3, +2, and −2 respectively)
Hence $V_\perp = x$, (= 0.16 at optimal doping — i.e. at maximal $T_c$), and this $x$ is taken to give directly the concentration of mobile holes. However, in the 1-2-3 materials, the stoichiometry can only give the *global* average oxidation state of the copper ions, and not the separate valuers for the CuI and CuII. Moreover, it is generally believed that the mobile charge carriers reside in the CuO$_2$ planes, and that in the 1-2-3 materials the chains serve primarily as a reservoir of charge; doping is effected by transfer of charge from the CuI layer to the CuII layers.

The principal motivation for performing BVS calculations for copper was the hope that they would enable one to find the average oxidation state of the CuII layer, and hence, by analogy with La$_{2-x}$Sr$_x$CuO$_4$, the concentration of mobile carriers. Tallon [13] [20], who followed Cava *et al.* [16] in taking $\xi = 0$, found that at optimum doping, $V_\perp^{YBCO} \approx 0.16$. This unfortunate coincidence led to a widespread belief that this value 0.16 was universal for optimally-doped high-$T_c$ cuprates. Furthermore, Tallon noted that in the calculation of $V_\perp$, the CuII–O$_p$ bonds play no role, as their contribution to BVS$_{CuII}$ and to BVS$_{O_p}$ exactly compensate, and that therefore only the CuII–O$_c$ bonds are relevant. (This may have been a reason for the belief that the apical oxygens were critically important.) Karpinnen and Yamauchi [17], relying on this compensation but once again taking $\xi = 0$, found $V_\perp = 0.99$. The discrepancy arises from the inconsistent use of $\xi = 0$, in calculating the BVS of the oxygen and copper. When the correct value of $\xi$ is used consistently, the two methods agree, and give $V_\perp = 0.105$ for optimally doped YBCO [11], forcing us to abandon belief in the existence of a universal value.

We can make a further claim — namely that although the BVS method can give the total charge concentration on the CuII layer, it does *not* give the mobile charge. The CLBLCO family $(Ca_xLa_{(1-x)})(Ba_{(1.75-x)})La_{(0.25-x)})CuO_y$ has the useful property that the average oxidation state of Cu is $\frac{1}{1}(2y - 7.25)$, independent of the Ca concentration $x$. For two different values of $x$, it was found [19] that in the underdoped regime, samples with the same $T_c$ but with different $y$ have the same resistivity $\rho$ and the same thermoelectric power $S$. Although there is no adequate theory for the thermoelectric power of the high-$T_c$
materials, we feel that we may safely assume that the equality of $\rho$ and of $S$ for equal $T_c$ means that they have the same mobile-carrier concentration, and also from Uemura’s \[22\] $\mu$sr results, we know that samples of YBCO with the same $T_c$ also have the same concentration of Cooper pairs. However, from the BVS calculations, our samples of CLBLCO with equal $T_c$ do not have the same total charge concentration. This surely means that they have about the same concentration of mobile holes, although they clearly do not have the same values of either $p_{\text{Tallon}}$ or $p_{\text{Brown}}$ (see Table 9). Not all the charges are mobile!

Another interesting new result for CLBLCO is that the average oxidation states of CuII (calculated by Brown’s method) for different $x$ but for the same $y$ are equal (Fig.3). At present we have data for only two values $x = 0.1$ and $x = 0.4$, but provided that this result is not accidental, it means that CLBLCO is fully charge-compensated with respect to Ca and La; not only is the global average oxidation state of copper independent of $x$, but the average oxidation states of the CuI and CuII layers are separately independent of $x$. This means (see Fig. 4) that in CLBLCO the plot of $T_c$ versus $p_{\text{Brown}}$ is essentially the same as its plot against the oxygen concentration $y$. (Note that this will not be true for $p_{\text{Tallon}}$; this is one of our reasons for tentatively preferring $p_{\text{Brown}}$.) The fact that the two Ca concentrations ($x = 0.1$ and $x = 0.4$) have such different $T_c$’s for the same value of $p$ strengthens our view that some of the holes are not mobile.

The fraction of the hole concentration residing on the CuII layer is $C = \frac{2p}{(V_{\text{Avg}} - 2)}$. Zhu and Tafto \[21\], using a novel electron-diffraction method, have been able to measure $C$ directly for YBCO. They find that, close to optimal doping, $C = 0.76 \pm 0.08$. In Table 10, we give the values of $p_{\text{Tallon}}$, $p_{\text{Tallon}}$, and $p_{\text{Brown}}$ for YBCO, (from ref. \[16\]) together with the values of $C$, calculated from these $p$’s. We see that $p_{\text{Brown}}$ is in fair agreement with the Zhu–Tafto results, while neither of the other estimates of $C$ is at all close.

Note that the present values of $p_{\text{Brown}}$ and $p_{\text{Tallon}}$ for CLBLCO differ slightly from those presented in ref. \[11\], for two reasons: (a) the calculations in our earlier paper did not include the effect of the displacement of $O_c$ and $O_\alpha$ from their “ideal” positions, and (b) the
old values of the oxygen concentration $y$ were taken from titration, while the present ones were derived from the Rietveld refinement.

In summary: the BVS method is found to be a very useful tool in improving the detailed knowledge of the crystal structure. In addition, it appears to provide a good representation of the oxidation states of the CuI and CuII layers and thus to give the number of Cu$^{+3}$ ions \textit{(i.e. holes)} in the CuII layer. But we are forced to conclude, regretfully, that because the BVS method gives neither the concentration of mobile charges nor that of Cooper pairs (which can be determined from $\mu$sr experiments), it does not contribute to our understanding of the superconductivity of the cuprates. Although the method is empirical, and therefore there is no \textit{a priori} way to determine whether Brown’s or Tallon’s method is most reliable, it appears to us that Brown’s method is preferable for the following reasons: (a) the better agreement with the results of Zho and Tafto, (b) the fact (see Fig. 3) that $p_{\text{Brown}}$ follows the oxygen concentration $y$ linearly (while $p_{\text{Tallon}}$ does not) appeals to us.

The value of BVS$_{O_{\alpha}}$ and the adp $U_{\text{CuI}}$ are still slightly anomalous; this is probably a consequence of neglecting the displacement of CuI from its ideal position when those of its neighboring O$_{\alpha}$ sites which are occupied are not arranged symmetrically. However, this will not exert any significant influence on the CuII layer.

\textbf{X. TABLE I}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
Ion & Cu$^{+}$ & Cu$^{+2}$ & Cu$^{+3}$ & Y$^{+3}$ & Ca$^{+2}$ & La$^{+3}$ & Ba$^{+2}$ \\
\hline
$r_{0}$ (Å) & 1.600 & 1.679 & 1.730 & 2.019 & 1.967 & 2.172 & 2.285 \\
\hline
\end{tabular}
\end{table}
| Ion        | $\xi$ | $\eta$ | $\zeta$ |
|------------|-------|--------|---------|
| CuI        | 0     | 0      | 0       | 2.34    |
| CuII       | 0     | 0      | 4.121   | 0.63    |
| Ca         | 1.940 | 1.940  | 5.856   | 0.69    |
| La(Y)      | 1.940 | 1.940  | 5.856   | 0.69    |
| Ba         | 1.940 | 1.940  | 2.122   | 1.04    |
| La(Ba)     | 1.940 | 1.940  | 2.359   | 1.04    |
| O$_{\alpha}$ | 1.940 | 0   | 0       | 7.13    |
| O$_{p}$    | 1.940 | 0     | 4.271   | 0.74    |
| O$_{c}$    | 0     | 0     | 1.805   | 1.35    |

| Lattice const. | $a$ | $b$ | $c$ | adp. |
|----------------|-----|-----|-----|------|
|                | 3.879 | 3.879 | 11.702 | $(U)$ |
XII. TABLE 3

(a)

| Calcium conc. $x$ | 0.1 |
|-------------------|-----|

| Oxygen conc. $y$ | 7.022 | 7.056 | 7.136 | 7.232 | 7.282 |
|------------------|-------|-------|-------|-------|-------|
| $T_c$            | 30.9  | 42.6  | 52.6  | 41.4  | 5.0   |
| $r$(CuI to $O_α$)| 1.953 | 1.952 | 1.953 | 1.953 | 1.954 |
| $r$(CuI to $O_c$)| 1.838 | 1.844 | 1.850 | 1.862 | 1.864 |
| $r$(CuII to $O_p$)| 1.964 | 1.964 | 1.965 | 1.965 | 1.965 |
| $r$(CuII to $O_c$)| 2.243 | 2.228 | 2.215 | 2.192 | 2.178 |
| $r$(Ca to $O_p$) | 2.518 | 2.517 | 2.517 | 2.523 | 2.535 |
| $r$(La$_{(Y)}$ to $O_p$) | 2.518 | 2.517 | 2.517 | 2.523 | 2.535 |
| $r$(Ba to $O_α$) | 2.878 | 2.869 | 2.853 | 2.847 | 2.856 |
| $r$(Ba to $O_p$) | 2.921 | 2.928 | 2.943 | 2.937 | 2.912 |
| $r$(Ba to $O_c$) | 2.776 | 2.773 | 2.771 | 2.770 | 2.773 |
| $r$(La$_{(Ba)}$ to $O_α$) | 3.019 | 2.974 | 2.977 | 2.931 | 2.875 |
| $r$(La$_{(Ba)}$ to $O_p$) | 2.784 | 2.825 | 2.820 | 2.853 | 2.893 |
| $r$(La$_{(Ba)}$ to $O_c$) | 2.801 | 2.790 | 2.790 | 2.780 | 2.775 |
(b)

| Calcium conc.  \( x \) | 0.4 |
|------------------------|-----|

| Oxygen conc. \( y \) | 6.852 | 6.898 | 7.008 | 7.054 | 7.158 | 7.176 | 7.244 | 7.290 |
|------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| \( T_c \)              | 12.6  | 33.1  | 54.6  | 71.4  | 79.4  | 80.3  | 75.9  | 60.8  |
| \( r(CuI \text{ to } O_{\alpha}) \) | 1.941 | 1.940 | 1.939 | 1.938 | 1.938 | 1.937 | 1.937 | 1.938 |
| \( r(CuI \text{ to } O_{c}) \)       | 1.805 | 1.812 | 1.823 | 1.827 | 1.833 | 1.838 | 1.844 | 1.849 |
| \( r(CuII \text{ to } O_{\rho}) \)    | 1.946 | 1.946 | 1.946 | 1.946 | 1.946 | 1.945 | 1.945 | 1.945 |
| \( r(CuII \text{ to } O_{c}) \)       | 2.315 | 2.300 | 2.275 | 2.261 | 2.251 | 2.241 | 2.229 | 2.225 |
| \( r(Ca \text{ to } O_{\rho}) \)      | 2.505 | 2.503 | 2.502 | 2.502 | 2.502 | 2.501 | 2.502 | 2.506 |
| \( r(La(Y) \text{ to } O_{\rho}) \)    | 2.505 | 2.503 | 2.502 | 2.502 | 2.502 | 2.502 | 2.502 | 2.506 |
| \( r(Ba \text{ to } O_{\alpha}) \)     | 2.876 | 2.870 | 2.849 | 2.838 | 2.832 | 2.823 | 2.823 | 2.828 |
| \( r(Ba \text{ to } O_{\rho}) \)       | 2.895 | 2.898 | 2.915 | 2.920 | 2.925 | 2.928 | 2.928 | 2.918 |
| \( r(Ba \text{ to } O_{c}) \)          | 2.763 | 2.760 | 2.755 | 2.752 | 2.751 | 2.748 | 2.748 | 2.749 |
| \( r(La(Ba) \text{ to } O_{\alpha}) \)  | 3.054 | 3.055 | 3.041 | 3.023 | 3.001 | 2.998 | 2.979 | 2.966 |
| \( r(La(Ba) \text{ to } O_{\rho}) \)    | 2.724 | 2.721 | 2.729 | 2.740 | 2.759 | 2.757 | 2.772 | 2.782 |
| \( r(La(Ba) \text{ to } O_{c}) \)       | 2.800 | 2.797 | 2.791 | 2.785 | 2.779 | 2.776 | 2.772 | 2.770 |
### XIII. TABLE 4

(a)

| Ca conc. $x$ | 0.1 |
|-------------|-----|

| O conc. $y$ | 7.022 | 7.056 | 7.136 | 7.232 | 7.282 |
|-------------|-------|-------|-------|-------|-------|
| BVS$_{Ca}^0$ | 1.802 | 1.810 | 1.808 | 1.782 | 1.721 |
| BVS$_{La(Y)}^0$ | 3.137 | 3.150 | 3.147 | 3.101 | 2.995 |
| BVS$_{La(Ba)}^0$ | 1.702 | 1.680 | 1.704 | 1.724 | 1.738 |
| BVS$_{Ba}^0$ | 2.188 | 2.208 | 2.239 | 2.306 | 2.354 |
| BVS$_{Op}^0$ | 2.052 | 2.045 | 2.032 | 2.027 | 2.016 |
| BVS$_{O\alpha}^0$ | 1.747 | 1.777 | 1.818 | 1.854 | 1.854 |
| BVS$_{Oc}^0$ | 1.916 | 1.926 | 1.937 | 1.946 | 1.954 |

(b)

| Ca conc. $x$ | 0.4 |
|-------------|-----|

| O conc. $y$ | 6.852 | 6.898 | 7.008 | 7.054 | 7.158 | 7.176 | 7.244 | 7.290 |
|-------------|-------|-------|-------|-------|-------|-------|-------|-------|
| BVS$_{Ca}^0$ | 1.866 | 1.878 | 1.882 | 1.883 | 1.886 | 1.890 | 1.884 | 1.862 |
| BVS$_{La(Y)}^0$ | 3.248 | 3.268 | 3.275 | 3.277 | 3.283 | 3.289 | 3.279 | 3.241 |
| BVS$_{Ba}^0$ | 2.214 | 2.242 | 2.291 | 2.324 | 2.374 | 2.397 | 2.433 | 2.458 |
| BVS$_{La(Ba)}^0$ | 1.789 | 1.811 | 1.830 | 1.836 | 1.840 | 1.857 | 1.861 | 1.867 |
| BVS$_{Op}^0$ | 2.076 | 2.083 | 2.071 | 2.068 | 2.060 | 2.065 | 2.059 | 2.052 |
| BVS$_{O\alpha}^0$ | 1.710 | 1.726 | 1.782 | 1.815 | 1.855 | 1.874 | 1.894 | 1.895 |
| BVS$_{Oc}^0$ | 1.917 | 1.922 | 1.939 | 1.954 | 1.971 | 1.975 | 1.984 | 1.980 |
XIV. TABLE 5

| Ca conc. $x$ | 0.4 |
|-------------|-----|
| O conc. $y$ | 6.924 |
| $T_c$       | 33.1 |

| Lattice constants | $a$ | $b$ | $c$ | adp |
|-------------------|-----|-----|-----|-----|
|                   | 3.879 | 3.879 | 11.701 | $U$(Å$^2$) |

| Ion  | $\xi$ | $\eta$ | $\zeta$ |  |
|------|-------|-------|-------|----|
| CuI  | 0     | 0     | 0     | 2.39 |
| CuII | 0     | 0     | 4.110 | 0.58 |
| Ca   | 1.940 | 1.940 | 5.851 | 0.66 |
| La(Y) | 1.940 | 1.940 | 5.851 | 0.66 |
| Ba   | 1.940 | 1.940 | 2.334 | 0.90 |
| La(Ba) | 1.940 | 1.940 | 2.062 | 0.90 |
| $O_\alpha(1)$ | 1.940 | 0 | 0 | 1.80 |
| $O_\alpha(2)$ | 1.940 | 0.755 | 0 | 1.80 |
| $O_p$ | 1.940 | 0 | 4.267 | 0.76 |
| $O_c(1)$ | 0 | 0 | 1.818 | 0.73 |
| $O_c(2)$ | 0.266 | 0.266 | 1.818 | 0.73 |
| $O_c(3)$ | 0.451 | 0 | 1.818 | 0.73 |

XV. TABLE 6:

Calcium concentration: (a) $x = 0.1$, (b) $x = 0.4$,
next two pages
|          | Oxygen conc. y | 7.038 | 7.084 | 7.158 | 7.180 | 7.258 |
|----------|----------------|-------|-------|-------|-------|-------|
| $r$(CuI to $O_{\alpha(1)}$) | 1.953 | 1.952 | 1.953 | 1.953 | 1.954 |
| $r$(CuI to $O_{\alpha(2)}$) | 2.024 | 2.028 | 2.015 | 2.000 | 2.001 |
| $r$(CuI to $O_{\alpha(1)}$) | 1.869 | 1.868 | 1.867 | 1.869 | 1.869 |
| $r$(CuI to $O_{\alpha(2)}$) | 1.902 | 1.901 | 1.898 | 1.898 | 1.893 |
| $r$(CuI to $O_{\alpha(3)}$) | 1.920 | 1.917 | 1.926 | 1.927 | 1.936 |
| $r$(CuII to $O_p$) | 1.964 | 1.964 | 1.965 | 1.964 | 1.964 |
| $r$(CuII to $O_{\alpha(1)}$) | 2.210 | 2.203 | 2.197 | 2.184 | 2.172 |
| $r$(CuII to $O_{\alpha(2)}$) | 2.238 | 2.232 | 2.223 | 2.208 | 2.193 |
| $r$(CuII to $O_{\alpha(3)}$) | 2.253 | 2.246 | 2.247 | 2.234 | 2.230 |
| $r$(Ca to $O_p$) | 2.518 | 2.517 | 2.518 | 2.524 | 2.537 |
| $r$(La($Y$) to $O_p$) | 2.518 | 2.517 | 2.518 | 2.524 | 2.537 |
| $r$(Ba to $O_{\alpha(1)}$) | 2.934 | 2.921 | 2.913 | 2.892 | 2.865 |
| $r$(Ba to $O_{\alpha(2)}$) | 3.312 | 3.312 | 3.267 | 3.201 | 3.174 |
| $r$(Ba to $O_p$) | 2.866 | 2.877 | 2.882 | 2.891 | 2.901 |
| $r$(Ba to $O_{\alpha(1)}$) | 2.781 | 2.778 | 2.778 | 2.774 | 2.773 |
| $r_{\perp}$(Ba to $O_{\alpha(2)}$) | 3.132 | 3.132 | 3.117 | 3.101 | 3.074 |
| $r_{\perp}$(Ba to $O_{\alpha(2)}$) | 2.803 | 2.801 | 2.798 | 2.793 | 2.790 |
| $r$(La($Y$) to $O_{\alpha(1)}$) | 2.807 | 2.812 | 2.784 | 2.784 | 2.840 |
| $r$(La($Y$) to $O_{\alpha(2)}$) | 2.467 | 2.464 | 2.461 | 2.499 | 2.563 |
| $r$(La($Y$) to $O_p$) | 2.995 | 2.988 | 3.015 | 3.002 | 2.926 |
| $r$(La($Y$) to $O_{\alpha(1)}$) | 2.766 | 2.766 | 2.764 | 2.764 | 2.771 |
| $r_{\parallel}$(La($Y$) to $O_{\alpha(2)}$) | 2.414 | 2.410 | 2.423 | 2.436 | 2.470 |
| $r_{\perp}$(La($Y$) to $O_{\alpha(2)}$) | 2.793 | 2.793 | 2.789 | 2.786 | 2.788 |
| $r$(La($Y$) to $O_{\alpha(3)}$) | 2.476 | 2.479 | 2.453 | 2.454 | 2.442 |
| occupancy $n(O_{\alpha(1)}$) | 0.638 | 0.660 | 0.666 | 0.648 | 0.666 |
| occupancy $n(O_{\alpha(2)}$) | 0.400 | 0.424 | 0.492 | 0.532 | 0.592 |
| Oxygen conc. $y$ | 6.884 | 6.926 | 7.008 | 7.068 | 7.142 | 7.174 | 7.208 | 7.240 |
|-----------------|-------|-------|-------|-------|-------|-------|-------|-------|
| $r$(CuI to $O_{\alpha(1)}$) | 1.940 | 1.940 | 1.939 | 1.938 | 1.937 | 1.937 | 1.938 | 1.938 |
| $r$(CuI to $O_{\alpha(2)}$) | 2.082 | 2.081 | 2.040 | 2.030 | 2.027 | 2.181 | 2.015 | 2.012 |
| $r$(CuI to $O_{c(1)}$) | 1.813 | 1.818 | 1.829 | 1.832 | 1.838 | 1.842 | 1.847 | 1.852 |
| $r$(CuI to $O_{c(2)}$) | 1.853 | 1.857 | 1.863 | 1.865 | 1.869 | 1.871 | 1.875 | 1.883 |
| $r$(CuI to $O_{c(3)}$) | 1.863 | 1.873 | 1.876 | 1.875 | 1.880 | 1.896 | 1.893 | 1.897 |
| $r$(CuII to $O_p$) | 1.946 | 1.946 | 1.946 | 1.946 | 1.946 | 1.945 | 1.945 | 1.945 |
| $r$(CuII to $O_{c(1)}$) | 2.305 | 2.292 | 2.266 | 2.254 | 2.243 | 2.235 | 2.224 | 2.219 |
| $r$(CuII to $O_{c(2)}$) | 2.337 | 2.322 | 2.294 | 2.280 | 2.269 | 2.259 | 2.247 | 2.245 |
| $r$(CuII to $O_{c(3)}$) | 2.345 | 2.336 | 2.304 | 2.289 | 2.278 | 2.279 | 2.262 | 2.257 |
| $r$(Ca to $O_p$) | 2.506 | 2.504 | 2.502 | 2.503 | 2.502 | 2.502 | 2.504 | 2.508 |
| $r$(La$_{\gamma}$ to $O_p$) | 2.506 | 2.504 | 2.502 | 2.503 | 2.502 | 2.502 | 2.504 | 2.508 |
| $r$(Ba to $O_{\alpha(1)}$) | 3.041 | 3.035 | 3.019 | 2.998 | 2.984 | 2.979 | 2.963 | 2.952 |
| $r$(Ba to $O_{\alpha(2)}$) | 3.571 | 3.565 | 3.460 | 3.421 | 3.400 | 3.375 | 3.351 | 3.332 |
| $r$(Ba to $O_p$) | 2.736 | 2.739 | 2.749 | 2.762 | 2.774 | 2.773 | 2.786 | 2.793 |
| $r$(Ba to $O_{c(1)}$) | 2.795 | 2.791 | 2.785 | 2.779 | 2.775 | 2.772 | 2.768 | 2.767 |
| $r$(La(Ba) to $O_{\alpha(1)}$) | 2.840 | 2.831 | 2.810 | 2.799 | 2.797 | 2.788 | 2.789 | 2.794 |
| $r$(La(Ba) to $O_{\alpha(2)}$) | 2.389 | 2.378 | 2.417 | 2.420 | 2.424 | 2.429 | 2.438 | 2.451 |
| $r$(La(Ba) to $O_p$) | 2.930 | 2.937 | 2.954 | 2.959 | 2.960 | 2.963 | 2.960 | 2.951 |
| $r$(La(Ba) to $O_{c(1)}$) | 2.757 | 2.754 | 2.750 | 2.748 | 2.747 | 2.745 | 2.744 | 2.746 |
| $r$(La(Ba) to $O_{c(2)}$) | 2.376 | 2.380 | 2.396 | 2.403 | 2.409 | 2.417 | 2.422 | 2.407 |
| $r$(La(Ba) to $O_{c(3)}$) | 2.783 | 2.779 | 2.773 | 2.769 | 2.768 | 2.764 | 2.763 | 2.767 |
| occupancy $n(O_{\alpha(1)}$) | 0.480 | 0.516 | 0.514 | 0.542 | 0.566 | 0.578 | 0.596 | 0.582 |
| occupancy $n(O_{\alpha(2)}$) | 0.404 | 0.408 | 0.488 | 0.520 | 0.572 | 0.596 | 0.608 | 0.656 |
### XVI. TABLE 7

(a)

| Ca conc. \( x \) | 0.1 |
|------------------|-----|
| O conc. \( y \)  | 7.038 7.084 7.158 7.180 7.258 |
| \( \text{BVS}_{\text{Ca}} \) | 1.803 1.810 1.806 1.777 1.713 |
| \( \text{BVS}_{\text{La(Y)}} \) | 3.138 3.150 3.143 3.092 2.982 |
| \( \text{BVS}_{\text{La(Ba)}} \) | 2.799 2.848 2.890 2.844 2.797 |
| \( \text{BVS}_{\text{Ba}} \) | 2.024 2.026 2.040 2.062 2.092 |

(b)

| Ca conc. \( x \) | 0.4 |
|------------------|-----|
| O conc. \( y \)  | 6.884 6.926 7.008 7.068 7.142 7.174 7.208 7.240 |
| \( \text{BVS}_{\text{Ca}} \) | 1.865 1.876 1.882 1.881 1.882 1.883 1.876 1.854 |
| \( \text{BVS}_{\text{La(Y)}} \) | 3.245 3.264 3.275 3.273 3.276 3.278 3.265 3.226 |
| \( \text{BVS}_{\text{La(Ba)}} \) | 2.121 2.131 2.142 2.145 2.143 2.161 2.159 2.147 |
| \( \text{BVS}_{\text{Ba}} \) | 2.780 2.821 2.786 2.797 2.844 2.898 1.866 2.918 |
XVII. TABLE 8

(a)

| Calcium conc. $x$ | 0.1 |
|------------------|-----|
| Oxygen conc. $y$ | 7.038 7.084 7.158 7.180 7.258 |
| $T_c$ (K)        | 30.9 42.6 52.6 41.4 5.0 |
| $\xi_{\text{CuI}} = V_{\text{CuI}}^{\text{Avg}} - 2$ | 0.094 0.154 0.267 0.312 0.417 |
| $\xi_{\text{CuII}} = V_{\text{CuII}}^{\text{Avg}} - 2$ | 0.114 0.121 0.121 0.140 0.151 |
| $V_{\text{Avg}}^{\text{Global}}$ | 2.107 2.132 2.170 2.198 2.240 |
| $V_{\text{Stoich. Global}}$ | 2.275 2.306 2.355 2.370 2.422 |

(b)

| Calcium conc. $x$ | 0.4 |
|------------------|-----|
| Oxygen conc. $y$ | 6.884 6.926 7.008 7.068 7.142 7.174 7.208 7.240 |
| $T_c$ (K)        | 12.6 33.1 54.6 71.4 79.4 80.3 75.9 60.8 |
| $\xi_{\text{CuI}} = V_{\text{CuI}}^{\text{Avg}} - 2$ | 0.048 0.079 0.176 0.264 0.346 0.385 0.420 0.433 |
| $\xi_{\text{CuII}} = V_{\text{CuII}}^{\text{Avg}} - 2$ | 0.167 0.180 0.198 0.214 0.222 0.237 0.246 0.246 |
| $V_{\text{Avg}}^{\text{Global}}$ | 2.127 2.146 2.191 2.231 2.263 2.286 2.304 2.308 |
| $V_{\text{Stoich. Global}}$ | 2.173 2.201 2.255 2.295 2.345 2.366 2.389 2.410 |
### XVIII. TABLE 9

**Table (a):**

| Ca conc. $x$ | 0.1 |
|-------------|-----|

| $T_c$ | 30.9 | 42.6 | 52.6 | 41.4 | 5.0 |
| O conc. $y$ | 7.038 | 7.084 | 7.158 | 7.180 | 7.258 |
| BVS$_{O\alpha(1)}$ | 1.659 | 1.694 | 1.725 | 1.774 | 1.835 |
| BVS$_{O\alpha(2)}$ | 1.823 | 1.831 | 1.894 | 1.874 | 1.765 |
| BVS$_{O\alpha(3)}$ | 1.886 | 1.905 | 1.923 | 1.942 | 1.962 |
| BVS$_{O\alpha(4)}$ | 1.889 | 1.907 | 1.916 | 1.924 | 1.921 |
| BVS$_{O\alpha(5)}$ | 1.842 | 1.852 | 1.893 | 1.902 | 1.920 |
| $p_{Brown}$ | 0.284 | 0.294 | 0.298 | 0.319 | 0.334 |
| $\xi^{\neq 0}$ | -0.031 | -0.015 | 0.008 | 0.055 | 0.117 |

**Table (b):**

| Ca conc. $x$ | 0.4 |
|-------------|-----|

| $T_c$ | 12.6 | 33.1 | 54.6 | 71.4 | 79.4 | 80.3 | 75.9 | 60.8 |
| O conc. $y$ | 6.884 | 6.926 | 7.008 | 7.068 | 7.148 | 7.174 | 7.208 | 7.240 |
| BVS$_{O\alpha(1)}$ | 2.151 | 2.154 | 2.142 | 2.131 | 2.121 | 2.127 | 2.113 | 2.099 |
| BVS$_{O\alpha(2)}$ | 1.538 | 1.555 | 1.597 | 1.841 | 1.673 | 1.691 | 1.718 | 1.731 |
| BVS$_{O\alpha(3)}$ | 1.852 | 1.890 | 1.888 | 1.920 | 1.931 | 1.948 | 1.944 | 1.925 |
| BVS$_{O\alpha(4)}$ | 1.864 | 1.874 | 1.893 | 1.918 | 1.933 | 1.941 | 1.952 | 1.950 |
| BVS$_{O\alpha(5)}$ | 1.924 | 1.929 | 1.934 | 1.951 | 1.958 | 1.961 | 1.965 | 1.970 |
| BVS$_{O\alpha(6)}$ | 1.884 | 1.906 | 1.904 | 1.913 | 1.922 | 1.959 | 1.944 | 1.934 |
| $p_{Brown}$ | 0.213 | 0.231 | 0.261 | 0.284 | 0.302 | 0.322 | 0.335 | 0.339 |
| $\xi^{\neq 0}$ | -0.135 | -0.127 | -0.086 | -0.049 | -0.020 | -0.017 | 0.019 | 0.048 |
XX. ACKNOWLEDGEMENTS

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XXI. TABLE CAPTIONS

Table 1: Values of the BVS parameter $r_0$ for all the ions relevant to the present study [10].

Table 2: This is a specimen table, giving the coordinates and atomic displacement parameters of the ions in the unit cell, from the naïve Rietveld refinement when all ions are held to their “ideal” positions [14]. The full table is available by e-mail from charles@physics.technion.ac.il
Table 3: The naïve interionic distances, calculated by Rietveld refinement, when the O_c and O_α are not allowed to deviate from their “ideal” positions.

Table 4: Naïve bond valence sums for Ca, La, Ba, and O. Note the extremely poor values for La_{(Ba)}, indicating the presence of significant distortion away from the “ideal” structure. The oxygen BVS’s require the use of the mixing ratios ξ, which are introduced in §5.

Table 5: This specimen table [14] replaces Table 2, giving the coordinates and atomic displacement parameters of the ions in the unit cell, from the Rietveld refinement when the O_c and O_α ions are allowed to deviate from their “ideal” positions [14]. The full table is available by e-mail from charles@physics.technion.ac.il

Table 6: The distances in this table are calculated from the Rietveld refinement, when the O_c and O_α are allowed to deviate from their “ideal” positions. The suffix 1 refers to the undisplaced ion, and the suffixes 2 and 3 to the displaced one. Note that for the situations described in Fig. 2 D and E, there are two distinct distances of Ba and of La_{(Ba)} to O_c(2), corresponding to displacement along the line joining La to Ba (Case r∥) and to displacement orthogonal to the line joining the pair of similar ions (Case r⊥).

Table 7: The BVS’s of Ca, La, and Ba, recalculated using the “improved” Rietveld refinements from Table 6.

Table 8: Mixing ratios ξ_I and ξ_II; and comparison of the global average Cu valence from BVS and from stoichiometry.

Table 9: The BVS’s of all the oxygen ions, and the values of p_{Brown} and p_{Tallon}^{ξ≠0} for CLBLCO. Note that although most of the oxygen BVS’s are quite close to 2, those of O_α are rather poor, reflecting (a) the likelihood that some lattice distortion arises, due to the fact that there are many oxygen vacancies in the CuI layer, and (b) the possibility that at least some of the O_α ions do not lie exactly in the plane (i.e. that the dimerization of the La ions is incomplete).

Table 10: The values, for YBCO, of p_{Brown}, p_{Tallon}^{ξ≠0}, and p_{Tallon}^{ξ=0} are taken from ref. [16]. We have not included values of y less than 6.64, since they enter the region where ξ^{(I)} is
negative, i.e. the CuI layer contains electrons rather than holes. The charge concentration on the CuII layers is \( C = 2p/\left(V_{\text{Stoich.} Global} - 2\right) \).

**XXII. FIGURE CAPTIONS**

Fig. 1: Unit cell of YBCO, defining our labelling convention. CLBLCO is always tetragonal; since there are no chains, the \( a \) and \( b \) directions are equivalent. In the CuII layers, \( O_{pa} \) and \( O_{pb} \) need not be distinguished, and will be labeled \( O_p \). The oxygens in the CuI layer occupy the \( O_b \) and \( O_a \) sites with equal probability and are assumed to be distributed randomly; we will label them \( O_\alpha \).

Fig. 2: The six distinct environments of an \( O_c \) atom, showing the directions of possible displacement. In cases A, B, and C, by symmetry, the oxygen is not displaced from its “ideal” position. In case D, it is displaced towards the solitary La, in case E, away from the solitary Ba, and in case F, towards the La pair. Cases A and B are nondegenerate, C is doubly degenerate, and D, E, and F are fourfold degenerate.

Fig. 3: CLBLCO — Plot of \( p_{\text{Brown}} \) versus oxygen concentration \( y \), for nominal calcium concentration \( x = 0.4 \) (squares) and \( x = 0.1 \) (circles).

Fig. 4: CLBLCO — (a) Plot of \( T_c \) versus \( p_{\text{Brown}} \), and (b) plot of \( T_c \) versus \( y \), for nominal \( x = 0.4 \) (squares) and \( x = 0.1 \) (circles).
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[14] Note that, because the material is tetragonal, O\(_{\alpha}\) can be either O\(_{a}\) or O\(_{b}\) with equal probability. The coordinates in the Tables are given for the case where the oxygen sits on site a, but the calculation is the same for site b; we only need to interchange the
coordinates $\xi$ and $\eta$. The full tables of ionic positions, both for the naïve and improved analyses are available by e-mail, from charles@physics.technion.ac.il

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Fig. 2
