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# Lattice Pressure Creating and Annihilating Superconducting Subperoxides

H. Oesterreicher

*Department of Chemistry and Biochemistry, University of California at San Diego, La Jolla, California 92093-0506*

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**The involvement of $O^-$ in oxide superconductivity is indicated in a variety of phenomenological rules such as a universal scaling of $T_c$ with stoichiometric holes per O. Here, a crystal chemistry of $O^-$ creation and placement is developed, based on the competition of various types of planes ($CuO_2$, *E*, B1). Generally, cuprate structural stability is dictated by slab matching, conventionally expressed in tolerance factors (*t*). Electronic liquefaction through subperoxide formation can ameliorate *t*, indicating a decisive influence of lattice pressure on the limits of $O^-$ formation. Comparison of calculation with experiment indicates trends to lattice commensurable hole patterns, of which the one responsible for optimal $T_c$ is an alternate hole charge order (P2), for both simple and complex cuprates. For complex cuprates, tension on the layers containing *M* = Bi, Hg, T1 leads to additional reductive self-dopings. Calculations indicate that in optimally doped materials this leads universally to P2. The $T_c$ decreases beyond this optimal doping, usually referred to as "overdoping," are here related to overfilling of this pattern. An extreme case of this occurs with nonsuperconducting $Bi_2Sr_2CuO_6$, which appears to be P1. This overdoping is caused by severe lattice pressure causing the annihilation of superconducting pairs. A distinction has to be made with a second type of "early" $T_c$ decreases. They occur before attainment of P2 and are due to an unfavorable hole placement crystal chemistry. An example is the disorder in $[(LaSr)_2CuO_4]$. $T_c$ optimization involves navigating between these antagonistic principles.** © 2002 Elsevier Science (USA)

## INTRODUCTION

There are many reasons to consider cuprate superconductivity (1, 2) in a new perspective, namely as based on traveling $O^-$ charge orderings in the planar covalent system (3–8). The basic requirements for superconductivity have to be viewed in this new perspective in the light of its occurrence in materials such as doped $C_{60}$. Accordingly, covalent radical bonds in a stressed planar network appear as the common denominator and this covalent model promises to be universally applicable for materials based on electronegative components. This opens the challenge for an encompassing model. If this approach is based on realistic assumptions, then it should manifest itself repeatedly in a variety of related phenomenological traits. It should, so to speak, be a "natural", connecting diverse aspects of the phenomenology in a comprehensive understanding. It has been shown that this is indeed the case. The involvement of $O^-$, or subperoxides $O_q^{1-2q}$, is apparent with respect to the thermodynamics (7, 8) of the couples involved, or a universal scaling of $O^-$ radical density with $T_c$ (3, 4). Charge orderings manifest themselves in levels and limits of doping. As an example, the vexing self-doping question (4–6) can be quantitatively understood in terms of characteristic doping limits, which often produce an alternate hole charge order. The mode of charge ordering can influence electronic properties (5) such as resistivity–temperature behavior, distinguishing between various power laws. Even aspects of the fundamentals of superconducting subperoxidic pair formation, energetics, and mechanism of propagation can now be identified (5) within the constraints of charge ordering. Here we explore the influence of lattice pressure on the structural placement of $O^-$ and its relationship to $T_c$ within the anionic model. We demonstrate that Le Chatelier-type lattice pressure equilibria determine essential aspects of oxide superconductors such as hole densities.

Chemical concepts indicate unprecedented success in dealing with cuprate superconductors. A realistic pursuit of the crystal chemistry of $O_q^{1-2q}$ promises a comprehensive understanding and forms the key to the materials questions for quantitative and predictive formalisms for $T_c$. These concepts are here first briefly introduced and subsequently detailed. They are based on an $O^-$ charge ordering chemistry with rational fraction valencies and trends to subperoxide quantizations. $T_c$ values are universally predictable on stoichiometric hole ($h$) density per total O ($y$) for all relevant cuprates according to $T_c = T_c^* r$ with $T_c^* = 666\,\mathrm{K}$ and $r = h/y = 1/q$, referred to as the radical formula. Usually holes are stabilized in adduct states by a thermodynamically select (7) number of metals ($M$ = Cu, Bi, Tl, Hg). Energy scales of charge order correlations reflect covalent bond polarizations, elasticities, or melting temperatures. Relevant cuprates are the ones that exhibit infinite



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O contact and place $O^-$ on $CuO_2$ planes (referred to as planes or P). $O^-$ charge orderings indicate a staging type behavior with special stability for rational hole fractions per number of planes, $n$ (e.g., $h/n = 1/k = 1/2, 1/3, \ldots$), reflecting lattice charge order commensurabilities (the respective charge orders are designated P2, P3, … P$k$). The order, which appears connected with optimizing $T_c$, corresponds to an alternate hole pattern P2. It is characterized by $h = n0.5$. A schematic of P2 and a diluted pattern P3 with stripe formation is shown in Fig. 1.

Where $O^-$ holes are placed on sites other than within the plane, $T_c$ collapses (collapse) can occur. They are connected with structural anomalies (e.g., axial ratios). As will be outlined, a classification can also be made between the hole placement in $\sigma$ or $\pi$ O orbitals, with the former leading to relative plane contractions ($P^-$)and $d$ wave properties and the latter to plane expansions ($P^+$) and absence of $d$ wave properties. A distinction has to be made between materials that derive $h$ through simple overoxidation (Ox) or reductive self-doping (Red). As a result of a balance between these two influences $T_c$ can tend to a level scheme, reflecting the $M$/O ratios and subperoxide "quantization." These phenomena explain quantitatively the $T_c$ plateaus and stratified self-doping levels, including $T_c$ of unusual strength in $YBa_2Cu_3O_y$ materials near O half-filling. They also pertain to additional self-doping in complex cuprates (e.g., $Bi_2Sr_2CaCu_2O_{8+\delta}$). The presence of self-doping is often dramatically evident through volume expansion effects ($V^+$).

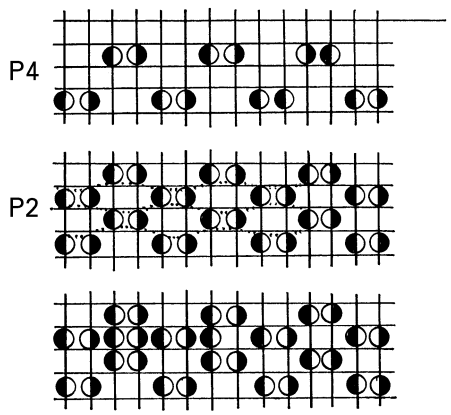


**FIG. 1.** Schematic of various P$k$ [under-, optimally, and P2 overdoped are represented] in the $CuO_2$ plane. Crosses correspond to Cu and only $O^-$ holes are represented. Lattice contraction waves are indicated, providing a pictorial representation based on "classical" materials concepts such as elastic energies and exchange for pair formation and propagation in short coherence length materials. P2 corresponds to a universal $T_c$ optimum at $O_4^{7-}$, or formal $Cu^{2.5+}$. Arguments for this order include subperoxidic lattice fit. On dilution of P2, one notes subperoxidic strings of pairs along $b$ (to shorten $a$) which may be a general element in superconductivity. In the underdoped region certain charge order harmonics are energetically favored, leading potentially to a "musical" $T_c$ level structure (e.g., $T_c$ plateaus and $T_c$ compound families). Propagation is hindered on approach of P1, as the expanded lattice regions are being filled by holes. Assumed adduct state Cu displacements can produce the magnetic doubling seen in diffraction.

*Details of subperoxide model.* The notion of subperoxides is based on comparable thermodynamic potentials for the relevant cationic and anionic systems. This leads to special polarization of the bonding electrons, with the possibility for anionic or O self-bonding contributions. This shall now be further expanded. A basic premise of this work will be the assumption that increasing formal Cu oxidation on the $CuO_2$ plane leads to a series of charge order commensurabilities (see, e.g., $T_c$ plateaus) and $T_c$ "optimizes" at $2.5^+$. The respective holes are considered as partly transferred to O in equilibrium Ox,

$$Cu_k^{2k+1}O^{2-} \rightleftharpoons Cu^{2+}O_q^{1-2_q},$$

where $k$ and $q$ are charge order repeat wavelengths. $q$ also represents the bond polarization as it indicates the number of O which are electronically displaced toward the hole.

There are several indications that Ox is shifted somewhat to the right (4). For our purposes the most important pertains to the experimental observation of a $T_c$ scaling with $r$. This indicates that the $p$ electronic system takes a decisive role in superconductivity. Accordingly, an adduct state $Cu^{2+}O^-$ is defined (3–5) in which Cu is not formally further oxidized, although its electronic system is drawn to $O^-$. A similar situation is indicated even in compounds such as $NaCuO_2$ where holes are also observed on O by spectroscopy (9). Compounds harboring $O_q^{1-2_q}$ have been generally termed subperoxides, with $O_2^{3-}$ as the limiting member. Their properties include spectroscopic $O^-$ observation, somewhat contracted O–O distances, and characteristic anomalous electrical resistivity properties, including superconductivity and a scaling of $T_c$ with $O^-$ radical density.

The origin of this $O^-$ formation is seen in a stabilizing of structure. This occurs through lattice pressure amelioration in the stacking of mismatched planes. It can take place in simple cuprates through overoxidation, e.g., on extra O uptake or substitutional doping. However, a second source for $O^-$ is self-doping through the partial reduction of a thermodynamically select (7) number of metals such as $M$ = Cu, Hg, Tl, Bi. This can be represented as equilibrium Red exemplified by

$$Hg^{2+}, O^{2-} \rightleftharpoons Hg_k^{2k-1}O_q^{1-2_q}.$$

For these complex cuprates, $T_c$ optima are observed, as a rule, on increasing doping. Conventionally, they are seen as a "common band" filling property. The $T_c$ decreases, observed thereafter, are usually referred to as "overdoping." Here an alternative explanation is given for these antagonists to superconductivity. A distinction is made between two types of overdoping, which we generally term $T_c$ collapse (collapse) effects. One is P2 overdoping in approaching P1.

The latter is here taken to be universally nonsuperconducting. Another type occurs at higher order P$k$ and is here referred to as a hole misplacement doping. An example is $(LaSr)_2CuO_4$, which can show $T_c$ decreases near $x = 0.17$ (P6). It is assigned to the partial placement of $O^-$ in the clusters of the disordered LaSr environments. Generally, placement equilibria of the type $O_q^{1-2q} \rightleftharpoons {}^cO^-$, where ${}^cO^-$ is the $c$ axis or apical O, will also depend on lattice pressure in a Le Chatelier sense. Indications are that these states still contain $O^-$ but do have distinctly different conductivity properties (see, e.g., 10).

Diffraction experiments (see, e.g., 11) can also indicate mobile charge ordering in superconductivity. Lattice displacement by the charge modulation usually occurs without special reference to the particular charges in question. Some techniques (12), however, are capable of locating the charge carries on the O. This corroborates the universal spectroscopic observation of $O^-$, while $Cu^{3+}$ is never observed.

Electronically optimized cuprate superconductors, above $T_c$, show abnormal linear resistivity–temperature behavior (8) for a metal, which we take as a hallmark for plane subperoxides. Power laws (10) are characteristic for some overdoped materials. For underdoped cuprates, a change in slope above a temperature $T_p$ is observed in properties such as resistivity, specific heat, or magnetic susceptibility (10). This is usually referred to as the pseudo gap. This gap will be interpreted as the onset of stripes of subperoxide ($O_4^{6-}$) pairs, without full correlation or phase coherence among the stripes, which occurs only below $T_c$. Some discussion of this phenomenon will be included for completeness.

## RESULTS

We shall first present some basic description of cuprate superconductivity, stability, and analysis of magnitude of $T_c$ in the subperoxide model. Subsequently we will introduce lattice pressure as the creator or annihilator of superconducting subperoxides. These ideas will then be discussed with an eye on applications for materials development.

### *Oxidation, $T_c$, and Charge Ordering*

The thermodynamic stability of oxide superconductors, that is plane-containing systems, places them in a precariously narrow window of synthesis conditions (7). In Table 1 examples are given for the general increase in formal Cu oxidation with decreasing synthesis temperature. The formal $Cu^{2.5+}$ oxidation on P, which in this paper is correlated with the condition for optimal $T_c$, is usually prepared in air near 800°C. Complex lattice pressure conditions lead to the existence and electronic liquefaction of P compounds and are discussed in this paper. At lower temperatures, materials with higher oxidation become competitive (e.g., $Ba_2Cu_3O_6$), which usually do not contain P (an exception is $Bi_2Sr_2CuO_6$ in P1) and make the P compounds universally metastable under those conditions. More details of the universal thermodynamics of oxide superconductor synthesis, the competition between plane and earth subperoxides, and their stabilization through a select number of metals are outlined elsewhere (7).

**TABLE 1**
**Thermodynamic Stabilities of Oxide Superconductors and Related Materials, Ordered in Terms of Synthesis Temperature $T_s$ and Oxidation State (More Details in Ref. 3)**

| $T_s$ (°C) | Formal oxidation | |
|---|---|---|
| 900 | $Cu^+/Cu^{2+}$ | $YBa_2Cu_3O_6$ |
| 700–800 | $Cu^{2.5+}$, $O_8^{13-}$ | $YBa_2Cu_4O_8$, P2 |
| | | $Bi_2Sr_2CaCu_2O_8$, P2 |
| 600 | $Cu^{2.67+}$, $O_3^{5-}$ | $Ba_2Cu_3O_6$ |
| 500–600 | $Cu^{3+}$, $O_2{}^{3-}$ | $KCuO_2$ |
| | $O_2^{3-}$ | $BaO_2$ |

The universal linear $T_c$ scaling with $r$ (radical formalism) is shown in two representations, namely vs $h/y$ (Fig. 2) and vs $h/n$ (Fig. 3). In the $h/y$ representation for simple overoxidized cuprates $T_c$ increases up to a maximum, which for hypothetical compounds based on infinite P stacking corresponds to $T_{c\,max} = 167^*$ K $= 666/4$ as a universal limit. This corresponds to $O_2^{3-}$, or $r = 0.25$. In this representation various $q$ families show independent optima on reaching P2. Fits with experiment are generally excellent and there are no obvious exceptions. As an example, for $YBa_2Cu_2Cu_2O_8$ one obtains $h = 1$ from stoichiometry. Accordingly, one calculates $T_c = 666/8 = 83^*$ K (asterisk denotes calculated). By comparison, experimental values are near 81 K and this holds for a variety of compounds with $q = 8 = y/h$. Simple cuprates with the highest overoxidations show a remarkable limit of stoichiometric $h/n = 0.5$ corresponding to $T_c$ optima (Figs. 1, 2, Table 2).

In order to demonstrate the universality of the condition for $T_c$ optima, Fig. 3 represents $T_c$ vs $h/n$. In this representation $T_c$ optima occur at $h/n = 0.5$ when one assigns total holes to the planes only. This corresponds to P2, indicating the importance of a charge order in the planes. This importance is further underscored in complex cuprates. When calculated on the radical formula (5, 8) and compared with optimized $T_c$, they are almost universally based on an assumption of $h/n = 0.5$, or P2 in a P$k$ notation (see Tables 2 and 3). This corresponds to the definition $T_{c.opt} = 0.5n666/y$. These hole concentrations are reached through a combination of Ox and Red self-doping. As an example, for $HgBa_2CuO_4$ one assumes $h = 0.5$ for P2, and accordingly $T_c = 0.5(666)/4 = 83^*$ K, compared to an experimental 90 K. This formalism works as a rule for optimized complex cuprates, although their somewhat higher observed values indicate a slightly higher $T_c^*$. The Tl

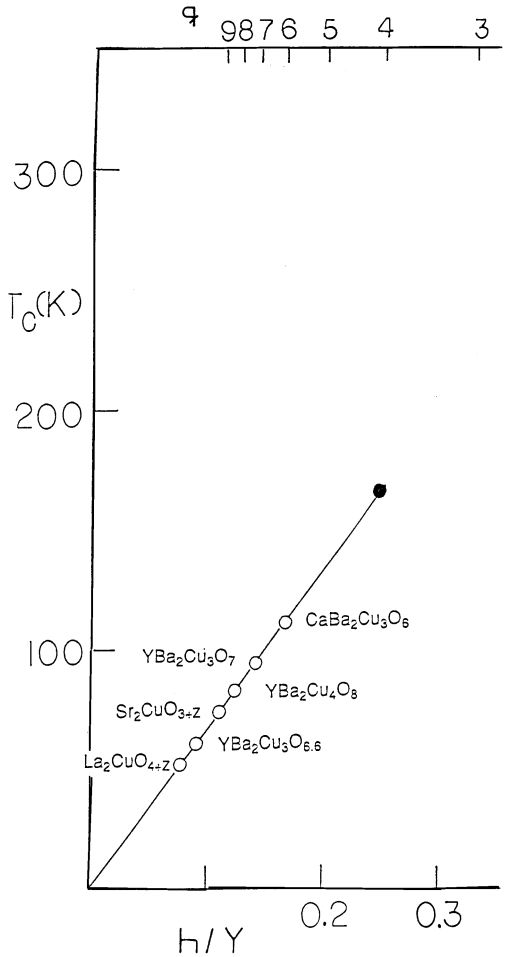


**FIG. 2.** $T_c$ scaling with $h/y$, according to $T_c = T_c^* h/y$ with $T_c^* = 666$ K and $r = h/y$. Open circles correspond to selected simple overoxidized cuprates for which $h$ can be determined by oxidation number calculations. Experimental values for simple oxide families fall within symbol size (e.g., other families with $q = 8$ such as $Pb_2Sr_2CaCu_3O_y$ with $y = 8$ also have calculated $T_c = 83^*$ K). P2 or $q = 4$ ($r = 0.25$) is considered to set a limit near $T_c \sim 167^*$ K as a universal maximum as predicted for infinite plane compounds doped to P2 (filled symbol). Higher $q$ families show $T_c$ optima at lower $r$ when P2 is reached.

double-layer analogs have yet higher observed $T_c$. This is related to the exclusion of some O (e.g., in the Tl layers) from the pool of common polarizations, presumably due to the unusually strong tension on the contracted Tl layer.

Generally, there exist, for overoxidized simple cuprates, trends to a variety of rational $h/n$ (P2, P3, ... ). Within one P$k$ family $T_c$ values are quantitatively calibrated with respect to $n/y$, reflecting the radical formula. Representative examples are also collected in Table 3. The list of materials in Fig. 3 for $h/n = 0.5$ is organized in terms of $Cu_nO_y$, where $y$ is the total O content. As an example, a family with $h/n = 0.5$ (that is, $k = 2$) includes $Cu_2O_8X$ where $X$ is $YBa_2Cu_2$, $Bi_2Sr_2Ca$, or $Pb_2Sr_2Ca$. It even reflects properties of $HgBa_2CuO_4$, as it has the same Cu/O ratio and $q$. There exist however also a variety of compounds with $h/n \sim 0.33$ (or P3), corresponding to $k = 3$, including $Sr_2CuO_{3+z}$. In this family, $T_c$ values again increase with favorable $n/y$ ratios.

For the purpose of exemplifying "early" $T_c$ collapse we finally select the behavior of $La_2CuO_{4+z}$. It is unusual in that doping through partial Sr substitution leads to collapse effects near $k = 6$ (P6), while O doping can produce higher $T_c$ up to $k = 3$ (P3). This indicates that crystal chemical rather than common band effects are at its origin and that $T_{c\,opt} \sim 83^*$ K. Another parameter of interest is $T_p$, which depicts the onset of charge striping. The general increase of $T_p$ with lower $h$ extrapolates roughly to the antiferromagnetic $T_n$. The magnitude of $T_n$(K) also appears to reflect bond polarizations or Cu/O ratios according to $T_n \sim 1200$ Cu/O and $T_p \sim T_n - ch$ where $c$ is a constant. Examples are $T_n$ of $\sim 500$ K and 300 K for $YBa_2Cu_3O_7$ and $La_2CuO_4$.

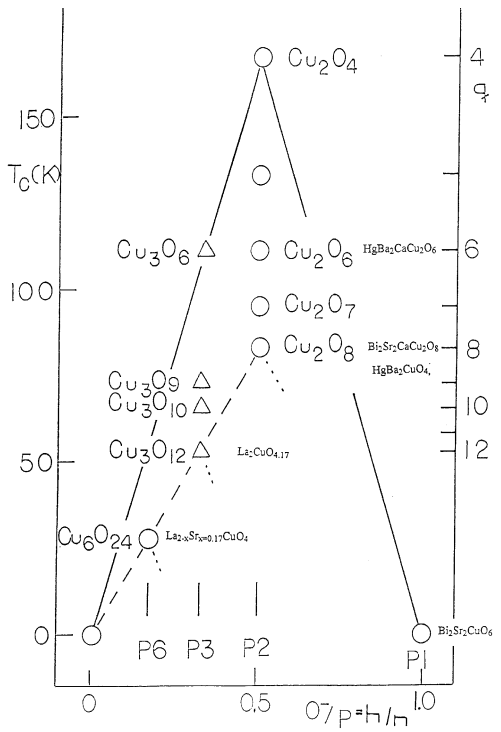


**FIG. 3.** $T_c$ organized in $h/n$ for selected cuprate superconductors, indicating charge order phenomenology, with P2 as a universal $T_c$ optimum among various $q$ families. Lines indicate range in doping with the highest line representing limiting $T_c$ values for infinite plane compounds (without spacer O). Circles represent calculated values on the radical formula, with experimental values generally fitting within the symbol size. For complex cuprates the assumption is attainment of P2 through a mixture of overoxidation and self-doping. The listing $Cu_2O_8$ indicates plane Cu and total O. Its $T_c$ for $h = 1$ (83* K) is characteristic for all members with $q = 8$ (e.g., with $n = 2$ and $y = 8$). Generally, one observes a grouping of materials according to charge ordering in rational $h$ fractions (P$k$). Collapse effects prevent materials with unfavorable lattice pressure (e.g., $La_{2-x}Sr_{x=0.17}CuO_4$) from attaining P2.

**TABLE 2**
**Limits of Oxidation State in Selected Overoxidized Cuprates[a]**

| Material | P*k* | *h* | $T_c$ (K), obs | $T_c$ (K), calc |
|---|---|---|---|---|
| $La_{2-x}Sr_{x=0.125}CuO_4$ | P8 | 0.125 | 24 | 21* |
| $La_{2-x}Sr_{x=0.17}CuO_4$ | P6 | 0.17 | 31 | 28* |
| $La_2CuO_{4+z(0.17)}$ | P3 | 0.33 | 49 | 53* |
| $Sr_2CuO_{3+z(0.17)}$ | P3 | 0.33 | 72 | 70* |
| $YBa_2Cu_2Cu_2O_8$ | P2 | 1.0 | 81 | 83* |
| $Bi_2Sr_2CuO_6$ | (P1) | 1.0 | — | (56*, P2) |

[a]Holes are stoichiometric. For $Bi_2Sr_2CuO_6$, *P*1 and $h = 1$ is assumed from doping behavior.

*General Lattice Pressure*

Figure 4 shows, for selected cases, the way in which the three basic layers reach compromises in a given structure leading to the buildup of lattice pressure. A point of reference is the "earth" ($E$ = alkaline earths Ba, Sr; rare earths = La, etc.) oxide plane. Where $E$ = BaO, a relatively large 3.86 Å (equivalent compared to the basis of P) is calculated from the atomic radii in Table 4. The examples given indicate that Ba analogs closely adhere to this spacing. This means, however, that P has to contract considerably. This contraction can be seen as inviting subperoxidic electronic liquefaction (and P buckling for $n > 1$). This contraction is yet more severe for $E$ = Sr.

The topmost example $La_{2-x}Sr_x\ CuO_4$ exemplifies a case of early $T_c$ collapse due to the combined effects of this lattice pressure and atomic disorder. $Bi_2Sr_2CuO_6$ analogs are also examples of strong lattice pressure which for $n = 1$ leads to a combination of partial Bi reduction and corresponding P oxidation, resulting in P2 overoxidation to P1 and nonsuperconductivity. The higher $n$ analogs can more successfully resist the P contractions and approach P2. This is especially pronounced for the single plane ($n = 1$) materials, which are nonsuperconducting. The more rigid $R_{n-1}Cu_nO_{2n}$-type units with spacer $R$ = rare earth or Ca maintain higher lattice parameters and are less prone to P2 overdoping effects. It is, however, interesting that $Bi_2Sr_2CuO_6$ can be made superconducting on doping according to $Bi_2Sr_{2-x}La_xCuO_6$, with an optimum $T_c$ (23 K) near $x = 0.4$. Assuming that this optimum corresponds to P2, one calculates the formal Cu oxidation for $x = 0$ as $2.9+$. It is likely that disorder effects have camouflaged the real optimum, which is assumed at $x = 0.5$. This indicates

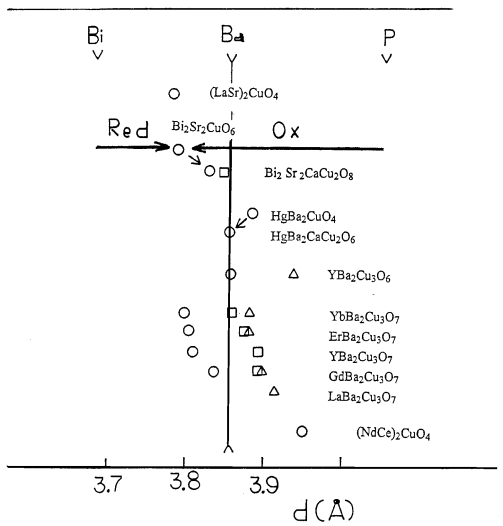


**FIG. 4.** Lattice dimensions in selected cuprates. Circles, squares, and triangles indicate *a*, *b*, and *c* axis. Also indicated are ideal slab dimensions of planes (P), the BaO and BiO layers. The small Sr dimension can lead to early $T_c$ collapse [(LaSr)$CuO_4$] or to P1 ($Bi_2Sr_2CuO_6$). In the latter, reductive self-doping (Red) on Bi leads to plane contractions (Ox). Hg analogs display strong changes in the step between $n = 1$ and 2 from $P^+$ to $P^-$. Selected $RBa_2Cu_3O_y$ are representatives of $P^-$ materials with hole placement on $\sigma$ O orbitals. It is suggested that materials such as $(NdCe)_2CuO_4$ with strong $P^+$ effects correspond to hole placement on $\pi$ O orbitals which do not involve Cu overlap and *d* wave property.

**TABLE 3**
**Calculated (Asterisk) and Observed (e.g., Refs. 1, 2) Optimal $T_c$ of Selected Complex Cuprates Together with Plane Dimensions[a]**

| Material | $T_c$, calc (K) | $T_c$, obs (K) | *a* (Å) | *b* (Å) |
|---|---|---|---|---|
| $HgBa_2CuO_4$ | 83* | 90 | 3.88 | — |
| $HgBa_2CaCu_2O_6$ | 111* | 120 | 3.86 | — |
| $HgBa_2Ca_2Cu_3O_8$ | 125* | 134 (164) | 3.85 | — |
| $Bi_2Sr_2CuO_6$ | 56* | – (23) | 3.79 | — |
| $Bi_2Sr_2CaCu_2O_8$ | 83* | 80–90 | 3.83 | 3.85 |
| $Bi_2Sr_2Ca_2Cu_3O_{10}$ | 100* | 110 | 3.82 | 3.86 |

[a]Calculations are performed on the radical formula assuming uniform doping to P2 through a combination of overoxidation and selfdoping. O contents are in some cases slightly higher than indicated. Bracketed values are described in text.

**TABLE 4**
**Diameters and Bond Lengths Used as Guides for Tension Doping Arguments[a]**

| Material | *d* (Å) | $d_{MO^{2-}}$ |
|---|---|---|
| $O^{2-}$ | 2.76 | |
| $Cu^{2+}$, (1)4 | 1.14 | 34.90 |
| $La^{3+}$ | | 3.58* |
| $Sr^{2+}$ | | 3.55* |
| $Ba^{2+}$ | | 3.86* |
| $Ra^{2+}$ | | 3.93* |
| $Bi^{3+}$ | | 3.65* |

[a]Asterisk denotes projection on P.

$Cu^{3+}$ and P1 for this extremely overdoped material. As such it represents an example for the nonsuperconducting nature of P1.

For $HgBa_2CuO_4$ analogs the situation is reversed, as the $n = 1$ analog has relatively expanded planes ($P^+$ effects). This is related to the larger Ba.

For $RBa_2Cu_3O_y$ the choice of $R$ determines the P dimension, which remains relatively contracted for $y = 7$ compared to the semiconductor at $y = 6$. These $P^-$ effects are here related to placement of holes on $\sigma$ O orbitals which are oriented toward Cu and therefore gain $d$ wave properties.

An unusual situation pertains to compounds such as $Nd_{2-x}Ce_xCuO_4$ which display strong $P^+$ effects and absence of $d$ wave properties. This is here related to hole placement in $\pi$ O orbitals extending within P. Where $\pi$ O orbitals are occupied which extend perpendicular to the plane (e.g., $R$ = Pr) nonsuperconductivity can result (13).

A large number of cases indicate that $T_c$ optima or limits reflect characteristic commensurability effects as expected for charge order phenomenology. A typical sampling is given in Fig. 3 and Table 2. As an example, a $T_c$ maximum obtains for $La_{2-x}Sr_{x=0.16}CuO_4$. This corresponds to $k \sim 6$ (P6 or one in six Cu being formally 3 +, while in the anionic representation this corresponds to one $O^-$ in 24, or $q = 24$). Onset of another type of metallicity with a different power law occurs near $k = 3$ or $q = 12$. This is here related to O placement solely on the apical positions, as born out in a reversal of $c$ axis trends with increasing oxidation. The $T_c$ anomaly for $x = 1/8$ is an example for P8.

### *Stratified Tension Self-doping*

In order to more fully appreciate the influence of lattice pressure on the stratified creation or annihilation of superconducting subperoxides or $T_c$, we will in the following briefly outline the situation on $YBa_2Cu_3O_{y\sim 6.5}$, which is nominally undoped. It can occur, however, in a variety of self-doped states, three of which are superconducting ($V^+$, $V^o$, $V^-$) while two ($C^-$, T3) are not. The origins of these changing self-dopings are found in changes with temperature of the O–O interaction potentials, establishing variations in lattice pressure and tension self-doping steps. Essential aspects of these ideas are presented in Refs. (5–8). *In situ*, high-temperature work indicates that at $y = 6.5$ the material has structural parameters characteristic of the tetragonal semiconductor designated T3, where 3 denotes the three-fold O coordination. Conventional slow cooling produces the cell volume contracted ($V^-$), alternate chain O42 superconductor. However, shot cooling can produce various degrees of V expanded, superconducting orthorhombics. One of them is a strongly V expanded version ($V^+$), based on O3. Its extrapolated $T_c \sim 100$ K indicates that $Cu(1)3^+$ exists, which self-dopes to P2. This tension self-doping results in a doubled $T_c$, compared to the conventional O42. When annealed for extended periods, a $c$ axis contracted ($C^-$), nonsuperconducting modification obtains.

## DISCUSSION

This work documents the operation of lattice pressure in creating subperoxidic pairs in oxide superconductors. Examples are the trends to early $T_c$ collapse and P2 overdoping with Sr, distinctions between the type of superconductivity ($d$ wave or not), or the absence thereof (e.g., Pr) depending on not yet fully understood details of three-dimensional lattice pressure.

The progress in the understanding of a connection between electronic liquefaction on P and lattice pressure has been based on a deeper understanding of superconductivity in the covalent model. This model views superconductivity as a last step in a stress relief sequence, employing lattice contracting pair lines. In fact it is now becoming possible, through the predictive qualities of the covalent model, to translate $T_c$ back into holes even in complex self-doped systems. This allows an understanding of the origin and extent of self-doping in the complex Le Chatelier-type equilibria. An example is the overdoping of $Bi_2Sr_2CuO_6$. We shall therefore begin with a brief summary of the phenomenological rules of the covalent model.

Generally, absolute magnitudes of $T_c$ scale universally with radical concentrations. In addition, phenomenology indicates that charge order regularities lead to an optimal alternate hole charge order (P2) as the basis of the highest routinely observed $T_c$. Within P2, the $T_c$ are calibrated through $r$, or parameters such as plane Cu to O ratios ($n/y$). In addition, trends to a series of more dilute charge orderings are apparent, displaying commensurability rules in rational fractions. This provides an unprecedented new understanding of oxide superconductors as "chemical" metals with trends to a series of self-bonding valency steps. The focus of this work is to discuss these regularities in terms of lattice pressure.

From the data of Fig. 3 it is possible to generalize that it is easiest to reach the highest $h/n$ and $T_c$ with materials based on $E$ = Ba (Ra may be yet more promising although impractical experimentally). This appears to reflect the relative spatial similarity with four-fold O-coordinated Cu in the stacking with the earth planes. It holds for a wide range of $YBa_2Cu_3O_y$ and related materials, including complex cuprates. By comparison, $E$ = Sr analogs are prone to two types of "overdoping." They show either early onset of collapse effects in the doping and do not attain maximum $T_c$ [$(LaSr)_2CuO_4$ with $T_p > T_c$], or they stay nonsuperconducting at high doping ($n = 1$ materials). Notable exception are analogs with $E$ = Sr and $M$ = Bi with $n = 2$ and 3, which also show high $T_c$, in line with the alternate hole charge ordering (P2). In this case, the relatively large spacer Ca allows the lattice parameters to approach the ones of the

Ba analogs. However, when this structural support is absent in $n = 1$, this produces especially contracted lattice dimensions, presumably due to trends to P1 and the Sr analogs as a rule loose $T_c$ in a collapse.

These concepts allow one to consider how to achieve yet higher $T_c$, based on lattice pressure-related strategies. A point of departure pertains to the pressure experiments (14) on Hg analogs (Table 2) which show strongly increasing $T_c$ presumably due to increased self-doping. Under pressure it is the rigid P that is preferentially forced to contract. It can for instance do so by accepting a higher concentration of lattice contracting subperoxides. At the same time, the less susceptible Hg stick configurations (lean balance) can actually become reduced, supplying the holes for the P contractions. The rather pronounced $T_c$ increases even beyond the straightforward calculations from the radical formula may suggest that external pressure also gradually removes the apical O from the pool of common polarizations. With a lower O count, the radical formula produces higher $T_c$, with a limit of $T_c = 167^*$ K, or up to 185 K, based on the somewhat higher $T_c^*$ in this case. This would represent the inherent $T_c$ limit for subperoxides and a downturn of $T_c$ under further pressure would corroborate this prediction. This uncoupling of "spacer O" could generally be used as a strategy for increasing $T_c$. Also, partly halogenated materials are of interest in this connection, as the halogens may not fully participate in the polarization.

Generally under compression, P can develop, through self-doping or overoxidation, lines of lattice contractions along axial stripes. Within these stripes, subperoxidic pair formation is strain and exchange energy favored and allows various degrees of elastically correlated motion. In fact, it is interesting that defects such as vacancies also have a tendency to travel in pairs, as this reduces the repulsive interaction. These lattice adjustments can be seen to belong to a variety of mechanisms, such as twin boundaries or dislocation structures, in which the solid can relieve stress (15). In fact remaining stress is often relaxed through tweed microstructures in oxide superconductors. By contrast, for the cationic nickelates, $Ni^{3+}$ has to be accommodated in diagonal charge ordering, to fit into the lattice. Questions of subperoxide pair formation and propagation can accordingly be couched within a language of materials parameters and structural rules (6–8).

These new phenomenological rules have helped to rewrite the basic aspects of the self-doping processes. They have also opened a wide variety of questions that so far have not been addressed experimentally because their importance was not realized. As an example, to date it is not known how the transition from semiconducting to self-doped occurs with temperature for isostoichiometric (*in situ*) $YBa_2Cu_3O_{y\sim 6.5}$. Only for quenched states is it known that structural ladder transitions are involved. It is hoped that the new understanding will lead to a renaissance of interest in variation of synthesis conditions for the textbook examples of stratified self-doping processes.

Lattice pressure on a covalent planar bond system is also causing $C_{60}$-type superconductivity and similar effects should be obtained with isoelectronic $B^-$ in layer networks. The experimental $T_c \sim 50$ K values for $C_{60}$-type superconductivity with three holes are far from optimized as they correspond to $q = 20$ and for $q = 4$; $T_{c\max}$ should accordingly be $\sim 250$ K. Extrapolations indicate the possibility of a doubling of $T_c$ at $h = 3$ and accordingly of $T_{c\max}$.

The main tenet of this work is that the achievement of superconductivity is basically a crystal chemical problem, with lattice pressure acting as an essential aspect in the creation or annihilation of $O^-$. In a most general way, superconductivity is born of and reflects a structure-stabilizing and chemical bond-related phenomenon. In fact, the electronic liquefaction inherent in all anionic metals (e.g., borides, carbides, nitrides, etc.) can be seen as an intriguing mechanism of mediating stress relief. This allows one to achieve stability in the stacking of basically incompatible layers. Superconductivity can be seen as a last step in this direction.

In summary, in the search for manifestations of $O^-$ in oxide superconductors one notices:

(A) A quantitative and universal relationship of $T_c$ with $O^-$/O-related parameters such as radical densities. This reflects a new concept of covalent bond polarization.

(B) An influence of lattice pressure on the level and limits of overoxidation and self-doping, resulting in $T_c$ optima for P2.

(C) Signs for an $O^-$ hole placement crystal chemistry, explaining a range of behavior from $T_c$ collapse to conductivity anomalies and the mode of pair formation.

## CONCLUSION

It is concluded that lattice pressure fosters subperoxide generation, in order to ameliorate slab matching. Stronger lattice pressure can result in higher $O^-$ radical concentration $r$ through self-doping or overoxidation. Phenomenological rules indicate that lattice pressure influences the degree of overoxidation and self-doping, with a common $T_c$ optimum in the alternate hole charge order. This P2 is attained when ideal P and $E$ plane dimensions are similar (e.g., with $E$ = Ba). Where they are not (e.g., $E$ = Sr), severe overdoping can occur. Combined with atomic disorder, $T_c$ collapse can be encountered early in the doping. The encompassing nature of the involvement of structure can be seen in the doping and self-doping limits or in the stratified doping plateaus. The structural chemistry of subperoxide creation and placement through lattice pressure can be utilized for further materials development. Strategies that employ the build-up of severe lattice pressure (e.g., films or thermal stress) are promising to raise $T_c$ to the assumed

general limit near 167–185 K for oxides and considerably higher for borides or C-based materials.

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