

Superconductivity in $Y(\text{Ba}_{1-y}\text{La}_y)_2\text{Cu}_3\text{O}_{9-\delta}$

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The superconducting properties of the $Y(\text{Ba}_{1-y}\text{La}_y)_2\text{Cu}_3\text{O}_{9-\delta}$ phase (note La solely substituting Ba) are studied over the entire homogeneity range, viz., $0.00 < y < 0.36(2)$ and $1.69(2) < \delta < 3.00(2)$ for well-defined samples prepared by the citrate gel method and annealed at controlled partial pressures of O_2 . Superconductivity (for $T_c > 5$ K, by ac susceptibility) is observed over a large range of compositions. In terms of oxygen content, the lower limit for superconductivity varies from $9 - \delta \approx 6.3$ for $y = 0.00$ to $9 - \delta \approx 7.05$ for $y = 0.20$. T_c increases with increasing oxygen content (referring to the oxygen saturation limit $9 - \delta = 6.95(1) + y$ for 320°C at $P_{\text{O}_2} = 100$ kPa), irrespective of the linkage of the copper-oxygen square chains when $9 - \delta$ exceeds 7. For $y = \text{const.}$, T_c is hence correlated with the overall hole concentration $p = (5 - 2\delta - 2y)/3$ per $(\text{Cu}-\text{O})^p$, and these correlations are in turn related to deformation of the structure. For $p = \text{const.}$, T_c decreases with increasing y , and a hole transfer from the Cu(2) to Cu(1) coordination sphere appears to be composed of: (i) a large contribution due to an increased number of oxygens bonded to Cu(1), (ii) a smaller contribution associated with a decrease in orthorhombic deformation, and (iii) an even smaller contribution [about half and of opposite sign to (ii)] attached to decreased tetragonal deformation. The direction of the hole transfer upon a change in the tetragonal deformation depends on the ratio of the partial deformations of the Cu(1) and Cu(2) coordination polyhedra in the crystallographic c direction, the condition of no hole transfer being established when the Cu(2) pyramid deforms about 7 times faster than the Cu(1) square. On the other hand, an increase in the orthorhombic deformation always causes a Cu(1) to Cu(2) charge transfer. All these effects are overshadowed when p changes with the oxygen content. The effects of La substitution are compared with those of Sr substitution, application of external pressure, and change in oxygen content. The occurrence of superconductivity is correlated with fractional occupancy of a single, non-bonding orbital leading to a metallic state, and this picture is discussed for various oxide systems. © 1992 Academic Press, Inc.

Introduction

A metallic, mixed valence state is considered as one prerequisite for the high T_c superconductors (1-4). In cuprates, the mixed valence state applies to the covalent copper-oxygen network, which may be either hole (5, 6) or electron (7, 8) doped. The superconducting state in $Y\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ is reached when certain concentrations of holes are attained in the copper-oxygen

square-pyramidal sheets (9-11). However, the mixed valence state in $Y\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ is not a sufficient condition for the occurrence of superconductivity (12). The favorable hole concentration is easily overshadowed when the Cu sites are partially occupied by other elements (13). Even when the electronic structure at the Cu site is neither perturbed through substitutions nor by changes in the hole concentration, T_c may be reduced as a result of subtle changes in the overall

crystal structure, as is believed to occur for $Y(\text{Ba}_{1-y}\text{Sr}_y)_2\text{Cu}_3\text{O}_{\sim 7}$ (14).

Substitutions induce changes in bond distances, which may influence the Fermi surface yielding a variation in T_c . Changing the hole concentration in $Y\text{Ba}_2\text{Cu}_3\text{O}_{9-\delta}$ through the oxygen content also alters the structural parameters which are supposed to be of major importance for superconductivity; for example, orthorhombic (15) or tetragonal (16, 17) deformation. The separation of the effects due to the hole concentration from those originating from the structural features represents therefore an important challenge.

$Y(\text{Ba}_{1-y}\text{La}_y)_2\text{Cu}_3\text{O}_{9-\delta}$ provides an interesting opportunity to approach this question experimentally. As reported earlier (18–20), substitution of La^{3+} for Ba^{2+} introduces additional oxygen atoms into the structure, while the overall formal Cu valence remains ~ 2.30 . Since La^{3+} does not substitute in the Y^{3+} site, the complexity of the structural impact (as evidenced from the changes in the structural variables) is minimized.

In order to deconvolute the effects of the Cu valence, the oxygen content, and the unit cell geometry on the superconducting transition temperature, T_c is determined over the entire homogeneity envelope with respect to La for Ba substitution and oxygen content. The variation of T_c is separated into effects caused by changes in the Cu(1), Cu(2), and Y coordination spheres, as well as changes in the oxygen content. In this process, the structural data for La substitution (20) are compared with data for Sr substitution (14) and application of external pressure (21).

Experimental

All samples were prepared by a liquid mixing technique followed by incineration of the formed citrate gels, and subsequent cycles involving homogenization, firing, and controlled oxidation. The amount of oxygen

in the samples was varied using controlled deoxidation by an exact amount of Ti powder in closed silica-glass ampoules. The oxygen content was determined iodometrically, with a reproducibility of ± 0.005 in units of the formal oxidation state of Cu. All samples were characterized by powder X-ray diffraction, using Guinier Hägg cameras. Structural parameters of the oxygen saturated $Y(\text{Ba}_{1-y}\text{La}_y)_2\text{Cu}_3\text{O}_{\sim 6.95+y}$ at room temperature were refined from powder neutron diffraction data. A more detailed description of the methods used in the preparation, analysis, and characterization is given in Ref. (20).

T_c and the degree of Meissner effect for temperatures down to 56 K were determined by measuring ac magnetic susceptibility. The sample (50 mg) was placed in a cylindrical ($l/r \cong \sqrt{3}$) sample holder inside a chamber with pick-up coils. The chamber was first field-cooled (~ 1 mT, frequency 300 Hz) by liquid nitrogen, followed by further cooling (to the triple point of oxygen) upon evacuation of the sample chamber. The voltage induced in the pick-up coils was amplified by a lock-in voltmeter. The Meissner fraction (MF) was determined as an absolute value of dimensionless diamagnetic susceptibility. A density of 3 g cm^{-3} for the powder samples was used to calculate the susceptibility (calibrated toward dysprosium oxide). T_c was determined upon temperature increase as the point with a residual MF = 0.002. For the temperature range 4 to 56 K, T_c was evaluated on the basis of magnetic susceptibilities measured using a SQUID magnetometer (MPMS, Quantum Design) in a magnetic field of 3 mT.

Results and Discussion

Composition Variables and T_c

Although the ionic radius of lanthanum is significantly smaller than that of barium, the substitution in $Y(\text{Ba}_{1-y}\text{La}_y)_2\text{Cu}_3\text{O}_{9-\delta}$ leaves

the sum of the a and b unit cell parameters practically independent of y (and smaller variations in δ),

$$(a + b)/2 = (383.8 \pm 0.8) + (7 \pm 5) \times 10^{-5}y + (0.77 \pm 0.12)\delta \quad [\text{pm}], \quad (1)$$

as obtained by least squares fitting of data for 48 compositions between $y = 0.00$, $\delta \in (2.0, 3.0)$, and $y = 0.20$, $\delta \in (1.8, 2.6)$. The difference between the a and b dimensions is largest for oxygen contents slightly below $9 - \delta = 7$, and a and b approach one another with increasing La^{3+} substitution (see Fig. 1B). The volume reduction is accomplished by a contraction of c , (approximately linear over the interval in question; Fig. 1A),

$$c = (1140 \pm 3) - (4.1 \pm 0.2) \times 10^{-3}y + (13.95 \pm 0.42)\delta \quad [\text{pm}]. \quad (2)$$

The compositional variation of $Y(\text{Ba}_{1-y}\text{La}_y)_2\text{Cu}_3\text{O}_{9-\delta}$ strongly affects the superconducting transition temperature T_c (Fig. 1C). The Meissner fraction varies correspondingly. For T_c above 90 K, $\text{MF} \approx 0.3$ is obtained, whereas $\text{MF} \approx 0.1$ for transition temperatures around 50 K and $\text{MF} \approx 0.03$ for T_c around 20 K. Due to this correlation to T_c , it is believed that the observed MF refers to a homogeneous superconducting phase.

As follows from Fig. 1C, T_c increases with increasing oxygen content up to the saturation limit (320°C , $P_{\text{O}_2} = 1 \text{ atm}$), at which the copper valence is $v_{\text{Cu}} \approx 2.30$. This behavior is seen whether or not the oxygen content exceeds $9 - \delta = 7$, suggesting that T_c correlates much more strongly with the formal valence of copper than with the linkage of the square Cu—O chains. The formal Cu valence can be expressed in terms of a (formal) overall amount ($p = v_{\text{Cu}} - 2$) of hole carriers per $(\text{Cu—O})^{p+}$, or in terms of compositional variables [$p = (5 - 2\delta - 2y)/3$]. Since p was found to be a function of the effective carrier density [by Hall coefficient measurements (22)], it is tempting at first to correlate T_c with the overall value of p . A more rigorous analysis is discussed later in which dis-

tinction has been made between the two crystallographically different Cu sites. In contrast, even for a constant p , one observes a decrease in T_c with increasing lanthanum substitution. This decrease may reflect a variety of possible changes in the electronic band structure, concerning the position, shape, and other characteristics of the Fermi surface, the density of particular states at and near the Fermi level, band gaps, and also more local features such as the charge distribution over the atoms. It is very likely that some of these changes are reflected in, or are consequences of, anisotropic variations in the structural parameters following from the substitution. Some of these possibilities are explored in the following subsections.

Unit Cell Deformations and T_c

As the first and most coarse measure for the induced anisotropic structural changes, the variation in the unit cell parameters may be considered. Two anisotropy gauge parameters, which respectively describe the tetragonal and orthorhombic character of a deformed, single perovskite unit cell, may be introduced. Here the term extension has been introduced in order to specify the nature of the deformation:

$$\mathcal{E}_T = 2c/3(a + b) \quad \text{and} \quad \mathcal{E}_O = b/a. \quad (3)$$

When the strongly correlated parameter p is constrained, viz., $p = \text{const.}$, it is evident that a correlation exists between T_c and \mathcal{E}_T , as depicted in Fig. 2A with p included as a third variable. The analogous plot for \mathcal{E}_O in Fig. 2B illustrates that correlation between \mathcal{E}_O and superconductivity is missing, but this may be explained away as due to disorder in the square chain arrangement (23). The nature of the correlation between \mathcal{E}_T and T_c suggests that \mathcal{E}_T may provide a too coarse measure, but may be justified by the fact that unit cell data are easily obtained and, moreover, often are the only structural

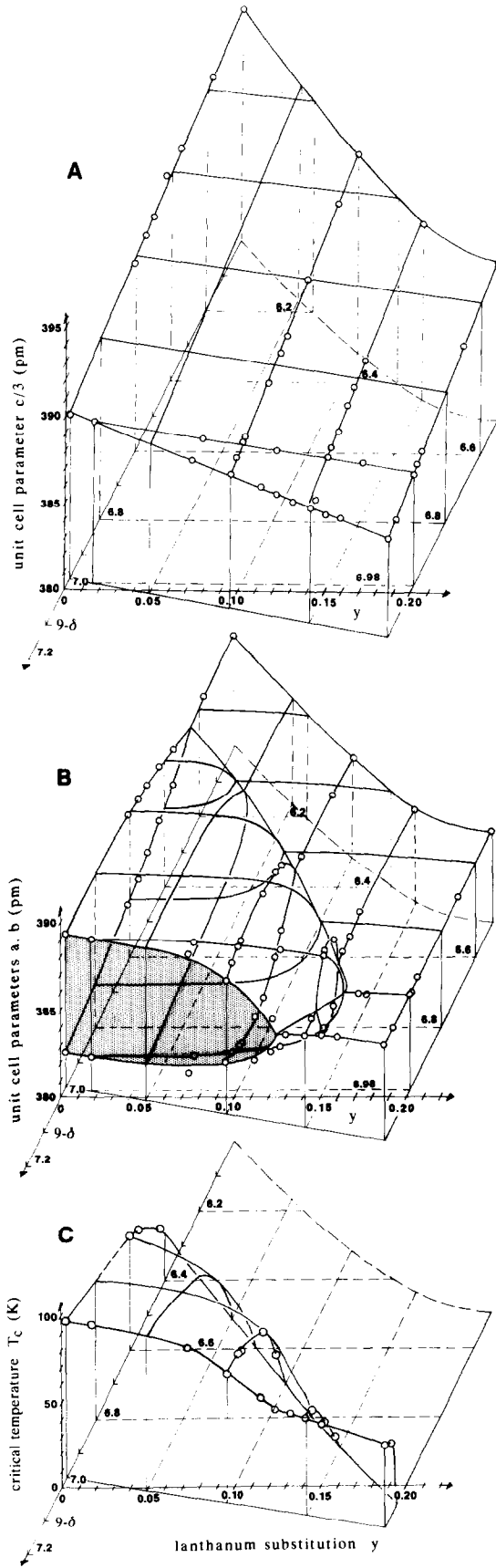


FIG. 1. Unit cell dimensions (A and B) and T_c (C) of $Y(\text{Ba}_{1-y}\text{La}_y)_2\text{Cu}_3\text{O}_{9-\delta}$ as functions of oxygen content δ and lanthanum substitution for $0.00 < y < 0.20$.

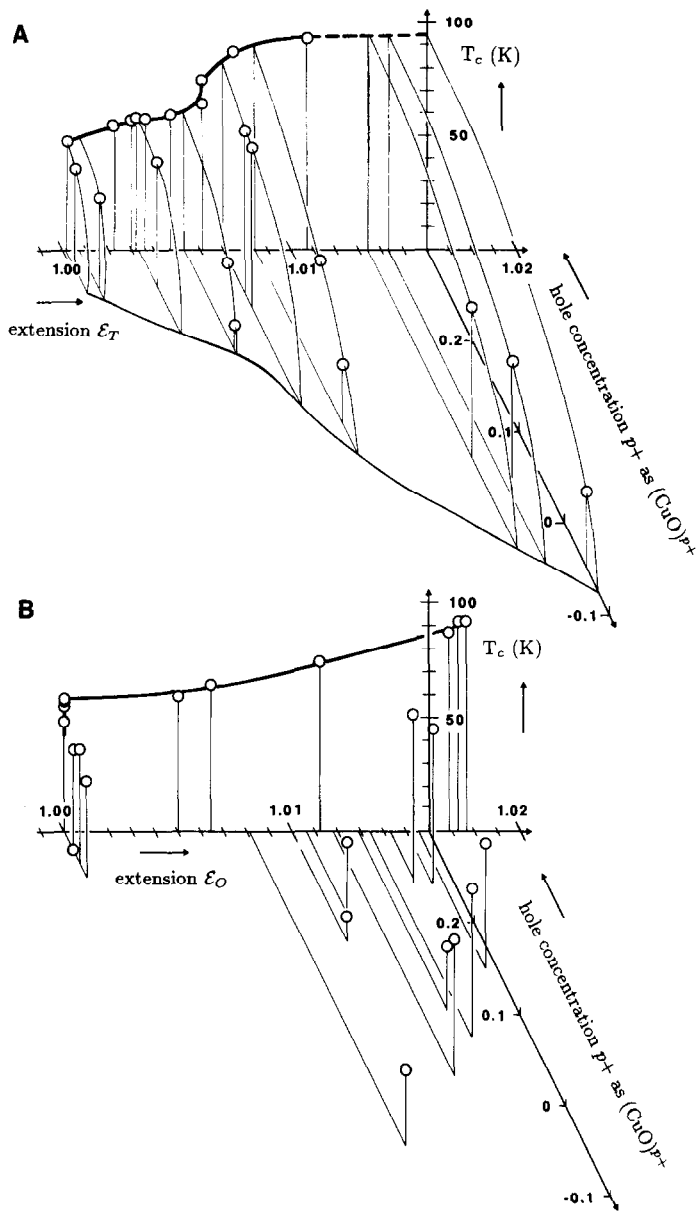


FIG. 2. T_c as a function of hole concentration p and (A) tetragonal [$\epsilon_T = 2c/3(a + b)$] and (B) orthorhombic [$\epsilon_O = b/a$] extension. Size of symbols is at least half the estimated standard deviation.

characteristics available for comparisons of the substituted $\text{YBa}_2\text{Cu}_3\text{O}_{9-\delta}$ phases.

However, even crude comparisons with ϵ_T and ϵ_O are of interest. When a small portion of oxygens in the ab plane is substituted by CO_3^{2-} , the c axis shortens consider-

ably, and although the phase still retains a high Cu valence [$p = 0.27$; (24)], no sign of superconductivity is observed down to 4 K. ϵ_T equals 0.999 and ϵ_O equals 1 for tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}(\text{CO}_3)_{0.2}$ as compared with $\epsilon_T = 1.011$ and $\epsilon_O = 1.018$ for the parent

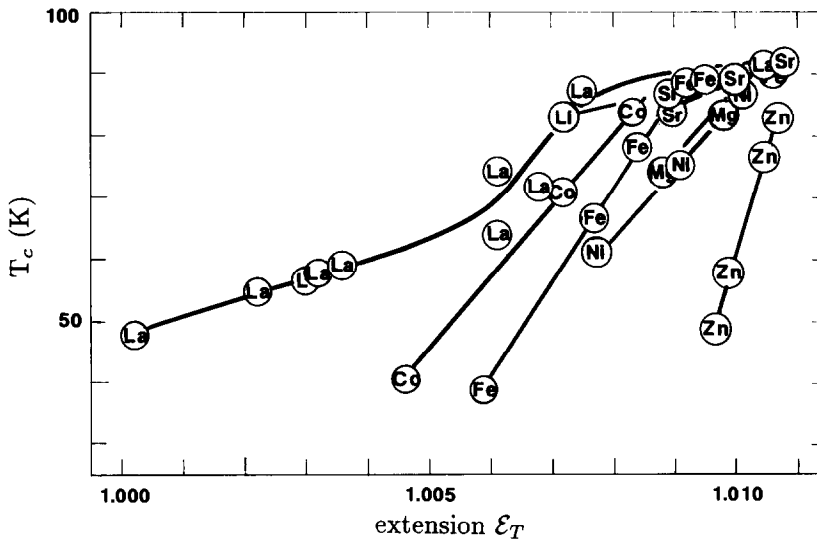


FIG. 3. T_c as a function of tetragonal extension [$\epsilon_T = 2c/3(a + b)$] for lanthanum, strontium (14), and d -metal (13) substituted samples of $\text{YBa}_2\text{Cu}_3\text{O}_{9-\delta}$, saturated in 100 kPa P_{O_2} (see text).

phase. Curiously, even when T_c is suppressed by substitution for Cu in $\text{YBa}_2\text{Cu}_3\text{O}_{9-\delta}$, ϵ_T decreases (Fig. 3).

Despite the overall rough correlations between T_c and ϵ_T , the striking diversity between the different substituents suggests that other structural variables reflected in the bond lengths should be considered. Hence one should search for correlations between variation in T_c and local, rather than overall, structural anisotropic changes; an approach more in line with the localized nature of the substitution intervention in the $\text{YBa}_2\text{Cu}_3\text{O}_7$ -type structure.

Partial Unit Cell Deformations and T_c

While the atomic framework of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ -type unit cell does not easily allow ϵ_0 to be divided into subcomponents, three components of ϵ_T can be identified, including the coordination spheres of Cu(1) (square chains), Cu(2) (square pyramids), and Y. These partial extensions are defined as

$$\epsilon_T^{\text{Cu}(1)} = 4D_{\text{Cu}(1)\text{O}(2)}/(a + b), \quad (4)$$

$$\epsilon_T^{\text{Cu}(2)} = 4D_{\text{Cu}(2)\text{O}(2)}/(a + b), \quad (5)$$

$$\epsilon_T^{\text{Y}} = 2D_{\text{Cu}(2)\text{Cu}(2)}/(a + b), \quad (6)$$

where the notation $D_{\text{Cu}(1)\text{O}(2)}$ refers to the interatomic distance between Cu(1) and the apical oxygen atom [O(2)] shared by the Cu(1) and Cu(2) coordination spheres. The sum of these partial extensions gives the overall extension per unit cell:

$$\epsilon_T^{\text{Cu}(1)} + \epsilon_T^{\text{Cu}(2)} + \epsilon_T^{\text{Y}} = 3\epsilon_T. \quad (7)$$

If the structure is subject to a perturbation (\mathcal{P} symbolizing here La for Ba substitution, Sr for Ba substitution, and applied pressure perturbations), the partial extensions tend to vary. Their variations are evaluated from room temperature structure data for oxygen saturated samples [see Refs. (20, 14, 21) and Table I]. The partial extensions (Fig. 4) vary differently with respect to the perturbations, but this very feature allows their individual influence on T_c to be separated. [$dT_c/dP = 0.65(15) \text{ K GPa}^{-1}$ (25) is used for the exter-

TABLE I
TRENDS IN STRUCTURAL CHARACTERISTICS UPON La AND Sr SUBSTITUTION
IN $Y\text{Ba}_2\text{Cu}_3\text{O}_{9-\delta}$; OXYGEN SATURATED

La y:	0.000	0.075	0.100	0.150	0.200	$\Delta f(y)/\Delta y$	$f(0)$
<i>a</i>	381.91(3)	381.87(3)	382.84(3)	385.39(4)	385.53(6)		
<i>b</i>	388.49(2)	388.59(3)	387.6(30)				
<i>c</i>	1167.9(1)	1165.1(1)	1163.0(2)	1160.0(3)	1156.7(2)	-55(2)	1168.3(3)
$D_{\text{Cu}(1)\text{O}(1)}$	194.25(1)	194.30(1)	193.80(5)	192.70(1)	[192.8]	-11(3)	194.7(4)
$D_{\text{Cu}(1)\text{O}(2)}$	188.9(8)	189.1(8)	189.0(9)	188.8(8)	[185.5]	-0.2(11)	188.98(12)
$D_{\text{Cu}(1)\text{O}(5)}$	190.96(1)	190.94(1)	191.42(3)	192.70(1)	[192.8]	+12(4)	190.5(4)
$D_{\text{Cu}(2)\text{O}(2)}$	227.9(13)	229.1(14)	227.0(14)	223.8(14)	[226.0]	-30(12)	229.3(13)
$D_{\text{Cu}(2)\text{O}(3)}$	193.4(2)	192.7(3)	193.1(3)	194.6(3)	[194.5]	+9(6)	192.7(6)
$D_{\text{Cu}(2)\text{O}(4)}$	193.33(15)	195.6(2)	195.3(2)	194.6(2)	[194.5]	-5(3)	195.6(3)
$D_{\text{Cu}(2)\text{Cu}(2)}$	334.5(12)	328.8(12)	330.9(12)	334.7(12)	[333.6]	+7(22)	331.7(24)
$n_{\text{O}(1)}$	0.90	0.94	0.90	0.54	0.56		
$n_{\text{O}(5)}$	0.05	0.06	0.11	0.54	0.56		
Sr y:		0.100	0.150	0.200	0.300	$\Delta f(y)/\Delta y$	$f(0)$
<i>a</i>		381.22(4)	381.11(5)	380.58(3)	379.98(5)		
<i>b</i>		387.99(4)	387.72(5)	387.37(3)	386.58(5)		
<i>c</i>		1165.4(1)	1163.0(2)	1162.6(1)	1160.0(2)	-27(2)	1167.8(4)
$D_{\text{Cu}(1)\text{O}(1)}$		194.00(1)	193.86(3)	193.68(1)	193.29(2)	-3.01(16)	194.26(3)
$D_{\text{Cu}(1)\text{O}(2)}$		189.6(8)	190.0(8)	190.1(8)	188.9 (8)	+0.5(3)	189.4(6)
$D_{\text{Cu}(1)\text{O}(5)}$		190.61(2)	190.55(3)	190.29(1)	189.99(2)	-3.28(11)	190.96(2)
$D_{\text{Cu}(2)\text{O}(2)}$		225.0(14)	224.6(14)	224.0	223.0(14)	-16(2)	227.3(5)
$D_{\text{Cu}(2)\text{O}(3)}$		193.4(3)	193.6(3)	193.2(3)	192.9(3)	-1.6(8)	193.55(13)
$D_{\text{Cu}(2)\text{O}(4)}$		194.82(16)	194.49(15)	194.09(11)	194.12(16)	-4.6(11)	195.22(19)
$D_{\text{Cu}(2)\text{Cu}(2)}$		336.1(9)	333.8(9)	334.4(9)	336.4(9)	+4(5)	334.7(10)
$n_{\text{O}(1)}$		0.90	0.89	0.89	0.88		
$n_{\text{O}(5)}$		0.05	0.06	0.06	0.07		

Note. From room temperature data (20) for $Y(\text{Ba}_{1-y}\text{La}_y)_2\text{Cu}_3\text{O}_{6.91(2)+y}$ [data for $y = 0.10$ and 0.15 are averages of two independent samples; data for $y = 0.20$ (in brackets) are excluded from regressions] and $Y(\text{Ba}_{1-y}\text{Sr}_y)_2\text{Cu}_3\text{O}_{6.95(1)}$ (14). Values for slopes [$\Delta f(y)/\Delta y$] and intercepts [$f(0)$] as obtained by least squares linear regression.

nal pressure effect.] In order to facilitate simple, rough comparisons, the partial extensions are approximated as linear functions of the perturbations (Fig. 4; the calculated standard deviations by linear regressions are comparable with errors from structural refinements). Moreover, the perturbation derivatives thus come out as simple slopes, which may be suitable for the comparisons. If one assumes, for the present system, that T_c is a function of, and only of, $\mathcal{E}_T^{\text{Cu}(1)}(\mathcal{P})$, $\mathcal{E}_T^{\text{Cu}(2)}(\mathcal{P})$, and $\mathcal{E}_T^{\text{Y}}(\mathcal{P})$ [a questionable assumption in the La case, *vide infra*], the effect of the partial extensions on T_c can

be approached via the perturbation differential of T_c :

$$\frac{\Delta T_c}{\Delta \mathcal{P}} = \frac{\Delta T_c}{\Delta \mathcal{E}_T^{\text{Cu}(1)}} \cdot \frac{\Delta \mathcal{E}_T^{\text{Cu}(1)}}{\Delta \mathcal{P}} + \frac{\Delta T_c}{\Delta \mathcal{E}_T^{\text{Cu}(2)}} \cdot \frac{\Delta \mathcal{E}_T^{\text{Cu}(2)}}{\Delta \mathcal{P}} + \frac{\Delta T_c}{\Delta \mathcal{E}_T^{\text{Y}}} \cdot \frac{\Delta \mathcal{E}_T^{\text{Y}}}{\Delta \mathcal{P}}. \quad (8)$$

Since $\Delta T_c/\Delta \mathcal{P}$ is approximately linear, the unknown partial extension differentials of T_c are obtained from a set of linear equations, based on Eq. (8) for each of the three independent perturbation systems. Using the ex-

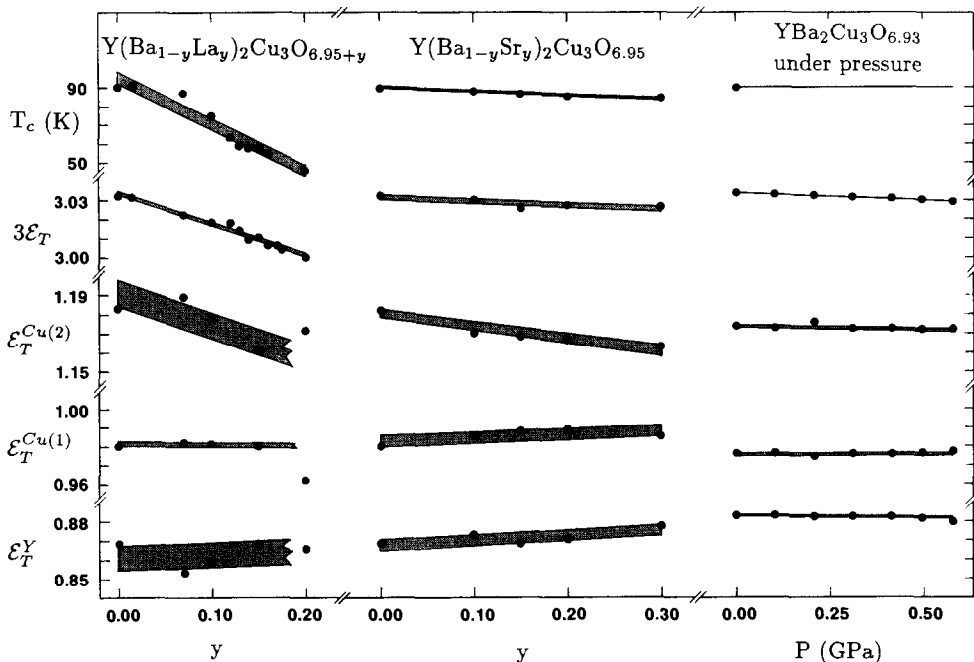


FIG. 4. T_c , overall tetragonal extension ϵ_T , and partial extensions $\epsilon_T^{\text{Cu}(2)}$, $\epsilon_T^{\text{Cu}(1)}$, and ϵ_T^{Y} of the oxygen saturated yttrium barium cuprate as functions of perturbations \mathcal{P} by La and Sr (\mathcal{A}) substitution for Ba and applied external pressure P (21). Shading indicates standard deviations of least squares linear regressions.

perimentally founded data in Table II, the following differentials are obtained:

$$\Delta T_c / \Delta \epsilon_T^{\text{Cu}(1)} = 3800(2600) \text{ K} \quad (9)$$

$$\Delta T_c / \Delta \epsilon_T^{\text{Cu}(2)} = 1400(600) \text{ K} \quad (10)$$

$$\Delta T_c / \Delta \epsilon_T^{\text{Y}} = -100(500) \text{ K}. \quad (11)$$

Despite the appreciable standard deviations, these results indicate that a decrease in T_c is correlated with decreasing extensions in *both* Cu coordination polyhedra, whereas it is rather insensitive to deformations within the Y coordination sphere. The last result complies with the fact that perturbations at the Y site (substitution by rare earth elements) have an effect on T_c (26) which is only one third of that induced by substitution at the Ba site (14). These findings stress the individual character of the

two Cu coordination polyhedra, which certainly deserves a further discussion.

Cu(1) and Cu(2) Valences and T_c

Since there appears to be a strong correlation between T_c and the overall hole concentration p , and it is generally accepted (27) that there exists a causal correlation between T_c and the charge at Cu(2), it is reasonable to examine whether structural deformations can cause an internal charge transfer between the two Cu coordination polyhedra (Fig. 5). Such an internal charge transfer is readily imagined due to the different bonding situations at Cu(1) and Cu(2). To further understand this problem, it seems useful to examine the charge distribution between the Cu(1) and Cu(2) polyhedra, subject to variation in \mathcal{P} . First, however, an

TABLE II
PERTURBATION DERIVATIVES OF T_c AND OF PARTIAL
TETRAGONAL EXTENSIONS

\mathcal{P} :	y_{La}	y_{Sr}	P
$\Delta T_c / \Delta \mathcal{P}$	-247(25)	-18(3)	+0.65(15)
$\Delta \mathcal{E}_T / \Delta \mathcal{P}$	-0.162(8)	-0.019(8)	-0.0073(3)
$\Delta \mathcal{E}_T^{\text{Cu}(2)} / \Delta \mathcal{P}$	-0.162(64)	-0.062(15)	-0.0036(19)
$\Delta \mathcal{E}_T^{\text{Cu}(1)} / \Delta \mathcal{P}$	-0.005(7)	+0.019(16)	+0.0014(16)
$\Delta \mathcal{E}_T^Y / \Delta \mathcal{P}$	+0.015(58)	+0.025(15)	-0.0048(15)

Note. For $Y(\text{Ba}_{1-y}\text{M}_y)_2\text{Cu}_3\text{O}_{9-\delta}$, $M = \text{La}$ ($0.00 < y < 0.150$), Sr ($0.00 < y < 0.30$), and $y = 0.00$ with external pressure P ($0.0 < P < 0.6$ GPa). All samples have a constant formal Cu valence of 2.29(1). For definition of \mathcal{E}_T , $\mathcal{E}_T^{\text{Cu}(1)}$, $\mathcal{E}_T^{\text{Cu}(2)}$, and \mathcal{E}_T^Y see Eqs. (3)–(7).

accessible variable should be found which is suitable for monitoring the charge transfers (or lack of transfer). Since the occurrence of superconductivity in $Y\text{Ba}_2\text{Cu}_3\text{O}_{9-\delta}$ structurally can be considered to be connected with filling vacancies by oxygen atoms, the phenomenon is related to the local transfer of electrons from non- or antibonding orbitals (bands) to bonding orbitals. The transferred charge is equivalent to the amount of holes created in the former orbit-

als. However, the actual location of the holes to Cu and/or O depends on the nature of the bonds formed, with the most even distribution occurring for high covalence. Even though this distribution is not known, a measure of the hole content per coordination polyhedron can be obtained using valences. The actual charge distribution between the bonding partners is outside the scope of the ideal valence concept, and hence either the formal ionic or covalent concept may be adopted to count electrons.

However, if the infinite network of a solid contains nonidentical coordinations around an atom which may take various oxidation states, the particular valences cannot be obtained without assumptions. The individual valences may be approximated according to Brown's (28, 29) scheme where formal valence is obtained from a large number of distance data for a particular bond, fitted to fulfill the Pauling's (30) valence sum rule. This provides parameters for an empirical relation between bond length $D_{\text{Cu}(i)\text{O}(j)}$ and bond strength $S_{\text{Cu}(i)\text{O}(j)}$, e.g.,

$$S_{\text{Cu}(i)\text{O}(j)} = (D_{\text{Cu}(i)\text{O}(j)} / D_0)^{-N}, \quad (12)$$

where $D_0 = 171.8$ pm and $N = 6.0$ (28) repre-

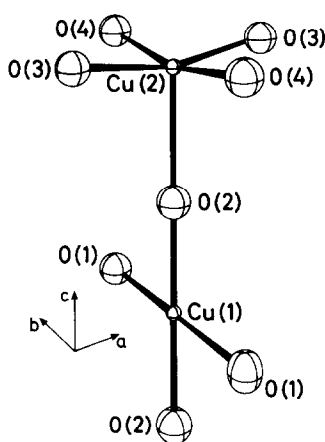


FIG. 5. The two Cu coordination spheres in $Y\text{Ba}_2\text{Cu}_3\text{O}_7$ with labeling of atoms as used in Refs. (14, 20). The O(5) site which becomes appreciably populated in $Y(\text{Ba}_{1-y}\text{La}_y)_2\text{Cu}_3\text{O}_{-6.95+y}$, is not marked, its location being at 90° to $\text{Cu}(1)\text{--O}(1)$ and $\text{Cu}(1)\text{--O}(2)$.

sent an average over a large number of compounds with Cu^{II} bonded to oxygen.

An *absence* of charge transfer between the Cu(1) and Cu(2) coordination polyhedra upon a perturbation \mathcal{P} , would thus require conservation of the valence ratio

$$r_{21} = \frac{v_{\text{Cu}(2)}}{v_{\text{Cu}(1)}} = \frac{\sum_j S_{\text{Cu}(2)\text{O}(j)}}{\sum_j S_{\text{Cu}(1)\text{O}(j)}}, \quad (13)$$

where the index j refers to the coordinated oxygen atoms. Using Eq. (12), the bond distances and the oxygen occupancies from Refs. (14, 20, 21), the calculated valence ratios r_{21} for oxygen saturated samples were regressed as linear functions of the perturbations by La substitution (20), Sr substitution (14), and external pressure [(21); in GPa]:

$$\begin{aligned} r_{21} &= 1.03(1) - 0.48(15) \cdot y_{\text{La}} \\ &= 1.03(1) + 0.10(7) \cdot y_{\text{Sr}} \quad (14) \\ &= 1.028(2) + 0.008(6) \cdot P. \end{aligned}$$

A notable feature is that La substitution gives rise to an appreciable decrease in r_{21} , whereas a (slight) increase in the relative hole concentration at Cu(2) is seen for Sr substitution and application of external pressure. Numerically, Eq. (14) shows that the effect of La substitution is about five times more powerful than, and of opposite sign to, that of Sr substitution. Including also the additional assumption that the sum of the formal valences at the Cu sites remains constant, it is possible to resolve $v_{\text{Cu}(1)}$ and $v_{\text{Cu}(2)}$. The valence sum was fixed at the calculated value for unperturbed $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$ [$2v_{\text{Cu}(2)} + v_{\text{Cu}(1)} = 6.23(7)$ and $6.29(3)$ for substitutions and pressure influence, respectively (14, 20, 21)]. The calculations were performed numerically "point by point" and, after regression as linear functions, the following relations for $v_{\text{Cu}(2)}$ are obtained.

$$\begin{aligned} v_{\text{Cu}(2)} &= 2.098(9) - 0.33(9) \cdot y_{\text{La}} \\ &= 2.097(7) + 0.07(4) \cdot y_{\text{Sr}} \quad (15) \\ &= 2.118(2) + 0.002(3) \cdot P. \end{aligned}$$

It is also interesting to compare the valence changes according to Eq. (15) with the case where the valence changes only with the oxygen content in $\text{YBa}_2\text{Cu}_3\text{O}_{9-\delta}$. Using the same procedure as above, but relinquishing the constraint on $2v_{\text{Cu}(2)} + v_{\text{Cu}(1)}$, one obtains (with $\delta' = \delta - 2$),

$$r_{21} = 0.93(3) + 0.33(4) \cdot \delta' \quad (16)$$

$$v_{\text{Cu}(2)} = 2.073(5) - 0.055(8) \cdot \delta', \quad (17)$$

on the basis of the bond length data of Jorgensen *et al.* (31). The variation in the constant terms of Eqs. (14) and (16), which originates from the different sources of the experimental data (14, 20, 21, 31), is of less importance in this connection. For the present purpose it is sufficient to note that $r_{21} \approx 1$ and focus attention on the markedly different response to the various perturbations. (Note also that $\delta' \approx 0.05$ corresponds to $y_{\text{La}} = y_{\text{Sr}} = P = 0$.) The average Cu valences [$(2v_{\text{Cu}(2)} + v_{\text{Cu}(1)})/3$] according to Eqs. (14)–(17) are distinctly lower than the values found by iodometry. This reflects either a methodical weakness of Brown's approach or that the values for D_0 and/or N are inappropriate to model the metallic nature of copper in these situations. Although the valences themselves are too low, the trends in their variation are more or less as expected. This suggests that the investigation of the structure variations in terms of r_{21} under constant valence sum is a useful approach to obtain the trends in the variation in the Cu valences. The deficiency in the numerical values for the Cu valences could easily have been mended by using the iodometrically determined values for $(2v_{\text{Cu}(2)} + v_{\text{Cu}(1)})/3$ instead of the structure based values which were chosen for reasons of consistency.

These findings encouraged us to search for a possible correlation between $v_{\text{Cu}(2)}$ and T_c for $\text{YBa}_2\text{Cu}_3\text{O}_{9-\delta}$ perturbed by the La and Sr substitutions and applied pressure. The result is shown in Fig. 6. The many sources of uncertainty for the structure-based Cu(2)

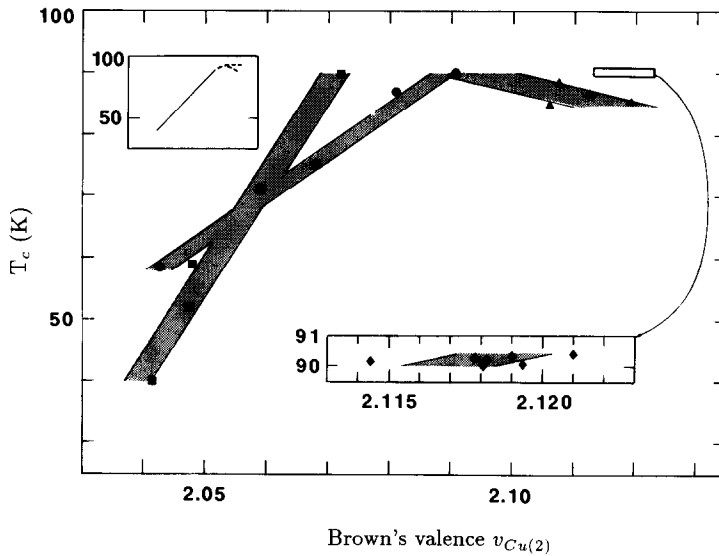


FIG. 6. T_c as a function of Brown valence for Cu(2) (see text) for substitutions of Ba by La (●) and Sr (▲) (14), application of external pressure (◆) (21), and deoxygenation (■) (36) on $Y\text{Ba}_2\text{Cu}_3\text{O}_{9-\delta}$. Width of shading indicates calculated standard deviations of least squares linear regressions. Calculated standard deviations of individual valence states are approximately three times larger than the shadings indicate. Inset in upper left corner gives *principle-sketch* interpretation, where it should be noted that the valence scale has been omitted intentionally.

valences lead us to include a *principle-sketch* interpretation in the inset on the left side of the figure. As a working hypothesis it is suggested that there occurs a charge transfer between the copper sites as a consequence of these perturbations. Since the above considerations on charge transfers and valence changes were based on the Cu–O bond lengths without discrimination, it may be of interest to attempt identification of main categories of structural changes contributing to the hole transfer.

Partial Extensions and Hole Transfer

The bonding situations at the two Cu sites are unequal, and are affected by changes in \mathcal{E}_O , \mathcal{E}_T , and the (more detailed) partial extensions. Any change in \mathcal{E}_O is likely to cause a charge transfer between the Cu atoms. A decrease in \mathcal{E}_O (on shortening of b , elongation of a , other parameters kept

constant) will according to bond strength considerations cause a hole transfer from the Cu(2) to Cu(1) coordination sphere. Such behavior in \mathcal{E}_O is observed for $Y(\text{Ba}_{1-y}\text{La}_y)_2\text{Cu}_3\text{O}_{-6.95+y}$, whereas only minor changes in \mathcal{E}_O occur for the corresponding Sr substitution and applied external pressure cases (note: the sum of the Cu valence is kept constant).

Analyzing the tetragonal extension, the partial extensions $\mathcal{E}_T^{\text{Cu}(1)}$ and $\mathcal{E}_T^{\text{Cu}(2)}$ will again be used. The variations in $\mathcal{E}_T^{\text{Cu}(1)}$ and $\mathcal{E}_T^{\text{Cu}(2)}$ upon a given perturbation \mathcal{P} are generally different, but a certain combination of their derivatives with respect to \mathcal{P} may conserve the charge distribution between Cu(1) and Cu(2). The expression for the valence ratio in Eq. (13) can be reformulated in terms of $\mathcal{E}_T^{\text{Cu}(1)}$ and $\mathcal{E}_T^{\text{Cu}(2)}$ as variables

$$r_{21} = \frac{v_{\text{Cu}(2)}}{v_{\text{Cu}(1)}} = \frac{4 + (\mathcal{E}_T^{\text{Cu}(2)})^{-N}}{2 + 2(\mathcal{E}_T^{\text{Cu}(1)})^{-N}}, \quad (18)$$

if the minor c displacements of the equatorial oxygen atoms at Cu(2) are neglected and all equatorial bond lengths are approximated by $(a + b)/4$, the O(1) site is considered completely filled, and the O(5) site is regarded as completely empty. The condition of no charge transfer upon perturbation would then imply

$$\frac{dr_{21}}{d\mathcal{P}} = 0, \quad (19)$$

and actually performing the derivation on the condition that $\mathfrak{E}_T^{\text{Cu}(1)}$ and $\mathfrak{E}_T^{\text{Cu}(2)}$ are proper functions of \mathcal{P} (see Fig. 4), one obtains

$$\frac{d\mathfrak{E}_T^{\text{Cu}(2)}}{d\mathcal{P}} = \frac{4 + (\mathfrak{E}_T^{\text{Cu}(2)})^{-N}}{2 + 2(\mathfrak{E}_T^{\text{Cu}(1)})^{-N}} \cdot \left(\frac{\mathfrak{E}_T^{\text{Cu}(1)}}{\mathfrak{E}_T^{\text{Cu}(2)}} \right)^{-(N+1)} \cdot 2 \cdot \frac{d\mathfrak{E}_T^{\text{Cu}(1)}}{d\mathcal{P}}. \quad (20)$$

The implications of this differential equation may either be discussed on its integral form, or, as we prefer later, using the differential version in Eq. (20). However, it is also instructive to establish the integral form which is obtained by separating the variables $\mathfrak{E}_T^{\text{Cu}(1)}$ and $\mathfrak{E}_T^{\text{Cu}(2)}$, noting that the first term at the right hand side of Eq. (20) is a constant according to Eqs. (18) and (19), and integrating the two sides between boundary conditions defined by $\mathcal{P} = 0$ and \mathcal{P} . After rearrangement, one obtains

$$(\mathfrak{E}_T^{\text{Cu}(2)})^{-N} = \frac{4 + (\mathfrak{E}_{T,0}^{\text{Cu}(2)})^{-N}}{1 + 1(\mathfrak{E}_{T,0}^{\text{Cu}(1)})^{-N}} \cdot [(\mathfrak{E}_T^{\text{Cu}(1)})^{-N} - (\mathfrak{E}_{T,0}^{\text{Cu}(1)})^{-N}] + (\mathfrak{E}_{T,0}^{\text{Cu}(2)})^{-N}, \quad (21)$$

which gives a non-linear relationship between $\mathfrak{E}_T^{\text{Cu}(1)}$ and $\mathfrak{E}_T^{\text{Cu}(2)}$ when $N \neq -1$. If N could have been considered as a variable, the case for $N = -1$ would have represented the solution for a situation specified by the condition for constant sums of bond lengths. In the present case, however, N is likely to vary only slightly around 6.0 (*vide supra*).

Fortunately, the product of the three non-differential terms on the right hand side of Eq. (20) varies relatively little. Over the full ranges of the perturbations in question, viz., La substitution, Sr substitution, and application of external pressure, the spans of the product are 6.9(2)–7.6(2), 6.1(3)–7.0(4), and 7.33(4)–7.42(4), respectively. Hence, 7(1) represents a reasonable average value [also bearing in mind the many other approximations which enter the expressions behind Eq. (20)], and, substituted into Eq. (20), one obtains

$$\Delta\mathfrak{E}_T^{\text{Cu}(2)}/\Delta\mathcal{P} = 7(1) \cdot \Delta\mathfrak{E}_T^{\text{Cu}(1)}/\Delta\mathcal{P}. \quad (22)$$

The message of Eq. (22) is that the charge conservation requires that the Cu(2)–O(2) bond must respond about seven times stronger to a given perturbation than the Cu(1)–O(2) bond in order to preserve status quo. The bonding situation around Cu(1) and Cu(2) is depicted in Fig. 5, where two notable features serve to emphasize the conclusion just reached. Firstly, the long Cu(2)–O(2) bond contributes much less to the bond valence sum at Cu(2) than do the short Cu(1)–O(2) bonds at Cu(1). Secondly, Cu(2)–O(2) represents one-fifth of the bonds around Cu(2), as compared with the two Cu(1)–O(2) bonds which correspond to half of the bonds around Cu(1).

These facts have to be considered when interpreting bond length characteristics in terms of charge transfer. The requirement for charge transfer according to the present model considerations is that the equals sign in Eq. (22) is replaced by an unequals sign. The condition for *hole transfer from the Cu(2) to Cu(1) coordination sphere* is, e.g.,

$$\Delta\mathfrak{E}_T^{\text{Cu}(2)}/\Delta\mathcal{P} > 7(1) \Delta\mathfrak{E}_T^{\text{Cu}(1)}/\Delta\mathcal{P}, \quad (23)$$

but it should be emphasized that the degree of hole transfer cannot be established by this approach. According to the slopes listed in Table II (see also Fig. 4), the above condition is not satisfied for any of the perturbations which, in the cases of Sr substitution

and applied external pressure, fully complies with the calculated valence increase at Cu(2). The calculated, rather large decrease in $v_{\text{Cu}(2)}$ for La substitution should come about as a contribution from other structural changes. Of these, the effects of the change in the "additional" oxygen content y of the $Y(\text{Ba}_{1-y}\text{La}_y)_2\text{Cu}_3\text{O}_{\sim 6.95+y}$ series have so far been neglected, and this key variable must be analyzed before further structural speculations are introduced.

Extra Oxygen and Hole Transfer

In addition to the direct structural consequences of the La substitution in $Y(\text{Ba}_{1-y}\text{La}_y)_2\text{Cu}_3\text{O}_{\sim 6.95+y}$, the variation in the extra oxygen content y gives rise to indirect structural changes. To correlate trends in the structural variations with the charge transfer between Cu(1) and Cu(2), the valence ratio r_{21} is once more calculated from the structural data for La substitution (Table I). This time only parameters specific to a selected structural change are allowed to vary, while all other variables are treated as fixed. For the present purpose, r_{21} is presumed to be a function of the CuO distances parallel (D_{para}) and perpendicular (D_{perp}) to c and the occupancy n of the O(1) and O(5) sites, viz.,

$$r_{21} = r_{21} [D_{\text{para}}(y_{\text{La}}); D_{\text{perp}}(y_{\text{La}}); n(y_{\text{La}})]. \quad (24)$$

Estimates for the partial derivatives of Eq. (24) give

$$\frac{\Delta r_{21}}{\Delta D_{\text{para}}} \cdot \frac{\Delta D_{\text{para}}}{\Delta y_{\text{La}}} = +0.07(2) \quad (25)$$

$$\frac{\Delta r_{21}}{\Delta D_{\text{perp}}} \cdot \frac{\Delta D_{\text{perp}}}{\Delta y_{\text{La}}} = -0.15(12) \quad (26)$$

$$\frac{\Delta r_{21}}{\Delta n} \cdot \frac{\Delta n}{\Delta y_{\text{La}}} = -0.52(13), \quad (27)$$

in reasonable agreement with the overall slope value $\Delta r_{21}/\Delta y_{\text{La}} = -0.48(15)$ ac-

ording to Eq. (14). The essential message of this little exercise is that the major source of the hole depletion at the Cu(2) site is the formation of the new Cu–O bonds in the Cu(1) coordination sphere [Eq. (27)], occurring as a consequence of the substitution of La^{3+} for Ba^{2+} . The next, but considerably less important contribution originates from the variation in the c -perpendicular component [Eq.(26)]. The least significant structural effect of the La for Ba substitution, with regard to the Cu to Cu charge transfer, is related to the variation in the c -parallel component [Eq. (25)]. The latter effect is seen to partially counteract the effects of the two former components. For the Sr for Ba substitution and application of external pressure, the hole concentration at Cu(2) is increased via both the c -parallel and the c -perpendicular component.

Conclusions on Structural Deformations versus Cu Valences

In conclusion, both orthorhombic and tetragonal extensions of the $Y\text{Ba}_2\text{Cu}_3\text{O}_7$ -type structure for constant oxygen content and constant overall Cu valence will cause charge transfer between the two different Cu coordination polyhedra. A decrease in the orthorhombic extension (as occurs most often in practice) always transfers holes from the Cu(2) to Cu(1) coordination sphere. The situation is less clear for the tetragonal extension, since the effect here depends on how the extension is separated between the Cu(2) square pyramid and the Cu(1) square. The condition for hole transfer from Cu(2) to Cu(1) under the influence of a purely tetragonal extension is that the apical distance of the square pyramid increases more (or decreases less if the extension is negative) than ~ 7 times faster than the adjacent Cu–O bond of the square. When the "tetragonal" perturbation acts oppositely (the apical distance increases less or decreases more than ~ 7 times faster) the hole transfer is from Cu(1) to Cu(2). If the oxygen content

is increased while the overall Cu valence is kept constant (which only can be accomplished in combination with substitutions by higher-valent elements), this will dominate the hole transfer from Cu(2) to Cu(1), (viz., the structural deformations become less important). The latter feature has the rather straightforward interpretation that new bonds are created at Cu(1) and increase the hole content there, while the overall hole content remains constant.

Structural Variables and Superconductivity

While the exact function of T_c on the hole concentration at the individual Cu atom is unknown, the present analyses suggest that the "gate keeper" for the correlation between T_c and the various structural variables is the distribution of holes between the two Cu coordination spheres. T_c is largely controlled by the hole concentration within the Cu(2) coordination sphere, viz., the generally acknowledged "pairing" center [as opposed to the "charge reservoir" at Cu(1)]. Thus perturbations which do not concern directly the Cu(2) site, but influence the hole balance between the two Cu sites [say, a simple increase in δ for $\text{YBa}_2\text{Cu}_3\text{O}_{9-\delta}$ or a replacement of the CuO square chains by TlO (32) or $\text{Pb}_2\text{CuO}_{2+\kappa}$ ($0.0 < \kappa < 1.9$) (33)] also affect superconductivity. However, for the two latter interventions, lack of superconductivity is obtained even for oxygenated samples, most likely because Tl or Pb may adopt mixed valence states which may serve as traps for holes, due to a relatively easy access to the higher valence states (Tl^{+3} and Pb^{+4}).

Certainly, mixed valence and metallic character are not sufficient conditions for the occurrence of superconductivity. Other variables must also be in play, since, say, $(\text{La}_{1-x}\text{Sr}_x)_2\text{MO}_4$, $M = \text{Mn-Co}$, which satisfies both the above criteria is not superconducting. Frustrated antiferromagnetism is

neither a sufficient condition for superconductivity, despite the fact that such a state precedes the hole-induced conversion to superconductivity in many solid solution oxide systems. The superconducting $(\text{Ba}_{1-x}\text{K}_x)\text{BiO}_3$ [with neither local magnetic moments nor magnetic ordering (34, 35)] and non-superconducting $(\text{La}_{1-x}\text{M}_x)_2\text{CoO}_4$, $M = \text{Sr or Ba}$ [metallic with antiferromagnetic ordering (36–38)] may serve as examples in this connection.

A possible approach to the question of preconditions for superconductivity in metallic oxide systems is to consider *all relevant* structural, physical, and chemical data for a variety of oxide superconductors and abstract common denominators. One such aspect, not yet mentioned, may be the conspicuous jump in two for the stable valence states of the key metal atoms, as originally pointed out by Simon (39) and later repeated by others (40, 41). However, neither this feature is per se sufficiently specific.

Combined with the condition of mixed valence, the jump in two valence units points at another feature, illustrated for example in compounds of Bi, Pb, and Tl. Two remarkably stable electronic configurations occur here, viz., $6s^2$ and $6s^0$. For the superconducting oxides of these elements, e.g., $\text{Ba}(\text{Pb}_{0.75}\text{Bi}_{0.25})\text{O}_3$ (42) or $(\text{Ba}_{0.74}\text{K}_{0.26})\text{BiO}_3$ (43), the metals in question adopt a mixed valence state between these two configurations, thus creating a deficient population in a single, non-bonding $6s^2$ orbital distributed among equivalent metal sites across the crystal structure. Formally, the orbital may be described as having *fractional occupancy*.

The natural question is then, whether such a single, partially filled orbital also may be traced to the cuprate (titanate, vanadate, etc.) superconductors. Whereas Ti and V may be considered analogous to the previous case, for Cu the only possible way of creating such single non-bonding orbital is energy splitting of the d -orbitals by the crys-

tal field. Copper in its higher oxidation states may variously take octahedral, square pyramidal, or square planar coordination (including deformed variants thereof) for the surrounding oxygens. Of these, only the ideal octahedral symmetry (O_h) does not give rise to *one* single, non-degenerate orbital available for partial filling.

The double and triple degenerate e_g and t_{2g} orbitals in octahedral field are further split when one or both of the ligands along, say, the z -axis are moved toward infinity (44, 45) thereby giving rise to square pyramidal (C_{4v}) or square planar (D_{4h}) coordination. For the superconducting cuprates in question, a minor tetragonal extension of the square pyramid or a large tetragonal extension of the octahedron is observed. A minimum in total energy is shown to occur for this kind of distorted clusters (46). It is therefore tempting to propose that a singular, partially filled, Cu orbital (here designated as $d_{x^2-y^2}$) acts as an analogue of the partially filled $6s$ orbital in the superconductors of Pb, Bi, and Tl. Although the incorporation of this single orbital feature from the simple crystal field model into a complete band picture may be complex, the Cu $3d_{x^2-y^2}$, O $2p_x$, and O $2p_y$ orbitals are shown (47–52) to participate at the Fermi level. Electronic band structure calculations and the occurrence of van Hove singularities in bands associated with the high T_c superconductivity (49, 51, 53) indicate that effects of the said singlet character are retained, at least for certain directions of the Brillouin zone.

Depending on the degree of filling of the Cu $d_{x^2-y^2}$, the average Cu valence across the structural network is $+1 \leq \bar{v}_{\text{Cu}} \leq +3$. This makes Cu the virtually single realistic candidate for such an intermediate electronic configuration (next to an unusual Ni in $0 \leq \bar{v}_{\text{Ni}} \leq +2$). In practice, two ways lead to the mixed valence state v in cuprates of the type $[(M_i)_{x_1}, \dots, (M_i)_{x_j}]^{c+}[\text{Cu}^v\text{O}_w]^{c-}$: (i) a change in w while $c+$ is kept constant, or (ii) a change in $c+$ upon substitution while

w is kept constant. The requirement of a certain degree of integrity for the structural networks (necessary for an itinerant character of the fractional, mixed valence charge) disfavors, e.g., deoxidation of the square coordination (electron doping). Another such possibility would be a substitutional hole doping for structures with low energy of formation for oxygen vacancies. A variety of structural arrangements in addition to that of $\text{YBa}_2\text{Cu}_3\text{O}_{9-\delta}$ comply with the assumption of a partially filled singlet orbital as a precondition for superconductivity.

For La_2MO_4 (T phases) of the K_2NiF_4 type structure, tetragonal extension of the coordination octahedron of M is observed, and as expressed using unit cell data and Eq. (3), \mathcal{E}_T increases from 1.08 for $M = \text{Co}$ (36) via 1.09 for $M = \text{Ni}$ (54) to 1.16 for $M = \text{Cu}$ (55). Superconductivity is obtained for La_2CuO_4 upon a substitutional hole doping of $d_{x^2-y^2}$ at a level of p between 0.15 and 0.25 (56). In the case of La_2NiO_4 , one would have to introduce a fractional number of electrons in $d_{x^2-y^2}$ by reducing the oxygen content so that a formal oxidation state below two is reached for Ni. Under strongly reducing conditions, superconductivity has actually been reported in a minority part of samples with non-substituted La_2NiO_4 and 20% Sr substituted nickelate (57, 58).

Similar behavior to that of the T phases is observed for a variety of similar structures containing square pyramidal sheets (59–62), which become superconducting when subject to the introduction of holes under oxygen saturated conditions (61–63). Remarkably, the Nd_2CuO_4 -type structure [T' phase, having planar nets with square Cu coordination (64)] gives rise to superconductivity upon a substitutional *electron* doping (7, 65, 66) to an overall level of ~ 1.15 electron per $d_{x^2-y^2}$ orbital. The hole doped superconductors SrTiO_3 (67), LiTi_2O_4 (68), and Li_xNbO_2 (69) may analogously be considered as derived from a $4s^2$ configuration at the metal atom.

In conclusion, it appears that a single, non-bonding orbital, with a fractional occupancy in a (nearly) metallic behaving solid, may possibly be a common denominator for superconductivity in oxide systems. In this respect, it may be worthwhile to consider remaining mixed-valent metallic oxides with a $6s^2$ -to- $6s^0$ configuration, such as Hg_2^{+2} . . . 2Hg^{+2} . It is, however, acknowledged that such analogies clearly have been the guidance for many laboratories in the discoveries of the bismuth and thallium based (cuprate) superconductors, toward investigations of multicomponent vanadium oxide systems, etc.

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