

Hole Concentration and T_c in $Tl_{2-y}Ba_2Ca_{1-z}Y_zCu_2O_{8-x}$

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The *p*-type copper-oxide superconductors all exhibit a maximum value of T_c at a saturation hole concentration p_s per Cu atom in the superconductive CuO_2 sheets. The maximum value of T_c varies from one structure type to another; it is not clear how p_s varies. After a brief review of this problem, the hole concentration in the system $Tl_{2-y}Ba_2Ca_{1-z}Y_zCu_2O_{8-x}$, $0 \leq z < 0.4$, is determined with the assumption that the number of Tl-6*s* electrons per Cu atom does not vary appreciably with *z* on going from an antiferromagnetic semiconductor ($z = 0.3$) to a superconductor with $T_c = 94$ K ($z = 0.0$). A $p_s \approx 0.17 \pm 0.02$ per Cu atom and a $T_c \approx (370p + 35 \pm 7)$ K are obtained. The defects in the $Tl_{2-y}O_{2-x}$ layer apparently trap out the Tl-6*s* electrons, probably at Tl(I) species, so the Tl-6*s* electrons contribute little to the electrical conductivity and the Seebeck coefficient, which were measured in sintered pelletized powders. An important expansion of the lattice *a*-parameter is noted on passing from the superconductive phase at $z = 0.2$ with $p = 0.10 \pm 0.02$ and $T_c = 72$ K to a semiconductive phase at $z = 0.3$ having, we assume, a $p = 0.02 \pm 0.02$. © 1992 Academic Press, Inc.

1. Introduction

It is now well established that the superconductive critical temperature T_c of the *p*-type copper-oxide superconductors increases with the hole concentration *p* in a superconductive CuO_2 sheet until it saturates at a $p = p_s$. The maximum value of T_c varies from one structure type to another, but the factor that governs p_s remains a mystery and the value of p_s for the few systems where a maximum T_c is known remains, in some cases, ambiguous.

In the system $La_{2-x}Sr_xCuO_4$, where $p = x$, a maximum $T_c \approx 40$ K is found at a $p_s \approx 0.15$ per Cu atom. In this simplest system, single CuO_2 sheets are separated by two (001) rocksalt planes, and the apical (*c*-axis) oxygen atoms coordinating a sixfold-coordinated Cu atom couple to La^{3+} ions on their

opposite side. There is no ambiguity in this case.

On the other hand, oxides with the $YBa_2Cu_3O_{6+x}$ structure have a maximum $T_c \approx 92$ K for $x \approx 0.95$. In this structure, a superconductive layer contains two CuO_2 sheets separated by a Y^{3+} -ion plane, and the fivefold-coordinated Cu atoms of a CuO_2 sheet have an apical oxygen that bonds on the opposite side to a Cu(1) atom of a CuO_x plane within a $BaO-CuO_x-BaO$ nonsuperconductive layer. At $x = 0.95$, the oxygens of a CuO_x plane are ordered onto *b*-axis sites, as the Cu(1) atoms are coordinated by either four or three coplanar oxygen atoms. Since the Madelung potential at the fivefold-coordinated Cu(2) atom of the CuO_2 sheets is larger than that at the Cu(1) atoms of the CuO_x planes, we may expect the Cu(1) atoms to have the formal valence Cu(II) in

the presence of a mixed Cu(III/II) valence in the CuO_2 sheets. This simple picture results in a $p_s = 0.45$ per Cu(2) atoms for a maximum T_c at $x = 0.95$. However, this simple picture carries implicit within it a strong covalent mixing of the partially filled orbitals. Within the CuO_2 sheets, covalent mixing of the Cu(2) : $d_{x^2-y^2}$ and O : p_x, p_y orbitals result in a narrow $\sigma_{x^2-y^2}$ band; the ratio of Cu-3d to O-2p character within the band remains a controversial issue, but the point of principal interest appears to be a sharp change in this ratio with increasing hole concentration in the CuO_2 sheets. Although the Cu-O distance along the c -axis is longer than that in the CuO_2 sheets, nevertheless the Cu(2) : $d_{x^2-y^2}$ -O : p_z -Cu(1) : $d_{z^2-y^2}$ interactions along the c -axis provide an important pathway for the transfer of holes back from the CuO_2 sheets to the CuO_x chains; the back transfer of holes is modulated by the location of the c -axis oxygen between the Cu(2) and Cu(1) atoms. This situation creates an ambiguity as to the number of holes in the $\sigma_{x^2-y^2}$ band of the CuO_2 sheets. However, a distinction can be made between mobile holes and trapped holes. Where there are a -axis oxygen that bridge two Cu(1)-O chains in the CuO_x planes, there a $\text{Cu(1)}_2\text{O}_9$ cluster contains two fivefold-coordinated copper in the CuO_x planes that compete for the mobile holes. Where the holes transferred back to the CuO_x planes are trapped at $\text{Cu(1)}_2\text{O}_9$ clusters, they cannot contribute to T_c ; however, all the mobile holes appear to determine the relationship between p_s and the maximum T_c . We call attention to the following experiments to justify this statement.

First, the muon-spin-rotation experiments of Uemura *et al.*(1) have established the relation $T_c \approx p/m^*$ for $p < p_s$. Whether the T_c vs p curve is in fact a straight line or is parabolic (2) for $p < p_s$ is not critical for the discussion of this paper.

Second, aliovalent cation substitutions for Y^{3+} or Ba^{2+} provide indirect confirma-

tion. In oxides with the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ structure, the equilibrium oxidation state of the Cu-O array in 1 atm O_2 at 400°C remains independent of any aliovalent cation substitution for Y^{3+} or Ba^{2+} (3, 4). In the system $\text{Y}_{1-z}\text{Ca}_z\text{Ba}_2\text{Cu}_3\text{O}_{6+x}$, for example, $x = 0.95 - 0.5z$; the Cu(1) atoms of the CuO_x planes remain in four or three coplanar coordination, and T_c decreases smoothly to 66 K at $z = 0.3$ (3). Whether this decrease is associated with a change in p_s remains to be explored. On the other hand, the system $\text{YBa}_{2-y}\text{La}_y\text{Cu}_3\text{O}_{6+x}$ for $y > 0.1$ has $x = 0.85 + 0.5y$; it exhibits a T_c that decreases linearly with increasing y at a rate corresponding to the capture of two mobile holes per excess (a -axis) oxygen in the CuO_x planes (4). In an independent experiment, Takita *et al.* (5) showed that the system $\text{NdBa}_{2-y}\text{Nd}_y\text{Cu}_3\text{O}_{6+x}$ had a similar variation of T_c with y for samples equilibrated at 400°C in 1 atm O_2 ; their Hall-effect measurements showed directly the decrease in p with y deduced by us from the variation of T_c with y . Although we originally interpreted the trapping out of mobile holes as due to peroxide formation, it now appears that the holes are trapped at the molecular orbitals of the two Cu(1) atoms of a $\text{Cu(1)}_2\text{O}_9$ cluster formed by an a -axis oxygen bridging two b -axis Cu(1)-O chains. Clearly two fivefold-coordinated Cu(1) atoms within such a cluster can compete for the mobile holes in the CuO_2 sheets (6). In fact, the system $\text{Y}_{1-z}\text{Ca}_z\text{Ba}_{2-y}\text{La}_y\text{Cu}_3\text{O}_{6+x}$, which has an equilibrium $x = 0.95 + 0.5(y - z)$, reveals this competition for the holes; modulation of the internal c -axis electric field by the Ca^{2+} substitution for Y^{3+} shifts to $x > 1$, the oxygen concentration at which holes are trapped out from the CuO_2 sheets (7).

The $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ structure also contains pairs of CuO_2 sheets, but they are separated in this case by Ca^{2+} rather than Y^{3+} ions. The superconductive CuO_2 -Ca-CuO₂ layers are separated by nonsuperconductive $\text{SrO-Bi}_2\text{O}_{2+x}$ -SrO layers, and the Cu of the

CuO_2 sheets have fivefold coordination as in $YBa_2Cu_3O_{6+x}$. In this structure, the CuO_x plane of $YBa_2Cu_3O_{6+x}$ is replaced by a complex Bi_2O_{2+x} layer, so only one type of copper is present (8). Substitution of Y^{3+} for Ca^{2+} in $Bi_2Sr_2Ca_{1-z}Y_zCu_2O_{8+x}$ gives $x = 0.17 + 0.3z$, which results in a depletion of holes in the CuO_2 sheets with increasing z (9). The shape of the resistance versus temperature curves indicates that T_c has its maximum value for $0 \leq z \leq 0.5$; in this range a $T_c \approx 86$ K is maintained. For $z > 0.5$, the resistance versus temperature curves exhibit an increase in resistance with decreasing temperature just above T_c , which is characteristic of a $p < p_s$. If we assume that the bismuth remain Bi^{3+} , a $p_s \approx 0.15$ per copper is estimated on the assumption of complete cation occupancy. Any cation deficiency (for example, loss of Bi^{3+}) would lower the value of p_s . However, substitution of Bi^{3+} for Sr^{2+} would increase p_s , and Lee *et al.* (10) provide structural evidence for some substitution of Bi for Sr in this phase. It therefore appears that $0.15 < p_s < 0.20$ per Cu in this system. Our failure to analyze for Bi frustrates a more accurate determination of p_s in this case.

Ever since the discovery of high- T_c superconductivity in the Tl and Tl_2 families with general nominal formulae $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ and $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ for $1 \leq n \leq 4$ (11–18), the chemical situation has been ambiguous due to the volatility of Tl and difficulties with the determination of both the thallium and oxygen contents. Therefore, although Nakajima *et al.* (10) have substituted Ln^{3+} ($Ln = Nd, Gd, \text{ or } Y$) for Ca^{2+} in nominal $TlBa_2Ca_{1-z}Ln_zCu_2O_7$ and found for $0 \leq z \leq 1$ a variation from superconductor to antiferromagnetic insulator, lack of chemical characterization of the product makes it impossible to correlate a maximum T_c with p_s . Similarly, the preliminary reports (20, 21) on $Tl_2Ba_2Ca_{1-z}Y_zCu_2O_8$ leave this question unanswered.

However, we (21, 22) have recently developed wet chemical techniques that solve the analytical problem; we used them to demonstrate that the Tl_2 family contains a deficiency of both thallium and oxygen to make its formula $Tl_{2-y}Ba_2Ca_{n-1}Cu_nO_{2n+4-x}$. Moreover, for small y the Tl-6s band was found to overlap the Fermi energy E_F , and an extrusion of Tl from the lattice of a quenched sample to form Tl_2O_3 occurs on heating in air in the temperature range $70 < T < 400^\circ C$ until all the thallium are converted to Tl^{3+} (21). The $n = 2$ member of the Tl_2 family has a structure similar to that of $Bi_2Sr_2CaCu_2O_{8+x}$, except that the Bi_2O_{2+x} layer is replaced by a $Tl_{2-y}O_{2-x}$ layer. For small y , the apical oxygen of the fivefold-coordinated Cu of a CuO_2 sheet bonds on the opposite side to a $Tl_{2-y}O_{2-x}$ layer having a partially filled Tl-6s band. Because of this situation, we decided to reinvestigate Y^{3+} substitutions for Ca^{2+} in the $n = 2$ member of this family in order to determine:

- (i) how the equilibrium oxidation state of the CuO_2 sheets varies with Y^{3+} substitution for Ca^{2+} ;
- (ii) how T_c varies with the hole concentration in the CuO_2 sheets; and
- (iii) the contribution of the partially filled Tl-6s band to the electrical conductivity and the Seebeck coefficient.

A modified procedure adopted by Gopalakrishnan *et al.* (23) following our method (21, 22) to obtain a direct determination of the concentration of holes in the CuO_2 sheets is not applicable to the Tl_2 family (24). Their method is based on a selective oxidation of bromide ions by holes in the CuO_2 sheets; but where the Tl-6s band overlaps E_F , there the reaction is accompanied by electron transfer between the CuO_2 sheets and the Tl-6s band. This situation has forced us to use an indirect method to obtain a value for p .

2. Experimental

The compounds $Tl_{2-y}Ba_2Ca_{1-z}Y_zCu_2O_{8-x}$ were synthesized by introducing into a muffle furnace, maintained at about 900°C in air, an intimate mixture of stoichiometric quantities of Tl_2O_3 , BaO_2 , CaO , Y_2O_3 , and CuO pelletized and sealed in a gold tube; the pellets were fired for 2 hr and quenched into liquid nitrogen. The black product was re-ground, repelletized, sealed again in a gold tube and introduced into a muffle furnace maintained at 880°C in air; after 4 hr at 880°C , the sample was quenched into liquid nitrogen.

The samples were characterized by x-ray powder diffraction recorded with a Philips diffractometer. TGA plots were recorded at $1^\circ\text{C}/\text{min}$ in O_2 atm with a Perkin-Elmer Series 7 Thermal Analysis System. Superconductive transition temperatures were obtained as the diamagnetic onset temperature taken from ac susceptibility measurements. The thallium and oxygen contents were determined by wet-chemical procedures reported elsewhere (21, 22). Resistivity and Seebeck coefficient measurements were performed on sintered pelletized powders.

3. Results and Discussion

Nearly single-phase (<5% $BaCO_3$ impurity) $Tl_{2-y}Ba_2Ca_{1-z}Y_zCu_2O_{8-x}$ samples were obtained in the composition range $0 \leq z \leq 0.3$. For $z \geq 0.4$, " $TlBa_2YCu_2O_7$ " impurity phase is formed.

Figure 1 shows the variations of the lattice parameters with z for $Tl_{2-y}Ba_2Ca_{1-z}Y_zCu_2O_{8-x}$. The decrease in the c -parameter and the volume V with increasing z over the range $0 \leq z < 0.4$ is due to substitution of a smaller Y^{3+} ion for Ca^{2+} . The increase in the a -parameter with z over this range reflects a reduction in the equilibrium oxidation state of the CuO_2 sheets, see Table I; a reduction of the CuO_2 sheets means an addition of antibonding electrons to the $\sigma_{x^2-y^2}$ band of

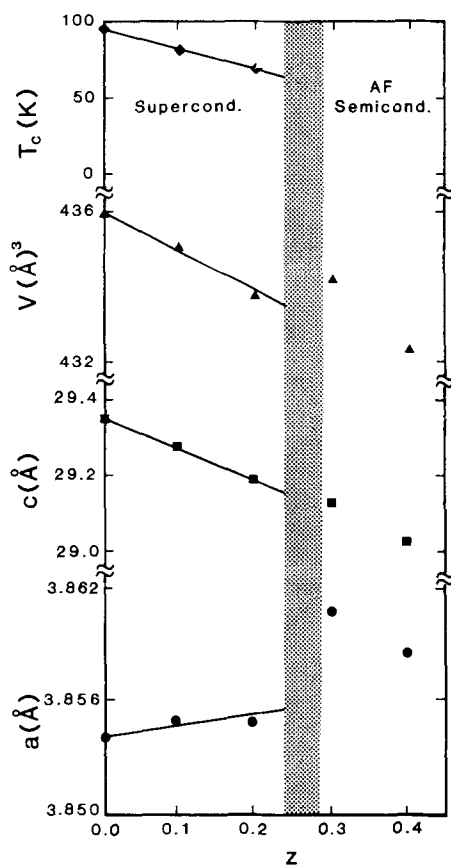


FIG. 1. Variation of lattice parameters, volume, and T_c with z for $Tl_{2-y}Ba_2Ca_{1-z}Y_zCu_2O_{8-x}$.

the CuO_2 sheets. However, at $z \approx 0.3$ there is an anomalous dilatation of the lattice, particularly in the a -parameter. The $z \geq 0.3$ samples are semiconductive, which signals a change from the superconductive to an antiferromagnetic state. We have noted such a dilatation in several systems (25); in particular, in the system $La_2CuO_{4+\delta}$ on passing from the superconductive to the antiferromagnetic state with loss of oxygen (26). It has been emphasized elsewhere (27) that the change from the superconductive to the antiferromagnetic state is associated with a change in the strength of the $Cu-O$ covalent bonding; this change in turn intro-

TABLE I
ANALYTICAL DATA OF $Tl_{2-y}Ba_2Ca_{1-z}Y_zCu_2O_{8-x}$

Nominal starting composition ^a	Analytical data		T_c (K)
	Tl content (2 - y)	Oxygen content (8 - x)	
$Tl_2Ba_2CaCu_2O_8$	1.79	7.59	94
$Tl_2Ba_2Ca_{0.9}Y_{0.1}Cu_2O_8$	1.73	7.51	82
$Tl_2Ba_2Ca_{0.8}Y_{0.2}Cu_2O_8$	1.70	7.49	72
$Tl_2Ba_2Ca_{0.7}Y_{0.3}Cu_2O_8$	1.78	7.58	Semiconductor

^a Analytical data for $z = 0.4$ are not given as it is contaminated with small amounts of impurity phases.

duces an important electron-lattice coupling that may give rise to dynamic charge fluctuations separating superconductive regions from antiferromagnetic spin fluctuations.

Figure 1 also shows the variation of T_c with z obtained from the diamagnetic onset temperature. A $T_c = 94$ K at $z = 0.0$ decreases linearly with z to 72 K at $z = 0.2$, but the $z = 0.3$ sample is semiconducting. If the overlap of the Tl-6s band with the Fermi energy E_F remains essentially independent of z , then the decrease in T_c can be attributed to a linear decrease in the hole concentration p in the CuO_2 sheets, see Table I.

The fact that the $z = 0.3$ sample is a semiconductor indicates not only that the valence state of the copper is close to Cu(II), but also that the electrons of the Tl-6s band are not itinerant. The fact that the $z = 0.3$ sample extrudes Tl_2O_3 on heating in air above 70°C demonstrates that the overlap of the Tl-6s band is present; but the semiconductive behavior of the sample indicates that the Tl-6s electrons are trapped within the $Tl_{2-y}O_{2-x}$ layers. The large defect concentration in this layer would be expected to create localized states in the bottom of the Tl-6s band. Moreover, a formal mixed valence between Tl(I) and Tl(III) generally results in a disproportionation into these

two species. Therefore we conclude that the Tl-6s electrons are most probably trapped at Tl(I) species in the $Tl_{2-y}O_{2-x}$ layer.

To proceed further requires that we make some assumptions. By analogy with the system $La_{2-x}Sr_xCuO_4$, semiconductive behavior implies a hole concentration in the CuO_2 sheets of $p \leq 0.04$ per Cu atom. Assuming a hole concentration $p = 0.02 \pm 0.02$ per CuO_2 sheet at $z = 0.3$, it then follows from Table I that a total of 0.52 electrons per formula unit (i.e., 0.26 ± 0.02 electrons per copper atom) are trapped in the $Tl_{2-y}O_{2-x}$ layer. If we further assume that the overlap of the Tl-6s band does not change appreciably with z in the range $0 \leq z \leq 0.3$, then we also obtain from Table I a hole concentration $p = 0.16 \pm 0.02$ per Cu atom at $z = 0.0$, where the critical temperature is $T_c \approx 94$ K and p appears to approach p_s .

Figure 2 shows the temperature dependence of the Seebeck coefficient α for different values of z . The curves for $z = 0.0$ and 0.2 are typical for $p < p_s$, but with p approaching p_s at $z = 0.0$ (27). Therefore we conclude that a $p_s \approx 0.17 \pm 0.02$ per Cu atom in the CuO_2 sheets holds for this system. Moreover, the linear relationship between p and T_c in the range $p < p_s$ gives

$$T_c \approx (370p + 35 \pm 7) \text{ K} \quad (1)$$

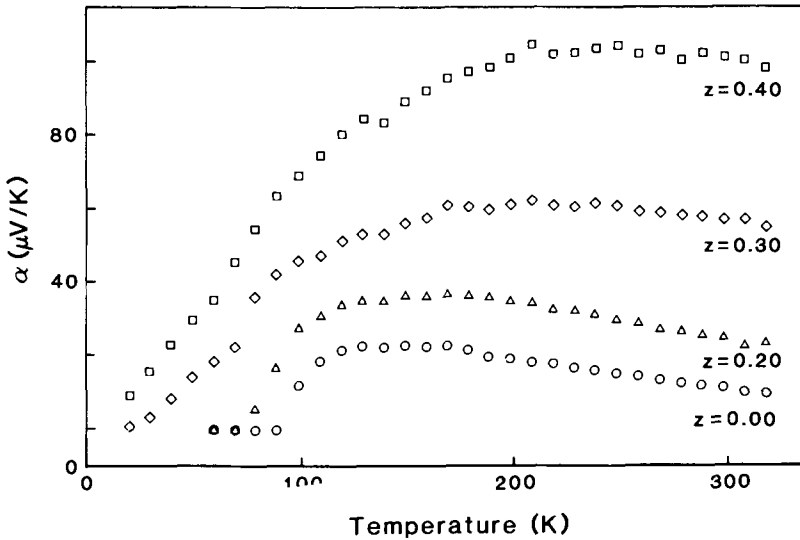


FIG. 2. Variation of Seebeck coefficient with temperature for $Tl_{2-y}Ba_2Ca_{1-z}Y_zCu_2O_{8-x}$.

The Seebeck coefficient for $z = 0.3$ is similar to that found in pelletized polycrystalline samples of $La_{2-x}Sr_xCuO_4$ for $x \approx 0.04$ where there is evidence for charge fluctuations at low temperatures, but there is no onset of superconductivity above 4 K.

4. Conclusions

Substitutions of Y^{3+} for Ca^{2+} in the system $Tl_{2-y}Ba_2Ca_{1-z}Y_zCu_2O_{8-x}$ reduces the equilibrium oxidation state of the CuO_2 sheets in samples retaining a Tl concentration $1.7 \leq (2 - y) < 1.8$, and the superconductive critical temperature T_c decreases linearly with hole concentration in the CuO_2 sheets from 94 K at $z = 0.0$ to 72 K at $z = 0.2$. The solid-solution range appears to be confined to $0 \leq z \leq 0.3$, and a marked dilatation of the lattice at the semiconductive end member $z = 0.3$ is characteristic of more ionic bonding and the appearance of a copper atomic moment.

Although a broad Tl-6s band overlaps the Fermi energy in all samples, a large defect concentration in the $Tl_{2-y}O_{2-x}$ layer introduces localized states at the bottom of the

band; the Tl-6s electrons are trapped in localized states. Oxidation of the reduced $Tl_{2-y}O_{2-x}$ layer in air above 70°C induces the extrusion of thallium to form Tl_2O_3 .

With the assumption that the number of trapped Tl-6s electrons remains essentially independent of z , it is possible to deduce a $p_s \approx 0.17 \pm 0.02$ for the hole concentration at which T_c would reach a maximum value and to obtain Eq. (1). The electrons of the Tl-6s band appear to contribute little to either the conductivity or the Seebeck coefficient. A $p_s \approx 0.17$ is in agreement with the deduction of Cava *et al* (28) from bond-valence sum arguments that $p_s \approx 0.20$ in $yBa_2Cu_3O_{6.94}$.

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