

## Structural Origin of Holes in the Tl-O Single Rock-Salt Layer Superconductor $\text{TlSrRCuO}_5$ ( $R = \text{La, Nd}$ )

M.-H. WHANGBO

*Department of Chemistry, North Carolina State University,  
Raleigh, North Carolina 27695-8204*

AND M. A. SUBRAMANIAN

*Central Research and Development, E. I. du Pont de Nemours & Co.,  
Experimental Station, Wilmington, Delaware 19880-0262*

Communicated by J. M. Honig, January 23, 1991

On the basis of tight-binding band electronic structure calculations, we examined why  $\text{TlSrRCuO}_5$  ( $R = \text{La, Nd}$ ) is a superconductor while its analog  $\text{TlBaRCuO}_5$  and its homolog  $\text{TlSrRCaCu}_2\text{O}_7$  are not. Our study strongly suggests that, for a Tl-O single rock-salt layer phase with very short in-plane Cu-O distance such as  $\text{TlSrRCuO}_5$ , the  $\text{CuO}_2$  layer  $x^2-y^2$  band is raised high enough in energy for the Tl-O layer to create holes in the  $\text{CuO}_2$  layer. © 1991 Academic Press, Inc.

The presence of holes in  $\text{CuO}_2$  layers is essential for superconductivity in *p*-type cuprate superconductors (1-5). These cuprates are divided into three classes, based on the cations occupying the 9-coordination sites adjacent to the  $\text{CuO}_2$  layers (5, 6). To first approximation, the superconducting critical temperature  $T_c$  of every class is represented by an inverted parabolic function of the hole density of the  $\text{CuO}_2$  layer (5, 7). Holes are generated in the  $\text{CuO}_2$  layer (i.e., the average formal oxidation state of copper is increased beyond +2) by several different mechanisms such as oxygen excess, cation vacancy, and cation substitution. In  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  ( $x = 0-1$ ), oxygen atoms loss from the Cu-O chain alters the formal oxidation states of the chain copper atoms and consequently changes the hole density of the  $\text{CuO}_2$  layer (8-10). In the Tl-O double rock-salt layer phases  $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ , the

bottom of the Tl *6s*-block bands lies below the Fermi level (11-13) so that the Tl *6s*-block bands remove electrons from the  $\text{CuO}_2$  layer  $x^2-y^2$  bands; i.e., the Tl-O layers create holes in the  $\text{CuO}_2$  layers. However, this is not the case for the Tl-O single rock-salt layer phases  $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$  (11-13). Earlier band electronic structure studies on  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ , in which ideal rock-salt structures were postulated for the Bi-O layers, suggested that the bottom of the Bi *6p*-block bands lies below the Fermi level, in disagreement with experiment (14-15). This incorrect conclusion is due to the use of ideal rock-salt structures for the Bi-O layers (16). The holes of the  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2}$  phases are generated in part by excess oxygen atoms in the Bi-O layers (17, 18).

Several modifications of the Tl-O single rock-salt layer phases  $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$

have been made, which include  $ASr_2Ca_{n-1}Cu_nO_{2n+3}$  [ $A = Tl_{0.5}Pb_{0.5}$  (19),  $n = 2, 3$ ;  $A = Tl_{0.5}Bi_{0.5}$  (20),  $n = 2$ ],  $TlBaRCuO_5$  ( $R = La, Nd$ ) (12, 13), and  $TlSrRCa_{n-1}Cu_nO_{2n+3}$  ( $R = La, Nd$ ) (21, 22). The  $ASr_2Ca_{n-1}Cu_nO_{2n+3}$  phases are superconductors, like their analogs  $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$  (19, 20). The formal oxidation states of the copper atoms expected for  $ASr_2Ca_{n-1}Cu_nO_{2n+3}$  are  $Cu^{2.5+}$  ( $Cu^{2+}$ ) $_{n-1}$  (23, 24), slightly smaller than  $Cu^{3+}$  ( $Cu^{2+}$ ) $_{n-1}$  expected for the copper atoms of  $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ . The  $TlBaRCuO_5$  phase is not a superconductor (12, 13), which is not surprising because the copper oxidation state is expected to be  $Cu^{2+}$ . However, its isostructural phase  $TlSrRCuO_5$  is a superconductor (21). On the other hand,  $TlSrRCaCu_2O_7$  ( $R = La, Nd$ ), for which the copper oxidation state is predicted to be  $Cu^{2+}$  as in  $TlSrRCuO_5$ , is not a superconductor (22). In the present work, we examine the origin of these apparently puzzling observations.

The crystallographic  $a$ -parameters of  $TlBaLaCuO_5$ ,  $TlSrLaCuO_5$ , and  $TlSrLaCaCu_2O_7$  are 3.849 (25), 3.761 (21), and 3.828 Å (22), respectively. These  $a$ -parameters are approximately twice the respective in-plane Cu–O bond lengths. Thus, the in-plane Cu–O bond of the superconducting phase  $TlSrLaCuO_5$  is considerably shorter than those of the nonsuperconducting phases  $TlBaLaCuO_5$  and  $TlSrLaCaCu_2O_7$ . The partially filled bands responsible for the superconductivity of the  $p$ -type cuprates are the  $CuO_2$  layer  $x^2-y^2$  bands, which are antibonding in nature and extend between the in-plane Cu and O atoms (5–7, 26). Therefore shortening of the in-plane Cu–O bond length should raise the  $x^2-y^2$  band in energy. When the in-plane Cu–O bond is significantly short as in  $TlSrRCuO_5$  ( $R = La, Nd$ ) the Fermi level could rise above the bottom of the Tl  $6s$ -block bands, so that the Tl–O layer creates holes in the  $CuO_2$  layer. We examined this possibility by performing extended Hückel tight-binding (EHTB) band

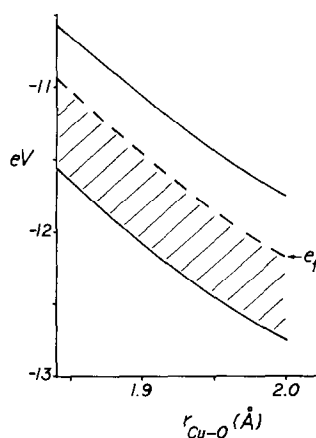


FIG. 1. Top and bottom of the  $x^2-y^2$  band calculated for a flat  $CuO_2$  layer as a function of the in-plane Cu–O bond length, where the Fermi level is for the half-filled case.

calculations (11, 14, 23, 27) on a flat  $CuO_2$  layer and a model Tl–O single rock-salt layer. The atomic parameters employed in this work were taken from Ref. (11).

Figure 1 shows the top and the bottom of the  $x^2-y^2$  band calculated for a flat  $CuO_2$  layer as a function of the in-plane Cu–O bond distance, where the dashed line refers to the Fermi level for the copper oxidation state  $Cu^{2+}$  (i.e., half-filled band). Note that the  $x^2-y^2$  band is raised as much as  $\sim 1.1$  eV when the in-plane Cu–O distance is shortened from 2.00 to 1.85 Å. To examine the Tl  $6s$ -block bands of the superconducting phase  $TlSrLaCuO_5$ , we construct a model Tl–O layer on the basis of its  $a$ -parameter (3.761 Å) (21). In general, the Tl–O layers of  $Tl_mBa_2Ca_{n-1}Cu_nO_{2n+m+2}$  do not adopt an ideal rock salt structure because such a structure leads to a long in-plane Tl–O distance of  $a/\sqrt{2}$  (e.g.,  $3.761/\sqrt{2} = 2.659$  Å for  $TlSrLaCuO_5$ ) (7, 11). The structures of the real Tl–O layers deviate from an ideal rock-salt structure to produce short in-plane Tl–O contacts, thereby leading to ladder-, chain-, or island-like patterns (7, 11, 14). As shown in Fig. 2a, we adopt a chain-like

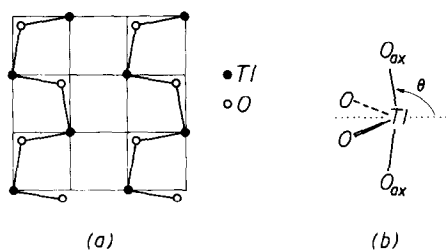


FIG. 2. (a) Chain-like pattern adopted for the Tl-O layer of TlSrLaCuO<sub>5</sub>. (b) Arrangement of the out-of-plane oxygen atoms (O<sub>ax</sub>) at each Tl atom above and below the Tl-O plane.

pattern for the Tl-O layer of TlSrLaCuO<sub>5</sub> with in-plane Tl-O of 2.30 Å. Then, two out-of-plane oxygen atoms (O<sub>ax</sub>) are attached to each Tl atom of Fig. 2a with the bond angle  $\theta$  as defined in Fig. 2b, where the dotted line bisects the in-plane O-Tl-O arrangement. Figure 3 shows how the bottom of the Tl 6s-block bands calculated for this Tl-O single rock-salt layer varies as a function of the Tl-O<sub>ax</sub> distance and of the bond angle  $\theta$ . The bottom of the Tl 6s-block bands is lowered in energy with increasing the Tl-O<sub>ax</sub> distance because this band is antibonding between the Tl and O atoms. It is also lowered when the bond angle  $\theta$  increases from 90° due to the mixing of the Tl in-plane 6p-orbitals into the Tl 6s-orbital, which leads to an in-plane

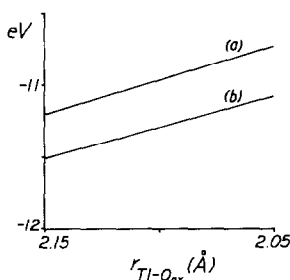


FIG. 3. Bottom of the Tl 6s-block bands calculated for the model Tl-O layer representing the Tl-O layer of TlSrLaCuO<sub>5</sub> as a function of the Tl-O<sub>ax</sub> distance for the cases of (a)  $\theta = 90^\circ$  and (b)  $\theta = 95^\circ$ .

hybrid orbital directed away from the chain atoms (28).

It is clear from Figs. 1 and 3 that, for a system like TlSrRCuO<sub>5</sub> ( $R = \text{La, Nd}$ ) for which the  $a$ -parameter is short, the Fermi level of the half-filled  $x^2-y^2$  band very likely lies above the bottom of the Tl 6s-block bands, so that the Tl-O layer creates holes in the CuO<sub>2</sub> layer. For a system with a longer  $a$ -parameter, the Fermi level of the half-filled  $x^2-y^2$  band would be lowered below the bottom of the Tl 6s-block bands, so that the Tl-O layer does not generate holes in the CuO<sub>2</sub> layer. This situation should be applicable for TlSrLaCaCu<sub>2</sub>O<sub>7</sub>, because this compound is not a superconductor and because its  $a$ -parameter is greater than that of TlSrLaCuO<sub>5</sub>. To summarize, the superconductivity of TlSrRCuO<sub>5</sub> is due most likely to the fact that its short in-plane Cu-O bond raises the  $x^2-y^2$  band high enough in energy to place the Fermi level above the bottom of the Tl 6s-block bands. The difference of TlSrRCuO<sub>5</sub> from TlBaRCuO<sub>5</sub> and TlSrRCaCu<sub>2</sub>O<sub>7</sub> in superconducting property originates essentially from the fact that the in-plane Cu-O bond length is strongly affected by the steric effects of the cations located at the 8- and/or 9-coordination sites adjacent to the CuO<sub>2</sub> layer (5-7). Solid solution studies of TlBaLaCuO<sub>5</sub> and TlSrLaCuO<sub>5</sub> reveal (29) that the  $a$ -parameter of the solid state Tl(Ba <sub>$x$</sub> Sr <sub>$1-x$</sub> )LaCuO<sub>5</sub> increases gradually with increasing  $x$ , and that the solid solution loses its superconductivity when  $x > 0.6$ . These results are consistent with our conclusions.

### Acknowledgments

This work was supported by the Office of Basic Energy Sciences, Division of Materials Sciences, U.S. Department of Energy, under Grant DE-FG05-86ER45259.

### References

1. A. W. SLEIGHT, *Science* **242**, 1519 (1988).
2. A. W. SLEIGHT, M. A. SUBRAMANIAN, AND C. C. TORARDI, *Mater. Res. Soc. Bull.* **XIV**, 45 (1989).

3. C. N. R. RAO AND B. RAVEAU, *Acc. Chem. Res.* **22**, 106 (1989).
4. R. J. CAVA, *Science* **247**, 656 (1990).
5. M.-H. WHANGBO AND C. C. TORARDI, *Science* **249**, 1143 (1990).
6. M.-H. WHANGBO, D. B. KANG, AND C. C. TORARDI, *Physica C* **158**, 371 (1989).
7. M.-H. WHANGBO AND C. C. TORARDI, submitted for publication.
8. J. K. BURDETT AND G. V. KULKARNI, *Phys. Rev. B* **40**, 8908 (1989).
9. M.-H. WHANGBO, E. CANADELL, M. EVAIN, AND J. M. WILLIAMS, *Inorg. Chem.* **27**, 2394 (1988).
10. J. ZAAENEN, A. T. PAXTON, O. JEPSEN, AND O. K. ANDERSEN, *Phys. Rev. Lett.* **60**, 2685 (1988).
11. D. JUNG, M.-H. WHANGBO, N. HERRON, AND C. C. TORARDI, *Physica C* **160**, 381 (1989).
12. J. B. GOODENOUGH AND A. MANTHIRAM, *J. Solid State Chem.* **88**, 115 (1990).
13. A. MANTHIRAM, M. PARANTHAMAN, AND J. B. GOODENOUGH, *Physica C* **171**, 135 (1990).
14. T. J. WAGENER, Y. HU, Y. GAO, M. B. JOST, J. H. WEAVER, N. D. SPENCER, AND K. C. GORETTA, *Phys. Rev. B* **39**, 2928 (1989).
15. M. TANAKA, T. TAKAHASHI, H. KATAYAMA-YOSHIDA, S. YAMAZAKI, M. FUJINAMI, Y. OKABE, W. MITSUTANI, M. ONO, AND K. KAJIMURA, *Nature* **339**, 691 (1989).
16. J. REN, D. JUNG, M.-H. WHANGBO, J.-M. TARASCON, Y. LE PAGE, W. R. MCKINNON, AND C. C. TORARDI, *Physica C* **159**, 151 (1989).
17. C. C. TORARDI, J. B. PARISE, M. A. SUBRAMANIAN, T. GOPALAKRISHNAN, AND A. W. SLEIGHT, *Physica C* **157**, 115 (1989).
18. Y. LE PAGE, W. R. MCKINNON, J.-M. TARASCON, AND P. BARBOUX, *Phys. Rev. B* **40**, 6810 (1989).
19. M. A. SUBRAMANIAN, C. C. TORARDI, J. GOPALAKRISHNAN, P. L. GAI, J. C. CALABRESE, T. R. ASKEW, R. B. FLIPPEN, AND A. W. SLEIGHT, *Science* **242**, 249 (1988).
20. S. LI AND M. GREENBLATT, *Physica C* **157**, 365 (1989).
21. M. A. SUBRAMANIAN, *Mater. Res. Bull.* **25**, 191 (1990).
22. M. A. SUBRAMANIAN, P. L. GAI, AND M.-H. WHANGBO, *Mater. Res. Bull.* **25**, 899 (1990).
23. D. B. KANG, D. JUNG, AND M.-H. WHANGBO, *Inorg. Chem.* **29**, 257 (1990).
24. S. LI, M. GREENBLATT, Y. JEON, J. CHEN, G. LIANG, AND M. CROFT, *Physica C*, in press.
25. M. A. SUBRAMANIAN AND A. K. GANGULI, *Mater. Res. Bull.*, in press.
26. M.-H. WHANGBO, M. EVAIN, M. A. BENO, AND J. M. WILLIAMS, *Inorg. Chem.* **26**, 1829 (1987).
27. M.-H. WHANGBO AND R. HOFFMAN, *J. Am. Chem. Soc.* **100**, 6093 (1978). For details of EHTB calculations, see Ref. (11).
28. T. A. ALBRIGHT, J. K. BURDETT, AND M.-H. WHANGBO, "Orbital Interactions in Chemistry," Wiley, New York, 1985.
29. M. A. SUBRAMANIAN AND A. K. GANGULI, to be published.