Possible pressure-induced valence changes in $Tl_2CaBa_2Cu_2O_8$ superconductors

B. Morosin and E. L. Venturini
Sandia National Laboratories, Albuquerque, New Mexico 87185
(Received 13 January 1992; revised manuscript received 2 March 1992)

The reported nonlinear pressure dependence of the superconducting critical temperature T_c in $Tl_2CaBa_2Cu_2O_8$ can be explained by valence changes deduced from the annealing behavior under various environments for single crystals of several Tl-Ca-Ba-Cu-O structure types. The pressure data are consistent with partial conversion of Tl^+ to Tl^{3+} with increasing pressure (decreasing c-axis length), resulting in electron transfer from the Tl-O layers to the Cu-O_2 sheets.

Recently, experiments on single-crystal $Tl_2CaBa_2Cu_2O_8$ (Tl 2:1:2:2) under essentially hydrostatic pressure conditions to ~6 GPa showed a nonlinear pressure dependence of the superconducting critical temperature, T_c.[1] Further, previous experiments on sintered samples had also indicated a nonmonotonic pressure dependence of T_c for Tl 2:1:2:2, initially increasing with increasing pressure, reaching a maximum, and then decreasing with further increasing pressures.[2,3] While the increase in T_c with increasing oxygen concentration in $YBa_2Cu_3O_{7-\delta}$ is consistent with the observation of increasing T_c with increasing pressure, the Tl-Ca-Ba-Cu-O systems shows a more complex behavior, including an increasing T_c with decreasing oxygen content,[4,5] but with a positive pressure dependence at low pressures.[6–8] Noting this inconsistent behavior, Moulton and co-workers recently suggested a theoretical explanation that is based upon the strong-coupling Eliashberg form of the BCS theory.[1] This theory, as applied to a two-dimensional-like system,[9] predicts a nonmonotonic dependence of T_c on the Fermi wave vector with a maximum T_c when $2k_F = q_c$, where q_c is the limiting value of the phonon momentum for the most important phonon mode. In turn, k_F is a function of both the interlayer spacing and the carrier concentration. Changing either (or both) of these will produce the nonmonotonic dependence on T_c that is observed in all the Tl-based cuprates.

The charge transfer effects induced by pressure changes from the apical oxygen above the Cu-O_2 sheets would be expected to be small but present.[10] Since to first order the compressibilities of the layered superconductors are similar, another more sensitive factor must be present for the Tl-containing materials. The present paper points out that an additional mechanism involving pressure-induced valence changes may be present in the Tl-containing material which would alter simultaneously the interlayer spacing and the carrier concentration in the Cu-O_2 planes. In fact, such valence changes lend support to the above mentioned general theoretical interpretation and provide an additional mechanism to explain pressure-induced effects.

Our recent structure studies on single crystals as a function of annealing have shown a rather complex behavior in the Tl-containing materials; namely, that addition or subtraction of oxide ions may result in oxidation-reduction *within* the charge reservoir rather than between it and the Cu-O_2 planes.[11,12] Further, these results clearly indicate the possibility of Tl^+ being present in the Tl-O layer even after many hours of oxygen annealing. The presence of such a Tl^+-Tl^{3+} equilibrium in the Tl-O layer can be inferred from the shift of the more accurately determined Ba positions in the lattice as the crystal is annealed in the case of both Tl 2:2:2:3 and Tl 1:2:2:3.[11,12] That is, as more oxygen goes into the vacancies in the Tl-O layer(s) of as-grown crystals, the remaining layers shift toward the Tl-O layer(s); this is best seen by examining the Ba position relative to the Tl-O layer.

Similar detailed data are not currently available for the Tl 2:1:2:2 system. On the other hand, several detailed structure studies have appeared in the literature on this crystal type and these are shown in Fig. 1. Note that

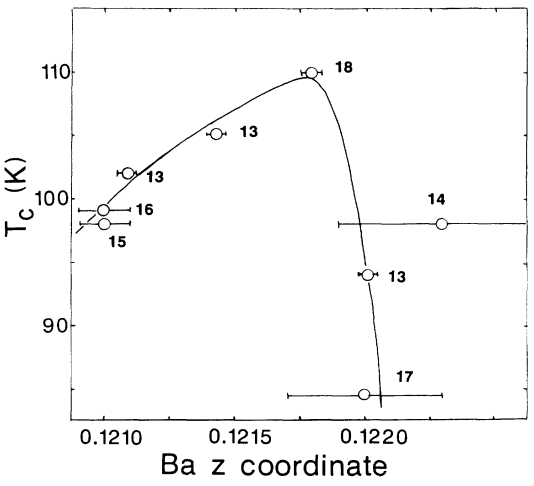

FIG. 1. T_c vs Ba z fractional coordinate. This coordinate scales with respect to the Tl^{3+} to Tl^+ ratio in the Tl-O layers; this Tl ratio affects the electron transfer to the Cu-O_2 planes, particularly as would be involved with a pressure-induced valence change. Numbers indicated by points refer to data from Refs. 13–18; the line represents a guide through the points. The number of carriers (holes) decreases as z increases. Increasing pressure increases z and decreases the number of carriers as the larger Tl^+ change to smaller Tl^{3+} ions.

there is a consistent trend of T_c with the position of the Ba in this structure type.[19] This is similar to the behavior found in Tl 2:2:2:3 and Tl 1:2:2:3 and can be explained by the presence of both Tl^+ and Tl^{3+} in the Tl-O layers depending on the growth conditions and subsequent annealing to which the crystal or ceramic sample may have been subjected.

It is also well known that pressure-induced valence changes occur in various materials, some discontinuous while others continuous, which are essentially driven by the difference of the ionic radii of the smaller, higher-valence compared with the larger, lower-valence state of a particular constituent.[20] In the present Tl-containing materials, the presence of some Tl^+ ions offers a route for carrier alteration as pressure is increased and these larger Tl^+ ions become smaller Tl^{3+} ions. Then the number of holes available to the $Cu\text{-}O_2$ sheets would be decreased as higher pressures are attained. (Further, the interlayer spacing is reduced with Tl^+ to Tl^{3+} conversion.)

Assuming that there is an optimal hole concentration in the $Cu\text{-}O_2$ layers (where $2k_F = q_c$ in the Eliashberg formulation) for a maximum T_c value, the nonlinear pressure dependence reported by Moulton *et al.*[1] is consistent with their as-grown Tl 2:1:2:2 single crystals being slightly overdoped. As increasing pressure is applied, the Tl^+ to Tl^{3+} conversion supplies additional electrons to the $Cu\text{-}O_2$ sheets (thus changing k_F), producing an initial increase in T_c as the optimal doping is approached. At higher pressures, the $Cu\text{-}O_2$ sheets become increasingly underdoped and T_c begins to fall. The initial doping is highly sample dependent because of Ca and/or Tl substitutional disorder and initial oxygen-vacancy concentration. Hence, the pressure for the maximum T_c will vary for different overdoped samples, while underdoped samples should have the highest T_c at ambient pressure.

This work performed at Sandia National Laboratories was supported by the U.S. Department of Energy under Contract No. DE-AC04-76DP00789.

[1]N. E. Moulton, S. A. Wolf, E. F. Skelton, D. H. Liebenberg, T. A. Vanderah, A. M. Hermann, and H. M. Duan, Phys. Rev. B **44**, 12 632 (1991).

[2]N. Mori, H. Takahashi, Y. Shimakawa, T. Manako, and Y. Kubo, J. Phys. Soc. Jpn. **59**, 3839 (1990).

[3]A. Allegeier, R. Sieburger, H. Grossner, J. Diedrichs, H. Neumair, W. Keith, P. Muller, and J. S. Schilling, Physica **C162-164**, 741 (1989).

[4]C. Martin, A. Maignan, J. Provost, C. Michel, M. Hervieu, R. Tournier, and B. Raveau, Physica **C168**, 8 (1990).

[5]E. L. Venturini, B. Morosin, D. S. Ginley, J. F. Kwak, J. E. Schirber, and R. J. Baughman, Mat. Res. Soc. Symp. Proc. **156**, 239 (1989).

[6]J. E. Schirber, B. Morosin, and D. S. Ginley, Physica **C157**, 237 (1989).

[7]J. Stankowski, B. Czyzak, M. Krupski, J. Baszynski, T. Datta, C. Almasan, Z. Z. Sheng, and A. M. Hermann, Physica **160**, 170 (1989).

[8]J. L. Zhang, C. G. Cui, S. L. Li, Y. L. Zhang, X. R. Chang, and Q. S. Yang, Mod. Phys. Lett. B **2**, 879 (1988).

[9]V. Z. Kresin and S. A. Wolf, J. Supercond. **1**, 143 (1988).

[10]Such charge transfer effects are documented in structural chemistry, see, for example, B. Morosin, Acta Crystallogr. B **26**, 1203 (1970); **32**, 1237 (1976) on the dependence of N-O bond lengths on the Cu-O separation (and induced charge transfer).

[11]B. Morosin, E. L. Venturini, and D. S. Ginley, Physica **C183**, 90 (1991).

[12]B. Morosin, E. L. Venturini, and D. S. Ginley, Physica **C175**, 241 (1991).

[13]B. Morosin, D. S. Ginley, E. L. Venturini, R. J. Baughman, and C. P. Tigges, Physica **C172**, 413 (1991).

[14]M. Kikachi, T. Kajitani, T. Suzuki, S. Nakajima, K. Hiraga, N. Kobayashi, H. Iwasaki, Y. Syono, and Y. Muto, Jpn. J. Appl. Phys. **28**, 382 (1989).

[15]D. E. Cox, C. C. Torardi, M. A. Subramanian, J. Gopalakrishnan, and A. W. Sleight, Phys. Rev. B **38**, 6624 (1988).

[16]A. W. Hewat, E. A. Hewat, S. Brynestad, H. A. Mook, and E. D. Specht, Physica **C152**, 438 (1988).

[17]Y. Shimakawa, Y. Kubo, T. Manako, T. Satoh, S. Iijima, T. Ichihashi, and H. Igarashi, Physica **C157**, 279 (1989); **157**, 97 (1988).

[18]M. A. Subramanian, J. C. Calabrese, C. C. Torardi, J. Gopalakrishnan, T. R. Askew, R. B. Flippen, K. J. Morrissey, U. Chowdhry, and A. W. Sleight, Nature (London) **332**, 420 (1990).

[19]The fractional coordinate position z of the Ba is an internal or "normalized" measure of the amount of Tl^{3+} to Tl^+ in this structure type. We have previously noted (see Ref. 13) the importance of Tl substitution for Ca and its affect on the c-axis parameter in the Tl 2:1:2:2 system. This uncontrolled substitution effect does not allow the direct comparison of T_c with the c-axis length. Note, however, that points in Fig. 1 for Refs. 15 and 16 scale on this "normalized" plot whereas their c-axis lengths, 29.420 and 29.260 Å, respectively, differ significantly because of such substitution.

[20]A. Jayaraman, P. D. Dernier, and L. D. Longinotti, High Temp. High Press. **7**, 1 (1975), and references therein.