Zero resistance at 107 K in the (Bi,Pb)-Ca-Sr-Cu oxide system

S. M. Green, C. Jiang, Yu Mei, H. L. Luo, and C. Politis*
Department of Electrical and Computer Engineering, University of California at San Diego, La Jolla, California 92093
(Received 21 April 1988)

The 110-K superconducting transition in the Bi-Ca-Sr-Cu-O system has been observed by many researchers. However, not even a filamentary path has been obtained connecting these regions in multiphase, polycrystalline samples. We have achieved zero resistance at temperatures exceeding 100 K in several samples by adding Pb to the system. The highest value we have observed is $T_{c,\text{zero}}=107$ K for $Bi_{1.8}Pb_{0.2}Ca_2Sr_2Cu_3O_y$.

The discovery of superconductivity in the Bi-Sr-Cu-O system by Michel *et al.*[1] was the first step toward high-T_c materials without the need for rare-earth elements. Superconducting transition temperatures were raised from ~20 K to over 100 K by the addition of Ca as reported by Maeda, Tanaka, Fukuitomi, and Asano[2] and Chu *et al.*[3] In the Bi-Ca-Sr-Cu-O system, two superconducting transitions with clear onsets at 110–120 K and 75–85 K have been reported.[2–8] Such steps in the resistivity have been observed after heat treatment at different temperatures in oxygen and air, by slow cooling and rapid cooling. Only in vacuum was no high-T_c observed. Thus, simply adding Ca does not yield zero-resistance temperatures above 100 K even though significant diamagnetic susceptibilities are observed. Rather, the bulk phase responsible for these high T_c's seem to occur in unconnected regions of the sintered polycrystalline samples, separated by a lower T_c phase. A residual resistance is always observed until the lower transition temperature, yielding $T_{c,\text{zero}}\sim 75$–80 K.[9] Varying the composition and heat treatment have not

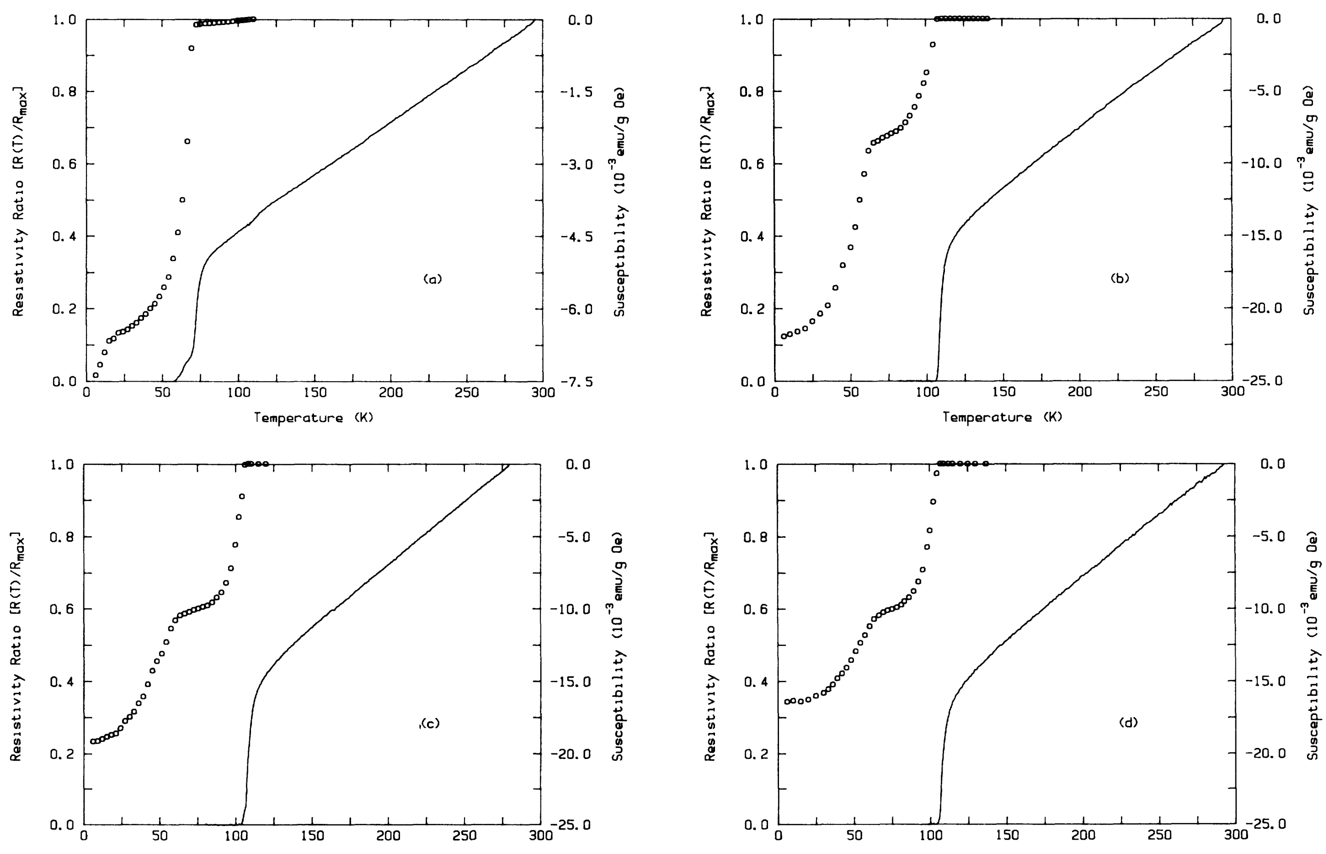

FIG. 1. Resistivity (solid line) and susceptibility (circles) of samples with nominal composition $Bi_{2-x}Pb_xCa_2Sr_2Cu_3O_y$ sintered for 60 h at 860–865 °C. (a) $x=0.0$; $R_{max}\simeq 2.4$ mΩ cm. (b) $x=0.2$; $R_{max}\simeq 5.5$ mΩ cm. (c) $x=0.4$; $R_{max}\simeq 3.3$ mΩ cm. (d) $x=0.6$; $R_{max}\simeq 4.0$ mΩ cm.

yielded the elusive $T_{c,\text{zero}} > 100$ K. We report here our success in preparing bulk polycrystalline samples with $T_{c,\text{zero}}$ as high as 107 K by chemical substitution of Pb in the Bi-Ca-Sr-Cu-O system. The substitution of Pb was first reported by Sunshine *et al.*[6] In their work, they note that the T_c of a multiphase lead-substituted sample was raised from 84 K as indicated by a ~10% Meissner signal beginning at 107 K, with zero resistance achieved near 100 K.[7]

Samples of nominal composition $Bi_{2-x}Pb_xCa_2Sr_2Cu_3O$ were prepared by solid-state reaction. Appropriate amounts of Bi_2O_3 (99.9%), PbO (99.999%), $CaCO_3$ (99.9%), $SrCO_3$ (99.999%), and CuO (99.9%) were well mixed and ground in an agate mortar and pestle. The powders were prefired in air at 800 °C for 16 h, then reground and pressed into pellets. The pellets were sintered at 860–865 °C for 60 h in air followed by furnace cooling to 350 °C, then removed to the laboratory bench.

Bars approximately $2\times1\times10$ mm^3 were cut from the center of the pellets for resistivity measurements from room temperature down to 77 K. Stainless-steel springs, arranged in the standard four-point configuration, were secured with silver paint. A 0.5–1.0 mA rms current was supplied at 40 Hz with the sample's voltage drop detected by a lock-in amplifier. Our minimum detectable resistivity with this setup is 0.5 $\mu\Omega$ cm for typically sized samples. dc susceptibility measurements were performed using a superconductor quantum interference device magnetometer.

The resistivity and susceptibility data of four samples with $x=0$, 0.2, 0.4, and 0.6 are presented in Figs. 1(a)–1(d). These samples were prepared simultaneously and are presumed to have identical thermal histories. Under these conditions, the addition of small amounts of Pb has a dramatic effect. Sample 1, which contains no lead ($x=0$), barely displays a resistive kink at 110 K, and shows no significant resistive transition down to 77 K. The susceptibility data confirm that the kink is associated with superconductivity; however, the majority transition occurs near 75 K, with an additional step evident below 25 K. Sample 2 ($x=0.2$) attains zero resistance at 105.7 K with an associated diamagnetic susceptibility of 8.3×10^{-3} emu/gOe. Sample 3 ($x=0.4$) contains a tiny foot in the resistive transition at about 106 K yet still reaches zero at 103.3 K. The diamagnetic signal for this transition is 10.4×10^{-3} emu/gOe. Sample 4 ($x=0.6$) has $T_{c,\text{zero}}=103.8$ K with the diamagnetic susceptibility for this phase also reaching 10.4×10^{-3} emu/gOe.

Based on the susceptibility data, all three Pb-doped samples contain a second phase with $T_c \sim 65$ K. The total diamagnetic susceptibilities at 6 K are 21.9, 17.0, and 16.1×10^{-3} emu/gOe for $x=0.2$, 0.4, 0.6, respectively. The 65-K phase is likely related to either the 25- or 75-K phase of the lead-free sample. One postulate is that Pb raised the T_c of the 75-K phase to ~105 K (Ref. 7) and the T_c of the 25-K phase to ~65 K, perhaps by increasing

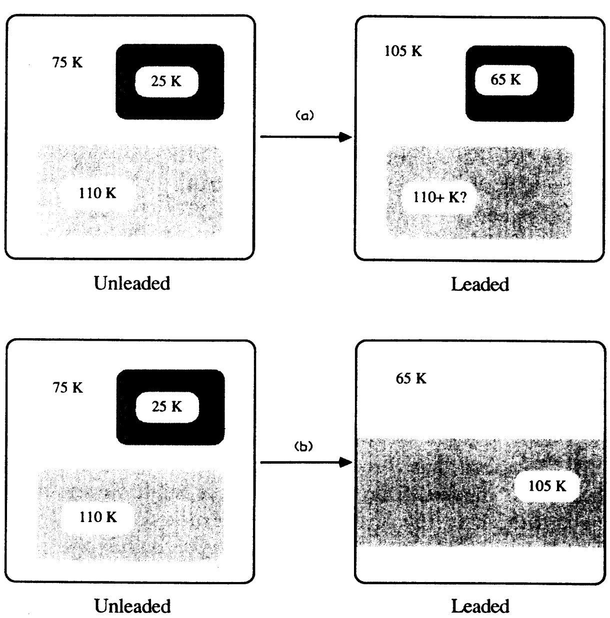

FIG. 2. Schematic representation of two conjectures. (a) Does Pb increase the T_c of each phase present in the Bi-Ca-Sr-Cu-O system? If so, might $T_c > 110$ K be eventually realized? (b) Or does Pb lower the T_c, acting instead to improve the connectivity of the highest T_c phase present?

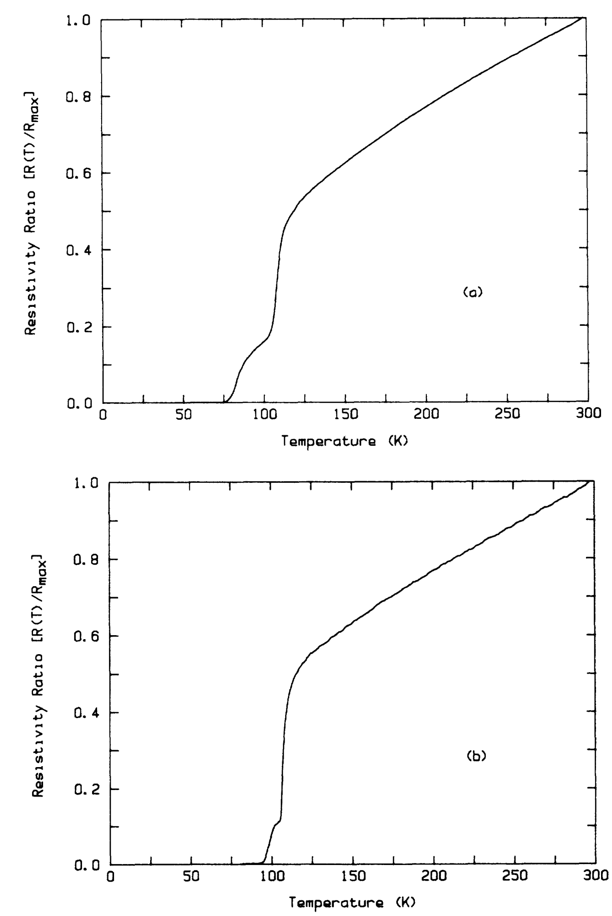

FIG. 3. Resistivity of samples with nominal composition $Bi_{1-x}Pb_xCaSrCu_2O_y$ demonstrate effect of Pb on the residual resistance step. (a) $x=0.0$ sintered at 870–875 °C; $R_{max} \simeq 2.8$ mΩ cm; $T_{c,\text{zero}}=75.0$ K (Ref. 7). (b) $x=0.2$ sintered at 870–875 °C; $R_{max} \simeq 8.1$ mΩ cm; $T_{c,\text{zero}}=91.2$ K.

the Cu^{3+}-to-Cu^{2+} ratio. In this fashion, connectivity would be readily achieved and zero resistance above 100 K easily attained. If this conjecture is correct, then incorporation of Pb in the 110 K phase, if possible, could lead to substantially higher T_c's.

Alternatively, the Pb may prevent the formation of significant amounts of the 25-K phase while reducing the T_c's of the 75- and 110-K phases to 65 and 105 K, respectively [Fig. 2(b)]. In this case, the Pb would also act to expand the 105-K phase so that connectivity is obtained. The microstructure of these samples will have to be thoroughly examined to ellucidate the actual situation. However, some other experimental results favor the former conjecture.

In another paper,[8] we report that significant amounts of the 110-K lead-free phase are formed if the nominal composition $BiCaSrCu_2O_y$ is sintered at temperatures between 870 and 875 °C. Thus, we prepared several samples with nominal composition $Bi_{1-x}Pb_xCaSrCu_2O_y$ and sintered them at temperatures ranging from 865 to 875 °C. The resistivity curve for a sample with $x=0.2$ is displayed in Fig. 3, along with a sample which contains no lead. The data tend to support the notion that Pb raises the T_c of the 75-K phase. Both samples demonstrate stepped resistive transitions. The step is most pronounced when $x=0$, but improves significantly ($T_{c,\mathrm{zero}}$ increases) for $x=0.2$.

With this in mind, we submitted sample 2 ($x=0.2$) [Fig. 1(b)] to an additional 16 h firing at 870–875 °C. The resulting resistivity curve is displayed in Fig. 4. A tiny foot is observable, yet zero resistance is achieved at 107.0 K. If the majority transition is extrapolated, zero resistance would occur at or slightly above 110 K.

There are now several known compounds with superconducting transitions above the boiling point of liquid nitrogen. Undoubtedly, there are more yet to be discovered. With the exception of the unleaded Bi-Ca-Sr-Cu-O system, all are capable of zero resistance at temperatures corresponding to the highest T_c phase present. The Bi-Ca-Sr-Cu-O system, however, suffers from a connectivity problem which prevents the zero resistance of the high-T_c phase from being achieved. As demonstrated in this work, connectivity can be readily achieved by adding lead to the system. Furthermore, lead would appear to affect the T_c's of the other superconducting phases in this system. Since zero resistance is obtained at temperatures well above these lower T_c's, this last point is evident only upon examination of the magnetic susceptibility data.

Note added in proof: High-resolution electron microscope images[10] indicated that the second conjecture [Fig. 2(b)] more likely reflects the actual situation.

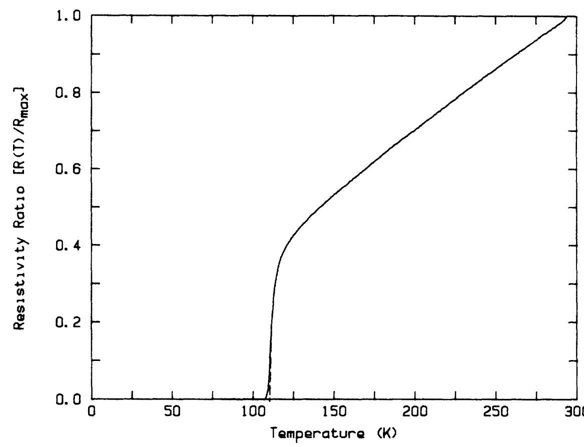

FIG. 4. Resistivity curve of sample from Fig. 1(b) refired at 870–875 °C for 16 h. $T_{c,\mathrm{zero}}=107.0$ K. The extrapolation (dashed line) indicates that $T_{c,\mathrm{zero}} \gtrsim 110$ K should be attainable.

This work was supported by the California MICRO program and Hughes Aircraft Co.

*Also at Kernforschungszentrum Karlsruhe, Institut für Nukleare Festkörperphysik, Postach 3640, D-7500 Karlsruhe, Federal Republic of Germany.

[1]C. Michel, M. Hervieu, M. M. Borel, A. Grandin, F. Deslandes, J. Provost, and B. Raveau, Z. Phys. B **68**, 421 (1987).

[2]M. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano, Jpn. J. Appl. Phys. Lett. **27**, L209 (1988).

[3]C. W. Chu, J. Bechtold, L. Gao, P. H. Hor, Z. J. Huang, R. L. Meng, Y. Y. Sun, Y. Q. Wang, and Y. Y. Xue, Phys. Rev. Lett. **60**, 941 (1988).

[4]R. M. Hazen, C. T. Prewitt, R. J. Angel, N. L. Ross, L. W. Finger, C. G. Hadidiacos, D. R. Veblen, P. J. Heaney, P. H. Hor, R. L. Meng, Y. Y. Sun, Y. Q. Wang, Y. Y. Xue, Z. J. Huang, L. Gao, J. Bechtold, and C. W. Chu, Phys. Rev. Lett. **60**, 1174 (1988).

[5]M. A. Subramanian, C. C. Torardi, J. C. Calabrese, J. Gopalakrishnan, K. J. Morrissey, T. R. Askew, R. B. Flippen, U. Chowdhry, and A. W. Sleight, Science **239**, 1015 (1988).

[6]S. A. Sunshine, T. Siegrist, L. F. Schneemeyer, D. W. Murphy, R. J. Cava, B. Batlogg, R. B. van Dover, R. M. Fleming, S. H. Glarum, S. Nakahara, R. Farrow, J. J. Krajewski, S. M. Zahurak, J. V. Waszczak, J. H. Marshall, P. Marsh, L. W. Rupp, Jr., and W. F. Peck, Phys. Rev. B **38**, 893 (1988).

[7]Cava (see Ref. 6) has reported that zero resistance above 100 K can be obtained in Pb-substituted ceramic samples (presented at *Proceedings of the International Conference on High-T_c Superconductors: Materials and Mechanisms of Superconductivity, Interlaken, Switzerland,* edited by J. Müller and J. L. Olsen [Physica C (to be published)].

[8]S. M. Green, Yu Mei, C. Jiang, H. L. Luo, and C. Politis, Mod. Phys. Lett. B (to be published).

[9]J. M. Tarascon has reported that millimeter-sized "pseudomorphs" plucked from the bulk sample can have zero resistance as high as 106 K (presented at *Proceedings of the International Conference on High-T_c Superconductors: Materials and Mechansism of Superconductivity, Interlaken, Switzerland,* edited by J. Müller and J. L. Olsen [Physica C (to be published)].

[10]R. Ramesh, G. Thomas, S. M. Green, C. Jiang, Yu Mei, M. L. Ruder, and H. L. Luo, Phys. Rev. B (to be published).

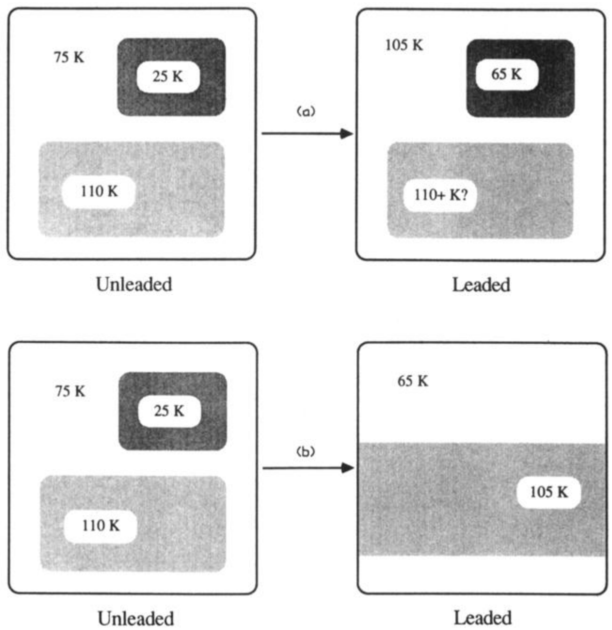

FIG. 2. Schematic representation of two conjectures. (a) Does Pb increase the T_c of each phase present in the Bi-Ca-Sr-Cu-O system? If so, might $T_c > 110$ K be eventually realized? (b) Or does Pb lower the T_c, acting instead to improve the connectivity of the highest T_c phase present?