

## Superconductivity up to 90 K in a New Family of the (Pb,Hg)Sr<sub>2</sub>(Ca,Y)Cu<sub>2</sub>O<sub>7</sub> System

S. F. HU AND D. A. JEFFERSON

*Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, United Kingdom*

R. S. LIU

*IRC in Superconductivity, University of Cambridge, Madingley Road, CB3 0HE, United Kingdom and Material Research Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan, Republic of China*

AND P. P. EDWARDS

*The School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom*

Communicated by J. M. Honig, November 30, 1992

A new family of superconductors were observed in the (Pb<sub>0.5</sub>Hg<sub>0.5</sub>)Sr<sub>2</sub>(Ca<sub>1-x</sub>Y<sub>x</sub>)Cu<sub>2</sub>O<sub>7-δ</sub> system for the composition range 0.5 ≤ x ≤ 0.2, with a maximum T<sub>c</sub> of 90 K (at x = 0.3) as determined by electrical resistance and magnetization measurements. We have investigated the crystal structure across the entire composition range by X-ray diffraction, by which we identify the phase responsible for the superconductivity to be similar to that of (Pb,Cu)Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>7</sub> (the so-called Pb-based 1212 phase) with a space group of *P4/mmm* and lattice constants of *a* ranging from 3.8159(6) Å for x = 0.5 to 3.8082(4) Å for x = 0.2, and *c* ranging from 11.950(2) Å for x = 0.5 to 12.022(2) Å for x = 0.2. Moreover, the chemical composition of one sample in the series having nominal composition (Pb<sub>0.5</sub>Hg<sub>0.5</sub>)Sr<sub>2</sub>(Ca<sub>0.5</sub>Y<sub>0.5</sub>)Cu<sub>2</sub>O<sub>7-δ</sub> (x = 0.5) was determined to be [Pb<sub>0.6</sub>Hg<sub>0.2</sub>Cu<sub>0.2</sub>]Sr<sub>2.0</sub>[Ca<sub>0.42</sub>Y<sub>0.51</sub>Hg<sub>0.07</sub>]Cu<sub>2</sub>O<sub>7-δ</sub> by energy-dispersive spectrometry. © 1993 Academic Press, Inc.

### 1. Introduction

Following the discovery of a nonsuperconducting lead-based 1212 cuprate, (Pb,Cu)Sr<sub>2</sub>(Ca,Y)Cu<sub>2</sub>O<sub>7</sub> (1, 2), numerous attempts have been made to induce or optimize superconductivity; these include the optimization of annealing conditions (3-8), the variation of the Ca and Y ratio (9), and

various chemical substitutions (10-15). (Pb,Cu)Sr<sub>2</sub>(Ca,Y)Cu<sub>2</sub>O<sub>7</sub> has a *P4/mmm* space group (*a* ~ 3.8 Å and *c* ~ 11.8 Å), characterized by an intergrowth of double rock salt-type layers {(Pb,Cu)O}(SrO) and double [Sr(Ca,Y)Cu<sub>2</sub>O<sub>5</sub>] oxygen-deficient perovskite layers, formed by sheets of corner-sharing CuO<sub>5</sub> pyramids interleaved with calcium and yttrium ions (1, 2, 16).

The structure of  $(\text{Pb,Cu})\text{Sr}_2(\text{Ca,Y})\text{Cu}_2\text{O}_7$  resembles that of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (123), with rock-salt-type  $(\text{Pb,Cu})\text{O}$  layers replacing the  $\text{CuO}$  chains, Sr atoms replacing Ba atoms, and  $(\text{Ca,Y})$  atoms replacing Y atoms. The main difference, however, is in the position of certain oxygen atoms; when those in the  $(\text{Pb,Cu})\text{O}$  planes of the Pb-based 1212 material are translated by  $(\frac{1}{2}, 0, 0)$ , they assume the positions of oxygen in the  $\text{CuO}$  chains in the 123 compound. However, there are extra oxygen atoms statistically present in the  $(\text{Pb,Cu})\text{O}$  layers at the site which corresponds to the chain site in the Pb-based 1212 material; the occupancy factors are around 0.025–0.054 (16). Oxygen in this position tends to trap holes within the rock-salt-type  $(\text{Pb,Cu})\text{O}$  layers and thus naturally to limit the  $T_c$  value to only around 45–67 K (17). It is therefore worth trying to replace the Cu in  $(\text{Pb,Cu})\text{O}$  by those elements favoring a rock-salt structure, in order to avoid hole traps within this layer. Generally, cations in the rock-salt-type layer (e.g., Tl) assume a distorted octahedral coordination; the axial metal–oxygen distance of the metal–oxygen bond is significantly shorter than the equatorial distance, for example 2.01(4) Å for the axial distance between Tl and O and 2.717(1) Å for the corresponding equatorial distance in  $\text{TlBa}_2\text{CaCu}_2\text{O}_7$  (18). This polyhedron can be best regarded as a dumbbell, a coordination typical for cations with the closed shell  $d^{10}$  electronic configuration.

An enhancement of  $T_c$  up to 70 K (19) and 92 K (20) by Cd-doping in the system  $(\text{Pb,Cd})\text{Sr}_2(\text{Ca,Y})\text{Cu}_2\text{O}_7$  has recently been observed; here it is assumed that  $\text{Cd}^{2+}$  (with a closed shell  $d^{10}$ ) substitutes for  $\text{Cu}^{2+}$  in  $(\text{Pb,Cu})\text{Sr}_2(\text{Ca,Y})\text{Cu}_2\text{O}_7$ . Although the  $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Ca}_{0.5}\text{Y}_{0.5})\text{Cu}_2\text{O}_7$  material exhibits onset diamagnetism as high as 92 K, the superconducting (Meissner) volume fraction is only a few percent of a perfect superconductor; in the normal state the material is a semiconductor with a very broad

superconducting transition temperature ( $T_{c(\text{onset})} = 90$  K and  $T_{c(\text{zero})} = 45$  K) as measured by electrical resistivity (20).

The  $\text{Hg}^{2+}$  ion which also has a closed shell  $d^{10}$  electronic configuration might be a possible substituent for  $\text{Cu}^{2+}$  in the Pb-based 1212 material. In this work, we report the synthesis and characterization of a new series of  $(\text{Pb}_{0.5}\text{Hg}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{7-\delta}$  superconductors by the substitution of Hg for Cu in the rock salt  $(\text{Pb,Cu})\text{O}$  layers of the Pb-based  $(\text{Pb,Cu})\text{Sr}_2(\text{Ca,Y})\text{Cu}_2\text{O}_7$  system.

## 2. Experimental

High-purity powders of  $\text{PbO}$ ,  $\text{HgO}$ ,  $\text{SrO}_2$ ,  $\text{CaO}$ ,  $\text{Y}_2\text{O}_3$  and  $\text{CuO}$  were weighed in the appropriate proportions to form nominal compositions of  $(\text{Pb}_{0.5}\text{Hg}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{7-\delta}$  ( $x = 0.5, 0.4, 0.3,$  and  $0.2$ ). The powders were then mixed using a mortar and pestle and pressed into pellets (10 mm in diameter and 3 mm in thickness) under a pressure of 5 ton/cm<sup>2</sup>. The pellets were wrapped in gold foil to prevent loss of lead and mercury and a possible reaction with quartz at elevated temperatures, then encapsulated in an evacuated (oxygen pressure  $\sim 10^{-4}$  Torr) quartz tube. Subsequently, the samples were heated inside of a furnace at a heating rate of 10°C/min up to 970°C for 24 hr, and then cooled down to room temperature at a cooling rate of 2°C/min. After heat treatment, all samples were black. Bar-shaped specimens ( $1.5 \times 2 \times 10$  mm) were cut from the sintered pellets and used for resistivity measurements.

X-ray diffraction (XRD) analyses were performed using a Philips PW1710 X-ray diffractometer with  $\text{CuK}\alpha$  radiation. The chemical composition of individual microcrystallites of the specimen was examined by energy-dispersive X-ray spectrometry (EDS) using a JEM-2010 electron microscope operating at 200 kV. Molybdenum specimen grids were used to check by re-

garding background spectra that no residual copper signal originated from the sample holder. Nearly monophasic  $(\text{Pb}_{0.75}\text{Cu}_{0.25})\text{Sr}_2(\text{Ca}_{0.5}\text{Y}_{0.5})\text{Cu}_2\text{O}_7$  was used as standard material (9). A standard four-probe method was used for electrical resistance measurements. The electrical contacts to the sample were made by fine copper wires with a conductive silver paint; the applied current was 1 mA. The temperature was recorded using a calibrated silicon diode sensor located close to the sample. Low field magnetization data were taken from a superconducting quantum interference device (SQUID) magnetometer (Quantum Design).

### 3. Results and Discussion

In Fig. 1 we show the powder XRD patterns of samples with nominal compositions

of the series of compounds  $(\text{Pb}_{0.5}\text{Hg}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{7-\delta}$  with (a)  $x = 0.5$ , (b)  $x = 0.4$ , (c)  $x = 0.3$ , and (d)  $x = 0.2$ . Most of the lines from the XRD pattern of the  $x = 0.5$  sample (Fig. 1a) can be fitted by using a space group of  $P4/mmm$  with a tetragonal unit cell of  $a = 3.8159(6)$  Å and  $c = 11.950(1)$  Å, which is similar to that observed from the so-called Pb-based 1212 phase for the corresponding composition  $(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{Sr}_2(\text{Ca}_{0.5}\text{Y}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$ , with lattice constants  $a = 3.818$  Å and  $c = 11.882$  Å. This result indicates that the Hg-containing sample has a slightly shorter  $a$ , and a longer  $c$ , than the Pb-based 1212 sample. This change in the  $c$ -parameter may correspond to the larger  $\text{Hg}^{2+}$  ion (1.02 Å for C.N. = 6) (21) which replaces the smaller  $\text{Cu}^{2+}$  (0.73 Å for C.N. = 6) (21) ions in the rock-salt (Pb,Cu)O layers. The XRD patterns of the  $x = 0.4$ , 0.3, and 0.2 samples

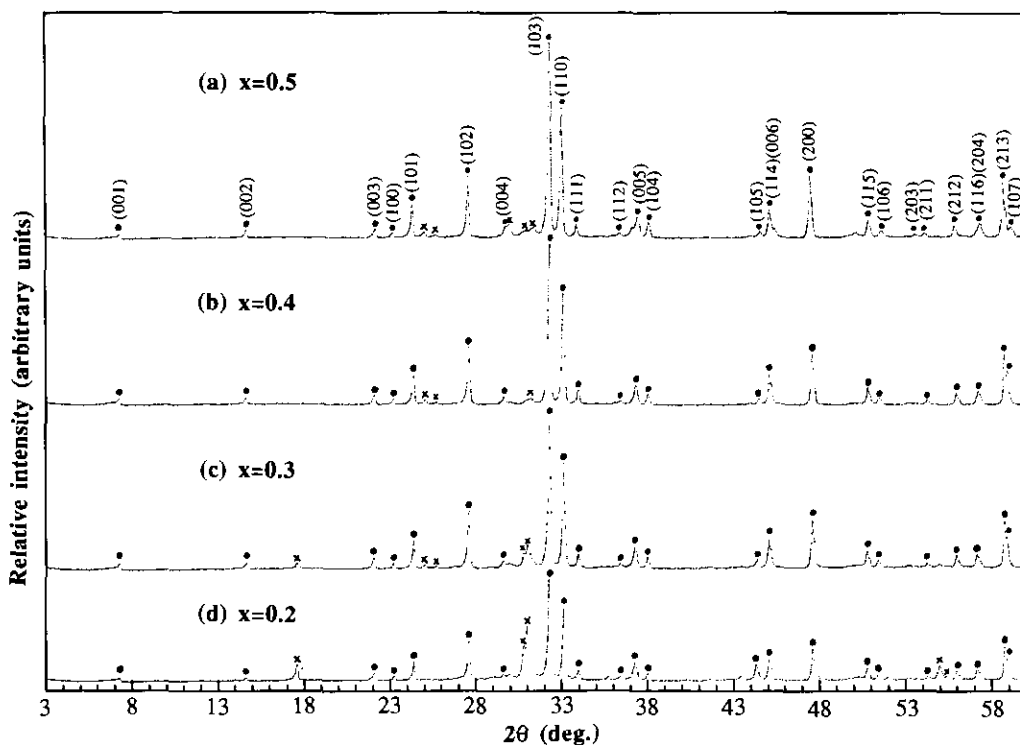


FIG. 1. Powder XRD patterns of samples with nominal compositions of the series of compounds  $(\text{Pb}_{0.5}\text{Hg}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{7-\delta}$  with (a)  $x = 0.5$ , (b)  $x = 0.4$ , (c)  $x = 0.3$ , and (d)  $x = 0.2$ .

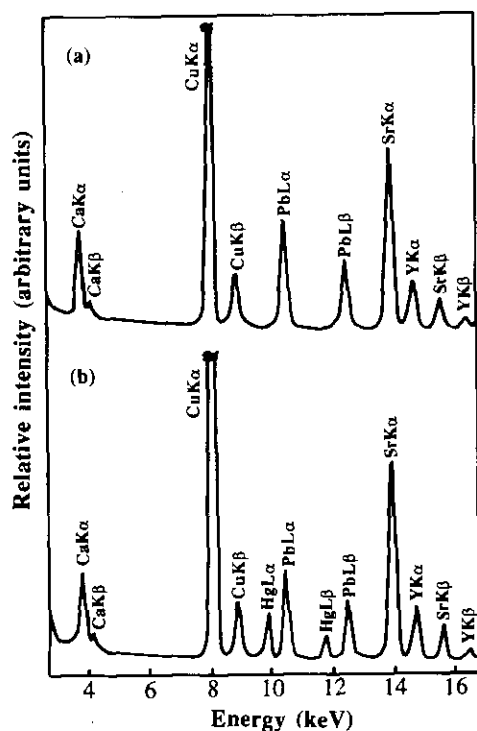


FIG. 2. The variation of the lattice constants (a)  $a$  and (b)  $c$  with  $x$  in  $(\text{Pb}_{0.5}\text{Hg}_{0.5})\text{Sr}_2(\text{Ca}_{0.5}\text{Y}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$ .

are similar to that of the  $x = 0.5$  sample, except that an increase in the concentration of an unidentified impurity phase with increasing Ca-doping (i.e., decreasing  $x$ ) (see Fig. 1a to d) was also observed and may indicate a solubility limit of  $\sim 70\%$  for the substitution of Ca for Y in  $(\text{Pb}_{0.5}\text{Hg}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{7-\delta}$ .

The variation of the  $a$  and  $c$  lattice constants with  $x$  in  $(\text{Pb}_{0.5}\text{Hg}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{7-\delta}$  is shown in Figs. 2a and b, respectively. Note that  $a$  increases with  $x$  (i.e., the contraction becomes less), whereas  $c$  shows the opposite behavior. We propose that the larger contraction in  $a$  with decreasing  $x$  in  $(\text{Pb}_{0.5}\text{Hg}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{7-\delta}$  may be attributed to an increase in the nominal copper oxidation state, arising from the substitution of  $\text{Ca}^{2+}$  for  $\text{Y}^{3+}$ , which in turn leads to shorter Cu–O distances within the copper oxygen sheets. The prob-

able reason for the expansion in  $c$  with decreasing  $x$  is that the  $\text{Ca}^{2+}$  ( $1.12 \text{ \AA}$  for C.N. = 8) is slightly larger than the  $\text{Y}^{3+}$  ( $1.019 \text{ \AA}$  for C.N. = 8) ion (21). A similar effect has been observed in the  $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{7-\delta}$  system (22).

We then chose one member of the series, with nominal composition  $(\text{Pb}_{0.5}\text{Hg}_{0.5})\text{Sr}_2(\text{Ca}_{0.5}\text{Y}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$  ( $x = 0.5$ ), to determine its actual chemical composition by EDS. In Fig. 3 we show the EDS spectra from the sample with this nominal composition (Fig. 3b) as compared to that of the standard sample  $(\text{Pb}_{0.75}\text{Cu}_{0.25})\text{Sr}_2(\text{Ca}_{0.5}\text{Y}_{0.5})\text{Cu}_2\text{O}_7$  (Fig. 3a). If it is assumed that  $\text{Sr}^{2+}$  sites are occupied solely by these ions, and that the overall occupancy of the (Ca,Y) sites must be unity, the occupancy of the rock-salt sites must then correspond to  $(\text{Pb}_{0.6}\text{Hg}_{0.2}\text{Cu}_{0.2})$ , and the chemical composition of the sample is determined to be  $[\text{Pb}_{0.60(2)}\text{Hg}_{0.27(3)}]$

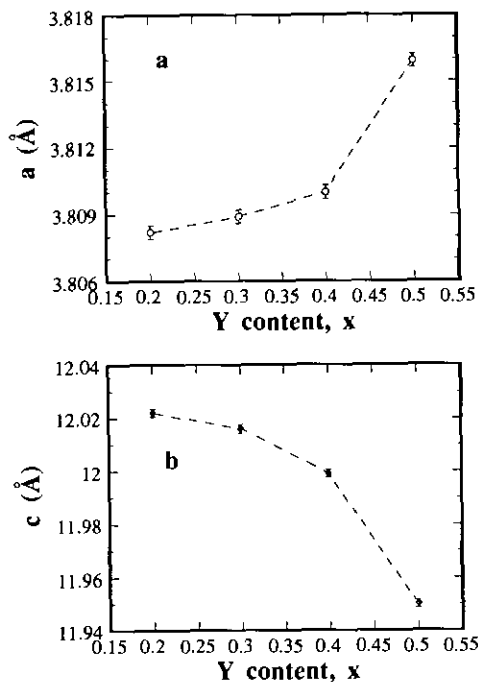


FIG. 3. EDS spectra from (a) a standard sample  $(\text{Pb}_{0.75}\text{Cu}_{0.25})\text{Sr}_2(\text{Ca}_{0.5}\text{Y}_{0.5})\text{Cu}_2\text{O}_7$  and (b) a sample with the nominal composition of  $(\text{Pb}_{0.5}\text{Hg}_{0.5})\text{Sr}_2(\text{Ca}_{0.5}\text{Y}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$  ( $x = 0.5$ ).

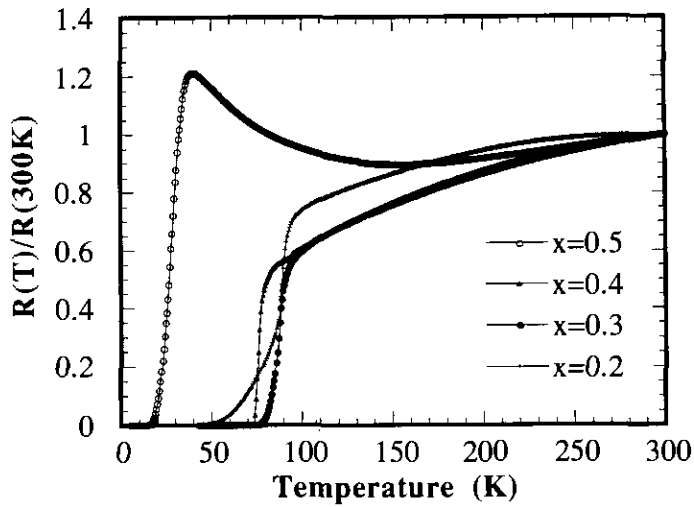


FIG. 4. Temperature dependence of normalized resistance for the series of samples  $(\text{Pb}_{0.5}\text{Hg}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{7-\delta}$  with  $x = 0.5, 0.4, 0.3,$  and  $0.2$ .

$\text{Sr}_{2.0(1)}[\text{Ca}_{0.42(6)}\text{Y}_{0.51(2)}]\text{Cu}_{2.2}\text{O}_{7-\delta}$ , corresponding to  $(\text{Pb}_{0.6}\text{Hg}_{0.2}\text{Cu}_{0.2})\text{Sr}_2(\text{Ca}_{0.42}\text{Y}_{0.51}\text{Hg}_{0.07})\text{Cu}_2\text{O}_7$ . Detailed structure refinements by XRD are currently underway.

In Fig. 4 we show the temperature dependence of the normalized resistance for the series of samples  $(\text{Pb}_{0.5}\text{Hg}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{7-\delta}$ . The substitution of  $\text{Ca}^{2+}$  for  $\text{Y}^{3+}$

increases the superconducting temperature from  $T_{c(\text{onset})} = 40$  K,  $T_{c(\text{midpoint})} = 28$  K, and  $T_{c(\text{zero})} = 14$  K for  $x = 0.5$  to  $T_{c(\text{onset})} = 100$  K,  $T_{c(\text{midpoint})} = 90$  K, and  $T_{c(\text{zero})} = 77$  K for  $x = 0.3$ . However for  $x < 0.3$ , the superconducting transition temperature then decreases and also becomes broader. We therefore propose that the substitution of

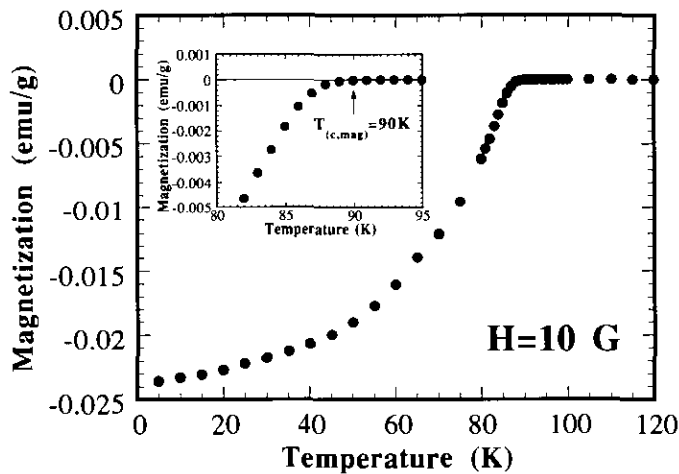


FIG. 5. Temperature dependence of low-field magnetization (10 Oe, field cooled) of the powdered sample with  $x = 0.3$  in  $(\text{Pb}_{0.5}\text{Hg}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{7-\delta}$ . The inset gives greater detail of the temperature dependence of magnetization of the sample over the temperature range 85–100 K.

low valent  $\text{Ca}^{2+}$  for high valent  $\text{Y}^{3+}$  in the system  $(\text{Pb}_{0.5}\text{Hg}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{7-\delta}$  gives rise to an increase in the hole concentration in the  $\text{CuO}_2$  sheets and enhances the  $T_c$  with decreasing  $x$  in the range of  $0.3 \leq x \leq 0.5$  via the removal of electrons from the  $\sigma_{x^2-y^2}^*$  band (23). This proposal is partly supported by the observed contraction of the lattice constant  $a$  with increasing Ca doping (as shown in Fig. 2a). For  $x < 0.3$ , the hole concentration could not be further increased, which may arise from the natural solubility limit of Ca in the Y sites. Consequently, a broadening of the superconducting transition temperature was obtained for the  $x = 0.2$  sample, perhaps due to the contribution from the unidentified impurity phase (as shown in Fig. 1d).

In Fig. 5 we show the temperature dependence of the low-field magnetization (10 Oe, field cooled) of the powdered sample with  $x = 0.3$  in  $(\text{Pb}_{0.5}\text{Hg}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{7-\delta}$ . The onset diamagnetism of the sample appeared at a temperature of 90 K (see inset of Fig. 5), consistent with the electrical resistance measurement of  $T_{c(\text{midpoint})}$ . We estimate a superconducting (Meissner) volume fraction of  $\sim 20\%$  of  $-\frac{1}{4}\pi$  at 5 K, which suggests that the sample essentially showed bulk superconductivity.

In summary, we have demonstrated that a new series of superconducting materials exists in  $(\text{Pb}_{0.5}\text{Hg}_{0.5})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_7$ . With increasing Ca doping (i.e., decreasing the compositional parameter  $x$ )  $T_c$  increases and a maximum value appears at  $x = 0.3$  with a  $T_c$  of 90 K.

### Acknowledgments

We thank the Fellowship of Engineering, BICC plc., SERC, BP, JEOL (UK) for support. We also thank R. W. Smith, glass blower in the Department of Physics, for help in encapsulating the samples. One of us (SFH) acknowledges financial support from Girton College (Cambridge) and the Cambridge Overseas Trust.

### References

1. M. A. SUBRAMANIAN, J. GOPALAKRISHNAN, C. C. TORARDI, P. L. GAI, E. D. BOYES, T. R. ASKEW, R. B. FLIPPEN, W. E. FARNETH, AND A. W. SLEIGHT, *Physica C* **157**, 124 (1989).
2. J. Y. LEE, L. S. SWINNEA, AND H. STEINFINK, *J. Mater. Res.* **4**, 763 (1989).
3. A. ONO AND Y. UCHIDA, *Jpn. J. Appl. Phys.* **29**, L586 (1990).
4. T. MAEDA, K. SAKUYAMA, S. KORIYAMA, H. YAMAUCHI, AND S. TANADA, *Phys. Rev. B* **43**, 7866 (1991).
5. S. ADACHI, H. ADACHI, K. SETSUNE, AND K. WASA, *Jpn. J. Appl. Phys.* **30**, L690 (1991).
6. S. F. HU, D. A. JEFFERSON, R. S. LIU, AND P. P. EDWARDS, *J. Solid State Chem.* **96**, 455 (1992).
7. X. X. TANG, D. E. MORIES, AND A. P. B. SINHA, *Phys. Rev. B* **43**, 7936 (1991).
8. A. MAIGNAN, T. ROUILLON, D. GROULT, J. PROVOST, M. HERVIEU, C. MICHEL, B. RAVEAU, R. S. LIU, AND P. P. EDWARDS, *Physica C* **177**, 461 (1991).
9. R. S. LIU, S. F. HU, I. GAMESON, P. P. EDWARDS, A. MAIGNAN, T. ROUILLON, D. GROULT, AND B. RAVEAU, *J. Solid State Chem.* **93**, 276 (1991).
10. S. ADACHI, H. ADACHI, K. SETSUNE, AND K. WASA, *Jpn. J. Appl. Phys.* **30**, L1099 (1991).
11. H. B. LIU AND D. E. MORRIS, *Phys. Rev. B* **44**, 5369 (1991).
12. T. ROUILLON, J. PROVOST, M. HERVIEU, D. GROULT, C. MICHEL, AND B. RAVEAU, *Physica C* **159**, 201 (1989).
13. T. ROUILLON, A. MAIGNAN, M. HERVIEU, C. MICHEL, D. GROULT, AND B. RAVEAU, *Physica C* **171**, 7 (1990).
14. S. KORIYAMA, K. SAKUYAMA, T. MAEDA, H. YAMAUCHI, AND S. TANAKA, *Physica C* **166**, 413 (1990).
15. R. S. LIU, S. F. HU, AND P. P. EDWARDS, *Appl. Phys. Lett.* **59**, 985 (1991).
16. T. MAEDA, K. SAKUYAMA, F. IZUMI, H. YAMAUCHI, H. ASANO, AND S. TANAKA, *Physica C* **175**, 393 (1991).
17. M. KOSUGE, T. MAEDA, K. SAKUYAMA, H. YAMAUCHI, N. KOSHIZUKA, AND S. TANAKA, *Physica C* **182**, 157 (1991).
18. B. BOROSIN, D. S. GINLEY, P. F. HLAVA, M. J. CARR, R. J. BAUGHMAN, J. E. SCHIRBER, E. L. VENTURINI, AND J. F. KWAK, *Physica C* **152**, 413 (1988).
19. R. S. LIU, D. GROULT, A. MAIGNAN, S. F. HU, D. A. JEFFERSON, B. RAVEAU, C. MICHEL, M. HERVIEU, AND P. P. EDWARDS, *Physica C* **195**, 35 (1992).

20. T. P. BEALES, C. DINEEN, W. G. FREEMAN, S. R. HALL, M. R. HARRISON, D. M. JACOBSON, AND S. J. ZAMMATTIO, *Supercond. Sci. Technol.* **5**, 47 (1992).
21. R. D. SHANNON, *Acta Crystallogr. Sect. A* **32**, 751 (1976).
22. R. S. LIU, P. P. EDWARDS, Y. T. HUANG, S. F. WU, AND P. T. WU, *J. Solid State Chem.* **86**, 334 (1990).
23. J. B. GOODENOUGH, *Supercond. Sci. Technol.* **3**, 26 (1990).