

## Pressure dependence of the superconducting transition temperature in the 94-K superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$

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(Received 13 April 1987)

We present the pressure dependence of the superconducting transition temperature for a variation of preparations of the 94-K superconductor Y-Ba-Cu-O. All preparations show a superconducting transition temperature near 90 K and a small positive derivative  $dT_c/dP = 0.07 \pm 0.02$  K/kbar.

There is enormous interest in the 90-K superconductors<sup>1</sup> and in incisive characterization leading to understanding of the mechanisms dominating their properties and in providing tests of model descriptions for these materials. The pressure dependence of  $\text{Y}_{1.2}\text{Ba}_{0.8}\text{CuO}_4$  was reported by Hor *et al.*<sup>2</sup> Unfortunately the sensitivity of their determination of the superconducting transition  $T_c$  was such that it was not possible to ascertain much more than the derivative was small in comparison to that observed<sup>3</sup> in  $\text{La}_{1.85}\text{Ba}_{0.15}\text{CuO}_4$ . Even the sign of the effect is indeterminate from their results. It is of considerable interest to know with more accuracy the magnitude and sign of the pressure or volume dependence of  $T_c$  for comparison with the various disparate model descriptions being advanced. It is reasonable to expect that such data may provide critical tests for these models.

Samples were synthesized from mixtures of BaO, CuO, and  $\text{Y}_2\text{O}_3$  or  $\text{BaCO}_3$ , CuO, and  $\text{Y}_2\text{O}_3$ . The BaO and  $\text{BaCO}_3$  were kept in an argon-atmosphere dry box prior to use. Mixtures of the materials were thoroughly ground and then pressed into pellets at 5.5 kbar in air. For the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  composition, the pellets were then sintered for 4 h at 950 °C in air with a slow cool. Samples were also initially sintered in  $\text{O}_2$  at 900 °C. The results for both sintering treatments were comparable. They were then annealed at 900 °C in 640 torr of pure oxygen for 12 h followed by a 5-h slow cool under  $\text{O}_2$ . This process resulted

in single-phase material when the mixtures were in stoichiometric ratio 1:2:3 for the yttrium, barium, and copper compounds, respectively. For this phase, x-ray diffraction patterns obtained on a commercial Siemens D-500 automatic diffractometer are in excellent agreement with previous reported values<sup>4</sup> with respect to both line position and intensity. For other mixtures investigated, such as that corresponding to  $\text{Y}_{1.2}\text{Ba}_{0.8}\text{CuO}_4$  and  $\text{Y}_{0.4}\text{Ba}_{0.6}\text{CuO}_4$ , several other nonsuperconducting phases are present with only a small amount of the  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . The  $\text{Y}_{0.4}\text{Ba}_{0.6}\text{CuO}_4$  material was processed in a way essentially identical to that for  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . For the  $\text{Y}_{1.2}\text{Ba}_{0.8}\text{CuO}_4$  material, the best results were obtained by air annealing at 1100 °C for 2 h followed by the normal  $\text{O}_2$  anneal. The high temperature appears to be necessary for generating a Ba-rich liquid phase which generates  $\text{YBa}_2\text{Cu}_3\text{O}_7$  as an intergranular phase.

The quality of our material is exemplified by the flux-expulsion (Meissner effect) data versus increasing temperature in an applied field of 0.3 mT shown in Fig. 1 and by the resistivity data versus temperature shown in Fig. 2. These data are for  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , but very comparable patterns are observed for  $\text{Y}_{1.2}\text{Ba}_{0.8}\text{CuO}_4$  even though the x-ray diffraction data show mixed phases in the latter material. We believe this stems from the finding that the superconductivity in the Y-Ba-Cu-O system is confined to thin shells of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  surrounding grains independent

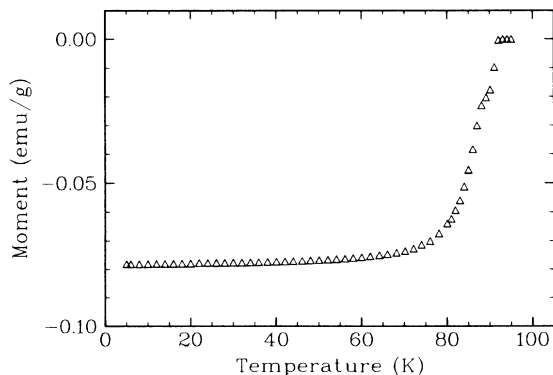


FIG. 1. Magnetization vs temperature for  $\text{YBa}_2\text{Cu}_3\text{O}_7$  in an applied field of 0.3 mT.

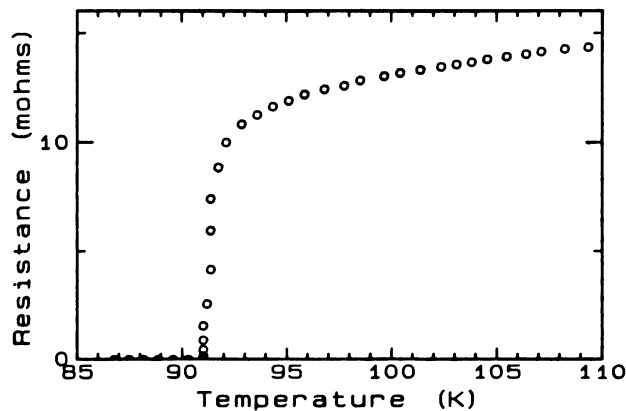


FIG. 2. Resistance vs temperature for  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .

of the starting mixtures.<sup>5</sup>

Pressure studies were made using gaseous He as the pressure medium up to 8 kbar. The transitions were monitored with the rf penetration technique<sup>6</sup> developed in our laboratory by L. J. Azevedo. The rf response just below the superconducting transition mimics the magnetization signature shown in Fig. 1 but typically "turns on" at slightly lower values of temperature because it is not as sensitive as the superconducting quantum-interference device (SQUID) to the changes in magnetization but nonetheless allows an accurate determination of the change in  $T_c$  with pressure.

Our technique allows a much more accurate determination of the derivative than that used in Ref. 2. This results from the combination of sharp transition temperatures in our material and the much greater control of pressure in a He-gas system, which is, of course, absolutely hydrostatic at the temperatures of interest.

A representative plot of  $\Delta T_c$  versus pressure is shown in Fig. 3. The two samples shown represent the widest variation of starting stoichiometry— $Y_{1.2}Ba_{0.8}CuO_4$  to  $YBa_2Cu_3O_7$ . Nonetheless, the transition temperature was always near 90 K, and the pressure derivative  $dT_c/dP$  equals  $0.07 \pm 0.02$  K/kbar for all the materials we investigated. This is consistent with the fact that a particular compound, with composition very close to  $YBa_2Cu_3O_7$ , is formed as one of the phases for the Y-Ba-Cu-O system irrespective of the original starting compositions.

This behavior is in sharp contrast with the  $La_{1-X}A_XCuO_4$  system, where  $A$  is Ba or Sr. In that system, the layered-perovskite,  $K_2NiF_4$ -like crystal structure tolerates a large amount of alloying with a large variation possible in the ratio of La to  $A$ . We find that  $La_{1.85}Ba_{0.15}CuO_4$  has a pressure derivative of 0.7 K/kbar in quantitative agreement with Ref. 1. This is an order of magnitude larger than what we observe in the Y-Ba-Cu-O system. Furthermore, when the La-Sr ratio is varied, both  $T_c$  and  $dT_c/dP$  change drastically.<sup>7</sup> As  $X$  is varied,  $T_c$  goes from 20 K at  $X=0.10$  through a maximum of 39 K at  $X=0.15$ , back down to 20 K at  $X=0.3$ . The pressure derivative changes from 0.2 K/kbar at  $X=0.1$  to a maximum of 0.4 K/kbar at  $X=0.17$  and is essentially zero at  $X=0.25$ . The variation of  $T_c$  in the La-Sr-Cu-O system appears to be consistent with the band pictures.<sup>8,9</sup> Both variations of Sr concentration and pressure apparently move the Fermi level over a sharp peak in the density of states. If this density-of-states picture is valid for  $YBa_2Cu_3O_7$ , the peak is much less pronounced than in the La-Sr-Cu-O system. It remains to be seen if band calculations support this contention.

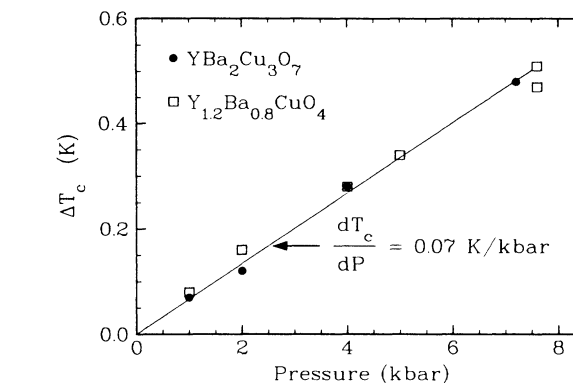


FIG. 3.  $\Delta T_c$ ,  $T_c(P) - T_c(P=0)$  vs pressure for  $Y_{1.2}Ba_{0.8}CuO_4$  and  $YBa_2Cu_3O_7$ .

In summary, in the Y-Ba-Cu-O we find constant values for  $T_c$  of near 90 K and of  $dT_c/dP$  equal to 0.07 K/kbar over a wide variation of starting compositions and in spite of mixed phases in some samples. This argues for a single superconducting composition near  $YBa_2Cu_3O_7$ . This is in sharp contrast to the La-Sr-Cu-O system where wide variations in both  $T_c$  and  $dT_c/dP$  are observed.

We are indebted to D. L. Overmyer for excellent technical assistance and to J. F. Kwak for the use of Fig. 2. This work was performed at Sandia National Laboratories supported by the U.S. Department of Energy under Contract No. DE-AC04-76DP00789.

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