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Comparison of the pressure dependencies of T_c in the 90-K superconductors $R\mathrm{Ba_2Cu_3O}_x$ (R = Gd, Er, and Yb) and $\mathrm{YBa_2Cu_3O}_x$

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We have determined the effect of pressure P on the resistance and superconducting transition temperature T_c of $R\mathrm{Ba_2Cu_3O}_x$ (R = Gd, Er, and Yb) and compare our results to those obtained on high-quality $\mathrm{YBa_2Cu_3O}_x$. The transition temperature, which is 90 K or greater at ambient pressure for all four compounds, is enhanced by pressure in each at rates between 0.09 and 0.19 K/kbar. Interestingly, the presence of a localized moment in the rare-earth compounds appears to have no influence on the pressure response. From the positive dT_c/dP we infer a positive change in the thermal expansion upon entering the superconducting state.

The discovery of superconductivity above 90 K in an Y-Ba-Cu-O compound[1] has stimulated the search for even more materials in this generic class, having comparable or higher transition temperatures. Subsequently, high-temperature superconductivity was reported by us[2,3] in rare-earth (RE) compounds and more recently by others.[4,5] These findings were particularly interesting because local magnetic moments are well known[6] to have a detrimental effect on superconductivity. The most notable previous exceptions to this "rule" have been certain $R\mathrm{Mo_6S_8}$ (Ref. 7) and $R\mathrm{Rh_4B_4}$ (Ref. 8) compounds (where R is a rare earth) in which antiferromagnetism and superconductivity coexist at low temperatures. Specific-heat measurements, in conjunction with electrical resistance and magnetic susceptibility experiments, on $R\mathrm{Ba_2Cu_3O}_x$ (R = Gd, Er, Ho, and Dy) suggest that superconductivity and magnetism coexist in these compounds as well.[3,9] Interestingly, to date there are no reports of superconductivity in the light rare-earth (Ce and Pr) analogues of these high-T_c compounds. Such an observation may suggest that the volume of the RE ion plays an important role in determining whether or not superconductivity appears.

To our knowledge, only two studies have been made on the volume (pressure) dependence of T_c in materials with $T_c > 90$ K. The first, reported by Hor *et al.*,[10] was performed on a sample of nominal composition $(\mathrm{Y}_{1-x}\mathrm{Ba}_x)_2\mathrm{CuO}_{3.6}$ having a resistive onset temperature greater than 91 K. In that study to ~19 kbar, the superconducting onset temperature increased weakly with pres-

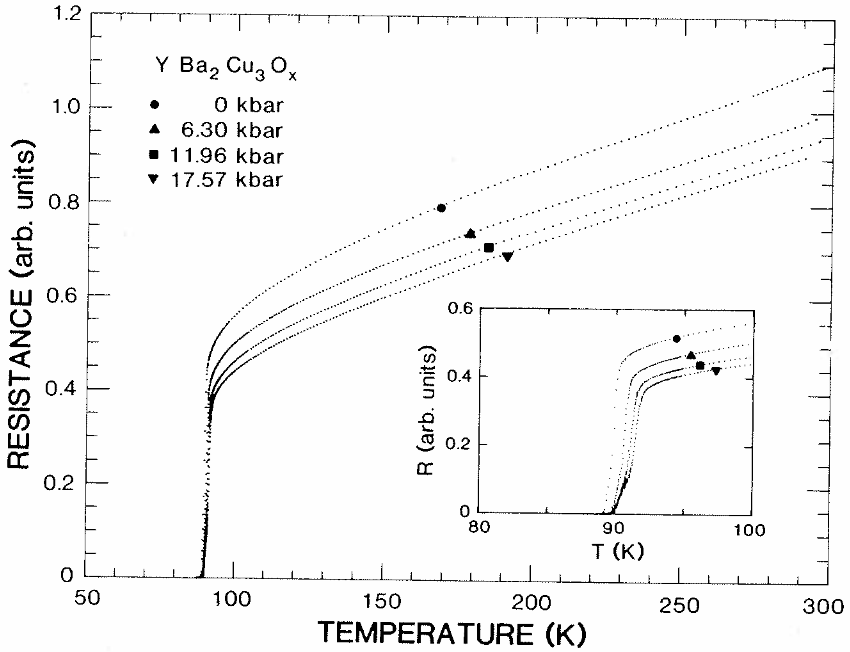

FIG. 1. Resistance of $\mathrm{YBa_2Cu_3O}_x$ at various applied pressures as a function of temperature. Note in the inset the additional structure developing near the completion of the transition at higher pressures.

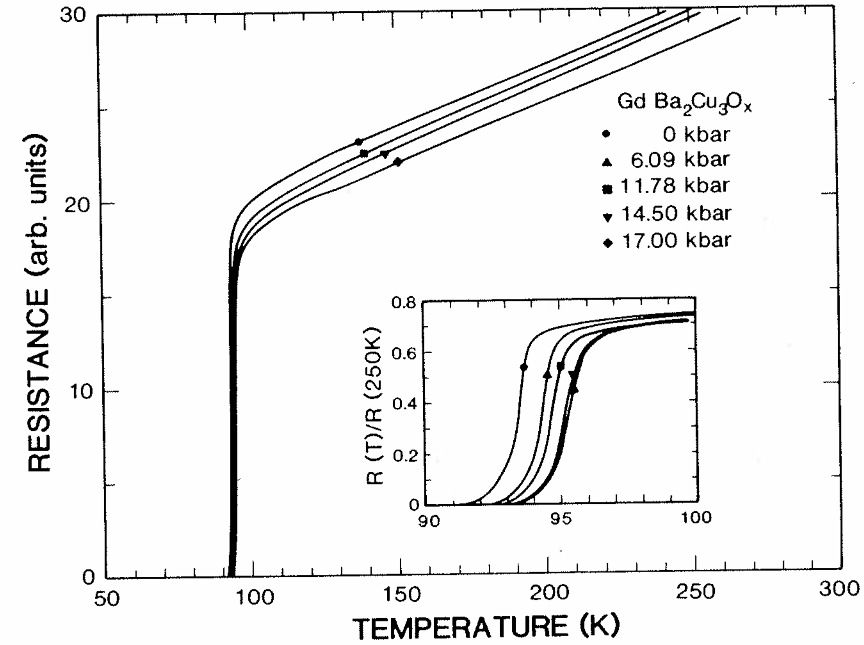

FIG. 2. Resistance vs temperature for GdBa$_2$Cu$_3$O$_x$ at various selected pressures. The inset provides an expanded view of the transition region.

sure and appeared to saturate ($dT_c/dP \simeq 0$) for $P > 12$ kbar, while the temperature at which superconductivity was complete decreased weakly for $P > 4$ kbar. We now know[2,11] that this composition was not optimal and that the intrinsic pressure dependence of the proper YBa$_2$Cu$_3$O$_x$ phase was undoubtedly masked in part by the presence of additional phases. A second study by Murata *et al.*[12] on nominal Y$_{1-x}$Ba$_x$CuO$_{2.4}$ showed the resistive midpoint transition temperature decreasing by ~2.5 K with the application of 8 kbar and considerable broadening of the transition width, as also found by Hor *et al.*[10]

Because it is important to know the pressure dependence of T_c in these materials, we have measured the effects of pressure to ~18 kbar on YBa$_2$Cu$_3$O$_x$ and RBa$_2$Cu$_3$O$_x$, where R = Gd, Er, and Yb. The samples were prepared by conventional ceramic powder techniques starting from oxides of Y, R, and Cu and BaCO$_3$. The samples were fired in oxygen at 900–950 °C to form the superconducting phase, then sintered into the shape of pills for measurement, and slowly cooled in oxygen after

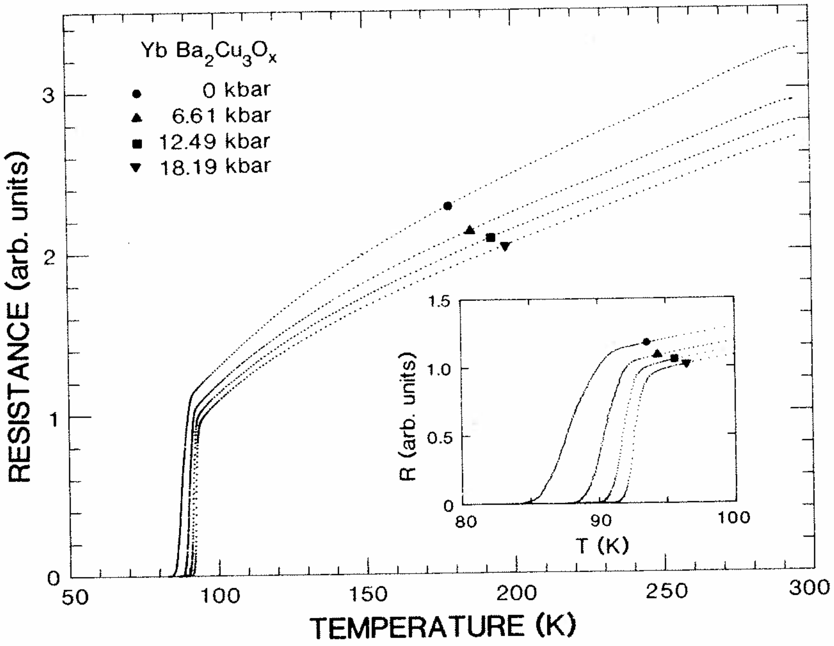

FIG. 3. Resistance of YbBa$_2$Cu$_3$O$_x$ at selected pressures vs temperature. The inset shows a sharpening of the resistive transition width with applied pressure.

the final heat treatment.

All samples showed greater than 90% of $1/4\pi$ diamagnetism when cooled in zero magnetic field to 7 K and then subjected to 100 G. Their electrical resistance was measured using a standard four-terminal ac technique. Electrical contact resistances to the sample were typically 10 Ω or less, thereby ensuring that Ohmic heating at a contact never exceeded 2 μW. Pressures were generated in a self-clamping cell, using a pressure medium of a 1:1 mixture of isoamyl alcohol and pentane and measured by a lead manometer. In determining $T_c(P)$ we have corrected the pressure, evaluated at ~7 K from the lead manometer, to account for known[13] pressure changes in the cell in going from 90 to 7 K. A calibrated carbon-glass thermometer measured the temperature over the entire range spanned in these experiments.

In Fig. 1 we show the resistance of $YBa_2Cu_3O_x$ as a function of temperature for four different pressures. At ambient pressure the resistance decreases linearly with temperature to about 150–160 K where it begins to fall more rapidly. Qualitatively, this same behavior is observed at all pressures, i.e., above ~160 K, dR/dT is approximately pressure independent; however, the temperature at which the resistance deviates from linearity increases with P. The rather strong decrease ~1%/kbar in the room-temperature resistance most likely arises[12] from changes in geometrical factors and not changes in the resistivity, although an increase in carrier concentration cannot be ruled out *a priori*. The inset shows an expanded view of $R(T)$ in the vicinity of T_c. At zero pressure, the transition width is reasonably sharp: The temperature interval ΔT_c over which the resistance drops from 90% to 10% of its value above T_c is ~0.6 K. With increasing pressure, T_c increases and ΔT_c approximately doubles upon going to the highest pressure. Part of the increase in ΔT_c arises from the appearance of additional structure in $R(T)$ near the completion of the transition. The origin of this structure is not known, but comparable behavior has been observed in $YBa_2Cu_3O_x$ and $GdBa_2Cu_3O_x$ (Ref. 12) as a function of applied magnetic field.

For comparison, we show in Fig. 2 $R(T,P)$ for $GdBa_2Cu_3O_x$. The response to pressure in this material is qualitatively similar to that found in $YBa_2Cu_3O_x$. However, in the inset, which shows the transition region in greater detail, we see no evidence for additional structure developing with pressure, instead only slightly more rounding near the end of the transition. Results for $ErBa_2Cu_3O_x$ (not shown) were very similar to those displayed in Fig. 2; however, the transition width was larger.

Somewhat different behavior was found in $YbBa_2Cu_3O_x$, as shown in Fig. 3. Unlike the other materials, the high-temperature resistance decreases, not so much because of geometrical factors which would cause an approximately constant offset in $R(T)$, but because of a change in slope dR/dT. We note, however, that like $YBa_2Cu_3O_x$, departure from linear behavior occurs also near 160 K. This deviation most likely is not due to superconducting fluctuations because the inverse magnetic susceptibility begins to fall below its high-temperature linear dependence at roughly the same temperature.[9] This is unlike the other $RBa_2Cu_3O_x$ compounds which show well-defined Curie-Weiss behavior to temperatures very near T_c.[9] Also unlike the other materials, the superconducting transition width (see inset in Fig. 3) sharpens with increasing pressure from almost 4 K at $P=0$ to about 1.5 K at 18 kbar.

Results for the pressure dependence of T_c are summarized in Fig. 4 where we plot the resistive midpoint transition temperatures versus pressure at 90 K. The vertical bars in these plots correspond to the transition widths ΔT_c. In all cases T_c is enhanced by pressure at a rate between 0.09 K/kbar for $YBa_2Cu_3O_x$ and 0.19 K/kbar for $YbBa_2Cu_3O_x$ above 6 kbar. Within the accuracy of our thermometry at 90 K (estimated to be ±0.15 K), we find no evidence for hysteresis in T_c upon reducing the pressure from its highest value to $P=0$. The initial nonlinear increase of T_c with P in $YbBa_2Cu_3O_x$ is not understood.

A few general inferences can be made on the basis of these results. From Ehrenfest's relation for a second-order phase transition,[14] we know that because dT_c/dP is

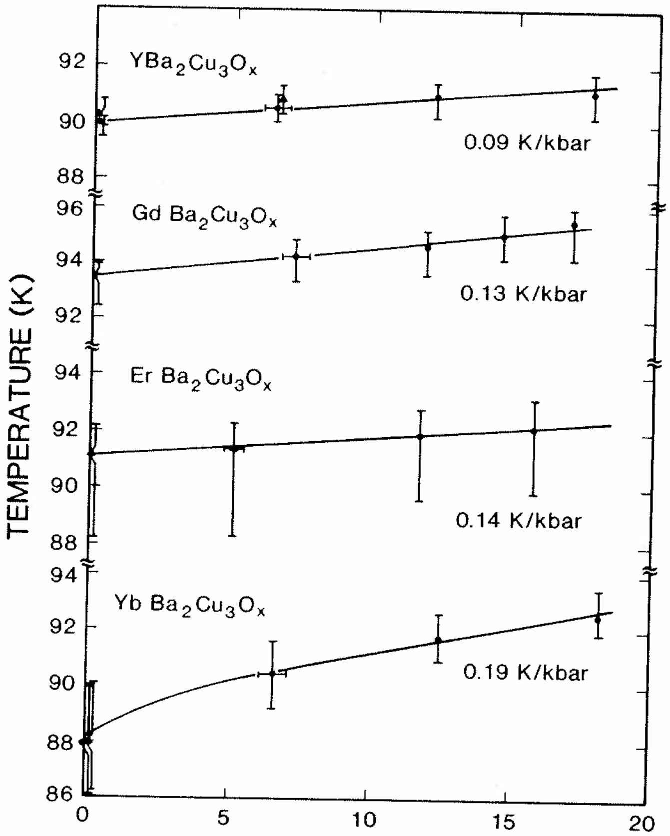

FIG. 4. Superconducting transition temperature vs pressure at 90 K for $YBa_2Cu_3O_x$, $GdBa_2Cu_3O_x$, $ErBa_2Cu_3O_x$, and $YbBa_2Cu_3O_x$. Filled circles correspond to resistive midpoints determined with pressure increasing, filled triangles with decreasing pressure. The vertical error bars correspond to 90%–10% resistive transition widths and the horizontal error bars to our estimated uncertainty in pressure. Note the linear increase in T_c with pressure for all samples except $YbBa_2Cu_3O_x$ at the lowest pressures. Estimated uncertainty in the slope dT_c/dP is ±10%.

positive, there should be a positive change in the thermal expansion α in going from the normal to superconducting states ($\Delta\alpha = \alpha_s - \alpha_n > 0$). For a crude estimate of $\Delta\alpha$, we assume that the specific-heat change in going through the superconducting transition is given by $\Delta C \simeq T_c \gamma/2$, where γ is the electronic specific-heat coefficient. Taking $\gamma \simeq 9$ mJ/mole Cu K^2, which is consistent with magnetic susceptibility, upper critical field near T_c, and resistivity measurements on our $YBa_2Cu_3O_x$ sample[15] as well as with literature values for these quantities,[11] we estimate $\Delta\alpha \simeq 6\times10^{-8}$/K. Such an estimate is accurate to within factors of order unity. Presumably comparable values for $\Delta\alpha$ would be inferred for the $RBa_2Cu_3O_x$ materials. The positive change in $\Delta\alpha$ further implies[16] an increase in the thermodynamic critical field near T_c with pressure.

In summary, we have determined the effect of pressure on the electrical resistance and superconducting transition temperature of four high-T_c samples (Y, Gd, Er, Yb) $Ba_2Cu_3O_x$. Qualitatively similar behavior is found in all four compounds, indicating that neither the local moment associated with the rare-earth atom nor the size of the substituted ion, which varies by as much as 7%–8%, has a profound effect on the pressure response. The positive change in T_c with pressure, which increases with the atomic weight of the substituted atom, implies that the thermal expansion change in going from the normal to superconducting state is positive and that the thermodynamic critical field increases with pressure.

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[1] M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, E. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).

[2] Z. Fisk, J. D. Thompson, E. Zirngiebl, J. L. Smith, and S-W. Cheong, Solid State Commun. (to be published).

[3] J. O. Willis, Z. Fisk, J. D. Thompson, S-W. Cheong, R. M. Aikin, J. L. Smith, and E. Zirngiebl, J. Magn. Magn. Mater. **67**, L139 (1987).

[4] S. Hikami, S. Kagoshima, S. Komiyama, T. Hirai, H. Minami, and T. Masumi, Jpn. J. Appl. Phys. **26**, L347 (1987); S. Hosoya, S. Shamoto, M. Onoda, and M. Sato, *ibid.* **26**, L325 (1987).

[5] E. M. Engler, V. Y. Lee, A. J. Nazzal, R. B. Beyers, G. Lim, P. M. Grant, S. S. P. Parkin, M. L. Ramirez, J. E. Vazquez, and R. J. Savoy, J. Am. Chem. Soc. (to be published); P. H. Hor, R. L. Meng, Y. Q. Wang, L. Gao, Z. J. Huang, J. Bechtold, K. Forster, and C. W. Chu, Phys. Rev. Lett. **58**, 1891 (1987).

[6] B. T. Mathias, H. Suhl, and E. Corenzwit, Phys. Rev. Lett. **1**, 922 (1958); also see, for example, M. B. Maple, in *Magnetism,* edited by H. Suhl (Academic, New York, 1973), Vol. V, p. 289.

[7] O. Fischer, A. Treyvaud, R. Chevrel, and M. Sergent, Solid State Commun. **17**, 721 (1985).

[8] H. C. Hamaker, L. D. Woolf, H. B. MacKay, Z. Fisk, and M. B. Maple, Solid State Commun. **32**, 289 (1979).

[9] S. E. Brown, R. M. Aikin, J. O. Willis, J. D. Thompson, Z. Fisk, J. L. Smith, and E. Zirngiebl (unpublished).

[10] P. H. Hor, L. Gao, R. L. Meng, Z. J. Huang, Y. Q. Wang, K. Forster, J. Vassiliou, C. W. Chu, M. K. Wu, J. R. Ashburn, and C. J. Torng, Phys Rev. Lett. **58**, 911 (1987).

[11] R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika, E. A. Rietman, S. Zahurak, and G. P. Espinosa, Phys. Rev. Lett. **58**, 1676 (1987).

[12] K. Murata, H. Ihara, M. Tokumoto, M. Hirabayashi, N. Terada, K. Senzaki, and Y. Kimura, Jpn. J. Appl. Phys. **26**, L471 (1987).

[13] J. D. Thompson, Rev. Sci. Instrum. **55**, 231 (1987).

[14] See, for example, P. M. Morse, *Thermal Physics* (Benjamin, New York, 1969), p. 133.

[15] G. Gruner, J. D. Thompson, E. Zirngiebl, S-W. Cheong, and D. Peterson (unpublished).

[16] See, for example, E. A. Lynton, *Superconductivity* (Methuen, London, 1969), p. 17.