Pressure dependence of the T_c of $YBa_2Cu_3O_7$ up to 170 kbar

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The superconducting onset temperature T_{co} of single-phased $YBa_2Cu_3O_{9-\delta}$ (with $\delta \simeq 2$) measured resistively in a diamond anvil cell is found to increase at a rate of $dT_{co}/dp = 0.043$ K kbar^{-1} up to 170 kbar. This is much weaker than for La-Ba-Cu-O for which $dT_{co}/dp = 0.64$ K kbar^{-1}. The pressure dependence of the high-T_c superconductors measured so far cannot be explained within a standard electron-phonon Bardeen-Cooper-Schrieffer theory. Predictions of resonating-valence bonds and bipolaronic theories are discussed.

In spite of the rapidly growing body of data on La-Ba-Cu-O, La-Sr-Cu-O, and Y-Ba-Cu-O the origin of high-T_c superconductivity in these metal oxides remains unclear. Until now, quantitative predictions about T_c have only been obtained within a "standard" BCS theory with strong electron-phonon interaction with so-called breathing modes. Using the results of band-structure calculations of Mattheiss[1] and infrared data[2] for the oxygen stretch modes for La_2CuO_4, Weber[3] calculated T_c for $La_{2-x}(Ba,Sr,)_xCuO_4$. The values for T_c at the lattice-instability limit are in the range 26–38 K depending on the exact values of the Cu-O force constant and of the Ba or Sr substitution concentration x. It is at present not clear whether or not the same approach is able to reproduce the much higher T_c's observed in Y-Ba-Cu-O and R-Ba-Cu-O compounds[4,5] (R: rare earths). For $T_c \simeq 95$ K, one expects that values substantially higher than 3 are required for the electron-phonon enhancement parameter λ. Under such conditions bi- or many-polaronic superconductivity is, however, likely to occur.[6-9]

Another difficulty of the standard theory is that Weber[3] had to assume spatial fluctuations in the dopant concentration (Ba,Sr) in order to explain the unusually large pressure dependence of the onset critical temperature T_{co} measured by Chu *et al.*[10] in Ba-La-Cu-O. The fact that not only T_{co} but also the midpoint transition temperature (and, in fact, the whole transition curve) is displaced to higher pressures (see Fig. 3 in Ref. 10) is, however, not consistent with the presence of concentration fluctuations (spinodal waves).[11]

These difficulties and the fact that dT_c/dp is probably strongly model dependent, motivated the present investigation of the pressure dependence of the T_c of Y-Ba-Cu-O at pressures much higher than reported until now.[12] The samples were prepared by standard powder metallurgical methods from high-purity Y_2O_3, $BaCO_3$, and CuO powders. After mixing in a dismembrator the powder was compacted under 4 kbar, heated up 950 °C in air during 6 h, and slowly cooled down to room temperature. After pulverization and mixing the same procedure was repeated for another 6 h in flowing oxygen. The oxygen concentration was determined thermogravimetrically, by means of a Mettler thermogravimetric analysis–differential thermal analysis system. As shall be reported elsewhere[13] we found that at 950 °C the composition of the samples was $YBa_2Cu_3O_{6.3}$. After slow cooling (2 K/min) down to room temperature the oxygen content increased by ~ 0.8 to give $YBa_2Cu_3O_{7.1}$. The samples were checked to be single phase by means of x-ray scattering. At room temperature the lattice parameters were found to be $a = 3.8239$ Å, $b = 3.8876$ Å, and $c = 11.6788$ Å in good agreement with previous data. The samples had typically an onset temperature of 92 K.

For the measurements of T_c at high pressure we used a beryllium-copper diamond anvil cell mounted in an optical cryostat similar to that described by Silvera and Wijngaarden.[14] As the diamond-anvil-cell system will be described in detail elsewhere[15] we mention here only that the heat exchanger of a continuous liquid-nitrogen or helium flow system is incorporated in the body of the cell. This is useful for rapid temperature sweeps over the whole operation range (1.5–300 K) of the diamond anvil cell. The force on the diamonds may be varied from 0 to 3×10^4 N at all temperatures. The resulting pressure is determined optically *in situ* by means of the ruby-fluorescence method[16] (Ramalog Double Spectrometer 1403, Spex Industries, Inc.).

Figure 1 shows schematically the experimental configuration used for resistive measurements of the superconducting transition of a small $YBa_2Cu_3O_{7.1}$ sample. As our

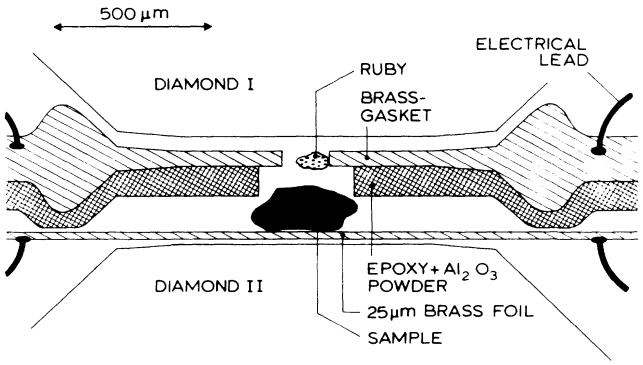

FIG. 1. Schematic representation of the pressure chamber of the diamond anvil cell. For clarity it is shown in the situation before pressurizing the sample into the gasket/epoxy hole.

cryogenic cell can generate a rather large force (3×10^4 N) we used beveled diamond anvils with a fairly large central flat region of 800-μm diameter. To insure a relatively good hydrostaticity of the sample environment we used a preindented brass gasket with a starting thickness of 150 μm. One side of the gasket is covered with an insulation layer made of epoxy reinforced with Al_2O_3 powder. A 150-μm hole is drilled at the center of the gasket and insulation is removed within a circle of 300μm diameter. A ruby grain and the sample are placed in this hole. Isolated by the reinforced epoxy layer a second brass gasket (25 μm in thickness) is placed on diamond II. Both brass gaskets serve as electrodes for resistivity measurements on the sample, which after slight compression, fits snugly in the gasket hole. Double contact leads soldered to the gaskets allow a semi-four-point measurement of the resistance. Test runs showed that reliable resistive measurements of superconducting transition temperatures are obtained by means of the configuration shown in Fig. 1 at pressures above 10 kbar. Even at the highest pressure chosen for this investigation (170 kbar) the width of the ruby line indicates that the pressure spread in the chamber is less than 30 kbar.

In Fig. 2 we show the pressure dependence of the onset temperature T_{co} and the completing temperature T_{cf} defined by Hor *et al.*[12] as the temperature determined by the intersection of the tangent at the inflection point of the $R(T)$ curve and the "zero-R" base line. From an experimental viewpoint it is gratifying that the present data agree quite well with those of Hor *et al.*[12] at low pressures ($p < 19$ kbar). Our results indicate clearly that T_{co} increases linearly up to 170 kbar with a slope $dT_{co}/dp = 0.043$ K kbar^{-1}, while T_{cf} decreases with $dT_{cf}/dp = -0.07$ K kbar^{-1}. The behavior of $YBa_2Cu_3O_{7.1}$ is thus completely different from that of Ba-La-Cu-O samples[10] in the K_2NiF_4 phase, for which $dT_{cf}/dp = 0.64$ K kbar^{-1} and $dT_{cf}/dp \approx 0.6$ K kbar^{-1}.

In the remaining part of this paper we indicate implications of the present results for the pressure dependence of the physical quantities which determine T_c within the standard electron-phonon BCS theory, the resonating-valence-bond theory or the bipolaronic models.

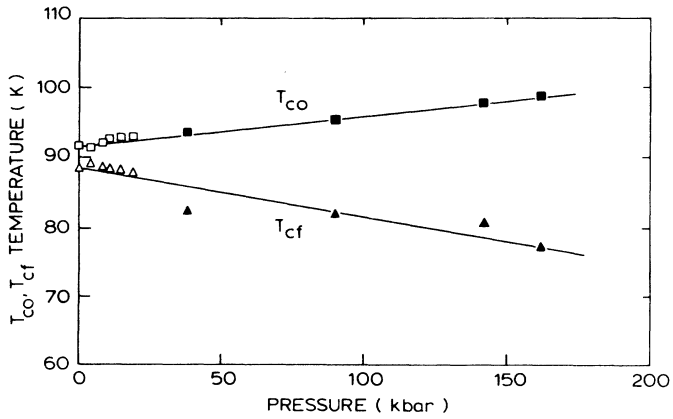

FIG. 2. Pressure dependence of the onset temperature T_{co} and the final temperature T_{cf} (see Ref. 12). ■, ▲, present work; □,△, low pressure results of Hor *et al.* (Ref. 12).

(i) *BCS theory.* Within this model the pressure dependence of T_c is most easily discussed on the basis of the relation proposed by Allen and Dynes,[17] with

$$k_B T_c = \frac{\hbar\omega_{\log}}{1.2} f_1 f_2 \exp\left[-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right], \quad (1)$$

where $\omega_{\log}$ is a weighted average of the Eliashberg $\alpha^2F(\omega)$ function and λ is the electron-phonon enhancement parameter. The parameter f_2 is in most cases not markedly different from unity so that we set $f_2 = 1$. For f_1 we use the standard value[3] $\mu^* = 0.13$ and consequently

$$f_1 = (1+0.142\lambda^{3/2})^{1/3}; \quad (2)$$

T_c depends then only on λ and $\omega_{\log}$. As the Eliashberg function has not been calculated yet for $YBa_2Cu_3O_7$ we assumed that $\omega_{\log}$ is similar to that for Ba-La-Cu-O. With $\hbar\omega_{\log} = 30$ meV we find $\lambda = 4.7$, i.e., a value which is typically three times higher than for "high-T_c" A-15 compounds.[18,19] Neglecting the volume dependence of μ^* we find[20]

$$\frac{d\ln T_c}{dp} = \frac{1}{B}\left[\gamma_{\log} - g(\lambda)\frac{\partial\ln\lambda}{\partial\ln V}\right], \quad (3)$$

with

$$g(\lambda) \cong 0.4 + \frac{1}{\lambda} \text{ for } 1.5 \le \lambda \le 10 \quad (4)$$

and

$$\gamma_{\log} \equiv -\frac{\partial\ln\omega_{\log}}{\partial\ln V}. \quad (5)$$

In the range of λ relevant to high-T_c superconductivity $0.4 \lesssim g(\lambda) \lesssim 1.1$. From thermal expansion and compressibility measurements (to be published elsewhere[13]) we estimate that $\gamma \cong 2.5$ for the Grüneisen parameter and $B \cong 1700$ kbar for the bulk modulus of Y-Ba-Cu-O. From $dT_{co}/dp = 0.043$ K kbar^{-1} and $\lambda = 4.7$ (corresponding to $\hbar\omega_{\log} = 30$ meV) we obtain then from Eqs. (3) and (4),

$$\frac{\partial\ln\lambda}{\partial\ln V} \cong 2.8. \quad (6)$$

A similar analysis of the data of Chu *et al.*[10] for Ba-La-Cu-O with $\lambda = 2.5$ would lead to

$$\frac{\partial\ln\lambda}{\partial\ln V} \cong -39. \quad (7)$$

As expected the volume dependence of λ which would be required to reproduce the experimentally determined dT_c/dp for Ba-La-Cu-O is much larger than the values observed for transition metals.[21]

(ii) *Resonating-valence bonds.* For the nearly half-filled Hubbard model with moderately large repulsion energy U which according to Anderson[22] leads to the resonating-valence-bond state in La_2CuO_4 and other high-T_c superconductors, T_c is of the order of t_b^2/U, where t_b is the site-hopping matrix element for noninteracting electrons. As U is basically an *intrasite* energy one ex-

pects that $d\ln U/d\ln V \simeq 0$ and consequently that

$$\frac{d\ln T_c}{dp} = -\frac{2}{B}\frac{\partial \ln t_b}{\partial \ln V} . \quad (8)$$

With $B = 1700$ kbar and the experimental values for dT_{co}/dp mentioned above we obtain that $\partial \ln t_b/\partial \ln V \cong -17$ for Ba-La-Cu-O. As t_b is mainly determined by the $(pd\sigma)$-energy-transfer integral for which Weber[3] found that $d\ln(pd\sigma)/dr \cong -1.6 \pm 0.1$ Å^{-1}, we obtain after multiplication by the shortest Cu-O separation, that

$$\frac{\partial \ln t_b}{\partial \ln V} \cong \frac{d\ln(pd\sigma)}{3d\ln r} \cong -1 . \quad (9)$$

This is comparable to our experimental result for $YBa_2Cu_3O_{7.1}$ but is much too small (in magnitude) to explain the behavior of Ba-La-Cu-O.

(iii) *Bipolaronic superconductivity.* In the limit of large electron-phonon coupling ($\lambda \gtrsim 2.5$ according to Chakraverty[6]), Anderson,[23] Alexandrov, Ranninger, and Robaszkiewicz,[7,8] and Nasu[9] have shown that bipolaron formation occurs. In the strong-coupling limit the electron spectrum is strongly renormalized and the bare electronic band is drastically reduced in width to a narrow polaronic band. Migdal's theorem breaks down and the Eliashberg theory is not applicable. The critical temperature for bipolaronic superconductivity is instead given by an implicit equation derived by Alexandrox, Ranninger, and Robaszkiewicz [Eq. (3.26) in Ref. 8]. As shown by Griessen,[20] this equation leads to the following relation for the pressure dependence of T_c:

$$\frac{d\ln T_c}{dp} = \frac{1}{B}\left[(4g^2-1)\frac{d\ln W_b}{d\ln V} + (4g^2+1)\frac{d\ln\lambda}{d\ln V} - 4g^2\frac{d\ln\omega}{d\ln V}\right] , \quad (10)$$

where W_b is the *bare* electronic bandwidth, ω a typical phonon frequency, and $g^2 \equiv W_b\lambda/(2z\hbar\omega)$ with z the number of nearest neighbors. In the strong-coupling limit $g^2 \gtrsim 2$ so that $d\ln T_c/dp$ is essentially determined by $[d\ln(\lambda/\hbar\omega)]/d\ln V$. For the Cu-O stretch modes we expect $d\ln\omega/d\ln V \cong -1$ in analogy with the results obtained by Sugiura and Yamadaya[24] for $BaBiO_3$. For the width of the electronic band[3] we have $d\ln W_b/d\ln \simeq -1$ so that

$$\frac{d\ln T_c}{dp} \cong \frac{1}{B}\left[(4g^2+1)\frac{d\ln\lambda}{d\ln V}+1\right] . \quad (11)$$

Equation (11) shows explicitly that very large values of $d\ln T_c/dp$ may be obtained with "normal" values for $d\ln\lambda/d\ln V$ (e.g., $d\ln\lambda/d\ln V \cong 2.7$ with $g^2 = 3$ would reproduce the very large dT_{co}/dp observed in Ba-La-Cu-O). However, $d\ln T_c/dp$ in Eq. (10) depends sensitively on the magnitude and sign of the three terms in the parentheses so that both large values and small values for $d\ln T_c/dp$ are, in principle, possible.

In conclusion, we have shown that both the standard electron-phonon BCS theory and the resonating-valence-bond model are able to explain the weak pressure dependence of the T_c of $YBa_2Cu_3O_{7.1}$ measured in a diamond anvil cell up to 170 kbar. These models are, *however*, unable to reproduce the large dT_c/dp observed in the Ba-La-Cu-O system. The bipolaron theory of superconductivity, on the other hand, can easily lead to unusually large values of dT_c/dp. For a quantitative test of the various models both accurate measurements of Grüneisen parameters and compressibilities, and calculations of the volume dependence of the electron bandwidth and λ are required.

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