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Pressure Dependence of T_c and Charge Transfer in $YBa_2Cu_3O_x$ ($6.35 \leq x \leq 7$) Single Crystals

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The superconducting critical temperature T_c of $YBa_2Cu_3O_x$ single crystals ($6.35 \lesssim x \lesssim 7$) has been measured resistively as a function of pressure P ($0 \leq P \lesssim 20$ kbar). The initial rate dT_c/dP exhibits three distinct regimes, a narrow plateau near $x \approx 7$ with $dT_c/dP \approx 0.04$ K/kbar, a plateau in the range $6.4 \lesssim x \lesssim 6.8$, where $dT_c/dP \approx 0.43$ K/kbar, and a maximum value ~ 0.8 K/kbar at $x \approx 6.35$. An analysis of the $T_c(x,P)$ data using a phenomenological model yields a pronounced peak near $x = 6.8$ in $d\Delta n_h(x)/dP$, where $\Delta n_h(x)$ is the change in the hole density in the CuO_2 planes relative to the value corresponding to the fully oxygenated sample.

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Veal and co-workers [1] have prepared single-crystal specimens of $YBa_2Cu_3O_x$ and demonstrated that the superconducting critical temperature T_c depends on the degree of oxygen ordering in the CuO chain sites in addition to the oxygen concentration x [2]. The oxygen ordering is manifested in dramatic increases in T_c with time in samples that have been quenched from high temperatures and annealed at room temperature [1]. Presumably the number of mobile holes in the CuO_2 planes that are involved in superconductivity and which determine T_c is controlled by both the concentration and degree of ordering of the oxygen ions. In order to elucidate the relationship between T_c and the number of holes in the CuO_2 planes and the transfer of charge between the CuO chains and the CuO_2 planes, we have measured the pressure P dependence of T_c between 0 and ~ 20 kbar as a function of x ($6.35 \leq x \lesssim 7$) on high-quality single crystals of $YBa_2Cu_3O_x$ prepared in the same manner as those originally studied at atmospheric pressure by Veal *et al.* [1]. For all values of x investigated, we have found that T_c increases linearly with P at a rate dT_c/dP that increases by more than an order of magnitude with decreasing x between $x \approx 7$ and $x = 6.35$. An analysis of the $T_c(x,P)$ data within the context of an inverted parabolic relationship between T_c and the concentration Δn_h of mobile holes in the CuO_2 planes, as proposed by several groups, yields a monotonic variation of Δn_h with x similar to that of $T_c(x)$. The dependence of the amount of charge transferred from the CuO chains to the CuO_2 planes under pressure, $d\Delta n_h/dP$, shows a pronounced peak near $x = 6.8$. The Δn_h and $d\Delta n_h/dP$ vs x data provide important input for microscopic models of the distribution of charge in the $YBa_2Cu_3O_x$ system; in particular, the value of $d\Delta n_h/dP$ at $x \approx 7$ is consistent with recent calculations by Gupta and Gupta [3].

Measurements of the temperature dependence of the electrical resistivity under nearly hydrostatic pressures up to 20 kbar were carried out on eleven high-quality single crystals of $YBa_2Cu_3O_x$ ($6.35 \leq x \lesssim 7$) grown at Argonne National Laboratory in gold crucibles using the self-flux method [4]. The single crystals have a typical size of $1.2 \times 1.1 \times 0.26$ mm^3, with the c axis along the shortest dimension of the crystals. For the single crystals with $6.35 \leq x \leq 6.85$, the oxygen content was set using the procedure described in Ref. [5]. One crystal was annealed in oxygen at 400 °C for 24 h under 3 kbar pressure. While the stoichiometry was not measured, x should be significantly increased relative to ambient-pressure treatments; we estimate that $x \approx 7$.

Figure 1 shows a typical set of R vs T curves for a $YBa_2Cu_3O_x$ ($x = 6.6$) single crystal measured at different pressures. The normal-state resistance shows metallic be-

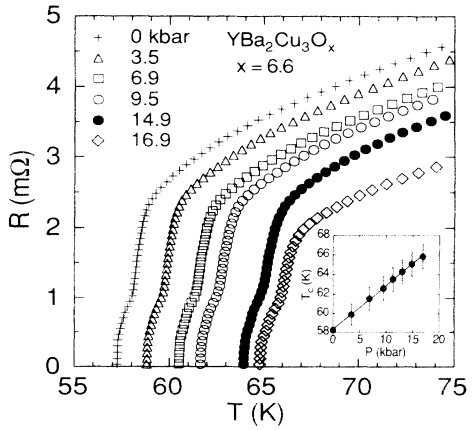

FIG. 1. Resistance R vs temperature T for a $YBa_2Cu_3O_x$ ($x = 6.6$) single crystal measured at pressures $0 \leq P \leq 16.9$ kbar. Inset: A plot of T_c vs P. The vertical bars indicate the superconducting transition width defined as the temperature difference between 10% and 90% values of the extrapolated normal-state electrical resistance.

havior. The magnitude of the room-temperature resistance measured at different applied pressures, normalized by the resistance at ambient pressure R_0, decreases linearly with increasing pressure at a rate $(1/R_0)dR/dP=(-1.1\pm0.2)\times10^{-2}$ kbar^{-1}. This value is independent of the oxygen content x for $6.4\leq x\leq6.95$. For polycrystalline samples, Borges *et al.* [6] and Medvedeva *et al.* [7] obtained a value of -1.2×10^{-2} kbar^{-1} over the same range of x values.

In this study, the superconducting transition temperature measured at different pressures P is defined as the temperature at which the electrical resistance R drops to 50% of its extrapolated normal-state value. The observed structure in the transition region (as shown in Fig. 1) might be related to oxygen inhomogeneity or sample impurities. The superconducting transition width ΔT_c, defined as the temperature difference between 10% and 90% values in the extrapolated normal-state electrical resistivity, appears to be independent of pressure. This assures that the extracted values of dT_c/dP from the resistivity data are independent of the definition chosen for T_c. The advantage of using single crystals is that they are free of grain-interaction stresses that are impossible to avoid in sintered ceramic samples. Such stresses could significantly alter T_c, especially in oxygen-deficient samples, since T_c of these samples depends strongly on pressure.

The inset of Fig. 1 depicts the linear increase of T_c with pressure at a rate $dT_c/dP=0.45\pm0.01$ K/kbar for an oxygen-deficient crystal with $x=6.6$. This value is comparable to the values reported by other groups for oxygen-deficient polycrystalline samples [7,8]. The vertical bars indicate the transition width. For all the single crystals studied at pressures up to 18 kbar, T_c exhibits a linear increase with pressure at a rate which depends on x, as will be discussed below.

Figure 2 shows the resistive T_c measured at ambient pressure along with dT_c/dP as a function of x. The plot of dT_c/dP vs x includes data from Ref. [8] which complement the data reported herein; the two sets of data provide a complete picture of the variation of T_c with pressure over the entire range of x values. The two remarkable features of the plot of dT_c/dP vs x are as follows: (i) dT_c/dP increases markedly with decreasing x from 0.04 K/kbar at $x\approx7$ to 0.8 K/kbar at $x=6.35$. (ii) There are three distinct regimes in the behavior of dT_c/dP: a wide plateau in dT_c/dP vs x at 0.43 ± 0.07 K/kbar for $6.4\leq x\leq6.8$, a steep linear decrease of dT_c/dP with increasing x which sets in at $x\approx6.8$, near the beginning of the 90-K plateau in $T_c(x)$, and a second plateau in dT_c/dP at ~0.04 K/kbar for $6.9\leq x\leq7$. The small increase observed at high x is within the experiment error which is ±0.07 K/kbar for the dT_c/dP values within the plateau. To the best of our knowledge, this is the first report of the existence of a plateau in dT_c/dP vs x for $6.4\leq x\leq6.8$. Two crystals were measured for $x=6.35$. Neither crystal exhibited a complete transition to zero resistance at ambient pressure down to 1.5 K. However, zero resistance appeared at 5 kbar above which $dT_c/dP=0.8\pm0.02$ K/kbar.

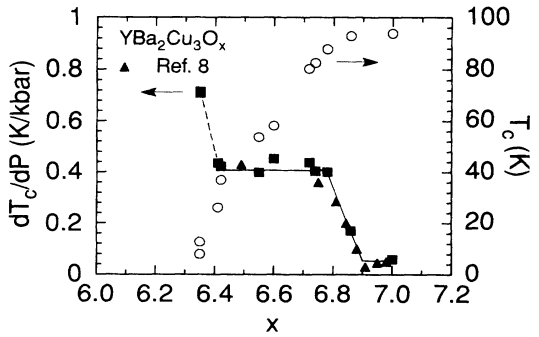

FIG. 2. Resistive superconducting transition temperature T_c measured at ambient pressure and dT_c/dP as a function of x for eleven single crystals of $YBa_2Cu_3O_x$. The solid triangles represent data from Ref. [8].

It has been suggested [9–12] that T_c is an inverted parabolic function of $\Delta n_h(x)\equiv n_h(x)-n_h(7)$, where $\Delta n_h(x)$ is the change in the hole density in the CuO_2 planes relative to the value corresponding to the fully oxygenated sample, and that there is an optimum hole density at which T_c attains a maximum value T_{c0}. Whangbo and Torardi suggested that this is true for every class of p-type cuprate superconductor [12]. Based on an analysis of experimental results on the $Y_{1-x-y}Ca_yPr_xBa_2Cu_3O_{6.95}$ system, Neumeier *et al.* [10] were the first to suggest that T_c of $YBa_2Cu_3O_{7-\delta}$ could be increased to $T_{c0}=97$ K by decreasing the hole concentration of the fully oxygenated sample by $n_0=0.05$ hole per CuO_2 plane. The relationship between the hole carrier density and T_c has been investigated experimentally for several cuprate superconductors [13]. An abrupt onset of superconductivity in which T_c increases sharply with increasing hole carrier density was found for hole concentrations $n_h>0.06$ hole/(CuO_2 plane). For even higher hole concentrations, T_c increases parabolically and attains a maximum at $n_h\approx0.25$ hole/(CuO_2 plane) ($x\approx6.91$) for $YBa_2Cu_3O_x$. This behavior is in agreement with calculations by Brown that are based on a bond-valence-sum model and have been corrected for geometrical stress [14].

In order to analyze the dT_c/dP vs x data, we have assumed that the dependence of T_c on Δn_h is governed by the following phenomenological model, generalized to include pressure [15],

$$T_c(x,P)=T_{c0}(P)-A[n_0+\Delta n_h(x,P)]^2, \quad (1)$$

and that the rate of increase of T_c with pressure is given by

$$\frac{dT_c}{dP}(x)=\frac{dT_{c0}}{dP}-2A[n_0+\Delta n_h(x)]\frac{d\Delta n_h}{dP}(x), \quad (2)$$

where T_{c0} is the maximum attainable T_c and $\Delta n_h<0$

represents the decrease in the number of holes in the CuO_2 plane from the value corresponding to $x \approx 7$. The first term in Eq. (2) insures that dT_c/dP has the experimentally measured positive value for the fully oxygenated sample. While the second term in Eq. (2) represents the contribution of the change in the number of holes in the CuO_2 planes under pressure to the change of T_c with P, the first term, dT_{c0}/dP, includes the contribution of all the mechanisms which would produce a linear increase of T_{c0} with P. Hence, according to this phenomenological model, the increase of T_c with P may be produced by pressure-induced charge transfer as well as other mechanisms provided that they yield a linear $T_{c0}(P)$.

Calculations of the rate of charge transfer under pressure based on neutron diffraction data and a bond-valence-sum analysis yielded $d\Delta n_h/dP = 8\times10^{-4}$ and 6.5×10^{-4} hole/kbar for $x = 6.6$ and 6.93, respectively [16]. These two values, the corresponding measured values of dT_c/dP, and the conditions $T_c = 0$ K for $\Delta n_h = 0.25$ hole/(CuO_2 plane) and $T_c = 93.87$ K for $\Delta n_h = 0$ holes/(CuO_2 plane) were used to solve Eqs. (1) and (2), yielding the parameters $T_{c0} = 94$ K, $dT_{c0}/dP = 0.048$ K/kbar, $n_0 = 0.007$ hole/CuO_2, and $A = 1587$ K.

Figure 3 shows a plot of the change in the number of hole carriers in the CuO_2 planes, Δn_h, vs x, calculated from Eq. (1). Clearly, the $\Delta n_h(x)$ data follow the same trend as the $T_c(x)$ data, in agreement with previous results which established that the value of T_c is related to the density of hole carriers in the CuO_2 planes [17–19]. A plot of Δn_h vs T_c given by the parabolic relation [Eq. (1)] with the above-mentioned parameter values is shown in the inset and is the basis upon which the values of Δn_h and $d\Delta n_h/dP$ were calculated from T_c and dT_c/dP. The open circles represent the values of T_c for the crystals that were investigated.

Figure 4 shows $d\Delta n_h/dP$ vs x calculated from the phenomenological model [Eq. (2)] and the experimental values of dT_c/dP. The pressure-induced charge transfer $d\Delta n_h/dP$ displays a pronounced peak near $x = 6.8$ and then decreases with increasing x, reaching a value of $\sim3\times10^{-4}$ hole/kbar for $x \approx 7$. This small change in Δn_h with pressure for the fully oxygenated samples is consistent with the small measured value of dT_c/dP and the parabolic dependence of T_c on Δn_h. Gupta and Gupta [3] reported a value of 1.7×10^{-4} hole/kbar derived from a bond-valence-sum model, while Reyes *et al.* [20] recently reported a value of 12×10^{-4} hole/kbar for $x = 6.62$ and 6×10^{-4} hole/kbar for $x \approx 7$, from an analysis of high-pressure nuclear-quadrupole-resonance data based on the charge-transfer model. Within experimental error, these values are in good agreement with our results in Fig. 4.

The study by Jorgensen *et al.* [16] indicated that the charge transfer between chains and planes was essentially identical for the $x = 6.6$ and 6.93 samples (the data are included in Fig. 4); rather small changes in the pressure dependence of the lattice parameters were observed for these samples. However, Fig. 4 implies that significantly larger changes in the pressure dependence of the lattice parameters and bond lengths will be observed for samples with x near 6.8.

In summary, our $T_c(P)$ measurements reveal that the dT_c/dP vs x curve of $YBa_2Cu_3O_x$ has the following features: dT_c/dP attains a maximum value of ~0.8 K/kbar for $x = 6.35$, displays a wide plateau at ~0.43 K/kbar for $6.4 \lesssim x \lesssim 6.8$, decreases with increasing x for $6.8 \lesssim x \lesssim 6.9$, and exhibits a second plateau at ~0.04 K/kbar for $6.9 \lesssim x \lesssim 7$. We calculated $\Delta n_h(x)$ and $d\Delta n_h(x)/dP$ from the values of $dT_c(x)/dP$ reported herein and in Ref. [8], using an inverted parabolic dependence between T_c and Δn_h in which pressure was included as an independent variable. The calculated values of $d\Delta n_h(x)/dP$ are in excellent agreement with previous theoretical [3] ($x \approx 7$) and experimental [20] ($x = 6.62$ and $x \approx 7$) results, indicating that a parabolic model is appropriate for the oxygen-deficient $YBa_2Cu_3O_x$ system. Within the context of this phenomenological model, the increase of T_c with pressure is produced by pressure-

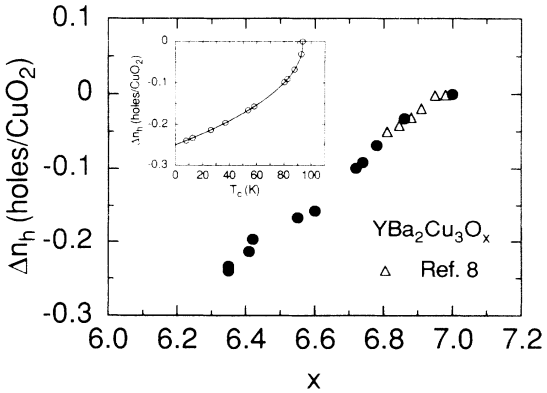

FIG. 3. Change of the number of hole carriers in the CuO_2 plane, Δn_h, vs x for $YBa_2Cu_3O_x$ single crystals. Inset: A plot of Δn_h vs T_c given by Eq. (1). The open circles represent the values of T_c for the measured crystals.

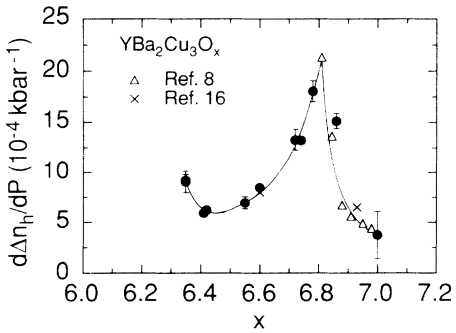

FIG. 4. Calculated values of $d\Delta n_h/dP$ vs x based on the phenomenological model [Eq. (2) in the text] and using the experimental values of $dT_c(x)/dP$ for the $YBa_2Cu_3O_x$ single crystals. The solid line is a guide to the eye.

induced charge transfer between CuO chains and CuO_2 planes, as well as other mechanisms which yield a linear dependence of T_{c0} on P. In contrast to previous reports, $d\Delta n_h/dP$ exhibits a dramatic peak near $x=6.8$ and then decreases with x, attaining a value of $\sim 3\times 10^{-4}$ hole/kbar for $x \approx 7$.

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