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Evidence for chain superconductivity in near-stoichiometric $YBa_2Cu_3O_x$ single crystals

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Specific-heat measurements on a high-quality, 63-mg $YBa_2Cu_3O_x$ single crystal, in the range $6.94 \leq x \leq 7.0$ (overdoped regime), are presented. The oxygen concentrations were determined independently by neutron scattering. It is observed that the mean-field value of the specific-heat jump at T_c increases by about 45% between 6.94 and 7.0. In contrast, T_c decreases by about 4%. It is also observed that the fluctuation contributions to the specific heat are greatly reduced near $x = 7.0$. The observed behavior is attributed to induced superconductivity in the CuO chains.

The overdoped regime ($6.94 \leq x \leq 7.00$) of the $YBa_2Cu_3O_x$ system is of special interest because it culminates at $x = 7.0$ in perfect stoichiometry without any lattice defects in the conducting CuO chains. It has therefore been proposed that, in addition to the CuO planes, the CuO chains also become superconducting.[1-3] As a consequence, the superconducting state becomes more three dimensional. Both the appearance of the chain gap as well as the increasing three-dimensional behavior of the superconducting fluctuations should be observable in specific-heat measurements. However, so far, no systematic study of $YBa_2Cu_3O_x$ single crystals, in the overdoped regime, has been reported in the literature. The main reason for this is the difficulty in controlling and determining the oxygen concentration to the accuracy required.

In this paper we report systematic specific-heat measurements on a large $YBa_2Cu_3O_x$ single crystal in states of different oxygen concentration in the overdoped range, $6.94 \leq x \leq 7.00$. One important feature of our investigation is that the oxygen concentration of each state was determined independently by neutron scattering. A careful analysis of the specific-heat jump at T_c reveals that with increasing x, the mean-field jump of $C(T)$, $\Delta C/T_c$, increases by about 45%, whereas T_c decreases by about 4%. This behavior is in contrast to the behavior of $La_{2-x}Sr_xCuO_4$ (Ref. 4), as well as $Y_{1-x}Ca_xSr_2Cu_2Tl_{0.5}Pb_{0.5}O_7$ (Ref. 5) and $Tl_2Ba_2CuO_{6+x}$ (Ref. 6), where both $\Delta C/T_c$ and T_c go through a maximum at the optimum doping level. The main difference between those systems and $YBa_2Cu_3O_x$ is the presence of the conducting CuO chains in the latter. We thus argue that the anomalous increase in $\Delta C/T_c$ near $x = 7.0$ in $YBa_2Cu_3O_x$ is due to progressively induced superconductivity in the chains,[1] in agreement with recent results by Tallon *et al.*[7]

The single crystals were grown in Y_2O_3-stabilized ZrO_2 crucibles.[8] They displayed the usual twinning.[8,9] Extensive neutron-scattering experiments revealed that they were of very good quality.[9] In particular, the Cu sublattice as well as the apex oxygen was found to be fully occupied. Thus, the only defects observed were the oxygen vacancies in the CuO chains. This allowed for a very accurate determination of the oxygen concentration to within ±0.01.

For the present study, we concentrate on one crystal with a mass of 63 mg. To produce various oxygen concentrations the crystal was subject to various annealing treatments under different oxygen pressures. The annealing times varied between 10 days, for the highest-temperature anneal, to 4 weeks for the low-temperature anneals. The resulting oxygen concentrations were determined by neutron-scattering ex-

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TABLE I. Annealing temperature T_A, oxygen pressure during the anneal p_{oxy}, oxygen concentration x, as determined from neutron scattering, transition temperature $T_{c,\mathrm{mag}}$, as determined from the midpoint of the diamagnetic transition, $T_{c,\mathrm{sp.h.}}$, as determined from the inflection point of the specific-heat jump, $T_{c,\mathrm{fit}}$, $\Delta C/T_c$, and the other fitting parameters are determined as described in the text.

T_A (°C)	p_{oxy} (bar)	x	$T_{c,\mathrm{mag}}$ (K)	$T_{c,\mathrm{sp.h.}}$ (K)	$T_{c,\mathrm{fit}}$ (K)	$\Delta C/T_c$ (mJ/mol K^2)	a_1 (mJ/mol K^2)	a_2 (mJ/mol K^2)	c_2 (mJ/mol K)	c_2/c_1
480	1	6.94	91.2	91.4	91.0	30	−3	−24	260	0.75
440	1	6.98	89.7	89.4	89.0	39	7	−25	240	0.73
380	70	6.99	88.0	87.8	87.5	40	−5	−25	200	0.70
380	200	7.00	(87.6) [a]	87.5	87.2	44	−11	−32	170	0.74

[a] Estimated.

periments, performed on the four-circle diffractometer P110/5C2 at the reactor Orphée, Centre d'Etudes de Saclay, as described by Schweiss *et al.* in Ref. 9. They are listed together with the annealing temperature and oxygen pressure during the anneal in Table I. Also shown are the superconducting transition temperatures in the various states of the crystal as determined from the midpoint of the diamagnetic transition in 1 G (parallel to the ab plane) and also from the inflection point of the specific-heat anomaly. The widths of the magnetic transitions are less than 1.0 K.

Figure 1 displays T_c vs oxygen concentration. The oxygen concentration of the circles and squares was determined from neutron scattering. The circles are present results (Table I) and the squares are previous results on two other crystals.[9] The smooth variation of T_c vs x confirms the high accuracy of the oxygen concentrations. The crosses are earlier data, the concentrations of which were previously estimated from the normal-state resistivity.[10] The solid line through the data is just to guide the eye. To be compatible with our absolute values of the oxygen concentration, the crosses were shifted by 0.05 to higher x values as compared to our earlier publications.[10] The optimum doping level (highest T_c) is now at $x = 6.94$ in agreement with data on ceramic samples.[11,12] In the overdoped regime, T_c decreases with increasing x by about 4 K to 87.6 K, i.e., a 4% decrease from its maximum value. Despite this decrease in T_c, the hole concentration continues to increase.[13] Measurements of the normal-state resistivity of our crystals confirm this trend.[10] In addition, our measurements of the penetration depth show that the superconducting pair density also continues to increase in the overdoped regime.[14]

Specific-heat measurements were performed by a continuous heating technique. Figure 2 displays the specific-heat data of our crystal in three of the four states listed in Table I. For display purposes, all curves were scaled at 110 K (this required shifts in C/T of less than 1%, somewhat larger than the absolute accuracy of our specific-heat measurements). Also shown are data of a 3% Zn-doped ceramic sample with a T_c of about 55 K which is below the temperature range of the graph. We use this curve as the normal-state background for our crystal. Investigations on Zn-doped $\mathrm{YBa_2Cu_3O}_x$ ceramics showed that the substitution of Zn for Cu (same valency, 3% difference in atomic mass) as well as our small variation of the oxygen content, hardly affects the normal-state heat capacity.[15–17] This is demonstrated in the inset of Fig. 2. After scaling the data at 110 K, the maximum deviation at 200 K is less than 1%. The same is true for the other oxygen concentrations.

The width of the specific-heat anomaly for the 6.94 state is somewhat smaller than for the other states. 6.94 is right at the maximum of the T_c vs x curve (Fig. 1), thus any small oxygen concentration gradient causes the smallest smearing

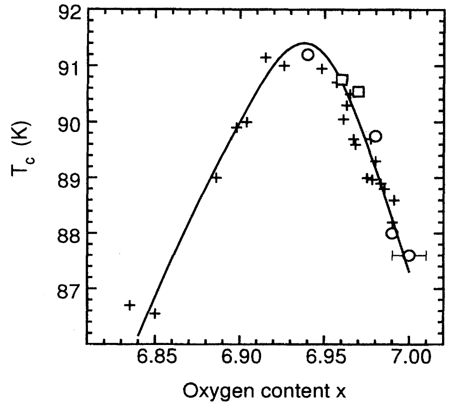

FIG. 1. T_c, as determined from the midpoint of the diamagnetic transition in 1 G, vs oxygen concentration x. The x values of the circles (present results) and squares (Ref. 9) are from neutron-scattering experiments. The crosses are earlier results (see text).

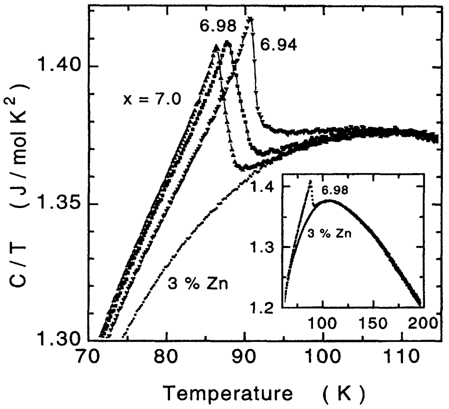

FIG. 2. Specific-heat data (scaled at 110 K) for various oxygen concentrations. The dots are data for a $\mathrm{YBa_2(Cu_{0.97}Zn_{0.03})_3O}_x$ ceramic sample. Inset: specific-heat data over an extended temperature range.

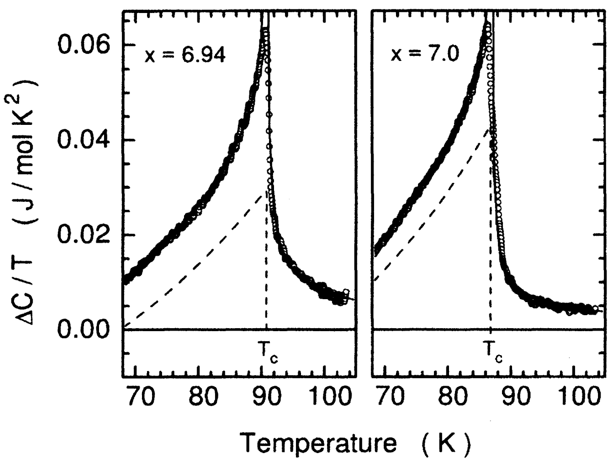

FIG. 3. Specific-heat anomaly for two states, obtained by subtracting the normal-state background (Zn doped sample, see text) from the measured data. The solid line through the data points is the fit to the data, as described in the text. Also shown is the mean-field contribution, $a_2+b_2T^3$ (dashed line).

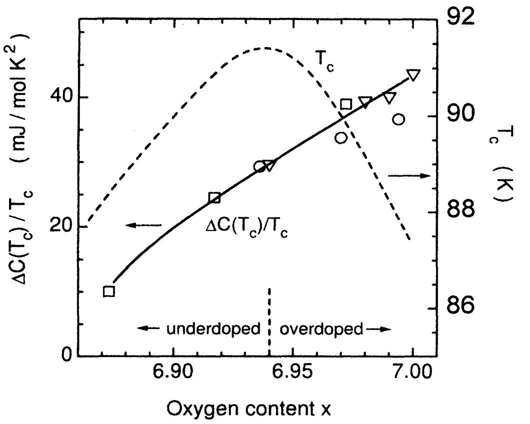

FIG. 4. Mean-field jump in $C(T)$, as determined from Fig. 3, vs oxygen concentration. Triangles are the present results. Squares and circles are from earlier measurements (Ref. 10), reevaluated with the present method. The dashed line represents T_c vs x from Fig. 1

of the transition for this concentration. There is no systematic increase in the width of the transition with increasing x, in particular no structure in the transition is observed, in contrast to certain ceramic samples.[12]

Figure 3 displays the specific-heat anomalies for two oxygen concentrations with the normal-state background (3% Zn-doped sample) subtracted. To obtain values for the mean-field jump in $\Delta C/T$, the fluctuations have to be modeled in a consistent way. From our experience and that of others,[18,19] this can be achieved by either assuming Gaussian or critical fluctuations. Only the presence of a magnetic field requires a description in terms of critical finite-size scaling.[18]

Our data can be satisfactorily described in terms of three-dimensional Gaussian fluctuations. The strong-coupling character of $YBa_2Cu_3O_x$ near $x=7.0$ (comparable to the coupling strength of Pb) (Ref. 18) has been taken into account by a T^4 dependence of the mean-field contribution to $C(T)$ below T_c. After subtracting the $C(T)$ data of the Zn-doped sample, we only have to allow for differences in the linear term of specific heat between sample and background. We therefore use the following expressions for the fitting procedure: $C(T)=a_1T+c_1(T/T_c-1)^{-0.5}$ for $T>T_c$ and $C(T)=a_2T+b_2T^4+c_2(1-T/T_c)^{-0.5}$ for $T<T_c$. For display purposes we have subtracted the linear term a_1T from the data in Fig. 3. Thus, the data above T_c only represent the fluctuation contribution.

Allowing for some rounding of the anomaly due to sample inhomogeneities, especially for the $x=7.0$ state, an excellent fit of the data in the temperature range from 70 to 105 K is obtained as demonstrated in Fig. 3 (solid line through the data points). The only adjustable parameters were the temperature range for the fitting procedure and, to some small degree, the critical temperature, $T_{c,\mathrm{fit}}$. An equally good fit is obtained for the other oxygen concentrations. The values of all parameters as well as the mean-field jump at T_c (equal to the numerical value of the mean-field term, $a_2+b_2T^3$, at T_c, dashed line in Fig. 3) are listed in Table I. The values of the fluctuation parameters are consistent with three-dimensional fluctuations of a two-component order parameter $(c_1/c_2=0.71)$.[18] The systematic decrease of c_1 and c_2 with increasing oxygen concentration points to an increasing three-dimensional nature of the superconducting state. The mean-field jump in $\Delta C(T_c)/T_c$ increases by about 45% as x increases from 6.94 to 7.00.[20] This compares to a 30% increase of the superconducting condensate density as observed by Tallon *et al.*[7] in the overdoped regime. The parameter a_1 becomes negative when the linear term of the subtracted background is larger than that of the sample. Despite the fairly large scatter in this parameter, there seems to be a trend for the linear term of the sample to decrease with increasing oxygen content. However, a quantitative discussion of the parameters a_1 and a_2 is not justified due to their large uncertainty.

Assuming a T^3 dependence, instead of the T^4 term, yields different but less consistent parameters. However, a similar strong increase of $\Delta C(T_c)/T_c$ is observed. Assuming a gradual transition from less strong coupling (T^3) to a strong coupling (T^4) behavior with increasing oxygen content, causes an even larger increase in $\Delta C(T_c)/T_c$. Using a linear approximation of the mean-field (BCS) electronic contribution near T_c with variable coupling parameter,[18] again yields the same trend in $\Delta C(T_c)/T_c$.

Figure 4 displays the concentration dependence of the mean-field jump $\Delta C/T_c$ vs the oxygen concentration. The triangles are from Table I. The squares and circles are from earlier measurements,[10] analyzed with the present method. Their oxygen concentration was determined from their T_c values, using the solid line in Fig. 1. The increase in $\Delta C/T_c$ with increasing x, in the underdoped region $(x<6.94)$ is well established.[16,21,22] In the overdoped regime, where T_c decreases again with increasing x, $\Delta C/T_c$ continues to increase. This continued increase of the mean-field jump in the overdoped regime is also confirmed by recent measurements of the magnetization which yielded values for $\Delta C/T_c$ [calculated from $B_{c,th}(x,T)$], which showed the same strong increase in the overdoped regime as $\Delta C/T_c$ in Fig. 4.[14,23]

The monotonic increase in $\Delta C/T_c$ is in contrast to other high temperature superconducting (HTSC) materials, where $\Delta C/T_c$, as well as T_c, display a maximum at the optimum doping level.[4–6] There is growing evidence that in the underdoped regime, the strong decrease of $\Delta C/T_c$ with decreasing oxygen concentration is due to a reduction of the apparent density of states at the Fermi energy, probably because of the opening of a gap in the spin excitations.[24–26] In the overdoped regime, the observed decrease of $\Delta C/T_c$ in the case of nonchain HTSC, and the corresponding decrease in the pair density, may be due to pair breaking.[6] In $YBa_2Cu_3O_x$, distinguished by its CuO chains, a competition between superconductivity induced in the highly conducting chains and pair breaking due to chain fragmentation, as described by Kresin and Wolf,[1] has to be taken into account. Near $x=7.0$ pair breaking is expected to be minimized because the chains become fully occupied (i.e., defect-free) and therefore, the condensation energy to be maximized. Thus, through the increase in $\Delta C/T_c$, the defect-free state of stoichiometric $YBa_2Cu_3O_x$ allows the direct observation of superconductivity in the CuO chains.

The parabolic T_c dependence on x might still be ascribed to the superconductivity of the planes since, in the Kresin-Wolf model, the feedback of the chains to the planes is weak due to a phonon mediated charge transfer in addition to the internal proximity effect.[1] Therefore, $T_c(x)$ may still reflect the common behavior of nonchain HTSC. In this scenario, a possible decrease of the density of states associated with the planes is overcompensated by the added chain phase space now participating in the superconducting transition. When $YBa_2Cu_3O_x$ is overdoped beyond the level corresponding to perfect stoichiometry,[27,28] one again expects the normal decrease of $\Delta C/T_c$. Indeed, recent penetration depth investigations by μSR measurements on Ca doped $Yb(Ba_{1.6}Sr_{0.4})Cu_3O_x$ showed, in the overdoped regime, a reduction in the condensate density despite an increased normal-state carrier concentration.[28]

In summary, we have shown that in the overdoped regime $x>6.94$, the mean-field jump in the specific heat at T_c continues to increase, despite the observed decrease of T_c. We attribute this anomalous increase to the increasing participation of the Cu-O chains in the superconducting transition. As a consequence, the superconducting state becomes more three dimensional, thus reducing the superconducting fluctuations near $x=7.0$.

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[20] In our earlier work (Ref. 10), we neglected this change in fluctuation contribution in evaluating the mean-field jump. This, and the lack of precise knowledge of the oxygen concentrations, led us to an erroneous conclusion that $\Delta C/T_c$ remains constant near $x=7.0$. A similar conclusion was obtained in Ref. 16 for ceramic $YBa_2Cu_3O_x$ samples, probably for similar reasons.

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