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Variation of superconductivity with carrier concentration in oxygen-doped $YBa_2Cu_3O_{7-y}$

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The Hall coefficient R_H, the volume fraction f showing the Meissner effect, and the superconducting transition temperature T_c have been measured in the high-T_c oxide $YBa_2Cu_3O_{7-y}$ for a range of oxygen vacancy concentration $0.0 < y < 0.7$. We find that R_H, f, and T_c are insensitive to y over the range $0.1 < y < 0.5$. In this range, superconductivity at 55 K is possible (with a carrier density of 1.4×10^{21} cm^{-3}), even with severe loss of connectivity in the CuO chains. The data are consistent with superconductivity occurring only in the CuO planes. A sharp transition in R_H is also seen when y exceeds 0.50.

Progress in understanding the mechanism for superconductivity[1] in compounds based on La_2CuO_{4-y} (Ref. 2) and $YBa_2Cu_3O_{7-y}$ (Ref. 3) relies on the clarification of the normal-state electronic properties. Because the charge carriers in both systems are believed to be confined to the band formed from the $Cu(d_{x^2-y^2})-O(2p)$ bonds, it is natural to ask how the superconducting properties of $YBa_2Cu_3O_{7-y}$ scale with the carrier density n. In $La_{2-x}Sr_xCuO_4$ (for $x < 0.15$) the carrier density,[4] T_c (transition temperature[5]), and f (the fractional volume showing the Meissner effect[5]) increase monotonically as x increases from 0.05 to 0.15. Several studies[6] attempt to account for the nearly linear relationship between T_c and n in this range of x. In $YBa_2Cu_3O_{7-y}$ the existence of two inequivalent sites[7] for the Cu ions [two-dimensional (2D) sites in the planes and one-dimensional (1D) sites on the chains] complicates a similar analysis. The related issue of how crucial the 1D chains are to the occurrence of high-T_c superconductivity is also an interesting and open question. To investigate these issues we have exploited the ease with which oxygen is removed[8,9] from the as-grown material to tune the carrier concentration.

Rectangular bars of size $8 \times 4 \times 0.25$ mm were sliced from the as-grown sintered pellet. The bars were individually heated at a controlled rate of 4 °C/min in an Ar atmosphere in a thermogravimetry apparatus. When the desired weight change was attained the sample was cooled to room temperature. The starting material was determined[10] to have an oxygen content of 7.0 ± 0.1. Hall measurements were performed in Bitter magnets. The averages of 10 readings for both field directions were usually taken to determine[11] the Hall constant R_H.

The variation of the Hall coefficient R_H (all holelike) between 290 and 77 K is shown in Fig. 1 for 7 samples with Δy varying from 0.0 (as grown) to 0.66. In contrast to $La_{2-x}Sr_xCuO_4$ the as-grown material here has a pronounced T dependence in R_H (solid circles.) As Δy increases to 0.11, R_H (open circles) is enhanced by a factor of 2–3. Thereafter, further reduction has no dramatic effect on R_H until Δy exceeds 0.50. In particular, R_H measured at 95 K shows a jump by a factor of 3 when Δy increases from 0.44 (solid squares) to 0.51 (solid triangles.) The interesting variation of R_H vs Δ_y is shown in Fig. 2, where the same data at 95 and 290 K are reproduced. As discussed above, R_H initially increases rapidly when Δy increases from 0.0 to 0.11. Then it remains pinned to the value 4.5×10^{-9} m^3/C over a wide range of Δy until the oxygen content drops below 6.5. The plateau in R_H implies that the system maintains the same carrier population despite a severe depletion of oxygen. T_c (defined as the midpoint of the susceptibility transition) and the fractional volume f (open diamonds in Fig. 2) showing the Meissner effect have also been measured. The three features of $1/R_H$ vs y, viz., the initial cusp near $y = 0.0$, the plateau, and the sharp decrease for $y > 0.5$, are reflected in the behavior of T_c and f.

We show in Fig. 3 the variation of T_c and f with respect to $n_H \equiv 1/R_He$ (normalized to the unit cell: e is the electronic charge.) Both T_c and f increase very rapidly as n_H exceeds 0.04 carriers per cell. When the oxygen content increases beyond 6.5 (n_H exceeds 0.12 per cell) the increase in both T_c and f become much weaker. The clustering of data around $n_H = 0.24$ per cell reflects the pinning of all three quantities T_c, f, and R_H at the plateau (Fig. 2) for $0.11 < \Delta y < 0.44$. Similarly, the kink in the plots at $n_H = 0.12$ per cell signals the sharp transition in R_H at an oxygen content of 6.5. The lattice parameters of these samples have also been measured by x-ray diffraction. The othorhombic-to-tetragonal (O-T) transition is observed[12] to occur at 6.4, rather than 6.5 where sharp changes in the electronic properties are seen in both Figs. 2 and 3.

The data on T_c and f vs R_H confirm that the superconducting properties are strongly correlated with the carrier density. From the variation of T_c and R_H in Figs. 2 and 3 we may distinguish three regions of oxygen doping of relevance to superconductivity. In region I, which extends from $y = 0$ to $y_1 (< 0.1)$, the chains have few defects and T_c occurs above 60 K. In region II ($y_1 < y < y_2 = 0.5$) f, T_c, and n_H are relatively insensitive to changes in y. In region III ($y > y_2$) T_c, f, and n_H decrease rapidly as y increases.

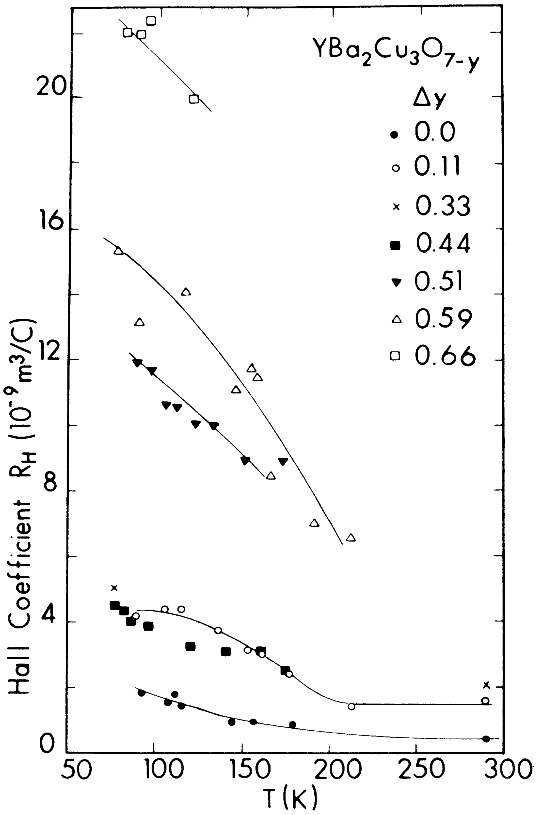

FIG. 1. Temperature dependence of the Hall coefficient for seven samples of $YBa_2Cu_3O_{7-y}$ with different oxygen contents. Δy is the increase in oxygen vacancies (per formula unit) from the as-grown material (in which y is measured to be 0.0 ± 0.1.) The solid lines are drawn to guide the eye.

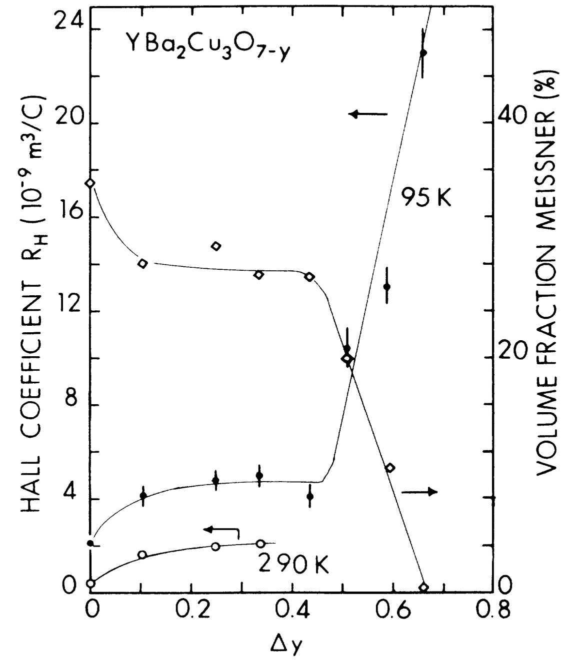

FIG. 2. The variation of the Hall coefficient with (change in) oxygen vacancies Δy at two temperatures 77 K (solid circles) and 290 K (open circles.) The volume fraction f showing the Meissner effect is also plotted (open diamonds.) Three regions of y separated by $y_1 \sim 0.1$ and $y_2 = 0.5$ are distinguished in the text. Solid lines are guides to the eye.

Since R_H is strongly T dependent we will interpret the Hall data using a two-band Drude model. The carriers are from two bands at the Fermi energy ϵ_F, with (predominantly) 2D and 1D dispersion. In region II the wide range of y over which R_H, T_c, and f are insensitive to y suggests the presence of a *sink* (a narrow band of localized states) which absorbs the donated electrons (as y increases), leaving the normal and superconducting transport properties unaffected. The obvious candidates for this sink are the cations Cu(1) on the 1D sites closest to the created oxygen vacancies. Because current transport along the 1D chains is readily disrupted by oxygen vacancies, the electrons donated to the Cu(1) ions by the vacancies are strongly localized. Over the range of y in region II the Hall effect simply measures the density of mobile holes n_{2D} associated with the cations Cu(2) in the 2D planes. We assume that the density of states at energy ϵ [comprised of a narrow 1D peak $N_1(\epsilon)$ and a 2D band $N_2(\epsilon)$] is as shown in Fig. 3 (inset). In region II all the states in $N_1(\epsilon)$ are strongly localized and ϵ_F is pinned at the peak. If the chains have strictly 1D behavior the usual two-band expression[13] for $H_H(T)$ reduces to $\mu(T)/[n_{2D}e\mu(T)+n_{1D}e\mu'(T)]$ where $\mu'(\mu)$ are the mobilities in the 1D chains (2D planes), and n_{1D} and n_{2D} are the corresponding carrier densities. The observed T dependence of R_H is due to the variation of $\mu(T)/\mu'(T)$.

In region II the contribution of the 1D states to the current is assumed to vanish. Thus, $n_{2D} \sim 1/R_He$. This implies that R_H should become T independent. Although a strictly T-independent R_H is not observed in any sample, the data in Fig. 1 do show a decreasing trend in the variation of the R_H with T as Δy increases from 0.0 to 0.44. (More measurements to test this hypothesis are needed.) Nevertheless, the persistence of R_H at the plateau value (4.5×10^{-9} m^3/C) over a large range of y and T reflects a stable structure in the oxygen-doped system. Using this value, n_{2D} equals 0.24/cell or $\frac{1}{8}$ hole per Cu(2) ion. Note that this is close to the value $\frac{1}{7}$ hole per Cu found[4] in $La_{2-x}Sr_xCuO_4$ with $x = 0.15 (T_c = 40$ K). The observation of T_c near 55 K in $YBa_2Cu_3O_{7-y}$ over the range of oxygen content in region II was reported by Tarascon *et al.*[8] With the assumption that T_c is determined by n_{2D} we interpret the ubiquitous 55-K transition as probably due to the clamping of n_{2D} to the value $\frac{1}{8}$ hole per Cu(2) ion in this range of y. Since high-T_c superconductivity (55 K) is observed even when the 1D chains are severely disrupted ($y \sim 0.4$) we conclude that connectivity of the 1D chains is *not essential to the superconductivity at 55 K*.

We turn next to region I. As the number of oxygen vacancies y decreases below y_1 a sharp increase in T_c, f, and n_H is observed. Two different interpretations are possible. In the first, the growing length of intact 1D segments plays a crucial role in augmenting the superconductivity

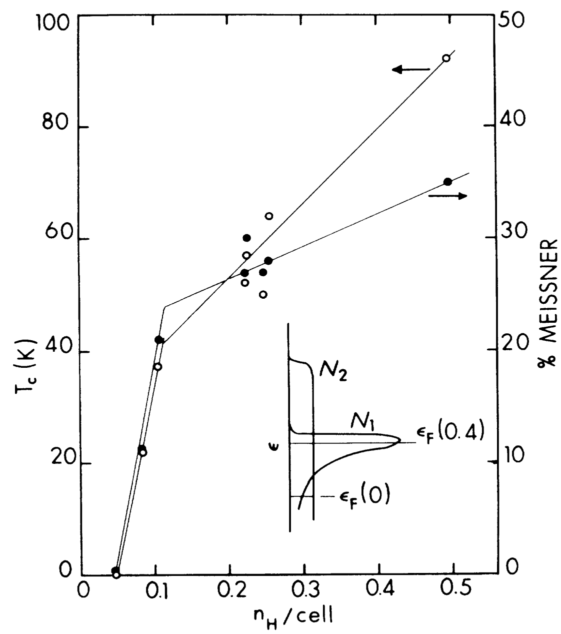

FIG. 3. Plot of the superconducting transition temperature T_c and volume fraction showing the Meissner effect f vs the effective carrier density $n_H \equiv 1/(R_H e)$ normalized to a unit cell. The cluster of data around $n_H = 0.24$ per cell reflects the plateau in all three quantities for y between 0.11 and 0.50. Inset: the proposed density of states with a narrow peak due to the 1D states. The Fermi level is 0.1–0.2 eV below the peak when $\Delta y = 0$. When Δy exceeds 0.11, ϵ_F is pinned at the peak.

already existing in the 2D planes. In the second, a further increase in n_{2D} is responsible for driving up T_c. Because the first interpretation requires two distinct superconductivity mechanisms (one operating at 55 K, the other at 90 K), we will restrict our discussion to the second. (The data, however, do not rule out the first.)

Assuming that the second interpretation is valid we expect n_{2D} to increase by roughly 50% (assuming T_c scales linearly with n_{2D}) to approximately 0.4 per cell. This enhancement in n_{2D} requires the pinning of ϵ_F to be relaxed. It is plausible that ϵ_F has decreased below the peak in $N_1(\epsilon)$ into the tail (Fig. 2 inset): In region I $N_{1F}[=N_1(\epsilon_F)]$ is comparable to, or smaller than, $N_{2F}[=N_2(\epsilon_F)]$. Thus the lowering of ϵ_F proceeds relatively rapidly as $y \rightarrow 0$, thereby generating the rapid increase in n_{2D} required by the second interpretation. Further, in region I the chains are reasonably intact, so they carry a substantial fraction of the normal current (above T_c). Since a reduction of y by 0.1 adds 0.2 electrons to the cations per cell, the peak in $N_1(\epsilon)$ is located 0.1–0.2 eV above ϵ_F in the $y=0$ compound, assuming that $N_{1F}+N_{2F}$ is $\sim$2/eV cell. The band-structure results of Massidda, Yu, Freeman, and Koelling[14] actually demonstrate the existence of a sharp peak (F) of width 0.1 eV which arises from the π-bonding band of the Cu(1)-O(1)-O(4) ions. For this band to be identified with our proposed peak, however, it would have to be 0.1–0.2 eV *above* ϵ_F in the $y=0$ sample.

Next, we discuss the interesting behavior around $\Delta y = 0.50$. When Δy exceeds 0.50, rather abrupt decreases in $1/R_H$, f, and T_c are observed in our data (Fig. 2). The coincidence of this abrupt transition with the oxygen level which corresponds to having all the Cu ions in 2+ oxidation state is quite intriguing from the point of view of large positive-U models.[15] (From simple valence counting the number of Cu^{3+} ions is reduced to zero when the oxygen content decreases to 6.50. As ϵ_F is pushed into the Mott-Hubbard gap with further oxygen depletion the system becomes insulating.) The occurrence of the sharp transition in R_H at 6.50 is clearly strongly correlated with the number of Cu^{3+} ions. However, there are two features of the data which are hard to fit into the usual Hubbard scheme. First, $YBa_2Cu_3O_{7-y}$ becomes progressively less metallic as Δy exceeds 0.50, whereas in the simple Hubbard model filling of the upper Hubbard band is to be expected. The occurrence of the O-T transition may alter the electronic structure enough to make such a simple application of the Hubbard model unwarranted. Second, the pinning of both T_c and R_H to their values at the plateau until the oxygen content reaches 6.50 is hard to reconcile with simple valence counting, according to which both T_c and $1/R_H$ should reach *zero* at 6.50.

In summary, we have studied how the superconducting properties change with carrier density when the oxygen content in $YBa_2Cu_3O_{7-y}$ is altered. We propose that the plateau in T_c, f, and R_H results from a narrow peak of 1D states which sits 0.1–0.2 eV above ϵ_F when $y=0.0$. With moderate oxygen doping ϵ_F moves into the peak, becoming pinned over a wide range of y (region II). Because the states in the peak are strongly localized in this range only the holes in the 2D planes participate in transport. Assuming that T_c is determined by n_{2D} (rather than the *total* hole density) we find that the 55-K transition corresponds to n_{2D} of $\sim 1.4 \times 10^{21}$ cm^{-3} [or $\frac{1}{8}$ per Cu(2) ion]. These numbers are rather close to the 40-K system, and suggest a common mechanism. At $y=0$ we determine that the Fermi wave vector in the 2D band[16] k_F is $< 3.2 \times 10^7$ cm^{-1}. From this number the parameter $k_F \xi_0 = 2\epsilon_F/(\pi\Delta)$, where ξ_0 is the Pippard length and Δ the gap, may be reassessed.[17] The 1D chains (which are badly disrupted in region II) do not play any role in the 55-K superconductivity. At $y=0$, where the chains carry a substantial fraction of the normal current, they may be important. However, the increase of T_c to 90 K may also arise solely from a 40% increase in n_{2D} (going from regions II to I). The latter possibility has the merit of requiring a common mechanism for both the 55- and 90-K transition.

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[10]$\Delta y = y - y_0$, where y_0 (starting material) is determined to be 0.0 ± 0.1. Δy is determined to higher accuracy, ± 0.01, than y.

[11]Severe contact noise (5–20 μV) obscured the signal at high T, for $\Delta y > 0.4$. The data reported here are restricted to V_H which are linear in B (± 6, 10, and 15 T) *and* current I (30, 50, and 100 mA.)

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[16]Since $n_H = n_{2D} + n_{1D}(\mu'/\mu)$, we have $n_{2D} < n_H = 0.5$ holes per cell at $y = 0$. For strictly 2D dispersion we have n_s (areal density) $< 1.7 \times 10^{14}$ cm^{-2}, $k_F = \sqrt{(2\pi n_s)} < 3.2 \times 10^7$ cm^{-1} and $\epsilon_F < 0.39(m_0/m^*)$ eV, where m^*/m_0 is the effective mass ratio.

[17]For example, John Bardeen, D. M. Ginsberg, and M. B. Salamon, in Ref. 1. Assume a value for k_F twice as large as the bound here.