Chain-Fragment Doping and the Phase Diagram of $YBa_2Cu_3O_{7-x}$

J. Zaanen, A. T. Paxton, O. Jepsen, and O. K. Andersen

Max-Planck-Institut für Festkörperforschung D-7000 Stuttgart 80, Federal Republic of Germany

We show, using a proposed oxygen-defect structure for $YBa_2Cu_3O_{7-x}$ and a tight-binding model based on density-functional calculations, that the distribution of holes between planes and (fragmented) chains causes jumps and plateaus for the hole counts in the planes as a function of the nonstoichiometry, x. These features can be correlated with the occurrence of the antiferromagnetic as well as the 60- and 90-K superconducting phases. Our findings are supportive of the view that the hole count is the controlling parameter for the superconductivity.

$YBa_2Cu_3O_{7-x}$ has a remarkable phase diagram as a function of the oxygen-vacancy concentration, x.[1-5] As seen in Fig. 1 the $T_c = 90$-K superconductors are found for $0 \leq x < 0.2$. T_c then decreases to 60 K, where it remains up to $x = 0.5$.[5] Beyond $x = 0.5$, T_c deteriorates[1,2] and it has been established that the $x \approx 0.7$, 0.85, and 1.0 materials are antiferromagnets.[3-5] We will argue that this phase diagram can be understood in detail given that the hole count in the planes is the controlling factor in the formation of both the antiferromagnetic (AF) and superconducting (SC) phases.

For $La_{2-y}Sr_yCuO_4$ the importance of the hole count (n_p) in the CuO_2 planes is rather obvious. There is gen-

eral agreement that near the Fermi level only one band exists, namely the antibonding band from the in-plane Cu $x^2 - y^2$ orbitals and the O x or y orbitals. At $y = 0$, this band is half filled ($n_p = 1$) and gives rise to antiferromagnetism in the presence of strong Coulomb interactions on the Cu ions. By doping with Sr, additional holes are introduced in the planes ($n_p \approx 1 + y$), destroying the long-range AF order with y as small as 0.03.[6] As y increases, the $T_c \cong 35$-K SC phase is stabilized until beyond $y = 0.20$, where oxygen vacancies are built in,[7] thus bringing down the hole count and destroying the superconductivity. This hole concentration plays a central role in many theories of high-T_c superconductivity. For instance, in the resonating-valence-bond theory,[8] or in the spin-bag theory,[9] the holes give rise to exotic quasiparticles, while in the more conventional theories, they act to stabilize a normal Fermi-liquid state.[10]

At first sight, the relationship between the hole counts and doping in $YBa_2Cu_3O_{7-x}$ is not as obvious as in $La_{2-y}Sr_yCuO_4$. If we consider the oxygen vacancies merely as donors of electrons, neither the AF state for $x = 1$ nor the sudden jumps between the different phases as a function of x can be explained. A first important clue is that the vacancies are not distributed randomly through the crystal, but often form ordered defect structures. For $x = 0$, the structure is well known,[11] consisting of two planes and one chain per $YBa_2Cu_3O_7$ unit cell. As x increases, the planes remain intact, while oxygen vacancies appear in the chains. The chains run along the b direction and consist of oxygen-linked CuO_2 units directed along the c axis. At $x = 1$, all the oxygen links are removed and the structure comprises intact planes and isolated CuO_2 units (empty chains).[12] It has been found that for $x = \frac{1}{8}$,[13] $\frac{1}{2}$,[14] and $\frac{7}{8}$,[13] the oxygen vacancies order in the a and b directions. In accordance with these observations, we use the following defect-structural model for the chains in $YBa_2Cu_3O_{7-x}$: In a unit cell which is doubled along the a axis, we regard the two chains as inequivalent. One of the chains will be either intact ($0 \leq x \leq \frac{1}{2}$) or empty ($\frac{1}{2} \leq x \leq 1$), and the other chain will have oxygen vacancies arranged with regular spacing so as to satisfy the nonstoichiometry. In
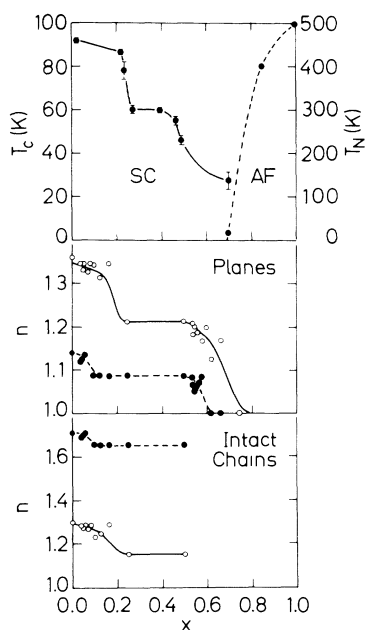

FIG. 1. Experimental phase diagram of $YBa_2Cu_3O_{7-x}$ from Refs. 1–4 (top) together with hole counts calculated for a plane (center) and an intact chain (bottom). The parameters used in the calculations were the ones reproducing the LDA results shown in Fig. 2 (filled circles), and the ones giving the band lineup shown in Fig. 3 (open circles).

the simplest case, this broken chain will then comprise fragments of v CuO_2 units connected by $v-1$ oxygen links, where for $0 < x \leq \frac{1}{2}$, $x = 1/2v$; and for $\frac{1}{2} < x \leq 1$, $x = \frac{1}{2} + 1/2v$. For values of x for which $1/2x$, or $1/(2x-1)$, is not an integer, the broken chains will be made up of two different lengths such that the oxygen vacancies are kept as far apart as possible.

We now need to consider the electronic structure. The local-density approximation (LDA) is expected to describe the general features of the band structures reliably, but the details could be misleading in the light of the correlated nature of these materials. Several groups[15] have shown that the planes in La_2CuO_4, $YBa_2Cu_3O_7$, or $YBa_2Cu_3O_6$ and the intact chains in $YBa_2Cu_3O_7$ give rise to highly dispersive bands crossing the Fermi level (E_F). We have performed an LDA linear muffin-tin-orbital method in the atomic-sphere approximation calculation[16] for $Y_2Ba_4Cu_6O_{13} = 2(YBa_2Cu_3O_{6.5})$. Per primitive cell there are two planes each with two CuO_2 cells, one intact chain, and one broken chain with $v=1$. In Fig. 2 we show the bands near E_F. Each of the two plane bands are doubly degenerate, the band from the intact chain, $E(k)$, is drawn with a heavy line in those regions where it hybridizes little, and the broken-chain levels are below the frame of the figure.

The intact-chain band is well described in the tight-binding approximation as the antibonding band obtained from the Cu $z^2 - y^2$ orbital, the z orbitals on the two oxygens in the c direction, and the y orbital on the oxygen along the chain. Its dispersion is

$$E(k) = \frac{1}{2}\Delta + [(\frac{1}{2}\Delta)^2 + 2t^2(\alpha^2 + 1 - \cos k)]^{1/2}. \quad (1)$$

Here, $k \equiv \mathbf{k} \cdot \mathbf{b}$, and $-\pi < k \leq \pi$. The bottom of the band is at $k = 0$ and the top is at π. The zero of energy is taken at the Cu d level, and Δ is the energy of the oxy-

gen p level. The hopping integral from Cu to O along the chain is t, and to one of the oxygens in the c direction, which are 5% closer, is αt. With n holes in the intact-chain band, we have

$$k_F = \pi(1 - n/2) \text{ and } E_F = E(k_F). \quad (2)$$

The parameter values $\Delta \cong 0$ eV, $t = 2.4$ eV, and $\alpha = 1.3$ describe the antibonding LDA band both for $x = 0$ and for $x = \frac{1}{2}$.

The electronic structure of a broken chain may be obtained with fair accuracy from that of the intact chain by our removing linking oxygens, without changing the values of the parameters. In this approximation the states for a fragment of length v, with oxygens removed from the positions $y = 0$ and v, and with CuO_2 units at $y = \frac{1}{2}, \ldots, v - \frac{1}{2}$, simply equal those infinite-chain states which have the Bloch factor $\cos(ky)$ and the wave vectors $k = q\pi/v$, with integer values of q from 0 to $v-1$. The reason is that these states have the same amplitude for the $z^2 - y^2$ orbitals at $y = \pm \frac{1}{2}$, as well as at $y = v \pm \frac{1}{2}$, so that they cannot couple via the removed oxygen y orbitals. The antibonding levels for a fragment of length v are thus $E(0), E(\pi/v), \ldots, E(\pi(v-1)/v)$. As seen in the right-hand side of Fig. 3, the lowest level $E(0)$ is the same for all fragments. It is below E_F for the systems considered, and this implies that the hole count in the $v=1$ fragment is zero [i.e., it is $Cu^+(O^{--})_2$]. If we now form $v=2$ fragments by adding oxygen atoms to an ensemble of $v=1$ fragments, we effectively add two holes and one level at $E(\pi/2)$ per oxygen. If this level is above E_F it will be occupied by the two holes so that no doping occurs. By continuing this argument for longer and longer fragments, we see that doping does not occur before $E(\pi/v)$ drops below E_F. The length v_c of the longest nondonor fragment is therefore given by
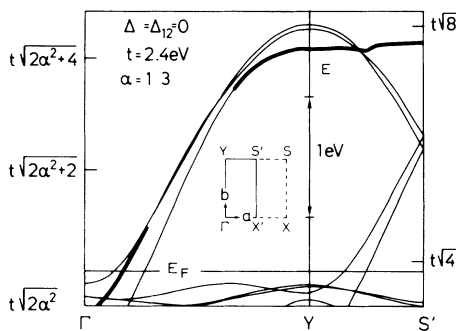
$$E(\pi/(v_c + 1)) < E_F \leq E(\pi/v_c). \quad (3)$$

FIG. 2. LDA energy bands of $2(YBa_2Cu_3O_{6.5})$ near E_F. The heavy line indicates the intact-chain band in regions where the hybridization is small. Inset: The Brillouin zone of $YBa_2Cu_3O_7$ folded in the a direction, perpendicular to the chains. The positions of the top ($n=0$), center ($n=1$), and bottom ($n=2$) of the model intact-chain band (1) are marked to the left. The positions of the top ($n_p = 0$) and center ($n_p = 1$) of the model plane band (Ref. 17) are marked to the right.
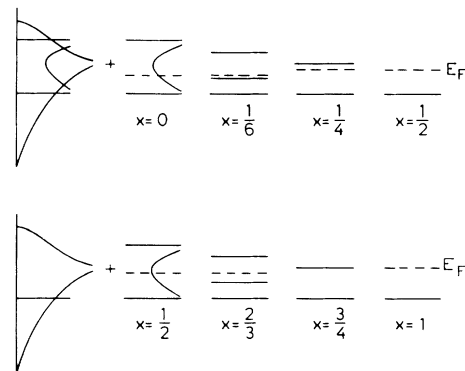

FIG. 3. Schematic densities of states (Ref. 17) for the plane and intact-chain bands, the broken-chain levels, and the Fermi level for $YBa_2Cu_3O_{7-x}$. With the chosen parameter values ($\alpha = 1$, $\Delta = \Delta_p = 0$), the centers of the plane and intact-chain bands are lined up.

This fact, that fragments with lengths less than or equal to a critical one do not act as dopants, taken together with our model for the fragment-formation sequence, leads to characteristic plateaus in the curves of hole count versus oxygen-vacancy concentration. In the center and bottom parts of Fig. 1 we show respectively the calculated[17] hole counts for a plane, $n_p(x)$, and for an intact chain, $n(x)$. The filled and open circles were obtained with parameters characterizing the band lineups in, respectively, the LDA situation (Fig. 2) and the situation where the centers of the plane and intact-chain bands coincide (Fig. 3).

If we begin now with $x = 1$, the plane band is half full, $n_p(1) = 1$, so that the situation is exactly as in AF La_2CuO_4. Addition of oxygen ($\frac{1}{2} < x < 1$) does not change the hole count before the first fragment of length $v_c + 1$ occurs. This happens at the critical concentration $x_c = \frac{1}{2} + 1/2v_c$ where, for our two parameter sets, $v_c = 4$ and 2, respectively.

Also the filling of the second chain ($0 < x < \frac{1}{2}$) leads to pinning of the Fermi level. Here, the length of the plateau is directly related to the hole count for the intact chain, because from (2) and (3) we obtain the bounds $v_c \leq 1/[1 - n(\frac{1}{2})/2] < v_c + 1$, in terms of the critical fragment length. Replacement of the latter by the plateau length, $L \equiv \frac{1}{2} - x_c = \frac{1}{2}(1 - 1/v_c)$, yields

$$4L \leq n(\tfrac{1}{2}) < 1/(1 - L), \qquad (4)$$

with $1/(1 - 2L) = v_c$ being an integer. This relation allows us to deduce the hole count from experimental plateau lengths. For the plane the hole count is $n_p(\frac{1}{2}) = \frac{3}{2} - n(\frac{1}{2})/4$. At this second plateau E_F is lower than at the first one. The length of the second plateau therefore exceeds, or equals, the length of the first.

Outside the plateaus the hole counts depend on the densities of states. The ratio $[n_p(0) - n_p(\frac{1}{2})]/[n(0) - n(\frac{1}{2})]$ between the second jumps in the hole counts for the plane and the intact chain equals the ratio N_p/N between the appropriately averaged state densities, for instance. Since the hole counts at $x = 0$ are related by $n_p(0) = 2 - \frac{1}{2}n(0)$, the ratio between the first and the second jumps in the plane hole count can be expressed as

$$[n_p(\tfrac{1}{2}) - n_p(1)]/[n_p(0) - n_p(\tfrac{1}{2})] = 1 + \tfrac{1}{2}N/N_p.$$

With equal average state densities, the ratio is $\frac{3}{2}$. This is approximately what is found with either parameter set (and for T_c), as seen in Fig. 1.

The experimental data are in significantly better agreement with our calculation for the parameter set with $\alpha = 1$ (Fig. 3) than for the set with $\alpha = 1.3$ (Fig. 2), which more properly takes the smaller Cu-O distance in the c direction into account. Since only the lineup near E_F is important, the same good agreement could, however, be obtained with $\alpha = 1.3$, provided that the plane band is shifted by the amount $\Delta_p \cong t[(2\alpha^2 + 2)^{1/2} - 4^{1/2}]$, so that the centers of the plane and intact-chain bands

are lined up. This shift seems to be missing in the LDA.

It is remarkable that such a simple model is able to reproduce the phase diagram of $YBa_2Cu_3O_{7-x}$ over the entire range of x between 0 and 1, and it is therefore essential that we comment on the assumptions made.

We have assumed ordered vacancy structures following Refs. 13 and 14, although long-range order is not observed in all specimens; e.g., disordered samples with $x > 0.5$ have often been found. Long-range order itself is, however, not essential for our argument, which only relies on the relation between oxygen concentration and chain-fragment length. But this does impose strong constraints on the short-range order. We expect sharp jumps in the phase diagram to be associated with crystal perfection.

One of the controversial questions in this field is to what extent the new superconducting materials should be viewed as itinerant- or localized-electron systems.[18] The controlling parameter here is the p-d splitting, Δ. We have assumed the itinerant-electron situation ($\Delta = 0$), but the hole counts are rather insensitive to the precise magnitude of Δ. In particular, we have seen that, given the defect-structural model, the critical concentrations where the jumps occur only depend on the band lineups, and, secondly, that the ratio between the jumps in the hole count for the plane merely depends on the ratio between the average plane and intact-chain state densities. Therefore, our model does not discriminate between the itinerant- and localized-electron pictures. Equally controversial is the nature of the quasiparticles and, hence, the densities of states in the planes and chains. However, our basic argument only assumes that the spacing between the discrete levels decreases when the size of the fragments increases, which is a universal trend. The finer details of our curves of hole count versus concentration, i.e., the sizes of plateaus and jumps, do not depend on the detailed shapes of the densities of states either.

We finally turn to the absolute numbers of holes in the planes and in the intact chain. We have argued that the length of the 60-K plateau provides upper and lower bounds for the hole counts at this plateau. From the T_c measurements our model yields $1 \leq n(\frac{1}{2}) < \frac{4}{3}$ for the intact-chain hole count, and $\frac{7}{6} < n_p(\frac{1}{2}) \leq \frac{5}{4}$ for the plane hole count. The hole counts thus seem to be similar, as one expects when on-site Coulomb interactions are strong.

In summary, we have proposed a model for the defect structure of nonstoichiometric $YBa_2Cu_3O_{7-x}$, which combined with a tight-binding picture reproduces the phase diagram of this compound, given that the hole counts are responsible for the SC and AF phases. We have seen that, in this way, the "magic numbers," 0, 60, and 90 K, can be traced back to the energy-level structure of broken-chain fragments of increasing lengths. Further, we have argued that stoichiometric $Y_2Ba_4Cu_6$-O_{13} should have $T_c \cong 60$ K and about equal hole counts

(≈ 1.2) in the planes and in the chains. This work confirms earlier views[7] that the hole counts are of decisive importance. This may be a guideline in the quest for higher superconducting transition temperatures.

We have enjoyed stimulation from A. Simon.

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[16]We used the structural data from Ref. 14. The ratios of the sphere radii were those of Fujiwara and Hatasugai (Ref. 15). The self-consistent calculation used 30 points in the irreducible Brillouin zone, two energy panels, and s, p, and d orbitals, plus f orbitals on Ba.

[17]The densities of states actually used in our calculations of the hole counts were, for the intact chain,

$$N(E) = \frac{4|E - \frac{1}{2}\Delta|/\pi}{\{[E - E^-(\pi)][E - E^-(0)][E - E(0)][E(\pi) - E]\}^{1/2}}$$

with $E^-(k)$ being the bonding tight-binding band obtained with the minus sign in front of the square root in (1). For the plane,

$$N_p(E) = \frac{1}{(\pi t)^2} \frac{E - \Delta_p - \frac{1}{2}\Delta}{1 - \epsilon^2} \int_0^{\theta(\epsilon)} \left[1 - \frac{\sin^2\phi}{\sin^2\theta(\epsilon)}\right]^{1/2} d\phi,$$

where $\epsilon^2 \equiv (E - \Delta_p)(E - \Delta_p - \Delta)/8t^2$, $\theta(\epsilon) \equiv \pi/2$, for $0 \le \epsilon \le 1/\sqrt{2}$, and $\sin\theta(\epsilon) \equiv \epsilon^{-2} - 1$, for $1/\sqrt{2} \le \epsilon \le 1$. This plane band is the antibonding band formed from the Cu $x^2 - y^2$, the O x, and the O y orbitals in the tight-binding approximation. It extends from $\epsilon = 0$ to 1, and is half full at $\epsilon = 1/\sqrt{2}$. Its dispersion is

$$E_p(\mathbf{k}) = \Delta_p + \frac{1}{2}\Delta + [(\frac{1}{2}\Delta)^2 + 2t^2(2 - \cos k_a - \cos k_b)]^{1/2}.$$

Δ_p is the position of the Cu d level in the plane relative to that in the chain. The hopping integral t was taken to be the same as along the chain, because the Cu-O distances differ by less than 1%. Also the p-d separation Δ was taken to be the same as in the chain. This band with $\Delta = \Delta_p = 0$ and $t = 2.4$ eV is a reasonable approximation to the LDA plane bands calculated for $x = 0$, $\frac{1}{2}$, and 1 (Ref. 15 and Fig. 2). (The value $t = 1.85$ eV given in Ref. 15 yields the best fit to the antibonding *and* bonding bands.) To the accuracy of the hole counts in Fig. 1 the hybridizations between the plane, chain, and chain-fragment states are found to be negligible in the LDA. So are the x dependences of the fitted tight-binding parameters, specifically that of the Madelung shift, Δ_p, between planes and chains.

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