Spin Polarons, Hole Filling, and High-T_c Superconductivity in $YBa_2Cu_3O_7$ and $PrBa_2Cu_3O_7$ Alloys and Layered Films

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Using results from previous work on a spin-polaron model of high-T_c superconductivity, together with a hole-filling mechanism, excellent agreement with experimental data for T_c in Y-Ba-Cu-O and Pr-Ba-Cu-O alloys and layered structures is obtained without introducing either pair breaking by the Pr ions or pairing interactions between unit cells.

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Several groups[1] have reported on the superconducting properties of alloys of $YBa_2Cu_3O_7$ (YBCO) and $PrBa_2Cu_3O_7$ (PBCO) and more recently superconductivity in layered structures of YBCO and PBCO has been extensively studied.[2] In the $Y_{1-x}Pr_xBa_2Cu_3O_7$ alloys, T_c shows a monatomic decrease with x from ~ 91 K at $x=0.0$ to 0 K at $x \simeq 0.60$. A complex dependence of T_c on the structure of the YBCO and PBCO supercells making up the layered films is found. The results are frequently discussed in terms of pair breaking by the Pr ions and/or filling of holes in the CuO_2 planes.[3] In this Letter it is demonstrated that the T_c data on both the alloys and the layered structures can be fitted with precision and self-consistency using results from a spin-polaron model,[4,5] together with the hole-filling concept.

In the spin-polaron model of Ref. 4, holes moving primarily on the oxygen sublattice of the CuO_2 planes polarize the unpaired spins in the $3d(x^2-y^2)$ orbitals of the Cu^{2+} ions to form the spin polarons. Since the Cu^{3+} d^8 configuration has low probability of occurrence,[6] these may be referred to as d^9 spin polarons.[5] The mechanism for their formation is similar to that discussed by Mott[7] for a one-dimensional (1D) antiferromagnetic (AF) chain. Essentially, it is due to the fact that in certain materials with a tendency toward AF alignment, a carrier's kinetic energy may be reduced if reversing the spins on neighboring ions allows the carrier to pass more freely over those ions.

Pairing of spin polarons occurs because a tendency toward short-range AF alignment of the Cu^{2+} spins associated with two different polarons persists even after long-range AF order is destroyed. These ideas can be incorporated into equations for the gap and T_c that may or may not be considered to fall within BCS theory, depending on the generality with which "BCS theory" is viewed. Solution of the equation for T_c, under certain simplifying assumptions about the Fermi surface, leads to the curves in Fig. 1. Since the curve for YBCO is an essential ingredient of the present work, its origins will be explained.

It is known from Hall-effect measurements[8] and from other sources that the single hole in a unit cell of $YBa_2Cu_3O_7$ is distributed approximately 0.6 on the chain plane and 0.20 on each of the CuO_2 planes; in Ref. 4 the numbers turned out to be 0.56 and 0.22, respectively. Removal of oxygen from the chain plane depletes Z_p, the number of holes in the CuO_2 plane, but this depletion is not linear in x, which gives rise to the well-known plateau region[9] in $T_c(x)$ around 50–60 K for $YBa_2Cu_3O_{7-x}$. Hall-effect and normal-state resistivity measurements[10] establish that superconductivity in $La_{2-x}Sr_xCuO_4$ does not occur until $x \simeq 0.07$. It is difficult to determine experimentally if a similar situation exists in $YBa_2Cu_3O_{7-x}$ when $x \simeq 0.5$, but it seems reasonable to assume that it does.

In the d^9 spin-polaron model, the electronic structure of a CuO_2 plane, with no holes present, is that of a generalized Mott-Hubbard insulator. As holes are added, the Fermi level moves down from the top of the valence band in a manner dictated by the band structure. In

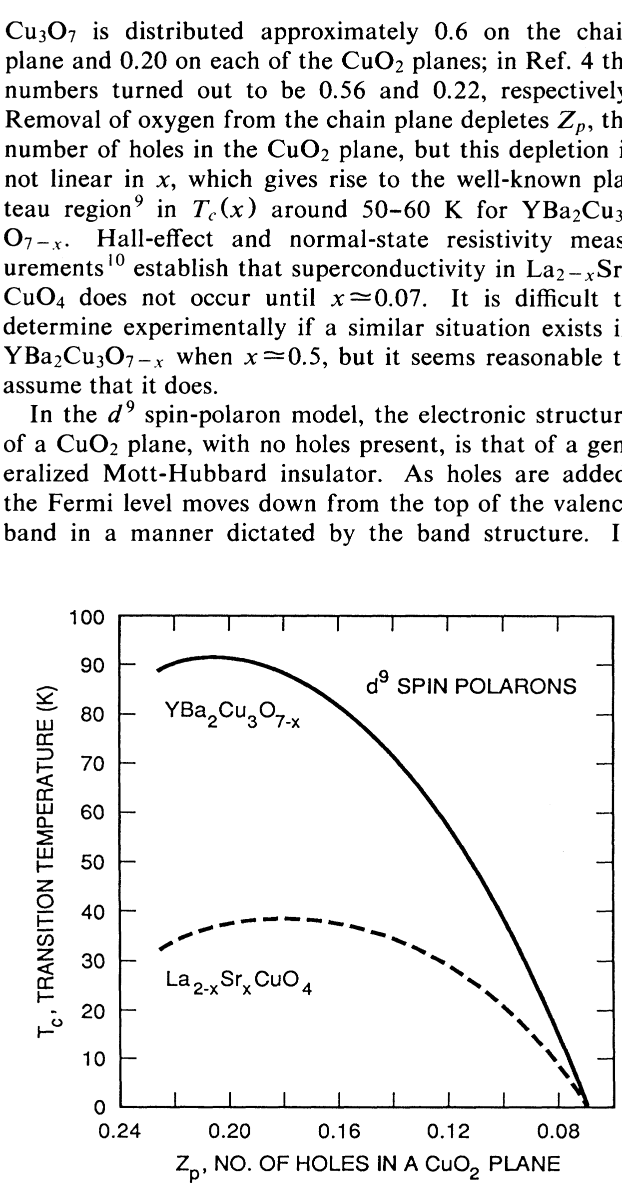

FIG. 1. Transition temperature as a function of hole number in a single CuO_2 plane.

Ref. 4 it was assumed that superconductivity does not occur until $x=0.07$ in $La_{2-x}Sr_xCuO_4$ because the holes initially go into O $2p\pi$ orbitals for which spin polarons do not form. There are other reasons why this may occur (e.g., the gradual destruction of long-range 2D AF ordering may enhance spin-polaron formation) but a discussion of them is not important to the present work. In any case, $T_c \rightarrow 0$ K at $Z_p=0.07$ in Fig. 1 because the number of "superconducting holes" goes to zero as the Fermi surface approaches the band edge. The overall shapes of the curves are determined by solutions of the equation for T_c which involve Brillouin-zone summations. An initial steep rise from $T_c=0$ K occurs as more **k** space becomes available for pair formation. The maximum in $T_c(x)$ occurs because certain **k**-dependent "form factors" in the T_c equation outweigh the effect of increased **k**-space availability; such an intrinsic effect occurs in $La_{2-x}Sr_xCuO_4$.[11] The results in Fig. 1 are taken directly from Ref. 4 (where Z_p is broken down into the number of holes in O $2p\sigma$ and $2p\pi$ orbitals).

$Y_{1-x}Pr_xBa_2Cu_3O_y$ alloys.—$PrBa_2Cu_3O_7$ has the same structure as $YBa_2Cu_3O_4$ and the lattice mismatch is small. In YBCO, Pr^{4+} supplies electrons that are shared among the chain and CuO_2 planes, with the average number of holes per unit cell being $1-x$ and the average distribution obeying $Z_c+2Z_p=1-x$, where Z_c is the number of holes on the chain plane. It will be assumed that Z_c is a linear function of x, and therefore the two equations

$$Z_c=ax+b,\quad Z_c+2Z_p=1-x \tag{1}$$

determine Z_p. [As already noted, Z_c varies as oxygen is depleted from the chain planes of YBCO, but the first of Eqs. (1) does not hold because electrons can be trapped in the chain planes.[8]] From the experiments of various groups it is found that T_c goes to 0 K for values of x in the range 0.5–0.6. Choosing the value 0.6 from Dalichaouch *et al.*,[7] requiring that $Z_p \rightarrow 0.07$ when $T_c \rightarrow 0$ K and putting $Z_c=0.56$ at $x=0$, establishes $a=-0.5$. A more restrictive assumption keeps the ratio Z_c/Z_p constant at its value for $x=0$, giving $a=-0.56$ and $b=0.56$. With values of a and b established, Z_c and Z_p can be determined for any x and then T_c can be extracted from Fig. 1. In Fig. 2, the theoretical curves of $T_c(x)$ vs x are compared to the experimental data of Dalichaouch *et al.*; a curve for the case in which $T_c \rightarrow 0$ K at $x=0.55$ is also shown. Since the transition widths can become quite large in the alloys, some ambiguity exists but clearly there is a very good overall fit to the 50% T_c points for $a=-0.5$, $b=0.56$.

Layered structures.—When YBCO/PBCO films layered in the c direction are formed, the electrons from the Pr redistribute to minimize the total energy. Denote the number of YBCO and PBCO cells in a supercell by N_Y and N_P, respectively, and the net charge in the ith YBCO cell by Q_{Yi} and in the ith PBCO cell by Q_{Pi}. Then the energy of a supercell with N_Y and N_P layers can be denoted by $\mathcal{E}_{NY,NP}(Q_{Y1,Y2},\ldots,Q_{P1},Q_{P2},\ldots)$, which is to be minimized subject to the constraint of charge neutrality on the entire supercell. This assumes that the charge distribution in a unit cell is much less important than the magnitude in determining the energy. In this way, the problem of calculating $\mathcal{E}$ is decoupled from that of determining the distribution of the charge within a cell. The charge distribution is assumed to be given in the ith YBCO cell by Eqs. (1), again with $a=-0.5$ and $b=0.56$, but with $x=Q_{Yi}$.[12]

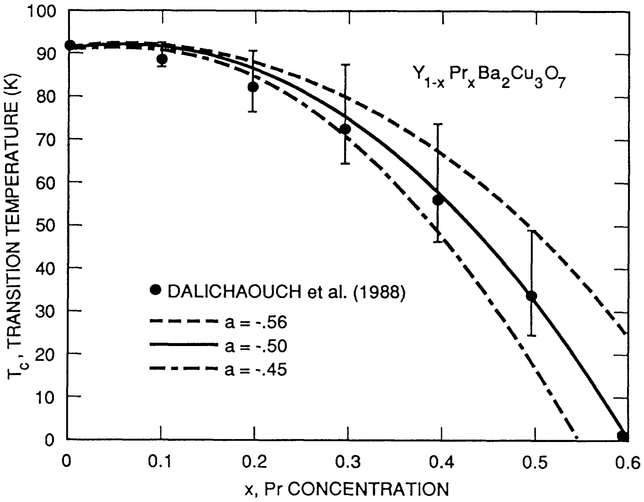

FIG. 2. Transition temperature as a function of x for $Y_{1-x}Pr_xBa_2Cu_3O_7$.

Let us first compare YBCO and PBCO cells before they are allowed to interact. A PBCO cell has one more ionic charge and one more electron than a YBCO cell. As with most all oxide materials, it is energetically favorable for electrons to fill O $2p$ orbitals because the nucleus is not strongly screened. In a crystal lattice this tendency to complete O $2p$ orbitals is greatly aided by the establishment of Madelung potentials, thus allowing the unstable O^{2-} ion to be formed. Calling the potential due to such chemical and crystal effects V_{cY}, the energy to put charge Q_{Yi}, in the ith YBCO cell is $V_{cY}Q_{Yi}$ from this term. However, a repulsive energy also enters and this is proportional to Q_{Yi}^2, so that the energy for the ith YBCO cell is

$$\epsilon_{Yi}=-V_{cY}Q_{Yi}+BQ_{Yi}^2\,. \tag{2}$$

In a PBCO cell, the chemical term in the potential is approximately the same as V_{cY} but the attractive interaction due to the additional charge of the Pr^{4+} ion modifies the linear term and so $\epsilon_{Pi}=-V_{cP}Q_{Pi}+BQ_{Pi}^2$.

The expression for $\mathcal{E}_{NY,NP}$ can be written as

$$\mathcal{E}_{NY,NP}(Q_{Y1},Q_{Y2},\ldots,Q_{P1},Q_{P2},\ldots)$$
$$=\sum_i^{N_Y}\epsilon_{Yi}+\sum_i^{N_P}\epsilon_{Pi}+\frac{1}{2}\sum_{i,j}{}'\frac{\bar{Q}_i\bar{Q}_j}{|X_i-X_j|}\,. \tag{3}$$

The last term gives the energy of interaction of the effective charges ($\bar{Q}$) setup in the unit cells at X_i and X_j as electrons are transferred from PBCO and YBCO. Since $Q_{Yi}=0$ in a neutral YBCO cell, $\bar{Q}_{Yi}=Q_{Yi}$, but in a neutral PBCO cell $Q_{Pi}=1$ and $\bar{Q}_{Pi}=1-Q_{Pi}$. The single summations go over the central supercell only, while the double summations must be extended until convergence is obtained. $\mathcal{E}_{NY,NP}$ is minimized subject to the charge-neutrality condition on a supercell, i.e.,

$$\sum_{i=1}^{N_Y} Q_{Yi} + \sum_{i=1}^{N_P} \bar{Q}_{Pi} = 0 . \tag{4}$$

For the purpose of determining the Q's, Eq. (3) can be parametrized with only two quantities. One of these was chosen to be $A \equiv (V_{cP} - V_{cY})/B$. The other is a parameter that allows the Coulomb sums to be evaluated in a simple approximate manner. It is apparent that if the $\bar{Q}_i$ were point charges located at the center of each cell, any contributions to the double sum could be expressed in terms of one over integer multiples of the lattice parameters X_c in the c direction. Since the X_c are essentially equal in YBCO and PBCO, a typical Coulomb term could be written as

$$\bar{Q}_i \bar{Q}_j / |X_i - X_j| = \bar{Q}_i \bar{Q}_j / X_c |n_i - n_j| \tag{5}$$

in an obvious notation. However, the Q's are not point charges but are distributed among the chain and CuO_2 planes in the manner already discussed above. To keep the simple structure of Eq. (5), a quantity C_{1nn} can be introduced so that

$$\bar{Q}_i \bar{Q}_j / |X_i - X_j| \simeq \bar{Q}_i \bar{Q}_j C_{1nn} / |n_i - n_j| . \tag{6}$$

C_{1nn} is the interaction energy between a distributed unit charge in one cell and a similar, but not identical, distribution in the first-neighbor cell. Clearly, C_{1nn} is not a constant and for Eq. (6) to be useful, C_{1nn} should be slowly varying as the charge distributions change within the range expected in the calculations. This was studied by calculating C_{1nn} for specific distributions. For those cases actually arising in the layered structures, it is unlikely that C_{1nn} varies by more than ~15% and hence it is reasonable to treat it as a single parameter.

Only two different values were allowed for both Q_Y and Q_P in the present calculations, i.e., Q_{Y1}, Q_{Y2} and Q_{P1}, Q_{P2}. This covers most cases of interest since it treats up to $N_Y=4$, $N_P=4$ exactly and all other cases to a good approximation. Q_{Y1} and Q_{P1} are always in first-nearest-neighbor cells, i.e., those forming the interface between YBCO and PBCO. Figure 3 shows the results for the calculation in which $N_P=16$ while N_Y is varied from 1 to 8, and Fig. 4 shows the results as N_Y is held fixed at the values indicated and N_P is varied. The experimental data are from Lowndes and co-workers.[13] The values of A and C_{1nn} (in units of B) are 1.22 and 0.56.

It is informative to consider the magnitudes of the Q's in some special cases. For $N_Y=1$, $N_P=1$ in Fig. 4, with the YBCO-PBCO sequence $\cdots PYPYPY \cdots$, $Q_{Y1} = \bar{Q}_{P1} = 0.318$. Each YBCO cell has acquired 0.318 electron from a PBCO cell and this is the maximum number of electrons a PBCO cell ever gives up in the layered structures. For $N_Y=1$, $N_P=2$, the sequence is $\cdots PPYPPYPP \cdots$ and $Q_Y=0.376$ but each PBCO cell gives up only 0.188 electron. For $N_Y=1$, $N_P=16$, the sequence is $\cdots P_2P_2 \cdots P_2P_1YP_1P_2 \cdots P_2P_2 \cdots$ and $Q_{Y1}=0.446$, $\bar{Q}_{P1}=0.115$, $\bar{Q}_{P2}=0.015$. Q_{Y1} is still well below 0.60, the approximate value at which $T_c \rightarrow 0$

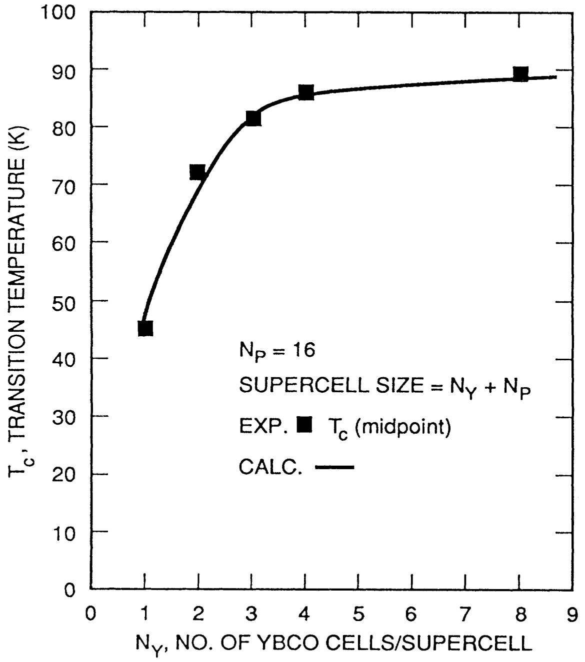

FIG. 3. Midpoint transition temperatures for layered structures with N_P held at 16 while N_Y is varied.

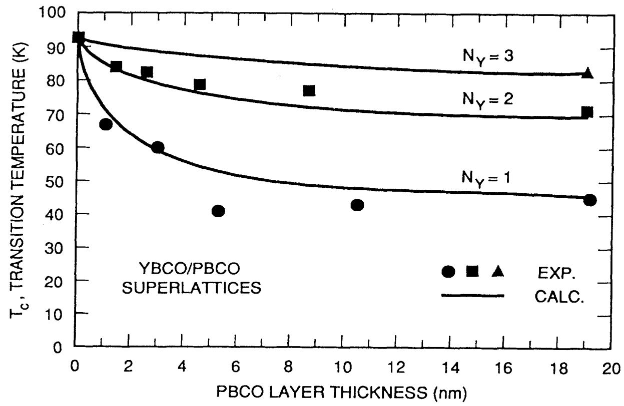

FIG. 4. Midpoint values of T_c for $N_Y=1$, 2, and 3 as N_P is varied.

K for the alloy. Thus, although the valence of Pr was assumed to be +4 initially, such an extreme value is not necessary for the alloys nor for the layered materials.

The calculations underlying Fig. 3 provide some other interesting insights. For $N_Y=1$ and 2 there are only Y_1 cells, while for $N_Y=3$, a Y_2 cell occurs (sequence $\cdots P_2P_2\cdots P_2P_1Y_1Y_2Y_1P_1P_2\cdots P_2P_2\cdots$), with $Q_{Y1}=0.312$ and $Q_{Y2}=0.231$. The concentration of holes in the CuO_2 planes of the Y_2 cell is well above that in the Y_1 cell and so the former goes superconducting before the latter. All YBCO cells that are added beyond $N_Y=3$ are isolated from the YBCO/PBCO interfaces and so T_c increases much less rapidly with increasing N_Y, giving rise to the kneelike shape of the curve.

Space limitations preclude further consideration of the details of the calculations and the results, but a few concluding remarks are needed. Neumeir *et al.*[3] interpreted their results on $(Y_{1-x-y}Ca_y)Pr_xCu_3O_{7-\delta}$ alloys as giving evidence for both hole filling and pair breaking. Although it was unnecessary to introduce pair breaking here, it also cannot be ruled out. Further refinements and extensions of the experimental work on layered systems, especially those containing Ca, will be very useful in this connection. As for the spin-polaron mechanism, it may be that other pairing mechanisms, together with appropriate densities of states, can lead to curves resembling those of Fig. 1 and no claim of uniqueness is made. Regardless of what the pairing may be within a single CuO_2 plane or in a unit cell, the results given here strongly suggest that pairing interactions *between* unit cells are not the origin of the high-T_c values in the copper-oxide superconductors.

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[12] The second of Eqs. (1) does not hold for all cells, but for most important cases, e.g., $N_Y=1$, $N_Y=3$, etc.; it either does or should be a good approximation.

[13] I would like to thank these authors for providing data in a form not appearing in their paper cited in Ref. 2. I would also like to thank Li *et al.*, Ref. 2, for a preprint of their work. Limited fitting of the data therein was attempted with good results.