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Particle-hole doping asymmetry in $Pb_2Sr_2YCu_3O_8$-class superconductors

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Charge transfer in $Pb_2Sr_2YCu_3O_8$ (PSYCO) compounds is evaluated using the self-consistent bond/charge model. When Ce^{+4} or Am^{+4} replaces Y^{+3}, the resulting *n*-type material does not superconduct. When the rare-earth replacing Y is trivalent (e.g., Y^{+3}, Tb^{+3}, or Pr^{+3}) and the PSYCO compound is doped *p* type (e.g., with >15% Ca), PSYCO exhibits superconductivity. This lack of *n-p* doping symmetry is inconsistent with most cuprate-plane models of high-temperature superconductivity, but is consistent with oxygen models.

I. INTRODUCTION

The compound PSYCO ($Pb_2Sr_2YCu_3O_8$) (Refs. 1–3) is structurally similar to $YBa_2Cu_3O_7$ (Y123-7), except that (i) its Ba ions are replaced by isoelectronic Sr ions, and (ii) its CuO chain layers are replaced by /PbO/Cu/PbO/ layers in the crystal structure[2–7] (Fig. 1[8,9]). Pure PSYCO homologues themselves probably[10,11] do not superconduct, but the PSYCO compounds with *trivalent* rare-earth ions do superconduct[1,2,7] with T_c in the range of 50–84 K,[9,11,12] when the rare-earth site is doped with more than 0.15 Ca.[13]

Here we consider PSYCO to be the compound without oxygen in its Cu^{+1} layer, and with eight oxygen ions total, while recognizing that between 8 and 9.4 oxygen have been observed per unit cell, with much of the extra oxygen adjacent to the Cu^{+1}.[14–17]

The conventional cuprate-plane viewpoint is that the charge-reservoirs dope its cuprate-planes (CuO_2 layers) with holes or electrons, causing these planes to superconduct, with critical temperatures in the range of 50 to over 80 K.[12] The combination of PSYCO's /PbO/Cu/PbO/ layers and its SrO layers are its charge reservoirs. Hole doping occurs for most rare earths, namely the trivalent ones, for modest amounts of Ca^{+2} co-doped with the $(\text{rare-earth})^{+3}$ ions, but electron doping is associated with rare-earth ions Ce^{+4} or Am^{+4} [even *n*-type material can be co-doped with as much as ≈30–50 % Ca^{+2} (Ref. 13)]. The *n*-type materials should superconduct in the cuprate-plane models.

Opposing this conventional viewpoint is the charge-reservoir oxygen picture,[18–23] which assigns the primary superconductivity to the charge-reservoir layers, rather than to the cuprate planes, and only allows holes as carriers of cuprate superconductivity. In this model, trivalent rare-earth ions co-doped with as little Ca^{+2} as 0.15 should produce *p*-type superconductivity, but tetravalent rare-earth ions, whether co-doped with Ca^{+2} or not, should not produce superconductivity, because the material is *n* type.

PSYCO represents a wonderful comparative testing ground for these two models, since it can be doped (i) by different rare-earth ions than Y, including Ce (which assumes the +4 ionic state[24]) and actinide Am [which also is +4 (Ref. 24)], as well as by such rare-earth ions as Tb and Pr [which are both +3 (Ref. 24)], and (ii) with Ca^{+2} partially replacing Y^{+3}.[25] This allows continuous variation of the doping on the rare-earth sites from *p* type to *n* type. We predict that only the *p*-type materials superconduct in the charge-reservoir oxygen model. Since both *n*-type and *p*-type materials superconduct in the cuprate-plane model, analyses of potential *n*-type superconductors should reveal if a cuprate-plane model or a charge-reservoir model is appropriate for high-temperature superconductivity.

II. PARTICLE-HOLE SYMMETRY IN PSYCO

In a charge-reservoir oxygen model,[19,21] the *pure* compounds $Pb_2Sr_2RCu_3O_8$, where *R* is a *trivalent* rare-earth ion, should not superconduct because their ionic charges all balance when O is assumed to be O^{-2}; they apparently do not

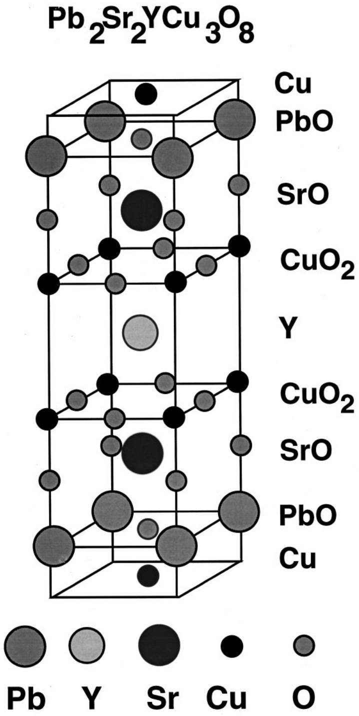

FIG. 1. Crystal structure of $Pb_2Sr_2YCu_3O_8$.

TABLE I. Bond-valence-sum charges (in units of $|e|$) and Madelung potentials (for ideal integral valences) (in V) for $Pb_2Sr_2YCu_3O_3$ (PSYCO), extracted from the data of Ref. 2, and computed using the self-consistent bond/charge method (Ref. 21). The absolute values of the ionization potentials (Ref. 32) of the relevant ions are listed in the last column (in V), with the final charge-state of the ionization process. Clearly the cations are in the charge-states Pb^{+2},Sr^{+2},Y^{+3},Cu^{+2} (in the cuprate-plane), and Cu^{+1} (in the charge-reservoir). The oxygen anions are all nearly O^{-2}. The holes are mainly in the SrO and PbO layers. On the Y site, all rare-earth ions will be in the $+3$ charge state, except Ce, which will be Ce^{+4}. Actinide Am may also be in the $+4$ charge-state, because its ionization potential to Am^{+4} is between 36.76 V and 38.98 V. (The fact that it is Am^{+4} indicates that its ionization potential is between 36.76 V and 37.85 V, the Madelung potential.)

Site	Charge	Potential	Ionization potentials
Pb	2.00	-16.25	15.03(+2), 31.94(+3), 42.32(+4)
Sr	1.63	-25.99	11.03(+2), 42.89(+3)
Y	2.83	-37.87	12.24(+2), 20.52(+3), 60.60(+4)
Cu in charge-reservoir: Cu(1)	1.17	-6.74	7.73(+1), 20.29(+2), 36.34(+3)
Cu in cuprate plane: Cu(2)	2.24	-34.62	
O in CuO_2 layer: O(1)	-2.06		
O in Sr layer: O(2)	-1.82		
O in Pb layer: O(3)	-1.64		

superconduct when their ionic charges all balance, namely when they are pure and undoped.[26]

The introduction of Ca^{+2} to the *trivalent* rare-earth sites of these PSYCO compounds should lead to an average valence on the rare-earth site between $+3$ and $+2$ and to *p*-type conductivity and superconductivity (for Ca doping >0.15). In *both* the charge-reservoir oxygen picture and in the cuprate-plane picture, Ca-doped PSYCO compounds with *trivalent* rare-earth ions are expected to superconduct—and do.

For *tetravalent* rare-earth ions *R*, such as Ce^{+4} or Am^{+4}, both of which prove to be stable ionic charge-states in at least Ce-PSYCO and Am-PSYCO compounds, the cuprate-plane picture predicts that Ca-doped $Pb_2Sr_2RCu_3O_8$ will be *n* type and will superconduct, while the charge-reservoir oxygen model predicts that such *n*-type $Pb_2Sr_2RCu_3O_8$ cannot superconduct (for $R=Ce^{+4}$ or Am^{+4}), even if heavily doped with Ca^{+2}. (Ce^{+4} and Am^{+4} have ionization potentials of 36.76 V and perhaps about 1 V more, respectively, while the Madelung potential at the rare-earth site is approximately 37.85 V.[27,28])

In contrast to the charge-reservoir oxygen model, all cuprate-plane theories that feature particle-hole doping symmetry assume that the *n*-type, electron-doped materials will superconduct, especially if the corresponding *p*-doped materials also superconduct. This is what is meant by particle-hole doping symmetry: both the *n*-type and the *p*-type materials will superconduct, provided the number of carriers is sufficient. Hence all cuprate-plane models with particle-hole doping symmetry predict implicitly that $Pb_2Sr_2RCu_3O_8$ compounds will superconduct *n* type for $R=M_{1-x}Ca_x$, where *M* is any *tetravalent* rare-earth or actinide ion (e.g., Ce^{+4} or Am^{+4}).

Experimentally, the particle-hole doping symmetry expected of a cuprate-plane model does not occur for *n*-doped cuprate-planes, as in $Pb_2Sr_2RCu_3O_8$ with $R=Ce^{+4}$ or Am^{+4}. Instead, these materials behave as expected in a charge-reservoir oxygen model: the *p*-type materials superconduct, and the *n*-type materials do not. Further investigation of this point is needed, because, if it is true, then the major theoretical picture of high-temperature superconductivity, the cuprate-plane model, is wrong: there is no particle-hole doping symmetry in the $Pb_2Sr_2RCu_3O_8$ experiments.

III. BOND VALENCE SUM METHOD

In order to verify that our statements about the sizes of ionic charges of PSYCO are valid, we executed bond valence sum computations[29] of the ionic charges. The bond valence sum method follows the empirical chemical binding ideas of Pauling:[30] the charge on the σth ion is a function of both (i) the bond lengths $|\mathbf{r}_{\sigma',\sigma}|$ to those neighboring ions (σ') directly bonded to the σth ion and (ii) the site occupancies $w_{\sigma'}$, according to the expression[29,31]

$$|Q_\sigma|=|e|\Sigma_{\sigma'}w_{\sigma'}\exp\{[R_\sigma-|\mathbf{r}_{\sigma',\sigma}|]/\beta\},$$

where one has $\beta=0.37$ Å, and the parameters R_σ are known in terms of the bond lengths of many chemical compounds—see the tabulation of Ref. 31. Therefore using a table of ideal bond lengths, it is straightforward to extract ionic charges from neutron diffraction data—with a typical absolute accuracy of $\approx\pm0.1|e|$.

Results obtained by applying the self-consistent bond/charge model[21] to PSYCO are presented in Table I,[32] and are similar to those reported previously for various PSYCO compounds.[9]

To an adequate approximation, PSYCO contains Pb^{+2}, Sr^{+2}, Y^{+3}, cuprate plane Cu^{+2}, Cu-layer Cu^{+1}, and oxygen ions in the SrO, PbO, and CuO_2 layers, which are all nearly O^{-2}. The oxygen ions in the PbO layers and the SrO layers are somewhat electron deficient, however, being hypocharged: O^{-Z}, where we have $Z<2$: $Z=1.64$ and 1.82 for the PbO and SrO layers, respectively. In the PSYCO compounds, the demonstration that there are holes in the vicinity of the oxygen in the PbO and the SrO layers is afforded by the fact that in these layers, the oxygen ions have too few electrons, when the simple valence rules would have them be O^{-2} (see Table I). As expected, the charge reservoirs in

PSYCO are in the vicinity of the PbO layers, where the hypocharged $O^{-1.64}$ is found, and quite possibly also in the SrO layers, where oxygen ions are charged to $O^{-1.82}$. This means that there are 0.36 holes per oxygen ion in the PbO layer, for example.

Although $Pb_2Sr_2Y_{1-u}Ca_uO_x$ (doped PSYCO) is known to experience a wide variety of oxygen concentrations, ranging from $x \approx 8$ to about $x \approx 9.4$ per unit cell,[14–17] most of the oxygen ions beyond $x = 8$ end up in the /PbO/SrO/PbO/ charge-reservoir layers (about 8 Å from the rare-earth site), where they may change the valences of the cations Pb or Cu (e.g., $Pb^{+2} \rightarrow Pb^{+4}$ or $Cu^{+1} \rightarrow Cu^{+2}$). (Room for O^{-2} is lacking in the layers closer to a rare-earth ion.) Such cation doping in the charge-reservoir layers of PSYCO normally *decreases* T_c while possibly removing the affected cations from the superconducting condensate. If we assume (incorrectly) that these oxygen ions are uncompensated by a higher valence cation such as Pb^{+4}, a singly charged ion provides an additional voltage of only ~1.7 V at the rare-earth site. With compensation by other defects in the charge-reservoir layers, the net voltage at the rare-earth site is further reduced so that the rare earth is not significantly altered (being still at a site with a voltage of about 36.8–37.8 V for Ce and Am). Therefore, despite considerable uncertainties in the data and variations both in the oxygen content and in T_c, PSYCO should still superconduct in its /PbO/SrO/PbO/ layers, because the main superconductor in this and all high-temperature cuprate superconductors is hypocharged oxygen.

IV. THE TRIPLET STATE OF Pr

Soderholm *et al.*[24] identify the ground state of Pr in Pr-PSYCO($Pb_2Sr_2PrCu_3O_8$) as a triplet state, as found also in $PrBa_2Cu_3O_7$, but not as found in $Pr_{2-z}Ce_zCuO_4$, which has a singlet ground state. All of these three materials superconduct. This means that the magnetic state of the rare earth does not play a major role in determining whether the material superconducts. It also implies that the usual models of hybridization in $PrBa_2Cu_3O_7$, which involve coupling of the cuprate-plane oxygen to the Pr, are not generally valid for explaining either the occurrence or nonoccurrence of high-temperature superconductivity.

V. ALL HIGH-TEMPERATURE SUPERCONDUCTORS ARE *p* TYPE

In summary, the superconducting PSYCO compounds are all *p* type, and superconduct in the charge reservoirs, which are mainly in the PbO layers, and perhaps also in the SrO layers. The Sr-O bonds are stretched, and dopant oxygen can sometimes be found in the Cu layers (which complicates analyses of the structure). The $Pb_2Sr_2R_{1-x}Ca_xCu_3O_8$ structure is rigid enough that pair breaking defects such as Pr_{Sr} defects are rather rare, and the PSYCO materials appear to be natural superconductors of rather high T_c.

These findings complement the demonstration that perfect $Nd_{2-z}Ce_zCuO_4$ also lacks particle-hole doping symmetry,[19] and has Ce in the Ce^{+3} charge state rather than the Ce^{+4} required for *n*-type doping.[21] Instead Ce appears to form $(Ce, O_{\text{interstitial}})$ pairs,[19,20,22,33] which makes $Nd_{2-z}Ce_zCuO_4$ a *p*-type superconductor.[34–36]

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[28] Upon further consideration, it may seem that substitution of Ca^{+2} for $(\text{rare earth})^{+3}$ would tend to drive the potential at the remaining rare-earth locations more negative, yielding, for example, Pr^{+4} or Tb^{+4}. However, the hole produced by this substitution migrates to adjacent oxygen ions, raises the potential at the rare-earth site, and makes the trivalent state more stable than prior to the substitution.

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