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Linear Electron-Hole-Electron Pair Model of High-Temperature Superconductivity in $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$. 2. Dependence of the superconducting transition temperatures on pressure and on hole concentration.

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Abstract (For Chemical Abstract use only)

On the basis of the linear electron-hole-electron (e-h-e) pair model, we discuss how the number of holes (i.e., formal Cu^{3+} sites), and an applied pressure, affect the superconducting transition temperatures T_c of $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ and $\text{LBa}_2\text{Cu}_3\text{O}_{7-y}$ ($L = \text{Y, Sm, Eu, Gd, Dy, Ho, Yb}$). We also examine the origin of the plateaus in the T_c vs oxygen content plot of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ within the framework of the linear e-h-e pair model.

Sir:

To provide a systematic rationale for understanding the properties of the high-temperature superconductors $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($\text{M} = \text{Ba}, \text{Sr}$) and $\text{L}\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ ($\text{L} = \text{Y}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}, \text{Ho}, \text{Yb}$), we proposed the linear electron-hole electron (e-h-e) pair model in the previous paper.² This model reconciles several important observations that phonons play an important role in the electron-pairing of the copper oxide superconductors,³⁻⁶ that Cooper pairs of those superconductors are small,⁷ that in $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ the copper atoms of both the CuO_2 layers and the CuO_3 chains participate in electron-pairing,⁸ that the 93 K superconductivity of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ might involve Cooper pair formation across the $\text{Cu}2\text{-O}4\text{-Cu}1\text{-O}4\text{-Cu}2$ linkages,⁹ and that mixed-valence fluctuations¹⁰ in a linear $\text{Cu}^{2+}\text{-O-Cu}^{3+}\text{-O-Cu}^{2+}$ unit coupled with its concerted breathing-mode vibration can induce the two electrons confined in such a unit to effectively move as an entity.² On the basis of the linear e-h-e pair model, we examine in the present work how the number of holes,¹¹ and an applied pressure,¹² influence the superconducting transition temperature T_c of the copper oxide superconductors, and discuss the origin of the plateaus in the T_c vs oxygen content plot of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$.^{9,13}

Dependence of T_c on n_H . According to the linear e-h-e pair model,² atoms involved in the pairing must undergo concerted breathing-mode vibrations. However, atoms not involved in the pairing are not constrained in their vibrational modes, and hence may engage in certain vibrational modes that disrupt linear e-h-e

pairing. Such pair-breaking vibrations are generally suppressed by lowering the temperature of a crystal lattice. If more holes are present in the lattice, more atoms are involved in linear e-h-e pairing, and fewer atoms remain to provide pair-breaking vibrational modes. Consequently, a crystal with more holes requires less cooling to suppress the pair-breaking vibrational effect thereby leading to a higher T_c value. This accounts for why the T_c of $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ is observed to increase almost linearly with the number of holes, n_H , for $x \simeq 0.05-0.15$.¹¹

Dependence of T_c on pressure. The copper oxide superconductors have 'two-dimensional' layered structures, so an applied pressure will exert its strongest effect along the direction perpendicular to the CuO_4 layers in $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ and perpendicular to the $\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ slabs in $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ (See Ref. 16a, p. 1831). The CuO_4 layers of $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ are made up of axially elongated CuO_6 octahedra by sharing their equatorial oxygen atoms (O_{eq}). The axial oxygen atoms (O_{ax}) of each CuO_6 octahedron have short contacts with La^{3+} cations (and with M^{2+} cations at La^{3+} sites as well) along the $\text{Cu}-\text{O}_{ax}$ bond direction to form linear $\text{La}\cdots\text{O}_{ax}-\text{Cu}$ units perpendicular to the $\text{Cu}(\text{O}_{eq})_2$ plane.¹⁴ Thus an applied pressure along the $\text{La}\cdots\text{O}_{ax}-\text{Cu}$ units will help suppress the vibrational modes arising from the $\text{Cu}-\text{O}_{ax}$ bond stretching.¹⁵ Electronic structure studies^{9b,16} on the copper oxide superconductors show that the half-filled x^2-y^2 level of each Cu^{2+} site, or the empty x^2-y^2 level of each Cu^{3+} site, of the CuO_4 layer has no orbital contribution from the O_{ax} atoms. Thus, only the concerted breathing-mode vibrations associated with the $\text{Cu}(\text{O}_{eq})_2$ plane are essential for linear e-h-e pairing, and

the vibrational modes of the Cu-O_{ax} bond stretching will disrupt linear e-h-e pairing. Since this pair-disrupting effect can be suppressed by an applied pressure, $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ requires less cooling to reach a superconducting state thereby leading to a higher T_c under an applied pressure than under ambient pressure. This explains why the T_c of $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ increases substantially with an applied pressure (i.e., $dT_c/dp = 0.64 \text{ K/kbar}$).¹²

Consider now why the T_c of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ is only slightly affected by pressure (i.e., $dT_c/dp = 0.04 \text{ K/kbar}$).¹² The crystal structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ shows¹⁷ that the capping oxygen atom O4 of each $\text{Cu}_2\text{-O}_4$ unit, aligned perpendicular to the CuO_2 layers, does not make any contact with Y^{3+} or Ba^{2+} along the direction of the $\text{Cu}_2\text{-O}_4$ unit. Thus, the $\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ slabs of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ may not possess such pair-breaking vibrational modes as those present in the CuO_4 layers of $\text{La}_{2-x}\text{M}_x\text{CuO}_4$. Therefore linear e-h-e pairing in the CuO_2 layers will be only slightly affected by pressure. Since an applied pressure will decrease the $\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ slab thickness and hence the $\text{Cu}_2\text{-O}_4\text{-Cu}_1\text{-O}_4\text{-Cu}_2$ linkage distance, we may speculate how linear e-h-e pairing in the linkage might be affected by pressure under the assumption that an applied pressure, and temperature lowering, have a similar effect on the crystal structure. Upon lowering the temperature from 298 to 5 K, the long $\text{Cu}_2\text{-O}_4$ distance decreases ($2.298 \text{ \AA} \rightarrow 2.264 \text{ \AA}$), but the short $\text{Cu}_1\text{-O}_4$ distance increases ($1.846 \text{ \AA} \rightarrow 1.855 \text{ \AA}$).^{17a} Therefore, an applied pressure will significantly change neither the vibrational modes associated with the O4 atom movement along the $\text{Cu}_1\text{-Cu}_2$ axis nor the linear e-h-e pairing in the $\text{Cu}_2\text{-O}_4\text{-Cu}_1\text{-O}_4\text{-Cu}_2$ linkages.

Plateaus of the T_c -vs-oxygen-content plot in $YBa_2Cu_3O_{7-y}$. The origin of the plateaus in the T_c vs oxygen content plot of $YBa_2Cu_3O_{7-y}$ ($T_c \simeq 93$ K for $y \simeq 0.15-0.25$; $T_c \simeq 55$ K for $y \simeq 0.4-0.5$)^{9,13} may now be explained. The distance of the Cu2-04-Cu1-04-Cu2 linkage increases with increasing y ,⁹ which is unfavorable for linear e-h-e pairing to occur across the linkage even if a hole is present in it. Thus the lower plateau at $T_c \simeq 55$ K might mean that linear e-h-e pairing occurs only within the CuO_2 layers.⁹ This proposal is consistent with our explanation of why the T_c of $YBa_2Cu_3O_{7-y}$ is nearly insensitive to pressure: The linear e-h-e pairing in the CuO_2 layers is not under the influence of such pair-breaking vibrations as the Cu-O_{ax} stretching modes in the CuO_4 layers of $La_{2-x}M_xCuO_4$. Effectively, the T_c associated with linear e-h-e pairing in the CuO_2 layers of $YBa_2Cu_3O_{7-y}$ should be similar to the T_c of $La_{2-x}M_xCuO_4$ under pressure in which the pair-breaking effect of the Cu-O_{ax} stretching vibrations is suppressed. In fact, the T_c of $La_{2-x}M_xCuO_4$ is ~ 53 K under ~ 12 kbar,^{12b} close to the T_c of the lower plateau in $YBa_2Cu_3O_{7-y}$.

Within the linear e-h-e pair model,² the observation of nearly constant T_c , which defines each plateau region, implies that the number of holes does not significantly change for the range of different y values in that region. In stoichiometric $YBa_2Cu_3O_7$, all the Cu1 atoms of the CuO_3 chains (1) are tetragonal four-coordinate (2). As the oxygen atoms O1 are removed, the CuO_3 chains are broken thereby leading to T-shape three-coordinate (3) and/or linear two-coordinate (4) Cu1 sites. According to electronic structure studies on $YBa_2Cu_3O_{7-y}$,^{9b,16} it is most likely that the oxidation state of

the Cu2 atom is +2, while that of the Cu1 atom is +3 for 2 but +1 for 3 and 4. Suppose that removal of the O1 atoms generates only three-coordinate Cu1 sites 3 (Case_1). Since removal of one O1 atom produces two three-coordinate Cu1 sites leaving behind only two electrons, for these two Cu1 sites to achieve the Cu⁺ state, two additional electrons must be received from the CuO₂ layers. Therefore, removal of one O1 atom destroys two holes in the CuO₃ chains but creates two holes in the CuO₂ layers. This explains how the total number of holes in YBa₂Cu₃O_{7-y} can remain unchanged for a range of different y values.

Case_1 is relevant for small y, when more holes are present in the CuO₃ chains than in the CuO₂ layers. Then the upper plateau at T_c 93 K, for example, is dominated by linear e-h-e pairing in the Cu2-O4-Cu1-O4-Cu2 linkages. Therefore the two different ⁶³Cu nmr spin-relaxation times observed for YBa₂Cu₃O_{7-y}⁸ may mean that there is one pairing energy set primarily by the linear e-h-e pairing in the Cu2-O4-Cu1-O4-Cu2 linkages, and the Cu1 and Cu2 atoms in each linear e-h-e pair have different spin-relaxation times due to their different environments.

Removal of the O1 atoms in YBa₂Cu₃O_{7-y} may generate both three-coordinate sites 3 and two-coordinate sites 4 (Case_2), which is a good approximation for large y. Case_2 allows the CuO₂ layers to be free of holes if the numbers of Cu³⁺ and Cu⁺ sites in the Cu1 atom plane ([Cu³⁺] and [Cu⁺], respectively) maintain the ratio [Cu³⁺]/[Cu⁺] = (1-y)/y.^{9a} Such a case is relevant in understanding the nonsuperconducting and semiconducting properties of YBa₂Cu₃O_{7-y} (y > 0.5).^{9a}

As discussed above, the linear e-h-e pair model provides a systematic rationale for understanding the properties of the copper oxide superconductors. In view of its apparent success, the linear e-h-e pair model deserves further experimental verification and quantitative theoretical development. It will be interesting to perform ^{63}Cu nuclear spin-relaxation measurements on $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ as a function of its oxygen content covering both the upper and lower plateaus in the T_c vs. oxygen content plot.

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