

Two-component superconductivity. II. Copper oxide high- T_c superconductors

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A systematic relationship between the Cu-O-based high- T_c materials and a two-component theory is developed. The two components are mobile-single-particle states associated with Cu-O planes and localized paired (negative- U) states associated with oxygen vacancies. The focus is on identification of the relevant electronic states in theoretical calculations and experimental observations. The family of Cu-O-based materials is discussed and an understanding is developed of the implications of layering and dimensionality, oxygenation, and doping. The relationship to superconducting properties is developed through the pair-density dependence and single-particle-density dependence of superconductivity. Comparisons with existing experimental data are made, distinctive experimental results are predicted. New directions for finding high- T_c materials are suggested both within the Cu-O-based family and in the more general class of materials which share with the Cu-O-based family the structure of metal-semiconductor layering and can be formed with off-stoichiometric compositions.

I. INTRODUCTION

In an earlier article¹ henceforth referred to as (paper I) a two-component theory of superconductivity was developed including a description of basic phenomenology. Superconductivity arises in the two-component theory through the joint action of two kinds of electronic states—localized paired states and extended mobile states. The hybridization of these states allows both mobility and pairing to combine. The phenomenology is quite different from the phenomenology of conventional BCS superconductivity and many promising comparisons with the phenomenology of Cu-O high- T_c superconductors were made. In this paper, emphasis is placed on understanding general trends and specific aspects of the family of Cu-O high- T_c materials in light of the two-component theory. The starting point is the proposal that experiments on Cu-O high- T_c materials can be understood if (1) locally paired states are associated with oxygen vacancies in Cu-O planes and (2) mobile single-particle states, are associated with Cu-O planes. Here, it is shown that electronic structure calculations and experiments reveal direct contact with the states needed in the two-component theory. Further theoretical discussion emphasizes the dependence of material property variation through the family of high- T_c materials. Emphasis is placed on understanding the effect of the oxygen vacancy concentration, doping, and layering. While it is shown that a variety of experiments can be understood using the starting point identification of electronic states, this identification must be viewed as tentative and key experiments and theoretical calculations are needed to verify or modify the identification of the essential electronic states in these materials.

I. LAYERING AND DIMENSIONALITY: METAL/SEMICONDUCTOR LAYERED STRUCTURES

Aside from the high T_c itself, the most noted feature of Cu-O-based superconductors is their layered or two-

dimensional structure. In the two-component theory the layering is a practical rather than fundamental aspect of the superconductivity, it establishes the environment for the two different types of electronic states. The two different types of electronic states are consistent with two kinds of electronic environments. Extended mobile states are associated with metals. Localized negative- U states are associated with defects in semiconductors. If the regions between the Cu-O layers are characterized, they should indeed be considered as semiconductor layers. As extensively discussed in the literature, they are essentially insulating, and can be doped. This doping is usually described by considering them as a reservoir of electrons for the metallic Cu-O layers. Thus, the Cu-O-based materials may be characterized as layered metal-semiconductor structures. This is directly reminiscent of metal-semiconductor alloys which motivated the introduction of theoretical work on negative- U impurity enhanced superconductivity.²⁻⁶ Significantly, supporting evidence for this theory was experimental evidence for a Fermi-energy dependence to the superconductivity also found in Cu-O-based superconductors. Much of this work expected that disorder was essential for the superconductivity. The existence of disorder in the Cu-O-based superconductors may yet show that this is correct.⁷ However, as described in paper I, in the two-component theory the superconductive properties do not appear to be directly linked to disorder. Whether disorder plays a role or not, this perspective implies a much more active role for the semiconductor layers in the superconductivity. Implications for the search for new high- T_c materials⁵ are discussed below.

Since the layering is not an intrinsic aspect of the superconductivity, three-dimensional structures may be directly included within this family of materials. However, the increased difficulty in having mobile states in a three-dimensional material may be understood. Essentially, the mobile states must travel around the semiconductor islands on an atomic scale, while these islands

must be sufficiently semiconductorlike to lead to localized states. A possible realization of a three-dimensional two-component superconductor is the high- T_c material $\text{Ba}_{1-x}\text{K}_x\text{O}_{3-\delta}$.⁸ It shares many of the phenomenological properties discussed in paper I of the Cu-O-based high- T_c materials. A negative- U theory for this material based on the local states of Bi atoms has been proposed.⁹ A two-component theory may also apply with negative- U paired states associated with vacancies.

The primary layering of metal and semiconductor layers is further complicated in many Cu-O-based materials, such as $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, by a secondary layering which breaks the symmetry between Cu-O layers. This symmetry breaking in these materials leads to much higher T_c because the defects responsible for the localized states are also disrupting the mobile states. Separating complete layers of the mobile states from layers with the defects leads to higher T_c .

It appears that a tertiary layering is also present in the Bi, Tl systems. These materials have layers which are metallic but not Cu-O based interleaved with Cu-O layers. These metallic layers serve in part as additional conductive states, a tertiary layering with an additional metallic system.

II. ELECTRONIC STATES

The nature of the electronic states required for the two-component theory is quite distinctive. Their signature should be found in both theoretical calculations and experiment. In theoretical electronic state calculations both a broad band and localized states (a flat band) are indeed found crossing or near the Fermi energy (Fig. 1). In experiment, signatures of a negative- U state in single particle excitations—empty and filled states equally displaced away from the Fermi energy—are also found in photoemission and inverse photoemission (Fig. 2). Predictions can be made for the behavior of both the experimental observations and theoretical calculations in further investigations.

A. Identification of mobile and paired states in theoretical calculations

Two kinds of electronic states in Cu-O based high- T_c superconductors: mobile states in the Cu-O plane and localized states at oxygen vacancies can be seen from detailed theoretical calculations^{10,11} and understood from tight binding arguments. Calculations show that Cu-O planes in the Cu-O-based superconductors, near the Fermi energy, are responsible for a single dispersive band. This band is the highest-energy combination of Cu d orbitals and O p orbitals. Introducing an oxygen vacancy into a Cu-O plane results in a localized orbital near the Fermi energy.¹⁰ In $\text{YBa}_2\text{Cu}_3\text{O}_7$ the chains of vacancies give rise to a flat band corresponding to one localized state per unit cell associated with the Cu-O chains.¹¹

The bands near the Fermi energy of Cu-O-based superconductors are composed of the highest antibonding or-

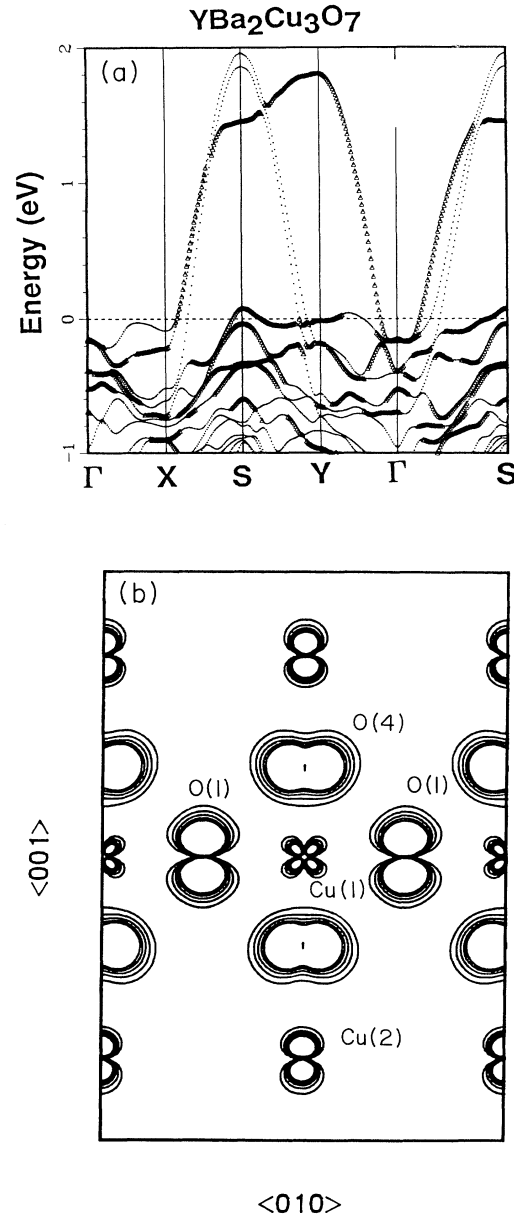


FIG. 1. Top: electronic states of $\text{YBa}_2\text{Cu}_3\text{O}_7$ from single-particle fixed-atom band-structure calculations taken from Ref. 11 (with permission from the author). Darker lines are associated with the Cu-O chains. This shows both the mobile states which cross the Fermi energy and the localized states which are manifest in a flat band near the Fermi energy. The actual transitions of the flat band which are to be associated with the oxygen vacancies are different from the single-particle transitions of this figure because of the assumed negative U . Two-particle transitions are at the Fermi energy, single-particle occupations are higher in energy. The related single-particle transitions are illustrated in Figs. 2 and 3. Bottom: charge density associated with the localized band of states at the Fermi energy showing the small Cu d and large O p character of these orbitals; O(1) and Cu(1) are the chain atoms, O(4) lies above and below the chain (reproduced from Ref. 11 with permission from the author).

bitals of Cu and O atoms. The highest levels of a complete Cu-O plane are the in-plane antibonding orbitals consisting of Cu $d_{(x^2-y^2)}$ and d_{xy} orbitals and oxygen p orbitals. The Cu $d_{x^2-y^2}$ -O $p_{x,y}$ antibonding orbital crosses the Fermi energy and is the dispersive band responsible for the mobile electrons in the two-component theory. The Cu d_{xy} orbital antibonding to the O $p_{x,y}$ orbitals is below the Fermi energy.

The electronic state of an oxygen vacancy, as for many defects, resides on neighboring atoms. The removal of a single oxygen atom in a plane leads to out of the plane antibonding orbitals being the highest energy. For an oxygen vacancy on an x -direction bond the antibonding (z,y) plane orbitals are highest. Cu $d_{z^2-y^2}$ can hybridize with the plane orbital, but the d_{zy} orbital is antisym-

metric with respect to the plane and does not hybridize with the highest energy orbitals of the complete plane. Therefore, this is a localized state found from calculations to be near the Fermi energy. The energy of this orbital should depend sensitively on the Cu-O distance above and below the plane. Such sensitivity may lead to a negative- U since a change in occupation of the orbital would result in a large change in location of the oxygen atoms above and below the plane. It is precisely these oxygen atoms which have the largest position uncertainty "thermal" ovals in neutron or x-ray diffraction in both $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-\delta}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (see discussion of isotope shift in paper I, III F). There are two Cu atoms adjacent to the oxygen vacancy, thus two localized orbitals should be formed. Without any symmetry breaking these orbitals are degenerate if they are weakly coupled to each other. A local pairing relaxation is thus reminiscent of a Jahn-Teller distortion. However, if they are weakly coupled these orbitals act independently, so that unlike a Jahn-Teller distortion, the pairing relaxation of one does not exclude the pairing relaxation of the other. If they are more strongly coupled they hybridize and act jointly.

The oxygen vacancy in the plane appears to be the natural candidate for introducing the negative- U localized state because of the importance of orbitals which lie perpendicular to the plane. It is also possible to suggest that an oxygen vacancy above or below the plane in the "semiconductor" layer (apical oxygen) may also introduce a localized state associated with the Cu d_{xy} and oxygen p orbitals in the plane. This state has not, to my knowledge, been calculated. In support of this second possibility one experiment has suggested that out-of-plane oxygen p orbitals are not empty at the Fermi energy in $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n-\delta}$.¹² (This experiment should be reevaluated in the context of shifts in excitations for negative- U states discussed below.) Since the local atomic environment of a Cu in the two different oxygen vacancy cases is the same, it is conceivable that similar states are generated in each case. The consideration of local environment, however, neglects the orbital symmetry with respect to the rest of the plane.

In $\text{YBa}_2\text{Cu}_3\text{O}_7$ a chain of oxygen vacancies exists. The narrow band at the Fermi energy which resides on the chain of Cu-O (Fig. 1) is consistent with an orbital composed of antibonding Cu d_{zy} and O p . The calculations further show that the amplitude on the Cu d orbitals is very small being predominantly O p .¹¹ This band has some dispersion along the chain due to hybridization. It might be possible to argue that localized states arise only from disruptions of the chain (either filling in vacancies or taking out chain O). This approach is not adopted here. Calculations which include the effect of structural relaxation are necessary to understand the details of the electronic state properties.

Calculations which have been performed to date have not included the effect of structural relaxation on the energy or dispersion of the flat band in $\text{YBa}_2\text{Cu}_3\text{O}_7$, or of states associated with isolated oxygen vacancies. The total energy calculations^{13,14} which must be performed to determine the relaxed position of atoms at a defect and

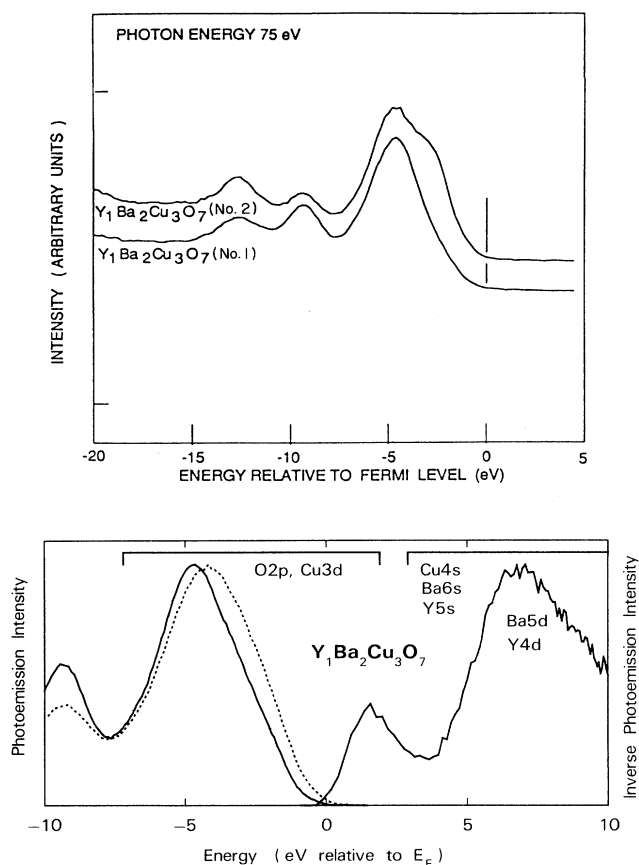


FIG. 2. Photoemission (PE) (top) and inverse photoemission (bottom, with PE) from $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ showing an O p -related shoulder 2.2 eV below the Fermi energy and a peak in the unoccupied oxygen p states 1.5–2 eV above the Fermi energy. These apparent empty and filled single-particle states are tentatively identified as being associated with the oxygen-vacancy-related localized negative- U states shown in Fig. 1 whose two-electron transition is at the Fermi energy (see Fig. 3 and text). The variability of the peaks with oxygen content has been noted as illustrated in the top photoemission figure showing two different samples. [Adapted from Ref. 32 (top) and Ref. 37 (bottom), with permission from the authors.]

the related electronic state changes are much more demanding computationally than the fixed atomic position electronic state calculations thus far reported.

In addition to introducing a localized state near the Fermi energy, the presence of an oxygen vacancy or a chain of oxygen vacancies disrupts the electronic states of the planes. Even though the adjacent Cu atoms still participate in the mobile states through their $d_{(z^2-y^2)}$ the x direction transport is interrupted. This can be seen in the lack of dispersion along the x direction in the (1D) mobile state chain band of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Fig. 1).

It should be noted that because the electronic states associated with oxygen vacancies are actually located on the neighboring oxygen atoms, the removal of the neighboring oxygen atoms does not serve to create more vacancy states. On the contrary, their removal destroys the oxygen vacancy associated flat band.¹⁰ In $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ this removal is the removal of oxygen chain atoms which occurs in the deoxygenation of $\text{YBa}_2\text{Cu}_3\text{O}_{\sim 7}$ to $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{\sim 6}$.

B. Identification of mobile and paired states in experiment

Direct experimental observation of the electronic states should be possible through electronic interband excitation. Both the mobile and the localized bands are observable.

The mobile band is manifest in a small though nonvanishing continuous DOS at the Fermi energy. This is to be contrasted with the possibility, not observed, of a semiconducting gap in the vicinity of the Fermi energy, with doping introduced carriers.

Localized states near the Fermi energy give rise to a distinctive signal. Since the localized states in the two-component theory are paired (also in the normal state) the lifetime of single-particle excitations in this band is short leading to an expected broadened band of excitations despite the narrow band of states. Furthermore, negative- U localized states lead to shifts in the energy of excitation and capture of electrons (Fig. 3) since single-particle states are higher in energy than the paired states at the Fermi energy. The symmetry of the localized states also forbids some excitations, though residual excitation is possible because of hybridization with the mobile states and symmetry breaking due to disorder and structural distortions such as the tetragonal distortion in $\text{La}_2\text{CuO}_{4-\delta}$. An important experimental tool for observations of negative- U centers is photoinduced absorption spectra.¹⁵⁻¹⁷ This is particularly important when lifetimes of single-particle states are short. By first exciting the material, there are created many single particles in the paired band which can be optically excited significantly increasing the absorption signal and shifting the energy of the excitation (Fig. 3).

These expectations are met by experiments in both $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-\delta}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The mobile band of states is found through the presence of a nonzero density of states at the Fermi energy.¹⁸

The key signature of a negative- U localized band—a broad-band excitation in photoinduced IR absorption is observed.¹⁹⁻²¹ These experiments further show a strong

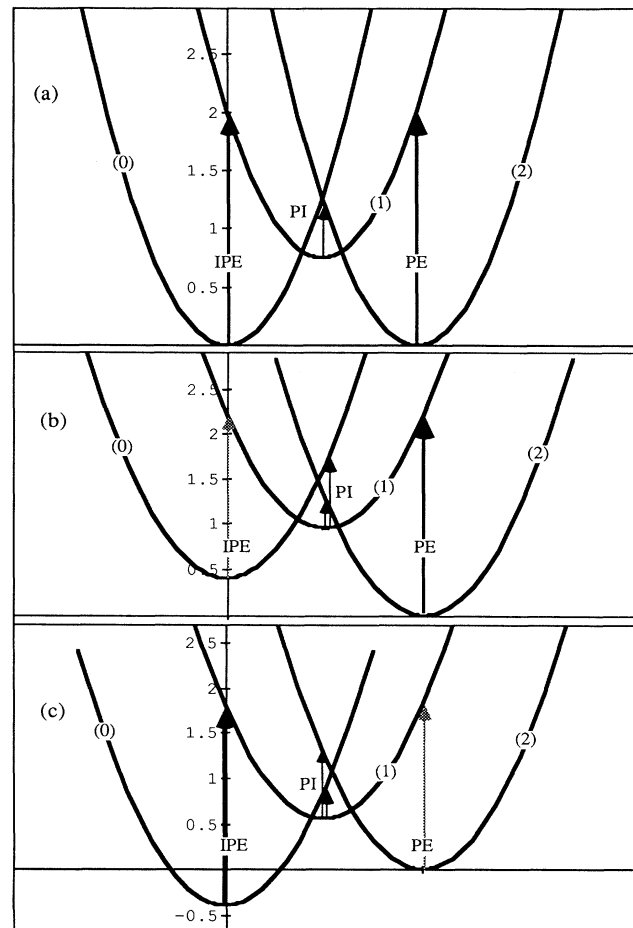


FIG. 3. Diagram representing the relationship between the negative- U -center total-energy curves and single-particle excitations. The three curves represent the configuration coordinate energy dependence of the three possible occupations of the negative- U center. In (a) the unoccupied (0) and the doubly occupied states (2) are degenerate at their respective lowest energy configurations. This corresponds to $\mu = \mu_B$ —the two-particle transitions are at the Fermi energy. A shift in the Fermi energy changes the occupation of the states to more occupied (b) or less occupied (c). Thus even though the transitions are far from the Fermi energy their intensity is dramatically affected by shifts in the Fermi energy. The energy of a defect when singly occupied is higher than the unoccupied or doubly occupied cases, this energy difference in (a) is half of the negative- U : $U_{\text{eff}} = E^2(2) + E^0(0) - 2E^1(1) = -2E^1(1)$ for this choice of μ and reference energy. Not shown in this figure are the effects of anharmonic terms which make the excitation energies (1/0) and (1/2) as well as the (0/1) and (2/1) inequivalent. The (2/1) transition is measurable in photoemission (PE) as the difference in excitation energy of an electron from an extended state at the Fermi energy and from the occupied negative- U center. The (0/1) transition is similarly measurable in inverse photoemission (IPE). The (1/2) and (1/0) excitations are measurable in photoinduced absorption (PI) or through virtual occupation of (1) near $\mu = \mu_B$. The energies of these excitations in the figure are suggested by experimental signatures in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Fig. 2 and text).

electron-phonon coupling consistent with the requirements for a negative- U . Since the measurements are performed when the material is (un)doped or deoxygenated into the insulating regime, the excitation energies may be shifted from the excitations expected in the superconducting state as shown in Fig. 3 for doping, and due to the essential disruption of states in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ from deoxygenation. This may account for the difference in the energy of the photoinduced signal 0.2–0.5 eV in $\text{La}_2\text{CuO}_{4-\delta}$, and 0.18 eV in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, thus particularly the latter does not reflect the value of the negative- U excitation energy for vacancies active in the superconductivity when T_c is 91 K. Note that if the identification of the negative- U with oxygen vacancies is correct the photoinduced signal in $\text{La}_2\text{CuO}_{4-\delta}$ should be sensitive to the oxygen vacancy concentration.

There is also an infrared excitation of energy similar to the photoinduced signal observed in reflectivity experiments, which is dependent on doping and oxygenation and has been correlated by some experiments with the superconducting state.^{22–26} This excitation at a sample dependent energy 0.5 eV in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ and 0.2–0.4 eV in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ may be related to the virtual occupation of the singly occupied vacancy state. This occupation which is maximum for a Fermi energy at the pair transition energy $\mu = \mu_B$ should be very sensitive to the Fermi energy and the oxygen vacancy concentration as reported in these experiments. In addition, the matrix element may depend sensitively on disorder and diminish as a result near O_7 . In contrast, T_c is relatively insensitive to the Fermi energy and oxygen vacancy concentration (Fig. 6 of paper I and below). Thus, the variability of this experimental signal in some samples²⁴ and its absence in high-quality thin films²⁷ may be accounted for. In particular, the oxygenation of thin films depends on surface charging and may exceed that of bulk materials. Possible intentional use of this effect is suggested in the section on new materials.

To build a more complete picture of the excitations of the negative- U states we must look in these materials for single-particle excitations which are essentially equally spaced from the Fermi energy and have the expected character of oxygen p orbitals. These requirements are explicitly met by excitations in superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ at $\sim \pm 2$ eV with oxygen p character, there is also evidence for such states in superconducting $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ but weaker, consistent with a lower concentration of vacancies and the associated paired states.

Figure 2 displays experimental curves showing electronic states associated with oxygen $2p$ states both above and below the Fermi energy in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ at a distance of ~ 2 eV from the Fermi energy. The strong oxygen p character of these states is consistent with electronic structure calculations on the localized band. The interpretation of the electronic excitations at ± 2 eV as associated with the negative- U centers leads to a number of specific predictions of the dependence of these excitations on doping and oxygen content of the Cu-O superconductors. As a function of doping, the prediction is particularly dramatic since filling the localized band would make

the inverse photoemission peak, which seems to be 2 eV above the Fermi energy, disappear while emptying the band would make the photoemission peak disappear 2 eV below the Fermi energy. The effects of oxygenation in creating or eliminating the paired states should also have direct effect on the intensity of these excitations. For $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, where most experiments have been performed, the removal of oxygen leads to elimination of the negative- U states so both peaks above and below the Fermi energy should have their shape, not just intensity, affected.

The peak or shoulder in the photoabsorption showing filled states at ~ 2.2 eV below μ ,^{28–33} is sensitive to the oxygen content and decreases over time due to loss of oxygen. This sensitivity has also been ascribed to a purely surface effect. Inverse photoemission experiments reveal a peak in the density of states in the empty states 1.5–2 eV above the Fermi energy in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and a weaker one in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$.^{34–37} A substantial absorption feature is also found from reflectivity experiments at these energies.^{23,24,26} X-ray spectroscopy shows the active hole states introduced by oxygenation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ to be oxygen- p related,³⁸ but unlike a usual Fermi energy shift, these hole states are shown by inverse photoemission to be far from the Fermi energy. X-rays have attributed³⁹ the low energy empty oxygen p states to be oxygen vacancy related in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$. These are the only hole states in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ which can be associated with the oxygen p hole related states in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, strongly suggesting the association of the $\text{O}p$ holes in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ also with vacancies.

Thus, experimental evidence linking the intensity of both the photoemission and inverse photoemission peaks to oxygenation or the position of the Fermi energy are known. Wendin⁴⁰ has noted the connection between the behavior of the photoemission and inverse photoemission peaks in deoxygenation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and the existence of similar peaks in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$. Doping and oxygenation are often interrelated in the high- T_c materials. In the original parent material $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ varying the oxygen annealing⁴¹ should enable a separation of the two providing unambiguous experimental tests on the unusual prediction of the doping dependence.

Combining the interpretation of the photoemission and inverse photoemission peaks at ~ 2 eV with the photoinduced IR absorption excitation at ~ 0.5 eV an estimate of the effective- U is possible $U_{\text{eff}} = \mathbb{E}^0(0) + \mathbb{E}^2(2) - 2\mathbb{E}^1(1) \sim -1.5$ eV. Where the seemingly redundant notation $\mathbb{E}^n(n)$ is the total energy with n electrons at its minimum energy coordinate R_n . The magnitude of the negative- U is large compared to a T_c and w consistent with the formalism. It is consistent on the high end with values for negative- U in semiconductors which have been found in the range 0.1–1 eV.^{42–46} The high value may be reasonable if bond stretching Cu-O modes are responsible for the relaxation.

The interpretation of single-particle excitations given here has neglected the on-site repulsion of the mobile states believed to be responsible for the antiferromagnetism. This is likely to be an oversimplification which should be corrected in more detailed treatments.

It is essential to emphasize that while the spectral density of the single-particle electronic transitions is *far* (2 eV) from the Fermi energy these transitions appear to probe the one-electron transitions of states associated with two-electron transitions which are *at* the Fermi energy.

III. OXYGENATION AND DOPING

One of the remarkable properties of the high- T_c family of materials is the ease of flow of oxygen in and out of many of these materials. Oxygenation is an essential step in the processing of many of the superconductors, while deoxygenation is essential for others. In most theoretical approaches to superconductivity this property is incidental. Here, the ability to have 1–10% oxygen vacancy concentration without decomposition is essential to the introduction of a substantial density of paired states. The experimental necessity of adding oxygen to the material for the superconductivity to occur in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ suggests the natural conclusion that oxygen vacancies disrupt superconductivity. In contrast, a whole family of new materials, the “electron-doped” materials, require removal of oxygen in order for superconductivity to exist. This contradiction may be resolved by the suggestion emphasized here, that oxygen vacancies introduce paired states but also disrupt the extended states and the necessity of both leads to a balance requiring a concentration of vacancies smaller than naturally found in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ but more than naturally found in the “electron-doped” materials. There are inherent difficulties in measuring the oxygen concentration accurately in these materials. An estimate of the optimal vacancy concentration in a complete layer is 1–2% as suggested by studies on “electron-doped” materials.⁴⁷

There are two thermodynamic driving forces governing the removal of oxygen from $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ at high temperatures. First is the lowering of the chemical potential of oxygen in the gas phase with increase in temperature. Second is the temperature and oxygen content dependence of the Fermi energy in these materials. It is widely acknowledged that the flow of oxygen into Cu-O based materials should shift the Fermi energy of the material. This is based on the ionic nature of the material, considering oxygen as an O^{2-} ion. The charge added by the oxygen atoms must be compensated in the material. Emphasizing the charge states of the vacancy and neglecting the interactions between oxygen atoms in the material and the existence of structurally different kinds of vacancies, the relationship between the concentration of oxygen n , the partial pressure of oxygen p and the density of states at the Fermi energy $D(\mu)$, in terms of reference values n_0 , $p_0(T)$, and $\mu_0(T)$ can be written in as

$$\begin{aligned} n/n_0 &= 1/[(p_0/p)\exp(q(\mu - \mu_0)/kT) + 1] \\ &= 1/[(p'_0/p)\exp\{[q^2(n - n_0)/D]/kT\} + 1], \quad (1) \end{aligned}$$

where q is the effective charge on the oxygen atom compared to the oxygen vacancy. p'_0 includes both the temperature dependence of the gas chemical potential and

the temperature variation in μ_0 . This shows that for a significant change in oxygen density the pressure must be raised exponentially. For a density of states of 1 state/cell/eV and a charge of 2 and a temperature of 700°C, a change from vacancy concentration of 50% to 1% requires a change of ~ 12 orders of magnitude in pressure.

In the two-component theory, the oxygen vacancies have at least two possible charge states differing by two electrons. The effective charge of the oxygen ion compared to the vacancy is expected to be roughly -2 and 0 , corresponding to one unoccupied and doubly occupied vacancy orbital, respectively. The effective charge may differ from these values because of modification of the local density of states at the vacancy site compared with the oxygen atom. In this case the charges may be written to first order as $-2+q$ and q . For q positive, if the Fermi energy lies below the electronic transition of the vacancy, the Fermi energy is shifted down by the addition of oxygen and if the Fermi energy is above the electronic transition there is a small shift up. Intermediate behaviors are possible depending on the Fermi energy and the change in D as the oxygen vacancies are introduced. For q negative, the addition of oxygen always shifts the Fermi energy down but the rate will be dramatically different for the Fermi energy above or below the electronic transition of the vacancy. The application of Eq. (1) is relevant to the Fermi energy location at the annealing temperature of oxygenation. The relative location of the Fermi energy and the vacancy electronic transition may change from low to high temperature.

While expression (1) neglects effects of different oxygen populations and the local interactions of oxygen atoms, it suggests that a systematic study of oxygenation may show dramatic behavior changes as a function of doping or temperature as the effective charge of the introduced oxygen vacancies changes. The several different types of oxygen sites and therefore oxygen vacancies in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ makes interpretation of experiment more difficult. Expression (1) appears consistent with an experimentally observed pressure dependence of $n(p)$ measured at a particular temperature.⁴⁸ A systematic $n(p, T)$ dependence as a function of doping, as may be possible in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$, is needed in order to investigate the possibility of changes in charge state of the vacancies.

Doping generally is achieved through substituting ions in the semiconductor layers between the Cu-O planes. It is widely believed (consistent with a conventional one-band model), that doping has the sole effect of shifting the Fermi energy of the single-particle states, adding holes or electrons. However, since oxygen ions are charged, the doping may be compensated by changes in the oxygen vacancy concentration. This has been found experimentally to occur.⁴¹ If a dopant is compensated by oxygen vacancies, these vacancies are likely to be attracted to the dopant and a correlation between dopants and vacancies should be found. New evidence for the correlation of dopants and oxygen vacancies has indeed been found.⁴⁹ In the two-component theory, vacancies have two charge states, depending on the position of the Fermi energy, thus the compensation by vacancies occurs only

when the charge on the vacancies has the right sign. The compensation of dopants by vacancies according to the standard charge assignment occurs by having one vacancy for two dopants since the vacancies are doubly charged. However, this depends also on the average occupation of the vacancies, if the Fermi energy is at the two-particle transition ($\mu = \mu_B$) then half the vacancies are occupied and effectively one vacancy compensates one dopant. These considerations are to be implemented at the relevant temperature—the temperature of oxygenation for the vacancy concentration, and the temperature at which oxygen atoms cease to move locally, for the coupling between oxygen and dopants.

IV. PAIR DEPENDENCE OF SUPERCONDUCTIVITY

In order to make systematic comparison of the variation of material properties with oxygenation, the variation with concentration of paired states is needed. The original two-component model used to obtain generic superconductive properties assumed one-single particle state and one paired state per unit cell. Changing the relative number of the two types of states can be done in a variety of ways. Diminishing the number of paired states would result in a relevance of band-structure effects since the unit cell periodicity of the lattice would be broken. Even assuming a super cell periodicity would lead to additional difficulties in the solution process. To obtain the dominant dependence of the superconductivity on the paired concentration it is simplest to consider having more than one paired site per unit cell, each of which is connected identically to the single particle states. This problem may be solved similarly to the original problem with the results in Table I, corresponding to Table I of paper I with the dependence of the paired concentration given explicitly by M_B .

Several interesting points can be made. First, the ratio $2\Delta/kT_c$ is sensitive to $D_c(\mu)$ not M_B . The condensation energy density $\Delta F = \Omega_0 H_c^2 / 8\pi$ is sensitive to the pair density and the ratio $\Delta F/kT_c$ is sensitive to M_B not $D_c(\mu)$. The behavior of $\Delta F/kT_c$ states that the condensation energy is $kT_c/2$ per paired site. Thus a cohesive energy comparison with experiment requires accurate knowledge of the pair site density (paper I, III C).

It is important to recall that the oxygen vacancy density affects both the pair density and the single-particle density of states.

V. THE FAMILY OF HIGH- T_c MATERIALS

The picture which can be built of the family of Cu-O-base high- T_c superconductors is based on conductive Cu-O planes, and vacancies which have three properties: (1) they introduce localized states which are negative- U ; (2) they disrupt the single-particle (mobile) states; and (3) if there are too many of them in a plane, the localized states themselves are disrupted.

The second property arises because the vacancies are in the Cu-O planes. If they were in the semiconductor layers this might be avoided. The third property arises because, like most defects, the localized states introduced by the vacancies reside on the neighboring atoms, particularly on the second neighbor oxygen atoms, which if removed disrupt the localized states. This is clear in electronic structure of $\text{YBa}_2\text{Cu}_3\text{O}_6$ which no longer has the flat localized band of $\text{YBa}_2\text{Cu}_3\text{O}_7$.

Using these three properties of oxygen vacancies a picture emerges for the family of Cu-O-based high- T_c materials. The control parameters are the annealing in oxygen, and doping. Different oxygen concentrations or orderings are essentially different materials.

A. $\text{La}_{2-x}(\text{Sr},\text{Ba})_x\text{CuO}_{4-\delta}$

The original and parent compound of this family of high- T_c materials displays an ease of oxygenation and doping. A relatively simple picture of the effect of doping and oxygenation can be developed considering only oxygen vacancies present in the Cu-O plane. In this case the doping and oxygenation essentially explore a two-parameter subspace of the $\mu - \mu_B$, M_B and D_c dependence of the superconductivity. However, this is complicated by potentially important additional features such as interstitial oxygen, and oxygen vacancies directly associated to dopants. In this “parent” compound of the family, the introduction of vacancies leads to a direct competition between the introduction of paired states and the reduction of the single-particle state density.

The convenient starting point for describing the material, as for other theories, is $\text{La}_2\text{CuO}_{4-\delta}$. Most experiments indicate that this material is antiferromagnetic, generally understood to be due to an on-site electron-electron repulsion in the mobile electron band of the Cu-O planes which crosses the Fermi energy. Oxygen vacancies in the plane introduce localized negative- U states. The value of the transition energy is below the Fermi en-

TABLE I. Comparison of basic superconducting parameters for BCS theory of weakly paired mobile states, negative- U lattice theory of strong-pairing low-mobility states, and the two-component theory. This table improves on Table I of paper I by incorporating the dependence of the pair density M_B in a simplified model. For details see text and paper I.

	BCS	Negative- U lattice	Two-component
kT_c	$1.13 \hbar\omega_D e^{-1/D(\mu)V}$	$\lambda'(\mu)E_0$	$M_B \lambda(\mu)w^2 D_c(\mu) \ln(1.13/kT_c)$
Δ	$2\hbar\omega_D e^{-1/D(\mu)V}$		$M_B \beta(\mu)w/2$
$\Omega_0 H_c^2 / 8\pi$	$\Omega_0 D(\mu) \Delta^2 / 2$	$\delta'(\mu)kT_c/2$	$M_B \delta(\mu)kT_c/2$
$2\Delta/kT_c$	3.5		$4\beta / [\lambda w^2 D_c(\mu) \ln(1.13t/kT_c)]$
ξ	$\hbar v_F / \pi \Delta$	a	$a < \xi < \hbar v_F / \pi \Delta$ (Fig. 14)

ergy of the intrinsic material $\text{La}_2\text{CuO}_{4-\delta}$. Thus vacancies which are present in the material are electronically occupied at low temperature. A shift of the Fermi energy downward weakens the antiferromagnetism because of departure from one-half filling in the single-particle band, and brings the Fermi energy toward the energy of the negative- U states. In this material, it appears that the antiferromagnetic order is suppressed by the single-particle carriers, though competition with the superconducting order may contribute to its suppression.

The addition of dopants (Ba or Sr), shifts the Fermi energy downward with the charge being compensated not only by changing the mobile band occupation but also by introducing oxygen vacancies. In general the existence of a continuum of single-particle energies implies that for higher Fermi energies the compensation is by single-particle states and when the Fermi energy reaches a value at which the vacancies have the same energy as the single-particle states, vacancies will then compensate the doping. Systematic studies of doping and oxygenation have been performed,^{41,50} and indeed indicate that the initial effect of doping is to change the mobile band occupation and then at a particular doping level to compensate with oxygen vacancies. The doping level at which oxygen vacancies become the compensating charge species rather than carriers depends on the oxygen pressure at the temperature of oxygenation. For low pressures it is at the onset of T_c , for typical pressures it is in the vicinity of the maximum value of T_c . For high pressure it can be reduced below the doping region of high T_c . The association of the increase in vacancy concentration at the doping level associated with high T_c is not coincidental in this theory. Indeed this is direct evidence for the association of the oxygen vacancies with the superconductivity through their electronic transition. Vacancies cannot compensate significantly for the doping as long as the Fermi energy is above the oxygen vacancy transition energy (where a nominally charged $-2+q$ vacancy dominates). Thus the onset of oxygen vacancy compensation at the superconducting Fermi energy is consistent with the oxygen vacancy transition energy being at the Fermi energy of the maximum superconductivity.

The appearance of oxygen vacancies at the maximum value of T_c might have been explained through the destructive aspect of oxygen vacancies suppressing the superconductivity for higher doping levels. However, experiments⁴¹ show that decreasing the oxygen vacancy concentration by high pressure oxygenation, and extending the range of doping, still results in a decrease of T_c at higher doping levels. Thus, as predicted, there are two mechanisms for the eventual decline of T_c at high doping levels, destroying the single-particle states with too many oxygen vacancies (variation in D_c) and shifting the Fermi energy below the oxygen vacancy transition energy (variation in $\mu - \mu_B$). The latter behavior has been termed "anomalous."

The oxygen vacancy concentration is controlled by both oxygen partial pressure and also by doping because of their role in compensating the dopants. A schematic oxygen vacancy concentration as a function of doping is indicated in Fig. 4 for several different oxygen partial

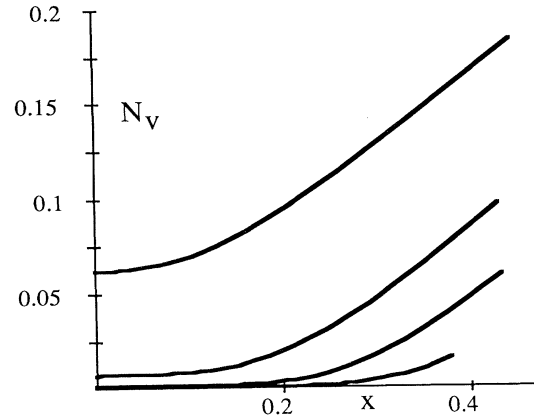


FIG. 4. Schematic dependence of the number of oxygen vacancies on the dopant concentration in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ for different oxygen partial pressures. This plot was made using a number of assumptions about formation energies for vacancies assuming only one vacancy type with two charge states -2 and 0 , where the oxygen ion is assigned a -2 charge. The actual situation is more complicated because of the existence of two types of vacancies [in the Cu-O plane and in the semiconductor plane (apical) oxygen atoms], and due to the association of dopants with vacancies.

pressures. In order to generate this figure assumptions were made about vacancy formation energies which determine the concentration of the different charged vacancies. The effective charge of the electronically unoccupied vacancy was assumed to be 0 compared to a -2 oxygen ion, while the doubly occupied vacancy was assumed to be -2 . For this assignment of charges, the doping does not affect the concentration of the doubly occupied vacancies, only the unoccupied vacancy. For oxygen vacancies directly associated with dopants the application of oxygen pressure is less effective at reducing their concentration because of their lower formation energy.

Relevant for the interpretation of experiment, four complications are important in the discussion and measurement of oxygen vacancy concentrations. (1) There are several different kinds of oxygen vacancies in the material and particular measurements may detect them differently. The categories are planar and apical vacancies, occupied or unoccupied, and associated or unassociated with dopants. For example, the oxygen vacancies which are occupied and unoccupied will lead to different changes in lattice parameters—a change which has been used to monitor vacancy concentration. Experiments⁴¹ have shown a decrease in lattice constants with the introduction of oxygen vacancies in the plane, these oxygen vacancies are to be interpreted as ionized oxygen vacancies since they compensate dopants. (2) The behavior of oxygen vacancies associated with dopants will be significantly different than the behavior of other vacancies in the plane. (3) Since the Fermi energy and thus the occupation of vacancies changes from annealing to the measurement temperature additional complications in interpretation may arise. (4) The presence of significant populations of oxygen interstitials has been found.⁵¹

Along with the ease of oxygen migration in these materials this suggests that low energy metastable arrangements of oxygen atoms are quite common including vacancy/interstitial pairs.

Note that the experimentally observed contraction of the lattice upon introduction of ionized vacancies is directly consistent with the pressure dependence of T_c . For Fermi levels above the oxygen vacancy transition, the application of pressure reduces the formation energy of the ionized vacancies, and the transition energy rises towards the Fermi energy increasing T_c as observed⁵² (see paper I, III D)

Indications for the existence of oxygen atoms in the plane of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ were found in early neutron diffraction experiments.⁵³ The measured value of $3 \pm 3\%$ is quite reasonable in view of the results on electron doped materials. This number is also reasonable if vacancies are assumed to be associated with the dopants. At the doping level $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_{4-\delta}$ direct compensation of dopants would require 0.075 vacancies per cell since vacancies are doubly charged, or 4% vacancies in the plane since there are two oxygen atoms in the plane per cell. Some compensation by carriers is expected so a lower number would also be quite reasonable. The similarity of the vacancy numbers obtained by doping compensation, neutron diffraction, and measurements in electron-doped materials reinforce this interpretation.

While neutron diffraction results are reasonable, it may be worth noting the the association of oxygen vacancies with dopants and/or with significant local structural relaxations leading to the negative- U also complicates the interpretation of neutron diffraction data. A potential difficulty in measuring the oxygen vacancy concentration by neutron scattering is the existence of thermal ovals. These may be better fit by two overlapping ovals corresponding to the two structures of the oxygen vacancy, and they are expected to be highly correlated with oxygen vacancies and related local atomic displacements. Since error bars are established assuming uncorrelated deviations, it is to be expected that the error bars in the fitting procedure are larger than usual. Nevertheless, systematic studies investigating the vacancy concentrations at the 1% level should be revealing in conjunction with other measurements such as photoemission.

A prediction of the T_c and Δ dependence on vacancy concentration is complicated by the coupling to the Fermi energy. For a fixed value of the Fermi energy, T_c should rise and fall as a function of oxygen vacancy concentration. The rise for small oxygen vacancy concentration occurs because of the introduction of paired states, while the decline for large concentration arises because of the disruption of the mobile states. Δ however, is controlled by the paired concentration rather than D_c . Thus, the dependence of Δ , also for fixed Fermi energy, is schematically as plotted in Fig. 5(a) and a plot of 2Δ with respect to kT_c is given in Fig. 5(b). This is dramatically different from BCS theory since BCS predicts a monotonic increase of Δ with kT_c while here Δ can increase while kT_c decreases. Functional dependences can also be described for the condensation energy from Table I. The realization of these predictions is somewhat complicated

by disorder of the oxygen vacancies.

Oxygen vacancies are disordered in the planes. Detailed studies of the averaged value of Δ and the BCS approximation to T_c in disordered negative- U systems have been presented.⁴⁻⁶ Here, it is significant to mention that because of the short coherence length in these materials, the local variation in pair density leads to a relatively poor sensitivity of the measured T_c to the pair density because only a small fraction of the material need have the optimal pair density for this to be the measured value due to the electrodynamic screening of the superconductive state. Within a coherence volume of the material there are likely to be only a few oxygen vacancies, thus the statistical variations are very large. It is well known in these materials that the active superconductive part of the material is significantly less than 100%. The variation of dopant density or oxygen vacancy density may be respon-

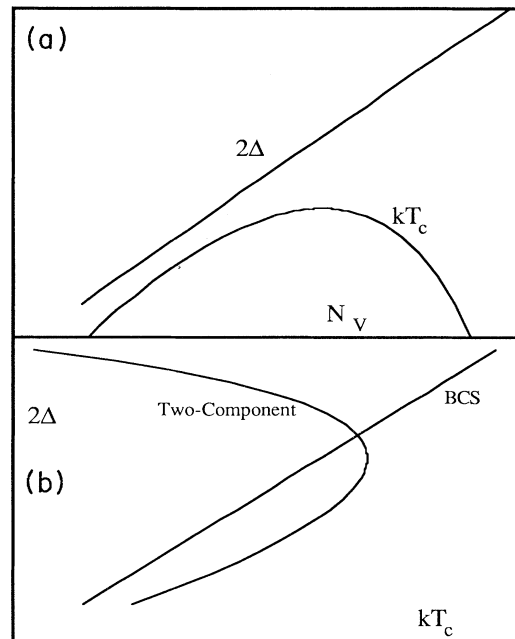


FIG. 5. Schematic dependence of kT_c and Δ on the number of oxygen vacancies (N_v) for fixed Fermi energy in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$. kT_c is the thermodynamic transition and Δ is the mean Fermionic gap (see paper I). For low oxygen vacancy densities, the introduction of vacancies primarily increases the pair density M_B while for high concentrations the single particle density D_c is reduced dramatically. As shown in Table I, T_c depends on the product $D_c N_v$ while Δ depends only on N_v . This leads to unusual dependences of 2Δ on kT_c as illustrated in (b). Since oxygenation and the Fermi energy are coupled, this curve is not for a fixed number of dopants. A systematic study of 2Δ vs kT_c as a function of doping and oxygenation should reveal such behavior. Disorder affects this curve by flattening the T_c curve at the top leading to a more vertical 2Δ vs kT_c curve. In contrast for cases where D_c is being varied and M_B is not, the curve will appear largely horizontal. For $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ deoxygenation leads to different behavior because the overly high density of oxygen vacancies disrupts the paired states (see text).

sible. This suggests that the active Meissner fraction of the material rather than T_c should have the functional dependence which corresponds to that described for T_c itself. Thus, the Meissner fraction should first rise and then fall with a rise in oxygen vacancy density. T_c should be relatively insensitive remaining relatively constant over a more extended range of vacancy concentrations.

Another aspect of the disorder of vacancies is that the superconductive coupling may very well play a role in the local arrangement of oxygen atoms if the material is annealed at low temperatures where the energy scale of the superconductivity is significant. Since the local arrangement of oxygen atoms is important for the superconductivity, the ability of oxygen atoms to rearrange themselves because of the low barrier to migration is important. Note that at 500°C long-range motion of oxygen is possible over experimental time scales. Thus over similar time scales, short-range motion is possible for oxygen at much lower temperatures. This trend to optimal arrangement also tends to lead to more optimal transition temperatures.

Sufficiently high pressures of oxygen or plasma annealing should lead to a reduced T_c in all materials due to the filling of oxygen vacancies. This should be easier to attain at low doping levels due to the association of vacancies with dopants. Thus, this effect is most likely for slightly underdoped samples of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$. A difficulty may remain since experimental evidence exists that at sufficiently high pressures, the additional oxygen entering the material does so interstitially rather than on the conventional oxygen sites.⁵¹ This implies that the oxygen vacancies do not get completely filled. Interstitial oxygen appears to be a dopant further complicating the picture.

In the extreme case where oxygen vacancies are not found in the material, superconductivity is not observed. This is to be associated with materials which have n -type doping as discussed below. In n -type doping dopants are not directly associated with oxygen vacancies and the Fermi energy shift does not introduce them.

Despite the complications of local pair density variations in a short coherence length superconductor, an indication of dramatic functional dependence should be available experimentally. Assuming that T_c does not vary despite the variation of oxygen vacancy density, but the average gap does vary with D_c still leads to the functional dependence of $2\Delta/kT_c$ shown in Fig. 4(b) but with a longer vertical part. Reports of $2\Delta/kT_c$ in this material have been quite varied, this sample dependence has frustrated research. The predicted functional dependence may be responsible. Systematic studies should be definitive.

An additional aspect of the properties of $\text{La}_2\text{CuO}_{4-\delta}$ based materials is a symmetry-breaking phase transition from tetragonal to orthorhombic where the lower symmetry orthorhombic phase is associated with superconductivity. For this discussion, the importance of this phase transition is that the symmetry breaking may enable a small hybridization of localized states to the extended states of the plane in which they are located. This is to be contrasted with the interplane coupling which is

to be expected otherwise. Since the hybridization controls the superconductivity, the importance of such symmetry breaking may be great, providing a tentative explanation for the apparent correlation of this transition with superconductivity in its phase diagram.^{54,55}

B. $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

There are a variety of differences between $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$. $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ has a different structure than $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ through a different stacking of Cu-O layers. It also has a more well-defined atomic structure where doping is not the basic variable, and disorder is not necessarily inherent. Oxygenation has been viewed through its role in shifting the Fermi energy. This is important in the two-component theory however, the oxygen concentration itself is important. The essential difference between these two materials in establishing the high- T_c for the two-component theory is a partial resolution of the conflict of the role of oxygen vacancies in both introducing paired states and disrupting single-particle states. The resolution is through a second level of layering in the material. Since the oxygen vacancies are associated with the Cu-O layers rather than the semiconductor layers, it is necessary to break the equivalence of the Cu-O layers in order to segregate the oxygen vacancies from the conductive Cu-O plane into a plane essentially dedicated to paired states induced by oxygen vacancies. By separating the oxygen vacancies from relatively complete Cu-O planes more oxygen vacancies can be present and T_c is higher because D_c remains high.

In $\text{YBa}_2\text{Cu}_3\text{O}_7$ there are 50% in-plane vacancies in one of three planes. This corresponds to 17% in-plane vacancies. Assuming a relatively similar D_c per plane in $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$, this explains why T_c in this material is substantially higher than that in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$. However, taking an estimate of $3 \pm 2\%$ vacancy concentration in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_{4-\delta}$, it suggests a ratio of 3–10 in T_c between the two materials, more than the observed ratio of 2–3 for the observed T_c 's of 30–45 K and 91 K. This might be accounted for by different interplanar w matrix elements in the two structures (by a factor of $\sqrt{2}$). Alternatively, the effective number of localized states introduced by a vacancy in the plane may be an important factor. An isolated vacancy may introduce two localized states, while because of the overlapping of states the vacancies in $\text{YBa}_2\text{Cu}_3\text{O}_7$ introduce only one localized state. In this case the 17% vacancies in $\text{YBa}_2\text{Cu}_3\text{O}_7$ would correspond to an effective concentration of 8% isolated vacancies. It seems consistent, however, to suggest that the almost complete disruption of the single-particle states in the plane of the oxygen vacancies is the most straightforward explanation. Specifically, it has been noted above that symmetry breaking such as achieved in the orthorhombic distortion of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ enables the localized states of the plane to couple to states in the same plane. This may be impossible or ineffective because of the disruption of the single particle states in $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_7$ reducing the effective w of the material. This suggests a speculation

that frequently observed trace metastable 240 K $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ material⁵⁶ are due to oxygen vacancy arrangements, possibly with higher oxygen content, which promote the mobility of extended states in the oxygen vacancy plane and, by some symmetry breaking, their hybridization to the localized states.

The segregation of oxygen vacancies to one out of three planes in $\text{YBa}_2\text{Cu}_3\text{O}_7$ is achieved by changing the relative potential of the three layers through the ions which are on each side of the layer. One of the three layers has two adjacent layers of Ba^{+2} ions while the other two have one Ba^{+2} and one Y^{+3} ion layer on each side. The potential profile can be inferred to be as in Fig. 6. The oxygen vacancies segregate to the unique layer associated with a lower potential as is appropriate for the relative positive charge of ionized vacancies with respect to the oxygen (i.e., they are repelled by the Y^{+3} ions). This directly measurable association of oxygen vacancies in Cu-O plane with the ions also lends support to the suggestion that in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ oxygen vacancies are also associated with dopants.

There is no fundamental reason in the two-component theory that the optimal T_c should be achieved for an oxygen concentration O_7 . This is particularly true since the Fermi energy is not separately controlled in this material. It should be noted that it is indeed not obvious that experimentally the Fermi energy is optimal for O_7 and it may be suggested that $\text{O}_{6.8-9}$ is the optimal value for the Fermi energy. As discussed above, the 0.35-eV excitation which appears to be associated with superconductivity is suppressed around O_7 and this is consistent with the suggestion that the material at O_7 has a Fermi energy displaced slightly from the two-particle transition energy. However, the relative lack of disorder in material with oxygen content O_7 may be responsible for improvement of some of the superconductive properties found in oxygenated thin films.

$\text{YBa}_2\text{Cu}_3\text{O}_7$, or 1:2:3:7, material has served as the model material for the comparison of theoretical and experimental results on T_c , Δ , H_c , ξ , and transport. It is the most studied material because of its high transition temperature but mostly because of the relative reproducibility

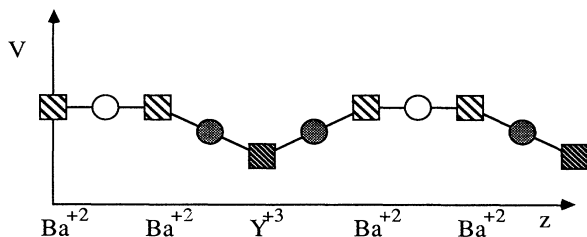


FIG. 6. Schematic illustration of the potential of different planes in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, showing the mechanism for the segregation of oxygen vacancies into one of the three planes—their association with the Ba “dopants” through the change in potential of the planes.

of its experimental results. This is understandable because the structure of this material also stabilizes an arrangement of oxygen atoms or vacancies. This leads to consistent experimental results rather than the large variability suggested by the theoretical discussion above for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$. However, several distinct oxygen concentrations for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ have been reported with transition temperatures and other properties varying. These correspond to different oxygen arrangements and are effectively to be considered different phases with T_c s of 40–60 K, 80 K, 91 K, 130 K, and possibly even 240 K. The 91-K material is the most extensively studied and has been used to make the comparisons of theory with experiment.

The second most studied phase formed by oxygen depletion⁵⁷ with a phase transition of 60 K no longer has the oxygen vacancy lattice of $\text{YBa}_2\text{Cu}_3\text{O}_7$; it has an approximate oxygen content of $\text{O}_{6.4}$. The primary effect is a complete disruption of the chains and thus of the negative- U states. A natural progression is obtained by assuming that as oxygen is removed, vacancies are introduced in the planes which formerly were full. Experimental association of vacancies with the semiconductor layers or apical sites has been made.⁴⁸ In-plane oxygen vacancies at the few percent level are also possible. Oxygen vacancies associated with the full Cu-O planes in this material have similar effects and problems as in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$. However, there are poorer contacts between the Cu-O double layers because of the effectively missing Cu-O layer, so the material is more intrinsically two dimensional.

In order to make a systematic comparison between theory and experiment, an explicit model for the superconductivity of 91 K $\text{YBa}_2\text{Cu}_3\text{O}_7$ material is necessary. The vacancies in this material are known to order into chains, these linear chains of vacancies run parallel to Cu-O chains. It is a matter of emphasis to call these ordered vacancies defects rather than part of the structure. This emphasis is justified because of the localized electronic states introduced by the ordered vacancies similar to the states associated with isolated vacancies. The electronic states, associated with the vacancies, located on the Cu-O chains, are at the Fermi energy. Thus, an ordered lattice of oxygen vacancies is manifest, and these are assumed to be negative- U sites introducing one paired state per unit cell. For the model the presence of additional vacancies aside from the ordered chain of vacancies was neglected. In $\text{YBa}_2\text{Cu}_3\text{O}_7$ there are two planes of almost full Cu-O, it was assumed that these can be represented as one electronic state per cell, taking only the actual density of states at the Fermi energy to be used in the theoretical model. Furthermore, the boson band was assumed to be at one-half filling. The self-hopping of a paired site onto itself $E\frac{1}{2}$ was neglected. The native hopping of the paired band and the electron-electron interaction in the single-particle band were assumed to be unimportant. Some of these assumptions may prove to be oversimplifications. The comparisons of this model with experiment, reported in paper I are made for the purpose of encouraging further efforts in comparison of theory with experiment.

C. More layers

The behavior of the sequences of materials $Tl_2Ba_2Ca_{n-1}O_{4+2n-\delta}$, $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n-\delta}$ with increasing numbers of layers of Cu-O suggests that their effect is to increase the single-particle density of states at the Fermi energy. As mentioned previously, these materials inherently have a metal interleaved with the CuO layers¹¹ and thus the modeling is complicated by the coupling of the Cu-O planes to these layers. The concentration of vacancies is not well established in these materials though one possibility for their identification lies in the layers of Cu-O which are completely missing one or both sets of apical oxygen atoms. Alternatively, like $La_{2-x}Sr_xCuO_{4-\delta}$ and more consistent with the "electron-doped" materials which do not have apical oxygen atoms and still require in-plane oxygen vacancies for superconductivity, there is very likely to be a concentration of vacancies in the plane of order a few percent.

In these materials there is little natural oxygen concentration change with temperature. The reason for the lack of natural evolution of oxygen may lie in a different Fermi energy behavior from $YBa_2Cu_3O_{7-\delta}$ and $La_{2-x}Sr_xCuO_{4-\delta}$ as a function of temperature due to the presence of other single-particle states associated with the metallic layers. Studies of the oxygen vacancy dependence of superconductivity in these materials achieved by more extreme oxygen annealing conditions should provide additional relevant information.

D. "Electron doped" materials

The "electron doped" materials^{58,47,59} present additional important evidence for the effect of oxygen vacancies and the two-component theory. It is worth noting that individual materials do not display electron/hole symmetry as would be expected for a one-band model of superconductivity. The electron-doped materials may be understood in the two-component theory by considering the oxygen vacancies in the planes of these materials. The Cu-O planes in electron-doped materials have a different structure from the Cu-O planes in $La_2CuO_{4-\delta}$ since there are no oxygen atoms above or below the plane (no apical oxygen atoms). The transition energy of the state associated with a vacancy in such a plane will be different than that in a plane of $La_2CuO_{4-\delta}$, and thus may lie above, rather than below half-filling of the mobile band of states. Doping upward would then be necessary for superconductivity and the active carriers are now due to a partially filled paired band (electronlike) rather than the partially empty (holelike) states for the doping of $La_2CuO_{4-\delta}$.

These materials do not normally contain oxygen vacancies. Doping should not be expected in this case to introduce vacancies. Assuming the conventional assignment of charge to oxygen ions and the two charge states of the vacancy, the vacancy cannot be negatively charged with respect to the oxygen ions and thus cannot compensate the *n*-type dopants. It has been shown³⁹ to be necessary to remove oxygen in order for these materials to become superconducting. This is the most direct evidence for the importance of oxygen vacancies for the superconductivity.

Note that the difference between a nonsuperconducting and an optimally superconducting sample consists of a change of only 1% in oxygen concentration. For other materials where dopants are naturally coupled to vacancies it appears that the number of natural vacancies exceeds the optimal amount.

VI. NEW MATERIALS AND DEVICES (REF. 60)

The two-component theory as described here suggests several new approaches for developing high- T_c superconductors, and possibly a new device.

New Cu-O-based materials. The importance of the control of oxygen in Cu-O-based materials has been apparent from experiment, and appears centrally in this theory. More specifically there is a need for independent control of the oxygen content and the Fermi level. Optimally the Fermi energy should be placed close to the center of the paired band. However, the oxygen content is related to the Fermi level at the time of oxygenation. In order to overcome this interdependence which is an obstacle to independent control it is possible to use thin films on a thin insulating layer above a metal substrate. By applying a bias field during the oxygenation, the Fermi energy in the thin film can be displaced affecting the energy of oxygen incorporation and thus the oxygen vacancy concentration. A similar arrangement may be used to evaluate the Fermi energy dependence for the superconductivity at low temperatures. Because of screening only very thin films can have their Fermi energy effectively controlled in this way.

It may be hoped, as discussed above, that the filamentary 240-K superconductivity⁵⁶ in $YBa_2Cu_3O_{7-\delta}$ -based materials corresponds to a particular choice of oxygen vacancy concentration and Fermi level which is unstable under normal circumstances. The experimental evidence describing the 240-K transition phase of $YBa_2Cu_3O_{7-\delta}$ in mixed systems is consistent with this phase arising from uncontrolled Fermi energy biasing in the mixed system. Fermi energy controlled annealing may achieve the same result in pure material. Recently reported⁶¹ careful oxygen annealing conditions which stabilize the filamentary 240-K phase are suggestive of this possibility.

A further suggestion can be made for developing independent control of oxygen vacancies and doping. In systems where oxygen vacancies active in the superconductivity are intimately coupled to dopants, one can control their density by overdoping and counterdoping to maintain the Fermi energy while introducing a larger number of active negative- U centers. This should be effective if the number of negative- U centers is below the concentration for which disruption of single particle states dominates. The technique of counter doping should enable a study of different regimes of the oxygen vacancy concentration/Fermi energy parameters.

New superconductors. Among the semiconductor defects studied in detail, a large proportion have been found to be negative- U centers.⁴²⁻⁴⁶ This suggests that many possible materials formed out of semiconductor-metal layers should be superconducting if the following conditions can be met. First that there be a large number of

defects, most easily accomplished by off-stoichiometry. Second, that the defect introduce negative- U states. Third that the Fermi energy be moved to correspond with the Fermi energy of the defect two-particle transitions. In the present class of high- T_c superconductors it appears that the defects are in the metallic layers. This may have advantages in some circumstances in high matrix elements connecting the localized and extended states, however, it has the disadvantage of disrupting the superconductivity unless the materials are further staged to separate the defects from the conducting states. If proper matching between the states can be achieved, it is likely that the active defects can be in the semiconductor layers. In order to study such layered metal-semiconductor materials in general, the problems of growing monolayered metal-semiconductor superlattices must be overcome, however, there are likely to be many materials which form naturally as such superlattices

which have not yet been studied in off-stoichiometric and doped regimes. These are promising materials for high- T_c studies.

New devices. The strong dependence of the superconductivity on the Fermi energy, suggests that a switch may be formed with its central element a thin film of superconductor with a Fermi energy away from the optimal value for superconductivity. If it is maintained at a temperature above its own T_c and below the T_c of the optimal Fermi energy then the superconductivity of the material may be switched on by a field which shifts the Fermi level. In essence such scheme makes use of large non-linear effects near the transition temperature for thin films with Fermi energy dependent superconductivity.

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