Understanding electron-doped cuprate superconductors as hole superconductors

J. E. Hirsch\textsuperscript{a} and F. Marsiglio\textsuperscript{b}

\textsuperscript{a}Department of Physics, University of California, San Diego, La Jolla, CA 92093-0319
\textsuperscript{b}Department of Physics, University of Alberta, Edmonton, Alberta, Canada T6G 2E1

Since their experimental discovery in 1989, the electron-doped cuprate superconductors have presented both a major challenge and a major opportunity. The major challenge has been to determine whether these materials are fundamentally different from or essentially similar to their hole-doped counterparts; a major opportunity because answering this question would strongly constrain the possible explanations for what is the essential physics that leads to high temperature superconductivity in the cuprates, which is still not agreed upon. Here we argue that experimental results over the past 30 years on electron-doped cuprate materials have provided conclusive answers to these fundamental questions, by establishing that both in hole- and electron-doped cuprates, superconductivity originates in pairing of hole carriers in the same band. We discuss a model to describe this physics that is different from the generally accepted ones, and calculate physical observables that agree with experiment, in particular tunneling characteristics. We argue that our model is simpler, more natural and more compelling than other models. Unlike other models, ours was originally proposed before rather than after many key experiments were performed.

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I. INTRODUCTION

Shortly after the discovery of high temperature superconductivity in cuprate superconductors in 1986 [1], it became clear that the carriers responsible for superconductivity in these materials were holes [2–7]. Upon changing the chemical composition of the parent insulating compound so that hole carriers were added to the copper-oxygen planes, the superconducting $T_c$ was found to increase, go through a maximum and then decrease to zero in the ‘overdoped’ regime [4, 8].

Then, on January 26, 1989 it was reported by Takagi, Tokura and Uchida [9] that by doping a parent insulating material with electrons instead of holes superconductivity also occurred, albeit with a smaller maximum critical temperature. Initially, experiments appeared to show very definitely that indeed the charge carriers in these electron-doped materials were electrons [9–11], as the title of Ref. [9] claimed: “A superconducting copper oxide compound with electrons as the charge carriers”.

The general reaction to this discovery was that it provided evidence for an approximate electron-hole symmetry [12–15]. For example, Art Sleight stated in March 1989 [16] “This symmetry between adding and subtracting electrons will have to be reflected in any theory that explains high-temperature superconductivity, and existing theories based on the supposition that there is something unique about hole carriers are ‘out the window’.”

Electron-hole symmetry is to be expected if the undoped parent insulating compound is assumed to be described by a half-filled band governed by the Hubbard Hamiltonian [17], which is particle-hole symmetric, and doping of holes or electrons results in changing the carrier occupation in this band. This was widely assumed to be the case at that time and continues to be widely assumed to be the case today.

Instead, immediately after the discovery of the electron-doped materials we pointed out [18–22] that a natural explanation existed for why hole carriers of the same nature as the hole carriers in the hole-doped materials [23] would be induced in the electron-doped materials, and we predicted that subsequent experiments would show that hole carriers exist and are responsible for superconductivity also in the electron-doped materials [18–22]. Figure 1 shows schematically how holes on $O^2$ can result from electron-doping of $Cu^{2+}$, we will delve into the details later. No experimental evidence suggesting neither that hole carriers existed nor that they were responsible for superconductivity in these materials existed at that time.

Already very soon thereafter, EELS experiments suggested the presence of holes at the oxygen sites in electron-doped cuprates [24]. That holes participate in the transport was shown by detailed and extensive magnetotransport measurements by several different experi-
mental groups extending over many years [25–35]. These experimental results and their analysis showed that there are both electron and hole charge carriers in the electron-doped cuprates, that hole carriers dominate the transport in the regime where electron-doped cuprates become superconducting, and that it is the hole carriers that likely drive superconductivity in these materials [25, 34, 35].

However several key questions remain unsettled. What is the nature of the electron and hole carriers in the electron-doped materials? Why, if there are hole carriers in electron-doped cuprates, aren’t there electron carriers in hole-doped cuprates? Are the hole carriers in the electron-doped materials of the same nature as those in the hole-doped materials? Even if they are, is the pairing mechanism the same? We argue that definite answers to these questions would go a long way towards elucidating the origin of superconductivity in both hole- and electron-doped cuprates.

In this paper we elaborate on the simple answers to these questions that we proposed 30 years ago [18–22], and argue that various experimental results obtained during these 30 years support our original proposal. We will also argue that other proposals to explain these questions are complicated, unnatural and implausible.

In a nutshell, our proposal was and is: hole carriers responsible for superconductivity in both hole-doped and electron-doped materials reside in a band resulting from overlapping oxygen $p\pi$ orbitals in the Cu-O$_2$ plane that point perpendicular to the Cu-O bonds, as shown in Fig. 2. This band is full in the undoped case and becomes slightly less than full both on the hole-doped and the electron-doped side, for reasons we will explain. The electron carriers in the electron-doped cuprates reside in the Cu–O band formed by the overlapping Cu $d_{x^2−y^2}$ and O $p\sigma$ orbitals pointing along the Cu–O bond. Proposals that hole carriers in the hole-doped cuprates reside in the O $p\pi$ orbitals were also made early on by Goddard et al. [36], Stechel and Jennison [37], Birgeneau et al. [38] and Ikeda [39].

II. TWO-BAND MODELS

As discussed above, experiments indicate [25–35] that hole carriers exist and are responsible for superconductivity in both electron-doped and hole-doped cuprate superconductors. Furthermore, these experiments show that in electron-doped cuprates there is two-band conduction in the normal state, with the other band being electron-like. The question is, where are these carriers? We start by giving a brief overview of three different possibilities that have been proposed: (i) Our two-band model, (ii) two-band $t−J$ model, and (iii) reconstructed Fermi surface models.

FIG. 2. Cu $d_{x^2−y^2}$ and oxygen orbitals in the Cu-O planes. In the undoped parent compound the nominal valence is $Cu^{++}$ and $O^−$ and there is one hole in the filled Cu $d^{10}$ orbital. The O $p\pi$ orbitals point perpendicular to the Cu-O bonds, the $p\sigma$ orbitals parallel. We propose that doped holes reside in a band resulting principally from overlapping O $p\pi$ orbitals for both hole- and electron-doped cuprates.

(i) Our two-band model

The simplest way to have two-band conduction for the system shown in Fig. 2 is if one band involves principally the O $p\sigma$ orbitals hybridized with the Cu $d_{x^2−y^2}$, which we will call the Cu-O band, and the other band involves principally the O $p\pi$ orbitals orbitals pointing perpendicular to the O $p\sigma$ orbitals in the plane, which we will call the O band. For the hole-doped materials we had proposed [23, 40], before the electron-doped materials were discovered, that their high $T_c$ could be understood as arising from hole carriers in the O band. Furthermore within this theoretical framework it is predicted that superconductivity can only arise from hole carriers in a nearly full band [41–43]. In other words, within this theoretical framework ‘A superconducting copper oxide compound with electrons as the charge carriers’, as announced [9] by Tokura, Takagi and Uchida on January 26, 1989, cannot exist. As we now know from experiments [25–35], it does not exist, at least to date.

There is a simple way to understand why doping with electrons can create holes in the O band, illustrated in Fig. 3, in the hole representation. First, we assume the O $p\pi$ energy level for a hole is lower than the O $p\sigma$ level, in other words it costs less energy to remove an electron from the O $p\pi$ orbital than from the O $p\sigma$ orbital. This is plausible for two reasons: first, as pointed out by Birgeneau et al. [38] and Goddard and coworkers [36], because there is more negative charge near the center of the plaquette than along the Cu-O-Cu line, it costs less Coulomb energy to remove an electron (create a hole) from the $p\pi$ orbitals that point towards the center of the plaquette from the $p\sigma$ orbitals directed along the Cu-O bond.
Second, as discussed in ref. [44], the orbital relaxation effect that occurs when an electron is removed from the \(O^=\) ion is stronger if the electron is in the \(p\sigma\) orbital that is doubly occupied (by electrons) in the undoped case than if it is in the \(p\pi\) orbital that is only about 1.5 occupied because of its hybridization with the neighboring Cu atoms. That lowers the energy for creating a hole in the \(p\pi\) orbital relative to creating it in the \(p\sigma\) orbital.

In the undoped case, there is one hole at each \(Cu^{++}\) site. For the electron-doped material, we assume the single-hole \(O\) \(p\pi\) energy level is lower than the \(Cu\) energy level. Nevertheless in the undoped compound the \(Cu\) hole doesn’t ‘fall’ onto the neighboring \(O^=\) ion because of the cost in Coulomb repulsion between neighboring holes at \(Cu\) and \(O\) sites. Upon electron doping the hole is removed from (electron is added to) a \(Cu^{++}\) ion, now the hole from a neighboring \(Cu^{++}\) can fall into the \(O^=\) ion without paying nearest neighbor Coulomb repulsion energy, as illustrated in the lower right panel of Fig. 3. The net result from adding an electron to a \(Cu^{++}\) is two \(Cu^{+}\) ions and one \(O^-\) ion, with the hole in the \(p\pi\) orbital. In other words, two extra electrons reside in the \(Cu-O\) band and one hole in the \(O\) band.

This process can (and will) happen in the electron-doped cuprate materials because of the absence of apical oxygens in their structure (\(T'\) structure), which increases the electrostatic potential at the \(Cu^{++}\) site relative to the case of the hole-doped materials (\(T\) structure). Because the apical oxygen is relatively closer to the \(Cu\) atoms than to the \(O\) atoms in the plane, the \(Cu\) hole energy level is relatively higher with respect to the \(O\) levels in the \(T'\) structure (right side in Fig. 3). This facilitates both the electron-doping of the material (it is not possible to dope electrons in the \(T\) structure) and the transfer of electrons from \(O^=\) sites to neighboring \(Cu^{++}\) sites, thus creating \(O\) holes. A detailed analysis of the energetics of these processes and the important role of reduction in getting the carriers to delocalize is given in ref. [45].

In all the other models that have been proposed to describe the electron-doped and hole-doped cuprate superconductors in recent years, the \(O\) \(p\pi\) orbitals are not included. It is assumed that the \(O\) band is far below the Fermi energy and can be ignored. We discussed in Ref. [44] why this may not be so.

(ii) Two-band \(t-J\) model

Another possible model to give rise to two-band superconductivity with electrons and holes was suggested by T. Xiang and coworkers [46]. They proposed that the two bands in question are a Zhang-Rice singlet band and the upper Hubbard band, both originating in the overlap of orbitals \(Cu_{d_{x^2-y^2}}\) and \(Op\pi\) shown in Fig. 2 (what we called the \(Cu-O\) band). The authors argue that both the Zhang-Rice singlet band and the upper Hubbard band should be described by effective one-band \(t-J\) models, or, more accurately, a ‘hybridized two-band \(t-J\) model’. Then, this model maps onto a one-band \(t-U-J\) model, using approximations that according to the authors ‘may not be fully satisfied in real materials’. The authors argue that this model gives results for a Fermi surface density map consistent with ARPES observations. However, they don’t explain how this model explains the transport experiments [25–35] that clearly show electrons and hole carriers in two different bands.

(iii) Reconstructed Fermi surface models

In these models it is suggested that some kind of translational symmetry breaking with wavevector \((\pi, \pi)\) doubles the unit cell and this gives rise to both electron and hole carriers. Lin and Millis [47] argue that this reconstruction of the Fermi surface occurs below Ce concentration \(x = x_c = 0.16\) due to antiferromagnetic long-range order, giving rise to electron pockets at \((0, \pi)\) and small hole pockets at \((\pi/2, \pi/2)\), while for \(x > x_c\) only a large hole-like Fermi surface exists occupying about half the Brillouin zone. However, Motoyama and coworkers report [48] that the antiferromagnetic order disappears already at \(x = 0.134\), and that in the doping regime where electron-doped cuprates superconduct, only short range antiferromagnetic correlation exists. This is incompatible with the hypothesis that the hole carriers responsible for superconductivity arise from reconstruction of the Fermi surface due to antiferromagnetic order. While it has been speculated that Fermi surface reconstruction may still occur in the electron-doped materials at high doping [49–51] due to some other mechanism, e.g. a hidden d-density wave order [52], no experimental evidence for this has been found so far.

We argue that our proposed model (i) is simpler and more natural than models (ii) and (iii). In the following sections we discuss in more detail experimental and theoretical reasons in favor of our model versus the other
models.

III. MAGNETOTRANSPORT

Initially, Hall coefficient measurements on electron-doped cuprates yielded a negative Hall coefficient [11], consistent with the expectation that these were superconductors ‘with electrons as the charge carriers’ [9]. Later this changed, when experiments were performed on single crystals and thin films.

Figure 4 shows measurements of the Hall coefficient versus temperature for a range of doping levels for a typical electron-doped material, $Pr_{2-x}Ce_xCuO_4$ [32], and a hole-doped material, $(La_{2-x}Sr_x)CuO_4$ [54]. Results for $T_c$ versus doping are also shown [53, 54]. There is a clear difference in the behavior of the Hall coefficient $R_H$ in both cases.

![Figure 4: Temperature dependence of Hall coefficient and $T_c$ versus doping for electron-doped (upper panels) [92, 53] and hole-doped (lower panels) [54] cuprates.](image)

In the hole-doped material, $R_H$ is almost temperature independent and positive over the entire doping range where superconductivity occurs (up to $x = 0.125$). For doping approaching $x = 0.125$ the positive Hall coefficient becomes very small. For doping $x = 0.15$ and above (not shown), the Hall coefficient is negative and no superconductivity exists [54].

These results for the Hall coefficient of hole-doped cuprates were initially qualitatively interpreted [54] as a crossover from a Mott-Hubbard regime ($R_H > 0$) at low doping to a Fermi liquid regime ($R_H < 0$) at high doping [55] in a single band model. However contrary to initial expectations it was found within dynamical mean field theory that the Hall coefficient of a half-filled Hubbard model doped with holes is negative for all dopings and given by the bare band structure results [56, 57]. At finite temperatures it was reported that the Hall coefficient can turn positive [57–59]; however the temperature and doping dependence does not resemble the experimental results shown in Fig. 4. In addition, these treatments predict that $R_H(\delta) = -R_H(-\delta)$, where $\delta$ is the doping away from half-filling, which is very different from the behavior shown in Fig. 4.

Instead, we argue that the results for $R_H$ for hole-doped cuprates shown in Fig. 4, namely the near temperature independence and the positive value decreasing with hole doping, are most simply interpreted as resulting from doping of a single band from an initial state where the band is completely full, as predicted by our model, where the band is the $Opn$ band. As hole carriers are added the magnitude of the Hall coefficient decreases as expected from the simple formula $R_H \sim 1/(n_{he}c)$. As the band becomes half full the Hall coefficient would change sign from positive to negative in a simple picture. The change in sign at high hole doping from positive to negative before the band is half-full can be simply explained as due to a high scattering rate that would prevent carriers from completing closed hole orbits without scattering, which is necessary for the Hall coefficient to be positive.

The behavior of the Hall coefficient for electron-doped cuprates as a function of temperature and doping shown in Fig. 4 is drastically different from a ‘mirror image’ of the hole-doped cuprates with a sign change, as would be predicted by a single band model. It shows unmistakable evidence for two-band conduction, one with electron carriers and one with hole carriers, with electrons dominating at low electron doping and holes dominating at high electron doping. For an isotropic two band model with electron and hole carriers of densities $n_e$ and $n_h$ the Hall coefficient is

$$R_H = \frac{1}{n_{he}c} \frac{1 - (n_h/n_e)(\mu_h/\mu_e)^2}{1 + (n_h/n_e)(\mu_h/\mu_e)^2}$$

and will be negative if the mobility of the hole carriers ($\mu_h$) is much smaller than that of the electron carriers ($\mu_e$). Wang et al [25] and Crusellas et al [27] have argued that the hole mobility increases rapidly as the temperature is lowered due to a decrease in the hole scattering rate, and have fitted the temperature and doping dependence of resistivity and Hall coefficient measured in experiments using reasonable assumptions for temperature-dependent electron and hole mobilities. Wang et al pointed out [25] the similarity in the temperature dependence of the scattering rate of the hole carriers in hole-doped cuprates inferred from the resistivity with that of the hole carriers in electron-doped cuprates inferred from $R_H$, suggesting it is the same carriers and the same scattering processes. Crusellas et al pointed out [27] that the measured hole mobility in electron-doped cuprates is very similar to that observed in hole-doped cuprates. Note also that in a single-band situation a temperature-dependent scattering rate does not result in temperature dependence of the Hall coefficient.
Further evidence for the existence of two-band conduction in the regime where electron-doped cuprates superconduct comes from the sign and magnitude of the magnetoresistance. Already in 1994 Jiang et al pointed out [29] that “we see a remarkable correlation between the occurrence of superconductivity and the appearance of a positive MR” and that a “signature of two-band conduction is a positive magnetoresistance”. Recently Li et al [35] pointed out that there is a considerable increase in the magnitude of the magnetoresistance in the region where bulk superconductivity is first seen, which reveals the underlying two bands. Jiang et al [29] as well as Fournier et al [30] also pointed out that the anomalously large Nerst coefficient they observed together with the measured small thermopower cannot be explained by a single band model and is direct evidence of two-band conduction with carriers of opposite sign in both bands.

Over the years Greene and coworkers have performed extensive measurements [29, 30, 32–34] on Hall coefficient, thermopower, magnetoresistance and Nerst effect in electron-doped cuprates, and carefully analyzed their data. They found compelling evidence from these measurements for two-band conduction, an electron-band and a hole-band, and dominant role of hole carriers in the regime where the materials are superconducting, and in particular that the regime where hole transport begins to dominate coincides with the onset of superconductivity. We believe that these together with other transport experiments and analysis [25, 28, 31, 35] have established experimentally that “in electron doped cuprates holes are responsible for the superconductivity” [34].

IV. QUANTUM OSCILLATIONS

In 2007, Shubnikov-de Haas oscillations in underdoped hole-doped cuprates provided clear evidence for the existence of closed small Fermi surface pockets in those materials [60, 61]. This was very surprising in view of the consensus that existed that Fermi liquid concepts did not apply to underdoped cuprates, and that the Fermi surface consisted of Fermi arcs rather than closed surfaces. The frequency of these oscillations was 530T in $YBa_2Cu_3O_{6.5}$ [60], corresponding to 1.9% of the two-dimensional Brillouin zone area, and 660T in $YBa_2Cu_4O_8$ [61, 62] with $T_c = 80K$, corresponding to 2.4% of the Brillouin zone. For the first case $T_c = 57.5K$ and $p = 0.10$ holes per planar Cu atom, for the second case $T_c = 80K$ and $p = 0.125$ [61] or $p = 0.14$ [62] holes per Cu atom. Quantum oscillations have also been observed in underdoped $HgBa_2CuO_{4+\delta}$ [63, 64], with frequency 840T corresponding to about 3% of the Brillouin zone, or 0.061 carriers per pocket. Several other such observations in hole-doped cuprates have been reported [65–67]. Whether these oscillations are due to hole pockets or electron pockets or both has been controversial [68, 69] and is unsettled. Quantum oscillations have also been observed in the overdoped regime of $Tl_2Ba_2CuO_{6+\delta}$ [70], with frequency 18,100T, corresponding to cross-sectional area 65% of the Brillouin zone.

Within our model, in hole-doped cuprates holes are doped into the $Op\pi$ band that is initially full, so we would expect small hole orbits around the $(\pi, \pi)$ point in the Brillouin zone, consistent with the Shubnikov-de Haas oscillations observed. It is not clear how these observations can be consistent with doping a half-filled Hubbard band with holes, since according to what we reviewed in the previous section the Hall coefficient at low temperatures in that model reflects the bare band structure.

In electron-doped cuprates, Shubnikov-de Haas oscillations first detected in 2009 in $Nd_{2-x}Ce_xCuO_4$ [71] showed that small Fermi surface pockets exist both in the optimally doped and overdoped samples [49, 50, 71]. The measured frequency is approximately 300T, corresponding to 1.1% of the Brillouin zone. As mentioned earlier, it is hypothesized that they originate in reconstruction of the Fermi surface, however no long range antiferromagnetic order exists in this doping range [48]. In addition, from the reconstructed Fermi surface scenario one would expect also quantum oscillations from electron pockets with frequency half of that produced by the hole pockets, however a single low frequency is observed. In $Nd_{2-x}Ce_xCuO_4$ at high doping, both low frequency and high frequency ($\sim 11kT$) oscillations are detected coexisting in the range $x > 0.15$ to $x = 0.17$ [49, 50], with the high frequency oscillations, corresponding to a Fermi surface area of $\sim 41\%$ of the Brillouin zone dominating at high doping, and the low frequency ones at low doping. The authors suggest that the reconstructed Fermi surface exists until the point where superconductivity disappears at $x \sim 0.175$ and that the high frequency oscillations originate in magnetic breakdown orbits, and they attribute the absence of evidence for electron pockets to damping. They acknowledge that “The mechanism responsible for the broken translational symmetry is still to be clarified”, and suggest “ ‘hidden’ d-density-wave ordering” as a possibility. Similar low frequency quantum oscillations are found in $Pr_{2-x}Ce_xCuO_4$, and $La_{2-x}Ce_xCuO_4$ [51].

Instead, within our model these observations are simply explained by the existence of a small number of hole carriers in the $Op\sigma$ band giving rise to the low frequency oscillations, and electrons doped into the $Cu-Op\pi$ band giving rise to a large Fermi surface corresponding to a more than half-filled band and corresponding high frequency Shubnikov-de Haas oscillations.

V. PHOTOEMISSION

Recent photoemission investigations on electron-doped cuprates were reviewed by Horio and Fujimori [72]. In particular they point out that the electron concentration inferred from the area of the electron Fermi surface measured by ARPES is significantly larger than the nominal Ce concentration. This was already found long ago by Alp and coworkers [73] via x-ray absorption spectroscopy.
It is consistent with our picture that electron doping induces hole carriers in the plane, hence by charge conservation this generates extra electron carriers in addition to the ones doped.

Horio and Fujimori (HF) emphasize the fact that annealing in a reducing atmosphere plays an essential role in giving rise to superconductivity, and point out that superconductivity can arise even in the absence of Ce doping. Contrary to earlier findings, they suggest that reduction removes oxygen from the rare-earth layers rather than from impurity oxygens at the apical sites. This is in agreement with our prediction [45].

The photoemission results reviewed by HF show a Fermi surface developing around $k \sim (\pi, 0)$. Upon further doping it becomes a large hole Fermi surface centered around $(\pi, \pi)$. Similar results are found in photoemission measurements by Song et al [74]. We infer that all these measurements are only detecting the quasiparticles residing in the $Cu-O\sigma$ band, that near half-filling are strongly affected by the Hubbard $U$ and for sufficient electron doping evolve into a simple Fermi surface centered around $(\pi, \pi)$. These measurements don’t show the hole carriers that according to the transport measurements must exist in a different band. We expect those hole carriers to be in the $O\sigma$ orbitals forming a small hole pocket at $(\pi, \pi)$, both for electron-doped and hole-doped cuprates. We conclude that because of the strong orbital relaxation effects in this purely oxygen band the quasiparticle weight is very small [75, 76] and not visible in current photoemission experiments.

VI. TUNNELING ASYMMETRY

Tunneling measurements have often been at odds with photoemission experiments; both types of experiments have unknown uncertainties because of the difficulties with surface preparation, etc. as discussed in Ref. [77]. Here we wish to focus on tunneling asymmetry, i.e. the difference in coherence peak heights, depending on whether the sample is negatively or positively biased with respect to the tip. For hole-doped cuprates, a large number of studies have found that tunneling spectra are asymmetric, with asymmetry of universal sign [78]. For electron-doped cuprates, much less tunneling work has been done. We will focus on data from Refs. [79–81], since specific details have been clarified through private communication. In particular in the raw data (Figs. 2 and 3 in Ref. [79]) the coherence peak is clearly higher when the sample is negatively biased with respect to the (normal) tunneling tip. The authors report (private communication) that this is universally true for all their measurements. Furthermore, this remains true for both Nd$_{1.85}$Ce$_{0.15}$CuO$_{4-x}$ at optimal doping (subject of Ref. [79]) and for Pr$_{1-x}$Ce$_x$CuO$_{4-y}$ as a function of doping, as shown in Ref. [80] (see their Fig. 1) and Ref. [81] (Figs. 1 and 2).

Tunneling spectra of Jubileo and coworkers [82] on $Pr_{1-x}LaCe_xCuO_{4-y}$ also show a clear asymmetry of the same sign (Figs.1 and 2), and this is also seen in tunneling on $Pr_{1-x}LaCe_xCuO_4$ by Miyakawa et al [83] (Figs. 1 and 3) and Diamant et al [84] (Fig. 1).

This tunneling asymmetry is important to confirm since the hole mechanism of superconductivity [41, 42] predicts an energy-dependent superconducting order parameter that results in a tunneling asymmetry [19] of universal sign, as observed in these experiments. Instead, the RVB model of Anderson and coworkers also predicts tunneling asymmetry [85] but of opposite sign for hole-doped and electron-doped cuprates [86]. Thus, establishing the sign of the tunneling asymmetry in electron-doped cuprates can rule out one of these two theories [87].

In the theory of hole superconductivity for a single band, the asymmetry predicted by this model is clear [19]. We will provide further model calculations in the next section, particularly in light of the fact that the tunneling data given in the different references give no indication of two-band behavior.

VII. MODEL CALCULATIONS

We consider a tight binding model for the orbitals shown in Fig. 2. There are 5 orbitals per unit cell $CuO_2$: one for the $Cu$ atom, and two for each of the oxygens. We denote the $d - \sigma\sigma$ hopping amplitude by $t_d$, and the direct hopping amplitudes between oxygen orbitals by $t_1$ for $\pi - \pi$ or $\sigma - \sigma$ hopping and $t_2$ for $\pi - \sigma$ hopping. Following estimates by McMahan et al [88] and Stechel and Jennison [37] we take $t_1 = 0.65$, $t_2 = 0.35$ and $t_d = 1.75$, all in eV. For site energies we take $\epsilon_d = -5.2$, $\epsilon_{\sigma\sigma} = -5.5$, $\epsilon_{\pi\pi} = -4.7$ eV. Because of electrostatics, $\epsilon_{\pi\pi}$ is higher than $\epsilon_{\sigma\sigma}$. The resulting 5 bands are shown in Fig. 5.

The bands of interest for us are bands 4 and 5. Figure 6 shows the weight of the atomic orbitals for the Bloch states of these bands. It can be seen that band 5 has similar content of $Cu - d$ orbital and $O\sigma\sigma$ orbital. This is the band that is generally considered to be the important one for both hole-doped and electron-doped cuprates. The Hubbard $U$ opens up a gap in the undoped compound in this band, rendering the system insulating. From this single band it is argued that both hole-like and electron-like carriers can result in the electron-doped cuprates according to the theories discussed in Sect. II.

Instead, in our picture band 4 is the more important one. As seen in Fig. 6, it is predominantly of $O\pi\sigma$ character, particularly as $k$ approaches the $(\pi, \pi)$ point in the Brillouin zone, when the band becomes full. Band structure calculations predict that it is about 1.5 eV below the Fermi energy and remains full under doping. Instead, we have argued [44] that strong oxygen orbital relaxation makes it easier to create holes in this band than what band structure predicts: qualitatively, when one electron is removed from the doubly occupied $p\pi$ orbital the remaining electron orbital shrinks, thus lowering its energy.
This local effect is not captured by band structure calculations.

Band 4 contains the hole carriers that we believe are responsible for superconductivity both in hole-doped and electron-doped cuprates. In the hole-doped cuprates, we argue that when holes are added to the undoped system they go into this band rather than into band 5. For electron-doped cuprates, we argue that adding electrons creates electron carriers in band 5 and through the process depicted in Fig. 3 also creates holes in band 4. We explained how this process works in the FeAs compounds in ref. [89] (Fig. 3) and argue that it is the same here. Thus there will be carriers at the Fermi energy both from band 4 and band 5.

We consider a reduced Hamiltonian to describe transport and superconductivity in those 2 bands. Following Suhl et al [90] we take

$$H = \sum_{\mathbf{k}\sigma} (\epsilon^a_{\mathbf{k}} - \mu) a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma} + \sum_{\mathbf{k}\sigma} (\epsilon^d_{\mathbf{k}} - \epsilon_0 - \mu) d^\dagger_{\mathbf{k}\sigma} d_{\mathbf{k}\sigma} +$$

$$\sum_{\mathbf{k}\mathbf{k'}} V^a_{\mathbf{k}\mathbf{k'}} a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k'-}\sigma} a_{\mathbf{k'}\sigma'} a^\dagger_{\mathbf{k'}\sigma'} + \sum_{\mathbf{k}\mathbf{k'}} V^d_{\mathbf{k}\mathbf{k'}} d^\dagger_{\mathbf{k}\sigma'} d^\dagger_{\mathbf{k'}\sigma} d_{\mathbf{k'}\sigma'} +$$

$$\sum_{\mathbf{k}\mathbf{k'}} V^{ad}_{\mathbf{k}\mathbf{k'}} (a^\dagger_{\mathbf{k}\sigma'} a_{\mathbf{k'}\sigma} d_{\mathbf{k'}\sigma'} + d^\dagger_{\mathbf{k}\sigma'} a_{\mathbf{k'}\sigma} a^\dagger_{\mathbf{k'}\sigma}). \quad (2)$$

As discussed in Ref. [91] we retain the simplest interband interaction, and in what follows adopt a constant interband potential: $V^a_{\mathbf{k}\mathbf{k'}}, V^d_{\mathbf{k}\mathbf{k'}} \equiv V_{ij}$. We have used a hole notation, so that the $a^\dagger$ and $d^\dagger$ operators correspond to hole creation operators in the $Op\pi$ and $Cu - Op\sigma$ band, respectively, and similarly for the annihilation operators. We adopt a flat density of states for both bands, each with bandwidth $D_i$. The single particle energies are measured from the center of each band, and the $Cu - O$ band is shifted by an amount $\epsilon_0$ with respect to the $O$ band.

The intraband potentials are assumed to have identical form; we adopt the form from Ref. [41]:

$$V^{ii}_{\mathbf{k}\mathbf{k'}} = U_i + K_i \left( \frac{\epsilon^a_{\mathbf{k}}}{D_i/2} + \frac{\epsilon^d_{\mathbf{k}}}{D_i/2} \right) + W_i \frac{\epsilon^a_{\mathbf{k}}}{D_i/2} \frac{\epsilon^a_{\mathbf{k'}}}{D_i/2}. \quad (3)$$

where $U_i$ corresponds to the on-site repulsion, $K_i$ the modulated hopping, and $W_i$ the nearest-neighbor repulsion ($i = 1, 2$ correspond to $a, d$ in Eq. (2)). These interactions lead to a BCS ground state that is superconducting, and an (s-wave) order parameter with the form

$$\Delta_i(\epsilon) = \Delta^{ii}_i (\epsilon_i - \epsilon / D_i / 2), \quad (4)$$

as found previously [41, 91]. Further details are available in these references.

Figure 7 shows $T_c$ versus hole concentration in the hole band for two sets of parameters given in the figure caption. We have taken into account the fact that within our model the bandwidth in the hole band increases with hole concentration [22], i.e. it is not a rigid band model. The behavior shown in Fig. 7 looks similar to the experimental results in Fig. 4, top right panel. If we were not to take into account the renormalization of the bandwidth with hole occupation the range of doping where superconductivity occurs would be about twice as large as shown in Fig. 7, which would be inconsistent with experiments.

The fact that the $T_c$ found in experiments (Fig. 4) starts at finite $Ce$ concentration rather than 0 would result if initially the doped electrons and induced holes remain localized, as discussed in Ref. [45] that also suggested an explanation why oxygen reduction is essential for hole delocalization.

Fig. 8 shows calculated tunneling spectra for our two-band model for parameters corresponding to the solid line in Fig. 7 just to the right of the maximum with
$T_c \sim 31K$, together compared with the Shan measurements. For this calculation we used a background density of states of the same shape as Shan’s, and assumed an intrinsic broadening with Dynes’ parameter $\Gamma = 0.5 \text{meV}^{-1}$. It can be seen that our results look very similar to Shan’s data.

We conclude that our model is compatible with the experimental tunneling results.

VIII. SUMMARY AND DISCUSSION

In this paper we have argued that a simple two-band model resulting from the orbitals shown in Fig. 2, where pairing originates in hole carriers in the $Op\sigma$ orbitals, can explain in a simple way a large variety of experimental findings in electron-doped cuprates obtained over many years, as well as in hole-doped cuprates. The basic principles of the model were proposed before electron-doped cuprates were even discovered. Our model says that pairing of the same hole carriers drives superconductivity in hole-doped and in electron-doped cuprates. The pairing mechanism is intimately tied to the hole nature of the carriers and gives rise to high $T_c$ when holes conduct through a network of negatively charged ions, as we have argued is the case in hole-doped cuprates, electron-doped cuprates, $MgB_2$, iron pnictides and chalcogenides and $H_2S$ [89, 91, 94–96].

In contrast, all other theoretical explanations of experimental observations in electron-doped cuprates assume that the only electrons involved are from $Cu d_{x^2-y^2}$ orbitals hybridized with $O p\sigma$ orbitals. To explain how clear experimental signatures of two-band physics arise from such a single band necessitates invoking electronic correlations, Fermi surface reconstruction and hidden exotic orders, which in our view are complicated and contrived explanations not supported by experimental observations.

In addition to the experiments already discussed, important information about electron-doped cuprates has been recently inferred from the behaviour of the superfluid density. The upward curvature of superfluid density versus temperature in electron-doped cuprates has been argued to be clear evidence for the presence of two types of superfluid carriers [92]. Li et al. [35] analyzed experimental results for upper critical field versus temperature and superfluid density versus temperature in electron-doped cuprates and concluded that they are consistent with a 2-band model where 25% of the carriers are hole-like and 75% are electron-like, that the dominant interaction giving rise to pairing is in the hole-like band, and that the interband coupling is small ($\lambda_{hh} >> \lambda_{ec}, \lambda_{ch} \sim \lambda_{he} \sim 0$ in their notation). Such models have also been used to model two-band superconductivity in $MgB_2$ [93]. The superfluid hole density inferred by Li et al. [92] matches the general scaling law between superfluid density and $T_c$ proposed by Uemura and coworkers [97].

The physics uncovered by the analysis of Li et al. is in agreement with what the model of hole superconductivity predicts, that was discussed in Sect. VII and in our earlier work on hole superconductivity in two-band models [89, 91]. In our model, the parameters $K_1$, $K_2$ and $V_{12}$ of Sect. VII are proportional to $\lambda_{hh}$, $\lambda_{ec}$ and $\lambda_{ch}$ of Li et al. [35]. In the Li et al. analysis the fact that holes drive superconductivity is derived from the experimental results. Instead, for us this is a prediction of the model: when there is two-band conduction with electrons and holes at the Fermi energy, it is necessarily the holes that pair and drive the entire system superconducting [91].

Li et al. conclude from their analysis [35] that it "points to a single underlying hole-related mechanism of
superconductivity in the cuprates regardless of nominal carrier type”. Dagan and Greene concluded from their analysis [34] that “in electron doped cuprates holes are responsible for the superconductivity”. Already in 1991 Wang et al had concluded [25] that “The similarity between the behavior of the hole-scattering rate and that in earlier “hole” superconductors suggests to us that the holes, in fact, may be driving the superconducting transition in Nd2−xCexCuO4−δ”. These conclusions agree with what our model has predicted since 1989. To further support this picture it would be important to confirm experimentally that tunneling asymmetry of the same sign as for hole-doped cuprates is the generic behavior in electron-doped cuprates, as initial experimental results appear to show [79–84]. This would rule out theories based on electron-hole symmetric models [85].

There has been conflicting experimental evidence on the question of the symmetry of the order parameter in electron-doped cuprates, as initial experimental results suggest that the fact that we formulated the model even before electron-doped cuprates were discovered and predicted the conclusions reached through thirty years of experimental work argues for the validity of the model to describe physical reality.

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