Particle-hole symmetry breaking in the pseudogap state of Pb$_{0.55}$Bi$_{1.5}$Sr$_{1.6}$La$_{0.4}$CuO$_{6+\delta}$: A quantum chemical perspective

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(Received 19 May 2010; published 24 January 2011)

Two Bi2201 model systems are employed to demonstrate how, beside the Cu-O $\sigma$ band, a second band of purely O 2$p_x$ character can be made to cross the Fermi level due to its sensitivity to the local crystal field. This result is employed to explain the particle-hole symmetry breaking across the pseudogap recently reported by Shen and co-workers [see M. Hashimoto et al., Nature Phys. 6, 414 (2010)]. Support for a two-bands-on-a-checkerboard candidate mechanism for high-$T_c$ superconductivity is claimed. Analysis based on band structures, partial density of states, and sum over states densities scanning-tunneling-microscopy-type images is provided.

DOI: 10.1103/PhysRevB.83.024508

PACS number(s): 74.72.–h, 71.18.+y, 71.20.Ps

I. INTRODUCTION

Generic electronic-structure features of hole-doped cuprate superconductors are presently being exposed at a renewed and even accelerating pace. The emerging consensus is that two energy gaps coexist in an electronically highly inhomogeneous state of matter. The gaps are associated with the superconducting state and a pseudogapped state,$^1$ respectively. The pseudogap function is discriminated by the fact that it displays only minor changes above and below the critical temperature for superconductivity. The ongoing progress is made possible by the combination of insights gained from the real-space scanning-tunneling-microscopy/scanning-tunneling-spectroscopy (STM/STS) technique$^2$–$^8$ and reciprocal-space angle-resolved photoemission spectroscopy (ARPES).$^9$–$^{20}$ These complementary techniques have acquired impressive precision over the years, partly driven by the unsolved riddle of high-$T_c$ superconductivity (HTS) found in said cuprates. Their success is proposed later in the paper to reflect fundamental complementarities inherent in the underlying physics of the HTS phenomenon.

One contemporary phenomenological perspective on the HTS property has the pseudogap state and the superconducting state reflecting two competing phases; see, e.g., Refs. 9 and 10. A complementary possible understanding is that the pseudogapped state signifies a segregated “preformed” pairs phase.$^{11}$–$^{19}$ A popular conceptual microscopic framework is the Anderson resonating valence bond (RVB) model$^{21}$–$^{23}$ based on the Gutzwiller method$^{24}$ akin to the treatment by Rice and Ueda$^{25}$ of the periodic Anderson model$^{26}$ for magnons in the doped AFM embedding.$^{27}$–$^{29}$ The rigidity of interplaquette entanglement is reflected in the SC gap function, while the rigidity of the virtual pair-susceptible AFM medium is reflected in the pseudogap function, which becomes renormalized due to the appearance of the former. This conceptual understanding is reminiscent of a spinon-holon terminology (see Refs. 21–23), where the spin-charge separation quality is replaced by the assumption that neither local spin nor local space symmetry are valid local descriptors in either the local AFM medium or the plaquette separately. It is the fact that the AFM + plaquette compound system does preserve local spin and symmetry in conjunction with the spatial extension of local AFM that enforces the entangled plaquettes’ ground state.

In light of this, any new information regarding the properties of the pseudogap is met with the utmost interest. Recently, the temperature evolution of the pseudogap was mapped out in detail by means of ARPES in terms of signatures of the band structure at the Fermi level in the vicinity of the superconducting gap function antinodal direction.$^{20}$ That study succeeded in monitoring the opening of the pseudogap, and even more interestingly, it claimed to demonstrate fundamental particle-hole asymmetry (PHA). Phenomenological modeling based on the sufficiency of charge-carrier segregation in the form of periodic checkerboard superstructures to achieve the PHA was attempted in Ref. 20. What adds to the drama is that the opening of a gap in a single-band scenario, that is, single-band Peierls instability,$^{30}$ does not per se render PHA. At least a two-band physics is required. Because conventional theory implies particle-hole symmetry conservation across the SC gap, the observed PHA across the pseudogap is effective in discriminating between the pseudogapped state and the superconducting state. However, this argument is equally valid in excluding the previously mentioned Peierls-type charge-density wave (CDW) as a candidate for the pseudogapped state. What is required for the particle-hole asymmetry is the existence of nonequivalent particle sink and source states. Such a situation may indeed be inferred from one of the central dogmas in contemporary HTS theory, that is, the validity of the local-density approximation (LDA) band structure in providing a general basis for interpretation of the HTS phenomenology in terms of the in-plane Cu-O $\sigma$ bands; see, e.g., Refs. 31–33. In these models, the required two bands for
particle-hole asymmetry would comprise the upper and lower Hubbard bands, the former acting as an electron sink and the latter as an electron source. Assumed instability toward hole segregation would result in the checkerboard observed directly by STM and indirectly as anomalous spectral broadenings in ARPES.

The purpose of the present study is to propose the complementary view to said upper-lower Hubbard band phenomenon. Hence, sufficient conditions for the hole-doped lower Hubbard band to act as an electron sink and a pure in-plane oxygen band of O 2pπ character to take the role of an electron source are demonstrated. Such a redistribution of holes can occur due to the innate inhomogeneous crystal fields as well as by the attenuation of the crystal field as caused by the displacement of cations relative to the CuO2 planes. The two model compounds Bi1.5,Pb0.5Sr1.5,La0.5CuO6 and Bi2Sr2CuO4 are employed here to demonstrate the two cases, respectively. In what follows, the contextual implications of our complementary understanding will first be reiterated. Second, the influence on the resulting band structure of the relative positions of the dopants Pb2+ and La3+ replacing Bi3+ and Sr2+, respectively, is demonstrated. Interpretation is provided by STM-type images generated by sum over states densities in the vicinity of the Fermi level. Third, the corresponding effects due to displacement of Sr2+ positions in pure Bi2Sr2CuO4 will be demonstrated by band-structure calculations in conjunction with partial density of states (PDOS) analysis and STM-type images. Finally, the proposed two-band scenario on a checkerboard framework will be employed to interpret the central observations of Shen and co-workers.20

II. A MULTIBAND SCENARIO FOR HIGH-CRITICAL-TEMPERATURE SUPERCONDUCTIVITY

The scenario for HTS formulated earlier27–29 includes three steps. (i) At elevated temperatures, mobile holes reside in the dispersive bands produced by the Cu-O σ states. (ii) Upon cooling, the charge carriers become trapped, such as with Zhang-Rice (ZR) singlets,34 or are transferred into bands of O 2pπ character. Indeed, recovery of local antiferromagnetic coupling15 requires such a transfer. The opening of the pseudogap has two contributions: one is the development of AF coupling among Cu 3d9 sites, and the second is the complementary clustering of holes in “superatom” states spanned by linear combinations of O 2pπ states. (iii) HTS emerges from a two-gapped “normal” state, such that resonant coupling of virtual hole cluster excitations and complementary virtual magnons contributes to the correlated ground state. Aspects of this understanding have been articulated in terms of a real-space analog27 to the Bardeen-Cooper-Schrieffer theory, and in an equivalent two-component RVB Bose-Einstein condensation (BEC) formulation.29 The latter implies that BEC among virtual hole cluster excitations is mediated by BEC of virtual magnons. Because the one provides the coupling required for the other to condense, the corresponding two signatures (superconductivity and spin-flip resonance36) appear at the same temperature, that is, at Tc. Our physical understanding27–29 is similar to that of Ref. 37. Yet the realization of said physics is different both with regard to the detailed mechanism and in the fundamental two-band origin of the electronic structure subject to segregation of charge carriers. The understanding developed for the cuprates29 was employed to formulate the superconductivity in FeSe,30 that is, in terms of an analogous multiband scenario to that developed for the cuprates. While such complexity is generally accepted in the case of Fe-chalcogenides and Fe-pnictides, Cu-O σ-band (see, e.g., Ref. 38) scenarios still dominate in the case of cuprates. The report by Shen and co-workers20 may provide the first solid ARPES-based evidence in favor of a multiband mechanism promoted by segregation in the case of HTS cuprates.

III. Bi1.5Pb0.5Sr1.5,La0.5CuO6 BAND-STRUCTURE DECONVOLUTION

Causes for the observations reported for Bi1.3Pb0.55 Sr1.25La0.75CuO6 ±1 in Ref. 20 are sought in the Bi1.5Pb0.5 Sr1.5La0.5CuO6 model system by means of spin-polarized general-gradient-approximation (GGA) Perdew-Burke-Enzenhofer (PBE) band-structure calculations. Taking the Bi2Sr2CuO4 crystal structure as a point of departure, in what follows, the influences of different structural replacements of Sr2+−Bi3+ by La3+−Pb2+ pairs on the resulting electronic structures are demonstrated.

In Fig. 1, we note that there are three distinctly different positions for the 25% replacement of Sr2+ by La3+, and the 25% replacement of Bi3+ by Pb2+. In all three cases, the density-functional-theory (DFT) ground state is a singlet. The band structures for the three cases are displayed in Figs. 2(a), 2(c), and 2(e). The most dramatic effect on the band structure due to the relative positions of Pb2+ and La3+ is seen in the vicinity of (π,π), where a band is shifted toward the Fermi level. To get a real-space representation of the electronic structure, sum over states densities is performed in the vicinity of the Fermi level at the two CuO2 planes in the unit cell [see Figs. 2(b) and 2(d)]. It is evident that the surfacing band at (π,π) has significant O 2pπ character. Apparently, the destabilization increases with increased distance between one of the CuO2 planes and the La3+ ion. Complementarily, the bands in the CuO2 plane vicinal to the La3+ ion experience stabilization due to the strong local crystal field. It is noted how the particle-hole symmetry in the structure of Fig. 1(a) reflects the exclusivity of Cu-O σ bands crossing the Fermi level in the vicinity of (0,π), as seen by inspection in Fig. 2(b). This property is retained for the CuO2 plane experiencing the strong crystal field; see Fig. 2(d1). However, in the case of the CuO2 plane experiencing the weak crystal field, clear particle-hole asymmetry emerges; see Fig. 2(d2). This is because the surfacing O 2pπ band in the vicinity of (π,π) renders the hole states O 2pπ character, while the particle states are still dominated by the bands crossings at (0,π).

IV. EMPLOYING Bi2Sr2CuO4 TO INTERPRET Bi1.5Pb0.5Sr1.5,La0.5CuO6

Also by comparing the band structure in Fig. 2 to that of native Bi2Sr2CuO4 [Fig. 3(a)], it is clearly seen how bands in the vicinity of (π,π) along the (0,π)−(π,π) direction become
shifted toward the Fermi level in the case of the La$^{3+}$-Pb$^{2+}$ doped samples. In addition, the apparent single Cu-O $\sigma$ band that crosses the Fermi level halfway between $(\pi, \pi)$ and $(0,0)$ [see Fig. 3(a)] is seen to split upon partial replacement of Sr$^{2+}$-Bi$^{3+}$ pairs by La$^{3+}$-Pb$^{2+}$ pairs; compare Fig. 2(a) and Fig. 3(a). This reflects the inherently lower crystal-field symmetry of the former compound. The fact that this is a crystal-field effect is demonstrated by displacing two Sr$^{2+}$ ions 0.1 and 0.2 Å away from one bracketed CuO$_2$ plane, thus artificially creating a weak-field–strong-field inhomogeneity between CuO$_2$ planes. The expected effect can be appreciated by comparing Fig. 3(a) to Figs. 3(c) and 3(e) at $(\pi, \pi)$-$(0,0)$, where the Cu-O $\sigma$ bands are seen to split.

Most importantly, it was reported that Bi$_{1.5}$Pb$_{0.5}$Sr$_{1.5}$La$_{0.5}$CuO$_6$ has characteristics of a band of O 2$p\pi$ character that may rise and touch the Fermi level in the $(0, \pi)$-$(\pi, \pi)$ direction; see Fig. 2. It is gratifying to note and indeed it is emphasized how this phenomenon can be reproduced by artificial Sr$^{2+}$ ion displacements in Bi$_2$Sr$_2$CuO$_6$; compare Figs. 3(a), 3(c), and 3(e) at $(\pi, \pi)$. Indeed, in the case of Fig. 3(e), the attenuated local crystal field causes the formation of a hole pocket in the vicinity of $(\pi, \pi)$. The fact that the surfacing band is of O 2$p$ character is concluded from the PDOS plots; see Figs. 3(b), 3(d), and 3(f).

Note, in particular, how the O 2$p$ states pile up at the Fermi level in Fig. 3(f). The $\pi$ character of the O 2$p$ states is again extracted by taking the real-space complementary perspective offered by sum over states densities in the vicinity of the Fermi level, producing STM-type images at the CuO$_2$ planes experiencing the weak and strong local crystal fields; see Fig. 4. Clearly, the planes experiencing weak and strong crystal fields exhibit different characteristics. Similar to the case of Bi$_{1.5}$Pb$_{0.5}$Sr$_{1.5}$La$_{0.5}$CuO$_6$, the strong local crystal fields display bias-independent Cu-O $\sigma$-band character at the...
FIG. 2. (Color online) (a) In-plane band structure (0,0)-(0,π)-⟨π,π⟩-(0,0) corresponding to the structures in Fig. 1(a). (b) Sum over states densities STM-type images in the case of the CuO₂ plane, which experiences strong (b1) and weak (b2) local crystal fields, illustrating particle-hole symmetry in both cases. (c) In-plane (0,0)-(0,π)-⟨π,π⟩-(0,0) band structure corresponding to the crystal structures in Fig. 1(b). (d) Corresponding sum over states densities STM-type images in the case of the CuO₂ plane, which experiences strong (d1) and weak (d2) local crystal fields illustrating particle-hole symmetry in the former, while particle-hole asymmetry in the latter. (e) In-plane band structure (0,0)-(0,π)-⟨π,π⟩-(0,0) corresponding to the structures in Fig. 1(c).
FIG. 3. (Color online) (a) Band structure and (b) CuO$_2$ PDOS for Bi$_2$Sr$_2$CuO$_6$ (compare Fig. 2). Also displayed are the band structure (c) and PDOS (d) for CuO$_2$ planes in Bi$_2$Sr$_2$CuO$_6$ caused to experience an artificially weak field (0.1 Å displaced Sr$^{2+}$ ions; see text). (e) and (f) are the same as (c) and (d) but with 0.2-Å Sr$^{2+}$ displacements. The PDOS display the Cu 3$d$ (red) and O 2$p$ (blue) contributions.

Fermi level, that is, qualitative particle-hole symmetry [cf. Figs. 4 (a1), (a2) and Figs. 4(c1), (c2)]. In the case of the CuO$_2$ plane experiencing weak local crystal field, the STM images acquire in addition significant O 2$p_{\pi}$ character. For the 0.1-Å Sr$^{2+}$ displacement, the particle-hole asymmetry observed qualitatively reproduces what was found for Bi$_{1.5}$Pb$_{0.5}$Sr$_{1.5}$La$_{0.5}$CuO$_6$ [see Fig. 2(d)]. In the case of 0.2-Å displacement, the hole pockets developing at ($\pi,\pi$) cause the particle-hole symmetry in the weak local crystal-field CuO$_2$ plane, and the characteristics of the O 2$p_{\pi}$ states become further accentuated; cf. Figs. 4(d1) and (d2). Essential here is the change in character of the particle states from Cu-O $\sigma$ in the case of strong crystal fields into O 2$p_{\pi}$ in the case of weak local crystal fields. The possible consequences of hole-pocket instabilities are discussed later.
V. POSSIBLE CAUSE OF PARTICLE-HOLE ASYMMETRY ACROSS THE PSEUDOGAP

Having thus made a connection between the two employed model compounds, attention is given to the $(-\pi,\pi)-(0,\pi)$ segment in the Brillouin zone, which was considered experimentally in Ref. 20.

The present interpretation assumes the Fermi surface of the hole-doped cuprates at $T > T^*$ to be well understood in terms of a hole-doped Hubbard-Mott insulator with a local Cu 3d$^9$ electronic structure. Upon cooling, band shoulders at $\sim (\pm 0.1,\pi)$ appear at $T \sim T^*$ and become saturated at $\sim (\pm 0.2,\pi)$ for $T < T^*$. Here, this phenomenon is arrived at by first considering how upon cooling, crystal-field inhomogeneities cause the trapping of charge carriers. Indeed, the a priori symmetry-broken crystal field may be insignificant at elevated temperatures due to the high mobility of the charge carriers at those temperatures, but may become decisive below $T^*$ and thus produce the observed temperature dependence of the ARPES signal. Secondly, this trapping acts to destabilize the holes a priori residing in the Cu-O $\sigma$ bands. Thus, holes become partially transferred to the O 2$p_\pi$ band. The destabilization of holes in Cu-O $\sigma$ bands has two origins, of which one is the competing local AFM order and the second is the thermally modified crystal field destabilizing the O 2$p_\pi$ band to the extent that it becomes a hole sink as manifested in the evolution of hole-pocket instabilities centered at $\pi$ in the ARPES signal. This understanding is summarized in Figs. 5(a) and 5(b), where the band folding is representative of twice doubling the unit cell to make a connection to the checkerboard superstructure. Figure 5(c) repeats the central part of Fig. 5(b) for the twice-folded O 2$p_\pi$ band. A qualitative connection to the ARPES band structure at $T < T^*$ is made by tracing the occupied and unoccupied electronic states in Fig. 5(c). This is the cause of the claimed particle-hole asymmetry understood to result from two disjoint bands crossing the Fermi level in conjunction with a four-unit-cell modulated stripe superstructure. The gap is due to two effects: (a) the stripes CDW in the O 2$p_\pi$ band, and (b) the antiferromagnetic fluctuations. Assuming further stabilization of the Cu-O $\sigma$ band and complementary destabilization of the O 2$p_\pi$ band upon further cooling, it is indicated in Fig. 5(d) how the U-shaped Cu-O $\sigma$ band is made to cross the first V-shaped segment of the O 2$p_\pi$ band. This gives the resulting band an additional complexity, similar to that observed in Ref. 20, upon approaching the critical temperature for superconductivity.

It is emphasized that said stripes phenomenology is a spectator to the HTSC. Essential to the HTCS is how the hole-pocket instability at $\pi$-pocket character of O 2$p_\pi$ character has a bearing along the SC gap function nodal $(0,0)$-$\pi$ direction. Indeed, a checkerboard superstructure, such as the generic charge-carrier segregated superlattice motif obtained for oxygen-doped Hg1201 (see, e.g., Fig. 6), is expected to produce additional Fermi-level crossing anomalies in the vicinity of both $(\pi/2,\pi/2)$ and $(\pi/4,\pi/4)$ due to the surfacing O 2$p_\pi$ band. This provides a complementary conceptual framework for the interpretation of such observations, contrasting, in particular, other proposed real-space inhomogeneities. Indeed, the spectral broadening, taken in Ref. 20 to reflect electronic inhomogeneities, supports an interpretation along
the line suggested in Figs. 5 and 6. This is partly because (a) instability toward hole clustering is conditional for the low-dispersive O 2$p_z$ bands to carry holes, and (b) $\sim$25% random replacement of Sr$^{2+}$ by La$^{3+}$ and Bi$^{3+}$ by Pb$^{2+}$ is expected to cause random zero-dimensional charge-carrier attractors due to the inhomogeneous crystal field. It is emphasized...
that such charge-carrier segregations preserve the inherent near-degeneracy in the hole clusters due to the small O 2$p_\pi$–O 2$p_\pi$ orbital overlaps across the unit cell. Note in Fig. 6 the apparent similarity to the ZR motif, although in our case the Cu$^{2+}$ ion, crucial to the ZR paradigm, is absent.

In conclusion, band structures, partial densities of states, and sum over states densities in the vicinity of the Fermi level have been employed to demonstrate sensitivity of the position of the O 2$p_\pi$ band to local crystal field in two Bi2201 model systems to the extent that this band crosses the Fermi level in the vicinity of ($\pi, \pi$). This result was employed to propose an alternative interpretation of the particle-hole asymmetry across the pseudogap reported by Shen and co-workers. The possible relevance of such an observation for HTS was discussed in the context of a quantum chemical formulation of high-$T_c$ superconductivity, the purpose of which is to serve as a conceptual tool for the discovery of new and improved superconducting materials.

VI. COMPUTATIONAL DETAILS

The band-structure calculations employ the CASTEP program package within the Material Studios framework. The GGA PBE functional was employed. Core electrons were described by ultrasoft pseudopotentials. O (6 electrons), Cu (11 electrons), Sr (10 electrons), La (11 electrons), Pb (14 electrons), and Bi (5 electrons), employing a 340-eV cutoff energy. Summations over the Brillouin zone employed a $7 \times 7 \times 1$ Monkhorst-Pack grid.

ACKNOWLEDGMENTS

The author wishes to thank Tord Claeson and Øistein Fischer for stimulating discussions.

43. Materials Studio 5.0, Accelrys Inc., simulation software.