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\[ Pb_{0.4}Bi_{1.6}Sr_2CaCu_2O_{8+x} \text{ and Oxygen Stoichiometry:} \]

Structure, Resistivity, Fermi Surface Topology and Normal State Properties

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Abstract

\[ Pb_{0.4}Bi_{1.6}Sr_2CaCu_2O_{8+x} \text{ (Bi}(Pb)\text{--2212) single crystal samples were studied using transmission electron microscopy (TEM), } ab-\text{plane (}\rho_{ab}\text{) and } c-\text{axis (}\rho_c\text{) resistivity, and high resolution angle-resolved ultraviolet photoemission spectroscopy (ARUPS). TEM reveals that the modulation in the } b-\text{axis for } Pb(0.4)-\text{doped Bi}(Pb)-2212 \text{ is dominantly of } Pb-\text{type that is not sensitive to the oxygen content of the system, and the system clearly shows a structure of orthorhombic symmetry. Oxygen annealed samples exhibit a much lower } c-\text{axis resistivity and a resistivity minimum at } 80-130K. \text{ He-annealed samples exhibit a much higher } c-\text{axis resistivity and } d\rho_c/dT < 0 \text{ behavior below 300K. The Fermi surface (FS) of oxygen annealed } Bi(Pb)-2212 \text{ mapped out by ARUPS has a pocket in the FS around the } \bar{M} \text{ point and exhibits orthorhombic symmetry. There are flat, parallel sections of the FS, about 60\% of the maximum possible along } k_x = k_y, \text{ and about 30\% along } k_x = -k_y. \text{ The} \]
wavevectors connecting the flat sections are about 0.72(\pi, \pi) along $k_x = k_y$, and about 0.80(\pi, \pi) along $k_x = -k_y$, rather than (\pi, \pi). The symmetry of the near-Fermi-energy dispersing states in the normal state changes between oxygen-annealed and He-annealed samples.

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I. INTRODUCTION

For cuprate superconductors, the shape of the Fermi surface and the properties of the normal state electronic states has been of continuing interest. The shape of the Fermi surface is of interest because it constrains theoretical models. In $YBa_2Cu_3O_{7-x}$, excellent agreement has been obtained between angle-resolved photoemission experiments $[1-4]$ and local density approximation (LDA) band structure calculations. $[5-7]$ More recently, K. Gofron et al. $[8]$ have reported an extended van Hove singularity for $YBa_2Cu_3O_{7-x}$. A. Abrikosov $[9]$ has argued that such a band structure feature is important in understanding the high superconducting transition temperature ($T_c$).

The symmetry of electronic states comprising the Fermi surface is identified in $YBa_2Cu_3O_{7-x}$ $[3,4]$ because the material is underdoped for $6.35 < x < 6.95$ and oxygen is removed predominantly from the chains. $[10-12]$ The $c$-axis resistivity $\rho_c$ increases as $x$ increases, and the interlayer coupling weakens. Several reports $[13]$ indicate that the chain electronic states are involved in the superconducting properties.

The situation is less clear in $Bi_2Sr_2CaCu_2O_{8+x}$ ($Bi-2212$). C. Olson and colleagues observed the Fermi surface in this material that appears to be consistent with LDA calculations. $[17,18]$ They have also reported the presence of an electron-like pocket around the $(\pi, 0)$ ($\bar{M}$) point for overdoped samples; the pocket was not observed after removing oxygen. $[14,15]$ These results are in qualitative disagreement with a rigid band model. Several other authors $[16]$ have, on a variety of grounds, criticized using a rigid band model. Further, an extended van Hove singularity along the $\Gamma - \bar{M} - Z$ direction in the Brillouin zone has been reported. $[19,20]$ The Fermi surface shape is not universally agreed on, although most reports argue that the Fermi surface exhibits orthorhombic $[13,21]$ rather than tetragonal $[20]$ symmetry.

$Bi_2Sr_2CaCu_2O_{8+x}$ is more complicated for three primary reasons, all material-related. The $BiO$ planes do not fit perfectly above/below the $CuO_2$ planes, so a buckling in the $\Gamma - Y$ direction of the Brillouin zone results. Also, oxygen is removed or added primarily to the
The BiO double layer. [16] Since the BiO layers possess electronic states near the Fermi energy, the interlayer coupling and $\rho_c$ can be changed dramatically by varying the oxygen stoichiometry. [17,18] Finally, small differences in cation stoichiometry, and hence disorder, affects the change of oxygen stoichiometry for the same annealing conditions. [16]

The Pb–doped BSCCO has attracted much attention since Sunshine et al. [23] found that the substitution of lead can enhance the superconducting temperature $T_c$ in BSCCO multiphase. It was then found that the lead substitution has a strong influence on the incommensurate modulation that exists in the $b$–axis. [24–29] in both Bi–2212 and Bi–2223. It appears that the lead doping could reduce the structure anisotropy (ratio of $\rho_c/\rho_{ab}$) which is always a factor complicating the interpretation of the experimental data. [29] It is generally believed that Pb-doping does not perturb the electronic state critical to forming the superconducting state in this system. [31]. Therefore the electronic structure of Bi(Pb)–2212 should be a proper representation of lead-free Bi(Pb)–2212.

We have performed extensive measurements on both oxygen annealed and helium annealed Bi(Pb)–2212 single crystals using Transmission Electron Microscopy (TEM), in-plane and $c$–axis resistivity, and Angle-Resolved Photoemission Spectroscopy (ARUPS). We have used Bi(Pb)–2212 samples due to the larger variation in oxygen stoichiometry that we have been able to reach with single crystal samples.

Our data in this paper lead to several conclusions for Bi(Pb)–2212: Bi(Pb)–2212 is structurally orthorhombic; oxygen stoichiometry can be very effective in changing the $c$–axis resistivity, and quite possibly changing the interlayer coupling; the Fermi surface exhibits orthorhombic symmetry, incomplete Fermi surface nesting, and, for sufficiently overdoped samples, a pocket around the $\bar{M}$ point in the Brillouin zone; the symmetry of the electronic states comprising the Fermi surface changes with oxygen stoichiometry; the rigid band model does not apply.
II. EXPERIMENTAL

The single crystal samples of $Bi_{1.6}Pb_{0.4}Sr_2CaCu_{2}O_{8+x}$ ($Bi(Pb)-2212$) were prepared using the method similar to that of Wu et al. [31]. The crystals were characterized using four-point resistivity, ac susceptibility, X-ray diffraction and transmission electron microscopy (TEM).

Transmission electron microscopy measurements were carried out with a JEOL 200CX microscope operating at 200 KV. The $Bi(Pb)-2212$ single crystal samples were cleaved repeatedly and thin flakes were then mounted on to a single-hole gold grid using M-bond adhesive. In order to examine the crystal from the [100] direction to study the structural modulation, the crystals were mounted so that the sample foil surface is perpendicular to the [100] direction. The samples were then mechanically polished and finally ion-milled at 4.5 KV.

The ARUPS experiments were performed using the four meter normal incidence monochromator at the Wisconsin Synchrotron Radiation Center in Stoughton, WI. The beamline provides highly (> 95%) linearly polarized light with the photon electric vector in the horizontal plane and with photon energy resolution better than 10 meV. The angle-resolved photoemission chamber includes a reverse-view low energy electron diffraction (LEED) optics used to orient the sample in situ after cleaving. The electron energy analyzer is a 50 mm VSW hemispherical analyzer mounted on a two axis goniometer, with an acceptance full angle of 2°. The base pressure is $6 \times 10^{-11}$ torr. The incidence angle between the photon Poynting vector and surface normal was 45° unless otherwise noted.

For photoemission studies, the samples were transferred from a load lock chamber with a base pressure of $5 \times 10^{-9}$ torr to the main chamber, and cleaved at 30K in a vacuum of $6 - 8 \times 10^{-11}$ torr. The sample holder includes the capability to rotate the sample in situ about the surface normal, at low temperatures, for precision alignment with respect to the photon electric field. To measure the normal state electronic band structure, the temperature was raised to 95K, above $T_c$. The stability of the temperature was $\pm 1K$. For
this study, the overall energy resolution employed was 55 meV unless otherwise stated.

For a quasi-two-dimensional system such as $Bi_2Sr_2Ca_1Cu_2O_{8+x}$ the initial state of the electron can be determined by measuring the component of the electron momentum parallel to the sample surface ($\mathbf{k}_{//}$). By measuring the energy distribution curves (EDC’s) for different directions ($\theta, \phi$) of the emitted photoelectron relative to the surface normal, the $\mathbf{k}_{//}$ of the initial state is derived from the relation:

$$\mathbf{k}_{//} = 0.512 \hat{A} \sqrt{E_{\text{kin}} \sin \theta \cos \phi \hat{k}_x + \sin \phi \hat{k}_y},$$

where $E_{\text{kin}}$ is the kinetic energy of measured photoelectrons in the unit of eV, $\hat{k}_x$ and $\hat{k}_y$ denote unit vectors along horizontal and vertical directions, respectively. A freshly in situ deposited gold film was used as a reference to determine the Fermi energy.

The modified modulation structure in $Bi(Pb)-2212$ due to lead substitution was confirmed by our in situ LEED study. At low electron beam energy (27 eV) the LEED pattern exhibits an almost 1×1 structure for $Bi(Pb)-2212$ whereas it is a 4.6×1 pattern for lead-free $Bi-2212$. At higher electron beam energies (above 40 eV) we do observe a modulation for the oxygen-annealed samples that is absent for the He/Ar-annealed samples. The sharp and intense LEED spots confirmed the high quality of the cleaved surfaces which is a prerequisite for performing ARUPS measurements.

### III. CRYSTAL STRUCTURAL AND TRANSPORT MEASUREMENTS

#### A. Crystal Structure of Bi(Pb)-2212

The chemical composition and the crystal structure of the $Pb$–doped $Bi-2212$ single crystals were examined by analytical electron microscopy. Energy dispersive X–ray spectroscopy confirmed the $Pb$ was incorporated into the $Bi-2212$ crystals. A twin-like domain structure was observed in the $Bi(Pb)-2212$ crystals, which has rarely been seen before in the lead-free crystals. Fig. 1 shows the [001](a) and [100](b) diffraction patterns on the oxygen annealed $Bi(Pb)-2212$ crystals. Both patterns show the modulated structure in the $Bi$ system which can be understood in terms of a basic structure (shown as the indexed
strong main spots) plus a superimposed displacement field (shown at those satellite spots marked by arrows). From the [100] pattern, there is only one type of modulation which parallels exactly with the $b-$ direction. This is the typical $Pb-$type modulation, as has been discussed previously. However, the modulation wavelength along the $b-$ direction is about $13b$ here, much longer than those reported previously (typically $8 - 10b$). Such an increasing of the modulation wavelength may be related to the $Pb$ content and the oxygenation effect. No $Bi-$type modulation was observed in this sample.

In order to identify the structure symmetry of the crystals, we have performed convergent beam electron diffraction (CBED) measurements. Care was paid to avoid any imperfect area when selecting regions to perform CBED measurements, since any defects or artifacts can break symmetry. CBED were performed many times at different locations in the crystals and Fig. 2 shows a typical example of the [001] CBED pattern of the oxygen annealed sample. It is evident that only one mirror plane can be identified, as indicated by the vertical line marked with $m$, implying a $2mm$ point-group symmetry of the orthorhombic system.

In a comparative study, we have performed the same CBED study on a $Pb-$free $Bi$−2212 single crystal and found that there are two mirror planes in the [001] pattern, implying a $mmm$ symmetry group, which also belongs to the orthorhombic structure. Therefore, it seems that the $Pb-$doping lowers the symmetry of the 2212 crystal. To date, reports on the precise symmetry of the $Bi(Pb)$−2212 system have not reached a consensus. Nevertheless, it is agreed that the structure of the $Bi(Pb)$−2212 studied here exhibits orthorhombic, not tetragonal, symmetry.

We also performed the same experiments on the helium annealed $Bi(Pb)$−2212 samples. Again, no $Bi-$type modulation was observed. The $Pb-$type modulation remained unchanged as comparing to the modulation observed in the oxygen annealed samples. This suggests that the change of the oxygen content does not affect the $Pb-$type modulation, which is consistent with the results reported by Chen et al. in their $Pb-$doped bulk 2212 samples. No noticeable changes were found in crystal symmetry as comparing to the oxygen annealed samples. Only one mirror plane was observed at the [001] CBED pattern,
similar to the results for oxygen annealed sample.

**B. In-plane and c-axis resistivity**

For lead-free $Bi-2212$, the in-plane resistivity is metallic and the out-of-plane resistivity is highly semiconducting. The resistivity anisotropy ratio of $\rho_c/\rho_{ab}$ near $T_c$ varies from $\sim 2 \times 10^5$ (lead-free, vacuum annealed) to $\sim 800$ (lead-doped, oxygen annealed). The transport measurements on the in–plane and $c$–axis resistivity were first performed on $Bi(Pb)-2212$ single crystal samples by Régi and co-workers. They demonstrated that lead substitution reduced the the resistivity anisotropy ratio $\rho_c/\rho_{ab}$ by two orders of magnitude near the transition temperature $T_c$, compared to the lead-free $Bi-2212$. Furthermore, they showed that the $c$–axis resistivity behaviour becomes metallic for lead-doped 2212. Our resistivity measurements on $O_2$ annealed $Bi(Pb)-2212$ have fully confirmed their results, as shown in Fig. 3(a). A linear behavior of $\rho_c$ occur in the temperature range of 125K–300K. The upward curvature near $T_c$ suggests $c$–direction localization of carrier.

However, as shown in Fig. 3(b), for He annealed $Bi(Pb)-2212$ we see the similar semiconducting behaviour in the $c$–axis transport as that for lead-free 2212. X-ray diffraction, TEM and LEED measurements exhibit no significant structural difference between He-annealed and $O_2$-annealed lead-doped samples. These data are thus a strong indication that it is the amount of oxygen incorporated into a $Bi(Pb)-2212$ sample that controls the $c$–axis transport property. The presence of lead has made it easier to get oxygen into or out of $Bi(Pb)-2212$ samples. As we will show in the next section, $O_2$ doping changes both the carrier concentration in $Bi(Pb)-2212$ (in turn changing the chemical potential), and also the electronic structure.

**IV. FERMI SURFACE TOPOLOGY**

The topology of the Fermi surface is an important measure of the electronic structure. The Fermi surface has been mapped out on lead-free $Bi_2Sr_2CaCu_2O_{8+x}$ ($Bi-2212$) in dif-
different oxygen-doped regimes using ARUPS by different groups [14,19,41,20]. Unlike what has been done for \( YBa_2Cu_3O_{7-x} \) (YBCO-123) [2,4], there has not yet been a systematic study of the Fermi surface versus oxygen stoichiometry for the \( Bi-2212 \) systems. We believe that the difficulty in obtaining totally consistent results from different research groups stems from the lack of control of oxygen stoichiometry compared to that available for the YBCO-123 system.

Due to the comparative ease with which the oxygen stoichiometry can be varied, the \( Bi_{1.5}Pb_{0.4}Sr_2CaCu_2O_{8+x} \) (\( Bi(Pb)-2212 \)) system appears to be an ideal system to study the Fermi surface topology. Figure 4 presents the complete set of angle-resolved photoemission spectra taken on the same oxygen overdoped \( Bi_{1.5}Pb_{0.4}Sr_2CaCu_2O_{8+x} \) single crystal sample. A photon energy of \( h\nu = 21 \) eV was used. The sample was oriented so that the \( \Gamma - X \) is in the horizontal plane which is also the photon polarization plane. The effect of polarization on the different orientations of the sample was very useful in determining the symmetries of the normal state bands and will be discussed in the next section.

In Fig. 4, the spectra in each vertical column were obtained by changing the angle \( \theta \) with fixed angle \( \phi \). The spectra have been aligned horizontally so that the spectra taken at the same \( \theta \) angle, but at different \( \phi \) angles are on the same horizontal level. By keeping \( \theta \) fixed, one can go along a direction parallel to the \( \Gamma - Y \) symmetry direction. Similarly, one can go along a direction parallel to the \( \Gamma - X \) direction by scanning \( \theta \) with \( \phi \) fixed. We shall discuss some of the spectra in detail, below.

Using the data of Fig. 4, a purely empirical construction of the Fermi surface of \( O_2 \)-annealed \( Bi_{1.5}Pb_{0.4}Sr_2CaCu_2O_{8+x} \) is illustrated in Fig. 5(a). We emphasize that no \textit{a priori} symmetry assumptions were made in constructing Fig. 5(a). The Fermi surface is orthorhombic, and \( \Gamma - X \) and \( \Gamma - Y \) are inequivalent. [19,21,31,11] Specifically, the shape of the Fermi surface around the \( X \)-point is very similar to that reported by P. Aebi et al. [11] We do not have conclusive data to comment on the presence or absence of the “shadow bands” reported by P. Aebi et al. [11] However, again similar to Ref. [11], the Fermi surface nesting is not complete. Instead, the portion of the Fermi surface parallel to \( \Gamma - X \) \((k_x = k_y)\)
is about 60% of the extent expected for perfect nesting, and the nesting wavevector is approximately $0.72(\pi, \pi)$. The portion of the Fermi surface parallel to $\Gamma - Y$ ($k_x = -k_y$) is about 30% of the extent expected for perfect nesting, and the nesting wavevector is approximately $0.80(\pi, \pi)$.

The above aspects are illustrated more explicitly in Fig. 5(b). We have assumed only $C_{2v}$ symmetry in constructing Fig. 5(b). Our nesting wavevectors can be directly compared to the predictions of Ruvalds et al. Ref. [40] predicts a marked decrease in the superconducting transition temperature ($T_c$) when the nesting wavevector decreases from $(\pi, \pi)$. Our results agree qualitatively with Ref. [40]: the $T_c = 75K$ of $O_2$–annealed $Bi(Pb)_{-2212}$ is lower than the $T_c = 90K$ of optimally doped $Bi_{-2212}$. Ruvalds et al. [40] do not obtain quantitative agreement with our data; their predicted $T_c$ for our samples is below 5K, compared to a measured value of 75K.

In addition, our data indicate a pocket around the $\bar{M}$ point, similar to that reported on $O_2$–annealed $Bi_{-2212}$ samples by C. Olson and colleagues. The portion parallel to $\Gamma - X$ (labeled “b” in Fig. 5(a)) merges with this pocket, while the portion around the $X$–point (labeled “a” in Fig. 5(a)) remains distinct from the pocket. These results further indicate that $\Gamma - X$ and $\Gamma - Y$ are inequivalent.

To validate the Fermi surface presented in Fig. 5, we present detailed spectra along particularly important directions. Fig. 6(a) illustrates the spectra taken along $\Gamma - X$ direction. A band disperses towards the Fermi energy ($E_f$) from more than 200 meV below $E_f$ at $\theta$ of 10° and crosses the Fermi level at $\theta = 14^\circ$ (note abrupt reduction of photoemission intensity). Along the $\Gamma - Y$ direction, as illustrated in Fig. 6(b), we observe an almost equally strong band dispersing towards $E_f$. The band crossed the Fermi energy at $\phi = 12^\circ$. The absolute positions of crossing are slightly different with respect to the $\Gamma$ point between $\Gamma - X$ and $\Gamma - Y$ directions, indicating that the Fermi surface around the $X$ point might be further away from $\Gamma$ than the Fermi surface around the $Y$ point. The difference of 2° is right at our combined experimental angular uncertainty.

The spectra along the $\Gamma - \bar{M}$ direction are illustrated in Fig. 6(c). A band with small
dispersion is observed near $E_f$ and crosses the Fermi energy at $\theta/\phi = 16^\circ/16^\circ$ (note reduction in photoemission intensity). We did not observe such a Fermi surface crossing for the lead-free samples. [19]

The spectra indicating the turning points where the flat sections of the Fermi surface (FS) around $X$ and $Y$ start to curve are presented in Fig. 7. In Fig. 7, the FS crossing happened at $\theta = 16^\circ$ for $\phi = 6^\circ$, whereas the FS crossings were at $\theta = 14^\circ$ for $\phi < 6^\circ$. Along the direction parallel to $\Gamma - Y$ at $\theta = 12^\circ$, the FS crossing was at $\phi = 14^\circ$, and the flat sections of FS were at $\phi = 12^\circ$ with $\theta < 14^\circ$.

The evidence of the existence of the pocket-like Fermi surface is shown in Fig. 8. For a direction parallel to $\Gamma - X$, at $\phi = 20^\circ$, a band emerges from above the Fermi energy at about $\theta = 18^\circ$ (Fig. 8(a)), with increasing photoemission intensity as the state disperses below $E_f$. At $\phi = 18^\circ$, a similar Fermi surface crossing was observed at $\theta = 16^\circ$ in Fig. 8. We already know (Fig. 8(c)) that there is a FS crossing at $\phi/\theta = 16^\circ/16^\circ$. Fig. 8(c) shows two FS crossings as one goes along a direction parallel to $\Gamma - Y$ at $\theta = 22^\circ$. The first crossing at $\phi = 12^\circ$ belongs to the FS around $X$ point. There is also a second crossing, at $\phi = 18^\circ$, that is part of the pocket and not part of the FS around the $Y$ point. The double FS crossings are also present in Fig. 8(d). The first FS crossing at $\phi = 10^\circ$ corresponds to the FS around $X$ point, and the second FS crossing at $\phi = 16^\circ$ is near $\bar{M}$ but away from $Y$ point. Finally, in Fig. 8(e), the first FS crossing at $\phi = 8^\circ$ belongs to the FS around $X$ point and the second crossing at $\phi = 16^\circ$ completes the pocket-like Fermi surface as indicated in Fig. 5. It was unfortunate that we were not be able to take data beyond $\phi = 20^\circ$ due to technical limitations of our sample holder arrangement, but the pocket-like FS, although incomplete, is clearly present in the spectra in Fig. 8.

In summary, the Fermi surface map (Fig 5) and supporting data (Figs. 4, 6–8) establish several important points:

- the Fermi surface exhibits orthorhombic symmetry;
- the Fermi surface nesting is quite incomplete for these HTSC’s ($T_c = 75K$);
• there is a pocket around the $\bar{M}$ point. Because we observe no Fermi surface crossing along $\Gamma - \bar{M} - Z$ for He annealed samples, the data indicate that there is no pocket around the $\bar{M}$ point for He-annealed samples. Thus, insofar as a pocket is concerned, the $Bi(Pb)-2212$ behaves in the same qualitative fashion as reported by C. Olson and colleagues [14,15] for $Bi-2212$.

There are at least two models that view the “flat band” around the $\bar{M}$ point as important: Abrikosov’s argument [9] about the effects of an extended van Hove singularity, and Dagotto et al. [42] electron correlation model. The model of Dagotto et al. [42] achieves quantitative agreement with our data on $Bi-2212$ samples. [19] To date, we are unaware of published calculations that predict the effects of a pocket on the superconducting properties. It is clear, however, that such a fundamental change in the Fermi surface topology can serve as a test for the above models when calculations are available. Let us now turn to the second part of this report, the symmetry of the normal state wavefunctions.

V. SYMMETRY OF THE NORMAL STATES: BLOCH’S THEOREM APPLIES

In this section, we present data demonstrating that the symmetry of the normal state wavefunctions changes with oxygen stoichiometry for $Bi(Pb)-2212$ samples. Because Bloch’s theorem applies, and X-ray diffraction, TEM, and LEED measurements indicate no structural change in the $CuO_2$ planes, there are very few plausible explanations for the data; these are discussed after the data are presented.

We employ a standard photoemission method, [44] using linearly polarized light to probe the symmetry of the normal state. A photoemission process can be described as a transition of the electron from the initial state $|\Psi_i >$ to a free electron final state $|\Psi_f >$ in vacuum. The differential photoionization cross section, to which the photoemission signal is proportional, can be derived from the Fermi-golden-sum rule as [44]:

$$\frac{d\sigma}{d\Omega} \propto |< \Psi_f | P \cdot A_0 |\Psi_i > |^2 \delta(E_f - E_i - h\nu),$$  \hspace{1cm} (5.1)
where \( \mathbf{P} \) is the momentum operator, \( \mathbf{A}_o \) the vector potential of photon electric field of the energy \( h\nu \). We define a plane of reflection symmetry by the \( z \)-axis (the surface normal) and the photoelectron emission direction. In order to detect a signal, the final state of the photoelectron must be even under reflection about this symmetry plane. Otherwise, there would be a node in the final state wave function in the symmetry plane and no signal would be observed under any condition. In our experimental setup, if the \( \mathbf{A} \) is in the \( x \)-direction, or \( \mathbf{A} = A_x \hat{x} \), the dipole operator \( \mathbf{P} \cdot \mathbf{A} = P_x A_x \) will be even under the reflection about \( xz \)-plane (\( y \rightarrow -y \)), and odd under the reflection through the \( yz \)-plane (\( x \rightarrow -x \)). By analysing the parities of the initial state of various possible spherical harmonics, \( s \), \( p \), and \( d \), under the same reflection operation, and comparing the \( \langle \Psi_f | \mathbf{P} \cdot \mathbf{A} | \Psi_i \rangle \) with the signals observed in the experiments, we shall be able to exclude the initial states of the spherical harmonics that are forbidden by the dipole selection rule. [45]

Figure 9 illustrates normal state angle-resolved photoemission spectra for an \( O_2 \)-annealed \( Bi(Pb)–2212 \) sample. The data include different geometries of photon electric field vector and sample orientation, including: (a) \( \Gamma - \bar{M} - Z \) oriented in the horizontal or vertical directions; (b) \( \Gamma - X \) oriented in the horizontal or vertical directions; (c) \( \Gamma - Y \) oriented in the horizontal or vertical directions. The insets illustrate the locations in the Brillouin zone where the spectra were obtained. The corresponding data for a \( He \)-annealed \( Bi(Pb)–2212 \) sample are illustrated in Figure 10. For the orientation that \( \Gamma - \bar{M} - Z \) is horizontal or vertical, the spectra are similar to Fig. 9(a), not shown. Consequently, we can directly compare Figs. 9(b) to 10(a), and 9(c) to 10(b).

Several important points emerge from the data of Figs. 9 and 10. Both types of samples exhibit the same symmetry (even symmetry) for the state along the \( \Gamma - \bar{M} - Z \) direction. However, there is a change of symmetry for the state along the \( \Gamma - X \) direction. \( O_2 \)-annealed samples exhibit a state of mixed (even and odd) symmetry along \( \Gamma - X \). By contrast, \( He \)-annealed samples exhibit a state of odd symmetry along \( \Gamma - X \). In addition, there is a change of symmetry for the state along the \( \Gamma - Y \) direction. For \( O_2 \)-annealed samples, the state along \( \Gamma - Y \) exhibits odd symmetry (note the strong dispersing peak in the vertical
orientation, Fig. 9(c)). This strong, dispersing, peak along \( \Gamma - Y \) is not observed in either orientation for \( He \)-annealed samples (Fig. 10(c)).

We have compared the data in Figs. 9 and 10 to the symmetry of various spherical harmonics. A similar analysis has been performed earlier by Kelley et al. for the superconducting state of \( Bi-2212 \) and by Ratner et al. for \( Pr \)-doped \( Bi_2Sr_2CuO_{6+y} \). We have assumed that the coupling between the photon electric field and the near \( E_f \) states along \( c \)-axis is so weak that the term \( P_z A_z \) in the dipole interaction can be ignored. Tables I and II present the comparison between experimental data of the states along the \( \Gamma - X \), \( \Gamma - Y \) and \( \Gamma - \bar{M} - Z \) directions to various spherical harmonics. For \( O_2 \) annealed \( Bi(Pb)-2212 \) samples the symmetry of the states along \( \Gamma - X \) is consistent only with either \( p_x \) or \( d_{xz} \) spherical harmonic, while the states along \( \Gamma - Y \) are consistent with only a \( d_{x^2-y^2} \) spherical harmonic. For \( He \) annealed \( Bi(Pb)-2212 \) samples, the states along \( \Gamma - X \) are consistent with a \( d_{x^2-y^2} \) spherical harmonic, while the states along the \( \Gamma - Y \) direction are not consistent with any single spherical harmonic.

The data of Figs. 9 and 10 establish that varying the oxygen stoichiometry changes the symmetry of the normal state dispersing wavefunction along both the \( \Gamma - X \) and \( \Gamma - Y \) directions. The data were taken in the normal state, so within a one electron picture Bloch’s theorem applies. Consequently, a change in symmetry is due to a change in the spatial orientation of the wavefunction. We have looked for, and found no indication of, a change in the structure of the \( CuO_2 \) planes. We have, however, observed a change in the interlayer coupling (Fig. 3). In the absence of a structural change in the \( CuO_2 \) planes, the data compel us to conclude that the change in wavefunction symmetry is caused by the change in interlayer coupling.

The above conclusion is within the context of a one-electron picture, for which Bloch’s theorem holds. However, as we mention earlier, Dagotto et al. recently obtained quantitative agreement with our data for the \( Bi-2212 \) system. Ref. argues that the dispersion relations arise from many-body effects, within the context of a \( t-J \) model. Calculations are in progress to extend these results by including next-nearest-neighbor in-
At present, we are unaware of any available many-body calculation to which we can compare our data.

VI. Bi(5d) AND Pb(5d) CORE LEVELS

As noted earlier, one motivation for our study was the earlier results of C. Olson and colleagues, which did not appear consistent with a rigid band picture. Other investigators have also argued that a rigid band picture is inappropriate for the cuprate superconductors. The change in wavefunction symmetry along $\Gamma - X$ and $\Gamma - Y$, as concluded in the previous section, are also inconsistent with a two-dimensional, rigid-band, picture. We used another method to determine whether a rigid band model is appropriate. In the rigid band model, changing the oxygen stoichiometry (the carrier concentration) will change the chemical potential. Such a change of chemical potential would produce a rigid shift of all electronic states, including the valence band and core levels.

We thus measured the valence band and $Bi(5d)$ core levels for three types of samples: as-grown $Bi-2212$ ($T_c = 90K$), $O_2$--annealed $Bi(Pb)-2212$ ($T_c = 75K$), and $He$–annealed $Bi(Pb)-2212$ ($T_c = 85K$). Fig. 11 illustrates the results. The data in Fig. 11 are inconsistent with a rigid band model. We first used the as-grown $Bi-2212$ samples as a reference. The conduction band of the $O_2$–annealed $Bi(Pb)-2212$ samples were shifted by 310 meV to lower binding energy. However, the $Bi(5d)$ core levels of the same samples were shifted by only 60 meV to lower binding energy. For the $He$–annealed $Bi(Pb)-2212$ samples, the conduction band was shifted by 160 meV to lower binding energy, while the $Bi(5d)$ core levels were shifted by 250 meV to higher binding energy. Thus, the rigid band model, which would result in the same shift of all states– is inconsistent with the data.

In addition, the rigid band model is also inconsistent with the data taken from only lead-doped samples. As Fig. 11 illustrates, we also measured the $Pb(5d)$ core level for such samples. Using $O_2$–annealed $Bi_{1.6}Pb_{0.4}Sr_2CaCu_2O_{8+x}$ samples as a reference, the shifts of the $He$-annealed $Bi_{1.6}Pb_{0.4}Sr_2CaCu_2O_{8+x}$ samples include the valence band (150 meV
higher binding energy), the $Bi(5d)$ core level (310 meV higher binding energy), and the $Pb(5d)$ core level (260 meV higher binding energy).

In summary, we do observe a shift of the chemical potential to lower absolute energy for $O_2$—annealed samples, as expected. However, the rigid band model is not consistent with our data.

VII. CONCLUSIONS

From our TEM data, we have demonstrated that $Bi_{1.6}Pb_{0.4}Sr_2CaCu_2O_{8+x}$ is structurally orthorhombic and its crystal structure is not sensitive to oxygen stoichiometry we applied. However, we have observed a large reduction in $c$—axis resistivity for $O_2$—annealed $Bi_{1.6}Pb_{0.4}Sr_2CaCu_2O_{8+x}$ samples, consistent with earlier reports. The Fermi surface of such samples exhibits orthorhombic symmetry, incomplete Fermi surface nesting, and a pocket around the $\bar{M}$ point (which seems absent for He-annealed samples).

In addition, there is a change in the symmetry of the normal state dispersing band along both the $\Gamma - X$ and $\Gamma - Y$ directions with oxygen stoichiometry. Within the one-electron band structure picture, the data indicate that the change in symmetry is caused by the change in interlayer coupling as indicated by the change of $c$—axis resistivity.

By measuring the shift in both the chemical potential (valence band) and core levels, we have established that the rigid band picture does not apply to the $Bi_{1.6}Pb_{0.4}Sr_2CaCu_2O_{8+x}$ system, consistent with earlier reports on other cuprate systems.

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FIGURES

FIG. 1. The [001](a) and [100](b) electron diffraction patterns (EDP) of the oxygen annealed Bi(Pb)–2212 single crystal samples. Diffraction spots are indexed based on the fundamental structure. Satellite spots, as indicated by arrows, are due to the modulated structure. Similar EDP were observed on the helium annealed Bi(Pb)–2212 single crystal samples.

FIG. 2. [001]Convergent beam electron diffraction (CBED) pattern of the oxygen annealed Bi(Pb)–2212 single crystal samples. The pattern has only one mirror plane as indicated by the vertical line marked m, implying a 2mm point-group symmetry of orthorhombic structure. A similar CBED pattern was observed on the helium annealed Bi(Pb)–2212 single crystal samples.

FIG. 3. Temperature dependence of the $c$–axis resistivity and in-plane resistivity for Bi$_{1.6}$Pb$_{0.4}$Sr$_2$CaCu$_2$O$_{8+x}$ single crystals (a) annealed in 1 atmosphere $O_2$ at 600 °C for 1 hour; (b) annealed in 1 atmosphere helium at 600 °C for 1 hour.

FIG. 4. The normal state (T = 95K) angle-resolved photoemission spectra (EDC) measured on a oxygen overdoped Bi$_{1.6}$Pb$_{0.4}$Sr$_2$CaCu$_2$O$_{8+x}$ single crystal sample of $T_c$ = 75K using photon energy $h\nu = 21$ eV. The photoelectron emission angle relative to the surface normal ($\theta$ and $\phi$) are marked. The spectra in each vertical column were taken by changing the angle $\theta$ with fixed angle $\phi$. The data were taken in the range $0 \leq \phi \leq 20^\circ$ and $0 \leq \theta \leq 40^\circ$ which covers almost 2/3 of the first Brillouin zone.

FIG. 5. (a). The experimentally determined Fermi surface of Bi(Pb)–2212 from EDC measurements using $h\nu = 21$ eV. The data were taken on 160 points in the first Brillouin zone. No symmetry assumption is used. All of data points are experimental ones. (b). The Fermi surface of Bi(Pb)–2212 constructed out of experimental data points and assumption of $C_{2v}$ symmetry.
FIG. 6. Normal state (T = 95K) angle-resolved photoemission spectra for an oxygen overdoped $Bi_{1.6}Pb_{0.4}Sr_2CaCu_2O_{8+x}$ single crystal of $T_c = 75K$ along (a) the $\Gamma - X$ direction; (b) the $\Gamma - Y$ direction; (c) the $\Gamma - \bar{M} - Z$ direction. The photon energy employed was 21 eV. The insets show the locations in the first Brillouin zone where the data were taken.

FIG. 7. Normal state (T = 95K) angle-resolved photoemission spectra for an oxygen overdoped $Bi_{1.6}Pb_{0.4}Sr_2CaCu_2O_{8+x}$ single crystal of $T_c = 75K$ along (a) a direction parallel to $\Gamma - X$ at $\phi = 6^\circ$, where the Fermi surface crossing happens at $\theta = 16^\circ$ instead of $\theta = 14^\circ$ for $\phi < 6^\circ$; (b) a direction parallel to $\Gamma - Y$ at $\theta = 12^\circ$, where the Fermi Surface crossing is at $\phi = 14^\circ$ instead of $\phi = 12^\circ$ for $\theta < 12^\circ$.

FIG. 8. Normal state (T = 95K) angle-resolved photoemission spectra for an oxygen overdoped $Bi_{1.6}Pb_{0.4}Sr_2CaCu_2O_{8+x}$ single crystal of $T_c = 75K$ along the directions parallel to $\Gamma - X$ (a) at $\phi = 20^\circ$; (b) at $\phi = 18^\circ$, and the directions parallel to $\Gamma - Y$ (c) at $\theta = 22^\circ$; (d) at $\theta = 20^\circ$; and (e) at $\theta = 18^\circ$. The pocket-like Fermi surface around $\bar{M}$ is derived from those cuts.

FIG. 9. Normal state (T = 95K) angle-resolved photoemission spectra for an $O_2$ annealed $Bi_{1.6}Pb_{0.4}Sr_2CaCu_2O_{8+x}$ single crystal of $T_c = 75K$ for different geometries of photon polarization vector and crystalline orientation. (a) $\Gamma - \bar{M} - Z$ is horizontal or vertical; (b) $\Gamma - X$ is horizontal or vertical; (c) $\Gamma - Y$ is horizontal or vertical. The photon polarization vector is always in the horizontal plane. The insets show the locations in the Brillouin zone where the spectra were obtained.

FIG. 10. Normal state (T = 95K) angle-resolved photoemission spectra for a helium annealed $Bi_{1.6}Pb_{0.4}Sr_2CaCu_2O_{8-x}$ single crystal of $T_c = 85K$ for different geometries of photon polarization vector and crystalline orientation. For the orientation that $\Gamma - \bar{M} - Z$ is horizontal or vertical, the spectra are similar to Fig. 9(a). However, the signal observed are quite different for the orientations (a) $\Gamma - X$ is horizontal or vertical; (b) $\Gamma - Y$ is horizontal or vertical. The insets show the locations in the BZ where the spectra were taken.
FIG. 11. (a) The $Bi(5d)$ core levels for as-grown $Bi-2212$ ($T_c = 90$K), The $Bi(5d)$ and $Pb(5d)$ core levels for $O_2$ annealed $Bi(Pb)-2212$ ($T_c = 75$K), and He annealed $Bi(Pb)-2212$ ($T_c = 85$K). The binding energies are labeled nearby the core level peaks. The photon energy $h\nu$ is 50 eV.

(b) The valence spectra for undoped $Bi-2212$ ($T_c = 90$K) and $O_2$ annealed $Bi(Pb)-2212$ ($T_c = 75$K) and He annealed $Bi(Pb)-2212$ ($T_c = 85$K). Notice the shifts of main feature which consists of mostly Cu(3d) valence. The photon energy $h\nu = 21$ eV is used. We emphasize that the core levels and valence spectra were taken on the same sample of different materials. Only the photon energy of the monochromator are different.
TABLE I. A list of possible $s$, $p$, or $d$ symmetries of the normal state with orientations for which a normal state band along $\Gamma - \bar{M} - Z$ and $\Gamma - X$ could be (Yes) or could not (No), by symmetry, be observed.

| Operation | $\Gamma - \bar{M} - Z$ | | | | $\Gamma - X$ | | |
|-----------|-------------------------|-------------------------|-------------------------|-------------------------|
| Orientation | horizontal | vertical | horizontal | vertical |
| $y \rightarrow -y$ | $y \rightarrow -y$ | $x \leftrightarrow -y$ | $x \leftrightarrow -y$ |
| Symmetry | $<e|e>e$ | Yes | $<e|o>e$ | No | $<e|e>e$ | Yes | $<e|o>e$ | No |
| $p_x$ | $<e|e>e$ | Yes | $<e|o>e$ | No | $<e|e+o>e$ | Yes | $<e|o+o>e$ | Yes |
| $p_y$ | $<e|e|o>e$ | No | $<e|o|o>e$ | Yes | $<e|e+o>e$ | Yes | $<e|o|o+o>e$ | Yes |
| $p_z$ | $<e|e>e$ | Yes | $<e|o>e$ | No | $<e|e>e$ | Yes | $<e|o>e$ | No |
| $d_{xy}$ | $<e|e|o>e$ | No | $<e|o|o>e$ | Yes | $<e|e>e$ | Yes | $<e|o>e$ | No |
| $d_{x^2-y^2}$ | $<e|e>e$ | Yes | $<e|o>e$ | No | $<e|o>e$ | No | $<e|o|o>e$ | Yes |
| $d_{3z^2-r^2}$ | $<e|e>e$ | Yes | $<e|o>e$ | No | $<e|e>e$ | Yes | $<e|o>e$ | No |
| $d_{yz}$ | $<e|e|o>e$ | No | $<e|o|o>e$ | Yes | $<e|e+o>e$ | Yes | $<e|o|o+o>e$ | Yes |
| $d_{xz}$ | $<e|e>e$ | Yes | $<e|o>e$ | No | $<e|e+o>e$ | Yes | $<e|o|o+o>e$ | Yes |

Experiment

$O_2 Bi(Pb)-2212$ | Yes | No | Yes | Yes
$He Bi(Pb)-2212$ | Yes | No | No | Yes
TABLE II. A list of possible $s$, $p$, or $d$ symmetries of the normal state with orientations for which a normal state band along $\Gamma - \bar{M} - Z$ and $\Gamma - Y$ could be (Yes) or could not (No), by symmetry, be observed.

| Orientation | Operation | $\Gamma - \bar{M} - Z$ | $\Gamma - Y$ |
|-------------|-----------|-------------------------|--------------|
| $\Gamma - Y$ | $\bar{M} - Z$ | | |
| Symmetry | | Horizontal | Vertical | Horizontal | Vertical |
| $s$ | $<e|e>$ | Yes | <e|o>e | No | <e|e> | Yes | <e|o>e | No |
| $p_x$ | $<e|e>$ | Yes | <e|o>e | No | <e|e>o | Yes | <e|o>e+o | Yes |
| $p_y$ | $<e|o>$ | No | <e|o>e | Yes | <e|e>o | Yes | <e|o>e+o | Yes |
| $p_z$ | $<e|e>$ | Yes | <e|o>e | No | <e|e> | Yes | <e|o>e | No |
| $d_{xy}$ | $<e|o>$ | No | <e|o>e | Yes | <e|e> | Yes | <e|o>e | No |
| $d_{x^2-y^2}$ | $<e|e>$ | Yes | <e|o>e | No | <e|e>o | No | <e|o>e | Yes |
| $d_{3z^2-r^2}$ | $<e|e>$ | Yes | <e|o>e | No | <e|e> | Yes | <e|o>e | No |
| $d_{yz}$ | $<e|o>$ | No | <e|o>e | Yes | <e|e>o | Yes | <e|o>e+o | Yes |
| $d_{xz}$ | $<e|e>$ | Yes | <e|o>e | No | <e|e>o | Yes | <e|o>e+o | Yes |

Experiment

| | $O_2 \ Bi(Pb)-2212$ | | $He \ Bi(Pb)-2212$ | |
| | Yes | No | Yes | No |
| | Yes | No | No | No |