

Local Electronic Structure of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ near Oxygen Dopants: A Window on the High- T_c Pairing Mechanism

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(Received 9 January 2006; published 15 May 2006)

The cuprate material $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (BSCCO-2212) is believed to be doped by a combination of cation switching and excess oxygen. The interstitial oxygen dopants are of particular interest because scanning tunneling microscopy (STM) experiments have shown that they are positively correlated with the local value of the superconducting gap, and calculations suggest that the fundamental attraction between electrons is modulated locally. In this work, we use density functional theory to try to ascertain which locations in the crystal are energetically most favorable for the O dopant atoms, and how the surrounding cage of atoms deforms. Our results provide support for the identification of STM resonances at -1 eV with dopant interstitial O atoms, and show how the local electronic structure is modified nearby.

DOI: 10.1103/PhysRevLett.96.197002

PACS numbers: 74.25.Jb, 74.25.Bt, 74.40.+k

STM measurements of impurities and other inhomogeneities in the cuprates have opened a new window on high-temperature superconductivity and raised a host of new questions about the way these impurities interact with their environment [1–3]. It has been traditionally assumed that an impurity acts as a localized screened Coulomb potential, and that its principal effect is the modification of quasiparticle wave functions nearby. This effect is large and observable as a consequence of the d -wave symmetry of the superconducting state [4]. Within such models, the superconducting order parameter is suppressed around the impurity, but this phenomenon is not usually essential for qualitative predictions. Recently, a phenomenological analysis [5] of STM experiments imaging interstitial oxygen atoms [6] suggested that such impurities might have a much more striking effect, to wit, the local modulation of the electronic pair interaction, leading to large amplitude modulations of the superconducting order parameter. If this is true, an understanding of the local changes in electronic structure and couplings to collective excitations of the material might tell us which aspects are of crucial importance to the pairing interaction itself.

Naturally occurring impurities which dope the CuO_2 planes in as-grown $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ crystals [7–9] include both the excess Bi substituting on the Sr sites, as well as oxygen interstitials. Both sets of dopant atoms have recently been imaged by STM [6,10]. In the case of the O interstitials, which appear as bright spots on the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ surface at a bias of -960 mV, a remarkable set of correlations was established by McElroy *et al.* [6] between the positions of the impurities and the magnitude of the local superconducting gap (as defined by the position of the coherence peak in the conductance signal), as well as the magnitude of the LDOS at different energies. Local doping disorder was therefore claimed to be responsible for the nanoscale inhomogeneities observed earlier in the same material [11–14], but the *positive* dopant-gap correlation observed contradicted earlier theoretical pro-

posals along these lines [15–17]. Nunner *et al.* [5] then proposed that the oxygen dopant increased the pairing strength g between electrons locally, and a simple model based on this ansatz was shown to explain all experimentally reported correlations at optimal doping. The results suggested that the range of the modulation was of order of a Cu-Cu distance. While such atomic-scale enhancements of pairing are outside the framework of standard BCS-type theoretical treatments of impurities in superconductors, they have occasionally been discussed in earlier treatments of the effects of impurities on s -wave systems [18].

If the theoretical proposal is correct, understanding where the O interstitials sit and how they distort the cage of atoms around them could be an important clue to the ingredients of the electronic pair mechanism in these materials. Even if not, the details of the local chemistry around interstitials can be important to understand the doping process in the cuprates. At present, there is no consensus as to the exact position of the defects imaged by STM, their chemical identity, nor the nature of the states they induce at -960 meV into which one tunnels in the experiment. We have therefore undertaken density functional calculations of BSCCO-2212 including O atoms placed in the most natural interstitial locations between the BiO and SrO , or between the SrO and CuO_2 planes. We regard locations between other layers as unlikely, since they are too far from the BiO layer, where the BSCCO-2212 crystal typically cleaves, to be the source of the strong STM signal observed. They are allowed to relax to lower the overall energy of the system, and ultimately several possible stable and metastable positions are found. Only one of these, close to but not identical to the position found by statistical analysis of the STM data, represents a clear minimum of the energy. We analyze the structural and electronic changes thereby produced in some detail.

The most important results include a displacement of the nearby apical (stoichiometric) oxygens from their naive positions on the Bi-Cu axis and the creation of states

centered primarily around -1 eV, not only associated with the interstitial O itself, but with the apical oxygens and nearby Cu sites. It is the unhybridized dopant $O2p_z$ states which give rise to the resonance seen by STM. It is remarkable that an *ab initio* calculation in an extremely complicated material is able to so quantitatively reproduce the energetics of such states.

Method.—In this work, density-functional theory (DFT) calculations have been used to determine all structural, energetic, and electronic results. The Kohn-Sham equations are solved self-consistently in a plane-wave basis set, in conjunction with Vanderbilt ultrasoft pseudopotentials [19,20], which describe the electron-ion interaction, as implemented in the Vienna *ab initio* simulation program (VASP) [21]. Exchange and correlation are described by local-density approximation (LDA). We use the exchange-correlation functional determined by Ceperly and Alder [22] and parameterized by Perdew and Zunger [23]. Details of the application of the method to impurity problems in $Bi_2Sr_2CaCu_2O_8$ have been given in [24]. It is known that LDA fails to give the correct band structure for cuprates in general, and, in particular, fails to describe the metallic or insulating character of the parent compounds. On the other hand, the bands and Fermi surface given by LDA agree relatively well with angle-resolved photoemission spectroscopy (ARPES) results on optimally doped BSCCO-2212, with minor exceptions (see below). Furthermore, as argued in [24], we are primarily interested in high-energy, localized impurity states which should be little affected by the strong electronic correlations which renormalize the band states near the Fermi surface.

For the calculation of the BSCCO surface in the presence of impurities, we use surface unit cells (super cells) with dimension of $(2\sqrt{2}a \times 2\sqrt{2}a)R45^\circ$ that contain 8 primitive unit cells in the xy plane. There is one O interstitial added to the stoichiometric sample of 120 atoms. The vacuum between neighboring slabs is about 15 Å thick.

Structural relaxation.—We compute the structure and electronic wave functions for the BSCCO-2212 surface first without and then with an O interstitial. In the latter case, the O is positioned somewhere in the lattice and the entire system is allowed to relax to minimize the total energy. Several metastable positions were found, summarized in Table I. It is seen that only one minimum thus found is a plausible location (position 1 in the table) for such a defect; others are higher in energy by at least 2.5 eV. Position 1 is located in the plane between 2 Bi atoms in the BiO layer and 2 stoichiometric oxygens in the SrO layer below, as shown in Fig. 1. This position is displaced by about 0.5 Å and has a different symmetry from that determined experimentally by the STM group [6] by doing a statistical analysis of their -960 meV signal. This may be attributable to a combination of dopant clustering effects and the distortions due to the incommensurate supermodulation in this material.

The displacements of atoms near the O impurity in position 1 are also shown schematically in Fig. 1, and

TABLE I. Stable or metastable positions of the O-interstitial found. Coordinates are relative to the central Bi atom in Fig. 1. Energies are per O interstitial measured relative to the crystal without interstitial.

No.	Location (Å)	Energy (eV)
1	1.09, 1.09, -0.93	-6.56
2	2.11, 0.00, -0.38	-3.91
3	2.60, 0.00, -0.38	4.38
4	2.60, 0.00, -4.81	14.97

summarized in Table II. The largest displacements are in the BiO and SrO planes. In particular, we note that the so-called apical oxygen in the SrO plane is moved by nearly half an angstrom away from the Bi-Cu axis, leading to an effective tilting of the semioctahedron of stoichiometric oxygens away from this axis. Crudely speaking, this tilting is of the low- T tetragonal type, which has been associated with the tendency towards stripe formation in the under-doped cuprates [25]. Finally, the Bi and O(Bi) atoms nearest the impurity in the BiO layer are also pushed away by displacements of the same order.

Changes in electronic structure.—Within the same framework, we now calculate the electronic structure and changes thereto caused by the O interstitials. To compare directly to the STM measurements, we should calculate the local density of states (LDOS) a tip height distance (~ 3.5 –4 Å) above the BiO plane. At present our numerical resolution is insufficient to address this question directly, but we can ask in which energy ranges new states are found, and roughly where in space they are localized. The partial density of states (PDOS) projected onto atomic species μ is defined as $\rho_\mu(\epsilon) = \sum_k w_k \sum_i \delta(\epsilon - \epsilon_{i,k}) |\langle \phi_{\mu,k} | \Psi_{i,k} \rangle|^2$, where $\phi_{\mu,k}$ are linear combinations of atomic wave functions consistent with the crystalline symmetry, and the $\Psi_{i,k}$ are Bloch wavefunctions for the i th

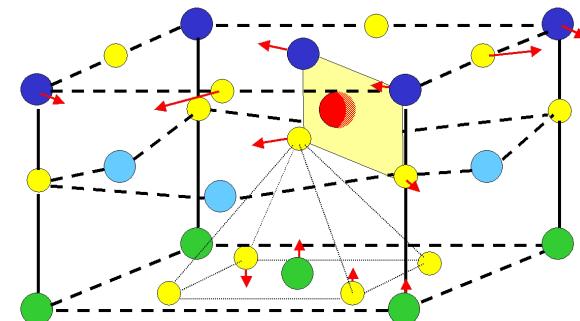


FIG. 1 (color online). Atomic displacements due to the presence of O interstitial at position 1 in Table I. Atomic species are color/ gray scale coded: Bi (blue/black), stoichiometric O (yellow/light gray), Cu (green/dark gray), Sr (light blue/medium gray), O interstitial (red/black). Arrows indicate rough measure of displacement of atoms from their positions without interstitial.

TABLE II. Initial positions \mathbf{r}_i , displacements $\mathbf{r}_f - \mathbf{r}_i$, and displacement magnitude of various nearby atoms in the presence of interstitial O at position 1 (see Table I). Atoms are those of a given species closest to the O interstitial, unless indicated by a' (second closest).

Atom	\mathbf{r}_i (Å)	$\mathbf{r}_f - \mathbf{r}_i$ (Å)	$ \mathbf{r}_f - \mathbf{r}_i $ (Å)
Bi	0,0,0	-0.34, -0.34, -0.14	0.50
Bi'	2.59,2.59,0	-0.17, -0.17, -0.08	0.25
O(Bi)	2.59,0,0.05	0.68, -0.31, 0.02	0.75
Sr	2.59, 0, -2.76	0.0,0.0,0.10	0.10
O(Sr)	0, 0, -2.05	-0.41, -0.41, -0.12	0.59
O(Sr)'	2.59, 2.59, -2.05	0.16, 0.16, -0.02	0.23
Cu	0, 0, -4.60	-0.02, -0.02, 0.14	0.14

band. Here $w_{\mathbf{k}}$ is the weight of each \mathbf{k} point and $\epsilon_{i,\mathbf{k}}$ is the dispersion of the Bloch state.

In Fig. 2, we plot the PDOS for relevant atomic orbitals in the absence of the O interstitial, together with the same quantities with the interstitial present. The spectra have been plotted relative to the absolute Fermi levels of 0.6527 and 0.4832 eV for the case without and with O interstitials, respectively. The PDOS and DOS for the crystal without interstitials are consistent with earlier LDA calculations for this material [26]. Upon addition of the O interstitial, one obvious change is the shift of the Cu and O(Cu) spectra towards the Fermi level, consistent with the hole doping of the CuO_2 plane by the interstitials. Another interesting feature is the shift of PDOS Fermi level weight on the Bi sites to above the Fermi level upon doping

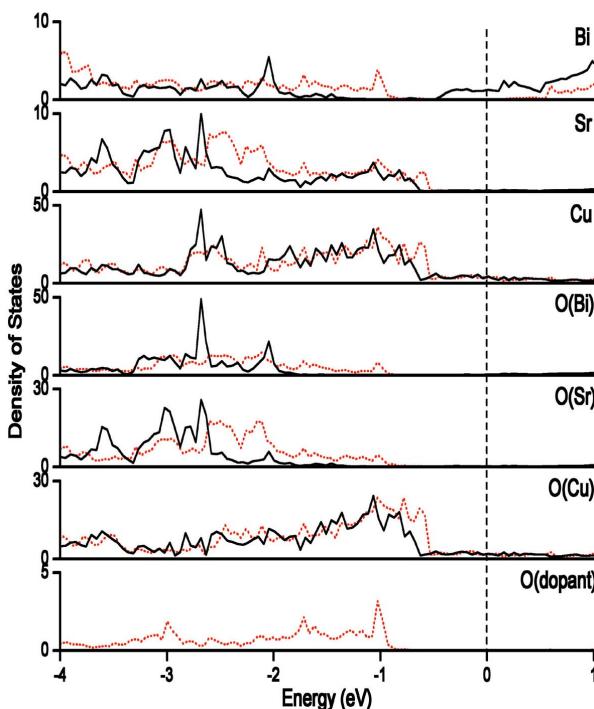


FIG. 2 (color online). Projected densities of states for different atomic species before (black solid line) and after (red dashed line) addition of O interstitial.

with O. All previous LDA-type calculations of stoichiometric Bi-2212 have found BiO-derived bands crossing the Fermi level, leading to BiO Fermi surface “pockets” [27]. These features have never been observed by ARPES [28], suggesting that the doping by excess O may be necessary to obtain the correct Fermi surface [29].

The primary effect of the interstitial O appears to be to contribute states in a range around -1 to -3.5 eV, with a sharp concentration of states around -1.0 eV itself. Since there are originally no Bi, O(Bi), or O(Sr) states in this range, the extra O apparently causes a significant change to the PDOS of these species, inducing peaks at -1.0 eV in all three cases. O interstitial states in the rest of the energy regions do not appear to induce qualitative changes in the PDOS of atomic species near the surface, and may therefore be expected to not cause significant qualitative changes to the LDOS measured by STM. The only expected strong signal of the presence of the O defects is therefore a concentration of (assumed) tunnelling states at -1.0 eV, nearly precisely where such a signal is found by STM [6]. This is a spectacular confirmation of the ability of DFT to predict electronic structure near impurities with high accuracy in these systems. We note that the rough magnitude of the binding energy of these states can be understood by recognizing the similarity to the *stoichiometric* $\text{O}2p$ -derived states (found at ~ -1.5 eV below the top of the Zhang-Rice band) in photoemission experiments on $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, which do not hybridize with Cu 3d states [30]. The peaks around -1 eV seen in the O(Cu) and Cu spectra in Fig. 2 which do not change significantly with the addition of O dopants are of this type.

We note finally the existence of a broad cluster of O (dopant) states centered around -1.7 eV which also appear to induce similar features in O(Bi) and Bi, and could lead to significant LDOS change at the BSCCO surface. This is an independent prediction which can be checked by STM.

Local density of states near -1 eV.—The PDOS is calculated for all atoms of a particular species and symmetry, but spatially resolved LDOS information is necessary to specify where these changes are taking place. To this end, we focus on the states near -1 eV, and plot a contour of the LDOS $\rho(\epsilon, \mathbf{r}) = \sum_{\mathbf{k}} w_{\mathbf{k}} \sum_i \delta(\epsilon - \epsilon_{i,\mathbf{k}}) |\Psi_{i,\mathbf{k}}(\mathbf{r})|^2$, integrated over a range of energies from -1.1 eV to -0.9 eV in Fig. 3. Inspection of various contours of this type leads to the conclusion that the states at -1 eV are dominated by unhybridized CuO_2 plane states [30], and induced states localized near the impurity. In particular, the slightly misoriented $\text{O}2p_z$ state on the O dopant is clearly visible. There is no other state in the vicinity close to the surface positioned and oriented to accommodate an electron transfer from an STM tip near the surface. We note the absence of any states localized on the Bi atoms, in apparent contradiction to the results shown in Fig. 2. This is because the Bi radius is 2 times larger, such that the PDOS weight appears at smaller LDOS values than depicted here.

The next fascinating change due to the O interstitial is the creation of new states on the closest Cu site which

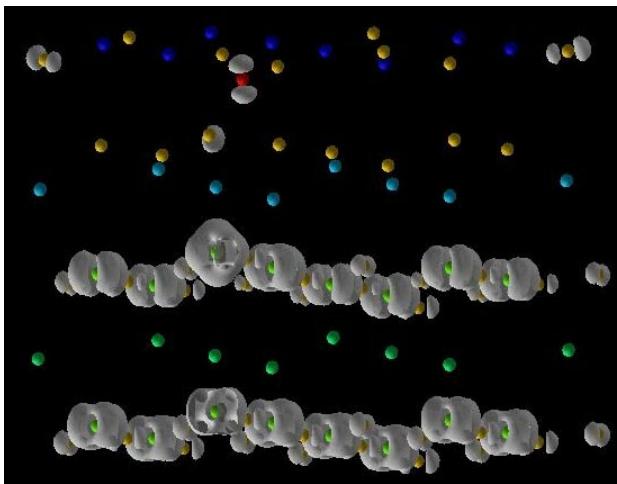


FIG. 3 (color online). Spatial distribution of LDOS integrating over states near -1 eV. The surface of the sample is at the top of the figure. Color coding as in Fig. 1 and, in addition, Ca between the CuO_2 planes.

appear to be of $3d_{3z^2-1}$ symmetry. This process is clearly mediated by the apical O(Sr), which also shows induced $2p_{x,y}$ symmetry states in this range. There is no obvious hybridization between these states; rather, these appear to be changes due to the displacements of the atoms in question, which transfer spectral weight from higher binding energy into this range, as seen in Fig. 2.

Conclusions.—Using density functional theory methods, we have shown that the excess O dopant atoms in the as-grown BSCCO-2212 material are located with high probability between the BiO and SrO layers in the plane containing Bi and O(Sr) atoms. These interstitials are responsible for the creation of a set of states narrowly localized near -1 eV, which we have investigated more closely. One unhybridized $2p$ state appears on the dopant itself, and is oriented in the z direction, strongly suggesting that this is precisely the state imaged in recent STM experiments [6] at -960 meV. This result is a strong confirmation of the ability of DFT to calculate high-energy impurity features even in strongly correlated systems, as emphasized in Ref. [24]. In addition, new states in this range are induced on the strongly perturbed nearby apical oxygen site, and even on the closest Cu atom. This suggests that the pairing of two electrons in the CuO_2 plane in this high-temperature superconductor may indeed be influenced by the presence of the nearby O interstitial, as suggested in Ref. [5], and that information on the modulation of the pair interaction may be gleaned by “downfolding” the DFT information to determine how the local change in electronic structure correlates with the superconducting gap.

This work was supported by ONR N00014-04-0060 (P.J.H.), DOE Grants No. DE-FG02-05ER46236 (P.J.H.), No. DE-FG02-97ER45660 (H.-P.C.), and No. DE-FG02-02ER45995 (H.-P.C.), and the NSF/DMR/ITR-medium program under Contract No. DMR-032553

(H.-P.C.), and the Alexander von Humboldt Foundation (T.S.N.). The authors acknowledge valuable discussions with B.M. Andersen, W.A. Atkinson, J.C. Davis, T. Devereaux, A. Kampf, A. Melikyan, G.A. Sawatzky, and L.-L. Wang.

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