Surface States and Angle-Resolved Photoemission Spectra from $Nd_{2-x}Ce_xCuO_4$ Superconductor

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By carrying out first-principles angle-resolved photoemission (ARPES) computations within the local-density-approximation-based band theory framework, we predict the existence of surface states on the (001) surface of the superconductor $Nd_{2-x}Ce_xCuO_4$ (NCCO). Two surface state bands are identified in the vicinity of the Fermi energy. The associated states possess quite different characteristics in terms of their binding energy, dispersion with $k_{\parallel}$, and the polarization and photon energy dependence. Our theoretical predictions offer new insight into the existing ARPES data on NCCO with which they are consistent.

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The possible presence of surface states (SS's) has substantial implications for the interpretation of angle-resolved-photoemission spectra (ARPES) in the high T_c's. In particular, SS's in the vicinity of the Fermi energy E_F would complicate the mapping of bulk bands and Fermi surfaces since SS's are expected to disperse as a function of $k_{\parallel}$ in a manner not unlike the bulk states. Further, SS's would affect spectral line shapes, and thus make it less straightforward to deduce via the ARPES the size and symmetry of the superconducting order parameter—a crucial piece of information which appears to be a "smoking gun" for discriminating between various mechanisms of superconductivity in new materials [1–7]. Finally, we note that SS's may induce higher T_c's in the surface layer compared to the bulk, and cause tunneling measurements—and thus the associated conclusions with regard to the symmetry of the gap—to be sensitive to the specifics of experimental method and geometry [8].

In this Letter, we predict theoretically the existence of SS's in a high-T_c compound for the first time using an *ab initio* local-density-approximation- (LDA-) based band theory framework. The specific material considered is the electron doped superconductor $Nd_{2-x}Ce_xCuO_4$ (NCCO). Our predictions give new insight into the existing ARPES data [9–11] on NCCO with which they are consistent, although further experimental work in this connection is warranted. Of the four unique ideal (001) surfaces permitted by the body centered tetragonal (bct) lattice of NCCO [12], only the two Nd-terminated surfaces ($Nd/CuO_2/Nd/O_2$ and $Nd/O_2/Nd/CuO_2$) are found to admit SS's. In both cases, the SS's are of the Shockley type; i.e., they arise from the imposition of changed boundary conditions on the wave functions in the presence of the surface [13]. The two SS's, denoted by SS1 and SS2, are predicted to lie a few tenths of an eV below E_F at the center of the Brillouin zone. Along the Γ-X direction, SS2 moves above E_F near the X point, but SS1 does not. On the other hand, both SS's move above E_F around the G_1 point. The spectral signal of SS1 is found to interfere significantly with

that of the CuO_2 plane bands, especially along the Γ-X direction. Finally, although the intensities of SS1 and SS2 possess a roughly similar dependence on the polarization of the incident photon, the two SS's differ substantially in their behavior as a function of the photon energy. These results show that the SS's can display a remarkable level of richness in complex systems.

Our calculations for obtaining the ARPES intensities employ the one-step model of photoemission [14] which we have recently generalized and implemented to treat arbitrarily complex unit cells. [See Refs. [7] and [15] for an application to the Y123 and Y124 (001) surfaces [16].] Briefly, the photointensities are evaluated for a Hamiltonian which consists of a semi-infinite crystal terminated by a potential step V_{inner} using multiple scattering theory techniques in the presence of the surface. Our bulk crystal potential is obtained via the charge self-consistent all-electron KKR methodology [17] for bct Nd_2CuO_4 [18]. Following common practice, the electronic structure of NCCO is treated within the rigid band model [9,10,19] which is reasonable because Ce doping serves mainly to provide a reservoir of additional electrons. Note that the band theory, of course, yields a *metallic* state for the parent compound Nd_2CuO_4 which is physically realized in the NCCO via Ce doping. Finally, as in Ref. [19], the Nd f bands were constrained to lie several eV away from the Fermi energy; we have, however, carried out a number of calculations which show that the influence of the f bands at E_F is relatively small on the ARPES spectra. Also, in order to highlight surface and bulk spectral features near E_F, we have chosen the imaginary part of the initial state self-energy to be a constant equal to -0.05 eV in the present computations; a larger, energy dependent value would be more representative of the experimental data [7,15].

Figure 1 shows theoretical spectra in the vicinity of the Fermi energy for four different (001) surfaces admitted by the NCCO lattice. The two Nd-terminated surfaces display the surface states SS1 and SS2. The bulk feature B, related to the CuO_2 planes, is most intense for the
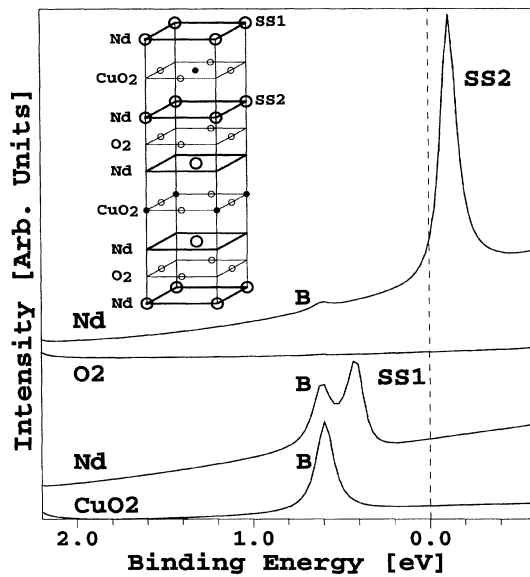
FIG. 1. A set of typical theoretical ARPES spectra from the Nd compound for four different surface terminations of the (001) surface (see inset for the schematic arrangement of layers in the lattice). SS1 and SS2 are the surface states, B is the bulk peak arising from CuO_2 plane bands. The spectra are for $h\nu = 17$ eV for an emission angle of 16° along the Γ-X line. The dashed vertical line marks the Fermi energy in NCCO for 15% Ce doping. The spectra have *not* been folded with the Fermi function; only the peaks below E_F would be observable in an ARPES measurement, the peaks above E_F being relevant for an inverse photoemission experiment.
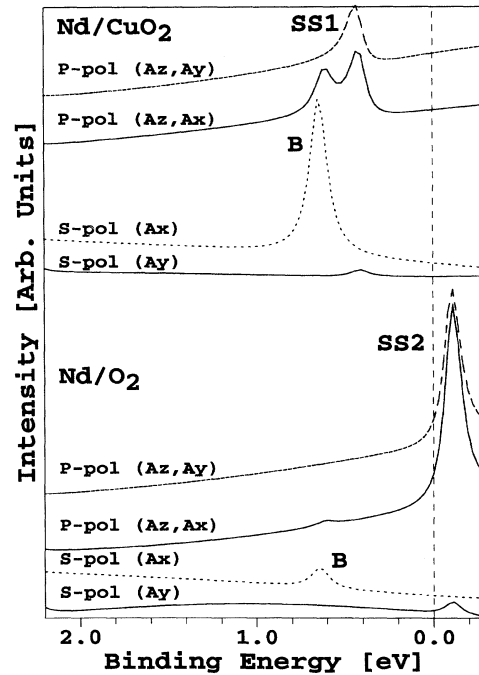

FIG. 2. The polarization dependence of the spectra of Fig. 1 for the two Nd-terminated surfaces which admit SS's (see caption to Fig. 1 for notation and other relevant details). Nonzero components of the vector potential $\mathbf{A}$ are indicated on each curve; s-polarized light corresponds to $A_z = 0$, p-polarized light to $A_z \neq 0$. A_x is parallel to the ΓY symmetry direction.

CuO_2-terminated surface, becoming less intense when CuO_2 is the second layer beneath the surface (third curve from top); B is barely discernible when the CuO_2 layer is deeper (the two topmost curves). For the $k_\parallel$ values of Fig. 1, SS1 and SS2 are predicted to lie above and below E_F, respectively. The SS's possess considerable dispersion, however, so that the relative binding energies of SS1 and SS2 vary with $k_\parallel$ (see below).

As already noted, SS1 and SS2 possess the characteristics of the so-called Shockley-type surface states. We have established this fact by carrying out a series of calculations for each termination of Fig. 1 by varying the position of the surface barrier, leaving all other parameters fixed. The binding energy of SS1, as well as SS2, was found to change as the position of the surface barrier was varied—a clear signature of a Shockley-type surface state localized in the region of the surface barrier. The bulk feature B, on the other hand, is insensitive to the barrier position [13]. Also, as expected for SS's, there are no bulk levels in the vicinity of either SS1 or SS2; in contrast, the position of B correlates well with that of an underlying bulk energy level.

Figure 2 delineates the polarization dependence of the spectra of Fig. 1. Since the behavior of SS1 and SS2 is similar, the main effects may be discussed with reference to SS1. We see that SS1 is excited mainly by p-polarized light, consistent with the expectation that SS's generally

couple with A_z; also, SS1 is insensitive to the component of $\mathbf{A}$ in the x-y plane (compare the two uppermost curves). The behavior of SS2 in the lower part of the figure is similar and does not require further comment. Incidentally, Fig. 2 shows that the bulk feature B possesses a substantial intensity only when the incident photon has $A_x \neq 0$, indicating that B is not excited by either A_y or A_z [20].

Figure 3 highlights dispersion and line-shape effects by considering spectra in the vicinity of E_F along two representative symmetry directions; the corresponding surface and bulk bands are shown in Fig. 4. Focus first on the left-hand pair of panels which refer to the Γ-G_1-Z direction. Here, SS1 and SS2 are seen to possess a similar dispersion although SS2 is flatter compared to SS1 around G_1 (middle of the figure); the two SS's nearly coincide in energy at G_1 with the separation increasing to a value of 0.7 eV at Γ. Both SS's lie below E_F at Γ, but above E_F at G_1. However, SS1 crosses E_F at about 0.78 and SS2 at about 0.47 of the Γ-G_1 distance, so that there is a range of intermediate $k_\parallel$ values where SS1 lies below and SS2 lies above E_F. The relative intensity of SS1 increases as one proceeds from Γ toward G_1 whereas, in the case of SS2, the intensity is more or less unchanged between Γ and G_1. In moving from G_1 toward Z, both states gradually diminish in intensity. These differences between the behavior of SS1 and SS2 reflect the differences in the nature of underlaying wave functions. Our analysis indicates
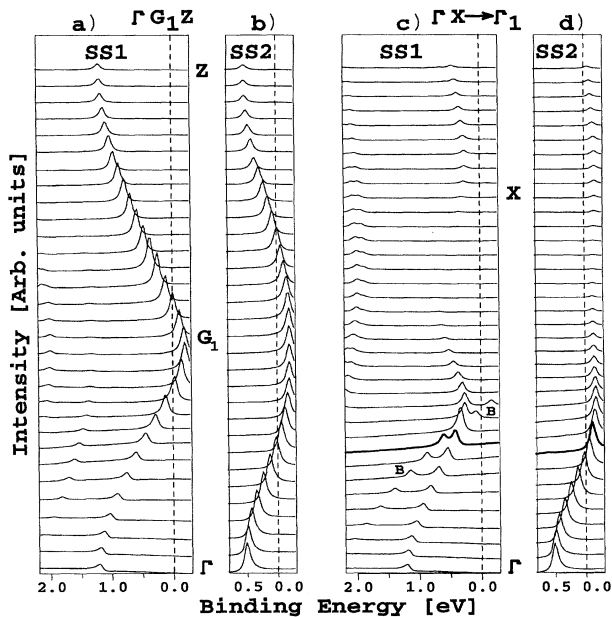
FIG. 3. Dispersion of the surface state bands associated with SS1 and SS2 along the Γ-G_1-Z (left pair of panels) and Γ-X directions. The spectra for SS1 in (a) and (c) are shown over a larger window of binding energies in order to highlight the interplay between bulk and surface features. The thick curves in (c) and (d) correspond to the $k_\parallel$ value of Fig. 1, with B denoting the bulk band. See caption to Fig. 1 for the value of photon energy, the meaning of dashed lines, and related details.

that, while SS2 is nearly completely localized in the region of the surface barrier and the topmost atomic layer, SS1 extends several layers into the crystal.

Many of the remarks of the preceding paragraph are qualitatively applicable to the behavior of SS1 and SS2 along the Γ-X line [Figs. 3(c) and 3(d)]. An interesting new twist is provided by the interplay between the bulk feature B and SS1 in Fig. 3(c) wherein, at around 0.52 of the Γ-X distance, SS1 and B cross each other, giving rise to an apparent single peak close to E_F. This circumstance may have important implications in the interpretation of the ARPES data from NCCO, a point to which we return below.

Figure 5 presents in the intensity of SS1 and SS2 as a function of photon energy $h\nu$, another parameter which may be used to probe the character of a state via the ARPES. The emission from SS2 is predicted to peak around $h\nu = 22$ eV with a full width at half maximum of 6.5 eV. The behavior of SS1 is remarkably different in that it displays a number of peaks in the range of 40–70 eV with the maximum around 53 eV. The presence of several peaks in the theoretical spectra of Fig. 5 over such a narrow energy range is unusual and suggests that photoelectron-diffraction [22] studies of NCCO may reveal interesting information concerning the geometrical arrangement of atoms in the surface layer.

We now turn to a discussion of available experimental ARPES data on NCCO, reported by three different groups
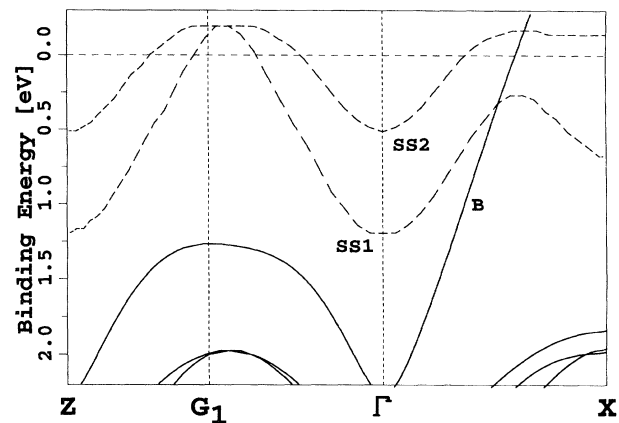
FIG. 4. Energy bands in the vicinity of E_F for the Γ-X and Γ-G_1-Z directions. Solid lines give the bulk bands, the dashed lines give the surface state bands related to SS1 and SS2.

[9–11], in the light of our theoretical results. Reference [11] observes a feature for 35–60 eV $h\nu$ values lying just below E_F with a dispersion of about 0.2 eV. (We are referring to the feature denoted by A in Ref. [11] whose dispersion is shown in their Figs. 6 and 7.) The behavior of this feature is qualitatively similar to that of SS1 above, including the $h\nu$ dependence of the intensity as seen from Fig. 5, some discrepancies notwithstanding [23]. Accordingly, feature A of Ref. [11] may be interpreted reasonably as the SS1 rather than the formation of a Kondo-type renormalized heavy-electron band as suggested by Ref. [11].

In ARPES data from NCCO, Refs. [9] and [10] report a dispersive feature which crosses E_F in reasonable accord with the band theory predicted Fermi surface. However, as seen from Fig. 3 of Ref. [9], the associated feature is quite asymmetric, and a rather high intensity remains at E_F even after the crossing of E_F. This behavior finds a natural explanation in terms of the results of Fig. 3(c) above, where SS1 stays below E_F. On the whole, it appears that
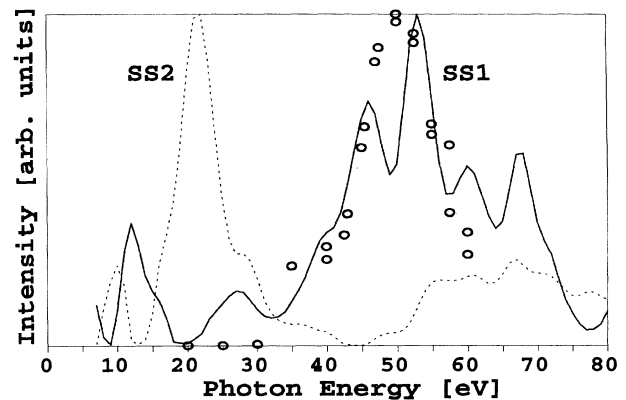

FIG. 5. The intensity of the peaks SS1 (solid) and SS2 (dashed) as a function of the photon energy (see caption of Fig. 1 for relevant details). Open circles give the results of Ref. [11] normalized to the theoretical peak for SS1 about 50 eV.

the data of Refs. [9–11] are consistent with the presence of SS1 in the spectra. If so, great care should be exercised in analyzing ARPES data from NCCO in terms of the bulk band structure. The presence of surface states close to E_F (occupied and/or possibly unoccupied) would induce substantial changes in line shapes and spectral weights, especially with electron doping.

We emphasize that electron correlation effects are obviously important in the high T_c's since the undoped parent compounds in most cases are insulating, and not metallic as predicted by the LDA. On the other hand, a number of high T_c's have been shown to possess Fermi surfaces in substantial accord with LDA predictions, indicating that the LDA, at least qualitatively, captures the physics of the metallic state. It will of course be crucial to include correlations beyond the LDA in treating problems where one goes across the metal-insulator transition. We have simulated the effect of correlations by adding an *ad hoc* self-energy correction to the Cu and O muffin-tin potentials which shifted the Cu-O complex of bands in Nd-Ce-Cu-O up by as much as 1 eV, but yielded only minor shifts of less than 0.1 eV on our SS's. We have also varied the relative position of the topmost layer with respect to the second layer by as much as 10% of the interlayer spacing to simulate effects of surface relaxation, but found only shifts of a few tenths of an eV in our SS's. Finally, the present SS's, being of Shockley type, are generally expected to be insensitive to the nature of crystal potential in the surface region, in sharp contrast with the behavior of the Tamm- or dangling bond-type SS's [24]. These results indicate that our main conclusion— the existence of SS's in the Nd compound—is a robust one, despite the limitations of our underlying model.

In summary, we predict the existence of two different Shockley-type surface states on the (001) surface of the superconductor $Nd_{2-x}Ce_xCuO_4$ based on our *ab initio* LDA band theory computations. The characteristic signatures of these surface states in the ARPES spectra are delineated in terms of the shape, dispersion, and polarization and photon energy dependence of the intensity of the associated spectral peaks. Our theoretical predictions give new insight into the existing ARPES data on NCCO with which they are consistent. Further high-resolution angle-resolved photoemission, as well as inverse photoemission measurements from well characterized surfaces of $Nd_{2-x}Ce_xCuO_4$, would be valuable. These results, including the fact that the signatures of SS1 and SS2 in ARPES spectra are quite different, establish clearly for the first time that a rich variety of surface states can exist in complex systems with implications for various physical properties.

[1] For recent discussions see, for example, the conference proceedings in Refs. [2–4]. For issues pertaining to ARPES line shapes, gap anisotropy, etc., see Refs. [5–7].

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