

No well-defined remnant Fermi surface in $\text{Sr}_2\text{CuO}_2\text{Cl}_2$

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In angle-resolved photoelectron spectra of the antiferromagnetic insulators $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ and $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, a sharp drop of the spectral intensity of the lowest-lying band is observed along a line in \mathbf{k} space equivalent to the Fermi surface of the optimally doped high-temperature superconductors. This was interpreted as a signature of the existence of a remnant Fermi surface in the insulating phase of the high-temperature superconductors. In this paper it is shown that the drop of the spectral intensity is not related to the spectral function but is a consequence of the electron-photon matrix element.

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It is of great interest to understand the changes the normal-state electronic structure of the high-temperature superconductors (HTSCs) undergoes when doped from an antiferromagnetic insulator to a metal. Angle-resolved photoelectron spectroscopy (ARPES) has played an important role in the study of the electronic structure of the HTSCs in the different regions of the doping phase diagram.¹⁻⁶ Recently ARPES experiments using $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ and $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ single crystals yielded information on the electronic structure of the HTSCs in the limit of very low hole doping.⁷⁻¹⁰

$\text{Sr}_2\text{CuO}_2\text{Cl}_2$ and $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ are closely related to the undoped parent compounds of the HTSCs as they are also antiferromagnetic insulators having Néel temperatures of 255 and 247 K, respectively.^{11,12} The CuO_2 planes in $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ and $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ are undoped (half filling); therefore the spectral intensity in an electron-energy distribution curve (EDC) from the CuO_2 plane gives information about the dynamics of a single hole (the hole created by photoionization) in a CuO_2 plane. Of primary interest are the lowest-lying states in an ARPES spectrum, the so-called first electron-removal states. These states in $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ and $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ show a well-developed peak only for \mathbf{k} vectors in the vicinity of $(\pi/2, \pi/2)$ (which in the following will be referred to as the low binding-energy peak) where it has its minimum binding energy.^{7-10,13} The low binding-energy peak is followed by additional spectral weight at higher binding energies. Outside this \mathbf{k} space region the first feature is a rather broad structure with its maximum located at higher binding energy.

In the published $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ and $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ ARPES data the spectral intensity of the first electron-removal states shows a sudden drop along a line in \mathbf{k} space which closely resembles the Fermi surfaces found in band-structure calculations (noninteracting Fermi surface) or ARPES data of optimally or overdoped HTSCs.¹⁰ Along the Γ to (π, π) Brillouin zone (BZ) cut the drop in spectral intensity of the low binding-energy peak is close to $(\pi/2, \pi/2)$, i.e., the crossing of this specific cut with the antiferromagnetic Brillouin zone (ABZ), which in Ref. 7 was interpreted as a signature for a possible description of the data in terms of a weak-to-intermediate-coupling Hubbard model. Insulators such as $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ and the undoped parent compounds of the HTSCs do not have partially filled bands and hence no Fermi surface, but it was argued that there exists a

remnant of the Fermi surface of their respective metallic phases in the sense that when the first electron-removal states of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ or $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ cross this remnant Fermi surface their spectral intensity suddenly drops, in analogy to the behavior of the ARPES spectral intensity related to the lowest-lying band of a metal when it crosses the Fermi surface. Comparing the binding energies of the first electron-removal states of the copper oxychlorides for \mathbf{k} vectors on the remnant Fermi surface one can formally define a gap which is zero for \mathbf{k} on the remnant Fermi surface where the low binding-energy peak has minimum binding energy and has its maximum for \mathbf{k} on the remnant Fermi surface where the low binding-energy peak has maximum binding energy. It was noted that the gap defined this way shows an analogous \mathbf{k} dependence as the superconducting gap of the HTSCs, i.e., a d -wave-like dispersion.¹⁰ This d -wave-like behavior of the first electron-removal states of the copper oxychlorides would quite naturally explain the \mathbf{k} dependence of the normal-state gap encountered in the underdoped HTSCs, upon hole doping the chemical potential drops to the maximum of the d -wave-like dispersion (the node of the “gap”) of the insulator. In the underdoped regime the Fermi level only touches states near the node of the d -wave-like gap of the insulator, forming small segments of the Fermi surface, while the portions of the remnant Fermi surface around $(\pi, 0)$ remain gapped.

One has to note, however, that in ARPES the spectral intensity of an EDC is directly proportional to the electron-photon matrix-element-weighted spectral function,¹⁴ and not the spectral function, $A(\mathbf{k}, E)$, itself. Calculations suggest that the relationship between ARPES intensities and the underlying electronic structure can be quite complicated due to matrix element effects and that caution should be exercised in interpreting detailed features of the ARPES intensities in terms of the spectral function.¹⁵ In a recent paper, using angle-resolved photoelectron spectra of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ as an example, it was experimentally demonstrated that for layered cuprates the electron-photon matrix element can have a significant impact on both the relative spectral intensity and the shape of a feature in an ARPES spectrum.¹⁶ In this paper, ARPES measurements on a $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ single crystal along the line Γ to (π, π) in \mathbf{k} space using different photon energies in the range from 20 to 24 eV are presented. It will be shown that the sudden drop in spectral intensity observed in

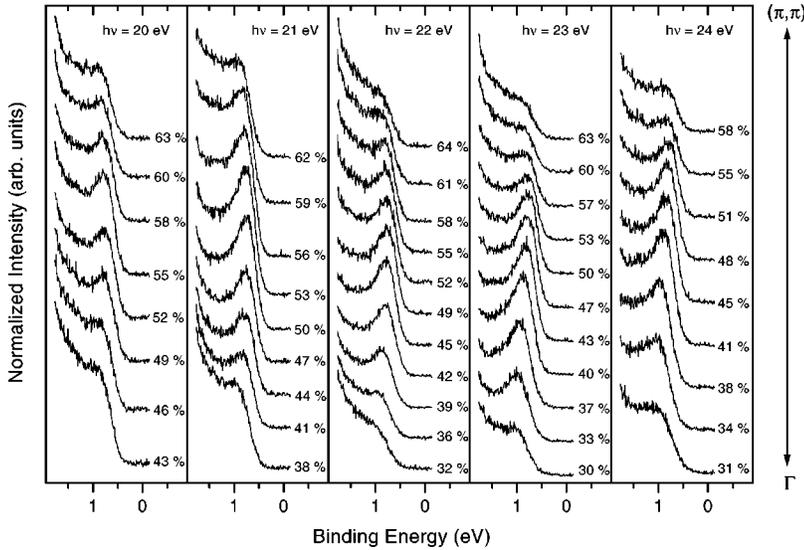


FIG. 1. The first electron-removal states of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ along Γ - (π, π) in the first BZ using 20- to 24-eV photon energy. The \mathbf{k} vectors are given in % of the distance between Γ and (π, π) .

the ARPES spectra of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ along a line in \mathbf{k} space similar to the Fermi surface of HTSCs is not due to a similar drop in the $A(\mathbf{k}, E)$ due to a remnant Fermi surface, but is caused by the electron-photon matrix element, i.e., is not a feature of the electronic structure of these compounds but an artifact of the photoexcitation. Along the Γ - (π, π) BZ cut we rather found the spectral weight of the low binding-energy peak to be of comparable strength on both sides of the ABZ in agreement with theoretical results using generalized t - J or Hubbard models.¹⁷

The angle-resolved photoelectron spectra were recorded on the storage ring Aladdin at the University of Wisconsin-Madison Synchrotron Radiation Center, on the Ames Laboratory/Montana State University ERG/SEYA beamline using a 50-mm radius hemispherical analyzer having a 2° full angular acceptance angle which corresponds to a \mathbf{k} resolution of 0.034 and 0.038 \AA^{-1} [6 and 6.8% of the distance between Γ and (π, π)] for the first electron-removal states with 20- and 24-eV photon energy ($h\nu$), respectively. The total energy resolution was 105 meV. The angle of incidence of the photons was $\sim 43^\circ$ with respect to the sample surface normal with the sample normal pointing down by $\sim 8^\circ$. The $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ single crystal was grown as described elsewhere.¹⁸ The sample was oriented *ex situ* by Laue back-scattering and mounted with the Cu-O oxygen bonds in a horizontal/vertical plane. The sample was cleaved (cleavage plane parallel to CuO_2 planes) in the experimental chamber in a vacuum better than 4×10^{-11} Torr and the sample alignment was confirmed *in situ* by using the symmetry of the dispersion of spectral features at high-symmetry points and the appearance of acute peaks associated with purely O $2p$ -derived states in the main valence band at ~ 2.5 and ~ 4 eV at (π, π) and $(\pi, 0)$, respectively.¹⁹ All EDCs were recorded at room temperature and were normalized to the photon flux. Although there is no long-range antiferromagnetic order at room temperature in $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, the antiferromagnetic correlation length is still two orders of magnitude larger than the Cu-O distance.¹¹ Therefore photoemission, as a fast and local probe, still sees the effect of antiferromagnetic order even 50 K above the Néel temperature.⁷ The

Fermi edge of a platinum foil in electrical contact with the sample was used as binding-energy reference. There were no indications of charging effects because repeating an EDC for a \mathbf{k} point after the beam had decayed to less than half the current when the first EDC was taken gave the same EDC, when normalized to the incident flux. All ARPES spectra shown were recorded within a period of five days after the cleave of the sample and in one experimental run, i.e., using the same sample cleave. We observed no signs of sample degradation during this span of time.

In Fig. 1 the first electron-removal states of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ for \mathbf{k} along Γ - (π, π) and photon energies from 20 to 24 eV are shown. For all photon energies a dispersing low binding-energy peak is observed which has its minimum binding energy at $(\pi/2, \pi/2)$. There is a significant change in the spectral intensity of the low binding-energy peak as a function of \mathbf{k} for different photon energies. For $h\nu=24$ eV the low binding-energy peak has non-negligible spectral intensity for \mathbf{k} from 38 to 51% of the distance between Γ and (π, π) , i.e., *inside* the ABZ. Upon lowering the photon energy the center of the \mathbf{k} span in which the low binding-energy peak exists along the line Γ to (π, π) shifts to larger \mathbf{k} vectors. For example, for 22 eV photons the low binding-energy peak can be observed for \mathbf{k} from 39 to 58% of the distance between Γ and (π, π) while for $h\nu=20$ eV it has significant spectral intensity only from 49 to 60% of the distance between Γ and (π, π) , i.e., for \mathbf{k} *outside* the ABZ. The fact that in all previously published Γ - (π, π) ARPES data there is a marked drop of the spectral intensity of the low binding-energy peak after crossing $(\pi/2, \pi/2)$ is therefore not unique but due to the specific choice of photon energy (larger than 22 eV in all previous publications).

Next we want to compare the spectral intensities of the low binding-energy peak at equivalent \mathbf{k} -space positions (with respect to the ABZ) inside and outside the ABZ. In Fig. 2 the first electron-removal states of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ are shown for \mathbf{k} at 44 and 56% ($\pm 1\%$) of the distance between Γ and (π, π) [i.e., equidistant to the Γ to (π, π) cut of the ABZ at $(\pi/2, \pi/2)$] for photon energies from 20 to 24 eV. Note that all spectra shown in Fig. 2 are on the same inten-

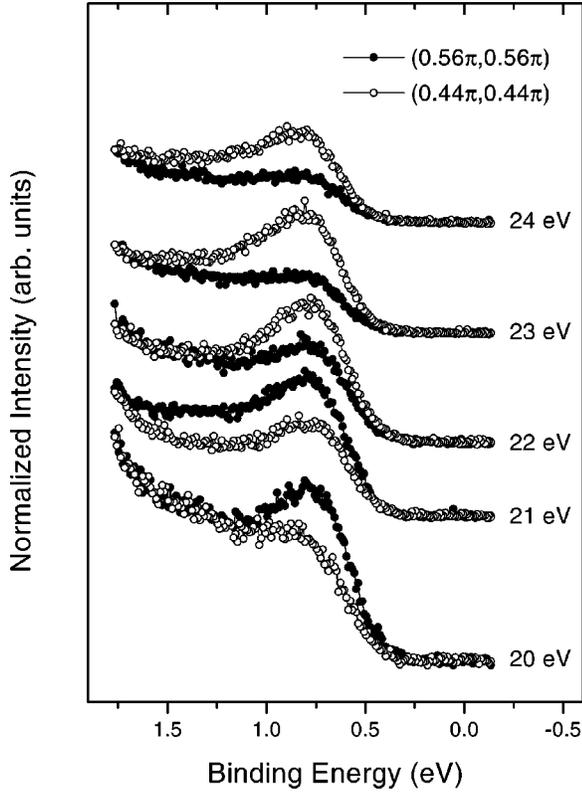


FIG. 2. Comparison of the first electron-removal states of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ recorded at 44 (open circles) and 56% (solid circles) of the distance between Γ and (π, π) for 20-24-eV photon energy. The spectra are offset vertically for clarity but are on scale otherwise.

sity scale and are vertically offset for clarity. At $(0.44\pi, 0.44\pi)$ the low binding-energy peak gains intensity on going from $h\nu$ from 20 to 24 eV and is best developed for 23 eV. For $(0.56\pi, 0.56\pi)$ the low binding-energy peak is strongest for $h\nu=21$ eV. It is evident from Fig. 2 that the maximum spectral intensities of the low binding-energy peak at 44 and 56% of the distance between Γ and (π, π) (at $h\nu=23$ and 21 eV, respectively) are comparable. This means that although the low binding-energy peak is highlighted in the ARPES spectra at $(\pi/2 + \epsilon, \pi/2 + \epsilon)$ (outside the ABZ, ϵ is a positive number understood to be in a range where the low binding-energy peak exists) for a different photon energy than at $(\pi/2 - \epsilon, \pi/2 - \epsilon)$ (inside the ABZ) it has similar maximum ARPES spectral intensity at equivalent \mathbf{k} -space positions inside and outside the ABZ.

We want to stress that Figs. 1 and 2 really represent the low binding-energy ARPES response of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ and that the observed differences between the series of EDC's are related to the electron-photon matrix element (see also Ref. 16). Sample variability can be excluded as the spectra presented in this paper were recorded using the same sample and sample cleave. Similar results were obtained on a second sample. Furthermore, our data are compatible with previously published $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ and $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ ARPES results (if recorded at the same photon energy) which eliminates a bad sample cleave or misalignment of the crystal as possible reasons. One could argue that, dependent on photon

energy, different initial states are observed, but this is not consistent with the continuous shift of spectral intensity of the low binding-energy peak to larger \mathbf{k} vectors evident in Fig. 1 when the photon energy is decreased. Moreover, up to now most authors ascribe the low binding-energy peak evident in the first electron-removal states of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ or $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ to a Zhang-Rice singlet (ZRS),^{20,21} i.e., one initial state. For an initial state with a given \mathbf{k} component parallel to the CuO_2 planes the momentum component perpendicular to the CuO_2 planes is dependent on the photon energy but a ZRS is derived from O $2p$ and Cu $3d_{x^2-y^2}$ orbitals, thus localized in the CuO_2 plane, so no dependence of the dispersion of the low binding-energy peak on the momentum component perpendicular to the CuO_2 plane is expected. Note also that the in-plane nature of the counterpart of the first electron-removal states in the unoccupied part of the electronic structure (which is derived from the same orbitals as the first electron-removal states) has been explicitly shown by x-ray-absorption spectroscopy.²²

$A(\mathbf{k}, E)$ itself does not depend on the photon energy used to excite the first electron-removal states. Resonant Cl $3s$ or Sr $4p$ photoemission can be excluded as reason for the observed photon energy dependence of the $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ ARPES spectra as the first electron-removal states are of O $2p$ and Cu $3d$ character. We do not think that these spectra are influenced by resonant O $2s$ photoemission. There is a report,²³ later challenged in Refs. 24 and 25, of resonant O $2s$ photoemission for states at the Fermi level for the related cuprate $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, but the enhancement of the photoemission intensity from states near the Fermi level was reported to be at $h\nu=18$ eV.

The Γ - (π, π) series of spectra shown in Fig. 1 are equivalent in the sense that they show the lowest-lying excitations associated with the motion of a hole in an antiferromagnetically ordered CuO_2 plane for \mathbf{k} along the Γ - (π, π) direction in the first BZ, i.e., the underlying spectral function is the same. The electron-photon matrix element $\langle i|\mathbf{p} \cdot \mathbf{A}|f\rangle$ (\mathbf{p} and \mathbf{A} are the photoelectron momentum and the vector potential, respectively), on the other hand, is affected by the photon energy as different final states are reached upon changing the photon energy and therefore is the factor which is responsible for the observed differences between the series of EDC's shown in Fig. 1.

From the foregoing discussion we can conclude that our data truly represent the low binding-energy ARPES response of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$. In the following we first recall our main experimental results, then discuss their implications for the theory of the hole dynamics in Cu-O planes. First, we showed that there is a well-developed low binding-energy peak for both $(\pi/2 - \epsilon, \pi/2 - \epsilon)$ and $(\pi/2 + \epsilon, \pi/2 + \epsilon)$. The peak is best developed at $(\pi/2 - \epsilon, \pi/2 - \epsilon)$ for a different photon energy (~ 23 eV) than at $(\pi/2 + \epsilon, \pi/2 + \epsilon)$ (~ 21 eV) due to the electron-photon matrix element. Finally, for photon energies from 20 to 24 eV the low binding-energy peak has similar maximum ARPES spectral intensity at $(\pi/2 - \epsilon, \pi/2 - \epsilon)$ and $(\pi/2 + \epsilon, \pi/2 + \epsilon)$. A possible interpretation of our spectra is that with 23- and 24-eV photons, a clear peak was seen just inside the ABZ, and with 20- and 21-eV photons the same peak was seen outside the ABZ via

an umklapp process. If so, the reciprocal-lattice vector responsible for the umklapp process also remaps the second ABZ into the first and any peak structure in $A(\mathbf{k}, E)$ just inside the ABZ boundary must have a counterpart along $\Gamma-(\pi, \pi)$ just outside that boundary. $A(\mathbf{k}, E)$ is then symmetric about the ABZ. Two peaks or a broad structure spanning the ABZ boundary are then expected,²⁶ but not found. Then our data indeed suggest that on going from Γ to (π, π) the low binding-energy peak in $A(\mathbf{k}, E)$ has similar strength on both sides of the ABZ. This result has two implications. First, note that this means that the first electron-removal states do not cross a remnant of a Fermi surface. In this scenario the lowest-lying band would disperse to lower binding energies on going from Γ to $(\pi/2, \pi/2)$ and cross the remnant Fermi surface before it disperses back to higher binding energies again, i.e., for \mathbf{k} less than $(\pi/2, \pi/2)$. This implies that on going from Γ to (π, π) the peak associated with the lowest-lying band should lose most of its intensity crossing $(\pi/2, \pi/2)$ in contradiction to our results.

The dynamics of a hole in an antiferromagnetically ordered Cu-O plane is often described using Hubbard or t - J models. Our results are not compatible with a Hubbard model in the weak- to intermediate-coupling regime which along $\Gamma-(\pi, \pi)$ yields a strong drop in the spectral weight of the low binding-energy peak after $(\pi/2, \pi/2)$.²⁷ Our ARPES data are, on the other hand, in agreement with results for a generalized Hubbard model in the strong-coupling limit and a generalized t - J model using accepted model parameters for the cuprates,¹⁷ as there is at most a 20% difference in the calculated spectral weights of the low binding-energy peak at

$(\pi/2 - \epsilon, \pi/2 - \epsilon)$ and $(\pi/2 + \epsilon, \pi/2 + \epsilon)$, compatible with our data, remembering again that ARPES spectral intensity is electron-photon matrix-element-weighted spectral function.

In conclusion, the spectral function associated with the motion of a hole in an antiferromagnetically ordered Cu-O plane has been probed by ARPES of the antiferromagnetic insulator $\text{Sr}_2\text{CuO}_2\text{Cl}_2$. Using a cut along the line $\Gamma-(\pi, \pi)$ in \mathbf{k} space we have observed that the strong drop of the spectral intensity of the lowest-lying states reported in the literature is not related to a crossing of the lowest-lying band of a remnant Fermi surface but is due to the electron-photon matrix element. The spectral intensity of the low binding-energy peak is found to be of comparable strength on both sides of the ABZ in agreement with theoretical results using generalized t - J or Hubbard models.

Ronning *et al.*²⁸ present extensive EDCs on $\text{Ca}_2\text{CuO}_2\text{Cl}_2$, scanning over the entire Brillouin zone. Perpendicular to the ABZ they also find there is always a drop in the intensity profile of the ZRS whose position in \mathbf{k} space depends on photon energy. However, parallel to the ABZ no similar correlation in the structure of the intensity profile is found. Ronning *et al.* use these facts to interpret the remnant Fermi surface as a “robust” feature whose details are dependent on the photon energy used.

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²⁶We think this assumption is reasonable. For 21- and 23-eV photon energy a low-binding-energy peak can be observed at a different \mathbf{k} window but for about the same \mathbf{k} span [$\sim 20\%$ of the distance between Γ and (π, π)] which would be unexpected if the strength of the electron-photon matrix element were very different.

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