Angle Resolved Photoemission from $Nd_{1.85}Ce_{0.15}CuO_4$ using High Energy Photons: A Fermi Surface Investigation

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We have performed an angle resolved photoemission study on a single crystal of the optimally electron doped (n-type) cuprate superconductor $Nd_{2-x}Ce_xCuO_4$ ($x = 0.15$) at a photon energy of 400 eV. The Fermi surface is mapped out and is, in agreement with earlier measurements, of hole-type with the expected Luttinger volume. However, comparing with previous low energy measurements, we observe a different Fermi surface shape and a different distribution of spectral intensity around the Fermi surface contour. The observed Fermi surface shape indicates a stronger electron correlation in the bulk as compared to the surface.

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Among the high-temperature cuprate superconductors only a small family can be doped with electrons (n-type), $Nd_{2-x}Ce_xCuO_4$ (NCCO) is one of them. The dominating amount of experimental work in this field has been devoted to the much larger family of hole-doped (p-type) materials and recent experiments have shown evidence for strongly contrasting behavior between the two families [1]. The undoped parent compounds of both p- and n-type cuprate superconductors are antiferromagnetic (AF) insulators [2]. An important aspect of cuprate high-T_c superconductivity is whether there exists a symmetry in the doping-temperature phase diagram when the AF parent is doped away from the insulating state with either electrons or holes. New studies of NCCO and the other n-type cuprates can give the information needed to resolve this issue.

Angle resolved photoemission spectroscopy (ARPES) is, because of its capability of directly measuring the spectral function $A(\omega, \vec{k})$, a very powerful technique in the study of the electronic structure of this class of materials. A number of recent ARPES studies of NCCO have shed new light on several central concepts of its electronic structure, for instance the symmetry of the superconducting gap [3], the doping dependence [4] and pseudogaplike effects [5].

The above-mentioned studies have been performed at relatively low photon energies (up to 55 eV), whereas the data we present here have been acquired at an excitation energy of 400 eV. High photon energy gives an increased photoelectron mean-free path and, hence, an increased bulk sensitivity. Increasing the kinetic energy from around 55 eV to around 400 eV roughly doubles the photoelectron escape depth. The use of high photon energies also gives the possibility to investigate whether features seen in low energy data could be caused by matrix-element effects. Furthermore, there is also a generally adopted belief that in the cuprates the Cu-O planes are the place where the mechanisms of high-T_c superconductivity originate. Results from measurements by ARPES, which at the typically used low photon energies is very surface sensitive, have been interpreted as reflecting the electronic structure of these Cu-O planes. However, cleaving a cuprate single crystal in many cases gives a sample where the first Cu-O plane is located at a depth of several Å and therefore a significant amount of the ARPES signal comes from other atomic layers closer to the surface. In the case of $Bi_2Sr_2CaCu_2O_{8+\delta}$ there are observations indicating that photoelectrons emitted from Sr and Ca core levels experience a strong inelastic scattering, which is also photon energy dependent, on their way towards the surface [6]. This results in a reduction of the photoelectron mean-free path and for electrons emitted from the deeper lying Cu-O planes this reduction should be even larger. Hence, several issues give the motivation for using high energy ARPES to study NCCO and the other high-T_c cuprates.

Here we report a high photon energy ($h\nu = 400$ eV) angle resolved photoemission study of a $Nd_{1.85}Ce_{0.15}CuO_4$ single crystal at a temperature $T \approx 24$ K. We observe a Fermi surface (FS) of hole-type with a volume respecting Luttinger's theorem [7], confirming previous measurements at lower photon energies [4,5]. A detailed analysis of the FS reveals several features which deviate from the characteristics observed at lower photon energies [4,5]. We see a different shape of the FS and a different variation of ARPES intensity around the surface contour at this photon energy.

Experiments were performed at beam line ID08 at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The beam line, which is equipped with a Scienta SES-2002 electron energy analyzer, has the capability to acquire ARPES spectra with an angular resolution of 0.15° along the slit and 0.2° in the perpendicular direction.

The Scienta analyzer was used in the angle mode; angular cuts were obtained parallel to the $\Gamma - (\pi, \pi)$ direction with a momentum resolution of 0.027 Å^{-1}. To obtain different angular cuts the sample was rotated in steps of 1.0° in relation to the analyzer, corresponding to a momentum step of 0.18 Å^{-1} perpendicular to the $\Gamma - (\pi, \pi)$ direction. Data were recorded using a total energy resolution of $\Delta E \approx 140$ meV. Circularly polarized synchrotron radiation with an energy of 400 eV was used throughout the measurement.

The single crystal of $Nd_{1.85}Ce_{0.15}CuO_4$ was grown by the travelling solvent floating zone method [8,9] and had a critical superconducting temperature of $T_c \approx 21$ K. Using a liquid He cold finger the sample was cooled down to a temperature of ≈ 24 K and then cleaved *in situ*. LEED was used to check the surface quality and the orientation of the sample. The base pressure in the experimental chamber was below 5×10^{-11} mbar and no signs of sample degradation were seen during the 38-h measurement period. To obtain a reference for the Fermi level of the sample a gold foil was mounted in electrical contact with it on the sample holder.

In Figs. 1 and 2 we present $E - \vec{k}$ image plots of the ARPES spectral intensity along two different high-symmetry directions in the Brillouin zone (BZ). In Fig. 1 one dispersive feature which is present in all the cuprates, is seen, while two different features are distinguished in Fig. 2. Besides the dispersive data in specific directions, we have also compiled a FS map by summing the ARPES intensity over a 136 meV energy window about the Fermi level, see Fig. 3. In agreement with data presented by Armitage *et al.* [4,5] the FS is of the hole-type.

In order to make a more detailed analysis of the FS shape we have added intensity contributions from $\vec{k}$-points equivalent by symmetry over almost the entire map displayed in Fig. 3. This results in a BZ octant, which in Fig. 4 has been duplicated 8 times to reproduce the complete FS.

The FS of Fig. 4 can be compared with the low energy data presented by Armitage *et al.* [4,5]. As noted above, the FS is of the hole-type and the volume is consistent with the value $1 + x$ given by Luttinger's theorem [7]. With a filling level of 1.16 ± 0.05 the Luttinger theorem gives a doping level $x = 0.16$, which is in good accordance with our sample ($x = 0.15$). Hence, in spite of the increased bulk sensitivity resulting from a high photon energy, we can confirm the doping level seen in low energy measurements. However, it is clear that our data deviates from that observed by these authors with regard to both the shape and the intensity distribution around the contour.

As noted previously we have used an energy window of 136 meV, which is several times wider than the 30 and 60 meV's previously employed in the low photon energy studies by Armitage *et al.* [4,5]. Depending on the dispersion of the integrated band, an increased energy win-

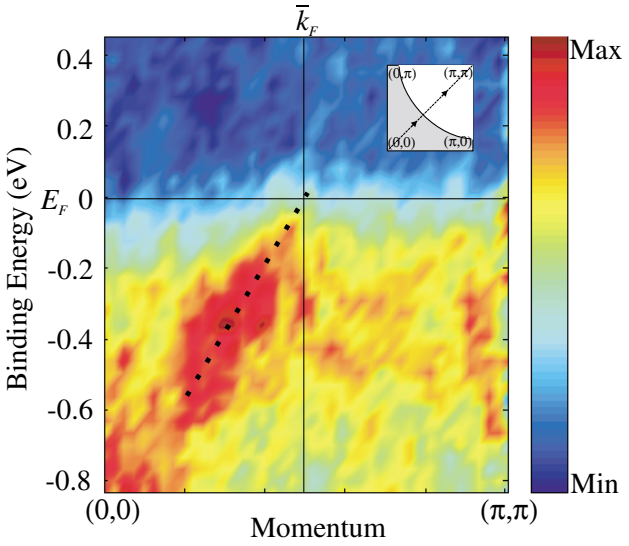

FIG. 1 (color online). ARPES spectral intensity at $h\nu = 400$ eV plotted as a function of binding energy and momentum for a cut in the $\Gamma - (\pi, \pi)$ direction, see schematic inset. A dispersive feature approaching E_F and crossing it at $|\vec{k}_F| \approx 49\%$ of the distance between Γ and (π, π) , is clearly seen. A dotted line in black has been added as a guide to the eye in order to show the dispersion. The approximate Fermi level crossing is an estimation by eye.

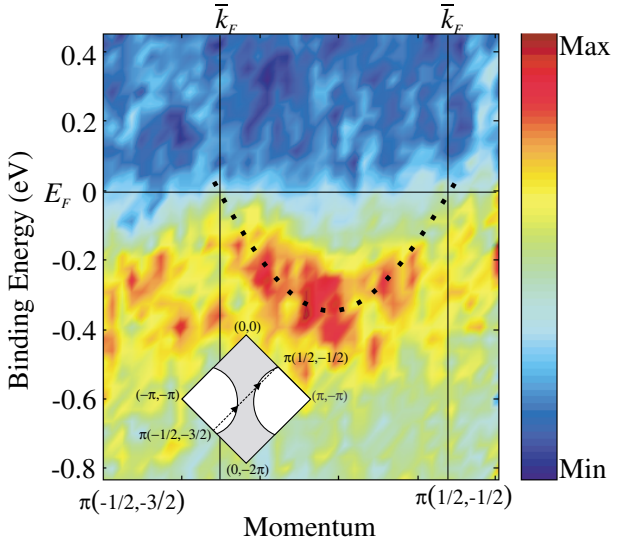

FIG. 2 (color online). ARPES intensity for a cut in the $(-\pi/2, -3\pi/2) - (\pi/2, -\pi/2)$ direction. Two dispersive features can be distinguished, one is crossing the Fermi level at $|\vec{k}_F| \approx 30\%$ and the other at $|\vec{k}_F| \approx 88\%$ of the distance between $(-\pi/2, -3\pi/2)$ and $(\pi/2, -\pi/2)$. A dotted line in black has been added as a guide to the eye in order to show the dispersion. The approximate Fermi level crossing is an estimation by eye.

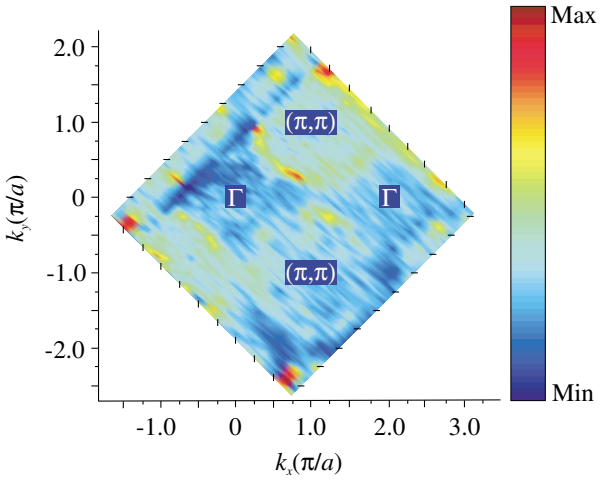

FIG. 3 (color online). FS plot obtained by energy integration of ARPES spectra over a 136 meV window ($\pm$ 68 meV) about the Fermi level [16]. About 2.5 repetitions of the FS are seen.

dow will change not only the integrated intensity, but possibly also the Fermi surface shape. A strong dispersion (large $|dE/d\vec{k}|$) close to the Fermi level gives a smaller shift of the FS and a smaller change in integrated intensity as compared to a case with low dispersion. These two aspects have been investigated close to the $(\pi, 0)$ point, where the dispersion is particularly large, comparing the present data with those of Refs. [5,10].

In Fig. 4 the intensity at the $(\pi, 0)$ crossing is low in relation to other parts of the FS, while it in Ref. [5] has a local maximum at the corresponding point. According to the dispersive data of Ref. [10] in the $(\pi, 0) - (\pi, \pi)$ direction, a change of integration limits from ± 15 to ± 68 meV accompanied by the corresponding decrease in energy resolution (here simulated by convolution with a Gaussian resolution function) shifts the FS position by 1.5% of the $(\pi, 0)$ to (π, π) distance. This shift is indicated by an error bar in the vertical direction in Fig. 4. Because of the sign of the dispersion the shift is in the direction from (π, π) towards $(\pi, 0)$. From Fig. 4 it is clear that an energy window of ± 68 meV neither results in drastically elevated ARPES intensity at the $(\pi, 0)$ point nor a significant FS shift in the $(\pi, 0) - (\pi, \pi)$ direction. Thus it is obvious that the disparities regarding distribution of spectral intensity and FS shape between the current study and previous ones at lower energy cannot be explained by our use of a wider energy window.

The data of Armitage *et al.* [5] show an NCCO FS where spectral weight is suppressed in regions near $(0.65\pi, 0.3\pi)$ and $(0.3\pi, 0.65\pi)$ as compared to other parts of the surface contour. Although differences in the intensity distribution between their 16.5 and 55 eV data indicate that matrix-element effects are present, these authors, on the basis of a line-shape analysis, draw the conclusion that the observed effect is real and not only caused by matrix-element dependencies. However, the intensity distribution around the FS in Fig. 4 shows no modulations of the type seen in the data of Armitage *et al.*

Armitage *et al.* [5] note that the regions where intensity is suppressed are located close to the intersections of the FS with the AF BZ boundary. Based on this and the fact that a line-shape analysis seems to indicate an increased scattering rate in the same regions, they argue that charge carriers there are subject to (π, π) scattering. After a comparison with our data this interpretation seems more unlikely. In Fig. 4 there is no sign of the intensity modulations on the FS contour presented by the authors in Ref. [5]. If there is a modulation in our FS data it is rather the opposite one to that displayed in Ref. [5] with increased intensity where they see suppressed and vice versa. The fact that we have used circularly polarized synchrotron radiation with $h\nu = 400$ eV, while Armitage *et al.* have used linearly polarized radiation with $h\nu = 16.5$ and 55 eV, suggests that matrix-element effects dependent on experimental geometry, photon energy and light polarization might be important for the modulations seen in the low energy data. The importance of matrix-element dependent effects [11] and photon energy dependence [12,13] in ARPES measurements on the cuprates, especially $Bi_2Sr_2CaCu_2O_{8+\delta}$, has been demonstrated several times. However, the FS shape is not affected by any such effects.

Previous ARPES measurements on $Nd_{1.85}Ce_{0.15}CuO_4$ performed at lower photon energies have shown a FS contour of rounded shape [4,5] roughly in agreement with results from local-density approximation (LDA) calculations [14]. However, a careful look at the data of Ref. [5] reveals differences in FS shape between the two photon energies used. While at 55 eV the contour is rounded, almost like a circle arc, the 16.5 eV data shows a flat area around the $(\pi/2, \pi/2)$ point. In terms of shape our 400 eV data is more similar to the latter of these than to the former. The high energy data of Fig. 4 shows a flat, almost linear, region about the $(\pi/2, \pi/2)$ point which is larger and even more pronounced than the corresponding feature in the 16.5 eV results, making the shape look more or less like a square with somewhat rounded corners. For the purpose of comparison, a contour (dashed white line) showing the FS shape according to the 55 eV data of Armitage *et al.* has been added to Fig. 4.

With a photon energy of $h\nu = 400$ eV we are probing the electronic structure at a larger depth as compared to the previous measurements by Armitage *et al.* performed at $h\nu = 16.5$ and 55 eV. By integrating along the surface contour we have verified that we have approximately the same doping level as these authors. This gives us reason to believe that the shape deviations we see could be caused by differences in the electronic structure between the outermost surface layer(s) and the deeper lying bulk structure.

A plausible explanation is that in the topmost surface layers the effects of electronic correlations are suppressed

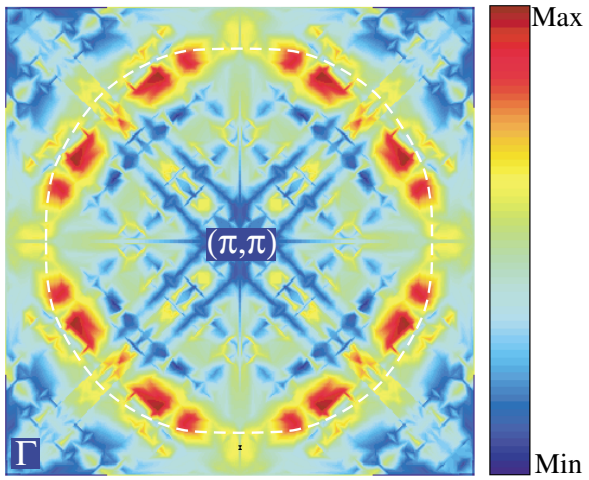

FIG. 4 (color online). Symmetrized FS plot obtained by adding intensities from symmetrically equivalent $\vec{k}$-points over the complete Fermi surface map of Fig. 3 [16]. The resulting BZ octant is repeated 8 times to get the shape of the complete FS. Above the $(\pi, 0)$ point an error bar indicates the shift in FS position [1.5% of the $(\pi, 0) - (\pi, \pi)$ distance] caused by the use of a wider energy window. The dashed white contour shows the FS shape according to the 55 eV data of Armitage *et al.* [5].

as a result of the structural differences between the surface and the bulk layers. In that case it is not surprising to find a variation of the FS shape as a function of probing depth. The observed shape with pronounced corners and straight segments could hence be related to an increased influence from electronic correlations in the bulk region, even though this might be counter intuitive at first sight. It is interesting to note that in terms of FS shape our data recorded at 400 eV is more similar to the 16.5 eV data of Armitage *et al.* than to the 55 eV results also presented by these authors. Since the universal curve of electron mean-free path as a function of kinetic energy has a minimum at about 50 eV, the 16.5 eV results possibly also reflect a situation with increased bulk-sensitivity. Furthermore, support for the presence of stronger electronic correlation effects in the bulk was recently found in high energy x-ray photoelectron spectroscopy (XPS) measurements on the related $Bi_2Sr_2CaCu_2O_{8+\delta}$ system [15]. There it was observed that the $2p^5 3d^9$ satellites in the Cu $2p$ spectrum were largely enhanced in the bulk thus indicating stronger correlation effects in the bulk of this system as well. It is therefore possible that the unexpected stronger correlation in the bulk of NCCO that we observe is a general feature common to several high-T_c compounds.

In summary we have conducted angle resolved photoemission on a $Nd_{1.85}Ce_{0.15}CuO_4$ single crystal at a photon energy significantly higher than previously presented ($h\nu = 400$ eV). Our dataset, covering more than two repetitions of the BZ, has been used to map out the FS. It is of the hole-type and has a volume in agreement with Luttinger's theorem ($\approx 1 + x$, where $x \approx 0.16$). In contrast to previous measurements at low energy we observe a FS of diamond like shape with almost straight sections. The increased bulk-sensitivity suggests that this difference could be caused by stronger electron correlation effects in the bulk as compared to the surface. Furthermore, the observed distribution of spectral weight lends no support to the proposal of strong (π, π) scattering in certain momentum space regions. In this case, the differences between our data and earlier low energy observations can most probably be attributed to matrix-element effects.

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[16] Before the FS map of Fig. 3 was obtained each ARPES spectrum was normalized in the following way. The data for each angle in an ARPES spectrum was normalized to the integrated intensity (i.e., summing over all energies) for that particular angle. However, the normalization used to obtain the map of Fig. 4 is different. Here each ARPES spectrum has been normalized to the intensity integrated over the entire spectrum (i.e., summing over all energies and angles) before the integration about the Fermi level was done. This allows us to make more distinct conclusions from the distribution of intensity around the FS contour.