New light on EuO thin films
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Chapter 8

Crossing the gap from \( p \)- to \( n \)-type doping: nature of the states near the chemical potential in \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) and \( \text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta} \)

We report on an x-ray absorption and resonant photoemission study on single crystal \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) and \( \text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta} \) high \( T_c \) cuprates. Using an internal energy reference, we find from the photoemission data that the chemical potential of \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) lies near the top of the \( \text{La}_2\text{CuO}_4 \) valence band and of \( \text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta} \) near the bottom of the \( \text{Nd}_2\text{CuO}_4 \) conduction band. The x-ray absorption data establish clearly that the introduction of Ce in \( \text{Nd}_2\text{CuO}_4 \) results in electrons being doped into the \( \text{CuO}_2 \) planes. We infer that the states closest to the chemical potential have a \( \text{Cu} \) 3d\(^{10}\) singlet origin in \( \text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta} \) and 3d\(^6\)L singlet in \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \).

8.1 Introduction

One of the long standing puzzles in the field of high \( T_c \) superconductivity concerns the nature of the charge carriers in doped high \( T_c \) cuprates [178]. Several photoemission studies [259–261] have revealed very little difference in the valence band spectra of the \( \text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta} \) system as compared to the \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \). In particular, the position of the chemical potential in the two different systems seem to be quite similar and is located in the middle of the gap of the parent compounds, while one would expect that the chemical potential should shift from the top of the valence band to the bottom of the conduction band by changing from \( p \)-type to \( n \)-type doping. From this unexpected behavior it was concluded that both hole and electron doping result in new states that fill the band gap. Several explanations have been proposed for this mid gap pinning of the chemical potential [259, 262–264], with
perhaps the scenario involving the occurrence of phase separation to be currently the most discussed [262, 264, 265]. In addition, for Nd$_{2-x}$Ce$_x$CuO$_{4-\delta}$ it becomes even an issue whether it can be regarded as a really electron doped system [266–268], since transport measurements on optimally doped Nd$_{2-x}$Ce$_x$CuO$_{4-\delta}$ have revealed a positive Hall coefficient [269, 270]. This has led to propositions that the charge carriers relevant for the superconductivity in Nd$_{2-x}$Ce$_x$CuO$_{4-\delta}$ are hole like.

In this paper we present a comparative x-ray absorption (XAS) and resonant photoemission (RESPES) study on Nd$_{2-x}$Ce$_x$CuO$_{4-\delta}$ and La$_{2-x}$Sr$_x$CuO$_4$ single crystals. To ensure that the spectra collected are representative for the bulk material, we rely on the bulk sensitivity of the x-ray absorption technique as well as of valence band photoemission measurements using high photon energies [271]. In addition, we use an internal energy reference within the CuO$_2$ planes as proposed earlier [262], in order to ensure a reliable measurement of the position of the chemical potential relative to the valence band. We find unambiguously that the chemical potential $\mu$ of La$_{2-x}$Sr$_x$CuO$_4$ lies near the top of the La$_2$CuO$_4$ valence band and $\mu$ of Nd$_{2-x}$Ce$_x$CuO$_{4-\delta}$ lies near the bottom of the Nd$_2$CuO$_4$ conduction band, and that the introduction of Ce results in electrons being doped into the CuO$_2$ planes. Resonance data suggest that the charge carriers in Nd$_{2-x}$Ce$_x$CuO$_{4-\delta}$ are different in nature than in La$_{2-x}$Sr$_x$CuO$_4$, in the sense that they are singlets of Cu 3$d^{10}$ character rather than of 3$d^9$L, where $L$ denotes an oxygen ligand hole. In addition we find that the presence of Nd 4$f$ states and a different O 2$p$ to Cu 3$d$ charge transfer energy cause Nd$_{2-x}$Ce$_x$CuO$_{4-\delta}$ to have an apparently similar chemical potential position as La$_{2-x}$Sr$_x$CuO$_4$ if the leading edge of the main valence band structure is used as reference.

### 8.2 Experimental

Single crystals of Nd$_2$CuO$_4$, Nd$_{1.85}$Ce$_{0.15}$CuO$_{4-\delta}$, La$_2$CuO$_4$, and La$_{1.85}$Sr$_{0.15}$CuO$_4$ were grown by the travelling solvent floating zone method [272–274]. The onset of the superconducting transition in the La$_{1.85}$Sr$_{0.15}$CuO$_4$ sample was found to be 35 K from ac-susceptibility measurements. The Nd$_{1.85}$Ce$_{0.15}$CuO$_{4-\delta}$ crystals show a critical temperature of 21 K after reducing them in flowing N$_2$ gas at 900°C for 30 hours. XAS and RESPES experiments were performed at the ID12B beamline of the European Synchrotron Research Facility (ESRF). The overall energy resolution was set to 0.3 eV for the XAS and 0.5 eV for the RESPES. The samples were both cleaved and measured at 20 K in a chamber with a base pressure below 5×10$^{-11}$ mbar. Core level x-ray photoemission (XPS) measurements were carried out in Groningen using a Surface Science Instruments system equipped with a monochromatized Al-$K\alpha$ source. The XPS energy resolution is 0.5 eV, and the samples were cleaved and measured at room temperature in a chamber with a base pressure below 1×10$^{-10}$ mbar.
8.3 Is Nd$_{1.85}$Ce$_{0.15}$CuO$_4$–δ electron doped?

Figure 8.1: Cu 2p XPS spectra of (a) Nd$_{1.85}$Ce$_{0.15}$CuO$_4$–δ and (b) Nd$_2$CuO$_4$.

Figure 8.1 shows the Cu 2p core level XPS of Nd$_2$CuO$_4$ and Nd$_{1.85}$Ce$_{0.15}$CuO$_4$–δ where we have used the standard labelling for the structures [261, 275–277]. We clearly observe that the 2p$3d^9$ 'satellites' decrease in intensity with Ce doping, and that also new structures start to appear on the low binding energy side of the 2p$3d^{10}L$ 'main lines', where the underline denotes a hole. These new structures have been assigned as 2p$3d^{10}$. These spectra imply that doping Nd$_2$CuO$_4$ with Ce results in a decrease of the Cu$^{2+}$ content with the 3d$^9$ and 3d$^{10}L$ configurations, and simultaneously an increase of the Cu$^{1+}$ with the 3d$^{10}$ configuration. In other words, Ce doping indeed introduces electrons into the CuO$_2$ planes in Nd$_{2-x}$Ce$_x$CuO$_4$–δ.

Figure 8.2 depicts the Cu L$_3$ XAS spectrum of Nd$_2$CuO$_4$ and Nd$_{1.85}$Ce$_{0.15}$CuO$_4$–δ normalized to the Nd M$_5$ absorption line as shown in the inset. The Cu white line is given by the transition 3d$^9$ + hν → 2p$3d^{10}$. One can clearly see that the Cu white line intensity has decreased appreciably when Ce is introduced into the system, consistent with the results from earlier electron energy loss studies on polycrystalline samples [278, 279]. This indicates again directly that the Cu$^{2+}$ content in the CuO$_2$ plane is reduced, i.e. Ce doping indeed means electron doping.
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8.4 Position of the chemical potential

Having established that \( \text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta} \) is an electron doped material, we now will shift our focus to the issue of the position of the chemical potential in \( \text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta} \) relative to that in the \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) as well as their parent materials. Figure 8.3 shows the on- and off-resonant photoemission spectra of \( \text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta} \), \( \text{Nd}_2\text{CuO}_4 \) \( \text{La}_2\text{CuO}_4 \) and \( \text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4 \). The on-resonant spectra are taken with the photon energy tuned at the \( \text{Cu} L_3 \) XAS white line, and the off-resonant spectra with a photon energy which is \( 5.0 \pm 0.1 \) eV lower. It has been demonstrated earlier [280–282] that the \( \text{Cu} L_3 \) resonant photoemission spectrum of \( \text{Cu}^{2+} \) oxides is dominated by the auto-ionization process of the type \( 3d^9 + h\nu \rightarrow 2p3d^{10} \rightarrow 3d^8 \), thereby enhancing the spectral weight of the \( 3d^8 \) final states considerably. Indeed, the spectra depicted in the top panel contain the characteristic \( ^1G \) and \( ^3F \) structures of \( 3d^8 \) [283, 284].

We now will use the \( 3d^8 \) \( ^1G \) peak to set the energy scale for all the photoemission spectra [262], since this will give us an energy zero that refers directly to the electronic structure of the \( \text{CuO}_2 \) plane, which is at the heart of the current discussion. Such an internal energy reference is much more reliable than using the leading edge of the main peak of the off-resonant valence band spectrum [259, 260], since

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Figure 8.2: \( \text{Cu} L_3 \) XAS spectra of \( \text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta} \) normalized on the \( \text{Nd} M_5 \) absorption intensity as shown in the inset.
8.4. Position of the chemical potential

Figure 8.3: Upper panel: resonant photoemission of Nd$_{1.85}$Ce$_{0.15}$CuO$_{4-\delta}$, Nd$_2$CuO$_4$, La$_2$CuO$_4$ and La$_{1.85}$Sr$_{0.15}$CuO$_4$ at the Cu $L_3$ edge. The energy of the spectra has been aligned on the Cu 3$d^8$ $^1G$ final states. Lower panel: off-resonant spectra of the same samples at a photon energy 5 eV below the resonance. The arrows indicate the valence band onset of Nd$_2$CuO$_4$ and the Fermi level of Nd$_{1.85}$Ce$_{0.15}$CuO$_{4-\delta}$.

in comparing the Nd$_{2-x}$Ce$_x$CuO$_{4-\delta}$ with the La$_{2-x}$Sr$_x$CuO$_4$ system one can suffer from differences due to the presence of different chemical species and charge transfer energies, as we will show later. It is also better to use the internal energy reference
rather than the Fermi level of the spectrometer [263], since the chemical potential of the undoped Nd$_2$CuO$_4$ and La$_2$CuO$_4$ is not well defined and in fact will even be pinned by impurities or defects of unknown nature and quantities.

With the $^1G$ peak position set to zero, we can clearly observe in the lower panel of figure 8.3, that the first ionization state of Nd$_{1.85}$Ce$_{0.15}$CuO$_{4-\delta}$ is about 1.0 eV further away than that of the undoped Nd$_2$CuO$_4$. Recalling that the onset of the optical gap in Nd$_2$CuO$_4$ is approximately 1.0 eV (with the first peak in the optical spectrum at 1.5 eV) [285–287], one can immediately conclude that the chemical potential of the Ce doped system lies near the bottom of the conduction band of the undoped Nd$_2$CuO$_4$. Contrary to earlier claims [259, 260], we find that the chemical potential for the doped material is not pinned in the middle of the gap of the undoped material. A similar conclusion can also be reached from recent doping dependent angle-resolved photoemission experiments [288], although there one needs to assume that one can align the spectrum of the undoped Nd$_2$CuO$_4$ with respect to those of the Nd$_{2-x}$Ce$_x$CuO$_{4-\delta}$ by using the leading edge of the valence band for small doping levels.

In comparing La$_{2-x}$Sr$_x$CuO$_4$ with La$_2$CuO$_4$ using the $^1G$ internal reference, we can also clearly see from the lower panel of figure 8.3, that the chemical potential in La$_{1.85}$Sr$_{0.15}$CuO$_4$ resides in the vicinity of the top of the valence band of La$_2$CuO$_4$, contrary to earlier reports in which the chemical potential was concluded to be pinned in the middle of the insulator gap [260, 263]. We suspect that this discrepancy is caused by the different method for the energy referencing, which can lead to hidden energy shifts, as we have explained above.

The lower panel of figure 8.3 also shows that the valence band spectrum of Nd$_2$CuO$_4$ is very different in intensity and also in energy position as compared to the spectrum of La$_2$CuO$_4$. We can identify two reasons for this. The first is that in the Nd$_{2-x}$Ce$_x$CuO$_{4-\delta}$ system the presence of Nd contributes significantly to the valence band spectrum, while this is not the case for La in La$_{2-x}$Sr$_x$CuO$_4$. From photo-ionization cross-section tables [289], one can estimate that the Nd 4$f$ is responsible for more than 50% of the signal in Nd$_{2-x}$Ce$_x$CuO$_{4-\delta}$ at the photon energies used, while in La$_{2-x}$Sr$_x$CuO$_4$ the spectrum is dominated by the Cu spectral weight. It is also important to realize that the Nd 4$f$ signal is present over the entire valence band energy range. This is demonstrated by figure 8.4, where we plot the resonant photoemission spectrum of the Nd$_2$CuO$_4$ and Nd$_{1.85}$Ce$_{0.15}$CuO$_{4-\delta}$ valence bands, with the photon energy tuned on the Nd 3$d$ absorption edge. A double peak structure is clearly visible, of which the higher-binding energy feature can be assigned to screening by charge transfer from the O 2$p$ orbitals (4$f^3$L final states) and the lower-binding energy peak which resonates most strongly is due to pure Nd 4$f$ hole states (4$f^2$ final states) [260, 290]. Similar resonances were found at the Nd $M_5$ [291, 292] and Nd $N_{45}$ absorption edge [259, 260, 293, 294]. From these data we can clearly see that the Nd 4$f$ component continues all the way up to the top of the valence band in Nd$_2$CuO$_4$. It is not inconceivable that the top of the valence
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Figure 8.4: On and off resonant photoemission spectra at the Nd M₅ absorption edge.

Band in the undoped Nd₂CuO₄ consists of Nd 4f states and not of Cu 3d⁹L⁹. It is interesting to note that this could provide a possible explanation why it is difficult to dope holes into the CuO₂ planes in cuprates with the T’-structure, as these holes would be doped into the Nd-O planes.

Another cause for differences in the valence band spectrum of Nd₂CuO₄ as compared to La₂CuO₄ is laid out in the upper panel of figure 8.3. A blow-up of the Cu L₃ on-resonant photoemission spectra shows that the leading edge of the valence band in Nd₂CuO₄ and also Nd₁.₈₅Ce₀.₁₅CuO₄₋δ is higher in energy by about 0.6 eV as compared to that of La₂CuO₄. This number agrees very well with the fact that the optical gap in Nd₂CuO₄ is about 0.5 eV smaller than in La₂CuO₄ (which has its first peak in the optical spectrum at 2.0 eV) [286, 295]. One could infer that this 0.6 eV difference reflects the difference in the effective O 2p - Cu 3d charge transfer
energy, since this parameter determines to a large extent the magnitude of the band gap of the insulating correlated insulator. On hindsight, it is perhaps not surprising to find such differences in view of the fact that Nd$_2$CuO$_4$ and La$_2$CuO$_4$ have different crystal structures and O-Cu bond lengths, resulting in differences in Madelung potentials and O 2p - Cu 3d hopping integrals. In fact, there is no compelling reason to believe that a comparative study of the development of the chemical potential in Nd$_{2-x}$Ce$_x$CuO$_{4-\delta}$ can be carried out using La$_{2-x}$Sr$_x$CuO$_4$ as a reference.

Figure 8.5: On and off resonant photoemission spectra at the Cu $L_3$ absorption edge.

8.5 Character of the states near the Fermi level

Finally, we will study the character of the states closest to the Fermi level ($E_F$) in the electron doped Nd$_{2-x}$Ce$_x$CuO$_{4-\delta}$ system. Figure 8.5 shows the on- and off-resonant photoemission spectrum of Nd$_{1.85}$Ce$_{0.15}$CuO$_{4-\delta}$ in the vicinity of the top
of the valence band and the near $E_F$ region. As expected, the on-resonant intensity is enhanced as compared to the off-resonant one. However, the enhancement is substantially smaller than that for the hole doped cuprates, as one can clearly see from figure 8.5, which also includes the on- and off-resonant data for $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$. Since at the $L_3$ resonance the Cu $3d^8$ spectral weight is being measured, the enhancements for the near $E_F$ states basically indicate the amount of $3d^8$ character that is mixed into these states. For the undoped cuprates, cluster calculations have shown that the top of the valence band consists of Zhang-Rice singletshavingmainlya$3d^9L$ character, and also about 8% $3d^8$ admixture due to the direct hybridization between these two local configurations $[296–298]$. Subsequent RESPES studies $[280, 299]$ have confirmed this picture. Also RESPES experiments on the hole doped cuprates have shown that the top of the valence band as well as the near $E_F$ intensity are of $3d^8L$ Zhang-Rice singlet nature $[282]$. The much smaller resonant enhancement factor for the near $E_F$ intensity in the $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4–\delta$ implies a much smaller admixture of the $3d^8$ states, indicating that these near $E_F$ states do not have a direct hybridization with the $3d^8$. We therefore conclude that these states are not of local $3d^9L$ character, and we infer that they are in fact doublet $3d^9$ final states that can be reached by the photoemission process starting from a $3d^{10}$ singlet initial state. In this framework, the doublet $3d^9$ has to hybridize first with the $3d^9L$ on a neighboring cluster, before it can acquire the $3d^8$ character of the neighboring cluster on which the resonance process takes place. These data therefore support the scenario that the charge carriers in $\text{Nd}_{2–x}\text{Ce}_x\text{CuO}_4–\delta$ are electrons of singlet $3d^{10}$ like nature.

### 8.6 Conclusions

To conclude, we have measured that the CuO$_2$ planes in the $\text{Nd}_{2–x}\text{Ce}_x\text{CuO}_4–\delta$ high $T_c$ cuprates are electron doped. Using a reliable internal energy reference we have established that the chemical potential in $\text{La}_{2–x}\text{Sr}_x\text{CuO}_4$ and $\text{Nd}_{2–x}\text{Ce}_x\text{CuO}_4–\delta$ is not pinned in the middle of the gap of the insulating parent compounds. Instead, it is located in the vicinity of the top of the valence band for $\text{La}_{2–x}\text{Sr}_x\text{CuO}_4$, and near the bottom of the conduction band for $\text{Nd}_{2–x}\text{Ce}_x\text{CuO}_4–\delta$. One might say that it crosses the gap upon going from $p$- to $n$-type doping. Important is to note that the existence of phase separation $[262–265]$ in the doped materials could involve the pinning of the chemical potential inside the gap, but that our results indicate that this pinning could not bring the chemical potential very far away from the band edges, with perhaps a value of 0.3 eV as an upper limit judging from our experimental resolution and uncertainties in determining the onset of the optical gap. Resonance data suggest that the charge carriers in $\text{Nd}_{2–x}\text{Ce}_x\text{CuO}_4–\delta$ are electrons of Cu $3d^{10}$ character, while in $\text{La}_{2–x}\text{Sr}_x\text{CuO}_4$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ they are $3d^9L$ like holes. As far as symmetry is concerned, the charge carriers in both the electron and hole doped cuprates are singlet in nature.