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# Doping dependence of the chemical potential in cuprate high- $T_c$ superconductors I. La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub>

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### Abstract

A systematic study is performed of the doping dependence of the chemical potential  $\mu$  in La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> as a function of the Sr content, using a well-characterized series of pellets and thin films. The measured shift of the chemical potential, as deduced from the changes in the photoelectron spectra, is compared with present models for the doping behavior of  $\mu$  in high- $T_c$  materials. The results obtained can be best described assuming  $\mu$  shifts due to the doping of a rigid narrow band.

# 1. Introduction

One of the major questions related to the microscopic mechanism of superconductivity in the cuprate high- $T_{\rm c}$  materials concerns the problem of the proximity of the superconducting compounds to a correlation-induced metal-insulator transition. In clarifying such questions, photoelectron spectroscopy has played a large role. With this technique no density of states is found near the Fermi energy  $E_{\rm F}$ for the parent insulating materials, whereas for the doped metallic samples a clear Fermi level is present in the measurements [1,2], proving the fermionic character of the states near  $E_{\rm F}$ . Another important result obtained with photoelectron spectroscopy is that angle-resolved measurements indicate a Fermi surface that agrees well in size and shape with predictions of band-structure calculations [3-7]. This

agreement is remarkable, because these calculations in general have difficulty in adequately taking into account the correlations between the charge carriers. It is by now widely accepted that such correlations do play a large role in the high- $T_c$  materials, most prominently visible in the fact that the parent compounds are insulators whereas band-structure calculations predict them to be metals.

In this study, we will use X-ray photoelectron spectroscopy for studying the behavior of the chemical potential  $\mu$  as a function of doping in the high- $T_c$  cuprates, especially in the neighborhood of the metalinsulator transition. This behavior of  $\mu$  can be directly related to the low-energy electronic structure of these materials. Concerning the question of how to describe the behavior of  $\mu$  as a function of doping, two possible descriptions are given in the literature up to now, schematically depicted in Fig. 1.

The first model assumes that the states created near the Fermi level upon doping are induced by impuri-

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Fig. 1. Schematic picture of the doping dependence of the chemical potential  $\mu$  in the high- $T_c$  superconductors. (a) Insulating parent compound with  $\mu$  located in the middle of the chargetransfer gap. (b) Doped compound, according to the "impurity model". The position of  $\mu$  is constant and the gap is filled with doping induced states. (c) Doped compound, according to the "semiconductor model". The chemical potential  $\mu$  has moved to the top of the valence band (VB) or to the bottom of the conduction band (CB), depending on the type of doping. A possible transfer of spectral weight caused by the doping process has been neglected in the picture.

ties. In the undoped material the chemical potential lies somewhere in the middle of the charge-transfer gap. Doping of the materials is achieved by the addition of impurities. These impurities create states near  $\mu$  that are either directly related to the impurities or more indirectly generated by an impurity potential that pushes states from the valence band up to the Fermi level. The consequence of doping, i.e. the addition of impurities, thus is a filling of the gap with states. The chemical potential will be more or less constant, near the middle of the gap. The increase of the density of states near  $\mu$  for finite doping is caused by the increase of the impurity-induced density of states in the gap (Fig. 1(b)). The second model assigns the increase of density of states near  $E_{\rm F}$  to a shift of the chemical potential. Again, in the undoped case the chemical potential is situated near the middle of the gap. If the material is doped with holes, the chemical potential rapidly moves to the top of the valence band. At still higher doping,  $\mu$  shifts further into the valence band. The increase in density of states near  $\mu$ thus (at least partly) arises from a change in position

of the chemical potential, with possible extra contributions of changes in electronic structure [8]. The behavior of  $\mu$  according to this model is depicted in Fig. 1(c). In the following we will refer to these two models as the "impurity model" and "semiconductor model", respectively. The latter name is because of the similarity of the behavior of  $\mu$  in this model to doping of a simple semiconductor.

Experimentally, the doping dependence of the chemical potential in a material can be measured with photoelectron spectroscopy (PES) by determining the binding energies of all core levels and the valence band. In a photoelectron spectrum, the binding energies are measured with respect to the common Fermi level of the sample and electron analyzer. If the reference level  $\mu$  changes upon doping of the material, this becomes visible as a collective shift of *all* core levels and the valence band.

Compared to the large amount of PES data in the literature, only a few serious studies devoted to the doping behavior of  $\mu$  have appeared. The main evidence in favor of the "impurity model" was put forward by Allen et al. [9]. They compared the valence band spectra of undoped and optimally doped  $Nd_{2-x}Ce_{x}CuO_{4}$  and  $La_{2-x}Sr_{x}CuO_{4}$  and found that the position of the Fermi level with respect to (the maximum of ) the valence band was essentially constant, and approximately in the middle of the gap. The data of Allen strongly conflict with the "semiconductor model", because there one would expect that for electron- or hole-doped samples, the chemical potential is at the bottom of the conduction band or at the top of the valence band, respectively (Fig. 1 (c)). Thus, the difference in position of  $\mu$  should be of the size of the gap (i.e. 1.5-2 eV [10-12]), which is not found in the measurements [9]. Recent measurements by the same group on higher-quality  $Nd_{2-x}Ce_{x}CuO_{4}$  samples covering the whole doping range confirm this result [7]. The chemical potential is constant as a function of doping, and the density of states at  $\mu$  increases with doping by an apparent filling of the gap with states.

On the other hand, the "semiconductor model" is supported by measurements of van Veenendaal et al. [13] in the Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>1-x</sub>Y<sub>x</sub>Cu<sub>2</sub>O<sub>8+ $\delta$ </sub> system. Here, the transition from insulator to superconductor is made by varying the Y content from 1 to 0. According to van Veenendaal et al.'s data, this transition is accompanied with a rather strong shift in chemical potential [13]. They find the same behavior in the core level positions as well as in X-ray and UV-light excited valence band spectra, which adds confidence to their results. In the metallic regime, the changes in chemical potential are small, and can be described with the doping of a rigid narrow band [13]. Such a small shift in the metallic regime was also found by Shen et al. who varied the doping in  $Bi_2Sr_2CaCu_2O_{8+\delta}$ by changing the oxygen content [14]. Prior to the study of van Veenendaal et al., at least two other groups have studied the Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>1-x</sub>Y<sub>x</sub>Cu<sub>2</sub>O<sub>8+ $\delta$ </sub> system with photoelectron spectroscopy. Itti et al. [15] measured all core-level positions over the whole doping range and essentially found the same results as van Veenendaal et al. [16]. However, they do not consider the possibility of changes in chemical potential and instead try to explain their data fully in terms of chemical shifts. Kusunoki et al. [17] limited themselves to the valence bands, from which they could defer only a small shift in chemical potential over the total Y doping range of x=0-0.6.

In this paper we present the results of a photoelectron study of  $La_{2-x}Sr_xCuO_4$  pellets and thin films, in the Sr doping range x=0-0.25. This range covers both the parent undoped insulating material and the doped metallic compounds. The choice for the  $La_{2-x}Sr_xCuO_4$  system was stimulated by the facts that it has a relatively simple crystal structure with only one CuO<sub>2</sub> plane per unit cell, and that it is hole-doped with the doping level rather well defined by the Sr content. Note that the difference between the data on  $Nd_{2-x}Ce_xCuO_4$  and  $Bi_2Sr_2CaCu_2O_{8+\delta}$  in principle could be caused by the unusual electron doping in the former compound.

The structure of the rest of the article is as follows. First we will describe the preparation and characterization of the samples used in this study, especially of the thin films. Then the XPS core level spectra will be quite extensively discussed, since not many photoelectron spectra of the  $La_{2-x}Sr_xCuO_4$  system have been published in the literature until now. Finally the results of the behavior of the chemical potential, as deduced from the shift in the photoelectron spectra, are presented and discussed.

## 2. Preparation and characterization

Starting materials for the preparation of the ceramic pellets are La<sub>2</sub>O<sub>3</sub>, CuO and SrCO<sub>3</sub> powders. The purity of the powders is better than 99.99%, except for SrCO<sub>3</sub> which is 99.5% pure with main contaminants Ca and Ba. The procedure followed in making the pellets is similar to that of Blank et al. [18,19] for the preparation of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> and briefly is as follows.

Carefully weighted amounts of the oxides are dissolved in nitric acid and mixed with citric acid monohydrate. After the addition of ammonium hydroxide to make the solution pH neutral (pH value approximately 6.8), it is heated to 300°C until a solidstate reaction occurs where a very fine powder is formed. The advantage of this technique compared with conventional mixing and grinding of the powders is a very homogeneous distribution of the elements in the final powder since the cations were mixed as ions in a solution. After the solid-state reaction, the powder is ground and annealed for 9 h at 920°C in flowing oxygen or air. Subsequently, the powder is reground and pressed under 15 tons into pellets with a diameter of 15 mm. The final preparation step consists of sintering at 1150°C in air for 5 h and an extra postanneal at 750°C in 1 bar oxygen during 11 h. In all cases, the cooling rate of the furnace is set to 1.5°C/min.

With this procedure, several samples of  $La_{2-x}Sr_xCuO_4$  were made with steps in Sr doping of 0.05, covering the total range x=0-0.25. It was not possible to prepare a pellet with x=0.30, since a suspension is formed in the acid solution after adding the ammonium hydroxide. This resulted in inhomogeneous samples.

After completion of all characterization and XPS measurements on this series of samples, the pellets were used as target in the laser ablation chamber for the in-situ growth of thin films. Since the pioneering work of Moorjani et al. [20], very little work has been published about the growth of  $La_{2-x}Sr_xCuO_4$  thin films with laser ablation. Only recently two papers have appeared on this subject. Yi et al. ablated from x=0.15 material and found a maximum  $T_c$  of 22 K for films grown at ~825°C in a 250 mTorr oxygen atmosphere [21]. Chern et al. deposited  $La_{2-x}Sr_xCuO_4$  films using a combination of pulsed

molecular oxygen and a continuous source of atomic oxygen, with a background pressure as low as 1 mTorr. For x=0.15 material grown at 700°C, they find a maximum  $T_c$  of 15 K [22]. The earliest in-situ growth of high-quality  $La_{2-x}Sr_xCuO_4$  films was done by Suzuki using sputtering techniques [23]. His films were well oriented, but also had lower critical temperatures with a maximum of 23 K. In a later study of the same author this was improved to 29 K [24]. The highest  $T_c$  so far of  $La_{2-x}Sr_xCuO_4$  thin films is approximately 35 K, obtained by Kao et al. for 8000 Å thick films [25]. According to all publications, the optimal growth conditions for in-situ growth of  $La_{2-x}Sr_{x}CuO_{4}$  thin films are similar to those of  $YBa_2Cu_3O_{7-\delta}$ . Thus, for the preparation of  $La_{2-x}Sr_{x}CuO_{4}$  films in our laser-ablation setup we have used the parameters that were optimal for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> thin-film growth. The temperature of the SrTiO<sub>3</sub> substrate during growth is 750°C and the oxygen pressure is 750 mTorr. Assuming an equal ablation rate for  $YBa_2Cu_3O_{7-\delta}$  and  $La_{2-x}Sr_xCuO_4$ , we estimate that the films are approximately 250 nm thick. After ablation of the film, the chamber is filled with 800 Torr oxygen and subsequently the sample is cooled in approximately 30 min in two steps to below 200°C.

The characterization of the pellets and thin films started with X-ray diffraction for determination of the structure and cell parameters, and detection of possible secondary phases in the samples. Temperature-dependent resistance measurements revealed the (super-) conducting properties and X-ray photoelectron spectroscopy (XPS) and electron probe micro analysis (EPMA) are used for compositional analysis. The results of this characterization will be presented and discussed here; the use of XPS for determination of the surface quality and shift in chemical potential versus doping is described in Section 3.

A typical result of an X-ray diffraction measurement of pellets and thin films is given in Fig. 2. The scans given in the figure are for samples with x=0.15and are typical for all samples. All peaks in the spectrum of the pellet can be assigned to the superconductor, and the majority of them are labeled in Fig. 2(a) with their Miller indices (*hkl*). For other doping levels, sometimes a faint reflection was found at  $2\theta=32.90^\circ$ , visible as a small shoulder on the (110) peak. This tentatively was identified as the (020)



Fig. 2. X-ray diffraction scans of a  $La_{2-x}Sr_xCuO_4$  pellet (a) and a  $La_{2-x}Sr_xCuO_4$  thin film (b) made by laser ablation from this pellet. The doping level of the samples is x=0.15; the scans given here are typical for all doping levels. Cu K $\alpha$  radiation with a Ni filter is used as radiation source. All peaks in the scans can be assigned to the superconductor or, in the case of the film, to the substrate. Within the sensitivity of the measurements, no secondary phases are detected. The majority of the peaks are labeled with their corresponding (*hkl*) Miller indices; substrate peaks are marked with S(*h*00) and X-ray satellites with an asterisk. Note the logarithmic intensity scale for the film (b).

diffraction peak [26] but also has been reported as due to the secondary phase material  $La_{2-y}Sr_yCu_2O_5$ [27]. As far as can be judged from the diffraction scans of the films, also these are free of secondary phases. The presence of sharp (00*l*) peaks indicates well-defined *c*-axis oriented material. Some films with non-zero doping have a small amount of *a*-axis grains. One film with x=0.15, grown under slightly different conditions, had deteriorated surface and transport properties and also had a small peak in the diffraction scan at  $2\theta = 44.20^\circ$ , probably from not fully oxidized copper. The results obtained on this sample are excluded from the present study.

Fig. 3 gives the room-temperature lattice parame-



Fig. 3. Room-temperature lattice constants a, b (a) and c (b) of La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> samples as a function of Sr doping x. Values for pellets and films are denoted by filled squares and circles, respectively. For comparison, values determined by Tagaki et al. are given as well (crosses) [28]. The lattice parameters of the pellets agree very well with these data. The films have significantly smaller *c*-axes, that only slightly increase after extra oxygen anneals (open circles). Note that for the orthorhombic samples, doping level x < 0.10, normalized lattice parameters  $a/\sqrt{2}$ ,  $b/\sqrt{2}$  and c are shown.

ters deduced from the  $\theta$ -2 $\theta$  scans, as a function of the Sr content x for both pellets and films. For comparison, also the values determined by Tagaki et al. are given [28]. Clearly, the lattice parameters of our pellets are in good agreement with these values. For the films, only the c-axis value can be determined from the scans. Similar to the trend seen in the data for the pellets, the c-axis increases for higher doping levels, but compared to the pellets the effect is significantly smaller. This cannot be caused by an oxygen deficiency of the films, since extra anneals of the films with x=0.15 and x=0.20 in 1 bar oxygen at 450°C and 900°C, respectively, hardly gave rise to larger values (open circles in Fig. 3(b)). The shorter c-axis is probably due to strain in the films. The in-plane lattice parameters of the films are  $\sim 3\%$  smaller than those of the SrTiO<sub>3</sub> substrates. The resulting in-plane strain causes a compressive strain in the perpendicular c-axis direction, resulting in a contraction of the c-axis. A similar relation between in-plane strain and c-axis length was found in multilayers of  $Nd_{1.83}Ce_{0.17}CuO_x$  and  $YBa_2Cu_3O_{7-\delta}$  [29].

In Fig. 4 we show the resistance curves of the doped samples, again for pellets and films. The curves were measured with a standard four-point measurement setup. Contact was made to the samples by pressing four gold-plated brass pins onto the samples. Since



Fig. 4. Temperature-dependent resistance of  $La_{2-x}Sr_xCuO_4$  pellets (a) and thin films (b) for different Sr dopings x. The films are prepared by laser ablation, where the pellets were used as target. Due to different contact geometries during the resistance measurements, absolute values of the resistance cannot be well compared with each other. Still, the observed decrease in resistance for increased Sr doping is significant. Note the constant onset temperature of the superconducting phase transition in the pellets and the similarly constant (but reduced)  $T_c$  values of the films.

the contact geometry was different for each sample, the absolute values of the resistance given in Fig. 4 cannot be compared with each other. However, the trend (visible for pellets and films) that the resistance decreases for higher Sr doping is still significant. The zero-doped samples all showed a semiconducting behavior of the resistance, without any sign of superconductivity above 4 K.

A phase diagram of the dependence of  $T_c$  on the Sr doping is given in Fig. 5. Shown are the values of  $T_{c,0}$ , defined as the temperature where the resistance is 10% of the value at the onset. Data of Tagaki et al. [28] are again included for comparison. The solid line in the figure is a guide to the eye through these data. For



Fig. 5. Dependence of the superconducting phase transition temperature  $T_{c,0}$  of  $La_{2-x}Sr_xCuO_4$  on the Sr doping x, for pellets (squares) and thin films (circles). Results of Tagaki et al. (crosses) are included for comparison [28]. The solid curve is a guide to the eye through these data. The dashed line is the value of  $T_{c,onset}$  of our pellets, which is remarkably constant. Open circles give the  $T_c$ 's of films after an extra anneal in oxygen.

the pellets the values of  $T_{c,0}$  closely follow this line. However, the onset of superconductivity in the R(T) curves is almost constant (dashed line in Fig. 5). A similar behavior of the onset temperature was found in magnetization data in a later study of Tagaki et al. on high-quality samples in the overdoped region (x>0.15) [30].

The  $T_{\rm c}$  values of the films are rather low and almost independent of Sr doping. The shape of the resistance curve near  $T_c$  is quite comparable for all films: the superconducting onset is near 16 K and the total width of the transition is approximately 5 K (Fig. 4(b)). As already mentioned above, all data in the literature to date show reduced  $T_c$  values for insitu grown thin films, ranging from 15 to 35 K [22,23,25]. Kao et al. have studied the dependence of  $T_c$  on the thickness of the films and found that on (100) SrTiO<sub>3</sub> substrates the  $T_c$  increased from approximately 20 to well above 30 K if the film thickness was increased from 2000 to 8000 Å [25]. They suggest that the low  $T_c$ 's for the thinner films are caused by strain. Indeed, combining known values of  $dT_c/dp$ , the compressibility of the lattice, and the lattice mismatch between substrate and film, we find a lowering of the critical temperature with at least 10 K, not even taking into account the anisotropy in  $dT_c/$ dp, as e.g. found in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> [31]. Additional evidence that strain indeed plays an important role lies in the fact that (110)/(103) oriented films have higher  $T_c$ 's than films with (001) orientation [25].

In the former case, the planes of the superconducting material are not parallel to the substrate so that the strain in these planes is reduced. Another reason for the lower critical temperatures was proposed by Suzuki, who assigned it to inhomogeneity of the Sr distribution [24]. Such an inhomogeneity always exists to a certain extent in a solid solution and may be intrinsic to single-crystalline  $La_{2-x}Sr_xCuO_4$  – also early bulk single crystals had lower  $T_c$ 's [32]. In addition, the double peak structure in the Sr core-level spectra (see Fig. 10) seems to indicate that strontium occupies two chemically different sites. Finally, the lower  $T_{\rm c}$  values could be related to an oxygen deficiency of the films. To test for this possibility, we have given the samples with x=0.15 and 0.20 an extra anneal in pure oxygen for 12 h at 500 and 900°C, respectively. After these anneals, the  $T_c$  was substantially higher, but still full superconductivity was not obtained above 20 K. Since the anneals are expected to be very effective in removing any oxygen deficiency, we do not think it plays a major role in causing the lower  $T_{\rm c}$ 's.

The composition of the samples is checked with XPS and EPMA. For the pellets, EPMA showed that the cation stoichiometry was within 5% equal to the starting composition in the preparation. With a slightly larger inaccuracy this is also true for the La/Cu ratio in the thin films. It is difficult to estimate the Sr content of the films with EPMA, since with the present thickness of the films (250 nm) also part of the SrTiO<sub>3</sub> substrate is probed.

Very similar results were obtained in XPS. Using the data in Figs. 8 and 9 (further discussed in the next Section) and calculated values for the photoelectron cross-section  $\sigma$  [33], furthermore assuming a homogeneous distribution of the elements in the samples, the composition of the pellets and the films is within the  $\sim 15\%$  accuracy of such an analysis equal to the desired ratios. The La and Sr intensities both follow the doping trend very well. In the case of the films, the assumption of a random distribution of the elements is not justified given the layered nature of the material and the c-axis orientation of the films. Analogous to an earlier study [34], we will therefore discuss the influence of the layeredness of the  $La_{2-r}Sr_{r}CuO_{4}$  material on the intensities in the XPS spectra. There are three possibilities for forming an ideal surface of c-axis oriented La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> depicted as model T1, T2, and T3 in Fig. 6. Since the



Fig. 6. Models for forming an ideal surface of c-axis oriented  $La_{2-x}Sr_xCuO_4$ . In (a) the three possible layer sequences T1-T3 are given (the first row is the top layer) for the  $La_{2-x}Sr_xCuO_4$  crystal structure as schematically depicted in (b) (from Hass [62]).

model assuming a random distribution of the elements describes the relative intensities of the photoelectron peaks very well, it is directly clear that termination T2 fits the data best. For model T1 or T3 the relative La intensity would be too low or too high, respectively. Also this intensity would further decrease or increase for larger exit angles of the photoelectrons, whereas in our measurements (not shown here) the relative intensities hardly show any change for varying exit angles. Of course, it is possible that in reality a combination of several terminations is present. For example, if the surface has equal amounts of terminations T1 and T3, this will give relative XPS intensities very similar to those of model T2.

#### 3. Photoelectron spectra

The pellets are attached with Ag paint [35] to stainless-steel sample holders, suited for transportation in our ultra-high vacuum (UHV) system. The as-prepared samples have highly contaminated surfaces, that are cleaned by scraping with a diamond file. This is done in the sample preparation chamber attached to the UHV transport chamber. The background pressure in this chamber during scraping is below  $2 \times 10^{-8}$  mbar. Several cycles of scraping – in total removing several hundred µm of material - are needed to obtain clean surfaces, as judged by a low C 1s peak and a small high binding-energy shoulder in the O Is spectrum. The sample with Sr doping x=0.05 was very hard and could not be cleaned sufficiently by scraping. Therefore, data of this sample have been omitted in this study. Apart from scraping,

we have also tried to clean the surfaces with ion etching. This always resulted in damage of the surfaces, almost independent of the ions used (Ar, Ne, O). Annealing the samples in the MBE system in an oxygen or ozone atmosphere is very effective in removing carbon contaminations but produces unwanted oxides at the surface. Thus to us, scraping seems the best method for preparation of clean surfaces of ceramic  $La_{2-x}Sr_xCuO_4$  pellets.

The in-situ growth and transport of the  $La_{2-x}Sr_xCuO_4$  thin films makes any further surface preparation of the films superfluous. Immediately after growth in the laser-ablation chamber and cool down to below 200°C, the samples are removed from the heater and the ablation chamber is quickly pumped down to  $10^{-5}$  mbar. Then, the films are transported via the UHV transfer chamber to the analysis chamber. The temperature at which the sample is removed from the heater block is critical. If sample transport is started at too high or too low temperatures, the samples are oxygen deficient or have contaminated surfaces, respectively.

Within half an hour after the preparation of the pellets and the films a complete set of photoelectron spectra is recorded, consisting of the strongest corelevel peak of each element and the valence band. Then, this series of spectra is repeated for approximately 7 h in order to obtain sufficient statistics. The pressure of the system with the X-ray source operating is in the low  $10^{-10}$  mbar region; the base pressure is an order of magnitude lower.

During the whole experiment no change was visible in any of the spectra, except for the O 1s spectrum. Due to the exposure of the surface to X-rays, possibly in combination with the low vacuum pressure, the main peak in this spectrum gradually shifted to higher binding energies (Fig. 7). Since this is already visible in spectra taken 30 min after the first spectrum, all XPS measurements were started with the O 1s line. Only these initial spectra are given in Figs. 8 and 9 and only these are used for the determination of shifts in the peak position. From the shape of the O1s spectrum it is clear that the main O Is line consists of two components which probably originate from the two inequivalent oxygen sites in the crystal structure (Fig. 6(b)). Apparently, due to the radiation, the low binding-energy component decreases in intensity or shifts to higher binding ener-



Fig. 7. O 1s core level of a  $La_{2-x}Sr_xCuO_4$  thin film (x=0.15) as a function of X-ray exposure time. Solid line: 2 min, and dashed line: 420 min. The shift of the main peak is 0.15 eV. The decrease of the high binding-energy shoulder with time points towards X-ray stimulated desorption of surface contaminants.

gies causing an overall shift of the main oxygen line. Similar shifts of the main O 1s line as a function of time were also found by Fowler et al. in their study of cleaved YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> single crystals [36]. In addition, they found an increase of the intensity of the high binding-energy shoulder due to the high background pressure in their system ( $\approx 1 \times 10^{-9}$  Torr). In our case, this shoulder *decreased* in intensity, probably due to X-ray stimulated desorption of surface contaminants. Also the small C 1s peak at 284 eV (Figs. 8 and 9) decreased in intensity after prolonged exposure of the surface to X-rays.

Other evidence for the influence of the X-ray radiation of the XPS source was found in room-temperature work-function measurements using our Kelvin probe setup. For the as-prepared pellets and films we on average find work function values of 4.7 and 5.6 eV, respectively. After 3 min exposure to X-ray radiation from the XPS source, operated at a quarter of the normal power, the work function had changed by  $\sim 30$  meV. At the end of the whole series of XPS measurements, the total change in work function typically was 50 meV. This indicates that most of the damage occurs in the early time of the X-ray exposure and then very rapidly saturates. The work function of the pellets increased, whereas that of the films always decreased.

An overview of all core-level and valence-band spectra of pellets and films is given in Figs. 8 and 9, respectively. For clarity, only the spectra for x=0, 0.10, and 0.25 are shown and offsets are given to

spectra of samples with non-zero doping. The spectra are measured using Mg K $\alpha$  radiation, and the pass energy of the hemispherical analyzer is set to 20 eV, giving an instrumental broadening of 0.4 eV. The energy scale of the spectrometer is calibrated using a freshly evaporated Cu film, and published values of the binding energies of Cu core levels [37].

## 3.1. La 3d<sub>5/2</sub> spectrum

The La  $3d_{5/2}$  spectrum consists of a double peak. For the undoped pellet, the main peak lies at 833.4 eV and a satellite is located at 4.40 eV higher binding energy. The splitting between the two features is independent of Sr doping. The separations found here are comparable with those in the La  $3d_{5/2}$  spectra of La<sub>2</sub>O<sub>3</sub> [38] and LaMO<sub>3</sub> (M=Fe, Co, Al) [39]. The much smaller value reported by Viswanathan for La<sub>2</sub>CuO<sub>4</sub> (3.1 eV [40]) and the larger value found in LaBaCuO by Steiner et al. (5.3 eV [41]) are probably caused by the low quality of their samples.

Fuggle et al. have shown that the core-level line shapes of, among others, the oxides of the early lanthanides can be explained as being composed of a well screened peak at low binding energy and a poorly screened peak at higher binding energy [42]. Screening arises from the coupling of (partially) empty 4f levels with the delocalized occupied O 2p states. For  $La_2O_3$ , the initially empty 4f<sup>1</sup> screening level is lowered in the final state of the photoelectron process to below the Fermi level. As a consequence, the total energy of the final state can be lowered if an electron is transferred from the occupied oxygen states to this 4f<sup>1</sup> level [43]. In general, the role played by such empty screening levels strongly depends on the initial position above  $E_{\rm F}$  and the coupling to the occupied levels [42]. The latter is directly reflected in the amplitude of the well screened peak. The former can be measured with inverse photoelectron spectroscopy (IPES). Data on  $La_{2-x}Sr_xCuO_4$ , e.g. those published by Gao et al. [44] and Riesterer et al. [45], indeed show unoccupied La states close to  $E_{\rm F}$ .

In comparing the La  $3d_{5/2}$  spectra for films and pellets, several small differences become visible. Both the relative intensity and the splitting of the two peaks in the spectra of the pellets greatly resemble those of La<sub>2</sub>O<sub>3</sub>. For the films, the splitting is 0.2 eV reduced and the intensity of the unscreened peak is somewhat



Fig. 8. Core-level and valence-band photoelectron spectra of  $La_{2-x}Sr_xCuO_4$  pellets as a function of Sr doping x. For clarity, the spectra for non-zero doping have been given an offset. The carbon spectra have been taken with lower resolution for higher sensitivity. Further discussion of the spectra is given in the text.

larger. Following the above explanation of Fuggle et al., this could reflect a smaller coupling of the 4f levels to the valence band. Most likely, the smaller coupling is due to oxygen defects, or an elongation of the La-O bond in the film because of the lattice mismatch between the SrTiO<sub>3</sub> substrate and the film. Also Sr disorder (see below) might play a role.

# 3.2. Cu 2p<sub>3/2</sub> spectrum

Just as in all other cuprate superconductors, the Cu  $2p_{3/2}$  spectrum closely resembles that of CuO, consisting of a main peak with  $|\underline{2p}_{3/2} \operatorname{3d}^{10}\underline{L}\rangle$  character and a  $|\underline{2p}_{3/2} \operatorname{3d}^{9}\underline{L}\rangle$  satellite peak. Here L de-

notes a hole on the neighboring ligand oxygen of copper. The relative intensity of the satellite and main peak does not change as a function of doping and is equal to ~0.36, both for pellets and films. Only the pellet with x=0.25 has a somewhat lower satellite intensity, 0.31 of the main line. This can be due to a lower oxygen content, since samples with doping levels x>0.15 tend to be oxygen deficient [46,47].

Accurate determination of the peak position – and shifts therein – is difficult, as the Cu  $2p_{3/2}$  spectrum is rather broad. Therefore, the leading edge of the spectrum will be taken as reference for determining shifts in the peak position as a function of doping. This will give the same results, assuming that the



Fig. 9. Core-level and valence-band photoelectron spectra of  $La_{2-x}Sr_xCuO_4$  thin films as a function of Sr doping x. For clarity, the spectra for non-zero doping have been given an offset. The carbon spectra have been taken with lower resolution for higher sensitivity. Further discussion of the spectra is given in the text.

spectra do not change shape as a function of doping. Inspection of Figs. 8 and 9 shows that this is indeed the case. Note that van Veenendaal et al. found a significant narrowing of the Cu  $2p_{3/2}$  main line with increased Y doping in Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>1-x</sub>Y<sub>x</sub>Cu<sub>2</sub>O<sub>8+ $\delta$ </sub>.

## 3.3. C 1s spectrum

The amount of carbon contamination of the pellets and the films is low. The spectra have been recorded with a higher pass energy of the electron analyzer (50 eV, total instrumental resolution  $\sim 1 \text{ eV}$ ), for higher sensitivity. Both pellets and films show a peak at 284 eV, the binding energy for carbon and carbon hydrides, and in addition the pellets have a peak around 289 eV, the binding energy of carbon oxides. The pellets have been scraped until this residual level of contamination was found. Spectra for x=0.15 and x=0.20 (not given in Fig. 8) have a lower intensity at 289 eV, but still it is not negligible [48]. This contamination is either due to impurity material between the grains of the pellets, or a residual amount of carbonate used as one of the starting materials in the preparation. The surface of the films is probably contaminated during the cool down after preparation or during the UHV transport of the sample. The increase in intensity below 282 eV for the doped sam-

ples is the high binding energy tail of the Sr  $3p_{1/2}$  peak at 278 eV.

#### 3.4. O Is spectrum

The O 1s spectrum is recorded using Al Ka radiation, because with the use of Mg Ka radiation the O 1s line is on the background of La MNN Auger peaks. The O 1s spectrum is dominated by a large peak at 528.7 eV (position for x=0) and a shoulder around 531 eV. Compared to the main peak, the shoulder is lowest for the undoped samples. For the pellets, there is a clear correlation between the carbon peak at 289 eV and the intensity of the high binding-energy shoulder in the O1s spectrum, but certainly not the entire shoulder originates from carbonates (see e.g. the spectra of the films). At present, no "shoulderfree" Ols spectrum has been published for the  $La_{2-x}Sr_{x}CuO_{4}$  compounds. Probably the best results have been obtained by Takahashi et al. in a combined XPS/UPS study of single crystals [49]. In their spectrum for undoped samples only an asymmetric tailing of the main line to higher binding energies is visible, comparable to our spectrum of the undoped film. For x=0.08, they also find a shoulder in the spectra, which they assign to deterioration of the surface. This deterioration occurred very rapidly at room temperature. As already discussed above, we do not find an increase of the shoulder in our spectra over the 8 h duration of our measurements - at most a small decrease is found (Fig. 7), probably due to Xray stimulated desorption of contaminants from the surface. Angle-resolved measurements confirm that the shoulder in the O Is spectrum is at least partly due to surface contamination.

## 3.5. Valence band

The valence-band spectra of the samples are broad and almost featureless, due to the low resolution of the measurements. For the same reason it is nearly impossible to detect the very small increase of the density of states near  $E_F$  with doping. In the figures, the spectra are scaled to the total intensity in the valence band after background subtraction.

In spite of the low resolution, a clear difference is visible between the spectra of the pellets and the films. All films give rectangularly shaped spectra, whereas for the pellets the valence band is more rounded. For the pellets, the spectra greatly resemble those of others [10,41,50]. Band-structure calculations indicate that the low binding-energy part of the valence band has more Cu weight and that the O 2p contribution is at higher binding energies [51,52]. The films seem to have extra intensity at around 2 and 5 eV, that thus originates from Cu and O, respectively. Especially, the increase of intensity at low binding energies is strong, indicating a significant difference in Cu 3d states between pellets and films. A possible explanation of this difference can be the presence of impurities in the pellets, e.g. oxygen deficiency at the surface, since it is known that impurities cause a smearing of the features in the valence band of the host material.

## 3.6. Sr 3d spectrum

The most puzzling core-level spectrum is the Sr 3d spectrum. With doping, La ions are replaced by Sr, and since there is only one crystallographic site for La in the  $La_{2-x}Sr_{x}CuO_{4}$  lattice (Fig. 6(b)) one would expect a single doublet in the Sr 3d spectrum. Instead, we find two doublets in this spectrum, both for pellets and thin films. To our best knowledge, only one spectrum of Sr in  $La_{2-x}Sr_xCuO_4$  is published in the literature, in an early study of Steiner et al. [53]. They also found double peaks in the Sr 3d spectrum, which might be due to the low quality of their material. Other references for Sr spectra come from the Bi cuprate superconductors [54,55], SrO [56,57] and SrTiO<sub>3</sub> [58]. For the superconductors always a second doublet is found, with an intensity depending on the quality of the samples and the cleanliness of the surfaces. The best samples seem to have a single doublet in their Sr 3d spectrum. However, the intensity ratio of the  $3d_{3/2}$  and  $3d_{5/2}$  peak in such spectra always exceeds 0.67, the value expected from the multiplicity of the two levels and which is also found in theoretical calculations of the relative cross-sections [33]. Experimentally, this ratio was found by van Doveren and Verhoeven in spectra of SrO [56] and in SrTiO<sub>3</sub> by Nagarkar et al. [58].

In Fig. 10 we give a compilation of Sr 3d spectra of several Sr containing conducting oxides. The lower spectrum is that of Sr in SrTiO<sub>3</sub> which clearly consists of a single doublet, and is shifted by -1.6 eV in order to put the chemical potential of the sample in



Fig. 10. Sr 3d core level spectrum of several Sr containing oxides, recorded with a Mg Ka radiation source. From top to bottom (symbols):  $La_{2-x}Sr_xCuO_4$  film,  $La_{2-x}Sr_xCuO_4$  pellet, Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8+8</sub> single crystal, and SrTiO<sub>3</sub> single crystal. The curves have been given an offset for clarity; each curve is scaled so as to give equal intensity of the low binding-energy component in the spectrum. The solid lines are fits to the spectra, assuming the presence of two chemically shifted doublets. The intensity of the high binding-energy doublet is (from to bottom) 1.0, 0.55, 0.12 and 0 times that of the low binding-energy one.

the middle of the gap [34]. Assuming Gaussian line shapes, the spectrum can be well fitted using an energy splitting in the doublet of 1.75 eV and a relative intensity of 0.70 (solid line in the figure). The second curve is of a single crystal of  $Bi_2Sr_2CaCu_2O_{8+\delta}$ , in-situ cleaved in the spectrometer chamber. This spectrum is entirely typical for the best spectra obtained for this material, e.g. those of Hill et al. and Hillebrecht et al. [54,55]. The top two curves are for the  $La_{2-x}Sr_xCuO_4$  thin films and pellets (x=0.15). Here, the background in the spectrum (probably originating from an energy-loss tail of the La 4d core level at 103 eV) was removed by subtraction of the spectrum for zero doping (Figs. 8 and 9). For SrTiO<sub>3</sub> and  $Bi_2Sr_2CaCu_2O_{8+\delta}$ , the background has been removed using the Shirley method [59]. If we take the energy splitting and intensity ratio from the Sr 3d spectrum of SrTiO<sub>3</sub> as reference, those of the three superconducting cuprates can be fitted with two doublets (solid lines in Fig. 10). The low binding energy doublet lies at 132.2 eV, except for the  $La_{2-x}Sr_xCuO_4$ thin film, where it is 0.5 eV higher; the high bindingenergy doublet has its 3d<sub>5/2</sub> peak at 134.1 eV. The relative intensity of the high binding-energy doublet is 0.12, 0.55, and 1.0 times the intensity of the low binding-energy peaks for  $Bi_2Sr_2CaCu_2O_{8+\delta}$   $La_{2-x}Sr_xCuO_4$  pellets and films, respectively. Note that the shape of the spectra for the  $La_{2-x}Sr_xCuO_4$  samples does not depend on the amount of Sr doping (Figs. 8 and 9).

An explanation of the double peak structure in the Sr 3d spectra is difficult. It is known that in the  $Bi_2Sr_2CaCu_2O_{8+\delta}$  material Sr-Ca disorder easily occurs. The second doublet in this case thus could be due to Sr located at Ca sites in the lattice. Alternatively, since the relative intensity of the second doublet is so low, the spectrum may be viewed as a single doublet with non-Gaussian line shapes (tail to higher binding energies). For the  $La_{2-x}Sr_xCuO_4$  samples, the intensity is too strong for such an explanation. In their study of  $La_{2-x}Sr_xCuO_4$  pellets, Steiner et al. assign the second doublet to oxygen vacancies [53]. Since the intensity of this peak increases for larger exit angles of the photoelectrons, they assume that the density of the vacancies increases near the surface. For our samples, we only find a very small increase of the high binding-energy part of the Sr 3d spectrum if the exit angle is increased. A pure surface phase, e.g. SrO, may thus be excluded. As already discussed in relation to the structural and transport properties of the samples (Section 2), we have tested for the possible presence of O vacancies by in-situ annealing the x=0.15 film at 450°C in oxygen. This hardly produced any difference in the Sr 3d spectrum. Therefore, a more probable origin of the double peak for the  $La_{2-x}Sr_{x}CuO_{4}$  samples is inhomogeneity in the Sr doping. This inhomogeneity should occur on very small length scales since the X-ray diffraction measurements do not give any indication of such an inhomogeneity [30]. XPS, on the other hand, is sensitive to the local chemical environment of the atoms. Note that due to the small coherence length, also the superconducting properties are sensitive to local changes in crystal or electronic structure. Further investigations, preferably using other analysis techniques that are sensitive to the local chemical environment of the ions, are certainly needed to clarify this point.

#### 4. Doping dependence of the chemical potential

The aim of the present XPS study was to find systematic shifts in the spectra as a function of Sr doping, signature of a doping dependence of the chemical potential. Fig. 11 shows the measured shifts for the pellets and the films, relative to the samples with x=0.15. For the determination of the shifts, we have taken the peak position in the O 1s and Sr 3d spectra. In the case of the Cu 2p, La 3d, and valence-band spectra, which are characterized by broad peaks, instead the leading edge of the spectrum has been used. Even though differences exist between the two sets of data in Fig. 11, the general trend is similar. In both cases, a significant shift is found if the doping is varied. Furthermore, this shift is smooth over the whole doping range. An important difference with the data of van Veenendaal et al. obtained on  $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$ , is that no large shift is found at the transition from the insulating, undoped (x=0)material to the (super)conducting, doped ( $x \ge 0.10$ ) samples. In this context it is important to mention that we have checked for the possible effect of charging during the measurements. In all cases, also for the undoped samples, we do not find a measurable change of the peak positions if the intensity of the X-ray source is varied.

The scatter of the core-level positions of the different elements around the average (solid line in Fig. 11), is caused by chemical effects, such as changes in Madelung potential or effective charge upon doping. As an example of the latter, one would expect that the LaO layers become more negative with Sr doping, since the La<sup>3+</sup> ions are replaced by  $Sr^{2+}$ . This will



Fig. 11. Core-level and valence-band positions of  $La_{2-x}Sr_xCuO_4$ pellets (a) and thin films (b) as a function of Sr content x. The positions are given relative to those of the x=0.15 samples. The dashed lines connect the positions of the valence-band leading edge; the solid lines follow the average core-level positions. Within a noise band of 0.2 eV, a clear shift is found in the spectra, indicating a doping dependence of the chemical potential.

result in a larger shift of the La and Sr spectra. The  $CuO_2$  planes, on the other hand, are doped with holes if the Sr content is increased, and consequently the Cu spectra will shift less. On average the shift of the core level spectra will of course reflect the changes in chemical potential.

The fact that there is not much difference in chemical potential shift for the pellets and the films indicates that the lower  $T_c$  of the films, the difference in Sr and valence band spectra, and the different levels of surface contamination for pellets and films apparently do not play a large role. Concerning the influence of contamination, it is illustrative to note that van Veenendaal et al., who claim to have very clean surfaces [13], also find almost the same shifts in the photoelectron spectra of Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>1-x</sub>Y<sub>x</sub>Cu<sub>2</sub>O<sub>8+ $\delta$ </sub> as Itti et al., whose surfaces clearly suffer from a nonnegligible amount of contamination [15,60].

#### 5. Discussion

The main result that can be deduced from the changes in the XPS spectra is that the chemical potential  $\mu$  in La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> shifts as a function of doping, without any discontinuity at the transition from metallic to insulating samples. Strong evidence that the shifts in the photoelectron spectra indeed are due to changes in  $\mu$  is provided by the great similarity of the average core-level shift and the shift of the valence band (compare the solid and dashed lines in Figs. 11(a) and (b)).

The behavior of the chemical potential found here in  $La_{2-x}Sr_xCuO_4$  is different from that in van Veenendaal et al.'s study of  $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$  and from that in Allen's study of  $Nd_{2-x}Ce_xCuO_4$ . Van Veenendaal et al. found a strong shift in  $\mu$  at the transition from metallic to insulating samples [13], which is clearly absent in our data. Also Takahashi et al. do not find a strong shift in  $La_{2-x}Sr_xCuO_4$ , comparing spectra of x=0 and x=0.08 cleaved single crystals [49].

Allen et al. report that in  $Nd_{2-x}Ce_xCuO_4$ , the chemical potential does not shift at all as a function of doping [9]. This conclusion is based on a valenceband study of an undoped and optimally doped sample. Recently this result was confirmed by the same group, using more samples in a wider doping range [7]. However, for  $La_{2-x}Sr_xCuO_4$ , we find that the spectra do shift if the doping is changed. The shift is quite comparable to that found by Shen et al. and van Veenendaal et al. in the metallic regime of  $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$ . Following their explanation, also in  $La_{2-x}Sr_xCuO_4$  the behavior of  $\mu$  can thus be described by the doping of a rigid band. In recent band-structure calculations by Czyzyk and van der Marel of  $La_2CuO_4$  [61], a shift of 0.15 eV is predicted, adopting a rigid band model, if the doping increases from x = 0 to 0.25. This is quite similar to the trend found in our experimental data.

In the above, we tacitly assumed that the measured behavior of the chemical potential is intrinsic to the  $La_{2-x}Sr_xCuO_4$  system. Especially regarding the behavior around the metal-insulator transition this is not evident since it is difficult to prepare stoichiometric undoped La<sub>2</sub>CuO<sub>4</sub>. Any excess oxygen in the material will produce holes, who in turn might pin the Fermi energy at the same energy as in the metallic regime. The agreement of the results on our pellets and films, and the single crystals in the study of Takahashi et al. [49], is an indication that the measured continuous change of the chemical potential in  $La_{2-x}Sr_{x}CuO_{4}$  indeed is intrinsic. Nevertheless, any definite conclusion would require careful analysis of the oxygen content and carrier concentration of the samples used in the photoelectron studies.

## 6. Conclusions

We have performed a systematic study of the behavior of the chemical potential as a function of doping in the  $La_{2-x}Sr_xCuO_4$  system. For this study, both pellets and films were made with Sr doping x ranging from 0 to 0.25. Extensive characterization of the samples shows that the pellets have good structural and electrical properties. The thin films are well-oriented but have reduced  $T_c$  values. Similar low  $T_c$ 's were found by others, who assigned it to strain in the layers. We found additional evidence for this assignment in the smaller increase of the *c*-axis length versus Sr doping of the films as compared to that of the pellets.

From the relative peak intensities in the XPS measurements we have deduced that if the surface has only one type of surface termination it must be the one starting with a LaO layer, and directly followed by a CuO plane. In the discussion of the separate XPS core-level spectra, special attention was paid to the Sr 3d spectra. In spite of the fact that the  $La_{2-x}Sr_xCuO_4$  crystal structure has only one crystallographic site for Sr, we find two doublets in all Sr 3d spectra indicating Sr occupies two chemically different sites. We suppose that this is caused by local inhomogeneity of the Sr doping.

The shift that is found in all photoelectron spectra upon doping, shows that the chemical potential of  $La_{2-x}Sr_xCuO_4$  continuously changes as a function of Sr content. The results obtained on pellets and films agree with each other, and also with measurements of Takahashi et al. on single crystals [49]. This indicates that the measured behavior of the chemical potential is intrinsic to the  $La_{2-x}Sr_xCuO_4$  system, although we cannot definitely exclude any possible influence of extra incorporated oxygen, especially in the undoped samples.

We do not find a large shift in  $\mu$  at the metal-insulator transition, in contrast with predictions of the "semiconductor model" of the doping behavior of  $\mu$ in high- $T_c$  materials. On the other hand, our data also do not support the "impurity model" where it is supposed that the chemical potential is constant as a function of doping. The results on  $La_{2-x}Sr_xCuO_4$  can be best explained assuming that the shift in  $\mu$  is caused by the doping of a rigid narrow band, lying near the middle of the gap.

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