Doping Dependence of the Chemical Potential in cuprate high $T_c$ superconductors II: $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$

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Using X-ray photoelectron spectroscopy, a systematic study is performed of the doping dependence of the chemical potential $\mu$ in two systems of $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$. The doping is varied by changing the O content of the sample. The measured shifts of the chemical potential are compared with present models for the doping behaviour of $\mu$ in high-$T_c$ materials.
I. INTRODUCTION

This paper is a sequel to Ref. [1], where we studied the doping dependence of the chemical potential of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ as a function of Sr content. In the present paper we present measurements of the behaviour of the chemical potential as a function of doping in $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$. Here, the doping is varied by annealing a sample in different oxygen atmospheres. As in the previous article, we will first discuss preparation and characterization of the sample, and subsequently the XPS measurements and the behaviour of the chemical potential in this material.

II. PREPARATION AND CHARACTERIZATION

The family of $\text{Bi}_2\text{Sr}_2\text{Ca}_n\text{Cu}_{n+1}\text{O}_{2n+6+\delta}$ materials is particularly suited for XPS studies because they are relatively inert and not sensitive to moisture and other contaminants in the environment. On the other hand it is difficult to prepare single phase material. The early Bi-Sr-Ca-Cu-O samples predominantly contained the $n = 1$ material, with certain fractions of the $n = 0$ and $n = 2$ phases, depending on the preparation. Later it was found that the addition of Pb stabilizes the structure. Especially the $n = 2$ material, used in this study, can not be made single phase without this addition.

Our $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ sample is prepared by a two-step ceramic route starting from $\text{Bi}_2\text{O}_3$, PbO, SrCO$_3$, CaCO$_3$ and CuO powders of approximately 99% purity. A Pb-free Bi-Sr-Ca-Cu-O precursor was first prepared by calcination at 800 and 840 °C. The required amount of PbO was then added, and a final sintering was performed in air at 860 °C, and then 850 °C for a total of 80 hours [2]. The nominal composition of the sample, as determined from the starting composition of the oxides in the preparation, is $\text{Bi}_{1.84}\text{Pb}_{0.34}\text{Sr}_{1.91}\text{Ca}_{2.03}\text{Cu}_{3.06}\text{O}_{10+\delta}$.

The sample was given four different surface preparation treatments in our UHV system, resulting in four different values of the oxygen content as determined from the relative in-
tensities of the XPS lines. Each time the sample surface was freshly scraped in situ with a sapphire plate, before it was heated and/or exposed to ozone. The pressures and temperatures used in the ozone anneals are typical for in situ growth of high-quality YBa$_2$Cu$_3$O$_{7-\delta}$ thin films in our system [3]. The freshly scraped surface always exhibited almost the same set of XPS spectra, from which we conclude that the changes in oxygen content due to heat/ozone treatment are the strongest in a top layer thinner than the 'scraping' depth (about 0.1 mm).

Treatment A was to transport the sample immediately to the measurement chamber under UHV. In treatment B the sample was heated to 330 °C in $3 \times 10^{-4}$ mbar ozone for 15 minutes, and the ozone delivery was stopped during cool-down. Treatment C was to anneal the sample at 450 °C in $6 \times 10^{-4}$ mbar ozone for 20 minutes, and cooled down to room temperature in the same ozone atmosphere. Treatment D consisted of heating to 100 °C in UHV for 15 minutes. The lower temperature for this vacuum anneal was chosen as the (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$ material is known to decompose when heated to high temperatures at low oxygen pressures.

We have characterized the sample with X-ray diffraction and resistance measurements it was introduced in the UHV system, and after the series of surface treatments and XPS measurements were completed.

The X-ray powder diffraction pattern of the as-prepared sample is displayed in Fig. 1. All peaks can be assigned to the $n = 2$ material. There is no indication of the presence of an $n = 1$ phase, which is the most frequently found impurity in Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$ samples. This is best visible from the narrow (0014) peak, which is considerably broadened by the (0012) peak of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ if this material is present. A least squares fit to the peak positions using a tetragonal unit cell, gives for the lattice parameters $a = 5.403 \pm 0.002$ Å and $c = 37.02 \pm 0.02$ Å, which are typical values found for this material.

The resistance was measured with a standard 4-terminal technique. The data shown in Fig. 2 are plotted relative to the resistance at 300 K. For the as-prepared sample the
resistance curve is almost linear above $T_c$. The onset critical temperature is 110 K. Zero resistivity is obtained at 99–103 K, slightly depending on the magnitude of the measuring current due to the granularity of the material. By comparison with the results of Ulm et al. [4], who studied the $c/a$ ratio and the transport properties of $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ after anneals at 700 °C in different oxygen pressures, we conclude, that the as-prepared sample is close to being optimally doped.

After completing the XPS analysis following the last surface treatment (annealing in vacuum), the X-ray diffraction pattern (Fig. 1) indicates that the material is still single phase. The $a$-axis value is unaltered within our experimental accuracy of 0.02 Å, but the $c$-axis is slightly expanded to $c = 37.10 \pm 0.02$ Å.

The resistance curve above $T_c$ has become non-linear, and the onset $T_c$ is lowered to 105 K. The sample is fully superconducting below 89 K. Comparing these results with the oxygen doping study of Um et al. [4] we see that the composition has moved in the direction of the metal-insulator transition. The smaller Cu $2p_{3/2}$ as determined with XPS (discussed in the following section) main peak [18] also points in this direction. It is important to notice, that the changes in the oxygen concentration at the sample surface are substantially larger than in the bulk, as follows from the intensities of the XPS lines. As the changes in $\mu$ are also measured with the same surface sensitive probe, we will use XPS as a quantitative measure of both the oxygen stoichiometry as well as the doping dependence of the chemical potential.

III. PHOTOELECTRON SPECTRA

After each treatmet of the sample surface in a UHV chamber using the different procedures described above, the sample was immediately transported to the analysis chamber without breaking the ultrahigh vacuum.

The core level and valence band spectra are displayed in Fig. 3. All spectra were measured with Mg $K\alpha$ radiation and an analyser resolution of 0.4 eV. The carbon contamination was
checked with 1 eV resolution, which gives a strongly increased sensitivity. The binding energies of the Bi 4f\textsubscript{7/2}, Pb 4f\textsubscript{7/2}, Sr 3d\textsubscript{5/2}, Ca 2p\textsubscript{3/2}, Cu 2p\textsubscript{3/2} and O 1s peaks of the as-prepared sample are 158.5, 137.4, 132.4, 345.0, 933.2 and 528.7 eV respectively.

The Bi 4f spectrum consists of two multiplet-split peaks, which have a slight asymmetry towards higher binding energy, which can be taken as an indication of a coupling of the core levels to excited states in the metallic or semiconducting BiO blocking layers. Also the Pb 4f\textsubscript{7/2} spectrum, shown in Fig. 3 together with the Sr 3d spectrum, has an asymmetric line shape. It is known that Pb substitutes for Bi in the Bi\textsubscript{2}Sr\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{10+\delta} superconductor. Unlike Golden \textit{et al.} who find a larger asymmetry for Pb than for Bi \cite{20}, the 4f line shapes in our case are exactly the same. Although the spectra can be fitted to a Doniach-Šunjić–like line shape \cite{7}, due to limitations imposed by the life-time broadening of the XPS lines as well as instrumental broadening, a small semiconductor gap may exist in the electron-hole shake-up tail. We observe that the lineshape is insensitive to the oxygen content. Hence, if the asymmetry should be interpreted as a mixture of two valencies (Bi\textsuperscript{3+} and Bi\textsuperscript{5+}) of Bi in this compound \cite{5,6}, the average valency of Bi has to be independent on the degree of oxygenation. The shift of the Bi 4f level (also found in the Bi 5d spectra [Fig. 3]) is much larger than the shift of the Cu 2p spectrum. Also the core levels of Pb and Sr (which is next to the BiO planes) show a larger than average shift [Fig. 4]. This indicates that the extra oxygen is introduced near the Bi- and Pb-atoms, supporting the point of view that the doping of the CuO\textsubscript{2} planes is controlled through the oxygen stoichiometry of the blocking layers. Together with the fact that the Bi line shapes remain unaffected, this indicates that the Bi core levels experience a decrease in binding energy due to the electrostatic potential surrounding the O\textsuperscript{2−} ions. In the Bi\textsubscript{2}Sr\textsubscript{2}Ca\textsubscript{1−x}Y\textsubscript{x}Cu\textsubscript{2}O\textsubscript{8+\delta} the Y\textsuperscript{3+} ions replace the Ca between the CuO\textsubscript{2} planes, resulting in a shift of the Bi core level which is smaller than the average, as has also been observed experimentally. \cite{17,18}

The Sr 3d spectrum of Sr containing high-\textit{T}_c superconductors is discussed extensively in Ref. \cite{1}. The spectrum of the (Bi,Pb)\textsubscript{2}Sr\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{10+\delta} material resembles that of Bi\textsubscript{2}Sr\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{8+\delta} \cite{1}. Thus either it consists of two components, one of them due to
Sr-Ca disorder, or it has only one chemical component, with an asymmetric line shape.

A single doublet is seen in the Ca 2p spectrum, very similar to the early spectrum of Steiner et al. [10]. Later spectra of highly oriented and of single crystalline Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ material showed at least two spin-orbit-split pairs marking Sr-Ca disorder [11,12]. The unusual background in our spectrum is caused by Cu LMM Auger peaks.

In the Cu 2p$_{3/2}$ spectrum, there is the familiar double structure typical for Cu$^{2+}$. After treatment A (only scraping) the intensity ratio of satellite and main peak is 0.33, somewhat lower than for e.g. La$_{2-x}$Sr$_x$CuO$_4$. This ratio is almost independent of oxygen treatment. After treatment D (annealing in vacuum) the main peak became somewhat narrower.

The O 1s core level is relatively broad, but in contrast with that of La$_{2-x}$Sr$_x$CuO$_4$ and YBa$_2$Cu$_3$O$_{7-\delta}$, almost free of a high binding energy shoulder. Similar oxygen core level spectra were measured on the Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ material [13,14]. The large width of the peak is probably caused by slightly different binding energies of the different types of oxygen in the material, e.g. as predicted in bandstructure calculations [14]. After treatment D a weak signal of carbon were present. All other treatments resulted in carbon-free surfaces.

IV. DOPING DEPENDENCE OF THE CHEMICAL POTENTIAL

Clearly visible in Fig. 3 is the systematic shift of the spectra as a function of oxygen treatment. For a useful plot of this shift, a quantitative determination of the oxygen content is necessary. Using the calculated cross-section for each level [15] and assuming a random distribution of the elements in the sample, we find that the surface composition after scraping (treatment A) is Bi$_{2.2}$Pb$_{0.26}$Sr$_{2.0}$Ca$_{1.6}$Cu$_{2.8}$O$_{9.4}$, which is close to the nominal value in the bulk. In this chemical formula we scaled the cation content such as to make the total charge on the cations equal to +20, taking Bi$^{3+}$, Pb$^{2+}$, Sr$^{2+}$, Ca$^{2+}$, Cu$^{2+}$ as the relevant formal valencies [16]. We define $\delta$ as the difference between the number of oxygen atoms based on the XPS peak intensities, and the number of O$^{2-}$ ions required for total charge compensation of the cations. This we interprete as a quantitative measure of the changes...
in oxygen content. After treatments D, A, B, and C this is $-0.9$, $-0.6$, $+0.2$, and $+1.3$ respectively. The result of the shift in each core level versus $\delta$ is given in Fig. 4. As before, the shifts in the Cu and valence band spectrum are determined from the leading edge of the spectra—for all other peaks, the peak position is used. Over the studied range of $\delta$-values, the average shift is reasonably linear with a small upturn after annealing in vacuum. By varying the source power during the XPS measurements we checked that the observed shifts in the spectra are not due to charging of the sample.

Similar to $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, the valence band follows the average core level shift quite well, indicating that the observed shift is due to a variation of the chemical potential. We see from Fig. 4 that there is a clear shift in chemical potential when increasing the oxygen content toward the metallic regime. The shift in $\mu$ as a function of doping is larger than in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [1] and in the $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ compounds [21]. We observe a stronger shifting of $\mu$ upon approaching the MI transition, which is in general agreement with previous results with $Y$-doping in Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$Cu$_2$O$_{8+\delta}$ [18,19]. This inconsistency would be removed if in the doped La and Nd copper oxides an additional band is formed within the charge-transfer gap, where the Fermi level remains pinned upon doping with holes or electrons. In principle such a band might exist due to the close proximity of the (disordered) layer of dopants to the metallic CuO$_2$ sheets. The doping layers are indeed further away in the BSCSO system, which would then explain the absence (or a different binding energy) of such a band in these materials. The question whether such a band could indeed exist, poses an interesting theoretical challenge involving both a quantative theory of the correlation induced insulating gap, and also a quantitative description of states within the gap induced by the dopant atoms.

V. CONCLUSIONS

We studied the doping dependence of the chemical potential in $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ as a function of O concentration $\delta$ with X-ray photoelectron spectroscopy. In the metallic
regime the shift is considerably larger than for the La$_{2-x}$Sr$_x$CuO$_4$ system. We observe that the chemical potential shifts more strongly, when we come closer to the metal-insulator transition by means of oxygen depletion. Differences between the Bi and Cu core level shifts indicate that the oxygen enters the crystal structure closer to the Bi sites than to the Cu atoms.

VI. ACKNOWLEDGEMENTS

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FIGURES

FIG. 1. X-ray powder diffraction pattern of the (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$ sample directly after preparation. All peaks can be ascribed to the $n = 2$ material; impurity phases, such as the frequently found $n = 1$ phase, are absent. The majority of the peaks is labeled with their Miller indices. Cu $K\alpha$ radiation with a Ni filter was used in the measurement.

FIG. 2. Temperature dependent resistance measurements of (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$ relative to the resistance at room temperature for the as-prepared and the vacuum annealed sample (solid and dashed line respectively). After vacuum anneal, both the lower $T_c$ and the non-linear behaviour of the resistance above $T_c$ indicate a lower quality of the sample.

FIG. 3. Core level and valence band spectra of the (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$ sample as a function of O content. From top to bottom: spectra after treatment D, A, B and C. Spectra were obtained using Mg $K\alpha$ radiation. Note the systematic shift in all spectra, indicating a variation in chemical potential.

FIG. 4. Observed shifts in core level and valence band position of (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$ as a function of oxygen content $\delta$. Here, $\delta$ is the difference between the measured O content and that based on the total cation content of the material. From left to right on the horizontal axis are data after treatment D, A, B, and C. The solid line gives the average shift found in the core levels. The dashed line follows the change in valence band position. The dotted band indicates the scatter in the data (with exception of Bi, see discussion in the text).