Evidence of Pseudogap Related Core Level Shifts in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$

O. Tjernberg,[1] H. Nylén,[2] G. Chiaia,[1,*] S. Söderholm,[1,5] U. O. Karlsson,[1] M. Qvarford,[2] I. Lindau,[2] C. Puglia,[3]
N. Mårtensson,[3] and L. Leonyuk[4]
[1]*Materials Physics, Royal Institute of Technology, S-100 44 Stockholm, Sweden*
[2]*Department of Synchrotron Radiation Research, Institute of Physics, Lund University, Box 118, S-221 00 Lund, Sweden*
[3]*Department of Physics, Uppsala University, Box 530, S-75121 Uppsala, Sweden*
[4]*Department of Geology, Moscow State University, 119 899 Moscow, Russian Federation*
[5]*Department of Materials and Chemical Engineering, ABB Corporate Research, S-721 78 Västerås, Sweden*
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Photoelectron spectroscopy data from $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$ single crystals, for $x = 0, 0.16,$ and 0.55, are presented. It is shown that there are core level shifts related to the opening of a pseudogap and that similar shifts are observed at the opening of the superconducting gap in optimally doped samples. This result is in agreement with pair formation above T_C as suggested by V. J. Emery and S. A. Kivelson [Nature (London) **374**, 434 (1995)]. [S0031-9007(97)03557-6]

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Since the discovery of the first high temperature superconductors (HTCs), much work has been performed in order to understand the electronic structure of these compounds. Several important facts have been established concerning the CuO based superconductors, e.g., the importance of hole doping, the strong correlation effects, and the charge transfer nature of the band gap in the undoped compounds. The importance of hole doping for the occurrence of superconductivity makes it natural to study the effect of changes in the doping. Several studies of doping dependence have been performed and one of the superconductors often studied by photoelectron spectroscopy (PES) is $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bisco) [1] and the related compound $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$ (Y-Bisco) [2–6].

Recent results concerning the existence of a pseudogap in underdoped HTCs [7–9] have further increased the interest for studies of doping effects in these materials. The existence of a pseudogap in the underdoped HTCs has raised the question about the nature of this gap and its relation, if any, to the superconducting gap. In this report, a study of *in situ* cleaved single crystals with $x = 0–0.45$ is presented together with data on optimally doped samples above and below T_C. It is shown that the Bi, O, and Cu core level binding energies are influenced by the opening of a pseudogap and that similar shifts in binding energy are observed at the opening of a superconducting gap. The result suggests that the pseudogap and the superconducting gap are similar in nature.

The samples were grown from melts in alumina crucibles [10]. Composition and structure were determined by x-ray diffraction (XRD) [11] and energy dispersive spectroscopy (EDS). The XRD results showed that the samples were all single phased with the same crystal structure. In the temperature dependent measurements, the samples were not from the same source but grown with a similar technique [12].

The measurements of the Bi $4f$ and $5d$, Sr $3d$, Ca $2p$ PES and O x-ray absorption spectra (XAS) were performed at beam line 22 [13] of MAX-Lab, the national synchrotron radiation facility in Lund, Sweden. The beam line enabled an energy resolution of 250, 60, 240, and 600 meV in the measurements of the Bi $4f$, Bi $5d$, Sr $3d$, and Ca $2p$ core levels, respectively, and a photon energy resolution of 300 meV at the O K edge. Both preparation and measurement were done at a base pressure in the 10^{-11} torr range. In order to obtain the best possible calibration the core level binding energies (BEs) were calibrated against the Bi $5d$ level, whose BE was determined by measuring the Fermi edge spectrum of a gold foil.

The O $1s$ and Cu $2p_{3/2}$ core levels were measured with a monochromatized Al Kα ($h\nu = 1486.6$ eV) rotating anode source and a 360 mm mean radius multichannel detector equipped hemispherical analyzer. The energy resolution was 250 meV and the base pressure $\sim 2 \times 10^{-10}$ torr.

In Figs. 1 and 2 the core level spectra and O XAS of Y-Bisco are displayed. In all figures, the bottom most spectrum corresponds to sample 1 ($x = 0$), the middle one to sample 2 ($x = 0.10$), and the topmost one to sample 3 ($x = 0.45$), i.e., the Y content increases in going from bottom to top. In each multiplot the spectra have been normalized to the same height. The thin lines at constant BE are included as guides to the eye.

Figure 1(a) shows the region from the Bi $5d$ levels to the Fermi level. The shape of the Bi $5d$ levels displays no noticeable changes upon Y substitution but the peak position is shifted towards higher BE for sample 2 and then back to approximately the original position for sample 3. The weak features at approximately 12, 18, 21,. and 23 eV BE are attributed to a Cu d^8 satellite [14,15], Sr $4p$, O $2s$, and Ca $3p$, respectively. A close study reveals only small shifts to higher BE of the valence band (VB) maximum as the Y content is increased. Moreover, the shape of the VB is changing upon Y substitution indicating other effects than a rigid shift. The

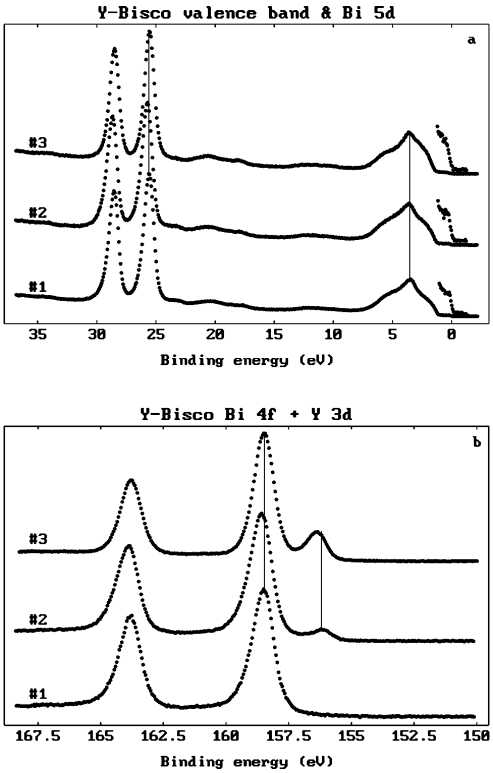

FIG. 1. (a) shows the valence band and Bi $5d$ core levels for samples 1–3, whereas (b) displays the Bi $4f$ and Y $3d$ core levels. Vertical lines are drawn for constant binding energy.

magnification of the intensity at the Fermi level shows that a distinct Fermi level is seen for sample 1, whereas a lower spectral intensity is noted for samples 2 and 3.

In Fig. 1(b) the spectra of the Bi $4f$, and for samples 2 and 3 also Y $3d$, are displayed. The increase in Y content is obvious from one spectrum to another and the intensity ratio is that expected from composition. It is also clear that the Y $3d$ level shifts to higher BE as the Y content increases while the Bi $4f$ level mimics that of the $5d$ level in Fig. 1(a), i.e., first shifting to higher BE and then back.

Figure 2(a) displays the O K edge XAS. The most significant difference between the spectra is that the prepeak at ~535 eV photon energy (PE) decreases when Y is introduced. As seen in Fig. 2(b) this correlates with the decrease in intensity of the shoulder on the low BE side of the O $1s$ spectra. The shoulder which is clearly visible in sample 1 is no longer visible in sample 3. This can also be seen as a decrease in full width at half maximum (FWHM). The correlation between the XAS prepeak and the low BE shoulder in the O $1s$ spectrum has been noted previously [4,16,17]. There is not only a change in the O $1s$ spectra shape but also a shift in energy as Y is introduced. The shifts seen here resemble the behavior of the Bi levels in the fact that there is first a shift towards higher BE and then back to approximately the original BE.

Also measured, but not displayed, were the Sr $3d$, Ca $2p$, and Cu $2p$ core levels. The shifts of these core levels are displayed in Fig. 3. The study of the Sr $3d$ levels revealed a slight decrease in FWHM upon Y substitution confirming that the Y-Sr intermixing is lower than the Ca-Sr intermixing [18].

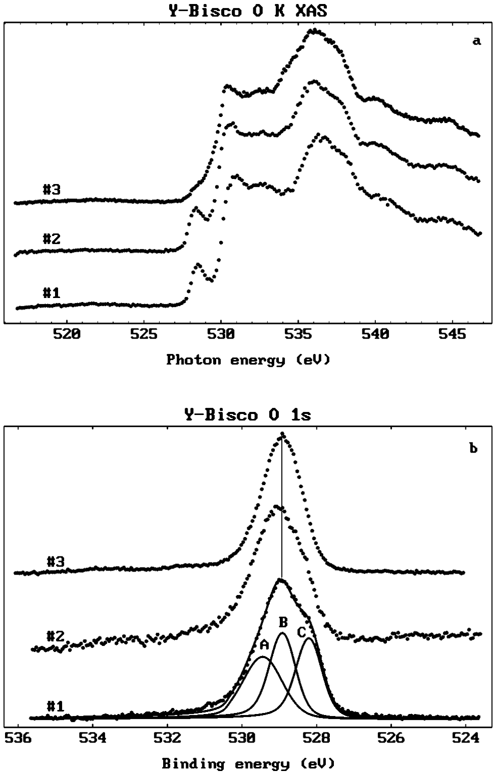

FIG. 2. Photoemission spectra of the O $1s$ core level for samples 1–3 are shown in (a) and x-ray absorption spectra for the same samples in (b). The absorption spectra were measured by means of O KVV Auger yield at normal incidence. Vertical lines are drawn for constant binding energy.

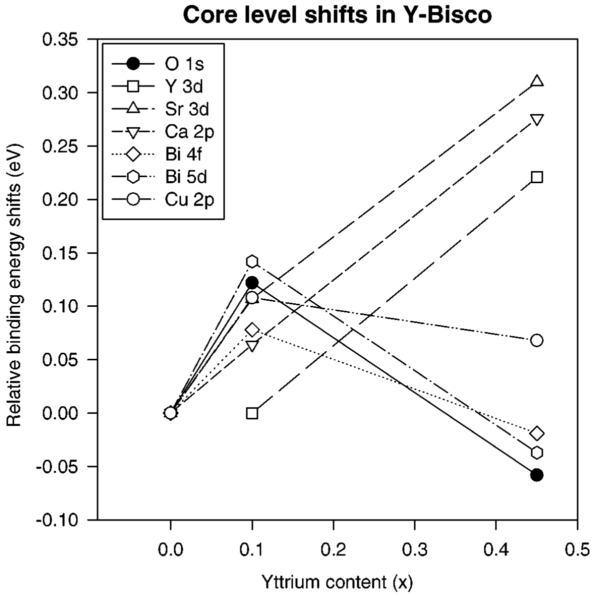

FIG. 3. A collection of the shifts of all core levels are displayed in the figure as a function of Y content.

It is clear that the observed shifts cannot be described by a simple shift of the chemical potential μ. The most obvious evidence is given in Fig. 1(b) where it is clearly seen that the distance between the Y $3d$ and Bi $4f_{7/2}$ peaks decreases with Y substitution. It is also very unlikely that the shifts are chemical shifts linked to Y since the shifts for Bi, O, and Cu change sign when the level of substitution is increased. The plausible cause for these shifts is the opening of a pseudogap as discussed below.

The correlation between the suppression of the prepeak in the O K edge XAS and the decrease of the low BE shoulder in the O $1s$ spectra is a strong indication that the O $2p$ holes connected to the XAS prepeak [16,17,19] are related to the shoulder on the O $1s$ core level [16,17]. It has been suggested that the O $1s$ core level consists of three lines and that they can be referred to as Bi-O, Sr-O, and Cu-O in order of decreasing BE [16]. In order to determine the behavior of these different components upon Y substitution curve fits of the O $1s$ spectra were performed. The fits were performed by first subtracting an integral background from each spectrum and then fitting three Doniach-Šunjić [20] functions convoluted with Gaussians. Peak positions and areas of all fits are presented in Table I [21]. The resulting fit for sample 1 is included in Fig. 2(b), where the three components labeled A through C are also seen. According to earlier results [16] the A component corresponds to Bi-O, the B component to Sr-O, and the C component to Cu-O in the Y free sample. From the data in Table I, it is seen that component C shifts towards the A and B components upon substitution, thus resulting in a reduction of the total width. The A and B components show first a small shift to higher BE and then back, while component C shifts markedly towards higher BE for low substitution but the BE increases only slightly for the high substitution case. It is possible that the A and B components exchange places between samples 2 and 3. This is supported by the peak areas found in the fits. Using the peak assignments in [16] and subtracting a shift in μ, this scenario implies that the Bi-O component displays the largest shift towards lower BE, while the Cu-O and Sr-O components shift less, irrespectively of any exchange between the A and B components. The fact that the width of component A remains the largest is probably due to satellite contributions on the high BE side [22].

TABLE I. The energy positions and areas of the three components fitted to the O $1s$ spectra [21].

Samples	E_A (eV)	Area$_A$ (%)	E_B (eV)	Area$_B$ (%)	E_C (eV)	Area$_C$ (%)
1	529.42	34.2	528.90	34.8	528.19	31.0
2	529.70	28.7	529.10	39.4	528.44	31.9
3	529.16	39.2	528.91	31.9	528.50	28.9
Above T_C	529.28	40.2	528.84	30.1	528.17	29.6
Below T_C	529.17	40.2	528.76	30.1	528.07	29.6

The relative peak positions of all core levels are compiled in Fig. 3. There are two visible trends. The Sr, Ca, and Y levels show an almost linear shift towards higher BE as the Y content increases while the Bi, O, and Cu levels shift first to higher BE and then back. The linear part of these shifts can be described by a shift in the chemical potential μ [2]. The shift of the O $1s$ level plotted in Fig. 3 is the shift of the spectrum peak position and thus an average of the shifts discussed above. Samples 1 and 2 are close to optimum doping, and the superconducting transition temperature T_C as well as the temperature T^* at which the pseudogap opens is far below room temperature [8,9]. For sample 3 the situation is quite different since this sample is strongly underdoped and a pseudogap exists even at room temperature (RT) [8] ($T^* >$RT). The linear increase in BE is apparently disrupted for Bi, O, and Cu when the pseudogap appears while Sr, Ca, and Y seem unaffected. In order to verify a possible relation between the superconducting gap and the pseudogap, the data presented so far have been compared to temperature dependent measurements on optimum doped Bisco with $T_C = 90$ K. In the temperature dependent measurements, the core levels of Bi, O, and Cu were measured below (78 K) and above (100 K) the superconducting transition temperature. The shifts measured were 81, 97, and 93 meV towards lower BE for the Bi $4f$, O $1s$, and Cu $2p$ peaks, respectively. In Fig. 4 the O $1s$ spectra of this measurement are displayed. Apparent from the raw data is that there is a change in the shape of the O $1s$ peak in this case as well. When the temperature is lowered below T_C the main peak narrows and the low BE shoulder becomes more pronounced. A corresponding effect has been observed in the O K XAS [23]. In order to study shifts in the constituting components the spectrum taken below T_C was fitted using the same parameters as in Fig. 2(b) except for a reduction of the Gaussian widths motivated by the lower temperature [21]. The spectrum recorded above T_C was then fitted by only moving the peak positions of the previous fit. The resulting peak

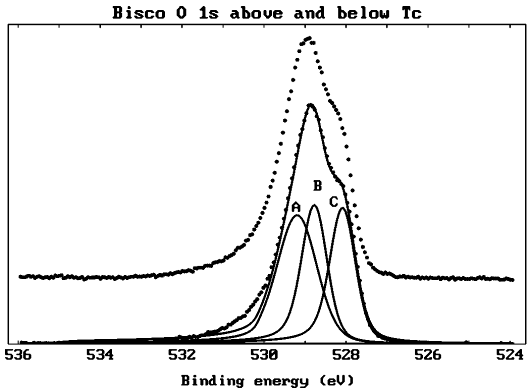

FIG. 4. Photoemission spectra of the O $1s$ core level measured above (top) and below (bottom) the superconducting transition temperature T_C.

positions are included in Table I and the result of the fit to the spectrum recorded below T_C is also displayed in Fig. 4. From the fit data it is seen that the Bi related component (A) is shifting the most, the Cu related component (C) less, and the Sr related component (B) the least, thus confirming that the narrower main peak and more pronounced low BE shoulder is due to a decreased A-B distance and an increased B-C distance. Comparing the doping and temperature cases, it is seen that in both cases the Bi, O, and Cu levels are affected by the opening of a gap. The behavior of the individual O components show that both at the opening of a pseudogap and at the opening of the superconducting gap it is the Bi-O related level which is most affected with the Cu-O and Sr-O levels less affected in both cases.

The fact that the levels most influenced by the pseudogap are those believed to be important for superconductivity is an indication that the pseudogap might be related to superconductivity. This assumption is further strengthened by the observation that the relative influence on the different O components for a pseudogap and a superconducting gap are similar. Since in both cases the shifts due to the gap are towards lower BE it seems plausible that the cause is an increased screening. In the case of a superconducting gap it is reasonable that the screening will be different as compared to the normal state since the nature of the quasiparticles and the density of states close to the Fermi level are both drastically changed. These being important factors for screening it is not surprising that the appearance of a superconducting gap induces a change in the screening. If, as suggested by Emery and Kivelson [9], the pseudogap is due to preformed pairs then it is natural that the shifts are similar in the case of a pseudogap and a superconducting gap. The similarities presented here are thus in support of their theory that the pseudogap is related to the superconducting gap in the sense that they are both due to pair formation. In the pseudogap case, phase fluctuations depress the superconducting transition temperature T_C below the pair formation temperature T^*.

In summation, there is a general shift towards higher BE when Y is substituted for Ca. This shift can be described by a shift in μ. At the point where a pseudogap is known to exist the Bi, O, and Cu core levels shift towards lower BE. This shift towards lower BE is also observed at the passing of T_C in optimum doped samples. A detailed study of the O 1s core level spectra shows that also the behavior of the three constituent components is similar in the two cases. This suggests that the pseudogap is similar in nature to the superconducting gap. A theory to this effect has been presented by Emery and Kivelson [9], in which the pseudogap is due to local pair formation and thus related and similar in nature to the superconducting gap. The data presented here are hence in support of their theory.

Further studies of underdoped compounds above and below T^* and T_C would be very interesting and could perhaps shed further light on the relation between the T^* and T_C transitions.

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*Present address: INFM-Dip. di Fisica, Politecnico di Milano, Piazza L. Da Vinci 32, 20133 Milano, Italy.

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