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Doping dependence of the chemical potential in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$

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A detailed study of the doping dependence of valence- and core-level spectra of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$ leads to the conclusion that the chemical potential shifts in a manner consistent with that of a simple doped semiconductor. The spectroscopically observed filling in of the gap upon doping of the correlated insulator is therefore not due to midgap states pinning the Fermi level, but most likely due to spectral weight resulting from the incoherent part of the one-electron Green's function.

The strong dependence of the properties on the hole concentration in the CuO_2 planes is one of the most striking characteristics of the cuprate-based high-T_c compounds.[1] The behavior of states near the chemical potential as a function of doping is of crucial importance for understanding the normal-state properties as well as the mechanism responsible for the superconducting state. In the strongly doped metallic state (hole concentration of 0.15–0.2 per Cu) photoemission has clearly established the existence of a Fermi level and therefore the fermionic character of states close to E_F.[2] Angular-resolved photoelectron spectroscopy data[3] also clearly exhibit a Fermi surface consistent in size with that determined by band-structure calculations, which is considerably larger than that based only on the expected number of doping induced states. Band-structure calculations predict only small changes in the Fermi surface between the metallic and "insulating" compounds. It is by now widely accepted that the insulating behavior of systems with one hole per CuO_2 unit cell is a direct result of strong correlations caused by the large Cu *d-d* on-site Coulomb interaction. These observations lead to one of the most intriguing and controversial questions concerning the evolution of the low-energy scale electronic structure from the antiferromagnetic insulator to the high-temperature superconductor upon hole or electron doping. Important questions related to this concern the position of the chemical potential, the influence of impurity potentials and the possibility of phase segregation as a function of doping.

Starting from the antiferromagnetic insulator in parent compounds of the high-T_c superconductors with the chemical potential somewhere in the 1.5–2 eV gap[4] the simplest picture would be that the chemical potential moves into the top of the valence band (bottom of conduction band) with hole (electron) doping. In this simple model the low-energy scale states of the doped system would correspond to the first ionization (affinity) states of the insulator. Most currently studied models are based on this assumption. For example, if we accept a much used parameter set[5] for the cuprates, the insulators have a charge-transfer band gap[6] and the first ionization states are ones in which the extra holes of largely O 2*p* character form local singlets (Zhang-Rice singlets[7]) with existing Cu 3*d* holes and the first affinity states are also composed of local singlets corresponding to filling the upper Hubbard band. The quasiparticle states close to E_F in the doped systems would correspond to holes forming local singlets and propagating in a magnetic background as described by the t,J model.[8] Such a t,J model is a special case of the more general three-band or multiband models.[9] Provided one does not have phase segregation into metallic and insulating regions, and if we neglect the impurity potentials due to the dopants, then the chemical potential in these models is expected to shift by amounts of the order of the band gap with doping.

Allen *et al.*[10] observed an apparent absence of such a shift when comparing electron- and hole-doped materials. They concluded that it looks like the chemical potential is pinned, which would necessarily require states to move into the gap to the chemical potential in order to form a metallic state. Perhaps the simplest possible way to realize this is by involving an impurity potential large enough to pull out bound states from the valence or conduction band to positions close to the center of the gap. At very low doping we retain an insulator because the empty states are bound to impurities. At higher doping these states form bands, which could eventually lead to metallic behavior similar to what happens in heavily doped semiconductors. However, to pin the chemical potential close to the center of the band gap of the insulators requires shifts of states by about 1 eV, which would require a very strong impurity potential. Such a strong impurity potential would modify the nature of the states from those corresponding to the first ionization states of the insulator. Phase segregation into a metallic and insulating phase could also result in apparent Fermi level pinning, since in thermodynamic equilibrium the chemical potentials of the insulator and metal would be the same.[11] It should be noted that Allen *et al.*[10] considered two systems, $La_{2-x}Sr_xCuO_4$ and $Nd_{2-x}Ca_xCuO_4$, with strongly different crystal structures, so that the first ionization states could be of a very different nature. As suggested by Hybertsen *et al.*[12] this could result in canceling effects of shifts in chemical potential and other sources.

Other evidence for a pinning of the chemical potential in the gap is the spectroscopic observation that the gap fills in with spectral weight[13] upon doping. The most straightforward explanation for this is that states move into the gap from the valence and conduction bands upon doping pinning the chemical potential. However, as we will show, this could also be the result of the incoherent part of the Green's function combined with a chemical potential shift.

In this paper we present a detailed photoemission study of the doping dependence of the Fermi level in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$, over a concentration range covering the insulators and the superconductors, including the valence band as well as the core levels. Previous studies by Takahashi *et al.* and Shen *et al.*[14] were limited to the metals and valance bands. Itti *et al.*[15] restricted themselves to core levels and interpreted their results in terms of chemical shifts. We note that a shift in E_F would result in a uniform shift of all the valence and core levels in x-ray photoelectron spectra (XPS) whereas local potential changes due to doping would result in different shifts in binding energy for the various core levels. The study of core- and valence-band energy shifts with doping presented here provides strong evidence for rather large shifts of the chemical potential consistent with a conventional model of doped semiconductors in the limit of small impurity potentials.

The $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$ compounds have been prepared by a spray-drying[16] technique to obtain a maximum homogeneity of the calcium and yttrium ions through the samples. According to x-ray diffraction the samples were single phase. Iodometry and inductive coupled plasma analysis were used to determine respectively the copper content and the bismuth to copper ratio of the pellets. Of the samples studied in this work the ones with $x = 0.0$, 0.1, 0.3, 0.4, and 0.5 were metallic. The 75 and 100 % yttrium-doped samples were insulating. The density of holes in the CuO_2 planes was determined by measuring the oxidizing power.[16] We notice that the samples with 100% yttrium doping have a formal valency of $+2.01$. Decreasing the amount of yttrium will increase the number of holes in the CuO_2 planes. The oxygen content was calculated from the formal copper valency. The metallic samples also become superconducting with a maximum critical temperature of 86 K for a density of 0.15 holes per CuO_2 unit. These results are summarized in Table I.

The x-ray photoelectron spectra have been measured with a "top hat" x-probe 300 spectrometer of Surface Science Instruments. The x-ray source is a monochromatized Al K_α line (1486.6 eV). The overall resolution, determined from the full width at half maximum of a Au $4f^{7/2}$ core level, was 0.65 eV with a 300 μm spot size and 1.0 eV for a 600 μm spot size. The former resolution was used during the measurements of the spectra close to the Fermi level. To obtain a clean surface the samples were scraped *in situ* with a diamond file. The samples were subsequently searched with XPS for regions with no significant traces of contamination, as evidenced by shoulders on the O 1*s* line or the presence of carbon. The base pressure was in the low 10^{-10} Torr range. To estimate the effects of charging spectra were taken at different beam intensities. The shifts due to charging were less than 0.1 eV for the insulating samples. The ultraviolet photoemission spectroscopy (UPS) data were taken using a He-I resonance line ($\hbar\omega = 21.2$ eV). The resolution was 100 meV.

In Fig. 1 we show the valence-band spectra. The zero of energy is at the Fermi level of the spectrometer, which is in good electrical contact with the sample so that the chemical potential of each sample is also at zero. The spectra have been normalized to the total area of the valence band after background correction.

The changes in the valence-band region with increasing Y content are characterized by a change in shape of the region from 1 to 7 eV, the disappearance of spectral

TABLE I. Several characteristics of the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$ samples. For the different values of yttrium doping (x), the oxygen content (δ), the number of holes per CuO_2 unit, the critical temperature, the shift needed to match the leading edge of the valence band for the XPS, and the shift needed to match the top of the UPS valence band, are given.

x	δ	Holes per CuO_2 unit	T_c (K)	Fermi level shift XPS (eV)	Fermi level shift UPS (eV)
0.00	0.23	0.23	70	0	0
0.10	0.23	0.18	85	0.03	
0.30	0.30	0.15	86	0.04	0.18
0.40	0.29	0.09	64	0.12	
0.50	0.33	0.08	40	0.15	0.22
0.75	0.41	0.03	<4	0.41	0.52
1.00	0.51	0.01	<4	0.64	0.60

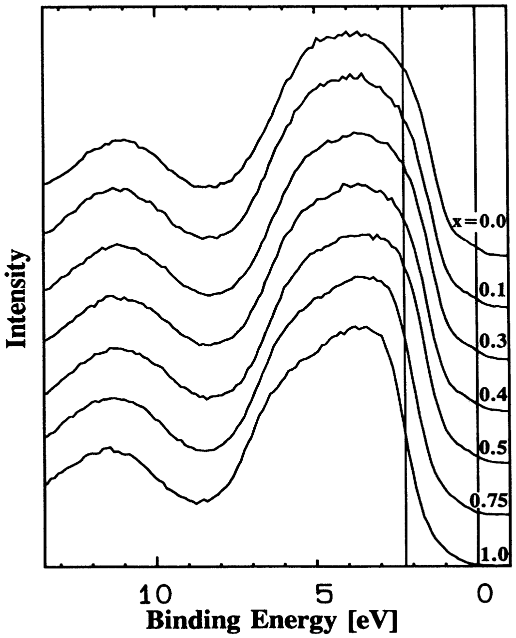

FIG. 1. Valence-band x-ray photoemission spectra of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$. From top to bottom x is 0.0, 0.1, 0.3, 0.4, 0.5, 0.75, and 1.0. The vertical lines are drawn to guide the eye. The spectra have been normalized to the total area of the valence band after background subtraction.

weight close to E_F, and a shift to higher binding energy of the onset of the large valence-band feature at about 1 eV. The main point of interest here is the origin of the apparent depletion of states at E_F with Y doping. Is this due to shifts in E_F or due to a real depletion of states? An expanded view of this region near the Fermi level is shown for some samples in Fig. 2. In the left part of Fig. 2 we see that the spectral weight near the Fermi level disappears on going from the metallic to the insulating samples. In the right half of Fig. 2, the spectra have been shifted in such a way that the onsets of the large valence-band structure, between approximately 1 and 1.5 eV, coincide. The required shifts are tabulated in Table I. Upon doing this also the region below this onset coincides indicating that the dominant difference in these spectra is simply a chemical potential shift and not a depletion of states. It should be noted that the shape of the structure between the main valence band and the Fermi level changes from a more rectangular shape for the metallic, $x=0.0$, sample to a more concave one for the insulating component, $x=1.0$.

Similar behavior of the valence band can also be seen in the UPS data; see Fig. 3. First of all, one observes a similar shift upon doping. This can be seen most clearly from the top of the valence band, which moves closer to the Fermi level when the number of holes in the CuO_2 planes increases. These shifts agree within 0.15 eV with those obtained from the valence bands, which were measured by XPS; see Table I. In the UPS valence-band spectra one also observes other changes especially in the region between 1 and 3 eV. These differences can be understood from the fact that for UPS the valence band not only comes from emission from the CuO_2 planes but involves all valence orbitals. When the system is doped with holes by replacing yttrium by calcium the O 2p states of oxygen in the vicinity of these ions will change

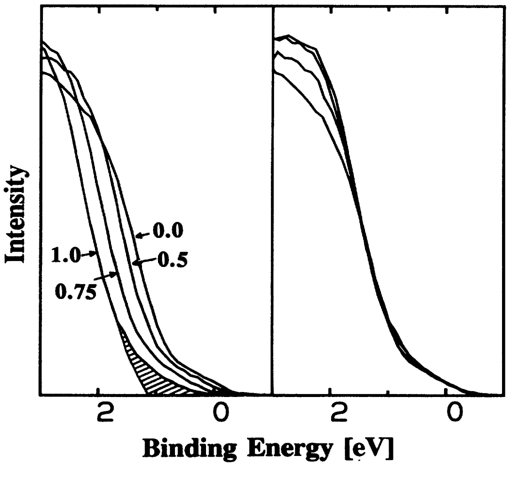

FIG. 2. The left part shows a blowup of the region near the Fermi level. For clarity only the spectra of the 0, 50, 75, and 100% yttrium-doped samples are shown. In the right half the spectra have been shifted to lower binding energies to match the large onsets. The required shifts are given in Table I. The shaded region for the insulator indicates the valence band into which the chemical potential moves upon doping.

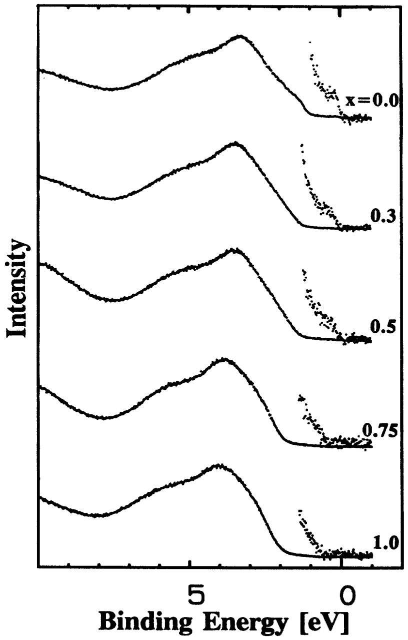

FIG. 3. UPS spectra of the valence band of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$. From top to bottom $x=0.0$, 0.30, 0.50, 0.75, and 1.0. The spectra have been normalized to the area of the main valence-band feature, after a background subtraction. The region near the Fermi level has been multiplied 20 times.

and thereby influence the overall shape of the valence band. Also a change in oxygen stoichiometry is expected to strongly influence the UPS spectrum. Therefore, it is more reliable to establish the existence of a shift of the valence band upon doping from the XPS spectra where the valence band consists mainly of Cu 3*d* emission due to the small cross section of oxygen 2*p* orbitals at x-ray energies.

The upper part of Fig. 4 shows the region near the Fermi level of the UPS spectra. At first glance it looks like doping causes new states to appear near the Fermi level. However, after shifting the spectra in such a way that the top of the valence band coincides, see Table I, one observes that for all the different doping percentages there is already spectral weight in the region from 0 to 0.5 eV and that the effect of doping is to increase the weight of these states, see the lower part of Fig. 4. Such a transfer of spectral weight is not unusual for strongly correlated systems; see, e.g., calculations for the Hubbard or charge transfer Hamiltonians.[17] These also show a transfer of spectral weight from high-energy states to states near the Fermi level upon doping the system with holes.

In other words, even for the insulating compounds there is a band of states between the onset of the large valence and the Fermi level, as indicated by the shaded area in the left part of Fig. 2. From this we conclude that a chemical potential shift is the dominant effect. This conclusion is confirmed by comparing the leading edges of the core levels in the same way.

In Fig. 5 the Cu $2p^{3/2}$ core level is shown. The vertical solid line is drawn as a guide to the eye to emphasize the shift of the leading edge to higher binding energies with Y doping. In addition we observe a broadening of the main line with increasing hole doping, a feature that is also observed in the O 1*s* core level. This could indicate inhomogeneities or a phase separation. However, the ab-

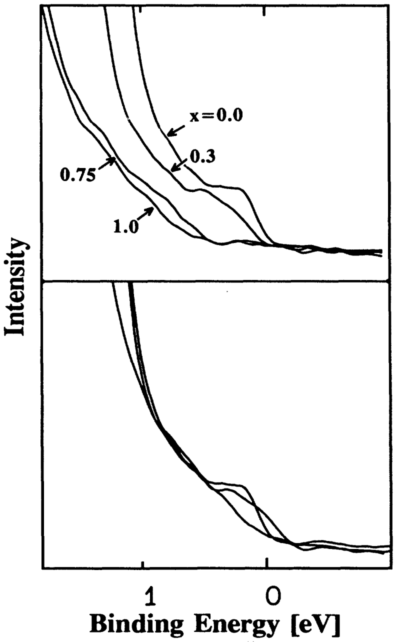

FIG. 4. The upper part shows the UPS spectra of the region near the Fermi level of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$. From left to right $x=1.0$, 0.75, 0.30, and 0.0. The lower half shows the $x=1.0$, 0.3 and 0.0 spectra, which have been shifted in such a way that the top of the valence band coincides. The required shifts towards the Fermi level are 0.6 and 0.18 eV for $x=1.0$ and the $x=0.3$ samples, respectively.

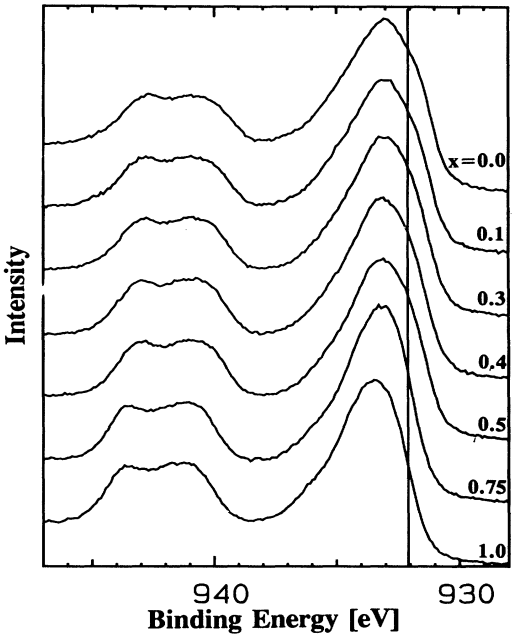

FIG. 5. Cu $2p^{3/2}$ core level of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$. From top to bottom $x=0.0$ 0.1, 0.3, 0.4, 0.5, 0.75, and 1.0. The vertical line is drawn to emphasize the shift of the leading edge with doping.

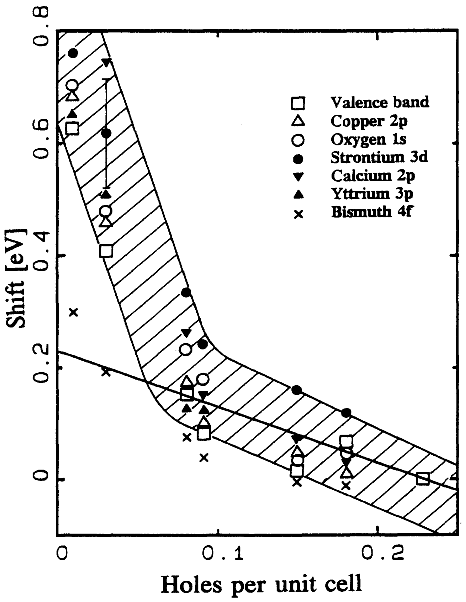

FIG. 6. Plot of the shifts needed to match the leading edges of the major core lines and the valence band. The line indicates the expected shift of the chemical potential for a model rectangular density of states with one hole per state and a bandwidth of 1 eV.

sence of such a broadening in the other major core lines indicates that this is only possible if the inhomogeneities were restricted to the CuO_2 planes, e.g., by differences in Cu valency. We note that a phase segregation into a metallic and an insulating phase[11] with a common Fermi level would result in a broadening of all the core lines.

Figure 6 displays the shift of the leading edges plotted versus hole concentration (decreasing Y content). We notice that all the core levels' leading edges, except perhaps those of Bi $4f$, exhibit nearly the same shift as that of the valence band. The only logical conclusion can be that the chemical potential is shifting, since this would cause a uniform shift of the whole spectrum. Of course in addition to this over all shift the core levels could also shift relative to E_F due to changes in the Madelung potential, effective charges, etc., upon doping. These changes, however, would be quite different and even in different directions for the different elements. Apparently, therefore, changes in the local potential are quite small (<0.2 eV).

We see two different regions as a function of doping in Fig. 6. At small hole concentrations (insulating samples) the shift is strongly dependent on the number of holes so that E_F shifts rapidly from a position in the 2.0 eV band gap[4] to one close to the top of the valence band. Upon further doping the slope is smaller, which is consistent with the Fermi level moving inside the valence band. The solid line is the doping dependence one would obtain for a rectangular band with a width of 1 eV and one hole per state as in a t,J-like model.[18] We note that Takahashi *et al.* and Shen *et al.*[14] observed, at most, very small shifts in the chemical potential. This is consistent with our findings, since their measurements were reported only for the metallic samples (number of holes per CuO_2 unit >0.15).

In conclusion, we find strong evidence for chemical potential shifts with doping consistent with a simple doped semiconductor picture and at most small impurity potentials. The many-body nature of these systems therefore does not result in Fermi level pinning or in so-called doping-induced midgap states.[19] Instead it reveals itself in the filling in of the gap with spectral weight due to the incoherent part of the one-electron Green's function[20] and transfer of spectral weights from the high- to the low-energy scale.[13,17] The data presented strongly indicate that correlated systems are not characterized by shifts in the energies of states with doping as occurs in most mean-field approximations but rather in shifts in spectral weights probably requiring theories that retain a coupling between the low- and high-energy scales.

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