Electronic States at the Fermi Level of Doped C_{60}

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The density of states of the lowest unoccupied molecular orbital band as a function of K doping was investigated by yield spectroscopy excited with visible and near-uv photons. The Fermi level position was determined at each composition with high precision. The superconducting phase K_3C_{60} exhibits a clear metallic edge, although the Fermi level is positioned at low state density $[N(E_f)=0.8\pm0.2$ states/eV molecule] past the band maximum. The K_4C_{60} phase is insulating. Correlation effects are necessary to explain the data as a function of doping.

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A large amount of work has been devoted recently to the understanding of the normal state of doped C_{60}, which becomes superconducting at relatively high temperature [1]. Special attention was paid to the evolution of the electronic state density at the Fermi level upon increasing the doping concentration. Despite the apparent simplicity of the charge-transfer doping process and the early suggestion of a rigid-band filling mechanism, experimental evidence piled up pointing to a much more complex situation. It was evident from photoemission spectra that the filling was not rigid-band-like, since a broad lowest unoccupied molecular orbital (LUMO) derived band was already present at low doping, whose intensity (but not the width) increased upon increasing x [2]. However, the early photoemission data [2-6], while showing clearly the insulating character of the A_6C_{60} (A standing for an alkali metal), were not able to establish conclusively whether a clear Fermi edge was present at lower concentration. In particular the Fermi edge position and the density of state at the Fermi level for the superconducting $x=3$ phase were not determined unambiguously. More recently, Takahashi *et al.* [7] questioned the presence of a distinct Fermi edge at the superconducting composition A_3C_{60} and presented data suggesting that a pseudogap opens at the Fermi level. Lof *et al.* [8] proposed that K_3C_{60} is a Mott-Hubbard insulator with a gap of $\simeq 0.7$ eV and that the actual superconductor has an off-stoichiometric composition, similar to the high-T_c cuprates. Very recently Merkel *et al.* [9] claimed the presence of a distinct Fermi edge for $0<x\leq 3.6$ and denied the presence of a pseudogap.

Most information came from photoemission experiments performed on samples doped *in situ* under ultrahigh-vacuum conditions. The main difficulty with these experiments resides in the absolute calibration of the alkali metal content and the singling out of homogeneous phases. Some discrepancies in the literature probably have this origin. Another difficulty stems from the steepness of the band edges that renders uncertain the identification of the Fermi function cutoff and the location of the Fermi level with the required precision to choose among insulating, metallic, or pseudogap regimes. In the present experiment these issues were addressed with the use of photoelectric yield spectroscopy (YS) with the exciting photons varying in the visible and near-uv ranges. The YS was operated in the constant final state mode; i.e., the photoemitted electrons of a chosen kinetic energy were collected as a function of photon energy. In this operating mode the signal for molecular and/or disordered solids [10] is directly proportional to the density of occupied states times the transition matrix element. This technique provides both a high resolution and a high dynamical range (up to 7 orders of magnitude in the state density variation as a function of energy can be followed) [11]. As a consequence the Fermi function cutoff was easily identified and the Fermi level located with high precision.

C_{60} samples were prepared *in situ* by evaporating powders provided by MER Corporation in a preparation chamber whose basic pressure was 8×10^{-11} Torr. Doping was obtained by evaporating potassium from well degassed SAES getter sources. The amount of evaporated C_{60} and K was measured during deposition by a quartz crystal thickness monitor. Two series of samples were prepared. In the first one, the required amount of potassium was evaporated on the clean surface of the C_{60} film. In the second series, after deposition of a thin C_{60} layer, the required amount of K for $x=6$ concentration was evaporated, followed by further C_{60} evaporation. The chosen K concentration in the thin near-surface region involved in the photoelectron measurements was therefore obtained by outdiffusion. This procedure resulted in a substantial uniformity of concentration in the investigated surface layer. All samples were characterized by monochromatized x-ray photoelectron spectroscopy (XPS) (total resolution 0.350 eV), ultraviolet photoelectron spectroscopy (UPS) (total resolution 100 meV), and photoelectric YS (total resolution 50 meV). Resolution and dynamical range were checked on the Fermi function cutoff of gold.

Since the correct evaluation of the K content is central to the problem of metallic or insulating ground state, we start the data presentation with a brief discussion of the procedure that was adopted. Full details will be presented elsewhere [10]. Three methods have been employed: quartz-crystal thickness monitor, analysis of the intensi-

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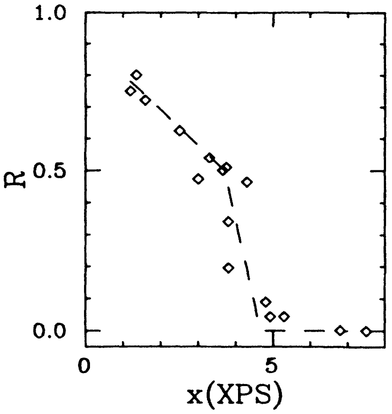

FIG. 1. Intensity ratio R of the two chemically shifted components of the K $2p$ core level, as a function of the doping concentration.

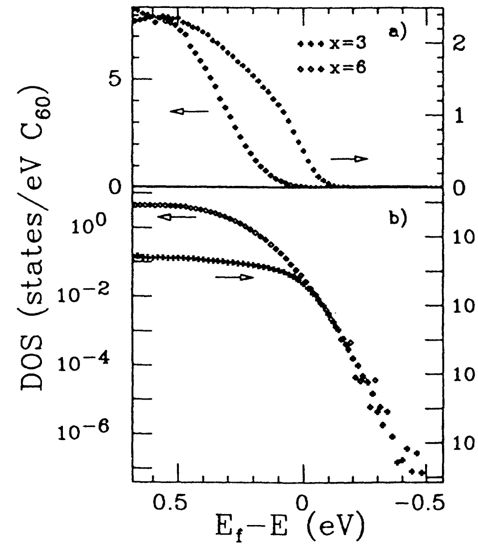

FIG. 2. Photoelectric yield spectra around the Fermi level for $x=3$ and $x=6$, shown on linear (upper) and logarithmic (lower) scales. The origin of the energy scale is taken at E_f, determined as explained in the text.

ties of the highest occupied molecular orbital (HOMO) and LUMO derived bands of the UPS spectra, and analysis of the XPS core level intensities, using table values for the cross sections [12]. We found the latter technique to be the most reliable. However, since we were trying to single out the $x=3$ phase with the best precision possible it was necessary to further test the XPS calibration and to find a reliable procedure to obtain a single phase. This was accomplished as follows. The K $2p$ core levels were quantitatively analyzed [10] as a function of doping. In the bcc phase the K sites are all equivalent and we expect a single spin-orbit doublet; in the fcc phase the potassium can occupy tetrahedral and octahedral sites and two chemically shifted components are foreseen. Therefore the relative intensity of the two doublets gives a direct indication of the phases present in the sample. Since there are two tetrahedral and one octahedral site occupied per C_{60}, a single $x=3$ fcc phase exhibits an intensity ratio $R=\frac{1}{2}$. However, $R=\frac{1}{2}$ does not necessarily imply a homogeneous $x=3$ phase, since regions of $x=0$ composition can be present that do not contribute to K core level intensity. The measured intensity ratio R of the two chemically shifted components is reported in Fig. 1 as a function of the K content x(XPS) as determined by the XPS calibration. We see that there is a very sharp decrease of R for $x(\text{XPS}) > \sim 3.5$, in agreement with previous findings [13] that $x=3$ and $x=4$ are stable phases. The spread of x(XPS) values for $R=\frac{1}{2}$ is attributed to the presence of $x=0$ regions whose amount is very sensitive to the preparation history. This interpretation was further corroborated as follows. Several samples of the second series, doped by outdiffusion of K deposited underneath, with K in the range $0<x(\text{XPS})<3$, were heated up to ~310° C. This caused C_{60} molecule evaporation and invariably resulted in a stable phase with $R=\frac{1}{2}$ and a narrow x(XPS) distribution in the range $3.65<x(\text{XPS})<3.8$. Clearly these samples were composed of a single $x=3$ phase. In conclusion we found a reliable way to obtain samples exhibiting a single $x=3$ phase and a calibration factor $C=0.81\pm0.02$ for the XPS concentrations. In the following, the samples are quoted with the corrected x values [14].

Next we discuss the YS data and the determination of the Fermi level position. In Fig. 2 the portion of the LUMO derived band close to E_f is reported on an expanded scale for $x=3$ and $x=6$ samples. We see in Fig. 2(a) that, thanks to the high resolution, the slope variation due to the Fermi function cutoff is clearly visible in the $x=3$ spectrum. No such cutoff is visible for $x=6$. In Fig. 2(b) the spectra are plotted on a logarithmic scale. Thanks to the high dynamical range, the exponential decay of the Fermi function can be followed over more than 5 orders of magnitude in both cases. Concerning the sample $x=6$ the Fermi cutoff starts in a region where the density of states (DOS) is approximately 2 orders of magnitude lower than the value at the maximum. These tail states are probably due to disorder and are localized. The spectrum shows, therefore, how the insulating LUMO band appears on a high dynamical-range scale. By fitting the exponential region in each measured sample the Fermi level position was determined with high precision. The estimated error is ±0.02 eV for the cases, like the $x=3$ sample, where E_f lies in a region of high DOS and ±0.05 eV when E_f is located at a much smaller DOS as exemplified by the $x=6$ sample.

The full YS spectra of the LUMO band for four representative K concentrations and the corresponding UPS spectra are reported in Fig. 3. In the UPS data the

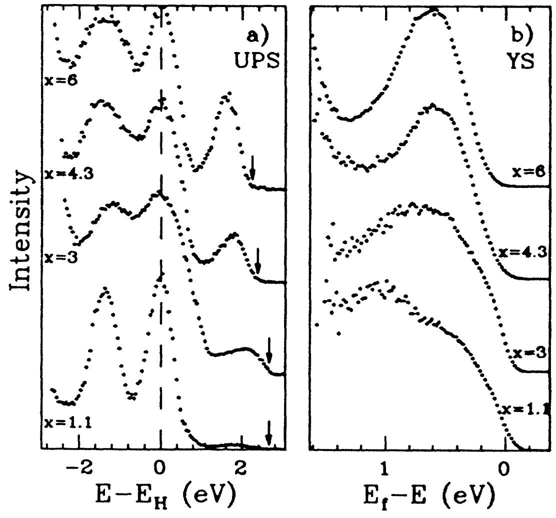

FIG. 3. (a) UPS spectra for four representative K concentrations. The origin of the energy scale is taken at the maximum of the highest HOMO band. The Fermi level position is indicated by arrows. (b) Photoelectric yield spectra of the same samples. The origin of the energy scale is taken at the Fermi level. The spectra of the $x=1.1$, $x=3$, and $x=4.3$ samples are expanded for the sake of clarity according to the following factors: 10, 3.2, and 1.5.

two uppermost valence bands only are shown. Several conclusions can be derived from the present data. Concerning the $x=3$ doping, the edge of the LUMO derived band is clearly metallic although the Fermi level is located in a region of low state density past the DOS maximum. Assuming a complete charge transfer from K to C_{60} we found $N(E_f)=0.8\pm0.2$ states/eV molecule (spin included), which is somewhat lower than previous estimates from UPS data [3] and more than 1 order of magnitude lower than NMR [15] and thermopower [16] values. We observe, moreover, that the band is rather broad. By subtracting the contribution due to the tail of the uppermost HOMO band with the help of the UPS data we find a width at half maximum of 1.0 eV.

Samples with $x<3$ always exhibit a double structure like that in Fig. 3(b) for the $x=1.1$ case, the peak at 1 eV being the dominant one at lower K concentrations. With increasing x the shoulder close to the Fermi level becomes stronger and eventually evolves toward the broad band characteristic of the $x=3$ concentration. Moreover, as exemplified by the $x=1.1$ case, E_f is always located in the low intensity side of the high energy shoulder. The DOS at E_f is still high and the edge metallic although $N(E_f)$ is a factor of ~ 3 lower than the DOS at the maximum, similar to the $x=3$ case. Clearly this behavior points to the simultaneous presence of different phases: the $x=3$ phase with metallic character, a diluted one accounting for the peak at 1 eV below E_f, and possibly regions of $x=0$ phase. This interpretation is corroborated by the analysis of the K $2p$ and C $1s$ core levels [10].

For $x\geq 4$ E_f is located in the band tail, i.e., in a region where the density of states is more than 1 order of magnitude lower than the value at maximum. This is the behavior of the insulating LUMO band as pointed out above. The YS data show that K_xC_{60} is already insulating at $x=4$. To our knowledge this is the first direct proof of the insulating character of K_4C_{60} and agrees with the conclusion derived from the coherent spin precession of muonium [17]. A further characteristic of the spectra at high x values is that the LUMO band is much narrower than in the $x\leq 3$ cases.

We now discuss the problem of the LUMO charge-transfer filling and the importance of correlation effects. Band calculations invariably predict a large HOMO-LUMO gap and narrow bands at all doping concentrations [18]. Furthermore, with increasing x the distance of the Fermi level from the HOMO band is expected to increase by an amount comparable to the narrow LUMO bandwidth. These would be the characteristic features of a rigid-band filling of the LUMO derived band upon doping and of negligible correlation effects. Our data confirm early observations based on UPS measurements [2,3,6] that the filling is not rigid-band-like. Indeed, upon inspection of the YS data, the UPS spectra aligned to the maximum E_H of the highest HOMO band, and the relative position of the Fermi level, the following features are immediately apparent. At low x values the LUMO derived band is already very broad and completely fills the energy region between E_f and the highest HOMO band. With increasing x there is a progressive creation of new filled states in the same energy region and the band remains very broad up to $x=3$. E_f moves closer to E_H with increasing x instead of moving farther as expected for rigid-band filling. Finally, there is the clear indication that K_xC_{60} is already insulating at $x=4$.

The observation that for every x value E_f is located past the peak maximum suggests the presence of an interaction which pulls down the LUMO states upon occupation. From this point of view our data are in qualitative agreement with the opening of a pseudogap as suggested by Takahashi *et al.* [7]. It is likely that electron correlation is responsible for the observed behavior as a function of doping. Indeed, while Jahn-Teller distortions are small [19], electron correlation is strong. It was estimated that there is a positive correlation energy U of ~ 3 eV for adding electrons on a C_{60} molecule [20]. Experimentally it was found $U=1.6$ eV for solid C_{60} [8]. It seems, therefore, that most of the experimental observations on doped C_{60}, including the present ones, can be explained within the framework of a correlated system with positive U. However, we emphasize that for $x=3$ the edge is still metallic and that this behavior is quite reproducible. It seems unlikely, therefore, that the $x=3$ phase is a Mott-Hubbard insulator [8] but rather that it is a correlated system in the intermediate coupling regime.

Finally, let us stress a feature which is difficult to understand not only with a model of rigid-band filling but also using the positive correlation concept and that is the observation that the distance of the Fermi level from the top of the HOMO band ($E_f - E_H$) does not increase (actually it decreases slightly) for $x > 3$ [21]. In a correlated system with positive U a jump $\Delta E = U/2$ is expected for E_f when the filling goes from half ($x=3$) to full ($x=6$) due to the double filling of the states. Since the estimated correlation energy for C_{60} is $\simeq 1.6$ eV, the distance $E_f - E_H$ going from $x=3$ to $x=6$ should *increase* by ~ 0.8 eV, contrary to what is experimentally observed. In order to keep constant the Fermi level position when going from half to full filling, a correlated system should have a *negative* U. This is certainly true in the strong correlation limit [22]. We arrive therefore at the rather intriguing conclusion that in order to explain the E_f behavior in solid C_{60} one of the following two possibilities should be investigated: either E_f remains constant for U positive in the intermediate coupling regime or a new effect should be looked for which offsets the positive correlation resulting in an effective negative U^* that tends to pair electrons. This possibility was suggested [23] as a mechanism for the superconductivity in these materials.

In conclusion, we have investigated the electronic states of doped C_{60} by means of photoelectron yield spectroscopy excited with low energy photons, a technique which allows both a high resolution and a high dynamical range. The Fermi edge on the decreasing side of the density of states was identified. It was found that for $x \leq 3$ the edge is metallic but K_4C_{60} is clearly insulating. The behavior as a function of doping is not one-electron-like and requires correlation effects in order to be understood. Puzzling enough the behavior of E_f for $x > 3$ resembles that of a correlated system with negative U.

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