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Electronic structure close to E_F in low-level alkali-doped C_{60}

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Abstract. High-resolution photoemission study of the valence-band electronic structure of A_xC_{60} ($A \equiv K$ or Cs ; $x \lesssim 3$) close to E_F reveals a phase separation into components exhibiting a dilute solid solution of alkali in fullerite (α - C_{60}) and A_3C_{60} . The α - C_{60} phase is found to be remarkably stable against oxidation. Our analysis shows a strongly correlated electronic system in this phase. The similarity of the present data to previously published results for Li-, Na- and Rb-doped C_{60} demonstrates the common character of the observed phenomena for this series of alkali-doped fullerenes.

1. Introduction

In spite of the large number of spectroscopic and theoretical studies of alkali-doped fullerenes A_xC_{60} [1–14] there is still no established interpretation of the electronic structure of those novel materials close to the Fermi level E_F . The analysis of the experimental spectra is complicated for several reasons, including

- (i) a phase separation into A_xC_{60} with components such as C_{60} , α - C_{60} , A_3C_{60} and A_6C_{60} [3, 9, 15],
- (ii) a possible strong electron–phonon (plasmon) interaction [8, 9] and
- (iii) correlation effects [5, 9, 16].

The photoemission (PE) structure close to E_F in superconducting A_3C_{60} as well as in A_4C_{60} , which originates from the lowest unoccupied molecular orbital (LUMO) of C_{60} , cannot be interpreted by only a simple filling of the LUMO band by valence electrons of alkali atoms as was expected earlier [11, 12]. The half-occupied LUMO-derived PE band in A_3C_{60} is even broader than that of the LUMO states in pure C_{60} [2, 17]; in addition, the A_4C_{60} phase reveals a rather insulating behaviour [7, 9]. These problems could also have their origin in the surface sensitivity of PE, which makes it difficult to obtain bulk information from molecular crystals, whose structural units have a diameter comparable with the electronic mean free path [6].

Recent observations [2, 7, 9, 18] reveal an additional structure for very low alkali concentrations in the energy region close to E_F , which can hardly be assigned in the

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framework of single-particle theories. On the other hand, some experimental studies even claim the existence of a gap at E_F in the electronic states of A_3C_{60} [4, 5], with the consequence that not this phase but an off-stoichiometric composition would be responsible for high-temperature superconductivity in A_xC_{60} [5]. The results of Lof *et al* [5] provide evidence that undoped C_{60} and probably also K_3C_{60} can be regarded as Mott–Hubbard insulators with a correlation energy of about 1.6 eV in C_{60} and a gap of about 0.7 eV in K_3C_{60} . Other workers [2, 9] have demonstrated the importance of Hubbard-like band splitting in K_4C_{60} and Rb_4C_{60} as well as in Li_2C_{60} and Na_2C_{60} , while the majority of studies reveal a finite electronic density of states at E_F in K_3C_{60} and Rb_3C_{60} [8–10].

The present study addresses some of these questions by the use of valence-band PE of C_{60} doped with K and Cs at relatively low concentrations.

2. Experimental details

The experiments were performed at the SU6 beam line of the SUPER-ACO LURE storage ring in Orsay using the 1.3 m undulator as a photon source. Photoelectrons excited at the photon energy of 22 eV were collected in normal-emission geometry at the VSW-ARIES set-up with a total system resolution of about 100 meV (FWHM). The photoelectron spectra were least-squares fitted with Lorentzian line profiles convoluted by a Gaussian to account for the finite experimental resolution.

The pure-phase C_{60} powder was sublimed from a degassed quartz crucible onto Ar-sputtered Ta or *in-situ* cleaved GaAs(110) substrates at room temperature. The evaporation of C_{60} was performed at a crucible temperature of about 400 °C, with the pressure rising to the low 10^{-9} Torr range. The amount of C_{60} deposited was determined with a quartz microbalance.

Solid films of A_xC_{60} were prepared by deposition of K and Cs from commercial SAES getter sources onto the C_{60} films at pressures better than 4×10^{-10} Torr. In order to achieve a homogeneous dopant concentration, the samples were subsequently annealed at about 120–160 °C. Dopant levels were estimated by direct comparison of the relative PE intensities of signals derived from the highest occupied molecular orbital (HOMO) and the LUMO state of C_{60} with those of A_6C_{60} as a reference with the highest possible alkali concentration [19]. These ratios were previously calibrated by core-level PE, which was performed together with valence-band PE in a wide range of photon energies including 22 eV.

3. Results

Valence-band PE spectra recorded at $h\nu = 22$ eV of C_{60} films (about 80 Å thick) doped with K are shown in figure 1. The spectra cover the region of the HOMO and the next-highest occupied molecular orbital (HOMO+1) states. For comparison, the PE spectrum of gas-phase C_{60}^- ions reported in [20] is reproduced as the thin full curve in the centre of the figure. A similar set of valence-band PE spectra was obtained for C_{60} films doped with Cs (not shown). The observed binding energy (BE) shifts and the broadening of the HOMO and HOMO+1 states upon alkali-metal doping are consistent with previous results [3, 21]. In the present study, emphasis was put on spectral structures close to E_F (with BEs less than 1.5 eV), which are shown enhanced in figure 1. The broken curve (component B) and the chain curve (shaded area) (component A) are the results of the least-squares fit analysis.

Note that, for doping levels $x \lesssim 3$, the present results clearly indicate a finite density of states at the Fermi level, in contrast with previous studies [4, 5].

For low doping concentrations of K ($x < 2.5$) a doublet structure with peaks A and B, located at BES of about 1.0 eV and about 0.4 eV, respectively, is observed. With increasing x , the relative weight of peak A increases up to $x = 0.8$ and then decreases to almost 0 at $x = 2.5$. In contrast the relative weight of peak B grows gradually in such a way that the integral intensities of features A and B linearly scale with the doping level.

Previously, similar effects have been observed in K-doped C_{70} [3] and Li- or Na-doped C_{60} [2], while no indications for the same phenomena in PE spectra taken at $h\nu = 65$ eV have been obtained upon doping of C_{60} with K [3] or Rb [2]. In contrast with the above observations, Takahashi *et al* [18] employing a lower photon energy of 20 eV have found the double-peaked PE structure close to E_F for very low Rb concentrations in C_{60} as well. Recent PE studies performed with He lamps [8, 9] resulted in similar effects for the K-doped fullerite. The representative PE spectra from [8, 9] together with the corresponding spectrum from the present study ($x = 1.7$) in the region of BES less than 1.5 eV are shown in the inset of figure 1. All three spectra have similar shapes in the energy region of feature A. The bottom spectrum measured at the temperature of 40 K [9] has a much sharper leading edge compared with the other two spectra taken at room temperature.

According to [3, 22] an exposure of C_{60} to K at room temperature produces a dilute solid solution, α - C_{60} , when the amount of K is below the solubility limit and the film is in thermodynamic equilibrium. Phase separation into α - C_{60} and K_3C_{60} occurs when the K concentration exceeds the solubility limit. In contrast with the low-BE feature B, structure A cannot be assigned to the K_3C_{60} phase [8, 9]. On the other hand the supposition that A relates to the α - C_{60} phase is supported by direct comparison of the $K_{1.7}C_{60}$ spectrum and the spectrum for one-electron-charged fullerene ions (C_{60}^-) in the gas phase [20] (figure 1). The gas-phase spectrum is positioned by alignment of the BE of its HOMO with the HOMO in the $K_{1.7}C_{60}$ spectrum. The observed 0.2 eV energy shift of the low-energy bump in the C_{60}^- spectrum compared with the position of feature A can be explained by the effect of the alkali environment, since energy separation of feature A from HOMO depends on the distance between the alkali and the centre of the C_{60} cluster [23].

On exposure of A_xC_{60} films to an oxygen atmosphere we have obtained an additional argument to assign feature A to the dilute solid solution of alkali in fullerenes. The PE spectra of $Cs_{2.1}C_{60}$ taken at a photon energy of 22 eV before and after oxidation are shown in figure 2. The different subspectra display the result of a least-squares fit analysis. Independently of the initial alkali concentration the signal in the energy region close to E_F (feature B) is suppressed for low oxygen exposure. At the same time the intensity of structure A grows, reaching a value close to the intensity of the related feature for the fullerenes with the doping level $x = 0.8$. Similar effects have been obtained for K-doped C_{60} with various doping concentrations. The suspicion that feature A relates to the formation of alkali oxide can be ruled out, since much higher O_2 exposure which cause the growth of new structures originating in the K-O interaction [24] (see inset in figure 2) results in the disappearance of structure A. Fullerene itself is stable against oxidation [25].

According to Benning *et al* [3], the oxidation of K_xC_{60} causes K to leave the film followed by K-O reaction at the surface. A high activation energy for O_2 diffusion through fulleride prevents K oxide formation internally. The deficiency of alkali in the fulleride results in a reduction in the number of electronic states at E_F , which is observed as the intensity suppression of feature B after O_2 exposure (figure 2). As a result of these processes, only a few alkali atoms remain in the bulk of the fulleride, forming the dilute solid solution characterized by feature A in the related PE spectra.

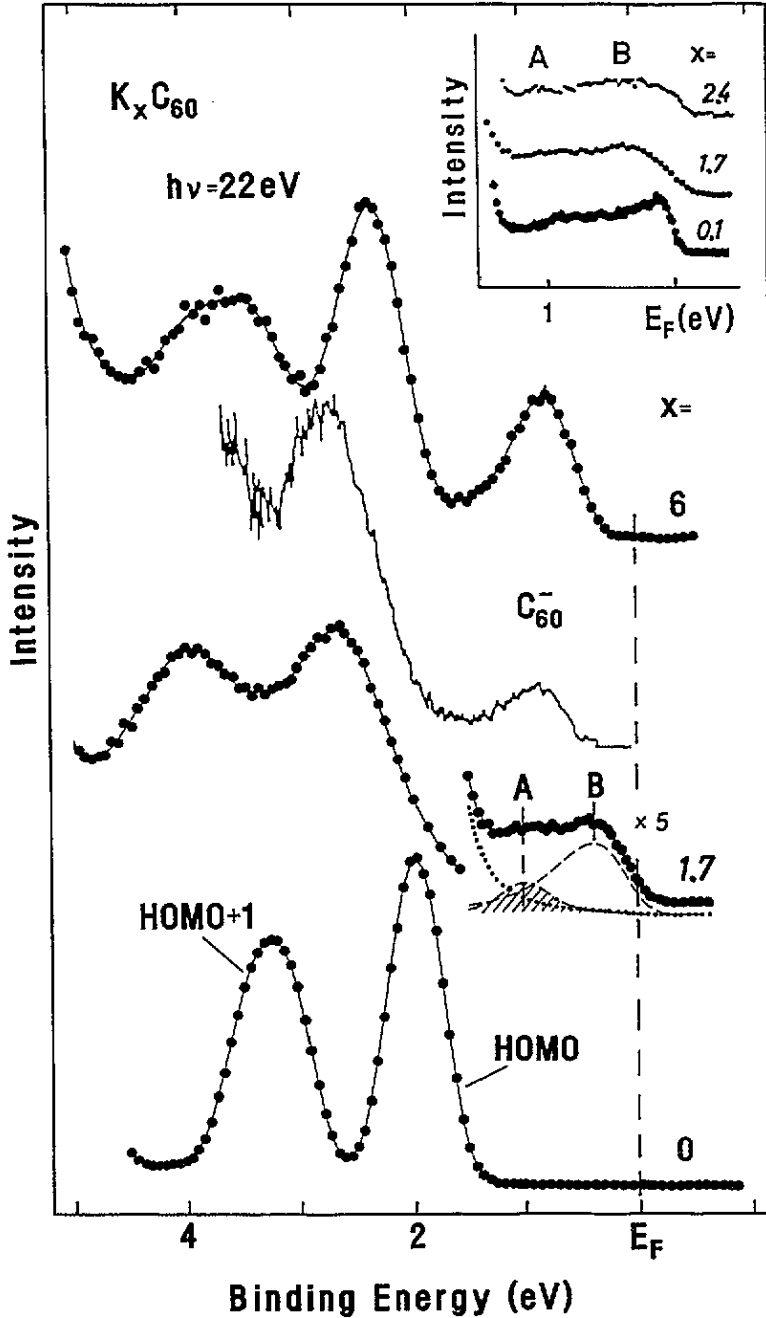


Figure 1. Valence-band PE spectra of K_xC_{60} taken at $h\nu = 22\text{ eV}$ for various doping concentrations x , together with the results of least-squares fit analysis of structure A (— · —, shaded area) and structure B (---). The spectra are normalized to the photon flux. The thin full curve in the centre represents the PE spectrum of C_{60}^- clusters in the gas phase measured at $h\nu = 6.4\text{ eV}$ [20]. The inset demonstrates correlation of spectral structures close to E_F obtained in the present study (middle curve) and reported in [7] (upper curve) and [9] (lower curve). The latter two spectra have been taken at $h\nu = 21.2\text{ eV}$.

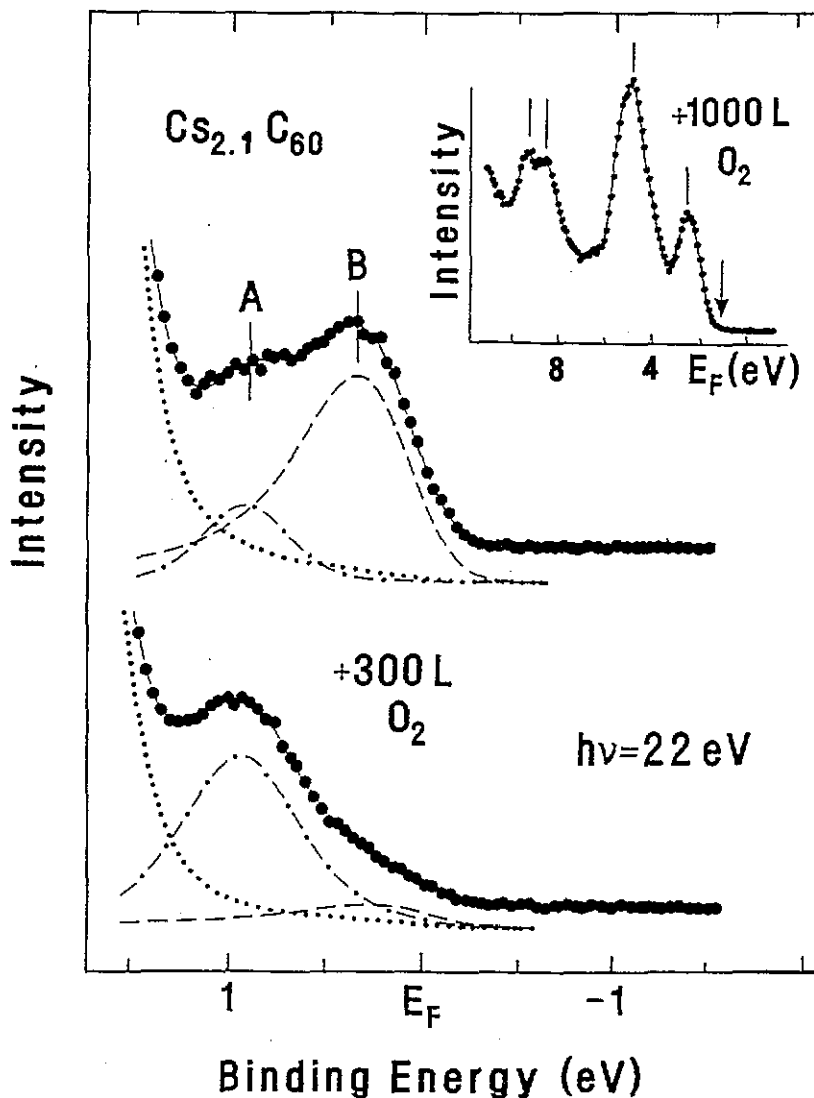


Figure 2. PE spectra in the region close to E_F taken at $h\nu = 22 eV$ for $Cs_{2.1}C_{60}$ as grown (upper spectrum) and after the exposure to an O_2 atmosphere at 300 L (lower spectrum). The inset shows the valence-band PE spectrum of K-doped C_{60} after its oxidation by O_2 at 1000 L.

Recently, incorporation of alkali into the solid C_{60} ($x \lesssim 3$) at room temperature and elevated temperatures has been investigated by core-level PE [22]. It has been found that, at room temperatures, K_xC_{60} ($x \lesssim 3$) consists of phase-separated $\alpha-C_{60}$ and K_3C_{60} . A reversible transformation with an invariant eutectic reaction $\alpha-C_{60} + K_3C_{60} \leftrightarrow KC_{60}$ was observed at elevated temperatures. The eutectic temperature is $150 \pm 10^\circ C$. The reactions observed were completed over approximately a $20^\circ C$ range of temperatures on a time scale of about 30 min. Raman-scattering experiments [26] have also indicated a KC_{60} phase, although at a lower temperature (about $80^\circ C$).

Figure 3 represents the cycle of the reversible spectral-shape transformation upon

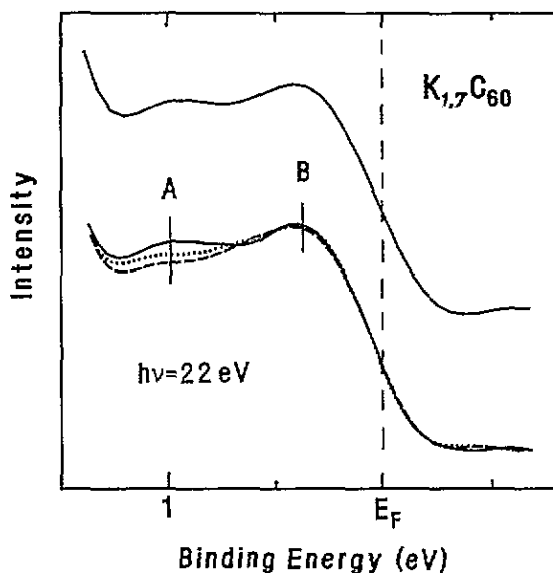


Figure 3. Valence-band PE spectra of $K_{1.7}C_{60}$ close to E_F measured as grown at room temperature (lower curves, —) and immediately after annealing for 10 min (lower curves, ·····) and 15 min (lower curves, - - -) at 150°C . The corresponding spectrum upon cooling the sample to room temperature is shown as the upper curve.

annealing of $K_{1.7}C_{60}$ at a temperature of 150°C for various periods of time (lower curves) and after cooling to room temperature (upper spectrum). The main differences are observed in the region of feature A, which almost disappears during annealing (from the full to the broken curve) and appears again upon cooling to room temperature. The PE spectra obtained at room temperature before and after annealing have similar shapes. On the basis of the previously reported results [22] these observations also support the assignment of the 1 eV PE feature to the α - C_{60} phase of fullerites.

The possible surface effects on the electronic structure of alkali-doped C_{60} have been studied by varying the electron detection angle. As in [8, 9] we did not find noticeable difference between the shapes of valence-band PE spectra recorded at normal and grazing electron emission.

4. Discussion

An alternative understanding of the structure of valence-band PE spectra could be based on the recent theoretical studies applying the Car-Parrinello method [27] or the Su-Schrieffer-Heeger model [28]. These studies claim an essential alkali-metal-induced distortion of C_{60} intramolecular bonds. As a result of this process, one energy level splits upwards from the fivefold-degenerate HOMO. These characteristic 'polaron excitation' changes [28] might be the origin of the experimental findings of electronic structure in alkali-doped fullerites close to E_F . However, our observations rule this possibility out. First, the PE signal of feature A is less than a thirtieth of the intensity of the HOMO-derived band, while according to [28] the ratio should be a quarter. Second, the energy shift of feature A relative to HOMO by far

exceeds the theoretically obtained value of about 0.35 eV. Finally, structure A shows no shift on doping, which is predicted in [28].

The linear scaling of the overall PE intensity in the region of low BEs (less than 2 eV) with doping supports the assumption that all PE structures appearing there originate from the LUMO-derived electronic states. Gu *et al* [2] on the basis of PE and inverse photoemission (IPE) studies of Na_xC₆₀ claim that feature A (PE) as well as the doublet structure of the LUMO-derived unoccupied band (IPE) for low alkali concentrations reflect the formation of a pair of non-degenerate unfilled bands and the additional LUMO-derived occupied band to be a simple result of the reduced symmetry in alkali-doped C₆₀ films. However, such a large crystal-field splitting between structure A and the LUMO-derived unoccupied bands (about 1.7 eV) seems unlikely; moreover other bands (HOMO, HOMO+1 etc) show no evidence for similar splitting.

The PE spectrum for the gas phase of C₆₀⁻ ions [20] presented in figure 1 proves that structure A cannot be directly related to the crystal-field splitting of LUMO nor to the effect of alkali atoms at all. It appears to be solely due to the charge of C₆₀ clusters by adding only one electron.

On the other hand, there are several indications that the alkali-doped fullerites can be considered to be highly correlated systems [5, 29]. Fairly localized electronic states in the LUMO of pure C₆₀ [17] cause a strong Coulomb interaction between the photoexcited alkali-transferred electron and the final-state localized hole in the LUMO. Note that there are almost no other electrons in the LUMO band of α -C₆₀ to screen this interaction. The weak screening of the localized final state results in an increase in the BE observed in PE compared with the ground-state value. This might give the obtained shift of about 1.0 eV away from E_F for feature A, especially as similar effects are known to result in even larger shifts of the localized weakly screened valence states in PE (e.g. about 6.0 eV for 3d valence states in metallic Ni) [16]. An increase in the number of electrons in the LUMO upon doping causes an improved screening of the final-state configuration, which drives the PE intensity back to E_F . The admixture of α -phase C₆₀ may serve as a reason for the observed broadening of PE electronic structure close to E_F in superconducting fullerides.

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