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Resonant photoemission study of *K*-derived valence-band states in K_XC_{60}

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Abstract. The electronic structure of K-doped C_{60} was investigated by photoemission (PE) and X-ray absorption near-edge structure (XANES) studies at the C-1*s* and K-2*p* thresholds. In addition, information on the local K-derived partial density of states in superconducting K_3C_{60} was obtained by resonant PE at the K-$2p_{1/2}$ threshold. The experimental observations support a complete charge transfer from K to C_{60} and we clearly observe a finite density of states at E_F. From resonant PE, occupied states with K-*p*, *d* character could be identified in the binding-energy region from 1.5 to 8 eV below, but not directly at the Fermi level. This partial-density-of-states structure agrees well with the results of our band-structure calculations based on the local-density approximation.

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I. Introduction

The recent discovery of superconductivity in alkali-doped C_{60} [1] has led to a series of experimental and theoretical activities in this field [2–11]. A detailed knowledge of the electronic structure close to the Fermi level, E_F, is of particular interest, since these states are directly involved in electrical transport and superconductivity. According to theoretical predictions, the alkali atoms transfer their valence electron to the fullerene [9–11], gradually filling up the lowest unoccupied molecular orbital (LUMO) of C_{60} and, in this way, leading to metallic properties.

Most studies of alkali-doped C_{60} compounds concentrated on the K_xC_{60} system. The structure of superconducting K_3C_{60} has been solved, with the K ions occupying the tetrahedral and octahedral interstitial sites of the fcc lattice; the LUMO-derived band is half-filled in K_3C_{60}. The insulating K_6C_{60} compound, with the highest K concentration possible, has a bcc structure, where the alkali ions occupy the tetrahedral interstitital sites; in this case, the LUMO-derived band is completely filled. For intermediate stoichiometries, the occurrence of a phase separation has been reported [2].

Previous photoemission (PE) [3–7], inverse photoemission (IPE) [3], and X-ray absorption near-edge structure (XANES) [4] studies have provided a wealth of information on the occupied and unoccupied density of states of alkali-doped fullerides. These methods are particularly useful for investigating C-derived electronic states due to the considerable excess of C atoms as compared to K. On the other hand, the K-derived valence electrons as well as the process of charge transfer from K to empty C_{60} states play a crucial role in the formation of these compounds as well as in the occurrence of superconductivity [9–11]. Until now, the nature of electronic states close to E_F is not fully understood, in particular, the degree of charge transfer from K to C_{60}. There is also a substantial discrepancy between experimental results for superconducting K_3C_{60} and the calculated electronic structure close to E_F [5, 11].

In the present study, we employ resonant PE at the K-$2p_{1/2}$ absorption threshold in order to obtain information on the partial K-derived electronic density of states close to E_F. Resonant PE is based on an interference between direct PE and a discrete deexcitation channel of the core-excited intermediate state leading also to the PE final state [12]. It can give rise to a strong resonant enhancement of the PE cross section if both the initial state and the core-excited intermediate state are at least partially localized [13]. While it is generally accepted that *p*-electrons are less localized than *d*- and particularly *f*-electrons in solids, the strong molecular origin of the electronic structure of the fullerenes is expected to favor the resonant PE channel.

The main results of the present study concern *(i)* the evolution of the LUMO-derived electronic states of K_xC_{60} with the level of K doping and *(ii)* the structure of the K-derived partial density of states in the binding-energy region close to E_F. The assumption of a complete charge

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transfer from K to C_{60} is confirmed, and we clearly observe a finite density of states at E_F in case of K_3C_{60}. The structure of K-derived valence-band states in the binding-energy region from 1.5 to 8 eV below E_F is in good agreement with the results of our band-structure calculations based on the local-density approximation. However, no K-derived states could be identified in the region directly below E_F.

II. Experimental procedure

The experiments were performed at the SX700/II beamline of the Freie Universität Berlin at the Berliner Elektronen-Speicherring für Synchrotronstrahlung (BESSY) [14], employing an experimental chamber equipped with a VG-CLAM electron-energy analyzer. The PE spectra were taken at a photon energy of 65 eV with a total-system resolution of 150 meV (FWHM); XANES spectra were recorded in the total-electron-yield mode with a resolution of 100 meV (FWHM).

C_{60} powder was produced by the contact-arc method [15] with subsequent purification by liquid-phase chromatography. Fullerite films with a thickness of ≅80 Å were prepared by in-situ deposition of pure C_{60} powder from a commercial UHV-Knudsen cell at a temperature of 400 °C onto an Ar-sputtered Ta substrate kept at room temperature; during deposition, the pressure rose to the low 10^{-9}-Torr range. Prior to deposition, the Knudsen cell was degassed at 200 °C for 24 h during bakeout of the experimental chamber; in the cooling phase, the cell temperature was increased for 1 h to 400 °C. The resulting C_{60} films were characterized by high-resolution PE ($\Delta E \cong 20$ meV, FWHM) in a separate experimental set-up equipped with a VSW-electron-energy analyzer at KFK Karlsruhe, using a He-discharge lamp. These HeI PE spectra (not shown here) confirmed the high purity of the C_{60} films obtained by this procedure [16, 17].

Solid films of K_xC_{60} were prepared by deposition of K from a well-degassed commercial $KCrO_3$ dispenser onto the C_{60} films. To achieve homogeneous dopant concentrations, the samples were subsequently annealed at ≅100 °C for 20 min; further annealing did not lead to noticeable changes of the doping quality. Dopant levels were determined by comparing relative intensities of C-1*s* and K-2*p* core-level PE lines for a given K_xC_{60} film with those obtained for the reference phase K_6C_{60} that containes the highest possible K content [2]. Also used was a direct comparison of HOMO- and LUMO-derived PE peak intensities, since these states are expected to have similar PE cross sections due to identical symmetry and parity [18]. The two methods, with quite different surface sensitivities, resulted in essentially the same K doping levels. This shows that the composition at the surface does not noticeably deviate from that in the bulk. The K concentrations obtained lead to reasonable agreement between the present valence-band PE spectra and previously published data [3, 6, 7, 19]. While samples for $x<6$ normally exhibit phase separation into C_{60}, K_3C_{60}, K_4C_{60}, and K_6C_{60} phases [3, 4], the compound with $x=3$ is expected to be single phase due to the higher stability of K_3C_{60} as compared to other phases [2]. However, in agreement with other authors [3, 20], we cannot fully rule out the presence of a certain amount of off-stoichiometric K_3C_{60}. We refer here to the claim of Lof et al. [20] that such off-stoichiometric components are even responsible for superconductivity in alkali-doped fullerites.

The electronic structure of fcc K_3C_{60} was calculated using the density-functional theory with the local-density approximation and the linear muffin-tin-orbitals-atomic spheres approximation with carefully chosen interstitial spheres [11]. As described in more detail in [11], the K atoms were placed in octahedral and tetrahedral interstitial positions. The lattice parameter and bond lengths were chosen to be 14.24 Å, 1.45 Å, and 1.37 Å, respectively; charge selfconsistency was obtained at three irreducible *k* points. The density of states for the selfconsistent potential was calculated using the full-zone tetrahedron method with 63 irreducible points in *k* space.

III. Experimental results and discussion

The preparation of solid films of K_xC_{60} was monitored by taking valence-band PE and C-1*s* XANES spectra as shown in Fig. 1. The PE spectra were recorded at a pho-

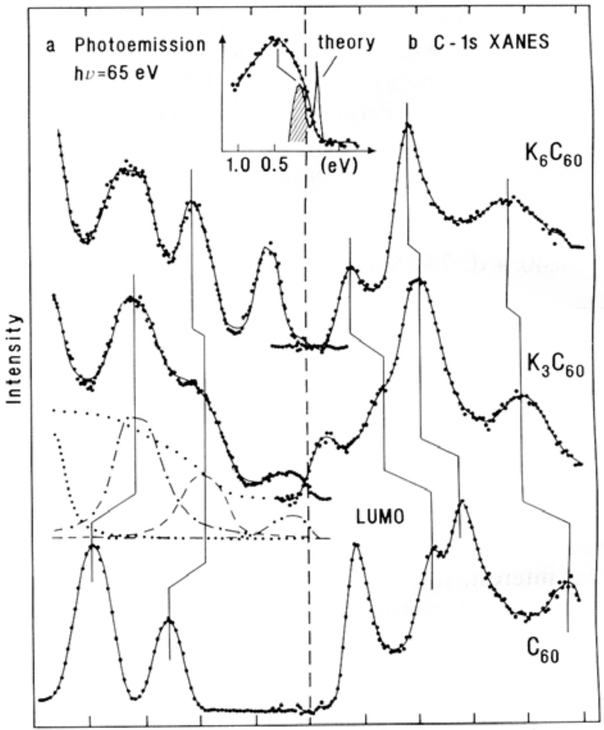

Fig. 1. a Valence-band PE spectra of solid films of C_{60}, K_3C_{60}, and K_6C_{60}, taken at a photon energy of 65 eV. The solid lines through the data points represent the results of least-squares fit analyses, with component lines given in case of the K_3C_{60} spectrum (see text). The inset shows the Fermi-level region of the PE spectrum of K_3C_{60} in comparison to the calculated LUMO-derived density of states. **b** XANES spectra at the C-1*s* threshold taken in total-electron-yield mode

ton energy of 65 eV in order to ensure similar cross sections for PE from HOMO and HOMO + 1 states [21]. In the XANES spectra, the energy scale relative to E_F was calibrated by assuming that the Fermi level crosses the LUMO-derived band in case of K_3C_{60}. In general, the results are in good agreement with PE and inverse PE data of Benning et al. [3, 7]. This shows that possible correlation and/or excitonic effects are not noticeably influencing the X-ray absorption spectra of pure and doped fullerenes. Both the occupied and unoccupied electronic states exhibit non-rigid shifts with increasing K content. Least-squares fit analysis show that the integral intensity of the LUMO-derived occupied states in the center K_3C_{60} spectrum is about 3 times smaller than that of the HOMO states; this is close to the theoretical prediction for K_3C_{60} [11]. While the spectra for undoped C_{60} and fully-doped K_6C_{60} are in conformity with insulating behavior, K_3C_{60} has states directly at E_F giving rise to the metallic properties of this phase. These states form an asymmetric PE peak at E_F, intersected by the Fermi distribution function (see inset in Fig. 1), in agreement with our calculations. The latter predict for K_3C_{60} that the Fermi level is situated in the center of the density-of-states doublet derived from LUMO, at the trailing edge of the low-binding-energy peak (see inset in Fig. 1). The observation of a finite density of states at E_F, as reported also by Chen et al. [4], is at variance with the recent claims [6, 20] that an insulating "pseudo-gap" opens up in K_3C_{60} at E_F. In agreement with previous results by Benning et al. [3], we also observe a shift of the LUMO states with increasing K concentration, favoring a gradual filling of LUMO states by valence electrons of K rather than the creation of a new "polaron-band" in the insulating gap of C_{60} [6].

Our PE spectrum of the half-doped film reveals a much broader structure originating from the LUMO-derived band ($\cong$1.0 eV, FWHM) than predicted by the single-particle approximation (see inset in Fig. 1); it is also broader than the LUMO structures observed for C_{60} and K_6C_{60}. This can result from phonon satellites [22] or from secondary-electron excitations, which – particularly in case of metallic K_3C_{60} – can give rise to energy losses of the photoelectrons. A different explanation is suggested by the observations of Takahashi et al. [5], who found double-peaked PE structures in the Fermi-level region for very low K concentrations. This suggests that the formation of K_xC_{60} can result in a rearrangement or hybridization of K- and C-derived states at the Fermi level in K_3C_{60}, contrary to expectations in a simple charge-transfer model. The additional peak in the Fermi-level region can also be interpreted on the basis of recent theoretical results [20, 23], which consider doped C_{60} as a highly correlated system.

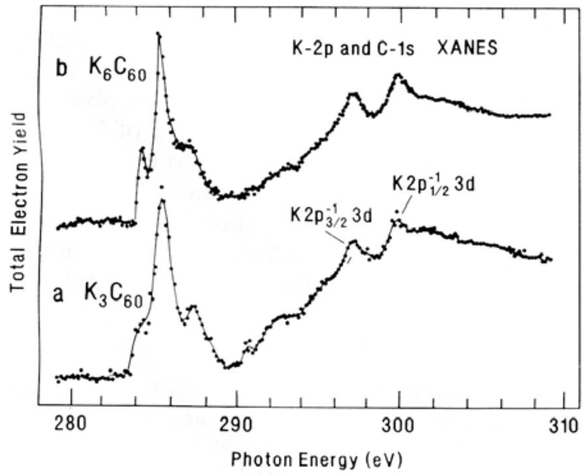

Fig. 2. XANES spectra of solid films of **a** K_3C_{60} and **b** K_6C_{60} taken at the C-1*s* and K-2*p* thresholds

A XANES spectrum of K_3C_{60} was recorded over a wide energy range including the C-1*s* and K-2$p_{1/2,3/2}$ thresholds (see Fig. 2a) in order to determine the energies of K-2$p_{1/2,3/2} \rightarrow 3d$ inner-shell excitations. The peaks at 297.0 eV and 299.7 eV, respectively, result from excitations of K-2$p_{3/2}$ and K-2$p_{1/2}$ electrons; this assignment is supported by the energy separation between these two peaks, which is identical to the $2p_{1/2} - 2p_{3/2}$ spin-orbit splitting as observed in K-2*p* core-level PE. A comparison with the XANES spectrum of K_6C_{60}, displayed in Fig. 2b, shows that the K-2$p \rightarrow 3d$ spectral features are indeed very similar for both phases.

In order to separate out a possible core-level PE signal due to second-order light originating from the grating monochromator [24], we studied the K-2$p_{1/2} \rightarrow 3d$ resonant excitation at $h\nu = 299.7$ eV. Here, less overlap between valence-band resonant PE and core-level PE due to second-order light is expected as compared to the K-

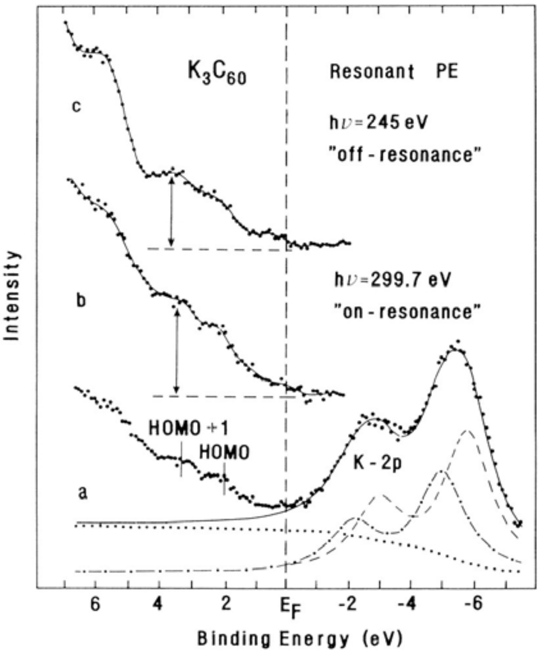

Fig. 3. a Resonant PE spectrum of K_3C_{60} at the $2p_{1/2} \rightarrow 3d$ threshold taken at a photon energy of 299.7 eV. The K-2*p* core-level PE doublet due to second-order light was described by a superposition of two doublets (see text), with the solid line through the data points representing the result of such a least-squares fit analysis. **b** Resonant PE spectrum of K_3C_{60}, with the contribution from second-order light subtracted. **c** Off resonance PE spectrum of K_3C_{60} taken at $h\nu = 245$ eV

$2p_{3/2} \rightarrow 3d$ excitation. The resulting PE spectrum of K_3C_{60} in the region of LUMO, HOMO, HOMO + 1, and HOMO + 2 states is shown in Fig. 3a. The strong doublet above E_F is due to PE from K-$2p$ core levels excited by second-order light. This doublet was least-squares fitted on the basis of a K-$2p$ PE spectrum taken in the second-order-light mode at a higher photon energy, where core-level PE and valence-band PE signals do no longer overlap. In agreement with Poirer et al. [2], the K-$2p$ PE spectrum consists of a pair of spin-orbit-split doublets with an energy separation of 1.05 eV, corresponding to the two inequivalent tetrahedral and octahedral sites for K atoms in the fcc lattice. The resulting on-resonance PE spectrum, after subtraction of the K-$2p$ contribution from second-order light, is given in Fig. 3b. For comparison, Fig. 3c shows also an off-resonance spectrum taken at $h\nu = 245$ eV.

Measurements of the off-resonance PE spectrum directly below threshold were not possible due to the PE signal by second-order-light from K-$2p$ and C-$1s$ core levels, which overlaps the normal valence-band PE signal in this case. The fact that the off-resonance PE measurements were performed at $h\nu = 245$ eV will unlikely effect the results, however, since at high photon energies changes of the PE cross section are usually much smoother functions of energy [25] than the differences between on- and off-resonance spectra.

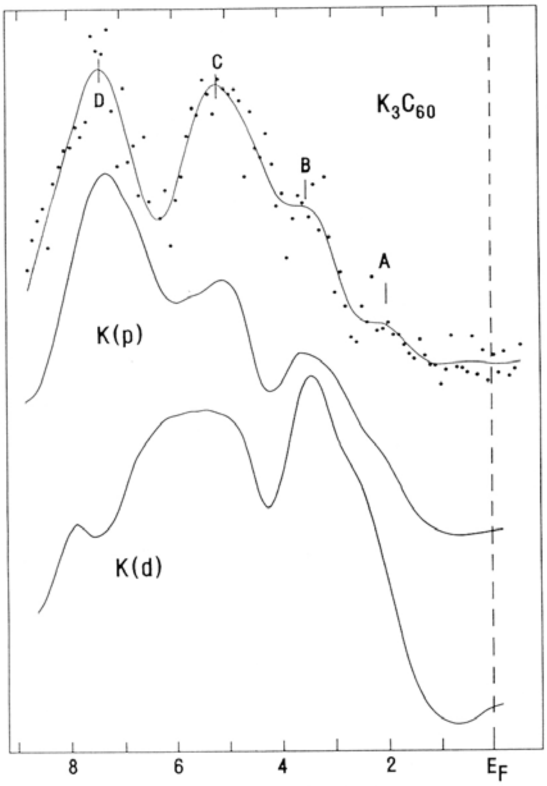

Fig. 4. Comparison of the net resonantly enhanced PE signal (difference of spectra *(b)* and *(c)* in Fig. 3) with theoretical results for the K (p) and K (d) partial density-of-states of K_3C_{60}; the latter were broadened in consistency with a finite experimental resolution of 0.45 eV (FWHM)

The spectra (b) and (c) were normalized to equal intensities at a binding energy of 9 eV, since our calculations show that there are practically no potassium-derived electronic states in this energy region. A comparison of the on- and off-resonance valence-band PE spectra reveals no difference in the spectral intensities at E_F. Instead, a resonant enhancement of the PE signal in the region of HOMO and HOMO + 1 bands can be clearly seen. This cannot be a simple cross section effect, since HOMO- and LUMO-derived states behave differently having the same symmetry and parity [18].

The pure resonantly enhanced PE signal in the region of the HOMO, HOMO + 1, and HOMO + 2 bands of K_3C_{60} was obtained by subtracting the off-resonance spectrum (Fig. 3c) from the on-resonance spectrum (Fig. 3b). The result is shown in Fig. 4, where – for comparison – also the calculated K-p and K-d partial density of states are plotted. The K-s partial density of states is negligible in this energy region as compared to K-p and K-d; in addition, it can hardly be observed with resonant PE due to its delocalized character. Both the experimental difference curve and the calculated partial density of states give no evidence for potassium-derived states close to E_F, at binding energies up to $\cong 1.5$ eV. For higher binding energies up to $\cong 5$ eV (maximum C), a gradual increase of the resonantly enhanced PE signal is observed (peaks *A* and *B*), decreasing again to a dip at $\cong 6.3$ eV and an additional peak *D* at $\cong 7.4$ eV.

A coincidence in energies of the calculated p/d-hybridized states with the peaks in the resonantly enhanced PE spectrum, particularly at binding energies from $\cong 1.5$ eV to $\cong 5.5$ eV, reveals the origin of the PE resonance in K_3C_{60}. The overlap of the K-p- and K-d-derived electronic states complicates an assignment of the resonant features to states with definite symmetry. We note, however, a better agreement of the experimental data with the theoretical K-p as compared to the K-d partial density of states, particularly, in the region of higher binding energies. The overlap of K-p/d hybridized states with C-derived states in K_3C_{60} can give rise to a broadening of valence-band PE structures in the region of the HOMO, HOMO + 1, and HOMO + 2 bands. The same argument, however, cannot be applied to explain the broadening of the LUMO state, since no K-p/d hybridized states were observed within 1.5 eV of the Fermi level. Therefore, correlation effects or electron-phonon interaction are more likely to be the cause of the observed broadening of the PE features in the spectra of K_xC_{60}.

In summary, the present study gives no evidence for potassium-derived localized occupied states at E_F. The highest occupied K-p/d-hybridized states are situated in the binding-energy region from 1.5 eV to 8 eV, i.e. in the region of bands derived from the HOMO, HOMO + 1, and HOMO + 2 states.

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