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ELECTRONIC STRUCTURE OF UNDOPED AND DOPED FULLERENES

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Abstract: The electronic structure of C₆₀ has been studied by electron energy-loss spectroscopy (EELS) in transmission, and by high resolution photoemission (PES) studies. Information on the occupied and unoccupied π , π^* , σ and σ^* band structure is obtained by photoemission and C1s absorption EELS measurements, respectively. In addition, the dielectric function of undoped C₆₀, as obtained from EELS measurements, show a clear gap of ~ 2 eV and several well pronounced $\pi \rightarrow \pi^*$ transitions. Upon doping with Li, Na, K, Rb, Cs and Ca, the filling of the lowest unoccupied molecular orbital (LUMO) band has been probed by both PES and EELS. For doping with divalent Ca, in addition the LUMO+1 band gets partially filled. Strong non-rigid-band behaviour is observed. The results are compared with theoretical calculations.

Introduction

The discovery of superconductivity in doped fullerenes, called fullerides, has lead to a large number of experimental and theoretical investigations in response to the challenge of understanding the electronic structure of these new and fascinating materials. In particular, knowledge of the electronic structure is a prerequisite for the understanding of the mechanism of high-T_c superconductivity. The question arises as to whether LDA calculations are adequate for this system, or whether electron-phonon coupling or electron-electron interactions are strong enough to cause serious deviations from the one-electron picture. Experimental determination of the electronic structure of the fullerenes has a vital role to play in this debate. Part of the data presented here have been published previously [1-3]. In the following, we discuss results from C₆₀, while analogous results from higher fullerenes as well as experimental details are found in Ref. 1-3.

Results

The photoemission data were recorded with a commercial VSW spectrometer, using a helium discharge lamp. The overall energy resolution was set to 25 meV for the present measurements. Synchrotron radiation photoemission and XPS measurements were recorded at the FLIPPER II beamline, HASYLAB. In Fig.1 we show the photoemission spectrum of the valence-band region of a C₆₀

film recorded with a photon energy of $\hbar\omega = 21.2\text{eV}$ for sample temperatures of 300K, 160K and 9K, together with the theoretical density of states (DOS) calculated in the LDA approximation [4]. The band structure results have been broadened to account for finite temperature and experimental resolution and shifted so that the onset of the h_{1u} -derived DOS matches the experimental result. The binding energy scale is referred to the Fermi level of a Au film. It can be seen that the widths and relative spacings of the bands are generally in good agreement between the calculation and experiment. The first two maxima at 2.3 and 3.6eV can be assigned to a group of 5 bands derived from the h_{1u} molecular levels, and a group of 9 bands derived from h_g and g_g states, respectively. Both have predominantly π electron character.

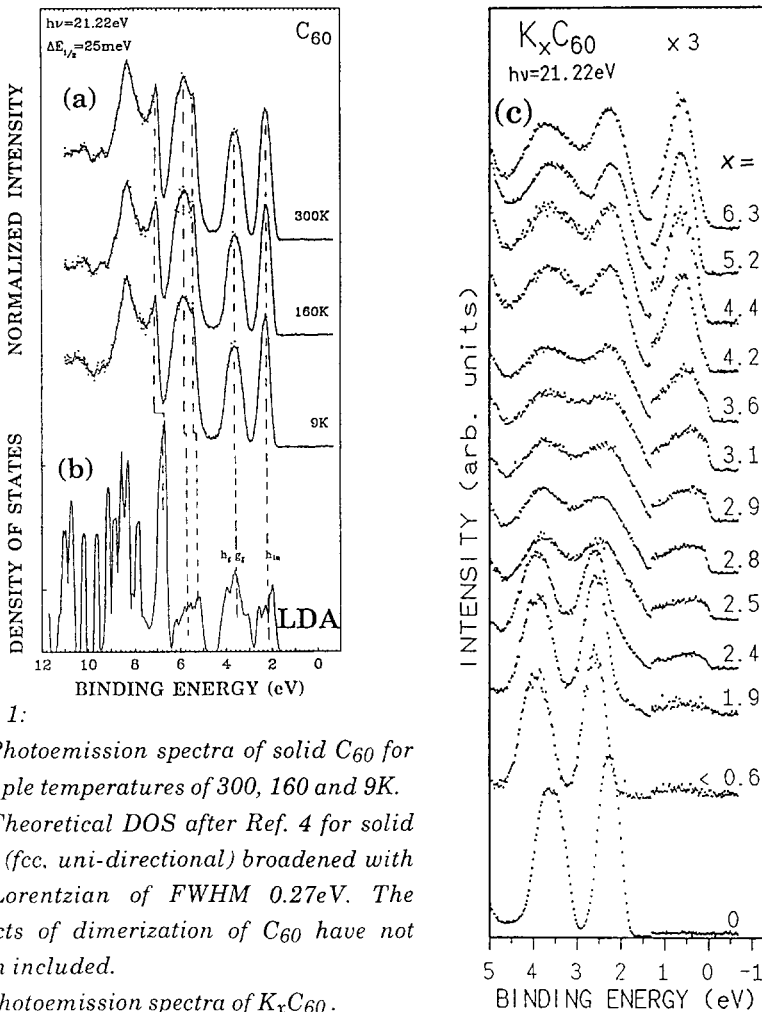


Fig. 1:

a) Photoemission spectra of solid C_{60} for sample temperatures of 300, 160 and 9K.

b) Theoretical DOS after Ref. 4 for solid C_{60} (fcc, uni-directional) broadened with a Lorentzian of FWHM 0.27eV. The effects of dimerization of C_{60} have not been included.

c) Photoemission spectra of K_xC_{60} .

The h_{1u} -derived bands (HOMO) have a total measured width of about 1 eV which is reproduced by the band structure calculation. However, the fine structure of the h_{1u} bands of Fig. 1b are not observed in the experiment, although the splitting between the maxima is an order of magnitude greater than the experimental resolution. In photoemission spectra of gas phase C_{60} [5], the line due to the h_{1u} state has a width of about 0.3 eV. The experimental width of the h_{1u} line in solid C_{60} may therefore be composed of a broadening due to band formation **and** due to excitations of intramolecular vibrations. In addition, there is a broadening due to lifetime effects, which can be estimated from the data on molecular C_{60} to be less than ~ 0.3 eV [5].

Various band structure calculations [4,6] predict considerable changes of the DOS due to structural changes at lower temperatures. Therefore, we have measured high resolution photoemission spectra as a function of temperature ($9K \leq T \leq 300K$, see Fig. 1a). Within experimental accuracy, no changes of the spectra have been observed indicating that spectral broadening due to various reasons is larger than changes of the DOS resulting from phase transitions.

Upon n-type doping with K a new peak close to the Fermi level appears due to the filling of the t_{1u} -derived conduction bands. At intermediate dopant concentrations a clear Fermi edge is observed, the spectral weight at E_F having a maximum at $x=3$, within error bars. The stoichiometry of the samples was monitored by XPS, thus giving an absolute value for the surface K-doping level. All spectra can be synthesised by a superposition of appropriately weighted spectra with $x=0, 3$ and 6 , confirming the three-phase nature of the K_xC_{60} system. Recently, an insulating phase due to correlation effects has been predicted for $x=3$ [7], and the existence of a pseudo-gap has been derived from photoemission and inverse photoemission data [8]. However, comparing the data of Ref. 8 to our data, we estimate their K-concentration to be near $x=5.5$ and not $x=3$, thus showing the gap of K_6C_{60} and not a pseudo-gap.

In K_3C_{60} there is a considerable broadening of the HOMO - and the (h_g, g_g) -derived bands compared to the undoped and fully doped case. The occupied part of the LUMO-derived bands is also broad: assuming half-filling this yields a total LUMO width of ~ 2 eV which is considerably larger than expected from band structure calculations.

There are several possible explanations for the broadening of the bands in the half-filled case. As a result of electron-phonon coupling, there may be a Jahn-Teller-like distortion of the C atoms within the C_{60} molecule, leading to a splitting of the molecular orbitals as a function of the filling of the LUMO level [9]. Calculations have been performed in the framework of a Su-Schrieffer-Heeger model leading to a maximal splitting of the molecular levels by some tenths of an eV for $x=3$ and a complete degeneracy for $x=0$ and $x=6$. In addition, the HOMO-LUMO gap is considerably reduced for $x=6$ in agreement with the experiment, which gives a value for the separation of the HOMO-LUMO maxima of 1.6eV. On the other hand, the anomalous broadening of the bands for intermediate x values could also be explained by correlation effects

on the C sites, although screening has been estimated to greatly reduce the magnitude of U in the metallic phase [10].

To probe the unoccupied DOS electron energy-loss data were recorded with a 170 keV spectrometer [11] in transmission. The energy and momentum resolution were set to 0.14eV and 0.04\AA^{-1} , respectively. For core excitation spectra, the momentum resolution was reduced to 0.2\AA^{-1} . In Fig. 2a we show the low-energy loss function, $\text{Im}(-1/\epsilon)$, of a C_{60} film measured by EELS for various momentum transfers, q . The peak at 2.2eV can probably be assigned as a singlet exciton related to the dipole forbidden h_{1u} - t_{1u} transition, which is enhanced with increasing momentum transfer up to $q \approx 0.9\text{\AA}^{-1}$, corresponding to a wavelength of $\approx 7\text{\AA}$, while it diminishes again at still higher momentum transfer ($q > 1\text{\AA}^{-1}$). Exactly this behaviour is expected for monopole transitions in C_{60} . The features at 2.7, 3.6 and near 6eV can be attributed to π - π^* transitions which may possess a degree of excitonic character. Having dipole character, their strength decreases with increasing momentum transfer ($q < 1\text{\AA}^{-1}$). Near 8.0eV, dipole forbidden but monopole or quadrupole allowed π - π^* transitions are observed. Using parameters refined from the fitting of photoemission data such as is shown in Fig. 1a, we have found that a majority of the transitions observed in the EELS studies can be assigned within an effective Su-Schrieffer-Heeger model. However, the validity of such a model in a system where electronic correlation may play an important role requires further consideration.

In Fig.2b we show the loss function of Rb_xC_{60} for $x=0, 3$ and 6 , and in Fig. 2c the C 1s absorption edges of the same samples. In the loss function for $x=3$, the gap is filled with two transitions, at 0.5eV and 1.2eV. The 0.5eV peak is assigned to a plasmon caused by an intraband transition within the LUMO-derived conduction bands. The second peak at 1.2eV is assigned to a transition between the partially filled LUMO-derived bands and the next group of π^* bands derived from the molecular t_{1g} level. The broadness of the structures compares to that of the UPS data for $x=3$. Due to the complete filling of the conduction bands, the lower energy peak disappears for $x=6$ and the peak at 1.2eV increases in intensity. The data shown in Fig. 2b are qualitatively in agreement with calculations of the loss function [12]. It is interesting to note that on going from $x=0$ to $x=6$ the peak at 3.6eV moves to 2.9eV. This again indicates a shrinking of the energy difference between π and π^* bands. This may be a result of a lowering of the dimerization in the doped case compared to the undoped case. This result is in agreement with theoretical calculations [9,10].

Neglecting core hole effects, the C 1s absorption edges shown in Fig. 2c represent the C2p-derived unoccupied DOS of Rb-doped C_{60} . They clearly illustrate the progressive filling of the LUMO with doping. This is manifest in the systematic reduction of the first peak, which results from transitions from the C 1s level to unoccupied LUMO states. The chemical shift of the C 1s core level on doping results in the shift of the spectra to lower energies with

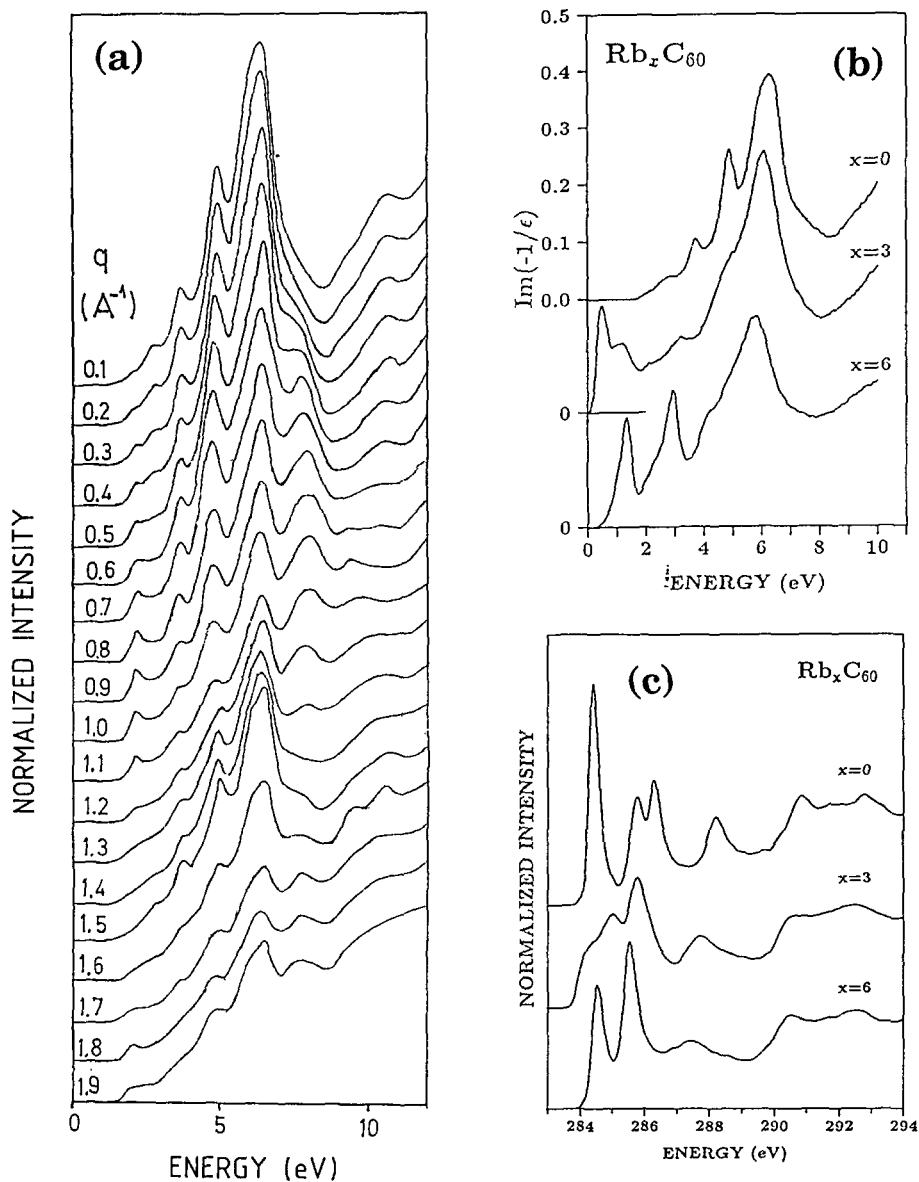


Fig. 2 a) Low-energy loss function of C_{60} for various momentum transfers, q (in \AA^{-1}) measured by EELS.
 b) Low-energy loss function measured by EELS for Rb_xC_{60} .
 c) C 1s absorption edges for Rb_xC_{60} measured by EELS.

increasing doping. A considerable broadening of the $1s-\pi^*$ transitions is observed for $x=3$. This may be explained in terms of Jahn-Teller-like distortions such as were mentioned in the discussion of the photoemission data of Fig. 1. Once more, the relative shift of the unoccupied π^* -states signals the non-rigid band behaviour of doped C_{60} .

Ca-doped C_{60} has been shown to contain insulating (Ca_3C_{60}) and superconducting (Ca_5C_{60}) compositions [13]. Calculations suggest there is a strong hybridisation of C2p and Ca4s orbitals [14]. Preliminary EELS measurements on $Ca_{5+x}C_{60}$ have revealed a filling of LUMO and a partial filling of LUMO+1 states. Thus, Ca_5C_{60} is a fulleride with partially filled LUMO+1 states.

Summary

Upon n-type alkali metal doping of C_{60} , there is a filling of the conduction bands. For $x=3$, the PES and EELS data are consistent with half filling of the conduction band and a metallic state. A clear Fermi edge was seen in the photoemission, the size of the edge having a maximum at $x=3$. The doping level was measured by XPS in situ on exactly the same sample from which PES data were taken. For $x=6$, the conduction bands are completely filled leading again to an insulating state. The changes of the electronic structure are not rigid-band like. There is a reduction of the energy difference between π and π^* bands due to a reduction in the dimerization with increasing x . At half-filling there may also be a Jahn-Teller-like splitting of the molecular π levels leading to a broadening of π bands in the solid. Upon Ca-doping of C_{60} , there is a filling of the LUMO and a partially filling of the LUMO+1 conduction bands due to hybridisation between C2p and Ca4s states.

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