

## Electronic Structure Close to the Fermi Energy in Alkali-Doped $C_{60}$

S.L. Molodtsov,\* A. Gutierrez, E. Navas, C.T. Simmons, M. Domke, and G. Kaindl  
Institut für Experimentalphysik, Freie Universität Berlin, W-1000 Berlin 33

M. Merkel, N. Nücker, and J. Fink  
Institut für Nukleare Festkörperphysik, Kernforschungszentrum Karlsruhe, W-7500 Karlsruhe

V.P. Antropov, O.K. Andersen, and O. Jepsen  
Max-Planck-Institut für Festkörperforschung, W-7000 Stuttgart 80

The detailed knowledge of the electronic structure close to  $E_F$  of alkali-doped  $C_{60}$  ( $A_xC_{60}$ ) is of particular interest, since some of these compounds are known to be superconductors [1]. According to theoretical predictions [2], alkali atoms transfer their valence electrons to fullerene, gradually filling the lowest unoccupied molecular orbital (LUMO) of  $C_{60}$  and, in this way, leading to metallic properties. However, this simple model developed in the framework of the single-particle approximation contradicts the recent experimental observations, which show an extra spectral feature close to  $E_F$ , in the energy region between the filled part of the LUMO and the highest occupied molecular orbital (HOMO) of  $A_xC_{60}$  for low A concentration. This spectral feature can be assigned to the correlated nature of the electronic states in fullerenes [3].

Our study addresses these questions by use of photoemission (PE), resonant PE, and x-ray absorption near-edge structure studies of  $C_{60}$  and fullerenes doped with K, Rb, and Cs. The experiments were performed at the SX700/II and TGM6 beamlines at BESSY using angle-integrating (Leybold EA-11) and angle-resolved (VSW-ARIES) electron spectrometers, respectively. All electron spectra were taken from *in-situ* prepared fullerene samples with controlled alkali concentration.

Resonant PE spectra of undoped  $C_{60}$  films show partly localized electronic states in the upper valence and the lower conduction bands of fullerene [4]. With this method, the partial density of states close to  $E_F$  can be studied in doped systems. As can be seen from the difference between the on-resonance and the off-resonance spectra (upper part of Fig. 1), no evidence was found for a localization of K-derived states at the Fermi level in  $K_3C_{60}$ . This is in agreement with the theoretical prediction of a charge transfer from K to  $C_{60}$ , and supports a model for electron pairing below  $T_c$  based on high-energy intramolecular phonons [5]. The structures of the difference spectrum agree in shape and energy positions with the theoretical K-derived partial density of states (especially K-p contents) shown in the middle and the bottom part of Fig. 1.

As demonstrated in Fig. 2, the charge transfer does not lead to a simple filling of the LUMO band. Low doping gives rise to the additional structure A on the expected tail of the LUMO-derived band (feature B). With further doping, the intensity of feature B increases, while signal A reaches an intensity maximum for

$x = 1$  and then decays to almost vanishing weight at  $x = 3$ . This fact plus the coincidence in energies of feature A and of the related feature in the PE spectrum of gas-phase  $C_{60}^-$  ion clusters [6] (middle spectrum), as well as a different behavior of features A and B upon oxygen exposure signal a phase separation of the two components  $A_3C_{60}$  and  $A_1C_{60}$ , which is remarkably stable against oxidation. A suspicion that feature A is related to oxidation can be ruled out, since higher doses of  $O_2$  exposure lead to a disappearance of structure A. An insulating nature of  $A_1C_{60}$  can be explained by electron correlation effects in low-level doped fullerites [3].

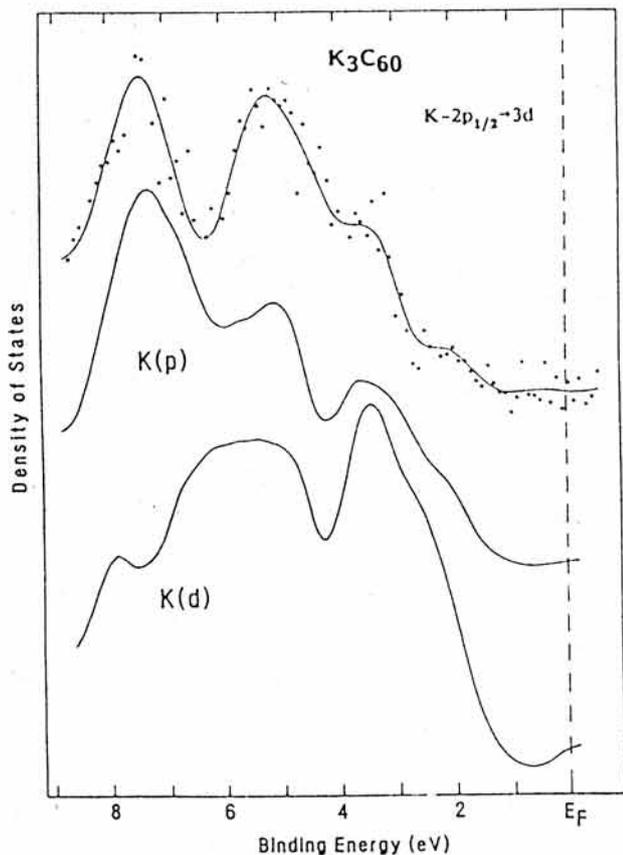


Fig. 1

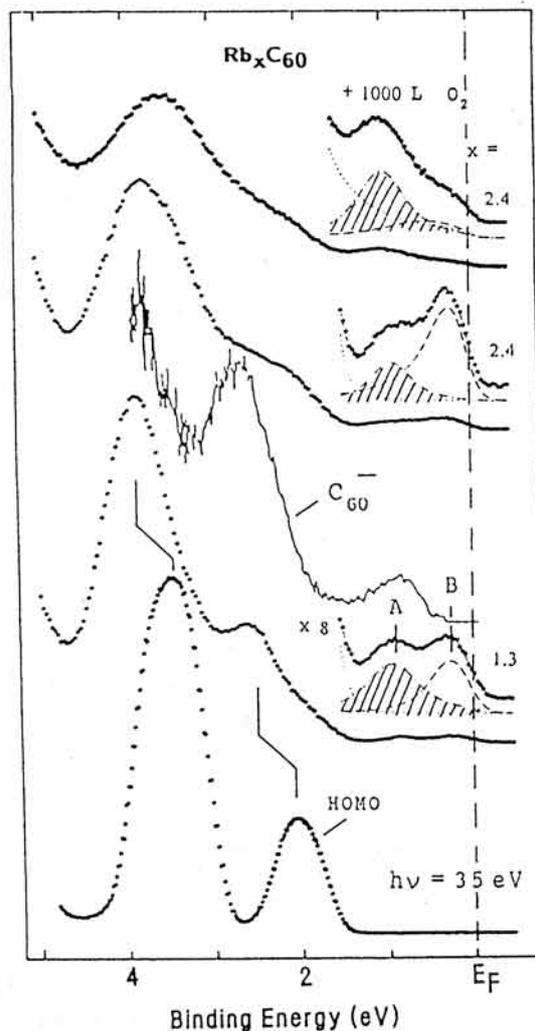


Fig. 2

The work in Berlin was supported by the BMFT, project 05-5KEAXI-7/TP01.

#### References:

\*On leave from Institute of Physics, St.-Petersburg University, 198904 St.-Petersburg

- [1] A.F. Hebard et al., *Nature* 350, 600 (1991).
- [2] S. Satpathy et al., *Phys. Rev. B* 46, 1648 (1992).
- [3] S.L. Molodtsov et al., to be published.
- [4] S.L. Molodtsov et al., *Europhys. Lett.* 19, 369 (1992).
- [5] M. Schluter et al., *Phys. Rev. Lett.* 68, 526 (1992).
- [6] S.N. Yang et al., *Chem. Phys. Lett.* 139, 233 (1987).