

## Evidence for Incomplete Charge Transfer and La-Derived States in the Valence Bands of Endohedrally Doped La@C<sub>82</sub>

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Photoelectron spectra from sublimed layers of chromatographically separated La@C<sub>82</sub> are presented. Using photon energies corresponding to the La 3*d* to 4*f* transition, a resonant enhancement of the La-derived valence states is observed. From the calculated resonant intensities of La 5*d* and 5*p* states in a La atom we estimate that about  $\frac{1}{3}$  of an electron charge is left in the La-valence orbitals for La@C<sub>82</sub>. In contrast to previous interpretations of La core-level photoemission studies our results demonstrate that the La valence electrons are not completely delocalized on the fullerene cage. [S0031-9007(97)04046-5]

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A few years ago the fascinating idea came up to create a whole new periodic system of elements consisting of endohedrally doped atoms in fullerene cages. Very soon problems became obvious: Some elements were never successfully incorporated and some endohedral materials could not be isolated because of their insolubility. One breakthrough occurred when the isolation of microgram amounts of La@C<sub>82</sub> by HPLC (high performance liquid chromatography) was successfully accomplished [1]. Many publications concentrate on this material [2]. Initially, theory predicted the La atom to be in the center of the fullerene cage and to donate two electrons to the cage [3]. Newer calculations predict an off-center position for the La atom and an electronic state corresponding to 3<sup>+</sup> for the La [4–7], which is in a better agreement with electron spin resonance, photoemission, and x-ray absorption fine structure results [8–12].

In order to test this charge-transfer model we use a tunable light source, i.e., synchrotron radiation from the Elettra storage ring, to perform resonant photoelectron spectroscopy at the La 3*d* to 4*f* transitions. We therefore have the advantage of an enhanced sensibility for any localized electronic density of states of the metal atom [13]. A calculation of the ratio of the resonant enhancement for the La 5*d* intensity relative to the La 5*p* peak for a La atom offers the possibility to estimate the amount of charge localized on La for endohedral La@C<sub>82</sub>. Studying the metal to cage charge-transfer process in La@C<sub>82</sub> might shed additional light onto some puzzling questions regarding the metallic properties and superconductivity of the alkali doped fullerenes. Presently the mystery remains unresolved why only some of the alkali and earth-alkali doped C<sub>60</sub> phases show metallic behavior and why only the A<sub>3</sub>C<sub>60</sub> components are superconducting [14,15].

Moreover, so far, no higher fullerenes have been reported to exhibit superconductivity or even metallic conductivity upon alkali doping [16–19]. This immediately poses the question about differences in the charge-transfer problems with symmetry.

The production and separation of La@C<sub>82</sub> by HPLC is described elsewhere [1]. The material was *in situ* evaporated from a resistively heated quartz crucible and deposited on an Ar<sup>+</sup>-sputter cleaned Au substrate. The energy was calibrated using the Au 4*f*<sub>7/2</sub> peak at a binding energy of 84 eV. From the overlayer induced reduction of the Au 4*f* peak by a factor of 250 we conclude that the La@C<sub>82</sub> layer was sufficiently thick to exclude any contribution from the Au substrate to the valence-band photoemission spectra. During the photoemission experiment the vacuum was better than  $1 \times 10^{-9}$  mbar. A He resonance lamp (21.22 eV) and synchrotron radiation from the SUPERESCA-beam line at ELETTRA (Trieste) were used as light sources for the *in situ* prepared films. The photoelectrons were detected by a hemispherical analyzer. The energy resolution for the spectra shown here varies between 0.3 eV for low photon energies and 1.2 eV for high photon energies. X-ray absorption near edge spectra (XANES) were recorded using a partial electron yield detector that discriminates against electrons with kinetic energies lower than 200 eV. All spectra have been taken with grazing light incidence (15°) and normal electron emission. During the preparation and the spectroscopy the samples were kept at room temperature. The sample was thick enough to exclude any contribution from the Au substrate to the observed valence-band spectra.

The valence-band region of La@C<sub>82</sub> measured with different photon energies is presented in Fig. 1. For the lower photon energies (21.2, 196, and 318 eV) the

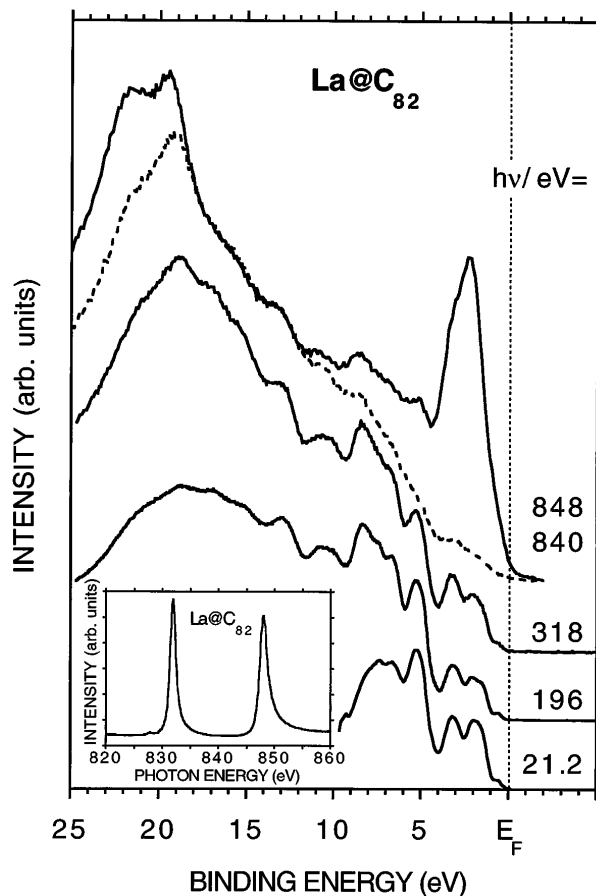


FIG. 1. Valence-band spectra of a thick layer of  $\text{La@C}_{82}$  at different photon energies. The bottommost spectrum has been recorded using a He lamp; the other spectra are taken with synchrotron radiation. The binding-energy scale is referenced to the Fermi level of the Au substrate. The intensity scale of the spectra at  $h\nu = 848$  eV (topmost curve) and  $840$  eV (broken line) has been normalized in the binding-energy region between about 12 and 18 eV. The inset shows an XANES in the region of the La  $3d$  core excitation threshold.

leading structures close to the Fermi level ( $E_F$ ) are clearly distinguishable and correspond nicely to the previously published data taken with a He lamp [11]. The missing intensity at  $E_F$  demonstrates the nonmetallic character of  $\text{La@C}_{82}$ . According to previous interpretations [4,6,10,11] the pronounced structure at binding energies higher than 6 eV belong to  $\sigma$ -derived states of the fullerene cage whereas the peaks at lower binding energy are mainly  $\pi$  derived. The three electrons from the La are believed to occupy former unoccupied orbitals of  $\text{C}_{82}$  now observed at binding energies less than 2 eV [10,11].

According to the theoretical prediction that three electrons are transferred from the La to the fullerene cage there should be no charge left in any La-derived state (neither  $5d$  nor  $6s$ ) close to  $E_F$  and the low-binding energy structures should correspond to  $\pi$  levels located on the fullerene cage [4,10,11]. We tested this model by resonant photoelectron spectroscopy (resonant PES) with a photon energy of 848 eV where a transition from the La  $3d_{3/2}$  core level

into the unoccupied density of states occurs. This transition corresponds to the high-energy peak in the absorption spectrum in the inset of Fig. 1. (The low-energy peak at  $h\nu = 831.2$  eV belongs to the corresponding transition from the La  $3d_{5/2}$  core level.) Apart from a resonant enhancement of the La  $5p$  intensity at high binding energy there are also some dramatic changes in the low binding energy region: Obviously there is a pronounced intensity increase for electronic states close to the Fermi level when the resonant photoemission spectrum (topmost spectrum of Fig. 1:  $h\nu = 848$  eV) is compared to the nonresonant emission spectrum taken at  $h\nu = 840$  eV. Both spectra have been normalized to equal intensity in the region between about 12 and 18 eV binding energy. In order to exclude any misinterpretation due to either Auger-electron emission or cross-sections effects, we compared the on-resonance spectra at  $h\nu = 848$  eV and at  $h\nu = 831.2$  eV (which corresponds to the La  $3d_{5/2}$  resonance) and we found no difference. We also observed a striking resemblance to the off-resonance spectra at  $h\nu = 840$  eV and at  $h\nu = 920$  eV (not shown). The apparent nonzero intensity right at the Fermi level is attributed to the reduced energy resolution at this higher photon energy but not to a metallic character of the sample.

The term “resonant PES” is used for an electron emission process where a direct photoemission process and a photoexcitation coupled with a radiationless (Auger type) deexcitation are leading to the same final states. Interference effects are observed since the initial and the final states are identical. At high photon energies, where the cross sections for direct photoemission from valence orbitals are orders of magnitude smaller than the core electron excitation cross sections, the resonant photoemission is completely dominated by the second channel, corresponding to core electron excitation followed by “Auger” decay. If resonance effects are observed in the valence state PES the structure of the Auger-matrix element allows the immediate conclusion that the involved states have a substantial spatial overlap with the core hole created in the excitation step. For resonant PES involving La  $3d$  core electrons these valence states therefore have to be located at the La atom.

Returning to the discussion of the spectra shown in Fig. 1, we observe a dramatic resonant enhancement in the low-binding energy region, apart from a (trivial) resonant enhancement of the La  $5p$  intensity at high binding energy. This resonant enhancement observed near the top of the valence band emission cannot be explained if the states close to  $E_F$  correspond to completely delocalized fullerene states. We therefore conclude that either some occupied density of states still are localized on the La atom, in contrast to the former interpretation that the La is in a complete  $3^+$  state, or there is a strong hybridization between La and fullerene orbitals.

In order to determine which orbitals are participating in the resonance we fitted the difference curve between the spectra on resonance (848 eV) and off resonance (840 eV),

the net resonance, using Voigt profiles for the subsequent peaks. The peak positions and the widths of the different peaks were determined by a fit of the data at  $h\nu = 21.2$  eV (bottommost spectrum of Fig. 1). No additional background intensity was taken into account. Figure 2(a) shows the result of this fit procedure: Nine peaks reproduce the valence-band structure quite well. The two peaks at the lowest binding energy (dotted curves) have been interpreted so far to fullerene states filled by charge transfer from the La atom. Thus the La  $5d$  and  $6s$  electrons are delocalized on the fullerene cage. The next two peaks on the binding-energy scale (solid curves) therefore correspond to the  $\pi$ -derived orbitals of  $C_{82}$ , and the rest of the

peaks (dashed curves) are mainly  $\sigma$ -derived states. The difference curve has been fitted using the same peak positions [Fig. 2(b)]. As free parameters of the fit the intensity and a common peak shape for all peaks (the ratio between Lorentzian and Gaussian peak width, in order to account for the lower energy resolution at the higher photon energies) were used.

The surprising result of this analysis is that the resonance is driven mainly by the two orbitals that correspond to the  $\pi$  states of the fullerene cage. The strong resonant enhancement of these peaks suggests that these orbitals contain significant La character. The localization of these states at the La site is even stronger than the localization of the topmost states, into which supposedly the La charge was transferred. This suggests a much more complex behavior than a simple charge transfer as is the case between alkali atoms and the fullerenes.

A comparison between the resonant enhancement of the valence-band features with that of the La  $5p$  peak offers the possibility for a rough estimate of the amount of charge that is localized on the La for  $La@C_{82}$ . From the calculation for a single La atom in a configuration  $5p^6 5d6s^2$  a ratio of 4 to 1 is expected for the peak areas of La  $5d/La 5p$ : From the ground state,  $La:5d^1:(g)$ , an electron may be excited optically from the occupied  $3d$  states to an empty  $4f$  state. The resulting intermediate states,  $La:[(3d^9, 4f^1)^1 P, 5d^1]^2(F, P):(i)$ , may decay via an Auger transition into either  $La:[(5p^5, \epsilon d)^1 P, 5d^1]^2(F, P):(f1)$ , or  $La:5d^0, ^2(\epsilon f, \epsilon p):(f2)$ . All states are determined by a nonrelativistic Hartree-Fock calculation [20,21] in the  $LS$ -coupling scheme as indicated. The results are for the excitation energies:

$$\Delta E_{g,i} = 851.39[\text{eV}],$$

$$\Delta E_{g,f1} = 25.8[\text{eV}],$$

$$\Delta E_{g,f2} = 6.46[\text{eV}],$$

for the transition probabilities into  $f1$  states with  $5p$  hole:

$$T(f1) \propto |\langle La(i) | W | La(f1) \rangle|^2 = 56.04 \times 10^{-6},$$

and into  $f2$  states without  $5d$  electron:

$$T(f2) \propto |\langle La(i) | W | La(f2) \rangle|^2 = 227.09 \times 10^{-6},$$

where  $W$  is the Coulomb-interaction operator and the matrix elements are given in atomic units. The ratio for the two decay channels in question is 1 to 4.

The result of a very crude fit for the net-resonance curve of endohedral  $La@C_{82}$  using Voigt peaks is shown in Fig. 3. From this fit the ratio of the peak close to the Fermi level (horizontal pattern, labeled La " $5d$ ") to the La  $5p$  derived features (vertical pattern) is about 7 to 5. Assuming that for any mixture between  $5d$ - and  $6s$ -derived orbitals a resonant enhancement is dominated by the  $5d$  part, we neglect the  $6s$  electrons. Therefore concentrating on the  $5d$  electron we conclude that roughly about  $\frac{1}{3}$  of the electronic charge of a  $5d$ -derived orbital is localized on La in the case of  $La@C_{82}$ . Since we have to take into

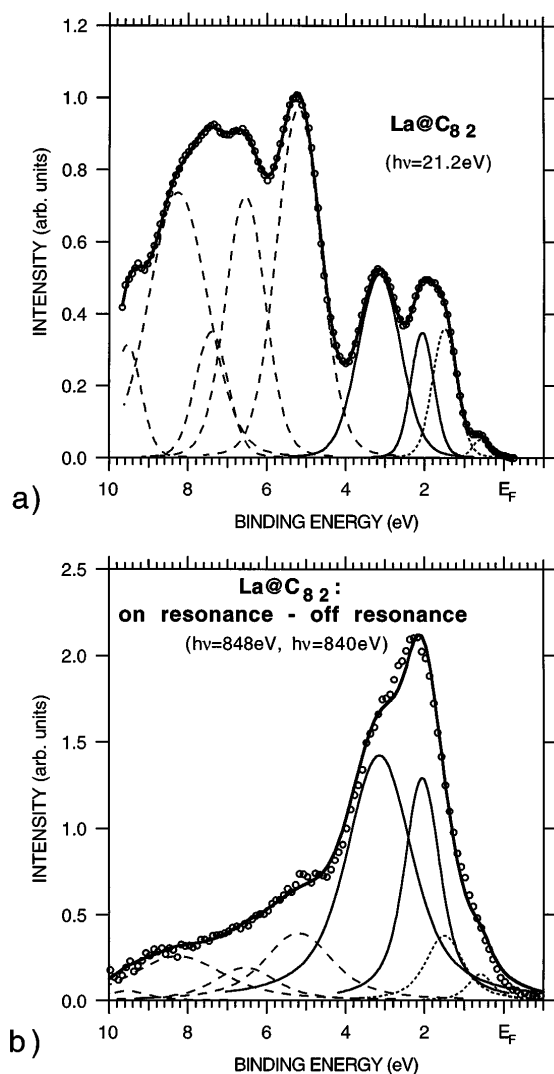


FIG. 2. (a) Valence-band spectrum of a thick layer of  $La@C_{82}$  at  $h\nu = 21.2$  eV (open circles), fitted by nine Voigt peaks (dotted curves, solid curves, dashed line: see text). Thick solid line: sum of the fit intensities. (b) Open circles: Difference curve between the valence-band spectra at  $h\nu = 848$  eV (on resonance) and  $h\nu = 840$  eV (off resonance) in Fig. 1, fitted by the same nine Voigt peaks as in (a) (dotted curves, solid curves, dashed line: see text) except for the width which was fitted by a common shape parameter that was allowed to differ from (a). Thick solid line: sum of the fit intensities.

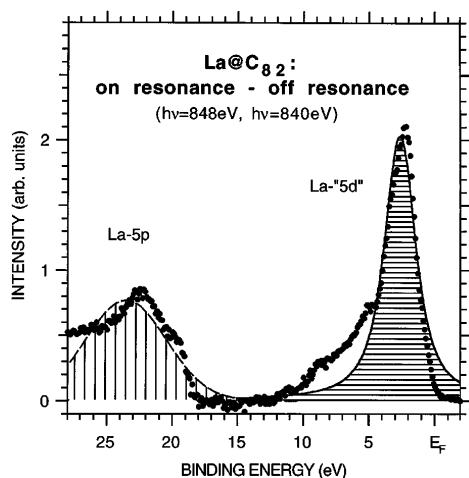


FIG. 3. Dotted line: Difference curve between the valence-band spectra at  $h\nu = 848$  eV (on resonance) and  $h\nu = 840$  eV (off resonance) in Fig. 1, fitted by two Voigt peaks (vertical and horizontal patterns). The vertical pattern gives estimate about resonant intensity corresponding to La 5p orbitals; the horizontal pattern gives estimate of valence-band resonant intensity associated with La 5d orbitals.

account that there is a strong hybridization between the different orbitals of the valence electrons, we cannot assign this electronic charge to a real 5d orbital; also the estimate of the amount of charge is crude and can be wrong by 50% in each direction.

Nevertheless a nonzero charge density localized on the La atom is obvious from our data. This contradiction to the photoemission cross-section data of Ref. [11] who found “essentially no La 5d character in the occupied states of La@C<sub>82</sub>” is attributed to the higher sensitivity of our resonant photoemission results. Any hybridization discussed in Ref. [11] concerns the La 5p states only. Newer calculations on the other hand show that a projection of the density of states onto the La atom for La@C<sub>82</sub> has a nonzero component around binding energies of about 3 to 8 eV that has been attributed to polarization effects [22].

In conclusion, our results on resonant photoemission at the La 3d<sub>3/2</sub> threshold show a resonant increase of the valence-band intensity that is not in accordance with a model in which all three valence band electrons of the La are completely transferred to the topmost orbitals of the fullerene cage. We find a significant La character in the occupied part of the valence bands, especially in the orbitals that so far have been interpreted to be mainly  $\pi$ -derived fullerene states. Thus a complex picture involving several La-fullerene hybridized states seems to better describe the electronic structure of La@C<sub>82</sub> than a simple charge transfer.

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