Surface electronic structure of fullerides
Macovez, Roberto

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Chapter 5

Surface Hubbard $U$ in alkali fullerides*

We report the combined photoemission (PES) and inverse photoemission (IPES) study of distilled, phase pure films of the monomeric fullerides $\text{Cs}_6\text{C}_{60}$, $\text{Cs}_4\text{C}_{60}$ and fcc $\text{RbC}_{60}$. The lowest PES-IPES energy separation (peak-to-peak), which is a measure of the barrier to hopping, is 1.45 eV in $\text{Cs}_4\text{C}_{60}$ and 0.7 eV in $\text{RbC}_{60}$. This difference is large enough to explain, in a correlated picture, the different electronic behaviour of the two stoichiometries. From a knowledge of the gap and Jahn-Teller pairing energies, the Coulomb contribution $U_C$ to the total Hubbard $U$ of these fullerides can be determined. While a similar value $\approx 1.5$ eV is found for closed-shell $\text{C}_{60}$ and $\text{Cs}_6\text{C}_{60}$, in $\text{Cs}_4\text{C}_{60}$ and $\text{RbC}_{60}$ the value of $U_C$ is reduced to $\approx 1$ eV and $\approx 0.8$ eV, respectively. This trend can be partially understood by taking into account the different molecular polarizability and crystal structure of the various stoichiometries. The relatively low values found for open-shell compounds are however surprising, given that these experimental values are upper limits for the surface $U_C$ which is higher than the corresponding bulk value. This suggests that the bulk $U_C$ is smaller in open-shell fullerides than usually believed, and that a different screening mechanism other than molecular polarization screening is available in these compounds, possibly related to the presence of free carriers.

Figure 5.2 (a) Vacuum level referenced PES and IPES from a thin $C_{60}$ film. (b) PES and IPES spectra of a distilled $Cs_6C_{60}$ sample.
5.1 Electron correlation in fullerides

Solids possessing strongly correlated charge carriers are usually described within the framework of fermion lattice models, in which the tendency toward metallicity is taken into account through hopping integrals and electron correlation is included via screened couplings between lattice sites \{Fazekas '03\}. The two most important parameters in such models are the Hubbard $U$ – defined as the energy needed to transfer an electron from a site with $n$ electrons to a distant equivalent site (i.e., $U = E_{n+1} + E_{n-1} - 2E_n$, where $E_n$ is the energy of a site with an occupancy $n$) – and the uncorrelated bandwidth $W$ arising from the hopping part of the Hamiltonian in the absence of correlation. The ratio $U/W$ determines the insulating or metallic nature of the ground state \{Georges '96\}. This is true also in the so-called extended Hubbard model which explicitly includes the nearest-site Coulomb interaction $V$, at least for small values of $V < U/2$ \{Meinders '94b, van den Brink '95\}, because the Hubbard $U$ is by definition a local quantity and does not contain contributions from the inter-site interaction. The non-degenerate Hubbard model and its extension to a degenerate band were initially devised and introduced \{Anderson '59, Gutzwiller '63, Kanamori '63, Hubbard '63, '64, '65\} for solid state compounds of $d$- and $f$-transition elements, after it was found that a number of these were insulating contrary to the predictions of standard band theory \{de Boer '37\}, see also \{Mott '85\} for a brief review).

Organic molecular solids are usually characterized by narrow bands with localized electrons, and hence usually display strong electron correlation. However, the electronic behaviour of molecular solids is largely determined by other factors besides the on-site electron-electron repulsion, such as the high lattice polarizability and the strong electron-phonon coupling (see Chapter 1), so that the experimental assessment and theoretical description of electron correlation in these materials is more problematic \{Silinsh '94\}.

As pointed out in Chapter 1, alkali fullerides display features similar to those of inorganic correlated systems with orbital degeneracy \{Imada '98, Tokura '00\}. In particular the critical ratio $(U/W)_c$ at which the Mott transition occurs depends on the effective degeneracy \{Lu '94, Gunnarsson '96, '97b; Koch '99b\} of the LUMO-derived level (three-fold degenerate in the isolated molecule), which can be easily lifted \{Manini '02\} by crystal field splitting or by a dynamic or cooperative Jahn-Teller (JT) effect \{Gunnarsson '97a\}.

As discussed in Chapters 1 and 4, the phase diagram of monomeric fullerides as a function of intercalation is considered to be largely determined by the interplay between the local couplings, namely the on-site electron-electron
repulsion, the JT coupling (which wins over the on-site exchange), and the crystal
field, which may lift the effective degeneracy of the frontier states. Despite the
qualitative success of this approach, a full quantitative understanding is still
lacking. While on one side odd-stoichiometry compounds should be
characterized by a large $U$ and lie close to the edge of a correlated metal-insulator
transition \cite{Fabrizio97,Durand03}, theoretical calculations point out that
Coulomb interactions must be effectively screened to allow for superconductivity
in these salts, since retardation effects are ineffective \cite{Koch99a}. The
magnitude of the electron-electron interaction and its role for fulleride
superconductivity remain highly controversial \cite{Gunnarsson97a, Chakravarty01, Capone02, Han03, Iwasa03}.

5.2 Experimental determination of $U$ in fullerides

In gapped correlated systems such as even-stoichiometry fullerides (see figure
5.1(a)), the total barrier to hopping ($\Delta E$) is the sum of the Hubbard $U$ plus the
energy gap $E_g$, which for a molecular insulator includes the effect of relaxation,
and Jahn-Teller coupling on the molecular orbitals. No gap is present instead in
odd-stoichiometry fullerides, where the Hubbard $U$ contains two contributions, a
screened Coulomb term $U_C$ and the JT pairing energy \cite{Auerbach94, Manini94}. The latter is instead included in $E_g$ in even stoichiometries where
$U=U_C$.

The highly symmetric structure of the C$_{60}$ molecule allows measuring the
hopping barrier $\Delta E$ and the Coulomb $U_C$ in fullerides independently by
combinations of electron spectroscopies \cite{Lof92a, Lof92b, Brühwiler92, Brühwiler93, Schwedhelm98}. $U_C$ can also be determined from the value of $\Delta E$, if the gap
and JT pairing energies are known. Estimates for the gap $E_g$ can be obtained
theoretically with the so-called GW approximation \cite{Hedin65} to the density
functional scheme, which has been shown to give quite accurate results for the
band gap of inorganic semiconductors. Experimental estimates may be derived
from the identification of direct (non-excitonic) transitions in high resolution
electron-energy loss spectroscopy (HREELS) (see Section 5.4). JT pairing
energies are known from calculations \cite{Auerbach94, Manini94}. 
Figure 5.1 (a) Energy level diagram for the isolated C\textsubscript{60}, C\textsubscript{60}(4–) and C\textsubscript{60}(6–) monomers. In the C\textsubscript{60}(4–) anion the molecular gap derives from the Jahn-Teller splitting of the t\textsubscript{1u} (LUMO) states. The molecular gap in the ground state of these fullerene molecules is responsible for the semiconducting character of condensed-phase C\textsubscript{60}, Cs\textsubscript{4}C\textsubscript{60} and Cs\textsubscript{6}C\textsubscript{60}. No gap is present in the C\textsubscript{60}(1–) or C\textsubscript{60}(3–) anion (and correspondingly in AC\textsubscript{60} and A\textsubscript{3}C\textsubscript{60} compounds). (b) Schematic top view of the surface of a fulleride (for simplicity taken here to have a hexagonal structure), showing the comparison between the PES and IPES processes.

The value of $U_c$ in the solid phase was calculated theoretically from the repulsion $U_c^{\text{mol}}$ between two electrons on the isolated C\textsubscript{60} molecule, assuming a reduction in the condensed phase due to the polarization screening contribution from nearest-neighbour molecules {Antropov '92, Pederson '92}. The value of the Hubbard $U$ can be measured using similar experimental techniques for the isolated C\textsubscript{60} molecule and for solid C\textsubscript{60} {Schwedhelm '98, Rudolf '99}, and indeed the difference is found to be consistent with calculations based on polarization screening. Instead, experiments have not yet been entirely conclusive on the value of $U_c$ in C\textsubscript{60} compounds, especially for metallic and superconducting phases {Brühwiler '93}. The value found in pristine fullerite is usually taken to be a good estimate also for alkali fullerides. However, it is likely that screening in C\textsubscript{60} salts is affected by the anionic charge state and that it is enhanced in open-shell compounds by multiplet effects, and, in metallic and superconducting phases, possibly by metallic-like screening. These effects have indeed been taken into consideration in some theoretical work {Koch '99\textsuperscript{a}, Guinea '94, Lammert '95}, but never directly explored by experiment.

The combination of photoemission and inverse photoemission spectroscopy near the Fermi level provides a direct measure of the hopping barrier $\Delta E$ in
fulleride thin films. In Figure 5.1(b) we present a schematic view of PES and IPES processes occurring at the surface of a C\textsubscript{60} compound (larger circles indicate the surface C\textsubscript{60} monomers, for clarity dopant ions are omitted and only the surface and first subsurface C\textsubscript{60} layers are shown). In both processes the probed film is initially in the ground state. In valence band PES a photon is absorbed by a molecular ion with \(n\) valence electrons and a photoelectron is emitted, leaving behind a molecule with \(n-1\) valence electrons (indicated as a positive charge in figure 5.1(b)). In the IPES process, an electron is captured by a molecule thereby resulting in an \(n+1\) state (a negative local excess charge).

When both processes are considered together, the net final state is equivalent to that produced when a valence electron is transferred from a molecule in the ground state to a (distant) equivalent molecule. Since the minimum energy required for the electron transfer is precisely the hopping barrier, when the features closest to the Fermi level in the PES and IPES spectra are considered their energy separation (centroid to centroid) is a direct measure of \(\Delta E\). It is clear that this definition of \(\Delta E\) includes all energy terms which are relevant for the charge transfer process, namely the relaxation energy at both sites, the Jahn-Teller pairing energy, and also the single-particle energy gap which separates the highest occupied and lowest unoccupied state, if present.

It is known that the PES and IPES features in C\textsubscript{60} compounds (and in organics in general) are wide due to Franck-Condon broadening (\{Macovez '07, Knupfer '93, Brühwiler '97, Goldoni '00\}, see also Chapters 1 and 4). Since phonon-loss satellites are more intense than those for phonon-gain \{Mahan '81\}, the energy distance between the Fermi level and the PES (or IPES) centroid is in general an overestimate of the true energy of the given electronic level (corresponding for an isolated molecule to the zero-phonon line), hence the value of \(\Delta E\) obtained with this method might lead to a (slight) overestimate of the true Hubbard \(U\) for the film. However, the comparison between the values of \(U\) measured at different stoichiometries, on which we focus in the following, is reliable as the same procedure is applied in all cases.

Because of the surface-sensitivity of the techniques employed, and due to the relatively low inelastic mean free path of electrons in fullerides (see previous Chapters), the value of \(U_c\) found with this approach is relevant for the surface of these solids. One should consider that screening is more efficient in the bulk than at the surface due to the higher coordination number \{Antropov '92\}. 
5.3 Experiments

Photoemission spectroscopy (PES) and inverse photoemission spectroscopy (IPES) measurements were carried out on well-ordered phase pure CsxC$_{60}$ ($x = 0, 4, 6$) and RbC$_{60}$ films grown on metallic single crystal substrates. The (angle resolved) IPES measurements were performed at the ISM IPES Trieste laboratory {Pedio '99}.* All IPES spectra are normalized at each point to the incident electron beam current.

The RbC$_{60}$ films were grown by the standard vacuum distillation procedure of {Poirier '95b}. The PES data of fcc RbC$_{60}$ are those of Chapter 4, and were collected at 525K with a photon energy of 129 eV in the ultra high vacuum experimental chamber of the SuperESCA beamline {Abrami '95} at ELETTRA. The photon energy calibration was obtained by comparing the first- and second-order photoemission signal from suitable core levels. The IPES spectrum of the same phase was measured at 470 K.

The Cs-doped films were prepared on a Au(110) substrate by modifications of the vacuum distillation procedure. The PES and IPES measurements on Cs$_x$C$_{60}$ were carried out at room temperature on films prepared under the same conditions and thoroughly characterized by Auger electron spectroscopy and low energy electron diffraction (LEED) to ensure that the desired phases were obtained. The PES measurements on the Cs-doped films were carried out with a standard He discharge lamp, using the He I resonance (21.2 eV). The energy resolution, as measured on the Fermi edge of the clean substrate, was 0.15 eV for PES and 0.45 eV for IPES. The energy scale for both PES and IPES spectra was referenced to the vacuum level.

5.4 Results

5.4.1 PES and IPES data

Figure 5.2 shows the PES and IPES spectra of C$_{60}$ and Cs$_x$C$_{60}$, normalized so that the area under the leading peaks is roughly proportional to the occupation of the corresponding energy bands. The energy and shape of the features in the spectra of pristine C$_{60}$ are in agreement with those of thick films available in the literature, demonstrating the good alignment of the Fermi level in our spectra, and that our film thickness is high enough so that screening from the metallic

*Details of the setup can be found at http://www.tasc-infm.it/research/ipes/instrume.php
substrate is negligible. The experimental HOMO-LUMO energy separation in pristine C$_{60}$ is 3.6 eV as previously observed {Lof '92a, Takajashi '92, Weaver '92}.

Both C$_{60}$ and Cs$_6$C$_{60}$ are insulators. As discussed in Section 5.2, in these closed-shell systems the smallest PES-IPES energy separation is $\Delta E = U_C + E_g$, where $E_g$ is the single-particle energy gap between the highest occupied band and the lowest empty band. The value of $E_g$ in solid C$_{60}$ calculated with the GW method is 2.15 eV {Shirley '93}, which coincides with the energy of the first direct inter-band (non-excitonic) transition observed with HREELS {Lucas '92}. This gives $U_C \approx 1.5$ eV, in agreement with previous estimates {Brühwiler '93, Lof '92a, Maxwell '96, Schwedhelm '98}.

We note that the HOMO-LUMO separation in the PES spectrum of Cs$_6$C$_{60}$ cannot be taken as a valid estimate for the fundamental gap in pristine C$_{60}$, as relaxation effects lead to a reduced value of the HOMO-LUMO distance upon (also partial) filling of the LUMO orbital (see also the discussions of figures 3.6(b) and 4.10(b) in Chapters 3 and 4, respectively). The HOMO-LUMO separation in Cs$_6$C$_{60}$ (1.6 eV, see figure 5.2(b)) is indeed found to be smaller than the theoretical GW band gap for pristine C$_{60}$.

In Cs$_6$C$_{60}$ the three-fold degenerate LUMO-derived band is filled completely by the six electrons per molecule provided by the Cs counter-ions. The LUMO-derived feature in the PES spectrum is centred 7.1 eV below the vacuum energy, while the LUMO+1-derived feature in IPES appears 4.4 eV below the vacuum level. To more accurately determine the energy of the latter feature, we have performed a fit of the lower energy part of the IPES spectrum using two Gaussians. The smallest energy separation between PES and IPES is 2.7 eV.

No GW calculation of the band gap is available for A$_6$C$_{60}$. HREEL spectra of A$_6$C$_{60}$, both in the reflection {Hunt '97, Ueno '01} and transmission {Sohmen '92, '93} modes, display the lowest most intense energy peak at 1.2-1.3 eV, which we take to be a measure of the bandgap $E_g$ in this material. A comparison between HREELS data on C$_{60}$ and A$_6$C$_{60}$ {Sohmen '93, Pichler '92} indeed shows that the energy of the first intense (non-excitonic) transition is reduced by roughly 1 eV in A$_6$C$_{60}$ with respect to pristine C$_{60}$, confirming our estimated value of the gap in Cs$_6$C$_{60}$. With this value we then find $U_C(C_6(CS_6C_{60})) \approx 1.4-1.5$ eV, in perfect agreement with the value reported for K$_6$C$_{60}$ (1.5 eV {Brühwiler '93}).
The PES and IPES spectra of Cs$_4$C$_{60}$ are shown in figure 5.3. The width of the first IPES structure is anomalously large with respect to the corresponding features in C$_{60}$ and Cs$_6$C$_{60}$. The first IPES feature in Cs$_4$C$_{60}$ results from the superposition between the empty LUMO-derived states and the LUMO+1 band, which shifts non-rigidly with increasing doping {Golden '95}. A similar overlap is observed in the IPES spectrum of Rb$_4$C$_{60}$ {Brambilla '05}. To separate the two contributions, we have subtracted the IPES spectrum of Cs$_6$C$_{60}$ from that of Cs$_4$C$_{60}$. The Cs$_6$C$_{60}$ spectrum was normalized and shifted so that the feature derived from the LUMO+2 orbital appeared at the same energy and had the same intensity as in the Cs$_4$C$_{60}$ spectrum, as shown in the inset of figure 5.3.

**Figure 5.3** Vacuum referenced PES and IPES spectra of a phase pure Cs$_4$C$_{60}$ thin film. The inset shows the method by which the centroid of the LUMO derived states was obtained (see text). The small dots represent the IPES spectrum of Cs$_6$C$_{60}$, the LUMO+2 feature of which has been aligned with and normalised to that of Cs$_4$C$_{60}$. The bold markers in the inset represent the difference between the Cs$_4$C$_{60}$ spectrum and the (shifted) Cs$_6$C$_{60}$ spectrum.
This procedure allows us to locate the intensity maximum corresponding to the unoccupied portion of the LUMO at 4.8±0.1 eV below the vacuum level. A small uncertainty exists in the position and shape of the LUMO-derived peak as obtained by the subtraction procedure due to differing backgrounds and lineshapes at lower energy in the IPES spectra of the two phases. The relative shift and intensity of the spectra was adjusted so that the subtraction procedure yielded a well-defined frontier peak. The energy separation between the filled and unfilled portions of the LUMO-derived band (marked by vertical lines in figure 5.3) obtained in this way is ΔE=1.5±0.1 eV.

The value of E_g for A_4C_60 (including JT effects) has been calculated \{Chibotaru '99\} with the GW method, and found to be 0.5 eV. A slightly higher value (0.6 eV) has been reported in HREELS studies \{Knupfer '97\}. The gap in A_4C_60 arises from the Jahn-Teller splitting of the t_{1u} states. The JT pairing energy for the isolated (C_60)^4– anion is calculated to be 0.2-0.4 eV \{Auerbach '94, Manini '94, Gunnarsson '95b\}, a good fraction of the bandgap. With the values for ΔE=1.5±0.1 eV and E_g=0.5 eV as given above we find U_C=1.0 eV (±0.1eV) in Cs_4C_60. This indicates that the bare U_C is better screened in A_4C_60 than in the closed-shell systems, which cannot be due to a higher coordination number as the number of first neighbours is lower in the body centred tetragonal (bct) structure of Cs_4C_60 than in the fcc structure of pristine C_60. In the following we show that U_C is greatly reduced in RbC_60 as well. We discuss in Section 5.4.2 the origin of this reduction of the on-site Coulomb interaction.

Figure 5.4 shows the PES and IPES spectra acquired on the high-temperature face-centred cubic (fcc) phase of RbC_60. The energy separations between the LUMO and LUMO+1 and the LUMO+1 and LUMO+2 features in the IPES spectrum are similar to those observed in C_60, but the width of the spectral features is much larger than in C_60 and Cs_4C_60, and the first peak around 6 eV below the vacuum level appears structured with a shoulder at lower energy. The PES valence band features are also anomalously broad. This suggests that different components contribute to the spectrum. As shown in Chapter 4, two different C_60 valence states, namely neutral (C_60(0)) and charged (C_60(1–)) are present at the surface of vacuum-distilled RbC_60 thin films. The same charge states should be visible in the IPES spectrum, and in the inset of figure 5.4 we present a model of the IPES spectrum of RbC_60 as the sum of two C_60 IPES lineshapes (the spectrum displayed in figure 5.2).
Figure 5.4 Vacuum referenced PES and IPES spectra of a phase pure RbC₆₀ thin film in the fcc phase. The inset shows a model of the IPES spectrum as the sum of two IPES spectra of pristine C₆₀, corresponding to the two different molecular charge states present at the film surface (see text for details).

The components are distant by 0.4 eV, an energy separation similar to the binding energy difference observed between the two components in the valence band PES spectrum (equal to 0.5 eV, see Chapter 4 and {Macovez '07}). We note that the component arising from the charged monomers could in principle be broader or more structured than the neutral one, as there are different possible final states in this case (corresponding to the different total-spin configurations of the two LUMO electrons). Our model provides nevertheless a reasonable fit of the IPES spectrum of fcc RbC₆₀.

The smallest LUMO-LUMO distance in the spectra of fcc RbC₆₀, which is a measure of the surface Hubbard $U$ in this phase, is 0.7 eV. This value is consistent with our model of the C 1s PES binding energy difference between the
two surface charge states (see paragraph 4.3.3.3). The IPES feature at lowest energy arises from a radiative transition into the lowest energy configuration of the (C$_{60}$)$_2^{2-}$ anion (which is the Jahn-Teller distorted low-spin state). Hence the measured $U$ contains a contribution from the Jahn-Teller pairing energy for the (C$_{60}$)$_{1-}$ anion, which is of the order of 0.1-0.15 eV \cite{Auerbach 94, Manini 94, Gunnarsson 95b}. The purely Coulomb contribution is then roughly $U_C \approx$0.8-0.85 eV. This value is much smaller than that found in C$_{60}$ and Cs$_6$C$_{60}$, while it is closer to that found for Cs$_4$C$_{60}$. This value is also close to the energy separation (0.7 eV) observed between the Auger fine structure and the self-convoluted valence band PES spectrum of K$_3$C$_{60}$ \cite{Brühwiler 93}.

Given this similarity of values in all open-shell fullerides, it is tempting to consider the energy separation of 0.7 eV found in \cite{Brühwiler 93} as a true measure of the (surface) Hubbard $U$ in K$_3$C$_{60}$, rather than assuming, as in \cite{Brühwiler 93}, that the Hubbard $U$ in K$_3$C$_{60}$ should be equal to that of pristine C$_{60}$. In RbC$_{60}$ (and also K$_3$C$_{60}$) the coordination number is the same as in C$_{60}$, hence we must look for alternative explanations for the more effective screening of $U_C$ in this compound.

### 5.4.2 Discussion

As mentioned in Section 5.2, the values of $U$ found in our study are appropriate for the surface, rather than the bulk, of each compound. Bulk values of $U_C$ are expected to be lower than those discussed so far, as the screening efficiency is enhanced in the bulk by a factor of $\sim$30% due to the higher coordination number \cite{Antropov 92}. In particular, the relatively low values of $U_C$ measured for the surface of open shell compounds (RbC$_{60}$ and Cs$_4$C$_{60}$, but arguably also K$_3$C$_{60}$ \cite{Brühwiler 93}) suggest that the bulk $U_C$ in these stoichiometries is very similar, and it is not much larger than the full uncorrelated bandwidth $W$. This allows, on one hand, odd-stoichiometry compounds to remain on the metallic side of the Mott-JT-Hubbard phase diagram, and on the other hand, it is a further confirmation of the idea that the JT coupling is the fundamental ingredient which determines the insulating nature of even-stoichiometry compounds \cite{Fabrizio 97, Chibotaru 99}.

The values of $U_C$ found in open-shell compounds are significantly lower than those found in closed-shells. Such low values might be somewhat surprising, if one considers that our experimental values represent over-estimates of $U_C$ at the film surface, where screening efficacy is supposedly rather poor. We have estimated the screening of $U_C$ in the bulk of the various phases by assuming the contribution of molecular polarization screening alone (the atomic polarizability
of the alkali counter-ions is, in comparison, negligible). Taking into account local field effects {Wang '80}, the reduction of $U_c$ due to molecular polarizability of the fullerene molecules can be written as {van den Brink '97}:

$$\text{Eq. (5.1) } \partial U_c = \frac{14.4 L(0)}{4\pi \cdot d} \left( 1 - \frac{1}{\varepsilon} \right) eV,$$

where $\varepsilon$ is the relative dielectric constant of the medium, $d$ the distance in Å between nearest neighbour molecules, and $L(0)$ is the appropriate lattice sum for the corresponding crystal structure, equal to 25.34 for fcc $C_{60}$, Rb$C_{60}$ and K$_3$C$_{60}$, and to 22.64 for bcc Cs$_6$C$_{60}$ {van den Brink '97}. For bct Cs$_4$C$_{60}$, the lattice sum was taken to be equal to that of the fcc structures, with an effective next-neighbour distance $d$ calculated as the cube root of the molecular volume. We estimate that the relative error associated with this procedure is less than 10% (the percent difference between the lattice sums for two cubic structures).

As for the relative dielectric constant $\varepsilon$, in the $C_{60}$ case the value available in the literature for $C_{60}$ films was used, namely 4.4 {Hebard '91a, Fartash '96}, while for the other fullerides we have calculated the dielectric constant from the Clausius-Mossotti relation using the theoretical molecular polarizability $\alpha$ for the $(C_{60})^n$-anion {Guinea '94}.

The theoretical values of the screened bulk $U_c$ obtained by this method are reported in Table I for the compounds studied here and for K$_3$C$_{60}$. We assumed that the Coulomb repulsion for the isolated molecule is the same for all charge states, namely $U_c^{\text{mol}} = 3.5$ eV (independent of $n$). This assumption is supported by theoretical calculations {Antropov '92} which indicate that the energy cost for introducing one electron into the $t_{1u}$ level of the isolated molecule is approximately the same regardless of the initial reduction state. In Table 5.1 also the comparison with the experimental (surface) values is presented.

The calculated values for the screened $U_c$ follow roughly the trend found experimentally. In Cs$_6$C$_{60}$ the enhanced anionic polarizability {Guinea '94} balances the effect of the reduced coordination number and the larger intermolecular separation with respect to the other compounds, resulting in a value of $U_c$ which is the same as for pristine $C_{60}$. In Cs$_4$C$_{60}$, the increased polarisation due to the available transitions within the multiplet structure of the open shell anion {Koch '99a, Guinea '94} compensates for the opening of the gap between the JT-split $t_{1u}$ states (figure 5.1(a)). This results in an experimental value of $\Delta E$ which matches accidentally the value of the Hubbard $U$ in pure $C_{60}$.
Chapter 5

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<th>$\varepsilon$</th>
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</tbody>
</table>

Table 5.1 Comparison between the experimental values of the surface $U_C$ in a number of fulleride compounds and the theoretical estimates of the same quantity in the bulk, calculated as $U_C = U_C^{\text{mol}} - \delta U_C$, where $U_C^{\text{mol}} = 3.5$ eV and $\delta U_C$ is determined from Eq. (5.1). The experimental value for $U$($\sim U_C$) in K$_3$C$_{60}$ is taken from {Brühwiler '93}. The relative dielectric constant $\varepsilon$ of the bulk fullerides was calculated using the Clausius-Mossotti relation from the theoretical molecular polarizability $\alpha$ of the corresponding anion, available from {Guinea '94}.

In closed-shell C$_{60}$ and Cs$_6$C$_{60}$, the theoretical bulk $U_C$ is smaller by 0.25 eV than the experimental surface value, as could be expected due to the lower molecular coordination at the surface. In contrast, in open-shell compounds the experimental values are lower than the theoretical ones, except for the RbC$_{60}$ case where, however, the calculation gives an unrealistic value of almost 200 for the relative dielectric constant. Even taking our estimate to be reliable, the theoretical value found for RbC$_{60}$ is still too low, because as discussed in the Chapter 4 the surface layer of RbC$_{60}$ is characterized by a charge reconstruction {Macovez '07} in which 50% of the surface monomers are neutral. As seen in Table 5.1, the neutral monomer has a polarizability which is half that of the singly charged anion, hence the difference in $\delta U_C$ between the surface and the bulk of RbC$_{60}$ should be much higher than that found in pristine C$_{60}$.

As the effect of molecular polarization screening does not explain the experimental values of $U_C$ in open-shell compounds, another source of screening must be present, which we propose is related to the presence of charge carriers. Free carriers definitely exist in odd stoichiometries, according to the metallic...
character of these compounds, and they are presumably present also in JT-Mott
insulators such as Cs$_4$C$_{60}$ due to thermal excitations across the relatively small gap,
while they are not so numerous in closed-shell compounds. Indeed, the resistivity
of K$_4$C$_{60}$ at 200 °C is the same as that of KC$_{60}$ and only about an order of
magnitude higher than that of K$_3$C$_{60}$, while K$_5$C$_{60}$ and pristine C$_{60}$ have a
resistivity which is at least two orders of magnitude higher than KC$_{60}$ and K$_4$C$_{60}$
{Hesper '00}.

Our results and those of {Brühwiler '93} show that a full metallic screening is
not operative at room temperature at the surface or in the bulk of fullerides. The
situation at low temperature is however more complicated. The procedure of
determining the Hubbard $U$ by comparing PES and IPES energy fails in odd-
stoichiometry fullerides at low temperature since the PES and IPES spectra of
these compounds are characterized by the presence of a sharp Fermi edge.
Moreover, the occurrence of superconductivity in A$_5$C$_{60}$ {Hebard '91b,
Holczer '91} and of long-lived spin-singlets in A$_3$C$_{60}$ {Brouet '99, '02b} suggests
that an effective screening of the on-ball Coulomb repulsion is available in the
bulk at low temperatures, so that the local Jahn-Teller pairing can become
effective against correlation. It is an attractive explanation that the reduction of $U$
at low temperature in bulk sc A$_3$C$_{60}$ and A$_5$C$_{60}$ due to free-carrier screening and
Jahn-Teller effects working in tandem is enough to allow the formation of a
superconducting ground state in the case of A$_3$C$_{60}$, and that of long-lived doubly-
charged states in the sc phase of CsC$_{60}$.

Our analysis shows that for a full understanding of the electronic structure
and transport properties of alkali fullerides the combined effects of electron
correlation and Jahn-Teller distortion, but also that of screening, must be
considered. To this aim, the development of a reliable method for calculating the
efficiency of screening in C$_{60}$ compounds beyond the molecular polarization
model is desirable.

5.5 Conclusions

This chapter focussed on the combined PES and IPES study of distilled
phase-pure films of Cs$_8$C$_{60}$, Cs$_4$C$_{60}$ and fcc RbC$_{60}$. The lowest PES-IPES
separation in RbC$_{60}$ and Cs$_4$C$_{60}$, which is a measure of the hopping barrier, is 0.7
eV and 1.45 eV, respectively. This difference is large enough to determine, in a
correlated picture, the different metallic behaviour of these compounds. The
Coulomb Hubbard $U_C$ was estimated for all compounds and found to depend
significantly on the stoichiometry. While the value of the screened $U_C$ is similar in
the close-shell systems C$_{60}$ and Cs$_8$C$_{60}$, it is strongly reduced in Cs$_4$C$_{60}$ and RbC$_{60}$.
This is only partially ascribable to the enhanced molecular polarizability of fullerene anions, indicating that a different source of screening, presumably related to the presence of charge carriers, is at work in open-shell fullerides. The combined effects of efficient screening and Jahn-Teller coupling may not only drive odd-stoichiometry fullerides to the metallic side of the Mott-Hubbard-Jahn-Teller phase diagram, but also favour the formation of Cooper pairs and long-lived spin singlets.