Chapter 4

Electronic structure and phase transitions in RbC$_{60}$

We present a combined core-level and valence-band photoemission and X-ray absorption study of the four phases – face-centred cubic (fcc), polymer, dimer, simple cubic (sc) – of a C$_{60}$-terminated RbC$_{60}$ crystalline film. The sc-to-dimer transition is found to be reversible at the surface of the film, in contrast to bulk results. We find evidence for an electronic charge reconstruction at the film surface in all phases, in which the electron density in the surface molecular layer is reduced to $-0.5e$ per cage, i.e., half that of corresponding bulk layers. This interpretation rationalizes the discrepancy between the theoretical DOS for RbC$_{60}$ and the experimental photoemission spectra. In the fcc phase the C$_{60}$(111) surface plane consists, on the photoemission timescale, for 50% of singly-charged monomers and for the remaining 50% of neutral molecules. These surface neutral monomers coexist with charged dimers and polymer chains in the corresponding phases. The X-ray absorption spectra of these phases are consistent with this interpretation.

The surface of the fcc phase appears weakly metallic, as has been found for the bulk. We confirm the previous conclusion on less crystalline films that the dimer phase is insulating. A metal-to-insulator transition is observed by electron energy loss spectroscopy at the surface of the polymer phase between 85 and 110 K, also confirmed by photoemission. A sharp Fermi edge is observed in the simple cubic phase, demonstrating the metallicty of this phase also in thin-film form. A lower limit of 0.5 eV (0.65 eV) is found for the surface Hubbard $U$ in

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the sc (fcc) phase, which shows that the surface of cubic RbC\textsubscript{60} is a strongly correlated system.

Three molecular charge states are identified in the valence and core photoemission spectra of the sc phase, two of which correspond to C\textsubscript{60} and C\textsubscript{60}\textsuperscript{1−} monomers as in the fcc phase, while the third arises from a minority of C\textsubscript{60}\textsuperscript{2−} anions, similarly to what observed by NMR in the sc phase of bulk CsC\textsubscript{60}. The strongly correlated surface character and the fact that the doubly-charged monomers directly contribute to the spectral intensity at the Fermi level in the photoemission spectrum of the sc phase, indicate that the (2−) anionic states occur only as short-lived charge fluctuations, and that the surface conductivity is hopping mediated in sc RbC\textsubscript{60}, as also suggested from the X-ray absorption spectrum of the same phase. The hopping time of charge carriers is longer than the photoemission timescale, being probably of the order of a few femtoseconds. Molecular charge fluctuations appear to be a fundamental ingredient of metallicity in fullerides.
4.1 $A C_{60}$ Phase Diagram

Alkali fullerides with stoichiometry $A C_{60}$ ($A = K$, Rb, Cs), among the last ones to be investigated {Winter ’92, Poirier ’94, Kosaka ’95, Zhu ’95}, are fascinating fullerene-derived salts displaying a variety of different structural phases as a function of temperature treatment (figure 4.1).

Four phases exist, two of which are thermodynamically stable while the other two are only metastable. Above 400K the stable form of $A C_{60}$ is a fcc lattice of rapidly spinning monomers with weak exchange interactions between them {Tycko ’93}. At room temperature a conducting phase of polymer chains sets in {Stephens ’94, Chauvet ’94, Pekker ’94}, which undergoes a magnetic ordering transition at lower temperature {Chauvet ’94}. The two metastable phases are obtained by fast-cooling (“quenching”) from the fcc phase: fast-cooling to about 50K results in an orientationally ordered simple cubic monomer phase {Kosaka ’95} with rather unusual metallic properties {Brouet ’99, ’02}; quenching to 200K leads to the formation of singly-bonded $(C_{60})_2^{2-}$ dimers {Oszlányi ’95, Zhu ’95, Thier ’97} which are isostructural and isoelectronic to the azafullerene molecule $(C_{59}N)_2$ {Pichler ’97}.

![Figure 4.1](image.png)

*Figure 4.1 The bulk phase diagram of $A C_{60}$ (after {Mehring ’00}).*
Upon annealing the sc phase, an irreversible phase transformation occurs in the bulk to the dimer phase. If the temperature is raised to slightly below room temperature, the dimer bonds are broken, after which the thermodynamically stable polymer chains form.

Each phase has characteristic electronic properties. NMR \{Tycko '93\} and ESR \{Chauvet '94\} investigations on the fcc phase revealed a high degree of localization of the unpaired electrons on individual \(C_{60}\) molecules. Optical conductivity measurements \{Martin '94\} found a metallic character, which suggests that the bulk fcc phase is a strongly correlated metal. Like solid \((C_{59}N)_2\), the metastable dimer phase is insulating and diamagnetic, which derives from the fact that one electron per cage participates in the dimer bond and the non-degenerate frontier orbital of the charged \((C_{60})_{2}^{2-}\) dimer is totally filled \{Pichler '97\}.

The sc phase differs from the fcc phase in that the molecular librations are frozen, and the orientation of the \(C_{60}\) monomers is fixed with respect to the cubic axes \{Kosaka '95\}. Though the sc phase was initially described as a simple metal \{Kosaka '95\}, a recent NMR study has shown that sc CsC\(_{60}\) is, in fact, characterized by a partial spin gap which is ascribed to the presence of a minority of stable doubly-charged molecules in spin-singlet state \{Brouet '99, '02b\}. The same authors suggest that spin-singlets might occur as short-lived charge fluctuations in the fcc phase of the same compound \{Brouet '02c\}. A number of NMR studies have in fact suggested the existence of charge fluctuations on different timescales in various fullerene compounds \{Brouet '01, '02a, '02c\}, but these were never yet observed directly, despite the fact that the fluctuations times conjectured by NMR are longer than the characteristic time of the PES process. The NMR results on sc CsC\(_{60}\) are peculiar because they point to an extremely long localization time of the spin singlets (up to few seconds), which is not expected in a strongly correlated system and has been partially ascribed \{Brouet '02b\} to the energy gain associated with the Jahn-Teller distortion of the \(C_{60}^{2-}\) anions \{Auerbach '94, Manini '94\}. The splitting of \(t_{1u}\) states due to the Jahn-Teller distortion also explains the non-magnetic (spin-singlet) nature of the \(C_{60}^{2-}\) anions (see section 1.4).

Few photoemission studies have appeared in the past years, limited to the investigation of the valence band. The valence band features of fcc \(A_{1}C_{60}\) were found to be much broader \{Lopinski '94, De Seta '96\} than those of solid \(C_{60}\) \{Hunt '97\}. The LUMO-derived band in particular was found to be much wider than predicted by band structure calculations for a partially filled \(t_{1u}\)-derived band (the full LUMO bandwidth is calculated to be 0.5 eV \{Erwin '91\}), a situation encountered also in other alkali fullerides such as Rb\(_3\)C\(_{60}\) and K\(_3\)C\(_{60}\). As in \(A_{1}C_{60}\)
at high temperature {Knupfer '93, Golden '95, Goldoni '98, '00, '01b}, the photoemission spectrum of the high temperature fcc phase of $A_{C_{60}}$ does not display a clear signature of a Fermi edge {Lopinski '94, De Seta '96}, contrary to the expectation for a simple metal. For the dimer phase as well, the disagreement between the calculated occupied density of states (DOS) and photoemission data for the valence band is marked. While the photoemission spectrum of solid $(C_{59}N)_{2}$ is identical to the theoretical DOS of the isolated azafullerene dimer {Pichler '97}, a much worse agreement is found in the case of dimerized Rb$_{C_{60}}$ (see figure 4.2).

Photoemission spectroscopy is particularly sensitive to the surface region of a probed sample, and modifications of the crystal and electronic structure are well known to occur at the surface of ionic compounds. As both pristine $C_{60}$ and $(C_{59}N)_{2}$ are van der Waals solids while Rb$_{C_{60}}$ is an ionic salt, it seems plausible that surface effects might be at least partially responsible for the discrepancy between calculation and experiment in Rb$_{C_{60}}$. The dimer and fcc phases of Rb$_{C_{60}}$ are simple systems on which to test the importance of surface effects on the electronic structure of molecular solids.

Figure 4.2 Left: valence band photoemission spectrum of solid $(C_{59}N)_{2}$ (dots) compared with the calculated DOS of the azafullerene dimer (solid line), after {Pichler '97}. Right: valence band photoemission spectrum of Rb$_{C_{60}}$ (circles) from {Poirier '95a}, compared with the theoretical DOS for the isolated $(C_{60})_{2}^{2-}$ dimer (solid line) {Pichler '97}. 
4.2 RbC₆₀ Experiments

The experiments were performed in the ultra high vacuum experimental chamber of the SuperESCA beamline {Abrami '95} at the ELETTRA synchrotron radiation facility (base pressure < 5×10⁻¹¹ mbar). A Ag(100) single crystal was mounted on a He-cooled manipulator and heated with a filament placed behind it. The temperature was monitored via a thermocouple inserted in a hole on the side of the sample. A phase pure RbC₆₀(111) thin film was grown by intercalating a C₆₀(111) film grown by physical vapour deposition with an understoichiometric amount of Rb, followed by a vacuum “distillation” at 525K to yield the fcc phase {Poirier '94}. The fcc phase was characterized by a faint (1×1) hexagonal LEED pattern, in agreement with earlier studies {Lopinski '94}. The polymer phase was obtained by slow cooling from the fcc to room temperature. The same growth procedure was repeated in the ultra-high vacuum chamber devoted to electron energy loss spectroscopy of the Zernike Institute for Advanced Materials, which is equipped with a DELTA 0.5 spectrometer (SPECS) to characterize the polymer phase by HREELS. The primary electron energy was 4 eV, and the resolution (defined by the full-width-at-half-maximum of the elastic peak) was better than 3 meV. The spectra were measured in specular reflection geometry at an incidence angle of 55°.

At Elettra, the dimer and sc phases were obtained by fast-cooling at a rate of 50 K/min (see below). Each phase was probed by PES and XAS at a temperature at which it is known to be stable in the bulk: 175 K for the dimer phase, room temperature and below for the polymer, 525 K for the fcc phase, and 50 K for the sc phase.

The photoemission spectra were acquired in two emission geometries to study the difference between the surface and bulk features of the film. In normal emission (NE) geometry photons impinge on the sample at 70° from the normal. In grazing emission (GE) the photon flux is normal to the surface and photoelectrons are analyzed at an angle of 70°. Due to the finite inelastic mean free path of electrons in a solid, the probed depth is lower in grazing than in normal emission. The binding energy was calibrated by recording the Fermi edge of the clean silver substrate. The Rb 3d and C 1s PES spectra were measured at a photon energy of 400 eV with a resolution of 0.15 eV, while for the valence band (VB) spectra the photon energy was 129 eV and the resolution 0.036 eV. The photon energies were chosen in order to assure that the photoelectron kinetic energy and hence the electronic mean free path were roughly the same for valence band and C 1s photoelectrons, and large enough so that the photoemission spectra were not sensitive to modulations in the empty density of
states.

The XA spectra were acquired by measuring the carbon KVV Auger yield at 250 eV kinetic energy as the photon energy was varied across the C 1s absorption edge, and corrected for beamline throughput by dividing by the current on a clean gold mesh. The photon energy calibration was obtained by comparing first- and second-order photoemission signals from suitable core levels.

4.3 Results

4.3.1 Sample quality, phase identification and termination of the film

Figure 4.3(a) shows the Rb 3d NE spectrum of all four phases (unless otherwise stated, in figures showing the comparison of spectra taken in different phases, each spectrum is normalized to the maximum of spectral intensity). In both cubic phases the spectrum consists of a single spin-orbit doublet with the expected intensity ratio (2:3) and an energy separation of 1.5 eV. This shows that only octahedral sites are occupied in the film. In fact, for higher Rb concentrations we observed a partial filling of tetrahedral sites, corresponding to the formation of a minority Rb$_3$C$_{60}$ phase. The tetrahedral sites give rise to a second Rb 3d doublet in the photoemission spectrum whose $j=5/2$ feature is indicated by an arrow in fig. 4.3(b).

The spectra of figure 4.3(a) indicate instead that in this film the tetrahedral sites are empty thereby ruling out the presence of minority Rb$_3$C$_{60}$ domains in the film. The spectrum of the sc phase is narrower than that of the fcc phase, and is asymmetric towards high binding energy, indicative of a metallic character (see Section 4.3.2 below).

The Rb 3d spectrum of the dimer phase is structured, revealing the presence of two non-equivalent Rb contributions of similar intensity, as expected since the dimerization requires the existence of two non-equivalent Rb sites (Zhu ’95, see also Section 4.3.8). As shown in Fig. 4.3(c), the dimer phase spectrum could be reproduced with two doublets of the same intensity ratio and energy splitting as observed in the fcc phase. In the fit, each component is taken to have a Voigt profile with a Lorentzian width of 80 meV (Coville ’91, Brühwiler ’02) and a Gaussian width of 0.22 eV. Negligible angle dependence is observed in all phases (not shown).
Figure 4.3 (a) Rb 3d core level spectra of the four phases of RbC₆₀, taken at normal emission with hν=400eV. (b) Rb 3d spectrum of an overdoped film, where the signal corresponding to tetrahedral (T) sites is visible (the arrow indicates the position of the j=5/2 feature of the spin-orbit doublet arising from Rb ions sitting in such sites). (c) Fit of the dimer phase Rb 3d spectrum with two spin-orbit doublets (each component is reproduced by a Voigt function); in each doublet the intensity ratio and energy separation are the same as in the cubic phases.
Figure 4.4 shows the normal emission valence band spectra of all four phases (left), and a close-up on the frontier states (right). It can be seen that the lineshape of the frontier states is characteristic for each phase. The valence band spectra measured on the fcc, polymer and dimer phases look virtually identical to those available in literature {Lopinski '94, De Seta '96, Pichler '97}, which shows that the desired stoichiometry is obtained and confirms the quality of our film. Since the highest occupied Rb core level (Rb 4$p$) lies around 17 eV binding energy, the valence band photoemission features in all four phases originate almost entirely from fullerene orbitals (though it should be noted that in the case of $K_xC_{60}$, some K $p$-$d$ intensity contributes to the valence band DOS below 1.5 eV {Molodtsov '93}. In potassium fullerides charge transfer is complete {Benning '91, Huang '92, Molodtsov '93}, and complete charge transfer occurs also for Rb {Satpathy '92}, as expected since the first ionization potential of Rb is smaller than that of K.

As mentioned in section 4.2, the LEED pattern of the fcc phase of RbC$_{60}$ is
hexagonal, which indicates that the film termination is the same as that of the precursor C_{60} film, namely a (111) plane. The RbC_{60}(111) film was observed to remain stable for several days in vacuum. The good stability of the surface implies that the film cannot be Rb-terminated, for surface Rb would react with gaseous species. Moreover, the ratio of the Rb 3d and C 1s photoemission intensities is less than expected for the RbC_{60} stoichiometry, indicating that the Rb signal is attenuated by a C_{60} surface layer. Hence the distillation procedure yields a C_{60}-terminated fcc RbC_{60}(111) film.

4.3.2 Reversible sc-to-dimer transition in the thin film

Figure 4.5 displays the temperature evolution of the frontier electronic states during the quench from the fcc to the dimer phase and as the temperature is further lowered.

![Graph showing the temperature dependence of the states closest to the Fermi level (EF) during fast-cooling from the fcc to the sc phase at an average rate of 50 K/min. The temperature to which each spectrum corresponds is not known with precision except for the first and last spectrum.](image)

**Figure 4.5** Temperature dependence of the states closest to $E_F$ during fast-cooling from the fcc to the sc phase at an average rate of 50 K/min. The temperature to which each spectrum corresponds is not known with precision except for the first and last spectrum.
The feature closest to the Fermi level \( (E_F) \) in the spectrum of the fcc phase arises from the partial filling of the \( \text{C}_{60} \) LUMO-derived band due to the complete charge transfer from Rb. The transition to the insulating dimer phase is visible as the opening of a gap at \( E_F \) in the density of states. The features around 1 eV in the three middle spectra arise from the highest filled molecular orbitals of the charged \( \text{C}_{60} \) dimer \cite{Poirier95a, Pichler97}, and could be observed in the temperature range between 250 and 140 K. As reported in previous studies \cite{Poirier95a, Pichler97}, there is a small spectral intensity between the dimer states and \( E_F \), which is indicative of a small percentage of charged monomers at the surface of the dimer phase.

As the temperature is lowered below 135 K the dimerized film undergoes a transition to a conducting phase characterised by a sharp Fermi edge. The sample could be annealed and cooled several times through this transition, which shows its reversible character. The reversible transformation undergone by the dimer phase cannot be a transition to the polymer phase, as once formed, the polymer chains are stable up to temperatures high enough to recover the fcc phase. Moreover, the \( \text{RbC}_{60} \) polymer phase undergoes a magnetic ordering transition at 50 K \cite{Chauvet94}, which is presumably preceded by a metal-to-insulator transition at higher temperature \cite{Oszlany95}, while our spectra clearly point to a strongly metallic character of the low temperature phase \cite{Kosaka95}. The sc phase is instead reported to be metallic \cite{Kosaka95}, which agrees with the observed Fermi edge in the low temperature spectra. Moreover, the transition temperature from the dimer to the low-temperature phase in the film corresponds to the temperature at which the sc phase transforms irreversibly into the dimer phase in bulk \( \text{RbC}_{60} \) (125 K) \cite{Kosaka95}. These observations in concert demonstrate the reversibility of the sc-dimer transition at the surface, in contrast to the bulk case \cite{Oszlany95, Zhu95}, and directly confirm the metallic character of the sc phase.

It may seem surprising that the dimer bonds can be cleaved as the temperature is lowered but one should note, however, that the formation of dimers costs elastic energy due to the ensuing structural distortion, and that this energy term plays a role in the free energy balance between the various phases. The reduced dimensionality and mechanical strain in the film, and electrostatic compensation issues at the film surface \cite{Oszlany95}, presumably contribute to the different character of the phase transformation at the surface. In bulk \( \text{RbC}_{60} \) in fact, the sc phase is obtained by quenching from the fcc phase so as to avoid the formation of the dimers (although in one case the sc to dimer
transformation appeared to be reversible also in a bulk RbC\textsubscript{60} sample\textsuperscript{*}). All quench attempts in our setup resembled the one displayed in Fig. 4.5, indicating that our cooling rate is too slow to avoid the formation of the dimer bonds.

### 4.3.3 Surface charge reconstruction

#### 4.3.3.1 Charge states at the film surface

The C 1\textsubscript{s} spectra of all four RbC\textsubscript{60} phases, shown in figure 4.6 for both emission geometries, are seen to contain (at least) two components, approximately half eV apart. The intensity of the two C 1\textsubscript{s} components varies with the emission angle in the same fashion in all phases, with the component at higher binding energy being more intense in grazing than in normal emission. Spectra from similar samples collected in normal emission and 80\textdegree grazing emission with a photon incidence angle of 40\textdegree in both cases, showed the same changes in the C 1\textsubscript{s} intensities (not shown). This implies that this intensity variation cannot be due to a polarization dependence.

The observation of the two-component feature in all four phases means that it is not due to a final state photoemission effect, but has instead a common origin in all phases. The C 1\textsubscript{s} binding energy of individual C atoms on a monomer or a dimer can in principle be slightly dependent on their position in the molecule, due to different values of the Madelung potential closer or farther from surrounding ions or intermolecular bonds. However, as discussed in detail in \{Schiessling\ '05\}, studies of chemisorbed C\textsubscript{60} suggest that intramolecular Madelung potential-like effects are quite small for C\textsubscript{60}, presumably due to the excellent internal polarization of the molecule upon charging \{Rotenberg '96, Shirley '96\}. Therefore, we attribute the observation of distinct components in the C 1\textsubscript{s} spectrum to the existence of different molecular sites, rather than to different atomic sites on the same molecule.

\textsuperscript{*} V. Brouet, private communication.
Figure 4.6 Normal (empty circles) and grazing (filled circles) emission C 1s spectra of the four phases of RbC$_{60}$. The normal emission spectra are normalized to the intensity maximum, while the grazing emission ones are normalized so that the lineshape at lower binding energy matches that of the normal emission spectrum of the same phase. In all phases at least two components are present, and the highest binding energy component (see arrow) has a higher relative intensity in grazing than in normal emission.

From the relatively high interlayer separation ($d \approx 9\,\text{Å}$) and the low electronic mean free path in C$_{60}$ compounds ($\lambda = 5-6\,\text{Å}$, see {Schiessling '05} and {Goldoni '01a}) at the kinetic energies of the photoelectrons in the present experiment, the expected contribution of the surface C$_{60}$ layer to the normal emission signal is $1 - \exp(-d/\lambda) \approx 75-80\%$ of the total intensity. Hence only the first two or three C$_{60}$ layers give a detectable contribution to the normal emission PES spectra, and these predominantly reflect the emission from the C$_{60}$ surface layer. The grazing emission spectra are practically sensitive only to the topmost layer, due to an increase of the exponent by a factor $1/\cos(70^\circ)$. The fact that the two C 1s components are present in the GE spectra (with only small intensity changes compared to the NE spectra), clearly indicates that the two non-
equivalent $C_{60}$ molecular sites are present at the film surface. Hence the origin of the two molecular components in the C 1$s$ spectra cannot be a surface relaxation or a surface core level shift \{Rotenberg '96, Shirley '96\}.

The comparison between the calculated DOS for the isolated $(C_{60})^{2-}_2$ dimer and the valence band spectrum of the dimer phase of RbC$_{60}$ brings further insight. It is seen that if the frontier states in the theoretical and experimental DOS are aligned, as shown in the left panel of figure 4.7, the shoulders to the low binding energy side of the main photoemission peaks are reproduced, but not the main peaks themselves. The energy separation between the main peaks is the same as that found in the $C_{60}$ monomer phases. In the right panel of figure 4.7 we have reproduced the valence band spectrum of the dimer phase of RbC$_{60}$ as the sum of the valence band lineshape of pristine $C_{60}$ and the theoretical $(C_{60})^{2-}_2$ DOS (the pristine $C_{60}$ spectrum was acquired on the multilayer film before Rb doping, in the same experimental conditions as the RbC$_{60}$ spectra). The two curves were broadened to mimic the effect of the crystal field and of inelastic electron scattering, shifted so that the energy separation between the leading features was similar to that in the C 1$s$ core level, and adjusted in intensity to best reproduce the dimer phase lineshape.

This analysis of the valence band spectrum of the dimer phase demonstrates that both charged dimers and neutral monomers are present at the film surface in this phase. The two components in the C 1$s$ spectrum of the same phase hence correspond to these two molecular species.

![Figure 4.7](image)

**Figure 4.7** Left: comparison of the theoretical density of states (DOS) of the isolated $(C_{60})^{2-}_2$ dimer \{Pichler '97\} and the valence band spectrum of pristine $C_{60}$ and that of the RbC$_{60}$ dimer phase. Right: model of the dimer phase spectrum as the sum of the $C_{60}$ valence band lineshape and the theoretical $(C_{60})^{2-}_2$ DOS.
The same considerations hold for the other phases as well. The valence band spectrum of the sc phase clearly shows the presence of at least two molecular components (see arrows in figure 4.4), and the same is true for the polymer phase (see figure 4.4 and paragraph 4.3.7). The spectrum of the fcc phase is also anomalously broad. In both cubic phases the relative intensity of the LUMO- and HOMO- derived states is much lower than the value 1:10 expected for a homogeneous matrix of $C_{60}^{1-}$ anions (Satpathy '92) (1:10 is the ratio between the number of LUMO to HOMO electrons in the $C_{60}^{1-}$ anion), which again indicates the presence of non-charged molecules in the film. The spectra of the cubic phases will be discussed in more detail in paragraph 4.3.4.

The arguments presented in this section therefore establish that the two-component feature of the C 1$s$ spectra of the four phases of RbC$_{60}$ is related to the presence of two distinct molecular charge states (neutral and charged) on the photoemission timescale at the film surface. We will now discuss the origin of such charge states.

### 4.3.3.2 Origin of the two molecular charge states

The simplest explanation for the presence of both charged and neutral fullerenes in the film is that they arise from domains of RbC$_{60}$ and pristine C$_{60}$, or from a nano-phase segregation as suggested in Na fullerides (Klupp '06). This, however, can be ruled out based on several reasons. The observed relative intensities of the two peaks are found to be the same regardless of the initial stoichiometry of the precursor film. The valence band spectrum of the polymer, dimer and fcc phases are indeed identical to those of previous studies, which shows that the double-component structure is an intrinsic feature of RbC$_{60}$ films, and can hardly be attributed to the presence of large domains of unreacted C$_{60}$ (different studies should otherwise find different valence band lineshapes due to the different average stoichiometry). Most importantly, however, pure C$_{60}$ sublimes at 455 K, i.e., much below the distillation and measurement temperature (525 K) of the fcc phase (Poirier '94), hence domains of unreacted C$_{60}$ would sublimate during the vacuum distillation procedure (see section 4.2).

The presence of a nano-segregated phase was suggested in Na fullerides. However, this hypothesis cannot explain the angle dependence of the C 1$s$ spectra. Moreover, a high mobility can be expected for the smaller Na and Li ions (as we showed in Chapter 3 for the case of Li), but it can hardly characterize the heavy Rb ions. Moreover, the chemical composition in bulk Na fullerides becomes homogeneous above 460 K (Klupp '06), which again is lower than the measurement temperature of fcc RbC$_{60}$. Hence an alternative explanation must
be sought for the occurrence of neutral charge states at the RbC\textsubscript{60} film surface.

The (111) surface of fcc RbC\textsubscript{60} is an example of a termination of an ionic compound with a maximum polarity plane. If the surface C\textsubscript{60} layer were fully charged, there would be an uncompensated negative charge at the film surface, leading to a net dipole moment perpendicular to the surface and such termination would be electrostatically unstable \{Fripiat '77\}. In fact, polar terminations with uncompensated dipoles are never observed in nature. There are various ways in which the instability of a fully polar surface of an ionic solid is avoided, the most common being relaxation and buckling reconstruction. A surface relaxation can be excluded for RbC\textsubscript{60}, as it does not introduce the nonequivalence between surface sites required to explain our C 1\textit{s} core level data. On the other hand, a buckling reconstruction would appear with a characteristic surface diffraction pattern, while the low energy electron diffraction (LEED) of the film showed simply a (1x1) hexagonal pattern, in agreement with previous studies \{Lopinski '94\}. Also, the size and mass of the C\textsubscript{60} molecule suggest that a structural surface reconstruction might not be as energetically favourable as in conventional solids where the ionic masses involved are much smaller.

A less common mechanism which can resolve the electrostatic instability of the RbC\textsubscript{60}(111) surface, and at the same time explain the observation of two nonequivalent surface sites, is an electronic reconstruction in which the surface C\textsubscript{60} layer carries a lower net charge than the corresponding bulk layers \{Hesper '00\}. This phenomenon has been observed on ultra-thin films of ionic compounds \{Hebenstreit '00\}, at the interfaces between transition metal oxides \{Nakagawa '06\}, and it was also recently proposed for fcc K\textsubscript{3}C\textsubscript{60}(111) \{Schiessling '04, '05; Hesper '00\}.

To obtain a plausible value for the surface charge density, we follow \{Fripiat '77\}. If one considers a thin slab or a semi-infinite crystal of a fcc ionic solid with (111) surface(s), the electrostatically-stable termination must carry a surface charge density reduced to half its value inside the solid in order for the total dipole moment perpendicular to the surface to vanish. This is shown in figure 4.8(a) and (b) for the A\textsubscript{3}C\textsubscript{60} case \{Hesper '00\}. 

**Figure 4.8** (a),(b) Schematic view of a finite charge-neutral slab of A$_3$C$_{60}$ in vacuum with (111) termination planes, and corresponding electrostatic potential (after {Hesper '00}). The termination planes are: (a) a fully charged C$_{60}$ plane on one side and a fully charged K plane on the other, which leads to a divergence of the potential; (b) half-charge C$_{60}$ plane (–1.5e per molecule) on both sides. (c) Schematic view of a finite, charge neutral slab of RbC$_{60}$ with (111) termination planes with the proposed charge reconstruction.

In the case of C$_{60}$-terminated RbC$_{60}$(111) the average charge in the surface layer is thus –0.5e per molecule, as depicted in figure 4.8(c).$^*$ Half-integer ionic charges are indeed observed in other examples of surface and interface electronic reconstructions, in particular in Na-terminated ultrathin NaCl films where the formal charge of the cations was reported to be +0.5e, implying a half-filled Na 3s band {Hebenstreit '00}. In RbC$_{60}$ the difference in energy between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is much less than that between the Na 2p and 3s states in NaCl, so that an electronic reconstruction is energetically more favourable.

$^*$ In our films as in the other examples of interfacial charge reconstruction one of the two surfaces is replaced by the interface between the film and the substrate, where interfacial dipoles and built-in electric fields may complicate the situation depicted in figure 4.8. The problem of electrostatic stability may however be considered a “local” issue at each interface: indeed structural reconstructions originate from electrostatic instabilities and are observed at the surface of a crystal regardless of its thickness or possible interfaces with other materials far away from its free surface.
Since in organic molecular solids in general, and in RbC\(_{60}\) in particular, the electrons are mostly localized on single molecules \{Chauvet '94, Tycko '93\}, a surface charge of \(-0.5e\) per \(C_{60}\) actually corresponds to a situation in which half the molecules are neutral and half carry a \(-1e\) charge (at least on short time scales such as that of the photoemission process, which is of the order of 10 \(\text{as}\)). Similar arguments should apply for the other phases, as it is likely that the local charge density at the surface is unchanged in a phase transition (the issue of electrostatic stability of the surface is always present for all phases). As the singly-bonded dimer is stable only when it carries a net charge, in the transition to this metastable phase only the charged \(C_{60}^{1}\) monomers take part in the dimerization, while the neutral monomers at the surface remain so also at low temperature, and similarly for the polymer phase.

### 4.3.3.3 Model for the binding energy difference

Within the present model, therefore, the two components visible in the C 1\(s\) spectra reflect the presence of 50% neutral and 50% charged fullerene molecules in the surface layer. We assign the component at lower binding energy to the charged \(C_{60}\) species and the one at higher energy to neutral \(C_{60}\), based on the relative intensity and angular dependence of the two C 1\(s\) components in both phases. This consideration is also true for the other molecular levels, for example the HOMO.

To support this assignment we can roughly estimate the C 1\(s\) or HOMO photoemission binding energy difference (\(\Delta\text{BE}\)) between the charged and neutral molecules, following the ideas of \{Schiessling '05\}. We take as an Ansatz a model in which the surface consists of alternate arrays of charged and neutral molecules (see figure 4.9(a)). The binding energy difference \(\Delta\text{BE}\) is approximately the difference in ionization potential between the two charge states. We start the calculation with the ionization of a neutral molecule by expelling an electron from the HOMO orbital. The difference in ionization potential is evaluated as the cost of transferring the resulting hole to a distant negatively-charged molecule. Such cost is in general the sum of an intra-molecular Coulomb energy term plus an inter-molecular Coulomb energy term (Madelung potential); the latter can be estimated in a simple way considering the contribution of nearest neighbours (n.n.) only \{Schiessling '05\}. A charged surface molecule has two charged n.n. in the surface plane and three in the subsurface layer, for a total of five, while a neutral molecule has four plus three, all other n.n. being neutral (see figure 4.9(a)).
Figure 4.9 (a) Top view of the first (outermost) and second molecular layers of the fcc RbC$_{60}$(111) surface. The dark circles are charged molecules, the bright ones correspond instead to the neutral surface monomers. The nearest neighbours of a charged and neutral surface molecule are indicated with arrows. (b) Top view of the same surface, after an electron has been extracted from the two molecules considered in (a): the previously charged molecule is now neutral but in an excited state (indicated by an asterisk); the previously neutral one is now positively charged and in an excited state (white circle with an asterisk).

The photoemission process from a neutral molecule leaves behind a C$_{60}^{1+}$ ion in an excited state (see figure 4.9(b), lower right corner). To move the hole in the HOMO of a C$_{60}^{1+}$ molecule to the HOMO of a distant C$_{60}^{1-}$ ion, we have to consider that there is an initial configuration Madelung contribution from the C$_{60}^{1+}$ of $-7\text{V}$ and from the C$_{60}^{1-}$ of $+5\text{V}$, for a total of $-2\text{V}$, where V is the screened Coulomb potential energy between singly charged n.n. ions. In the final state configuration both molecules are neutral, giving no terms in V, but the formerly negatively-charged molecule now contains an exciton (figure 4.9(b), upper left corner). The change in internal energy between the initial and final configuration of such a molecule is simply the exciton binding energy, or $U_{\text{ex}}$. If there is a difference in the ground state energy of the HOMO levels of the neutral and charged molecules due to solid-state effects, we postulate that to a large extent such difference is maintained in the final state of the PES process, as this occurs on fast timescales. Hence the binding energy difference is simply the ionization potential difference or $\Delta \text{BE}=2V-U_{\text{ex}}$, placing the spectrum from the negatively-charged molecules at higher energy (or lower BE). Using the values found for solid C$_{60}$, namely $U_{\text{ex}}=1.5\text{ eV}$ for surface excitons {Goldoni '96a, '96b; Schwedhelm '98} and V=0.3 eV {Antropov '92}, we find a binding energy...
difference of 0.9 eV, in reasonable agreement with our experimental value of 0.65 eV (see next paragraph). As the exciton binding energy is roughly the same for core and valence excitons {Schnadt '05}, our estimate is valid for the C 1s level as well as for higher-lying molecular orbitals. The slight overestimation of the binding energy separation is most probably related to the fact that the value of U (and presumably also of V) is lower in fcc RbC_60 than in pristine fullerite, as will be shown in Chapter 5, due to a more efficient screening of Coulomb interactions.

4.3.4 Charge states in the surface and subsurface layers in the cubic phases

In figure 4.10(a) a fit of the C 1s spectrum of the fcc phase is presented, using two Doniach-Šunjić {Doniach '70} components separated by 0.65 eV, to which a Shirley background {Shirley '72} is added to account for inelastically scattered electrons (for the Doniach-Šunjić components a Lorentzian width of 0.1 eV and Gaussian FWHM of 0.68 eV was used, and the asymmetry parameter was α=0.035). The spectral weight of the C_60\(^{1−}\) component is about 62%, implying that at normal emission only ~25% of the total spectral weight comes from the subsurface layers, in agreement with the low inelastic mean free path {Schiessling '05; Goldoni '01a}. The RbC_60 fcc valence band spectrum was modelled (figure 4.10(b)) using two C_60 lineshapes, corresponding to the neutral and charged monomers, with approximately the same relative intensity and energy separation observed in the core level spectra, as expected from our previous discussion of the binding energy difference between the two charge states. The energy separation between the HOMO of the negatively charged component and the LUMO-derived feature, which represents the band gap of the charged molecules in this phase, is found to be 1.7-1.8 eV (centroid to centroid). This value is intermediate between the gap found for the neutral molecules in pristine fullerite (2.15 eV, see Chapter 5) and that observed in A_6C_60 compounds {Rudolf '99}. This could be anticipated, as the lower filling of the LUMO entails a reduced relaxation of the molecular orbitals, and provides further support to our interpretation.

As visible in Fig. 4.6, the relative height of the two C 1s features in the sc phase is reversed compared to the fcc phase, which would seem to indicate that the percentage of neutral fullerenes in the film has increased and that the amount of C_60\(^{1−}\) ions decreased (this cannot be due to a higher surface sensitivity in the sc phase: as the two cubic phases are structurally very similar, the electronic mean free path should be the same in both, and the lower temperature of the sc phase
should, if anything, lead to higher mean free path than in the fcc phase). The lower energy component has a pronounced tail towards low binding energy, which cannot be due to metallic screening of the core hole nor to inelastically-scattered electrons, as both effects only contribute to the asymmetry towards high binding energy. Also, we do not expect an anomalous broadness of the charged component with respect to the neutral one in a cubic phase; this is indeed testified for by the Rb 3$d$ spectrum of the sc phase.

While it is possible to reproduce the core level and valence band spectra of the fcc phase with two components of the same broadness, a third less intense component must be introduced at low binding energy in the sc phase spectra (see figure 4.10). The relative intensity and energy position of the three components are consistent between the core and valence spectra, with an energy separation between adjacent components of approximately 0.5 eV, slightly smaller than that found in the fcc phase (0.65 eV).

The similar energy separation between the components, the shift of the minority component to lower binding energy, and the relative enhancement of the high binding energy component (neutral C$_{60}$) allow us to conclude that the new component arises from doubly-charged fullerene molecules present in the sc phase. The relative intensity predominantly reflects the abundance of each charge state in the first layers of the film, and it can be accounted for if, starting from the composition of the fcc phase, with the bulk consisting of C$_{60}^{1-}$ anions and the surface composed of 50\% C$_{60}^{1-}$ and 50\% neutral C$_{60}$, approximately 10-15\% of the molecules in the surface and subsurface layers assume a double-charge state. This must occur at the expense of singly-charged species, rationalizing the observed increase in neutral molecules to preserve charge balance. Thus, all our observations are consistent with the presence of doubly-charged molecules at the surface of the sample in the sc phase. This conclusion strongly supports the proposal based on NMR data of a minority of doubly-charged molecules in the spin-singlet state in the sc phase of CsC$_{60}$ {Brouet '99, '02b}. The percentage of doubly-charged anions is the same in the two systems, which lends support to the idea brought forth in {Brouet '02b} that the number of C$_{60}^{2-}$ anions is limited by their mutual Coulomb repulsion.
Figure 4.10 Model of the NE C 1s (left) and HOMO- and HOMO–1-derived region of the valence band (right) spectra of the fcc and sc phases, in terms of different molecular charge states (the valence band spectra are plotted with a vertical offset). (a),(b) model of the fcc spectra with two components; (c),(d) model of the sc spectra with two components; (e),(f) model of the sc spectra with three components. In the fit of the sc spectra with two components ((c),(d)), the arrows indicate the largest discrepancies between data and model.
4.3.5 LUMO-derived states in the fcc and sc phases

The spectra of the LUMO-derived states are compared in detail in Fig. 4.11 for both cubic phases. These states are interesting at least in two respects: while the spectra of C $1s$ and the higher lying C$_{60}$ molecular orbitals carry information on neutral and charged molecules, only charged species contribute to this part of the spectrum; moreover, the $t_{1u}$ states cross the Fermi level and thus convey information about the metallicity of each phase.

In the lower part of figure 4.11 we compare the grazing and normal emission PES spectra of the C$_{60}$ LUMO-derived feature in the fcc phase of RbC$_{60}$. The LUMO-derived spectrum looks practically identical in the two geometries, with a single broad feature centered at 0.5 eV binding energy and a very low but non-zero spectral density at and above the Fermi level as previously observed in both fcc RbC$_{60}$ and CsC$_{60}$ \cite{Lopinski94, DeSeta96, Poirier95}. As mentioned previously, the width of the fcc LUMO feature is much larger than $\sim 0.1$ eV predicted by band theory for the singly occupied $t_{1u}$ band, which points to an important role played by electron-electron and electron-phonon interactions. While both the electron-electron and the electron-phonon coupling in general lead to a narrowing of the electronic bandwidth, they also give rise to satellites in the photoemission spectra, as exemplified in section 2.6.3 of this thesis.

The LUMO spectrum of the sc phase displays a sharp Fermi edge followed by a maximum at 0.4 eV, which decays with a linear slope at higher energy. The observation of the Fermi edge clearly shows that the sc phase of RbC$_{60}$ is metallic also in thin-film form.

The spectral weight of the LUMO-derived states in the fcc phase extends well above E$_f$, and decays more slowly than the profile of the Fermi-Dirac distribution at the measuring temperature of 525 K. This is not expected for a Fermi liquid, where the photoemission profile is given by the density of states multiplied by the occupation factor at the measuring temperature (i.e. the Fermi-Dirac function), and signals an unconventional electronic behaviour. The same phenomenon was observed in previous studies of the fcc phase of RbC$_{60}$ and CsC$_{60}$, and in K$_3$C$_{60}$ and Rb$_3$C$_{60}$ at high temperature \cite{Knupfer93, Lopinski94, DeSeta96, Poirier95, Goldoni00}. The similarity between the high-temperature LUMO profile in $A_3C_{60}$ and $AC_{60}$ compounds shows that this phenomenon does not depend on the details of the band structure, but is instead related to electron-electron or electron-phonon interactions.
Electron correlation can give rise to quasiparticle satellites above $E_F$, which can determine a tailing of the spectral intensity as observed in some strongly correlated and Kondo systems {Reinert '01}. From our discussion of the binding energy difference in section 4.3.3 it is clear that correlation effects are important at the surface of RbC$_{60}$, as also found at the K$_3$C$_{60}$ surface {Schiessling '04, '05}. As reported in paragraph 2.6.3.3, calculations {Meinders '94a} of the spectral function for the three-fold degenerate Mott-Hubbard model in the localized limit with $U=0.7$ eV show that at low doping the spectral function has a pole near $E_F$ whose energy position depends on the number of electrons per site, being below the Fermi energy for $x=1$, at $E_F$ for $x=0.8$ and slightly above $E_F$ for lower filling levels such as that observed at the film surface ($x=0.5$). Interestingly, also for $x\approx 1.5$ the spectral function has a pole right above $E_F$. Hence correlation satellites might be partially responsible for the spectral tail above $E_F$ in the photoemission spectrum of odd-stoichiometry fullerides.

On the other hand, the broadness of the spectral features of the dimer phase, where no band- or correlation-effects are present, indicates that electron-phonon
broadening plays a dominant role in the photoemission spectra of RbC₆₀. Electron-phonon broadening is a well-known feature of organic solids and fullerides in particular. Franck-Condon broadening has been extensively observed in C₆₀, for example in PES experiments on C₆₀ and C₆₀¹⁻ in the gas phase {Gunnarsson '95a}, on C₆₀ films on graphite {Brühwiler '97, Manini '03} and on K₅C₆₀ and Rb₃C₆₀ films {Goldoni '98, '00, '01b; Knupfer '93}. The difference in lineshape between the spectrum of the high-temperature fcc phase and that of the sc phase in figure 4.11(a) is reminiscent of the temperature dependence of the LUMO-derived states in K₅C₆₀ and Rb₃C₆₀ {Knupfer '93, Goldoni '00}, shown in figure 4.11(b) for the K₅C₆₀ case. Also in the higher stoichiometries a sharp Fermi edge is visible at low temperature, which is smeared out with increasing temperature. A smooth evolution between the low- and high-temperature LUMO profiles is observed in A₃C₆₀, accompanied by a corresponding broadening of the other valence band features and the appearance of the intensity tail above E_F {Knupfer '93, Goldoni '00}. The similarity to our spectra strongly suggests that the non-Fermi liquid profile in odd stoichiometries is due to Franck-Condon satellites, with the intensity above E_F due to the gradual transfer of spectral weight to phonon-gain satellites (see paragraph 2.6.3).

While the C 1s and the higher lying C₆₀ molecular orbitals carry information on neutral and charged molecules, only charged species (in the sc phase, both singly- and doubly-charged anions) contribute to the LUMO-derived intensity. The similar energy position of the spectral maximum in the spectra of Fig. 4.11 suggests that the most prominent LUMO-derived feature arises in both cubic phases from C₆₀⁻ species. The relative energy position of the two charge components in the spectrum of the sc phase should follow that observed in the C 1s and HOMO and HOMO-1 spectra of the same phase, since it mainly reflects the contribution of the on-site Coulomb repulsion. Thus we find that the 2– component in the sc phase contributes to the spectral weight at E_F.

The more pronounced slope to the high binding energy side of the LUMO states in the sc spectrum might be due to the different electron-scattering mechanisms available in the sc phase {Brouet '02b} or to spectral satellites related to the 2– charge state, and possibly to the presence of a small minority of dimers in the sc phase, which might contribute some of the spectral intensity around 1 eV binding energy.

From the relative intensity of the C₆₀²– and C₆₀¹⁻ components in the C 1s spectrum of the sc phase we estimate that the contribution of the doubly-charged states to the LUMO spectrum is approximately 40% of the total intensity, which shows that at least some of the spectral intensity related to C₆₀²– species must be distributed into satellites below E_F.
4.3.6 Surface metallicity and charge fluctuations in the cubic phases

As visible in figure 4.11(a), no angular dependence is found in the LUMO-derived signal of the fcc phase, contrary to the observations on the other molecular levels. Since only half the surface layer contributes to the LUMO intensity, the ratio between subsurface- (“bulk”) and surface-derived intensity in the LUMO spectrum should be higher than the one found for the other levels. The fact that the binding energy of the LUMO-derived feature is the same in both geometries and that it crosses the Fermi level suggests that both the surface and the bulk of fcc RbC$_{60}$ are (weakly) metallic, since the similar binding energy would then result due to the alignment of the chemical potentials of bulk and surface.

Similarly, no dependence on the emission angle is observed for the LUMO-derived feature in the sc phase. The observation of the Fermi edge in grazing emission and the lack of angle-dependence demonstrates the conducting nature of the surface layer in the sc phase. Instead, the electronically-reconstructed K$_3$C$_{60}(111)$ surface was suggested to be insulating {Schiessling '04, '05}. This difference in behaviour between the two odd stoichiometries, both of which are metallic in the bulk, is a bit puzzling.

We can tentatively discuss the metallic character of the surface and the bulk of RbC$_{60}$ within the same model used to account for the binding energy differences. A long distance hopping process in the bulk of RbC$_{60}$ between two singly-charged molecules costs an energy amount equal to the bulk Hubbard $U_{\text{bulk}}$ in this phase. Despite this energy cost for hopping, the kinetic energy gain derived from hopping (of which the bandwidth is a measure) is apparently large enough to keep RbC$_{60}$ (as well as other alkali fullerides of odd stoichiometry such as K$_3$C$_{60}$) on the metallic side of a Mott-Hubbard transition {Koch '99b}. At the film surface a long distance hop from a charged molecule to a neutral one leads to a net intermolecular repulsive energy loss of $2V<U$ (these quantities refer now to surface values). In other words, although there is no on-site $U$ to pay for the hopping process to occur, the nearest-neighbour Coulomb repulsion acts as a hopping barrier for conduction in the surface layer. The same argument has been applied to the case of the K$_3$C$_{60}(111)$ surface {Schiessling '04, '05}.

It could be argued that although in a surface layer the bandwidth should be reduced, this reduction could be compensated by the decrease in the energy barrier for the hopping process, which is only $V_{\text{surf}}$ compared to the bulk where it is equal to $U_{\text{bulk}}$. This explanation would rationalize the similarity in the electronic character of the bulk and surface of RbC$_{60}$, but it is at odds with the suggested
insulating character of the surface of K$_3$C$_{60}$. The difference between the two cases could be related to the fact that, contrary to K$_3$C$_{60}$, in RbC$_{60}$ the same charge state (1–) appears both at the surface and in the bulk material and a charge density difference of only 0.5e per molecule exists between the surface and subsurface layers, which might perhaps render hopping between the two more favourable and thereby help establish the surface metallicity of RbC$_{60}$.

We now discuss the nature of conduction at the surface of the sc phase of RbC$_{60}$. The simultaneous presence in the photoemission spectra of a Fermi edge and of different molecular charge states is at odds with the expectation for a simple metal, where the conduction electrons are delocalized and core ions are all in the same charge state. The relatively small intermolecular hopping (compared to the intramolecular one) in molecular solids results in general in a localized electronic character. This is in fact what is observed in RbC$_{60}$, where the half-integer surface charge density does not result in the formation of a band of delocalized electrons, but in the observation, at least on the PES timescale, of several surface charge states. Such observation entails that the metallicity of the RbC$_{60}$ surface is not derived from delocalization, but from hopping processes, which is consistent with the expectation that the ground state of the Hubbard model at non-integer filling is a metal also in the limit of extremely localized electrons where $U$ is much larger than the bandwidth, which results from the possibility of electron hopping to empty sites (in the RbC$_{60}$ case, the neutral surface molecules). A “molecular” character of metallicity in RbC$_{60}$ can be also inferred from our XAS study (see paragraph 4.3.8).

The surface metallic character of RbC$_{60}$ implies that the localization of an electron on a specific molecule is limited to a finite time due to hopping processes. Our data show that the electronic localization time is longer than the PES timescale (tens of attoseconds). The 2– charge states in the sc phase also exist on a timescale longer than tens of attoseconds, and the obvious question is whether they are static entities or if they play an active role for metallicity. We can draw a parallel between our photoemission study and the NMR results {Brouet ‘99, ’02b, ’02c} on the electronic structure of A$_r$C$_{60}$. Given the identical phase diagram of RbC$_{60}$ and CsC$_{60}$, we do not expect any dependence on the intercalant, and base our discussion on the comparison between bulk and surface phases, which we have shown to have different properties, as exemplified by reversibility of the sc-to-dimer transformation at the surface or by the occurrence of the surface charge reconstruction. As mentioned in paragraph 4.1, the NMR studies on the sc phase of CsC$_{60}$ {Brouet ’99, ’02b} point to an extremely long lifetime (seconds) of the 2– states in the bulk of this phase. Although the stabilization of the spin singlets was attributed in part to the Jahn-Teller energy
gain associated with the formation of (distorted) C_{60}^{2–} anions (see section 1.4), and tentatively also to the possible presence of a trapping potential related to the orientational degree of freedom of the C_{60} molecule {Brouet ‘02b}, the origin of the long lifetime of 2– states was not understood quantitatively, as double site occupancy should be hindered in a strongly correlated system.

It is in fact reasonable that the interplay between electron correlation and Jahn Teller coupling, which, as stated in paragraph 1.4, determines the insulating or conducting ground state of cubic fullerides, plays a determinant role in establishing the occurrence (and lifetime) of different molecular charge states. The discussion of section 4.3.3 shows in fact that the surface of cubic RbC_{60} is a strongly correlated electron system. The binding energy difference between different charge components in the C 1s spectrum represents a lower limit for the value of the Hubbard U at the film surface, since the inter-molecular Coulomb repulsion term V appears with a negative sign (the same holds also for the sc phase). This implies that U_{surf}>0.5 eV (0.65 eV) in the sc (fcc) phase of RbC_{60}. These values are much higher than that of the Jahn-Teller pairing energy (see paragraph 1.4) for a phase of (C_{60})^{1–} anions (≤0.2 eV), which shows that the Jahn-Teller effect is not enough to stabilize long-lived doubly charged anions at the surface of the sc phase.

It should be noted that a number of NMR studies have suggested the existence of charge fluctuations on different timescales in various fullerene compounds {Brouet ’01, ’02a, ’02c}: with the notable exception of the bulk sc phase of CsC_{60}, the lifetime of such fluctuation was always found to range between one fs and few tens of fs. The lifetime of doubly-charged anions is reduced to a few femtoseconds in the bulk of the fcc phase {Brouet ’02c}. These studies show that the lifetime of such non-stoichiometric states is not fixed but depends on temperature and varies from phase to phase, and, possibly, between the bulk and surface of the same phase.

The large value of U_{surf} strongly suggests that the 2– states are not stable as long-lived entities. We have moreover seen that the 2– component contributes to the spectral intensity at E_F, which shows that the effect of the doubly charged anions is not simply to introduce vacant sites enabling the hopping of electrons between singly charged and neutral molecules, as suggested in {Brouet ’02b}, but instead points to an active role of this charge state for metallicity. These observations suggest that the 2– states are mobile, i.e., they are present only as short-lived charge fluctuations at the surface of the sc phase. Since the observed lifetime of charge states in the NMR studies is similar in all compounds {Brouet ’01, ’02a, ’02c}, it is tempting to associate the localization timescale with this common time scale, of the order of 10^{–15}-10^{–14} seconds. It is interesting to
note that such a timescale corresponds to the energy barrier for non-stoichiometric fluctuations to occur, as the (bulk) Hubbard $U$ in fullerides is usually of the order of 0.5-1 eV (see Chapter 5).

An important difference between the surface and the bulk of a material is the more efficient screening of Coulomb interactions in the bulk. In pristine $C_{60}$ the bulk value of $U$ is smaller by 0.3 eV than the corresponding surface value due to the lower coordination number at the surface \{Antropov '92, Gunnarsson '04\}. The difference should be even more marked in $RbC_{60}$, since the surface charge reconstruction leads to the presence of neutral surface monomers, which have a lower polarizability than the singly or doubly charged anions leading to a poorer screening of $U$ (see Chapter 5 for a further discussion). The enhanced screening in the bulk $sc$ phase may be large enough to rationalize a difference in the electronic properties of the surface and bulk of the $sc$ phase, and explain the long lifetime of doubly-charged states in the bulk. If we take $U_{surf}=0.5-0.6$ eV in $sc RbC_{60}$, the more effective screening in the bulk would in fact entail that $U_{bulk}$ is comparable to the JT pairing energy; in such case, the two strongest interactions cancel out and the (much weaker) trapping potential invoked in \{Brouet '02\} could indeed become effective in stabilizing the long-lived spin singlets observed in bulk $sc CsC_{60}$, thus rationalizing this puzzling aspect of this phase.

Our data provide evidence that conduction at the $RbC_{60}$ surface is mediated by molecular charge fluctuations, with a localization time of charge carriers longer than the PES time scale. This type of conduction is in fact an expected feature of metallic molecular solids. Since charge fluctuations in such systems are accompanied by modifications of the vibronic state of the involved molecules (which are even more important for Jahn-Teller systems) and of the polarization cloud surrounding the localized charge, they may be expected to occur on longer timescales than that of coherent processes in simple metals, which explains their observation on the PES timescale. We cannot, based on our data, rule out the presence of charge fluctuations also in the $fcc$ phase. The fact that such charge fluctuations were never identified in previous PES studies in fullerides, despite the fact that the fluctuations times conjectured by NMR are longer than the

* We argue that strong electron correlation prevents double site occupancy on longer timescales. Indeed, in a Hubbard picture and in the limit of electron wavefunctions localized on single sites, the characteristic time for a charge fluctuation which costs $\Delta E\sim U$ (the cost of a doubly occupied site) should be (through the uncertainty principle) $\tau\sim h/\Delta E\sim h/U$, which is of the observed order of magnitude in fullerides with $U = 0.5-1$ eV. An active role played by 2– charge states for metallicity implies that there is also a kinetic energy gain accompanying the 2– charge fluctuations, which might play a role for their occurrence.
characteristic time of the PES process, could be due to the more important role played by electron-electron interactions at surfaces, which are supposedly responsible for the insulating nature of the K$_3$C$_{60}$ surface {Schiessling '04, '05}.

### 4.3.7 Metal-insulator transition in the polymer phase

Figure 4.12 shows the fit of the normal emission C 1s spectra of the dimer and polymer phases with two components of different width. We assumed that in the dimer and polymer phases the charged component is slightly broader than the neutral one because of the molecular distortion induced by the formation of inter-molecular bonds, which leads to non-equivalent atomic sites on the molecular unit. The “bulk” to total-signal ratio is roughly 15% for the dimer and polymer phases, which is slightly lower than that found for the fcc phase. This difference is possibly related to the different surface morphology of phases characterized by intermolecular bonding (see paragraph 4.3.8).

Contrary to the dimer case, no density-of-states calculation is available for the charged isolated polymer chain (nor for the AC$_{60}$ polymer phase), but various theoretical studies have appeared on the electronic structure of the linear polymer (see e.g. {Tanaka ’95, Adams ’95, Pederson ’95}). Figure 4.13 shows the theoretical valence band electronic density of states (DOS), calculated in the tight-binding approach, for the isolated C$_{60}$ molecule and the neutral polymer chain (after {Belavin ’00}). A strong similarity is apparent between the two lineshapes. Apart from the region at 8-9 eV below the Fermi energy, where the $\sigma$ orbitals corresponding to the inter-molecular bonds in the polymer chain lie, the positions and relative intensity of the peaks in the polymer DOS are very similar to those in the isolated monomer, albeit the features are in general slightly broader.
Figure 4.12 Fit of the C 1s normal emission spectrum of the dimer (left) and polymer (right) phases with two Voigt components. In both cases the charged component (at lower binding energy) is assumed to be broader than the neutral one (see text).

Figure 4.13 Tight-binding theoretical electronic density of states for the isolated C$_{60}$ molecule (top) and for the neutral C$_{60}$ polymer chain bonded via [2+2]cycloaddition (after {Belavin '00}).
The comparison shows that the monomer DOS is not dramatically modified by linear polymerization, as also confirmed experimentally on photopolymerized C\textsubscript{60} \{Itchkawitz ‘95, Onoe ‘97\}. We have seen in Chapter 3 that the photoemission spectrum of the Li\textsubscript{4}C\textsubscript{60} polymer phase is also rather similar to that of a monomer phase, apart from the frontier states. These results suggest that the similarity in electronic structure between monomer and polymer phases persists also in alkali-doped fullerenes. The main difference between the RbC\textsubscript{60} polymer phase and other polymeric fullerenes such as Li\textsubscript{4}C\textsubscript{60} is that two charge states are present at the surface of RbC\textsubscript{60} due to the charge reconstruction.

We have accordingly modelled the normal emission valence band spectrum of the polymer phase as the sum of two C\textsubscript{60} lineshapes; the result is shown in figure 4.14. The remarkably good agreement found with this model in the “HOMO”-like and “HOMO–1”-like regions of the spectrum indeed shows that the monomer DOS is a good approximation for the occupied electronic states of charged polymers (apart from the “LUMO”-like level, which is not reproduced in the model), similar to what found for Li\textsubscript{4}C\textsubscript{60}.

![Figure 4.14](image)

**Figure 4.14** Model (bold line) of the normal emission valence band spectrum of the polymer phase (markers, displayed with a vertical offset) with two components, corresponding respectively to neutral surface monomers (thin line) and charged polymer chains (dotted line).
Contrary to the LUMO-derives states in monomer phases as fcc \(\text{RbC}_{60}\), where the LUMO orbital supposedly retains its three-fold degeneracy, the partially occupied frontier orbital in the polymer phase, shown in more detail in figure 4.15(a), is non-degenerate \{Tanaka '95\}. The intensity ratio between the frontier “LUMO”-like states and the “HOMO”-like states is the same in the fcc and polymer phases of \(\text{RbC}_{60}\). This shows that the formation of intermolecular bonds does not “use up” extra electrons with respect to the monomer, as all the charge donated by the Rb ions appears in the “LUMO”-like region of the spectrum.

The frontier polymer states display a maximum between 0.35 and 0.4 eV binding energy, followed by a slope towards the “HOMO-like” states. In the room temperature spectrum a finite spectral intensity is observed at and above \(E_F\), supposedly indicative of metallic behaviour. The tail above \(E_F\) is analogous to that observed in the PES spectrum of the LUMO-derived states of the fcc phase, indicating that electron-phonon broadening is also here responsible for the non-Fermi-liquid lineshape.

As the temperature is lowered, the spectral intensity at \(E_F\) decreases and a gap appears to open below the Fermi level. The slope in the spectral lineshape between 0 and 0.3 eV binding energy is not due to the Fermi-Dirac distribution, whose sharp slope is limited to a small range (tens of meV) around \(E_F\). The vanishing spectral intensity in the spectrum acquired at 55 K (figure 4.15(a)) suggests that the thin-film form of the polymer phase is insulating at 55 K. Given the important impact of electron-phonon coupling on the spectral features, it cannot be concluded from these data alone whether the temperature dependence in the lineshape is due to a transition from a metallic to an insulating state, or whether it is an effect due to electron-phonon satellites.

We have therefore performed HREELS experiments to further investigate the possible occurrence of a metal-to-insulator transition. Figure 4.15(b) shows the phonon spectrum measured on a \(\text{RbC}_{60}\) film in the same phase, at room temperature and at 85 K. While at room temperature a clear background is visible which rises towards the position of the elastic peak, suggesting that metallicity is present at ambient temperature, a very flat background can be observed in the spectrum acquired at 85 K, which confirms the insulating nature of the polymer phase at low temperature. The metallic-like asymmetry was observed also in the HREEL spectrum acquired at 110 K. The high number of modes visible in the HREEL spectrum of polymerized \(\text{RbC}_{60}\) (especially at low temperature), as compared to the few modes visible in the spectrum of pristine \(\text{C}_{60}\) (also shown figure 4.15(b)) is a result of polymerization, which as discussed in Chapter 3 for the \(\text{Li}_4\text{C}_{60}\) polymer phase lifts the degeneracy of the vibrational modes.
Figure 4.15  (a) Photoemission spectrum of the frontier polymer states at room temperature and at 55 K. (b) HREELS phonon spectrum of the polymer phase at RT and at 85 K, compared with the analogous spectrum of the pristine C_{60} film at room temperature. Note the metallic background at low loss energy in the room temperature polymer spectrum.

The comparison between the PES and HREELS results suggests that the opening of the gap in the spectra of figure 4.15(a) is the signature of a metal-insulator transition in the polymer phase, which occurs at the surface of the film between 110 and 90 K. Indeed, bulk studies on the RbC_{60} polymer phase report weak metallicity at room temperature {Stephens '94, Chauvet '94, Pekker '94}, while at 50 K a magnetically ordered phase sets in which has characteristic features of a charge density wave {Chauvet '94}. This magnetic ordering is accompanied by a metal-insulator transition {Bommeli '95, Mizoguchi '99} related to strong electron correlation effects combined with reduced
dimensionality {Chauvet '94}. The higher temperature observed for the metal-
insulator transition at the surface might be related to structural aspects (strain,
different lattice parameters in the film) influencing the dimensionality of the
electronic and magnetic structure, or to an effect of the film truncation on the
electronic properties (occurrence of the surface charge reconstruction, poorer
screening of Coulomb interactions at the surface).

4.3.8 X-ray absorption spectra

Our analysis of the photoemission results on the four phases of RbC$_{60}$ in
terms of different charge states of the surface molecules finds further
confirmation in the X-ray absorption (XAS) spectra of these phases. The XAS
spectra of all four phases of RbC$_{60}$ appear more structured than the
corresponding spectrum of pristine C$_{60}$, as shown for the fcc, sc and dimer
phases in figure 4.15. The features in the fcc RbC$_{60}$ XAS spectrum are broader
than those of pristine C$_{60}$, which is only partially due to the elevated temperature.

The XAS spectra presented in figure 4.16 are normalized to the area under the
curve between 285 and 287 eV photon energy. The features in this energy range
 correspond, in the monomer phases, to C 1$s$ → LUMO+1 and C 1$s$ →
LUMO+2 transitions. With this normalization the four spectra overlap also at
high photon energies. The height of the first absorption resonance,
corresponding to the C 1$s$ → LUMO transition, is reduced in both dimer and fcc
phases of RbC$_{60}$ by almost one half with respect to pristine C$_{60}$ (a bit less in the sc
phase spectrum), while the width of such feature is larger and appears structured.
This fits well with our model for the surface, since different charge states
contribute to the XAS spectrum. The total intensity (area under the curve)
between the onset and 285 eV in the RbC$_{60}$ spectra is reduced by 15% compared
to the total intensity of the C 1$s$ → LUMO transition in pristine C$_{60}$. This result,
given the uncertainty involved, is consistent with an average partial filling of the
LUMO molecular orbital in our RbC$_{60}$ film of close to or less than 1/6, as
expected for AC$_{60}$ stoichiometries.

The most intense absorption features in the RbC$_{60}$ spectra should arise from
the neutral surface monomers, which correspond to 50% of the surface layer in
the fcc and dimer phases (65% in the sc phase). The presence of neutral
monomers in all phases explains the evident similarity of all RbC$_{60}$ XAS spectra
to the spectrum of pristine C$_{60}$ (figure 4.16).

The C 1$s$ binding energy measured with PES (roughly 285 eV for the charged
component at lower BE, see figures 4.10 and 4.12) is higher than the XAS onset
in both cubic phases of RbC$_{60}$, which implies that metallic screening as it is found
in conventional metals, or in some $C_{60}$ monolayer systems, is not present here. This points to a predominantly “molecular” character of both phases, similar to what is observed in pristine fullerite \{Goldoni '96a, '96b; Krummacher '93\} and $K_3C_{60}$ \{Käämbre '07, Maxwell '94\}, see also Section V B of \{Brühwiler '02\} for a discussion.

The XAS spectra of the cubic phases of RbC$_{60}$ look very similar to that of the dimer phase, despite the fact that the unoccupied states of the C$_{60}$ monomer and those of the $(C_{60})_2^2$ dimer have quite different energy and degeneracy \{Pichler '97\}. This similarity confirms that an important contribution to the absorption spectrum of the dimer phase comes from the neutral C$_{60}$ molecules present at the film surface.

![C Kα XAS](image)

**Figure 4.16** $C\,1s$ (Kα) X-ray absorption spectra for the dimer, fcc and sc phases of RbC$_{60}$, compared to that of pristine C$_{60}$. The spectra are normalized to the area under the curve between 285 and 287eV photon energy (see text). The arrows indicate the onset of absorption (prepeak) in the spectra of the cubic phases.
Examining the spectra of fcc RbC$_{60}$ in more detail, we note that the main absorption peak at 284.5 eV is accompanied by a shoulder at lower photon energy (see the arrow on the fcc spectrum in figure 4.16), and a similar shoulder is visible slightly above 285 eV photon energy preceding the higher $\pi^*$-derived features between 285.5 and 286.5 eV. Similar, albeit less intense, features can be observed also in the sc spectrum. In both cubic phases the onset of absorption occurs at lower photon energy than in the dimer phase spectrum, and the peaks in the latter appear to be shifted to slightly higher photon energies. Since both features disappear in the dimer XAS spectrum, it is reasonable to assume that they have a common origin.

In the following we present a possible interpretation of the XAS spectra of the two cubic phases based on our model for the surface of RbC$_{60}$. Since the binding energy of charged monomers is lower than neutral ones, we can associate the pre-peak onset of absorption with processes involving charged molecules. Since the XAS were measured in partial yield collecting electrons at 250eV KE, we can estimate that 70% of the signal comes from the surface and 30% from the subsurface layers, similar to the PES case. In the fcc phase, this means that 65% ($=30%+(70%/2)$) of the signal should come from C$_{60}^{1-}$ molecules.

From the above discussion it follows that, for the fcc phase, the first absorption maximum at 284.5 eV photon energy can be attributed to neutral molecules, while the prepeak at 284 eV stems from C$_{60}^{1-}$ anions. For a singly charged molecule (with one unpaired LUMO electron in the ground state), two possible excited states can be reached upon absorption of an X-ray photon, as the spin of the unpaired LUMO electron in the initial state of the absorption process (ground state) can be parallel or antiparallel to the spin of the electron which is photoexcited (spin is conserved during the absorption process). These two types of transitions appear at different energies in the XAS spectrum because of the on-ball exchange energy (see e.g. {Lüders '03}) (and possibly also Jahn-Teller contribution) associated with each spin configuration. Because the final state (as the initial state) contains an odd number of electrons, and because of the presence of the core-hole in the final state, the Jahn-Teller term is probably negligible, and in any case smaller than the term arising from the exchange coupling between the two electrons sitting in the LUMO states. Since such exchange lowers the energy of the parallel spin-configuration, the parallel-spin C$_{60}^1$ $\rightarrow$ LUMO excitations should occur at lower photon energy, which means that they should correspond to the prepeak around 284 eV photon energy.

Not all parallel-spin excitations are allowed: since the spin-part of the wavefunction corresponding to two electrons with parallel spins is symmetric, the coordinate-component must be antisymmetric, hence the two valence electrons
with parallel spin after excitation must sit on different (orthogonal) $t_{1u}$ subshells. No limitations exist instead for antiparallel-spin excitations, implying that such transitions give a larger contribution to the XAS intensity than parallel-spin ones. The relative intensity of the prepeak at 284 eV and the absorption maximum at 284.5 eV in the fcc spectrum can be understood if we assume that the antiparallel-spin $C 1s \rightarrow t_{1u}$ excitations in the charged molecules and the $C 1s \rightarrow t_{1u}$ excitations in the neutral $C_{60}$ molecules both contribute to the main absorption peak (that is, these transitions occur roughly at the same photon energy), while only parallel-spin excitations in the charged molecules contribute to the prepeak intensity.

In the sc phase, the fact that the relative prepeak intensity is lower than in the fcc phase might be a further indication that the fraction of singly charged monomers has decreased due to the appearance of doubly-charged molecules. The low onset intensity (despite the observation of a sharp Fermi edge in PES) and the structured spectral lineshape in the sc spectrum indicates once more that the metallicity of this phase has a “molecular” character, that is, it is due to molecular (hopping-mediated) charge fluctuations rather than to electronic delocalization.

### 4.3.9 Surface morphology in the dimer and polymer phases

While in the monomer phase the surface layer is a $C_{60}(111)$ plane, in the dimer and polymer phases the symmetry is reduced from the cubic symmetry of the other phases, and two possibilities arise for the termination of the film. The $(C_{60})_2^-$ dimers and polymer chains can be either parallel to the surface plane or tilted at an angle of approximately 55° with respect to it. We will present our discussion for the dimer phase, but similar results, apart for the expected LEED pattern, hold for the polymer case.

A comparison between the cubic and dimer structures is proposed in figure 4.17. The direction of dimerization is along the $a_{\text{ortho}}$ axis of the dimer unit cell \{Zhu '95\}. The orthorhombic vectors $a_{\text{ortho}}$, $b_{\text{ortho}}$ and $c_{\text{ortho}}$ are related to the three cubic vectors $a$, $b$, $c$ pointing along the edges of the conventional cubic cell as follows:

\[
\begin{align*}
    a &= (a_{\text{ortho}}/2) - b_{\text{ortho}} \\
    b &= (a_{\text{ortho}}/2) + b_{\text{ortho}} \\
    c &= c_{\text{ortho}}/2.
\end{align*}
\]

Fixing the orientation of the dimers, four possible choices exist for the cubic (111) termination plane, shown as bold triangles in the upper panel of Fig. 4.17.
Figure 4.17 In the upper panel the four equivalent planes of triangular symmetry in the conventional fcc unit cell are drawn as bold triangles. The large spheres represent $C_{60}$ molecules while the smaller ones correspond to the positions of the Rb ions (for clarity the relative sizes and distances are not reproduced). The arrows indicate the directions of the dimers (in the polymer phase, they indicate the orientation of the polymer chains). The two choices shown in the upper left panel are fully equivalent, with the dimers lying in the surface plane (termination (041)). The corresponding surface pattern (without taking into account the electronic reconstruction) is shown in the lower left panel. The other two choices, corresponding to the (201) termination, are also equivalent and result in the same surface pattern (bottom right panel). In both lower panels, the large and middle-sized circles (in blue) represent the $C_{60}$ molecules of the first and second layer, respectively. The smaller (purple) circles represent Rb atoms. Note that in both cases two non-equivalent subsurface Rb sites arise.

These four choices coincide with the four diagonal planes of the fcc conventional cubic cell, that is, in terms of the vectors $a$, $b$ and $c$, to the planes $(1 1 1)$, $(1 -1 -1)$, $(-1 1 1)$ and $(1 -1 1)$. When expressed with help of the orthorhombic vectors they become, correspondingly, the planes $(2 0 1)$, $(-2 0 1)$, $(0 4 1)$ and $(0 -4 1)$. The first two choices are equivalent, and relate to the case...
where the \((C_{60})_2^2\) dimers are tilted with respect to the surface plane (right upper panel of figure 4.17). The last two correspond to the situation with in-plane dimers (left upper panel).

If the surface crystal structure were simply the truncation of the orthorhombic bulk structure at a (041) or a (201) plane, the surface pattern for both the in-plane and out-of-plane position of the dimer would be readily identified. In the lower right panel of figure 4.17 it is shown that the (201) termination plane of the dimerized film consists of two sublattices, one of neutral monomers and the other one of molecules which are linked to subsurface molecules via dimer bonds. In this case a hexagonal 2×1 LEED pattern would result. The pattern for the other case cannot be predicted \textit{a priori} because only half the dimers depicted in the lower left panel of Fig. 4.17 are present in the surface layer due to the reduced surface charge density.

Perhaps surprisingly, we observed no deviation in the LEED pattern of the dimer and polymer phases with respect to the hexagonal 1×1 pattern of the fcc phase. A possible reason for this could be that the surface of oligomerized RbC\textsubscript{60} resembles that of photopolymerized C\textsubscript{60} films reported in scanning tunnelling and atomic force microscopy studies, where strain in the film results in a disordered surface without long range order or gives rise, in some cases, to a herring backbone-like structure \{Makarova ’01\}. In such a case the lack of long range order could result in a hexagonal LEED pattern arising from the “average” triangular surface symmetry. A microscopy study is more suited to address this issue.

### 4.4 Conclusions

We have presented the results of a photoemission and X-ray absorption study of the four phases of a crystalline RbC\textsubscript{60} film, together with a characterization by HREELS of the polymer phase. In contrast to bulk results, the sc-to-dimer transition is found to be reversible at the film surface. We show that an electronic charge reconstruction characterises the surface of the RbC\textsubscript{60} in all phases, resulting in a reduced electron density in the surface layer of molecules with respect to corresponding bulk planes. The resulting half-filling of the surface LUMO-derived states, and the molecular character of fulleride result in the coexistence of different integer molecular valence states at least on the photoemission time scale. The X-ray absorption spectra of these phases are consistent with the presence of different reduction states of fullerene species at the film surface.

We confirm that the dimer phase is insulating. The polymer phase is
conducting at room temperature, while a metal-to-insulator transition is observed between 85 and 110 K. As in the Li$_4$C$_{60}$ case, the electronic density of states is not dramatically modified by polymerization in RbC$_{60}$. The surface of the fcc phase is probably weakly metallic, as the bulk of the same phase. A sharp Fermi edge is observed in the sc phase, which demonstrates the metallic nature of this phase also in thin-film form. A lower limit of 0.5 eV (0.65 eV) is found for the surface Hubbard $U$ in the sc (fcc) phase, which proves that the surface of cubic RbC$_{60}$ is a strongly-correlated electron system.

Three molecular charge states are identified in the photoemission spectra of the sc phase, two arising from C$_{60}$ and C$_{60}^{-1}$ monomers as in the fcc phase, and one corresponding to a minority of C$_{60}^{2-}$ anions, similarly to what is observed by NMR in the sc phase of bulk CsC$_{60}$. Our data provide evidence that conduction at the RbC$_{60}$ surface is mediated by molecular charge fluctuations, with a localization time of charge carriers longer than the PES time scale (but probably shorter than few tens of femtoseconds). The strongly correlated surface character and the fact that the C$_{60}^{2-}$ monomers directly contribute to the spectral intensity at the Fermi level in the photoemission spectrum of the sc phase indicate that the doubly-charged states do not exist as long-lived entities at the film surface. These results, and the comparison of the photoemission and X-ray absorption spectra of the sc phase, indicate that conduction is hopping-mediated near the surface of sc RbC$_{60}$.