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## The LUMO-derived band of the CsC<sub>60</sub> phases

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**Abstract.** The LUMO-derived band of the CsC<sub>60</sub> compound was investigated by means of x-ray and UV photoemission and photoelectric yield spectroscopies. A double-peak structure is found, with peak maxima at 1.1 eV and 0.35 eV. The relative magnitude of the two peaks is strongly temperature dependent: a large transfer of spectral weight from the lower- to the higher-binding-energy peak takes place upon cooling to 110 K. The peaks are tentatively attributed to the dimer and the polymeric phase respectively. However the behaviour as a function of temperature does not agree with the metastability of the dimer phase at room temperature. The position of the Fermi level is compatible with a correlated system on the border of the metal–insulating transition.

### 1. Introduction

Since the discovery of superconductivity in K<sub>3</sub>C<sub>60</sub> [1, 2], the properties of alkali-doped fullerides have been extensively investigated. A variety of stable phases have been identified [3, 4]. In this context the study of the recently discovered AC<sub>60</sub> (A=Cs, Rb, K) [3–8] compounds is of particular interest. All the AC<sub>60</sub> compounds exhibit a number of phase transitions. At high temperature the AC<sub>60</sub> system crystallizes in a face-centred cubic (fcc) rocksalt structure with the alkali ions occupying the octahedral sites of the host lattice only [6, 7]. Upon slow cooling a first-order transition takes place at about 400 K to a stable orthorhombic polymeric phase where the C<sub>60</sub> molecules are bonded into parallel charged chains [9–11]. A second metastable nearly orthorhombic phase is formed by quenching the fcc AC<sub>60</sub> from 500 K to temperatures below 270 K [11–16]. The formation of C<sub>60</sub> dimer pairs has been suggested as a possible structure. Finally, it was reported that rapid quenching below 150 K of the high-temperature phase can also promote the formation of another metastable phase with an orientationally ordered simple cubic structure [17, 18].

The electronic properties of the AC<sub>60</sub> compounds are still a matter of debate despite a number of theoretical [19–22] and experimental [4, 11–14, 17, 23–33] investigations. Few photoemission measurements have been reported. Early low-temperature data ( $T = 40$  K) on Rb and Cs compounds at low alkali concentration found a nearly Gaussian LUMO-derived band centred at  $\sim 0.3$  eV below the Fermi level  $E_F$ , characterized by a relatively high density of state at  $E_F$  [24]. Subsequently, the presence at room temperature of a second structure at  $\sim 1$  eV below  $E_F$  in Cs-, Rb-, K-doped compounds was reported [4, 34–36]. Two peaks at low Cs doping and room temperature were also reported by Gildemeister and Waltheim [25], who found that only one structure at 0.5 eV remained in the LUMO-derived band upon annealing at 180 °C, suggesting to the authors that the second structure

was related to Cs atoms present at the surface. Recently, Poirier *et al* [33] reported low-temperature photoemission data on  $\text{RbC}_{60}$  samples showing different LUMO-derived bands depending on the cooling procedure. They found a peak centred at  $\sim 0.3$  eV below  $E_F$  in the polymeric phase and a peak centred at 1 eV in the dimer phase.

As pointed out by several authors, the main difficulty in obtaining conclusive results stems from the fact that it is hard to reach the equilibrium conditions and that, quite often, the samples are multiphase, the composing phases depending on the growth and/or doping procedure. In this paper we present a detailed photoemission study of the electronic structure of  $\text{Cs}_x\text{C}_{60}$  samples in the low-doping regime at room and at low temperature ( $T = 110$  K). The samples were concurrently characterized by x-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS) and photoelectric yield spectroscopy (YS) operated in the constant-final-state mode (CFS). Core level measurements allowed us to monitor the surface stoichiometry and to get information on the dopant configurations and on the phases present in the samples as well as to find a procedure to obtain homogenous  $\text{CsC}_{60}$  layers.

## 2. Experimental details

The films were prepared *in situ* on copper substrates by evaporating 99.9% pure MER Corporation  $\text{C}_{60}$  powders in a preparation chamber whose basic pressure was  $8 \times 10^{-11}$  Torr. Doping was achieved by evaporating Cs from well outgassed SAES getter sources. The amount of evaporated  $\text{C}_{60}$  and Cs was determined during deposition with a quartz-crystal thickness monitor. Typical film thicknesses were in the range between 200 and 600 Å. According to the procedures established in previous works [4, 34, 37] the following doping method was used. After a first deposition of  $\text{C}_{60}$  and the subsequent evaporation of the Cs amount necessary for reaching the  $x = 6$  concentration, layers of  $\text{C}_{60}$  having the thickness suitable for the desired final concentration were successively deposited. In this way the doping of the thin near-surface layer investigated by the photoelectron spectroscopies was obtained by outdiffusion. As pointed out previously [4], this ‘backdoping’ procedure results in a substantial uniformity of concentration in the investigated surface layer and in better quality films closer to the thermodynamic equilibrium. Furthermore, it avoids the presence of non-diffused Cs on the surface.

The Cs concentration in the near-surface region of interest was determined from the intensity ratio between the C 1s and Cs 4d core level peaks, as measured by XPS. The ratio between the atomic sensitivity factors  $R = \sigma(\text{Cs } 4d)/\sigma(\text{C } 1s)$  was calibrated by assuming saturation at  $x = 6$ . The found value was  $R = 7.2$  in good agreement with the determination reported in [38], but somewhat larger than the table values  $R = 5.53$  of Yeh and Lindau [39] and  $R = 5.24$  by Band *et al* [40].

Frequent contamination checks were made by monitoring the O 1s core level intensity. The oxygen content at the end of measurements was always less than 0.4 at. %

XPS measurements were performed with a monochromatized ESCA system (PHI model 3057) equipped with a hemispherical electron energy analyser. The photon source was the Al  $K\alpha$  line ( $h\nu = 1486.6$  eV). The total resolution of the system (source + analyser) was 0.35 eV. UPS and YS spectra were recorded with a double-pass cylindrical mirror analyser (CMA PHI model 15-255 G). The photon sources used for these two kinds of measurement were the He I radiation ( $h\nu = 21.2$  eV) and a Xe lamp monochromatized with a double grating monochromator. System resolution was 70 meV for UPS excited with the He lamp, 100 meV for UPS excited with 6.2 eV photons and 70 meV for the YS. The resolution was checked on the Fermi function cutoff of gold. The UPS spectra excited with the He

lamp were corrected for the contributions due to the satellite lines of the He radiation. The YS was excited with photons in the range  $3.0 \leq h\nu \leq 6.4$  eV and was operated in the constant-final-state mode (CFS), i.e. photoemitted electrons of a chosen kinetic energy were collected as a function of photon energy. More details on the CFS-YS and on the information it provides can be found in [37].

UPS and CFS-YS low-temperature measurements were performed using an home-made liquid nitrogen cryostat. Typically the sample temperature dropped from 300 K to 110 K in 30–40 min. The temperature was measured by an Fe–Co thermocouple in contact with the copper substrate. The estimated error in the temperature determination was  $\pm 15$  K.

The Fermi level position was determined in two ways, by measuring the UPS spectrum of a freshly evaporated gold layer and by fitting the YS spectra according to the procedure reported in [34]. The two determinations agree within less than 100 meV.

### 3. Results and discussion

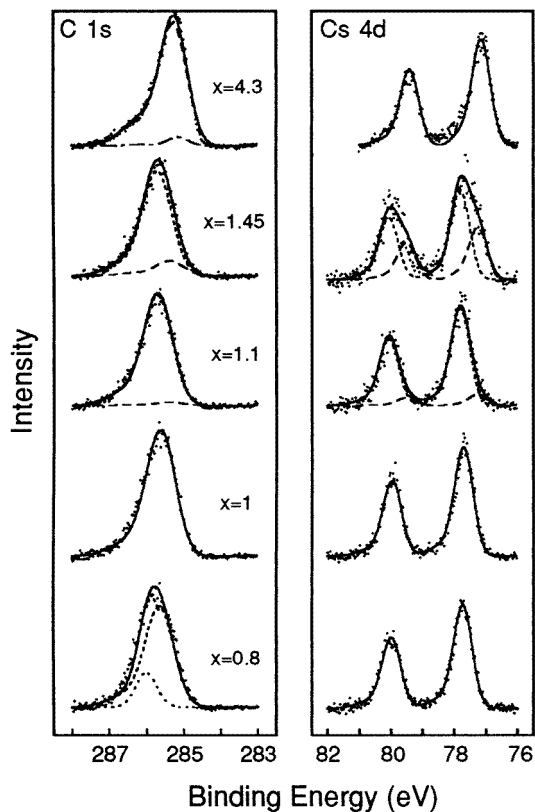
#### 3.1. Core level analysis

Core level spectroscopy provides precious information on the different phases present in the A<sub>x</sub>C<sub>60</sub> samples [4, 37, 38]. In particular, a large chemical shift is expected for the core level energies of the alkali atoms in the two stable phases CsC<sub>60</sub> and Cs<sub>4</sub>C<sub>60</sub> of the Cs–C<sub>60</sub> system due to the different Madelung energies and screening properties [38]. This property was used for determining the phase composition of our samples. The Cs 4d and C 1s core level spectra of a series of Cs<sub>x</sub>C<sub>60</sub> samples are shown in figure 1. The spectra labelled with  $x = 1$  refer to a homogeneous CsC<sub>60</sub> sample obtained with a ‘distillation’ procedure which will be explained later on. For  $x > 1$  the coexistence of the  $x = 4$  and the  $x = 1$  phases is expected, while that of the  $x = 1$  phase and pure C<sub>60</sub> is expected for  $x < 1$ . The contributions to the core spectra of these phases are also shown in the figure.

The Cs 4d core level is a spin–orbit doublet with the two components separated by 2.25 eV. A single doublet is present in both the CsC<sub>60</sub> and Cs<sub>4</sub>C<sub>60</sub> phases, since the sites occupied by the Cs ions in each phase are equivalent. The chemical shift of the levels due to the different chemical environment of the Cs ions in the two phases is large enough (0.55 eV) to allow an accurate determination of the percentage of the two phases in non-stoichiometric samples.

The lineshape of the Cs 4d and C 1s levels in the Cs<sub>4</sub>C<sub>60</sub> phase was obtained from the spectra of the  $x = 4.3$  sample after subtraction of the small contribution of the Cs<sub>6</sub>C<sub>60</sub> phase. As for the lineshape of the core levels in the  $x = 1$  phase, it was obtained from the spectra of the homogeneous  $x = 1$  sample singled out by using a distillation process previously used to obtain other stoichiometric phases [3, 34, 37, 41]. It consists in heating at 300 °C samples with an average concentration  $x < 1$  obtained via the backdoping procedure. This resulted in the evaporation of C<sub>60</sub> molecules. The evaporation ended when the concentration saturated to the  $x = 1$  value. Further annealing after the saturation was achieved did not cause further changes of concentration or core level lineshape. The features of this process can be followed by comparing the  $x = 0.8$  and  $x = 1$  spectra. The C 1s spectrum of the  $x = 0.8$  sample clearly indicates that a mixture of CsC<sub>60</sub> and pure C<sub>60</sub> is present. Upon annealing the higher-binding-energy component due to the pure C<sub>60</sub> decreases pointing to the evaporation of C<sub>60</sub> molecules.

In order to determine the percentage of the different phases in samples with intermediate  $x$  values, both the Cs 4d and C 1s level were fitted as a combination of CsC<sub>60</sub>, Cs<sub>4</sub>C<sub>60</sub> and pure C<sub>60</sub>. In each sample the phase content obtained from the Cs 4d core level was consistent



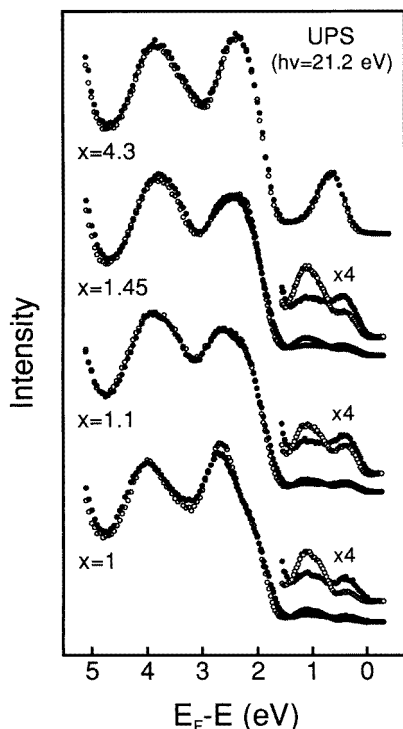
**Figure 1.** Room-temperature C 1s and Cs 4d core level spectra for samples with different Cs content. The dotted line represents the  $C_{60}$  contribution, the short-dash line the  $CsC_{60}$  contribution, the long-dash line the  $Cs_4C_{60}$  contribution, the dash-dot line the  $Cs_6C_{60}$  contribution and the solid line is their sum.

with that obtained from the C 1s core level.

### 3.2. LUMO-derived bands

The UPS spectra of samples corresponding to the  $Cs_4C_{60}$  and  $CsC_{60}$  single phases are shown in figure 2. Also shown are the spectra of two samples with mixed phases but average composition close to  $x = 1$ . The LUMO-, HOMO- and HOMO-1-derived bands are displayed. In figure 3 the LUMO-derived bands are shown on an expanded scale. The LUMO-derived band of the  $x = 4.3$  sample consists of a single peak centred at  $\sim 0.6$  eV. The Fermi level position is compatible with the insulating character of the  $Cs_4C_{60}$  phase. Upon decreasing the temperature down to 110 K the spectrum remains practically unchanged.

In the case of the  $x = 1$  sample two structures at 0.35 eV and 1.1 eV are present in the LUMO-derived band region. At room temperature the two peaks have approximately equal magnitude, although the ratio is slightly sample dependent. The relative intensity is strongly affected by the decrease of the temperature. Upon cooling to 110 K there is an almost complete transfer of spectral weight from the structure closer to the Fermi level to the structure located at higher binding energy. Furthermore, the width of both structures

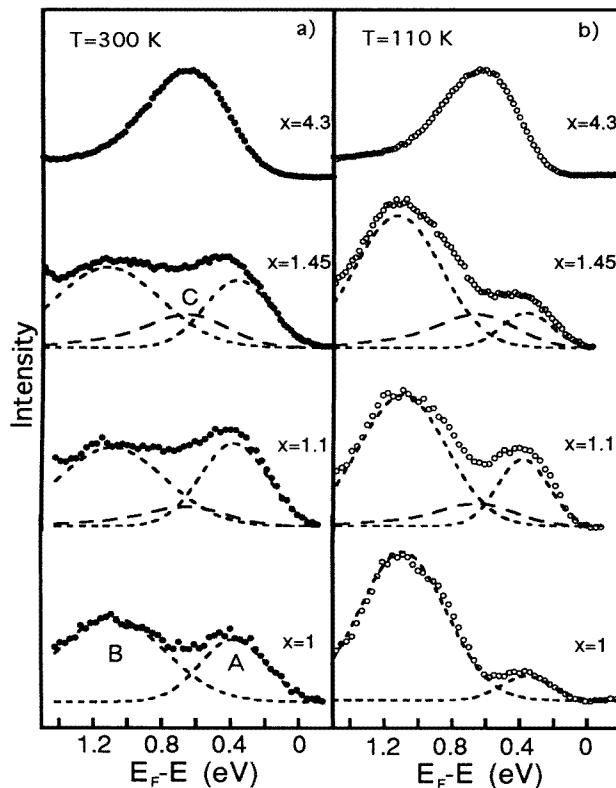


**Figure 2.** UPS spectra excited by 21.2 eV photons for samples with different Cs content. The spectra have been normalized to the area of the two uppermost HOMO-derived bands. Filled circles:  $T = 300$  K; open circles:  $T = 110$  K.

decreases by  $\sim 15\%$ . Minor changes can also be detected in the HOMO and HOMO-1 region. In order to quantify the relative magnitude of the two LUMO-derived structures, the spectra have been fitted with two Gaussians (labelled A and B, respectively), as shown by dashed lines in figure 3. The intensity ratio A/B varies from 0.67 at room temperature to 0.16 at low temperature. The total intensity of the two bands remains unchanged, showing that the temperature effect is, indeed, the transfer of spectral weight from one band to the other.

The curves of the  $x = 1.1$  and the  $x = 1.45$  samples in figures 2 and 3 show that the above characteristics of the LUMO-derived spectral region are not limited to homogeneous  $x = 1$  samples, but are also exhibited by mixed-phase specimens. The presence of some Cs<sub>4</sub>C<sub>60</sub> phase (curves C in figure 3) only adds a contribution at  $\sim 0.6$  eV, which does not change with temperature.

For a correct analysis of the UPS spectra it is important to ascertain whether the data can be interpreted solely in terms of initial-state effects, since final-state and matrix element effects could be equally important in photoemission processes excited with low-energy photons. A check on the relative magnitude of these effects was made by comparing the LUMO spectra measured in different operating modes, i.e. the UPS excited by  $h\nu = 21.2$  eV and  $h\nu = 6.2$  eV and the CFS-YS. As was discussed previously [37] the dependence on the photoelectron final state and on the matrix element enters these operating modes in a drastically different way. In figure 4 the data at room and low temperature are reported.

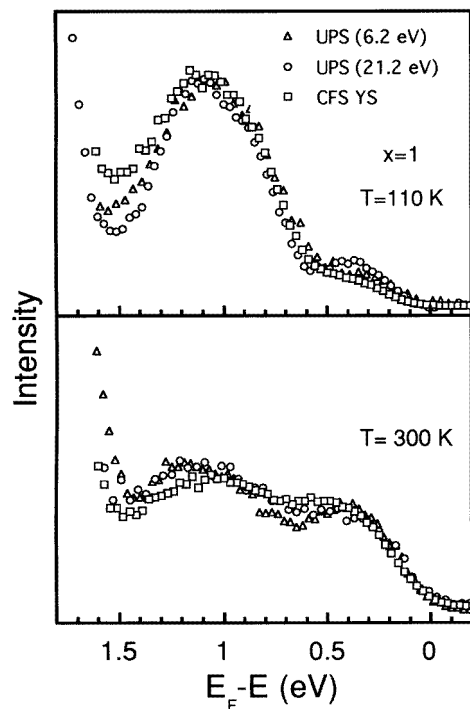


**Figure 3.** LUMO-derived band region of the spectra of figure 2 shown on an expanded scale and its decomposition in the  $\text{CsC}_{60}$  (peaks A and B) and  $\text{Cs}_4\text{C}_{60}$  (peak C) contributions (see text).

The three spectra are practically identical at both temperatures. Since in the UPS spectra the kinetic energy of the photoemitted electron is analysed at a fixed energy of the exciting photons, while the photon energy dependence at fixed electron kinetic energy is analysed in the CFS-YS data, and since, furthermore, the final states are different in the three kinds of spectrum, the coincidence of the spectral features shows unambiguously that they are due to initial-state effects.

The data of figure 4 allow us also a check on the possible surface inhomogeneity. Indeed, the presence of a double structure in the LUMO spectra was often interpreted in the past in terms of a bulk and a surface contribution. Since the escape depth of the photoelectrons increases by a factor of  $\sim$ eight by changing the exciting photon energy from 21.2 to 6.2 eV, the coincidence between the spectra rules out this kind of explanation as well as the surface contamination as the origin of one of the two peaks.

As already mentioned in the introduction, the properties of the  $\text{AC}_{60}$  samples depend strongly on their thermal history. Most of the investigations report that a slow cooling of the high-temperature fcc phase promotes the transition to the polymeric orthorhombic phase, which is the stable one at room temperature [3, 9–11, 33]. Quite to the contrary, a rapid quenching of the fcc phase below 270 K and a further cooling to lower temperature results in the dimer phase [12, 13–16, 33]. This phase is metastable and tends to revert to



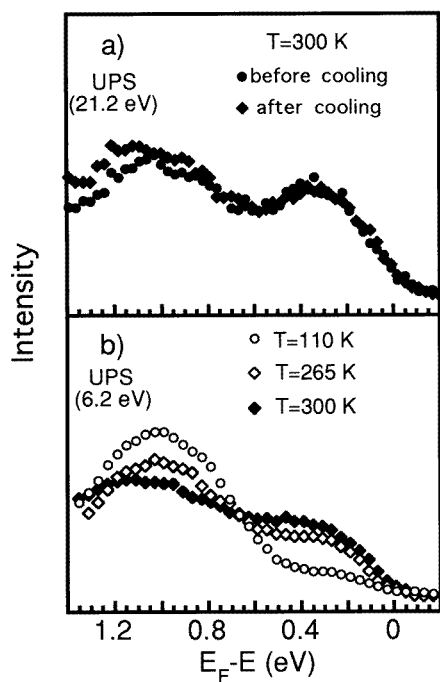
**Figure 4.** UPS spectra excited with 6.2 eV and 21.2 eV photons and CFS-YS spectrum of the LUMO-derived band of the CsC<sub>60</sub> sample.

the polymeric phase with a relaxation rate strongly dependent on temperature. For instance, in the RbC<sub>60</sub> system the relaxation time is  $\sim 700$  min at 260 K and  $\sim 10$  min at room temperature [11]. Some authors have also reported that, upon warming up the dimer phase, an intermediate metastable cubic phase appears in the range 250–300 K, which, eventually, reverts to the polymeric one [7, 42]. The recent photoemission measurements at 150 K on the RbC<sub>60</sub> system by Poirier *et al* [33] found that the LUMO-derived band consisted of a single peak centred either at 0.3 eV or at 1.0 eV below  $E_F$  depending on the cooling procedure. The LUMO-derived band centred at 0.3 eV was obtained by cooling the rocksalt phase at a rate of  $0.5 \text{ K min}^{-1}$ , while that at 1.0 eV was present upon quenching from 525 K to below 273 K in less than 15 s and then cooling further down to 150 K. These are the procedures to obtain the polymeric and the dimer phase, respectively.

By considering the above results an obvious interpretation for our data is that the peak in the LUMO band centred at 1.1 eV is due to the dimer phase and the peak at 0.35 eV to the polymeric one. Since the two peaks have a comparable magnitude at room temperature and are present also in samples doped by evaporating Cs on the surface of pure C<sub>60</sub> [4], a consequence of this interpretation would be that the two phases coexist in similar amounts in our samples, regardless of the doping procedure and the presence of some Cs<sub>4</sub>C<sub>60</sub> phase. Furthermore, the 1.1 eV peak is strong and the spectra are practically identical also for samples annealed at 300 °C and slowly cooled to room temperature. According to the literature, these are the conditions for obtaining the polymeric phase and the dimer phase should not be present. On the assumption that the two peaks are proportional to the extent

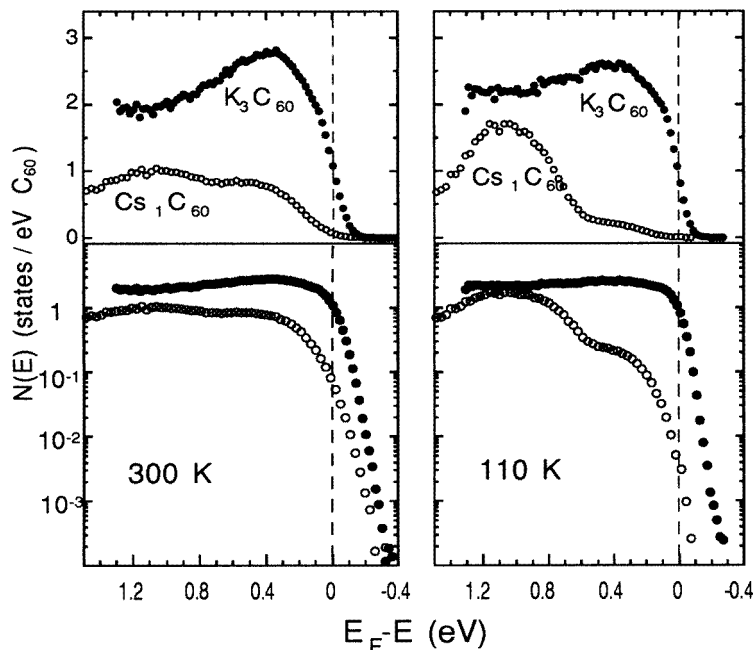


of the two phases in the samples, our experimental evidence would require, therefore, that in the  $\text{CsC}_{60}$  compound the coexistence of the two phases is easier than previously thought. It is worth pointing out that the presence of a structure around 1 eV in the LUMO-derived band at room temperature was reported by other investigations also [25,36] and that we have found a similar structure in  $\text{K}_x\text{C}_{60}$  ( $x \sim 1$ ) films too [4, 34]. In the case of K-doped compounds, however, the intensity of the structure turned out to be strongly dependent on the growth conditions and the observed behaviour was therefore compatible with the presence of a non-equilibrium phase (the dimer phase) promoted by the non-equilibrium nature of the sublimation growth and doping. A structure at slightly higher binding energy ( $E = 1.35\text{--}1.5$  eV) appears at room and low temperature in  $\text{Na}_x\text{C}_{60}$  samples ( $x \sim 2$ ) also [4, 43, 44].



**Figure 5.** (a) LUMO-derived band recorded at room temperature before and after cooling. (b) Evolution of the LUMO-derived band during a warming up cycle from 110 K to the indicated temperatures.

The behaviour as a function of thermal cycles also differs from that reported for  $\text{RbC}_{60}$ . The evolution of the LUMO bands as a function of the temperature is completely reversible, as shown in figure 5(a), where the UPS spectra recorded at 300 K before and after cooling are compared. In figure 5(b) the evolution of the lineshape upon heating from 110 K to the indicated temperatures is reported. It is evident that there is a continuous evolution of lineshape until the room-temperature lineshape is recovered. A substantial decrease of the intensity of the structure B (1.1 eV) is already observed at  $T = 265$  K during a warming up cycle that took 40 min for heating the sample from 110 K to that temperature. This behaviour differs from that of  $\text{RbC}_{60}$  where a negligible decrease was reported for temperatures up to 270 K [33]. Furthermore, in our case no evolution as a function of time was observed at



**Figure 6.** CFS-YS spectra of CsC<sub>60</sub> and K<sub>3</sub>C<sub>60</sub> samples taken at 300 K and 110 K. Top panels: linear scale; bottom panels: logarithmic scale.

room temperature once the original lineshape was recovered. This stability contrasts with the behaviour of RbC<sub>60</sub> where relaxation times of the order of 10 min have been reported for the transformation of the metastable dimer phase to the polymeric one [11].

As a final characterization, the spectral weight close to the Fermi level, which is used to define the ‘metal’ character of the CsC<sub>60</sub> phase, was investigated in detail by exploiting the high dynamical range of the yield spectroscopy [34, 37]. The CFS-YS spectra of the CsC<sub>60</sub> phase were compared with that of the K<sub>3</sub>C<sub>60</sub> single phase, since the  $x = 3$  compounds are the only ones that exhibit unambiguously metallic character. The YS spectra are shown in figure 6 on a linear as well as on a logarithmic scale. The spectra were normalized to one and three electrons per C<sub>60</sub> molecule, respectively, assuming a complete charge transfer from the alkaline atoms to the fullerene molecules in both cases. From the data at the room temperature we see that, while a clear Fermi edge is present in K<sub>3</sub>C<sub>60</sub> samples, in CsC<sub>60</sub> the Fermi level is located in a region of reduced spectral weight, its magnitude at the Fermi level being  $\sim 1/10$  of the value at the peak A maximum. Upon cooling there is a decrease of the spectral weight at the Fermi level far larger than the decrease of the peak itself, its magnitude becoming  $\sim 1/50$  of the peak maximum. On the assumption that the two peaks we observe are related to the dimer and to the polymeric phase, respectively, we can compare our results with previous reports on the metallic or insulating character of the two phases.

Previous results on the dimer phase [11, 13] showed unambiguously its insulating character and would agree with the identification of the 1.1 eV peak with the LUMO-derived band of the dimer phase. Indeed, the large energy separation from the Fermi level would require a gap as large as  $\sim 0.4$ – $0.5$  eV.

The metallic or insulating character of the polymeric phase is more controversial. Metallic properties were reported by several groups [11, 12, 26]. However the electronic properties are quite different in K, Rb, Cs compounds [29]. Especially in the case of the Cs compound, there are several anomalies [29]. The  $\text{CsC}_{60}$  samples are poor conductors and the resistivity increases with decreasing temperature; the optical conductivity  $\sigma(\omega)$  presents a strong peak in the FIR–MIR region and decreases in the range below 20 meV for  $T \leq 300$  K giving, on the assumption of a metallic behaviour, an unusually small plasma frequency and an unusually long scattering relaxation time; the spin susceptibility is temperature dependent [29]. According to energy band calculations the  $(\text{AC}_{60})_n$  polymeric chains have a half-filled conduction band due to the lifting of the threefold degeneracy of the parent  $t_{1u}$  state [21]. However, many theoretical investigations have pointed out the role of electron–electron and electron–phonon interactions in alkali-doped  $\text{C}_{60}$  compounds [45, 46]. It is expected, as a consequence, that the alkali-doped compounds are on the border of the metal–insulator transition, with the actual relative strength of correlation effects and crystal potential determining the metal or insulating character of each phase. Detailed photoemission characterization of the LUMO-derived spectral weight confirmed these theoretical arguments [4, 34, 37, 47]. The energy position of the Fermi level on the tail of the LUMO-derived band that we find presently for the  $\text{CsC}_{60}$  phase agrees with the picture of a highly correlated system on the metallic border of the metal–insulator transition. Furthermore, the observed decrease of the density of state at the Fermi level upon cooling correlates well with the temperature dependence of the optical conductivity of  $(\text{CsC}_{60})_n$  phase reported in [29]. The peculiarity of  $\text{CsC}_{60}$  compounds with respect to  $\text{KC}_{60}$  and  $\text{RbC}_{60}$  can be related to the larger size of the Cs ion and the consequently larger lattice parameter. It determines narrower bands and the enhancement of the correlation effect. Furthermore it can promote the transition to a quasi-one-dimensional structure [21, 22].

Finally, before closing this section, we would like to point out the following. The double structure present in the LUMO-derived band of our  $\text{CsC}_{60}$  data was interpreted in terms of two phases, the dimer and the polymeric, present in the samples. This explanation was the most natural one if the previous reports on these phases were taken into account. It was found, however, that the samples investigated exhibited a behaviour differing appreciably from that expected from the reported characteristics of the two phases. It would be tempting, therefore, to interpret both features in the LUMO band in terms of a single phase and to consider the observed transfer of spectral weight from low to high binding energy upon cooling as a characteristic of this phase. Although we have not been able to perform structural characterizations on our samples as yet that could support this second interpretation, we believe, nevertheless, it is important to point out that this possibility cannot be ruled out at present and that the Cs  $x = 1$  compounds could behave rather differently from the  $\text{KC}_{60}$  and  $\text{RbC}_{60}$  systems.

#### 4. Conclusions

We have investigated the LUMO-derived band of homogeneous  $\text{CsC}_{60}$  samples. It was found that it consists of two peaks, whose relative magnitude is strongly temperature dependent but time and temperature-cycle independent. We have shown that the two structures are due to initial-state effects and we have ruled out surface inhomogeneity or surface contamination as a possible origin of one of the two peaks. Based on the reported phase transitions and on the behaviour of the  $\text{RbC}_{60}$  compound, we have tentatively attributed the higher-binding-energy peak to the dimer phase and that closer to the Fermi level to the polymeric phase. It was pointed out, however, that the room-temperature stability and the temperature-cycle

independence of the relative magnitude of the two peaks are not compatible with the reported metastability of the dimer phase at room temperature. As a consequence, it is possible that both peaks are related to a single stable phase.

Finally, by taking advantage of the high dynamic range of the CFS-YS technique, it was shown that the Fermi level is located in a region of reduced spectral weight and is compatible with a highly correlated system on the metallic border of the metal-insulator transition.

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