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## Valence state evolution of C<sub>60</sub> deposited on Sm film

Xiao-Xiong Wang<sup>1</sup>, Hong-Nian Li<sup>1,3</sup>, Shao-Long He<sup>1</sup>, Kurash Ibrahim<sup>2</sup>,  
Hai-Jie Qian<sup>2</sup>, Run Su<sup>2</sup>, Jun Zhong<sup>2</sup>, Cai-Hao Hong<sup>2</sup> and M I Abbas<sup>2</sup>

<sup>1</sup> Department of Physics, Zhejiang University, Hangzhou 310027, People's Republic of China

<sup>2</sup> Laboratory of Synchrotron Radiation, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100039, People's Republic of China

E-mail: Phylhn@public.zju.edu.cn (H-N Li)

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### Abstract

Ultraviolet photoemission spectra of C<sub>60</sub> deposited on Sm film were measured. The results indicate that C<sub>60</sub> and Sm can combine with each other to form fulleride in the interface at room temperature. The bonding is mainly ionic with some covalent contribution. Both the lowest unoccupied molecular orbital (LUMO) and the LUMO + 1 orbital of C<sub>60</sub> are occupied at coverages less than about one monolayer. As for the second overlayer, only the LUMO orbital is occupied. The first and second C<sub>60</sub> overlayers are metallic and semiconducting, respectively.

### 1. Introduction

Alkali and alkali-earth-intercalated C<sub>60</sub> solids have been intensively studied in the past decade. A great deal of attention is now dedicated to the rare-earth-intercalated fullerides, mainly due to the observations of superconductivity [1–3], ferromagnetism and giant magnetoresistance [4–6]. For a good understanding of these novel physical properties, photoemission spectrum (PES) measurements are needed to study the electronic structures of the rare-earth/C<sub>60</sub> systems. Some results have been reported for both the interfaces between C<sub>60</sub> and rare-earth metals and the rare-earth-intercalated bulk fullerides. Ohno *et al* [7] studied the core-levels of Yb-intercalated C<sub>60</sub>, and drew the conclusion that the single phase of Yb<sub>2</sub>C<sub>60</sub> (actually Yb<sub>2.75</sub>C<sub>60</sub>) formed in the vacuum–vaporization–deposition–annealing process. Xia *et al* [8] researched the valence state evolutions of the Yb/C<sub>60</sub> interfaces. The electronic density of states near the Fermi level for well-defined single phase Yb<sub>2.75</sub>C<sub>60</sub> was reported by Li *et al* [9]. Li *et al* [9] also presented more detailed studies of the C<sub>60</sub>/Yb interface. The PES technique was also applied to the Eu/C<sub>60</sub> system to explore the ferromagnetic property and the Eu fulleride formation [10]. As

<sup>3</sup> Author to whom any correspondence should be addressed.

for the Sm/C<sub>60</sub> system, there is, to the best of our knowledge, no PES result reported so far, either for interface or for bulk fulleride.

In this paper, we present the ultraviolet photoemission spectra (UPSs) of C<sub>60</sub> deposited on the surface of polycrystalline Sm film at room temperature. The results can reveal the valence state evolution and the nature of the Sm–C<sub>60</sub> bonding in the interface. Some of the results can also be applied to the bulk Sm fullerides, for example Sm<sub>2.75</sub>C<sub>60</sub>.

## 2. Experiment

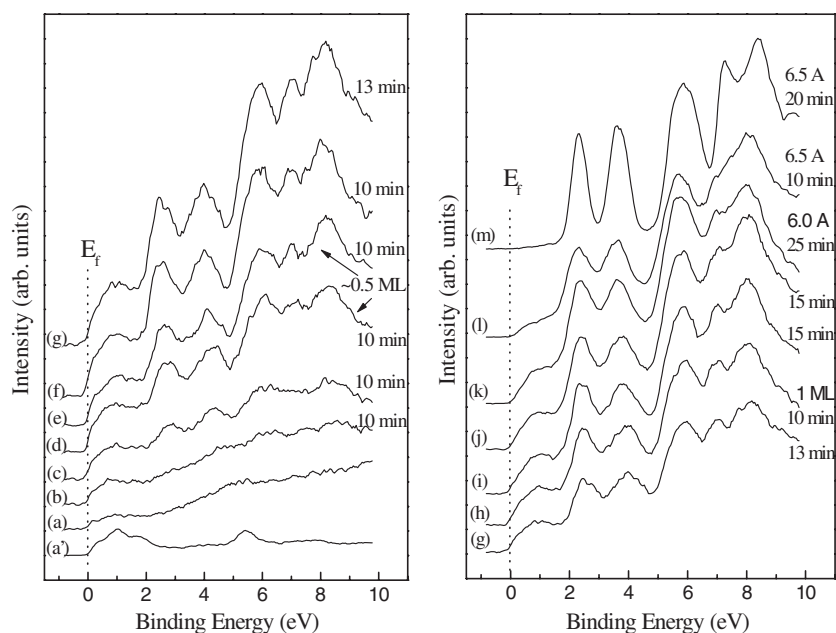
Sample preparations and measurements were performed in an ultra-high vacuum system. The base pressure was  $2 \times 10^{-10}$  Torr. Incident photons with energy of 21.0 eV were induced from the 4B9B beam line of Beijing Synchrotron Radiation Facility. The overall energy resolution was 0.1 eV. An angle-resolved spherical deflection analyser was used to collect the photoelectrons at normal emission.

Thoroughly degassed C<sub>60</sub> and Sm were sublimed from Ta boats located at about 11 cm from the surface of a chemically-etched Si:H (111). The Si:H (111) substrate was kept at room temperature during the Sm and C<sub>60</sub> depositions. To make sure of the purity of the C<sub>60</sub> raw material, we first grew the commercial C<sub>60</sub> powder as single crystals with the gas-phase method [11], and then ground the single crystals into powder by using an agate mortar. The high-purity Sm (99.99%) was purchased from Beijing Research Institute for Nonferrous Metals. A thick Sm film was prepared by evaporating Sm atoms onto the substrate until the signal of Si 2p could not be detected by the x-ray photoemission spectrum (XPS,  $h\nu = 650$  eV) measurements. The O 1s and the C 1s signals were not observed at all. Then we changed the spectrometry mode from x-ray photoemission to ultraviolet photoemission. Just before the UPS measurements, an additional large quantity of Sm was deposited to keep the Sm film fresh. The amount of C<sub>60</sub> deposited on the Sm film was controlled by the electric current through the Ta boat and the deposition time. We calibrated the deposition time and the electric current by the valence evolutions of C<sub>60</sub> on an Ag(111) surface, as the UPS of one monolayer (1 ML) C<sub>60</sub> on an Ag(111) surface has been well defined (especially the peak position of the highest occupied molecular orbital (HOMO)-derived band) [12]. We tested a very low deposition rate of (6.0 A, 60 min) to prepare 1 ML C<sub>60</sub> on Ag(111). The low deposition rate allowed us to study the valence evolution of C<sub>60</sub> on Sm film in detail. Although the above calibration could not be readily applied to the C<sub>60</sub>/Sm interface due to the different sticking coefficients of Ag(111) and polycrystalline Sm, it could serve as a useful reference. We also adopted an electric current of  $\sim 6.0$  A for most C<sub>60</sub> deposition trials onto the Sm film. The more accurate coverage of C<sub>60</sub> will be determined self-consistently by the UPS results.

To clarify the electronic state evolutions, the process of C<sub>60</sub> deposition was performed step by step. Once the deposition was over for each trial in the preparation chamber, the sample was transferred into the analyser chamber for UPS measurement.

## 3. Results and discussions

The UPS results are presented in figure 1. Those peaks located between the Fermi level ( $E_f$ ) and 5.0 eV binding energy (BE) are enlarged in figure 2 to clarify the valence evolution. All the spectral lines are normalized to the incident photon flux. The electronic current through the Ta boat and the deposition time for each trial are shown next to the lines and in the figure caption. Curve (a) is the spectrum of the clean Sm film. It exhibits the clear Fermi edge of the metal Sm 5d6s band (the conduction band of metal samarium is the hybridized 5d and 6s states, rather than the 6s state). Sm has very low photoionization cross section with an incident

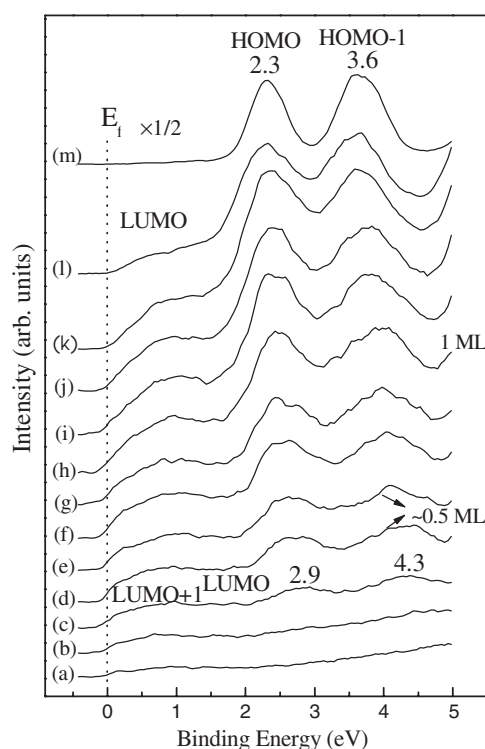


**Figure 1.** Synchrotron radiation photoemission spectra taken at normal emission with  $h\nu = 21.0$  eV for C<sub>60</sub> deposited on polycrystalline Sm. Spectral curves from (a) to (m) exhibit the phase evolution of the sample with increasing amount of C<sub>60</sub> deposited. The electric current through the Ta boat is 6.0 A for curves (b)–(k), and 6.5 A for curves (l) and (m). The deposition time is shown next to the curves. The curves were normalized to the incident photon flux. The coverages of C<sub>60</sub> are indicated in the figure for 1 ML (curve (h)) and  $\sim 0.5$  ML (curves (d) and (e)). Curve (a') is the spectral line recorded with a photon energy of 45 eV to clarify the 4f peaks of Sm.

photon energy of 21.0 eV. Thus we have the opportunity to observe the valence evolution of C<sub>60</sub> on Sm more clearly than C<sub>60</sub> on Yb [8, 9]. The latter has significant Yb 4f<sub>7/2</sub> and 4f<sub>5/2</sub> contributions to the spectral lines. We also measured the spectral line of the metal Sm with photon energy of 45 eV to exhibit the location of Sm 4f spectral peaks (curve (a')).

Before the detailed discussion on the electronic state evolutions, we would like to specify the coverages for each line in figures 1 and 2. With reference to the UPS results for C<sub>60</sub>/Ag(111) as mentioned above, curve (g) corresponds to the (6.0 A, 60 min) coverage, i.e., 1 ML coverage. Due to the unknown difference of the sticking coefficients between the C<sub>60</sub>/Ag(111) and the C<sub>60</sub>/Sm cases, it is necessary, if possible, to re-examine the calibration. The HOMO feature evolution in figure 2 offers this possibility. The intensity of the HOMO feature increases rapidly from curve (b) to curve (h). From curves (h) to (k), the intensity increases very slowly. The HOMO evolution thus reveals that the coverage for curve (h) is near to 1 ML, as the UPS measurement can detect only the top layer of C<sub>60</sub> [13, 14]. The two calibrations coincide with each other fairly well. In the following, we refer to curve (h) as the UPS of 1 ML C<sub>60</sub>. The coverages for most of the rest of the curves can be determined by the deposition time. The uncertainty is less than 1/6 ML according to the deposition time. After the coverage near to 2 ML (curve (k)), we increased the electric current from 6.0 to 6.5 A. Two rounds of deposition with a current of 6.5 A (total deposition time is 30 min) produce the UPS of pure C<sub>60</sub> (curve (m)). Curve (l) corresponds to a coverage slightly larger than 2 ML.

After the first deposition trial ( $\sim 1/7$  ML C<sub>60</sub>), the spectral weight between  $E_f$  and  $\sim 2.0$  eV BE increases significantly as compared to curve (a). The unique reason for the increased intensity is that some electrons transfer from Sm to C<sub>60</sub> (the photoionization cross section of



**Figure 2.** Part of figure 1 to clarify the valence evolution near the Fermi level. Peak assignments are given. There is no distinct separation between the LUMO and LUMO + 1 features. Curve (m) is multiplied by 1/2.

C 2p  $\pi$ -like states is considerably larger than that of the Sm 4f state with photon energy of 21.0 eV [15]). This observation reveals that Sm and C<sub>60</sub> can combine to form fulleride in the interface even at room temperature, and that the Sm–C<sub>60</sub> bonding should have large ionic contribution.

Figures 1 and 2 reveal that not only the lowest unoccupied molecular orbital (LUMO) but also the LUMO + 1 orbital is occupied below  $\sim 1$  ML coverage. The degeneracies of the LUMO and HOMO are threefold and fivefold respectively. The spectral intensity ratio between the LUMO and HOMO should be no larger than 3/5. However, the integral spectral intensity in the vicinity of  $E_f$  is larger than that of the HOMO feature in curves (c) and (d). Thus we can say that the LUMO + 1 orbital is occupied at low coverages.

The assertion of the LUMO + 1 occupation is further supported by the successive valence evolutions exhibited in figure 2. The HOMO and HOMO – 1 features locate at 2.9 and 4.3 eV in curve (c), respectively. The combined LUMO and LUMO + 1 feature has a width of  $\sim 2.0$  eV. With successive depositions of C<sub>60</sub>, the HOMO and HOMO – 1 move to the Fermi level, and the width of the combined LUMO and LUMO + 1 feature decreases. These observations coincide with the above assertion that the LUMO + 1 orbital is occupied. At very low coverage, there should be large number of Sm atoms around one C<sub>60</sub> molecule. With successive depositions, the average number of Sm atoms around each C<sub>60</sub> and the number of electrons occupying the LUMO + 1 orbital decrease. The Fermi level thus moves towards the LUMO feature, i.e., the LUMO feature together with the HOMO and HOMO – 1 features moves to  $E_f$ , and the width of the combined LUMO and LUMO + 1 feature becomes narrower.

The peak movements in figure 2 also reveal that the LUMO + 1 orbital can be partially occupied until 1 ML coverage because the HOMO peak moves towards lower BE continuously until curve (h) (or (i)). Other evidence for the above conclusion is that the integral intensity ratios between the combined LUMO and LUMO + 1 feature and the HOMO feature are no less than 3/5 for curves (c)–(h).

The LUMO and LUMO + 1 bands are not separated in figures 1 and 2. Although the signal-to-noise ratio of our spectrometer cannot let us draw the conclusion that the LUMO and LUMO + 1 bands combine, the results in figure 1 can reveal that the separation between these two bands is at least very narrow. For comparison, the LUMO and LUMO + 1 bands are separated by 1.5–2.0 eV in alkali-metal-intercalated solid C<sub>60</sub>. The conduction band electrons of alkali-metal fully transferred to the LUMO band of C<sub>60</sub> and the bonding is ionic [16]. Thus we suggest that the electronic states of Sm (5d6s, 4f) hybridize with the molecular orbitals of C<sub>60</sub> and the bonding between Sm and C<sub>60</sub> should have some covalent contribution. The analogous phenomenon was also observed in alkali-earth-intercalated C<sub>60</sub>, where the alkali-earth atoms hybridized with C<sub>60</sub>. Ca-intercalated [17] and Ba-intercalated [18] C<sub>60</sub> showed no separation between the LUMO and LUMO + 1 bands with the LUMO + 1 band partially occupied, and exhibited a narrow and shallow dip between these two bands when the LUMO + 1 band was fully occupied.

From 1 ML to the coverage slightly less than 2 ML (curve (k)), the spectral weight at  $E_f$  decreases to negligibility, but the decrease of the peak height around 1.0 eV is not significant. This observation reveals that Sm atoms can diffuse into C<sub>60</sub> thin film (at least into the second layer) even at room temperature and donate their electrons to the LUMO band of the second C<sub>60</sub> overlayer. Diffusion at room temperature was also observed in the Eu/C<sub>60</sub> system [10], but not observed in the Yb/C<sub>60</sub> system [9]. The difference may be due to the different formation enthalpies among these systems. The calculated formation enthalpies [19] for the Sm/C<sub>60</sub> and Eu/C<sub>60</sub> systems are more negative than that for the Yb/C<sub>60</sub> system.

With the LUMO + 1 occupation, the sample is metallic as there is remarkable spectral weight at  $E_f$ . Curve (k) has negligible spectral weight at  $E_f$ , which reveals that the second layer of C<sub>60</sub> attenuates the photoemission of the LUMO + 1 band from the first layer of C<sub>60</sub>. Only the LUMO band is occupied for the second layer of C<sub>60</sub>. The sample changes to become semiconducting. At the coverage larger than 2 ML, Curve (l) more clearly reveals the semiconducting property of the electrons occupying the LUMO band as there is no photoemission at  $E_f$ .

#### 4. Conclusions

C<sub>60</sub> and Sm can combine to form fulleride in the interface at room temperature. Sm can diffuse into at least the second layer of C<sub>60</sub>. The bonding is mainly ionic with some covalent contribution. The first layer of C<sub>60</sub> is metallic with both the LUMO + 1 and LUMO band occupied. For the second overlayer, only the LUMO band is occupied, and the C<sub>60</sub> overlayer converts to become semiconducting. The different electronic properties for the LUMO and LUMO + 1 bands in the Sm/C<sub>60</sub> system deserve further research.

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