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Superfulleride formation and electronic properties of C_{60} on K/Rh(111) surfaces

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Abstract

Despite the high electron affinity of C_{60} , photoemission and work function measurements of C_{60} on Rh(111) surfaces containing submonolayer amounts of K show that a low value of the work function is not sufficient to cause extensive charge transfer (> 1 electron) from the substrate to the C_{60} molecule. However, when appropriate amounts of C_{60} are evaporated onto potassium multilayers of controlled thickness at 100 K, interdiffusion occurs and potassium superfullerides, K_xC_{60} with $6 < x < 12$, form on the surface. The resulting phases can be purified by annealing the sample to ≈ 325 K for $x \rightarrow 12$, or higher temperatures for lower K stoichiometries, to drive out excess K.

1. Introduction

There has been increasing interest in the electronic structure of fullerene-based materials ever since the discovery of superconductivity at up to 30 K for alkali-metal-doped C_{60} . This fascinating material is much simpler from both a symmetry point of view and the number of elements involved compared to high T_c cuprate superconductors, and therefore it is particularly suitable for fundamental research. Recently, fullerene thin films were also found to be excellent templates for diamond growth [1] and the catalytic activity of fullerenes was demonstrated in hydrogen-transfer reactions [2]. New advances have suggested that alkali-metal-doped C_{60} may possess catalytic properties that resemble those of Pt or Pd, and that fullerene-based materials could be efficient hydrogen storage media, better battery materials, and useful optical devices^{#1}. Clearly, insights into the

electronic structure of C_{60} and its modification with metal intercalation have great implications in realizing these important potential applications.

Surface science studies have proven to be very powerful in the fundamental understanding of these new materials [4], as well as in the fabrication of novel devices such as fullerene-based quantum well structures and Josephson junctions [5]. Thin film studies do have limitations in some cases but they offer great control of many important factors such as the sample cleanliness, composition, and reaction conditions. Most of the previous experiments on electronic states were conducted for solid C_{60} surfaces as a function of alkali metal (A) exposure. This procedure leads to the formation of a series of fullerides, A_xC_{60} with $0 \leq x \leq 6$, which are characterized by the progressive filling of the t_{1u} band derived from the lowest unoccupied molecular orbital (LUMO) of C_{60} [4]. A higher doping level has been achieved for Li- C_{60} in an electrochemical study [6], and for Na- C_{60} by growth in a closed thermodynamic system [7]. Although the occupation of the t_{1g} band derived from

^{#1} See ref. [3] for a discussion of potential commercial uses of fullerenes.

the next unoccupied (LUMO+1) orbital was observed in the alkaline-earth-metal fullerenes [8], it is only very recently that partial [9] and nearly complete [10] occupation of the t_{1g} band were observed for alkali-metal-fullerene system in the 'reverse' deposition studies of C_{60} on potassium multilayers. The filling of the t_{1g} band is a signature for the formation of alkali metal 'superfullerides', A_xC_{60} with $6 < x < 12$.

This Letter focuses on the conditions for potassium superfulleride formation and its thermal stability. Temperature-dependent photoemission and work function (ϕ) measurements of C_{60} on K-precovered Rh(111) surfaces are presented over a large coverage range of both C_{60} and K, from submonolayer up to 20 monolayers so that our conclusions should be relevant to bulk synthesis and properties. Taking advantage of the ϕ tuning possible by varying submonolayer coverages of potassium, we also investigated the charge states of adsorbed C_{60} on metal surfaces over a very large work function range.

2. Experimental

The experiments were carried out in an ultra-high vacuum (UHV) chamber that has been described previously [10,11]. Photoemission measurements were made with 21.2 and 40.8 eV He I and II resonance radiation by using a double-pass cylindrical mirror analyzer. The work function was determined from the difference between the photon energy (21.2 eV) and the kinetic energy interval between the onset of secondary electron emission and the Fermi level (E_F) in the He I photoemission spectrum. A -5 V bias was applied to the sample in order to raise its work-function cutoff above that of the spectrometer. The Rh(111) sample could be cooled to 90 K or resistively heated to 1500 K. After initial sputter-anneal cycles, Rh(111) was cleaned by annealing at 1000 K in 1×10^{-7} Torr of oxygen followed by repeatedly flashing to 1400–1450 K in UHV. After extensive outgassing, high-purity C_{60} [12] was sublimed from a Ta boat at 600 K. The C_{60} coverage was controlled by the deposition time and the deposition rate was calibrated by Auger electron spectroscopy (AES) uptake and annealing experiments [11]. Potassium was evaporated onto the clean Rh(111) substrate from a thoroughly outgassed SAES getter source

and its coverage was determined by AES and temperature programmed desorption (TPD) [13]. The operating pressure was $\approx 6 \times 10^{-11}$ Torr during data acquisition and was maintained below 1.5×10^{-10} Torr during C_{60} and K deposition. All depositions of C_{60} and K were performed at a substrate temperature of ≈ 100 K. One monolayer (ML) of C_{60} and potassium corresponds to 1.1×10^{14} molecules/cm² ($\theta_{C_{60}}=1$) and 5.3×10^{14} atoms/cm² ($\theta_K=1$), respectively.

3. Results and discussion

Fig. 1a shows valence-band spectra (referenced to E_F) of 0.5 ML C_{60} on Rh(111) precovered with various amounts of potassium at 100 K. The binding energy of the h_u band, or the highest occupied molecu-

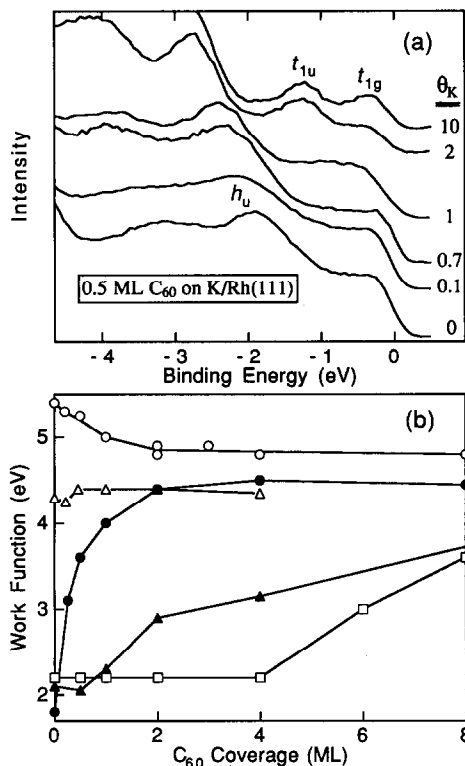


Fig. 1. (a) He I photoemission spectra for 0.5 ML C_{60} on Rh(111) with various potassium precoverages at 100 K. Each spectrum is individually scaled in intensity to emphasize its shape. (b) Work function of the K/Rh(111) substrates as a function of C_{60} coverage at 100 K. $\theta_K = (\circ)$ 0, (Δ) 0.1, (\bullet) 1, (\blacktriangle) 2 and (\square) 10.

lar orbital (HOMO) of C_{60} , is at ≈ 1.9 eV for C_{60} on clean Rh(111), which is considerably less than that of 2.2–2.4 eV found for C_{60} on surfaces partially covered with K. The Fermi level of clean Rh(111), which has a large ϕ of 5.4 eV, lies slightly higher (≈ 0.5 eV) than the ground state HOMO but significantly (≈ 1 eV) lower than the ground state LUMO of C_{60} which is 4.35 eV below the vacuum level [14]. The π -d bonding with delocalization of charge from C_{60} to the metal is more extensive than the d - π^* back-bonding and the net charge transfer is from C_{60} to Rh. This is supported experimentally by the decrease in ϕ upon C_{60} adsorption on clean Rh(111) shown in Fig. 1b and found also in our previous work [11]. For submonolayer K coverages on Rh(111) of $\theta_K \geq 0.1$, the drop in ϕ makes the substrate Fermi level lie above the C_{60} LUMO so that d - π^* back-bonding dominates the π -d interaction and charge transfer from the substrate to C_{60} occurs. This leads to the increase in ϕ upon C_{60} adsorption on submonolayer K-covered Rh(111) surfaces as observed in Fig. 1b. The C_{60} Fermi level, which lies near the middle of the HOMO–LUMO gap for pristine C_{60} , shifts toward the HOMO of C_{60} on clean Rh(111) due to the net loss of charge to the substrate, and moves toward the LUMO of C_{60} on surfaces partially covered with K due to charge transfer from the substrate. This explains why the work function saturates with increasing C_{60} coverage at a higher value for C_{60} on clean Rh(111) than on K-covered Rh(111) surfaces in Fig. 1b. The Fermi level alignment between C_{60} and the substrate leads to the lower binding energy of the HOMO of C_{60} on clean Rh(111) than on submonolayer K-covered Rh(111) surfaces.

The charge transferred to C_{60} from the substrate with $0.1 \leq \theta_K \leq 1$ is about 0–1 electron per C_{60} molecule as estimated from the initial slopes of Fig. 1b by using the Helmholtz equation $\Delta\phi = -4\pi p\theta$, where p is the dipole moment, with a dipole length of 5 Å which is the van der Waals radius of the C_{60} molecule. This charge transfer has been identified unambiguously by electron energy loss spectra since the relatively intense Rh emission between 0 and 2 eV binding energy for $\theta_K \leq 1$ and the photoemission satellite peaks from the h_u band obscure direct evidence for charge transfer from the photoemission data [10]. We note, however, that based on a comparison of the vibrational and electronic excitation spectra of an

adsorbed C_{60} monolayer and bulk K_xC_{60} , an earlier study [15] of the charge states of C_{60} on metal surfaces suggested significantly larger charge transfers from the substrate to C_{60} of 1 ± 1 and 3 ± 1 electrons for a C_{60} monolayer on Au(110) and K/Au(110) $c(2 \times 2)$, respectively. On the other hand, theoretical calculations [16] predict a transfer of one electron to the C_{60} molecule from any surfaces with $1.5 \leq \phi \leq 3.5$ eV, in excellent agreement with our interpretation for C_{60} on submonolayer K-covered Rh(111) surfaces.

In contrast to C_{60} on Rh(111) surfaces with $0 \leq \theta_K \leq 1$, the photoemission spectra of 0.5 ML C_{60} on potassium multilayers in Fig. 1a show new and different features. For $\theta_K = 2$, the t_{1u} (LUMO) band is completely filled and the t_{1g} (LUMO+1) band is partially occupied. The h_u band is also pushed to a higher binding energy of 2.8 eV. For $\theta_K = 10$, even the t_{1g} band is nearly completely occupied because emission from this band is as strong as from the t_{1u} peak. Since the t_{1u} or t_{1g} orbitals can accommodate only six electrons, the occupation of the t_{1g} band indicates a charge transfer of 6–12 electrons. Since little charge transfer was seen for C_{60} on surfaces with similar small values of the work function formed by submonolayer coverages of K on Rh(111), the large charge transfer observed for C_{60} on potassium multilayers is only possible if interdiffusion between C_{60} and K occurs. Potassium superfullerides, K_xC_{60} with $6 < x < 12$, form on the surface since each K atom can only donate one electron and 6–12 K atoms are required to occupy the t_{1g} bands. This interdiffusion is reasonable because K atoms in the multilayer are much more mobile for intercalation than those present on the surface at submonolayer coverages (small K coverages are very tightly bonded to the Rh surface, ranging from 70 kcal/mol near zero coverage to 20 kcal/mol near monolayer coverage [13]). The data in Fig. 1b for K multilayers and the C_{60} coverage-dependent photoemission spectra [10] show that, as long as the t_{1g} band is partially occupied, the work function stays low with increasing C_{60} deposition up to a certain C_{60} coverage that increases with θ_K , before rising gradually toward a saturation value of ≈ 4.4 eV.

It was concluded in an earlier study [15] of depositing a monolayer of C_{60} on a K double layer that 6 ± 1 electrons were transferred from K to C_{60} , but intermixing was not recognized. This leads to a small inconsistency that the charge transferred is more than

the entire amount available for bonding because there are only 5 K atoms per C_{60} molecule in a C_{60} monolayer on top of a K film. We also observed a charge transfer of six electrons from K to C_{60} for the same surface as evidenced directly by the completely filled t_{1u} band and the nearly empty t_{1g} band in photoemission, but we attributed it to the formation of K_6C_{60} [10]. Partial occupation of the t_{1g} band, corresponding to C_{60}^{3-} , has been reported for isolated C_{60} molecules deposited onto alkali-metal multilayers, but the coverage dependence was not investigated [9]. This result is a special case of our 0.5 ML C_{60} on a 2 ML K film where the t_{1g} band appears only as a shoulder. Our data for lower C_{60} coverages or thicker K films indicate that *twelve rather than six or eight is the upper limit of electron transfer from potassium to C_{60} .*

Clear evidence for the formation of potassium superfullerides when C_{60} is deposited onto K multilayers is seen in photoemission spectra such as shown in Fig. 2 for increasing C_{60} coverage on a 20 ML K film. The dashed curves are spectra prior to C_{60} deposition and the large feature at 3.8 eV in Fig. 2a taken with He I ($h\nu = 21.2$ eV) is due to the $M_{23}VV$ Auger transition of potassium [17], rather than contamination, as proven by its absence in Fig. 2b taken with He II

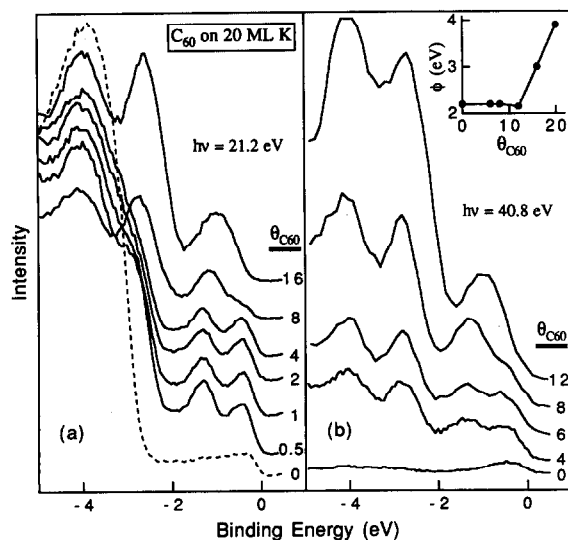


Fig. 2. Photoemission spectra for 20 ML K as a function of C_{60} coverage at 100 K with (a) $h\nu = 21.2$ eV and (b) $h\nu = 40.8$ eV. The work function versus C_{60} coverage of this surface is plotted in the inset of (b).

($h\nu = 40.8$ eV). The spectra are almost independent of $\theta_{C_{60}}$ from 1 to 6 ML, indicating that intermixing readily occurs for vapor deposited C_{60} on K multilayers even at 100 K. This behavior is similar to K deposition on solid C_{60} surfaces at room temperature [4]. The occupied t_{1u} and t_{1g} states at 1.3 and 0.4 eV closely resemble those observed for B_yC_{60} , where B is the alkaline-earth element Ca or Ba and y is close to 6 [8]. This suggests the formation of a K_xC_{60} species with $x \rightarrow 12$, but $K_{12}C_{60}$ is not quite reached yet because the t_{1g} peak is slightly weaker than the t_{1u} peak and a small tail still crosses E_F . The trend from Fig. 2 and the data from 2 and 10 ML potassium films as a function of C_{60} coverage [10] suggests that the photoemission spectrum will stay constant up to even higher C_{60} coverages if we further increase the thickness of the K multilayers. Thus the stoichiometry and the thickness of these superfulleride films can be controlled by the amount of C_{60} deposition and the thickness of the K film. The HOMO and HOMO-1 bands characteristics of C_{60} are obscured at small $\theta_{C_{60}}$ by the large potassium Auger feature at these K-rich stoichiometries in the He I spectra of Fig. 2a, but they are clearly seen in the He II spectra of Fig. 2b. Increasing the C_{60} coverage further leads to shifts of t_{1u} band to lower binding energy, reduced intensity of the t_{1g} band as it moves across E_F , and the growth of the h_u band. At $\theta_{C_{60}} = 16$, the t_{1u} band shifts to an even lower binding energy of 0.9 eV, the t_{1g} band becomes completely unoccupied, and the spectrum resembles that of K_6C_{60} [4]. This is consistent with the K: C_{60} absolute coverage ratios. The inset of Fig. 2b shows that the work function stays low up to 12 ML of C_{60} before rising, in agreement with the changes observed in Fig. 1b. In previous studies of exposing solid C_{60} to K vapor at room temperature, one starts with a C_{60} -rich environment and the saturation of potassium intercalation at K_6C_{60} is due to kinetic limitations and lattice constraints which, rather than unfavorable thermodynamics, prevent the achievement of full K coordination. Fig. 2 demonstrates that when low coverages of C_{60} are deposited onto K multilayers, full K coordination of C_{60} is achieved immediately as C_{60} diffuses into K multilayers even at 100 K.

The data in Figs. 1 and 2 show that potassium superfullerides can be prepared by evaporating appropriate amounts of C_{60} on potassium multilayers of

controlled thickness at 100 K. In order to determine the thermal stability of the superfullerides, photoemission spectra of 5 ML C_{60} deposited on 20 ML potassium were taken as a function of annealing temperature and these are presented in Fig. 3. With the expanded scale used in Fig. 3, it can be seen more clearly that the t_{1g} peak is slightly weaker than the t_{1u} peak for the as-deposited film. As the sample is annealed stepwise from 150 to 200 to 250 K, the intensities of both the t_{1u} and t_{1g} peaks drop while the difference between these two peak intensities becomes smaller. This can be understood by additional interdiffusion induced by annealing which makes the surface region probed by photoemission become K-rich; this region contains unreacted K so that the C_{60} features get diluted and attenuated. Upon heating to 300

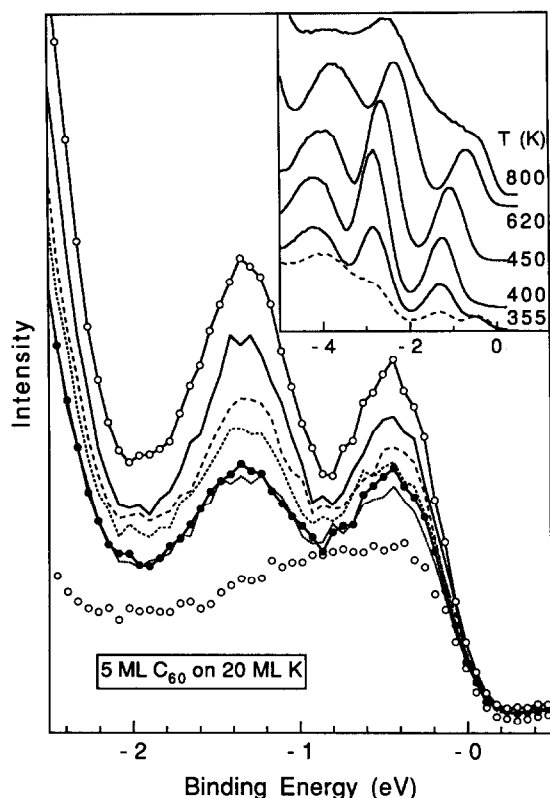


Fig. 3. He I photoemission spectra for 5 ML C_{60} on 20 ML K as a function of temperature. The annealing time was 30 s at each temperature. Spectra for $T \geq 325$ K are plotted in the inset, with the dashed curve corresponding to 325 K. The spectrum of 20 ML potassium at 100 K is shown by the broken open circles. $T =$ (—) 100 K, (---) 150 K, (---) 200 K, (---) 250 K, (●, —) 300 K and (○, —) 325 K.

K, the intensity of both peaks increases but the t_{1g} peak increases slightly more so that the two peaks have about equal intensities. At 325 K, the intensities of both peaks drastically increase, exceeding that for the as-deposited film. It is known from TPD studies [13] that potassium in the multilayer state starts to desorb near 300 K and the desorption rate is quite large at 325 K. The data in Fig. 3 for $300 \leq T \leq 325$ K can be explained therefore by the removal of excess K so that the superfullerides become more phase pure. Increasing the annealing temperature further leads to decomposition of the superfullerides and desorption of potassium. The t_{1g} peak becomes much smaller than the t_{1u} peak and is completely unoccupied at 400 K, as shown in the inset of Fig. 2. These studies suggest that the K_xC_{60} superfullerides prepared at 100 K can be purified by annealing the sample to ≈ 325 K for $x \rightarrow 12$, or even higher temperatures for lower K stoichiometries to drive out excess K. Since our work covers a large range of coverages, these conclusions should have impact on bulk synthesis and properties. We believe that these conclusions will also apply to other alkali metal superfullerides.

The temperature-dependent photoemission data establish the K_xC_{60} ($x \approx 12$) species as a distinct phase stable to 325 K. One important question arises as to whether this phase is crystalline, amorphous, or is composed of many individual clusters of C_{60} surrounded by ≈ 12 K ions. Proving the crystallinity of these samples will require structural experiments. We note, however, that based on X-ray powder diffraction data of $Na_{9.7}C_{60}$ [7], an fcc structure with an ideal composition of $Na_{11}C_{60}$ has been proposed in which the octahedral interstitial sites contain a nine-atom body-centered cluster of alkali atoms with the tetrahedral sites singly occupied. Since the sample in that study did not reach the ideal composition, possibly due to kinetic limitations, site occupancies of < 1 are needed. A feasible structural model for our potassium superfulleride is obtained from the same structure, but with site occupancies of unity (ideal composition) and the lattice constant expanded to take account of the larger size of K compared to Na. If this is the case, the structure of K_xC_{60} will change from fcc to bcc and back to fcc as x increases from 3 to 6 to 11. It is very important to test these proposals experimentally.

Photoemission spectra as a function of annealing

temperature were also taken for other coverages as presented in Fig. 4 in order to gain more insight into the interdiffusion process. Fig. 4a shows that the valence-band features of the film obtained by depositing 12 ML C_{60} on 2 ML K shift about ≈ 0.25 eV to lower binding energy upon heating to 350–500 K. This shift is the result of additional screening of the photoemission final state by the increased number of electrons occupying LUMO-derived states as potassium becomes mobile enough above room temperature to diffuse through the relatively thick C_{60} film. Above 500 K, the photoemission spectrum changes drastically because C_{60} multilayers start to desorb. The shifts of the valence features indicate that interdiffusion occurs readily near 200 K. This conclusion is strongly supported by the spectra in Fig. 4b where the LUMO-derived feature can be observed directly after annealing the 14 ML C_{60} film on 10 ML potassium to 200 K. The large drop in ϕ from 100 to 200 K, as shown in the inset of Fig. 4b, indicates that potassium atoms actually diffuse all the way to the top-most surface layer. The fulleride formed at 200 K has a stoichiometry close to K_6C_{60} because the t_{1u} band is below the Fermi level (completely filled). It is extremely stable thermally and the photoemission spec-

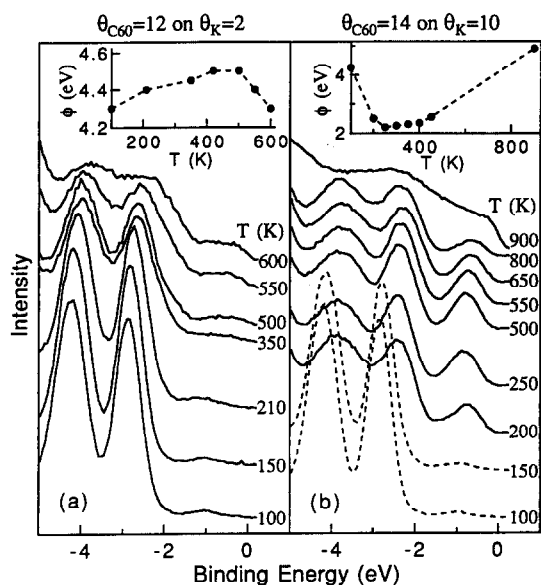


Fig. 4. He I photoemission spectra as a function of temperature for (a) 12 ML C_{60} on 2 ML K and (b) 14 ML C_{60} on 10 ML K. The annealing time was 5 s at each temperature. The insets show the work functions versus temperature.

trum is almost independent of annealing temperature up to 800 K.

Since the half-filled t_{1u} band is responsible for the superconductivity of K_3C_{60} , it will be interesting to study the transport properties, and particularly the possible superconductivity associated with the t_{1g} band (as in the case of Ca_5C_{60}) of K_xC_{60} for $x=6\rightarrow 12$. While magnetization experiments used to test superconductivity can be performed for samples prepared by depositing C_{60} on potassium multilayers, resistivity measurements are obviously very complicated, if not impossible, because the potassium multilayers deposited first will short circuit the probe wires. Samples prepared by exposing solid C_{60} to K vapor at room temperature are very convenient for resistivity measurements, but previous work (including ours) indicates saturation at K_6C_{60} , beyond which metallic K forms on the surface. The failure to increase K doping in this case might be due to the fact that room temperature deposition never creates enough K on the surface. In order to overcome these problems, we condensed 20 ML potassium on 8 ML C_{60} at 100 K (so that the K to C_{60} ratio is about 12) and tried to form potassium superfullerides by subsequently annealing the sample to higher temperatures. Fig. 5 shows that K_xC_{60} ($6\leq x\leq 12$) can be synthesized in this way by gradually warming up the sample to 300–310 K, as evidenced by the occupation of both the t_{1u} and t_{1g} bands. This result demonstrates the feasibility of preparing potassium superfullerides suitable for resistivity measurements and varying the stoichiometry by using the annealing temperature.

4. Conclusions

We have explored charge transfer to C_{60} from substrates with work functions over a very large range of $1.8\leq\phi\leq 5.4$ eV, as controlled by the coverage of strongly adsorbed K adatoms on Rh(111) in the submonolayer regime. The charge transfer is less than one electron even though C_{60} has a large electron affinity of 2.7 eV [18]. Also, in contrast to exposing solid C_{60} to K vapor at room temperature, full coordination of C_{60} with up to 12 K atoms can be achieved by depositing C_{60} on potassium multilayers so that potassium superfullerides, K_xC_{60} with $6<x<12$, can be pre-

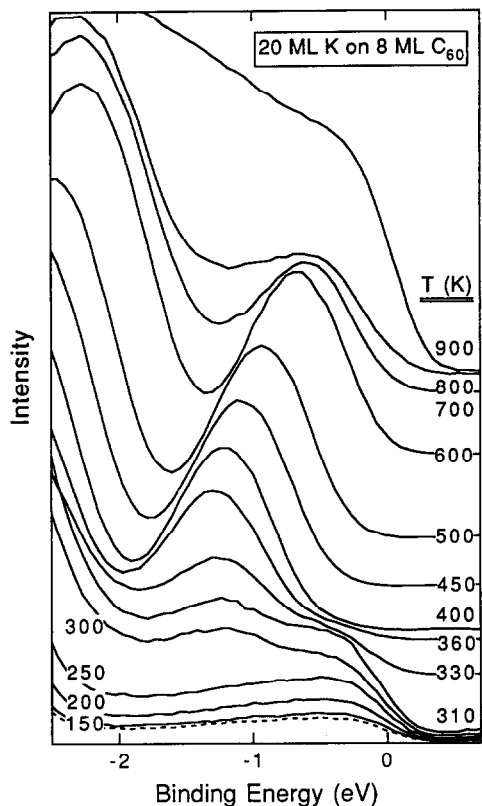


Fig. 5. He I photoemission spectra for 20 ML K on 8 ML C_{60} as a function of temperature. The annealing time was 30 s at each temperature. The dashed curve corresponds to the spectrum prior to annealing (taken at 100 K). The intensity of the spectrum at 330 K has been reduced by a factor of 4 and the intensities of the spectra for $T \geq 360$ K have been reduced by a factor of 8. Spectra for $T \geq 330$ K have been offset vertically in order to show the changes in the spectra more clearly.

pared. The stoichiometry and the thickness of these films can be controlled by the amount of C_{60} deposition and the thickness of the K film. Additional control of the resulting phases is provided by annealing. It is hoped that this work will inspire new structural measurements and a search for conductivity and superconductivity associated with the t_{1g} band of C_{60} in alkali metal superfullerides.

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