

Bulk and surface electronic structures of potassium fullerides

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Photoemission spectra from thin films of K_xC_{60} prepared by vapor-phase reaction of C_{60} with K vapor consist of superpositions of distinct bulk and surface contributions. The spectra of K_3C_{60} and K_6C_{60} are identified and shown to be in very good agreement with band-structure calculations. The surface layer of molecules does not contribute to the metallic conductivity for any bulk composition.

Although the general features of the transport properties¹⁻⁵ of K_xC_{60} are well understood, the detailed interpretation of photoemission spectra⁶⁻⁹ encounters various difficulties. While there is general agreement that the potassium donates its outer *s* electron into the lowest unoccupied molecular orbital (LUMO) of the host, there is only limited understanding of the rich phenomenology that results from this process. Among the outstanding problems are the small amplitude and large width of the conduction band of K_3C_{60} . Another concern is composition-dependent band shifts which are incompatible with the two-phase nature of K_xC_{60} in both the fcc regime with $0 < x < 3$ (Ref. 10) and the bcc regime for $3 < x < 6$.¹¹ It seems likely that these problems have their origin in the surface sensitivity of photoemission, which makes it difficult to obtain bulk information from molecular crystals whose structural units have a diameter comparable to the electron mean free path.¹²

The samples used in this work were prepared by the conventional method. Thin (100 Å) films of C_{60} were grown in UHV by vapor deposition onto a clean room-temperature W(100) substrate. These films were allowed to react at room temperature with K vapor obtained from an SAES Getters source. Data were taken directly after reaction and after an anneal at 150°C. Conductivity measurements have shown that the diffusion constant of K in C_{60} is sufficiently large at room temperature³ to penetrate these thin films in about 1 sec, which is short compared to the time between exposure and data acquisition. The fact that annealing up to 150°C did not produce a significant change in the photoemission spectra of such doped films confirms that these films rapidly approach an equilibrium K distribution at room temperature. (In a related experiment we observed the diffusion of K through a comparable C_{60} film in a matter of minutes at -40°C.) Nevertheless, in view of the two-phase nature of this system it is clear that the K is not uniformly distributed on a microscopic scale. In particular, it is likely that in the fcc regime K_3C_{60} will form preferentially near the surface exposed to K vapor.

The data were taken with He I resonance radiation (21.22 eV) using a Vacuum Science Workshop 50-mm hemispherical electron energy analyzer system controlled by an AT&T personal computer. A -3.0-V bias was applied to the sample in order to raise its work-function

cutoff above that of the spectrometer. The location of the Fermi level was checked prior to the deposition of the C_{60} film by recording the valence-band spectrum of the freshly cleaned W(100) surface. It was found to be reproducible to within 5 meV over the period of these experiments and in good agreement with the Fermi cutoff in the metallic K_xC_{60} samples that were prepared. Survey data were typically recorded with 100-meV instrumental resolution and 50-meV point spacing, covering the entire spectrum down to the work-function cutoff. Spectra with adequate statistics were obtained in 20 min. More-detailed data of the region near the Fermi level were taken with 50-meV resolution in order to minimize the broadening of the 88-meV room-temperature thermal width of the Fermi cutoff.

Data taken during the preparation of the clean C_{60} films (Fig. 1) show the valence-band spectrum of C_{60} mol-

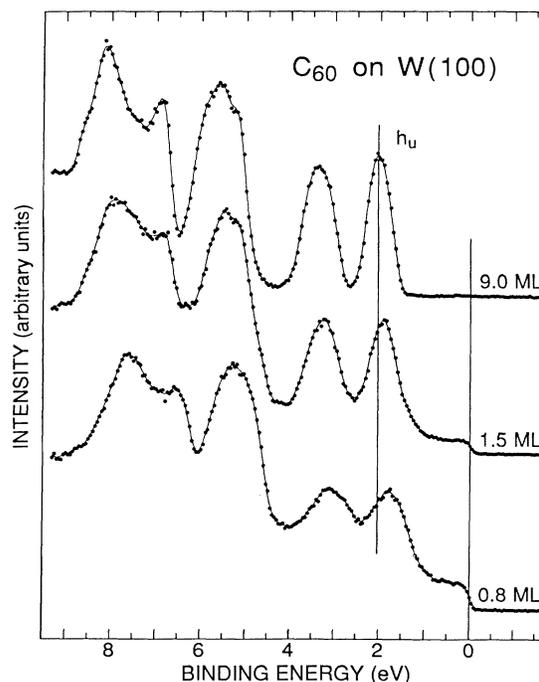


FIG. 1. Coverage-dependent valence-band spectra C_{60} deposited on a clean W(100) surface.

ecules in contact with the W surface both shifted and broadened compared to those obtained from the bulk solid. A similar shift has been reported for the C 1s core level of C_{60} in contact with Cu.¹³ The Fermi cutoff in these spectra is due to the W 6s band and not due to electrons in the t_{1u} band of C_{60} . The shift to smaller binding energy is probably due to final screening by the W conduction electrons, since the large work function of W makes electron donation into the LUMO of C_{60} in the initial state highly unlikely. The broadening may be attributed to the lower symmetry of a C_{60} molecule that is in contact with a metal surface. The samples used in the K doping work were sufficiently thick compared to the electron escape depth so that the effects of the tungsten substrate are completely attenuated by the additional C_{60} .

Survey data taken immediately after K exposure at room temperature are shown in Fig. 2. The data exhibit the development of a metallic Fermi edge at intermediate doping in (c)–(e) and then show a new filled band well below the Fermi level in (f)–(h). The work-function cutoff at high binding energy is extremely sharp in a well-prepared sample with uniform surface properties. In most of the data shown this width is due largely to the instrumental resolution (equal to twice the separation of the

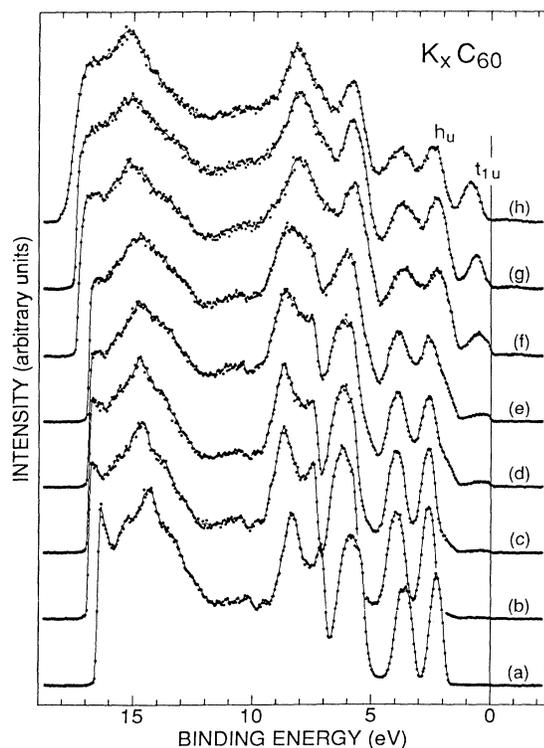


FIG. 2. Valence-band spectra of $K_x C_{60}$ prepared by exposing a 100-Å-thick film of C_{60} to K vapor at room temperature. The data were taken with 21.2-eV He I resonance radiation. The K vapor exposure times from (a) to (h) are proportional to 0, 2, 4, 6, 8, 12, 16, and 28, respectively. The corresponding bulk compositions are approximately $x = 0, 0.6, 1.2, 1.8, 2.4, 3.6, 4.8,$ and ~ 6 , respectively, but the surface layer is more weakly doped.

data points). For insulating C_{60} in (a) the Fermi level falls in the highest occupied molecular orbital (HOMO)-LUMO gap and binding energies are not strictly reproducible. (The HOMO generally lies between 2.0 and 2.3 eV.) After exposure to even small amounts of alkali vapor, the still largely empty t_{1u} band becomes pinned at the Fermi level [(b)–(e)] and the work function is 4.30 eV. Since this is slightly smaller than that of W there should be no electron transfer from W to C_{60} , as indicated above. In (f) the cutoff is relatively broad, indicating the presence of two phases at the surface. In (g), which is dominated by $K_6 C_{60}$, it is again narrow. The work function here is 3.79 eV. In (h) the work-function cutoff has become very broad, indicating that the surface is inhomogeneous, presumably due to the accumulation of excess K on the surface. However, there is not sufficient K to form a metallic layer, which would have an even smaller (2.2 eV) work function.

These data present an interesting problem. For x in the vicinity of 3, the half-filled t_{1g} band should have an amplitude comparable to that of the filled band in (h), but with a sharp Fermi cutoff at midband. That has never been observed.^{6–9} In fact, the conversion to $K_3 C_{60}$ appears to be much slower than suggested by the exposure. Since a large fraction of the signal comes from the outermost molecular layer,¹² it seems likely that a surface layer with unique properties is responsible for these anomalies. In the following analysis we seek to identify the bulk and surface contributions to these spectra.

In order to consider the behavior near the Fermi level in greater detail, we show data from samples annealed at 150°C in Fig. 3. The first spectrum shown (a) was taken after an exposure so small that there were only minor changes from the clean spectrum, except for an 0.3-eV shift to larger binding energy, which pins the largely empty t_{1u} band at the Fermi level. The h_u band, derived from the HOMO of the molecule, now lies 2.6 eV below the Fermi level, in agreement with earlier work.^{6–9} The fact that this is larger than the 1.5-eV HOMO-LUMO gap in the theoretical band structure¹⁴ is not necessarily in conflict with that calculation. It is simply an indication that the final-state screening in the insulator is less effective than that in the metallic $K_3 C_{60}$. In the insulator the hole in the h_u band is screened only by the polarization of the neighboring molecules, reducing but not eliminating the ~ 2.0 -eV Coulomb energy of the hole state. The residual Coulomb energy serves to increase the binding energy of the h_u band. The binding energy of the empty t_{1u} band relative to the Fermi level is not subject to such a shift. As a result the separation of filled and empty bands is increased by this Coulomb energy, which in this case is ~ 1 eV. In metallic $K_3 C_{60}$ the Coulomb energy is completely canceled out by screening charge in the t_{1u} band, making it possible to measure consistent binding energies for all bands.

Successive K exposures (b), (c), and (d) result in the growth of a signal at the Fermi level, which is due to the half-filled t_{1u} band, as well as the appearance of a new broad feature 1.5 and 2.0 eV. It is indicated by the vertical solid line at 1.7 eV in Fig. 3. The latter is due to the

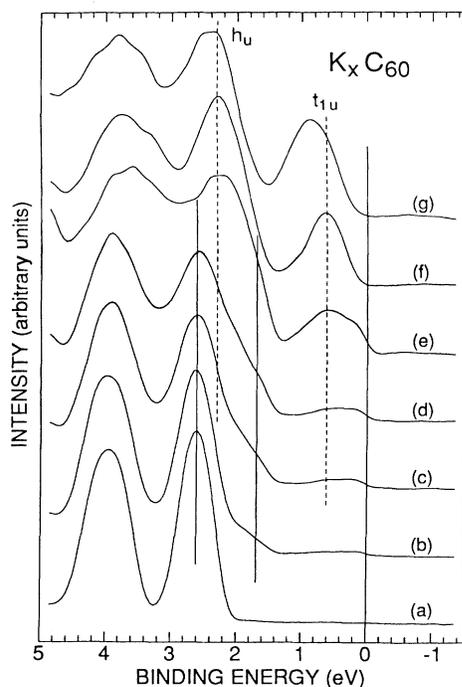


FIG. 3. Detail of the region near the Fermi cutoff of $K_x C_{60}$ prepared as in Fig. 1 and annealed for 1 min at 150°C. The K vapor exposure times from (a) to (g) are proportional to 1, 4, 6, 8, 12, 20, and 28. The bulk compositions for (a)–(f) are approximately $x = 0.3, 1.2, 1.8, 2.4, 3.6,$ and 6.0, respectively.

h_u band of molecules modified by charge donation. In light of the demonstrated two-phase character of this system for $0 < x < 3$,^{10,15} we identify these weak features with K_3C_{60} in the bulk, rather than with weakly doped C_{60} . The much-stronger and relatively narrow signal at 2.6 eV is due to unconverted C_{60} in the bulk as well as weakly doped C_{60} in the first molecular layer (see below). The ~ 1.7 -eV separation between the Fermi level and the broad feature is in very good agreement with the 1.8-eV separation in the band-structure calculation for K_3C_{60} .^{16,17} This is only slightly smaller than the 1.9-eV separation between the corresponding states of C_{60} . Since this is a two-phase system, we do not see the shifts associated with the progressive filling of the conduction band with increasing K content that would be expected if the rigid-band model were applicable.

A more-detailed analysis of 50-meV resolution data with $x \approx 2$ is shown in Fig. 4. The components of the spectrum were represented by five Gaussian profiles with free parameters, subject to a Fermi cutoff. The instrumental resolution and kT were fixed to known values. Although the determination of weak components located close to stronger ones results in considerable uncertainty, the results confirm the visual impression that there are two components separated by ~ 0.3 eV in the broad feature between 1.5 and 2.0 eV. This is in very good agreement with the theoretical splitting of the h_u band in K_3C_{60} obtained by Oshiyama and Saito.¹⁷ The binding

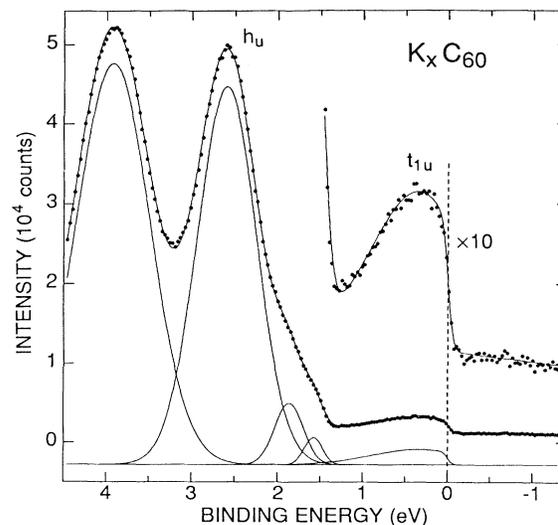


FIG. 4. Analysis of valence-band spectrum of relatively weakly doped $K_x C_{60}$. The two strong peaks are due to unmodified C_{60} . The three weak peaks are due to K_3C_{60} . The conduction band is also shown vertically magnified.

energies are also in good agreement with their theory. However, the large width of the conduction band, although in good agreement with earlier experimental data,⁸ represents a serious disagreement with theory. We show below that it arises from a superposition of a relatively narrow bulk conduction band at the Fermi level and a broader surface band well below the Fermi level. The important point that emerges from this analysis is that the conduction band is associated with the weak h_u components at 1.6 and 1.9 eV rather than with the strong peak at 2.6 eV. The latter is due in part to unconverted bulk C_{60} , but the broadening seen in Figs. 3(c) and 3(d) indicates that much of its intensity is due to a weakly doped surface layer with properties unlike those of the two bulk phases.

In order to demonstrate that the data in the region $0 < x < 3$ are not adequately accounted for by a superposition of the spectra of C_{60} and K_3C_{60} , we attempt to isolate the spectrum of K_3C_{60} by subtracting the spectrum of C_{60} from one with intermediate doping. This is illustrated in Fig. 5, in which the spectrum of pure C_{60} (a) is subtracted from that of a moderately doped sample (b), resulting in (c). It is interesting to note that (c) is broader, but otherwise quite similar to the spectrum of pure C_{60} , except for a shift to smaller binding energy. This demonstrates that the broadening produced by K doping is due to the growth of a shifted spectrum of which the bulk feature at 1.7 eV is the only part accessible by inspection. When considered in greater detail, the result of the subtraction is incompatible with the band structure of K_3C_{60} . The major problem is that the total intensity of the h_u band in (c) is much too large relative to that of the t_{1u} conduction band. This demonstrates that the assumption that (b) is a two-component spectrum is incorrect. There is an additional contribution

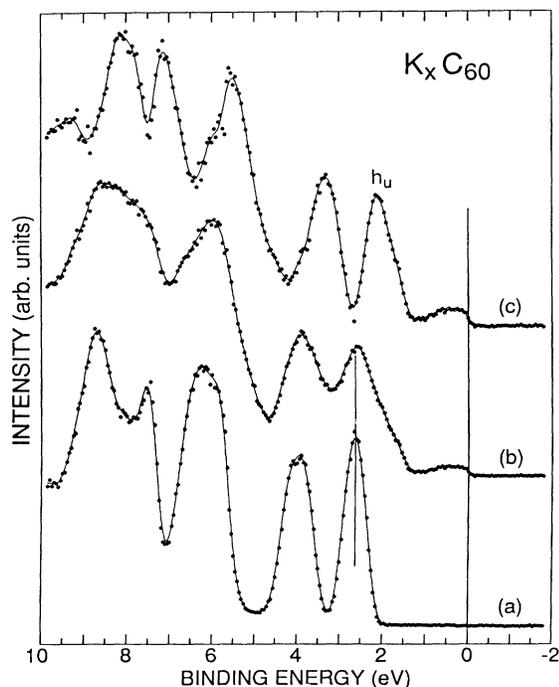


FIG. 5. Attempt to isolate the spectrum of K_3C_{60} by subtracting the C_{60} component from data in the two-phase region for $x < 3$.

from the surface layer, which has a spectrum unlike those of C_{60} or K_3C_{60} . The subtraction (c) must contain a distinct contribution from the surface layer of molecules. The latter is responsible for most of the h_u peak at 2.0 eV as well as for the lower part of the excessively broad "conduction band" (see below).

Returning to Fig. 3, we find that continued K exposure leads first to a broad spectrum (e), and then to a sharper (f). In (e) the contribution from undoped C_{60} at 2.6 eV has largely vanished and an indication of a new peak appears at 0.6 eV. In (f) the transformation is complete. The signal at the Fermi level has vanished and the peak at 0.6 eV can be identified as the filled t_{1u} band, which has now dropped below the Fermi level, indicating that we have reached the insulating state corresponding to K_6C_{60} . The structural phase transition from fcc to bcc stacking takes place between (d) and (f). In (f) the h_u band now lies at 2.3 eV, corresponding to a gap of 1.7 eV; see the dashed lines. The two occupied bands are significantly broader than those of C_{60} , but the only new features are the filled t_{1u} band and the shoulder at 3.4 eV. The agreement with the band-structure calculation for K_6C_{60} (Ref. 18) is gratifying, both with regard to the 1.7-eV band separation and to the larger bandwidths. Even the shoulder is accounted for in the density of states. This comparison confirms that we have successfully prepared K_6C_{60} . Spectrum (e) then represents a superposition of K_3C_{60} and K_6C_{60} rather than a Fermi cutoff in a single broadband. This confirms the conclusion reached in the discussion of the broadened work-function cutoff in

Fig. 2(f), which corresponds to the same doping level.

Additional exposure to K vapor shifts the entire spectrum to larger binding energy and produces some broadening of the bands; see Fig. 3(g). For this doping level the work-function cutoff, Fig. 2(h), indicates that excess K is present on the surface. A shift of the bulk spectrum is possible because the Fermi level of K_6C_{60} lies in the 0.48-eV gap between the t_{1u} and t_{1g} bands.¹⁷ The broadening suggests that bulk and surface do not shift by the same amount. In fact, continued exposure to K vapor makes the shift exceed the limit set by the band gap. This can be understood if the excess K on the surface donates its electrons into the t_{1g} band, making the surface layer metallic. Excess K on grain boundaries may be responsible for the reported tendency of the resistivity to decrease again after increasing from the K_3C_{60} minimum to K_6C_{60} .³

Up to this point the discussion has been concerned mainly with making assignments of the various spectral features seen during the reaction of C_{60} with K vapor. We now consider the intensities in greater detail. They can be understood only in the context of the escape depth of the photoelectrons. Experiments have shown that the electron mean free path at 21.2 eV is no larger than the 8.2-Å (111) layer spacing in C_{60} , so that the first molecular layer is responsible for most of the photoemission signal.¹² In the regime $0 < x < 3$, Figs. 2(b)–2(e), the slightly broadened h_u signal at 2.6 eV remains very large compared to the height of the Fermi cutoff. This and the constant work function are indications that little if any K remains on the surface while the near-surface bulk is converted to K_3C_{60} . This is reasonable from the point of view of the energetics, since a fully coordinated bulk interstitial site is more favorable for a K ion than a partially coordinated surface site. The absence of surface K is also in accord with the finding that these surfaces are stable in UHV for many hours.

In the absence of surface K, the surface layer of C_{60} molecules has a lower K coordination than those of bulk K_3C_{60} and will have a distinct spectrum. The subtraction shown in Fig. 5 suggests that the h_u band of the surface layer lies at 2.0 eV and that its t_{1u} band does not intersect the Fermi level. This is possible provided the t_{1u} band of the surface layer of molecules is split into two subbands by the lower symmetry at the surface. It seems likely that the splitting is due to the asymmetrical K environment rather than to the reduced C_{60} coordination, because the interaction with the K is much stronger. Takeoff angle experiments have shown that the occupied surface subband is responsible for the lower part of the broad t_{1u} band in Fig. 4 and only a narrow part near the Fermi energy to K_3C_{60} in the bulk.¹⁹ That assignment brings the spectrum of K_3C_{60} into good agreement with theory.¹⁷ The data in this regime then contain three contributions. The undoped regions of bulk and surface contribute a C_{60} -like spectrum. The doped bulk contributes a metallic K_3C_{60} spectrum, with a narrow conduction band and a split h_u band very much like the theoretical band structure in Ref. 17. The regions of the surface above K_3C_{60} clusters are weakly doped and contribute a

spectrum with h_u band at ~ 2.0 eV and a filled subband of the t_{1u} band at ~ 0.6 eV.

The fact that the height of the Fermi edge remains small compared to that of the t_{1u} peak in K_6C_{60} throughout the doping sequence confirms that the surface does not contribute to the Fermi edge even when the near-surface bulk has been converted to K_3C_{60} . This is in accord with the insulating grain boundaries found in conductivity measurements at minimum resistivity.³ The appearance of the filled t_{1u} band in Fig. 3(e) and its rapid growth to saturation indicates that the fcc-to-bcc phase transition is nucleated at the surface when the near-surface bulk has been fully converted to K_3C_{60} . In a thick film this may well happen before the bulk has been entirely converted to K_3C_{60} unless the exposure rate is kept very small. In fact, in a recent study²⁰ photoemission data corresponding to K_6C_{60} were obtained at the minimum in the bulk resistivity, confirming that the surface can have a stoichiometry corresponding to K_6C_{60} when the bulk is fully converted to K_3C_{60} .

The fact that the t_{1u} band approaches the intensity expected on the basis of its degeneracy indicates that the surface C_{60} molecules contribute to this peak, i.e. they reach the full K coordination of a bulk molecule after the bulk transition to K_6C_{60} . The decrease in work function that accompanies the formation of K_6C_{60} is in agreement

with the presence of K on the surface. (We have also found that samples which yield a K_6C_{60} spectrum are much less stable in the spectrometer vacuum than those which show only K_3C_{60} , confirming the presence of K on the surface.) It is likely that the splitting of the t_{1u} band disappears when the surface molecules are fully coordinated by K. These results indicate that the surface layer on K_3C_{60} is insulating because it is deficient in K, while that on K_6C_{60} is insulating because it has a full bulklike K coordination. The surface layer of K-doped C_{60} then does not contribute to the conductivity at any doping level.

We have presented an interpretation of the photoemission data obtained when thin films of C_{60} are exposed to K vapor. Our conclusions depend on the recognition that the data are dominated by emission from the outermost molecular layer, which has unique properties. We find that the spectra of K_3C_{60} are in very good agreement with band-structure calculations and that the surface layer remains insulating at all bulk compositions.

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