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Auger and photoelectron study of the Hubbard U in C_{60}, K_3C_{60}, and K_6C_{60}

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Comparison of valence-photoelectron to Auger-electron spectra has been carried out for three phases of K_xC_{60}, $x=0$, 3, 6, yielding Hubbard correlation energies, U, of 1.4 eV (1.5 eV) for $x=0$ (6), consistent with the results of Lof *et al.* [Phys. Rev. Lett. **68**, 3924 (1992)]. At $x=3$ the results are best described by intermolecular charge-transfer screening of the C 1*s* core hole in the Auger initial state, with U of the same magnitude as for $x=0$ and 6.

The discovery[1] of a method to mass produce C_{60} was followed quickly by studies of its solid phases and compounds, in particular compounds with alkali metals that exhibit superconductivity at relatively high temperatures.[2] Holczer *et al.*[3] rapidly made a positive identification of the superconducting K fulleride as K_3C_{60}. Since then there have been numerous experimental[4-6] and theoretical[7] studies of these materials aimed at understanding this new type of organic superconductor.

Photoemission (PES), which should play an important role in elucidating the electronic properties of the alkali fullerides, has suffered somewhat from variability in the results.[8-11] Phase separation and well-defined phases of K_xC_{60} were identified using PES early on,[8,9] consistent with bulk measurements.[3,12] The appearance of the K-induced band near E_F was not reproducible in photoelectron spectra until recently, when Merkel *et al.*[11] duplicated the results of Chen *et al.*[9] and confirmed the sharp Fermi level for $x \approx 3$. Recently Lof *et al.*[13] combined PES, inverse photoemission, and Auger-electron spectroscopy to study pure C_{60} films. They determined the Coulomb interaction of two excess charges on a single molecule ($U \approx 1.6$ eV), measured as the shift ΔE between the Auger and self-convoluted valence PES spectra, to be much larger than the bandwidth ($\sim \frac{1}{2}$ eV), and concluded that a large-U Hubbard model description of C_{60} and the alkali fullerides should hold. The implications of these results include the notion that conducting and superconducting phases of the alkali fullerides must be nonstoichiometric, and if confirmed require reevaluation of much of the theory developed so far to explain the high-superconducting transition temperatures in these compounds.

We present new measurements of the Hubbard U for three phases of K_xC_{60}, $x=0$, 3, and 6. U is within the range of 1.4 ± 0.2 eV for the phases $x=0$ and 6. We find the shift $\Delta E = 0.6 \pm 0.3$ eV between Auger and PES self-convolution for the metallic phase. We tentatively assign this to an effect of the core hole in the Auger initial state. We thus find that $\Delta E < U$ for K_3C_{60} because a new intermolecular screening is activated with the formation of a half-filled band; U is apparently of the same magnitude as for the other two phases studied here.

Pure C_{60} was prepared[14] at UCLA and evaporated at $T \approx 300\,^\circ\mathrm{C}$ from radiatively heated Ta crucibles onto Mo(110) substrates. Pressure during evaporation varied from 2 to 20×10^{-10} Torr, higher pressures corresponding to earlier evaporations, but the results did not depend on this. PES and Auger spectra were obtained with two spectrometers, Beamline 22 at MAX Lab in Lund,[15] and a high-resolution x-ray photoemission spectroscopy (XPS) system using monochromatized Al $K\alpha$ radiation at Uppsala.[16] The base pressure in the sample preparation chamber was about 1×10^{-10} Torr, and 5×10^{-11} Torr in the measurement chamber in Lund, and the pressures were about a factor of 3 higher in Uppsala. Energy resolution was, unless indicated otherwise in the figure captions, 0.3 eV (0.4 eV) for C_{60} and K_6C_{60} (K_3C_{60}), in all cases significantly less than the intrinsic broadening. Core and valence spectra were used to characterize the samples, and to monitor the effects of time, which were found to be negligible. We use SAES Getters sources to evaporate K onto clean C_{60} films, and prepared them in two ways. The intercalated samples studied at MAX Lab were annealed during and after evaporation (25 min total), which was crucial to prevent K segregation for $x \rightarrow 6$ at the evaporation rates used, and presumably enhanced the uniformity of the K intercalation.[9] The K_3C_{60} samples studied at Uppsala were made with lower K-flux density, and annealing brought about no changes in the C 1*s* and K 2*p* spectra.

We show valence spectra taken at MAX Lab in Fig. 1, and compare the spectra taken at both laboratories for K_3C_{60} in Fig. 2. For the case of K_3C_{60}, the valence spectrum at 110 eV compares reasonably well with others[9,11] shown to correspond to $x \approx 3$, including good alignment of energies, but contains extra broadening; we show it here to link the XPS valence spectrum, taken on the same sample as our Auger spectrum, to published valence data, which were acquired with much lower photon energies. The $h\nu = 1486.6$ eV spectrum is more in line with the previous data,[9,11] most notably in the free-electron-like line profile of the K-induced band. The K 3*p* line is split for this phase, which can be associated with the two sites occupied by K.[8,17] We note that there is almost certainly a minority phase component for these films.[8,9,11] For example, the intensity ratio of the two components of the K core levels, which should be exactly 2 for an idealized

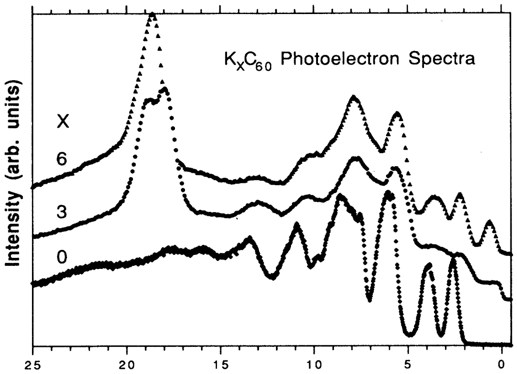

FIG. 1. Valence spectra of K_xC_{60} at the indicated compositions, taken at photon energy 110 eV (80 eV) for $x=0$ and 3 ($x=6$). Total energy resolution was 0.06 eV for $x=0$. Binding energies are referenced to the spectrometer E_F as determined from the Fermi edge of a comounted metallic sample.

bulk measurement, varied from 1.66 to 2.23 among the $3p$, $2p_{3/2}$, and $2p_{1/2}$ lines. In addition to the possibility of other phases, part of this variation stems from the difficulty in choosing the backgrounds for the spectra, which includes our uncertainty in the site dependence of the shake-up and shake-off contributions to the tails of the K core lines, and part may be due to the existence of a different surface composition for this phase. However, as shown in Fig. 2, using a higher photon energy to probe more deeply does not change the overall structure in the PES, with the exception of expected variations in cross section,[18] indicating surface effects do not dominate the measured electronic structure. For K_6C_{60} we find excellent agreement with prior measurements, consistent with K intercalation saturating at this concentration.

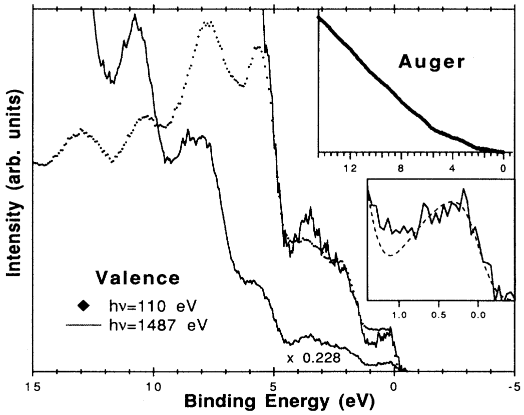

FIG. 2. Valence spectra of K_3C_{60} at widely different photon energies, to illustrate the small mean-free-path dependence of the spectra. Note that the valence spectrum at 110 eV is significantly broader than previously published K_3C_{60} spectra (Refs. 9 and 11) taken at comparable resolution, most importantly for the present work in the region between the Fermi-level band and the former highest occupied molecular orbital band. On the other hand, the XPS spectrum closely resembles the published data near the Fermi level, suggesting the measured electronic structure is not strongly dependent on the sample depth probed. Lower inset: Comparison of our XPS data to the room-temperature He I excited data of Merkel *et al.* (Ref. 11) convoluted with a 0.35-eV-wide Gaussian (dashed line). Upper inset: Auger spectrum from the same sample as the $h\nu=1486.6$ eV spectrum.

In Fig. 3 we compare the C 1*s* line for K_3C_{60} to that of pure C_{60} and of a monolayer[19] of C_{60} on Au(110). The width of the main line increases to 1.5 eV for K_3C_{60} as previously noted.[8] Some broadening could be expected because of the variation in chemical environment of the C atoms for this phase, and similar widths have been observed, e.g., for K-intercalated graphite.[20] However, the nonzero value of ΔE we obtain points to the importance of screening effects for the interpretation of the K_3C_{60} data. When the C 1*s* hole is created, the system may end up in two different final states, "fully relaxed" and "satellite," where an electron in the lowest unoccupied molecular orbital (LUMO) band has been transferred or not, respectively, from a neighboring C_{60} molecule to that in which the core hole was created. From studies of, e.g., CO on surfaces, it is known that the satellite peak can obtain most of the weight if the ground-state coupling to the surface, or in the present case the intermolecular coupling, is weak compared with the Coulomb interaction U_c between the core hole and the LUMO.[21-23] As a measure of the coupling one may use the LUMO bandwidth W, which is calculated to be $\sim\frac{1}{2}$ eV,[24,25] though this could be reduced due to polaronic effects. In either case, $U_c > W$ assuming $U_c \sim U = 1.4$ eV. If the core-hole lifetime broadening $\gamma \ll W/2$ the screening of the core hole will, nevertheless, take place before the Auger process occurs. For conjugated carbon compounds, $\gamma \approx 0.1$ eV,[26] i.e., $\gamma \sim W/2$, placing this system in an intermediate regime.

If one neglects the effects of the hopping on the energies, neglects all Coulomb integrals except U and U_c, and

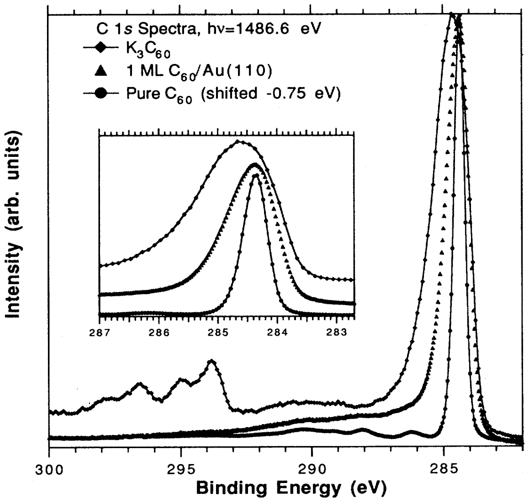

FIG. 3. Comparison of C 1*s* spectra for C_{60}, one monolayer of C_{60} on Au(110) with a resolution of $\sim$0.3 eV (Ref. 19), and K_3C_{60}. Note that the intramolecular shake-up features of pure C_{60} are preserved but broadened for the monolayer. This suggests that the very broad structure for K_3C_{60} in the same energy range is due to similar excitations, smeared by chemical shifts and modified by the fact that the t_{1u} orbital is now half filled.

assumes total charge transfer from K to C_{60}, i.e., no K-induced orbital hybridization,[24] one can envision the following possibilities: (i) intermolecular screening of the core hole does not take place, in which case $\Delta E = U$; (ii) intermolecular screening of the core hole does not take place, but in the Auger process an electron is transferred to the LUMO from a nearest neighbor, thus effectively removing one hole in the final state to a nearest neighbor and yielding $\Delta E = 0$; (iii) intermolecular screening does not take place in the XPS process, but does occur before the Auger decay, so that $\Delta E = U_c - U$; (iv) intermolecular screening takes place in the XPS process, in which case $\Delta E = 0$. Since the core hole is more localized than the LUMO and will effectively localize screening charge to itself, one may expect that $U_c > U$, in agreement with a recent determination of $U_c = 2.2 \pm 0.2$ eV.[27] All of the arguments above rely on one's ability to accurately choose the location of the C 1*s* line. Because U as used here should have a similar value for all x,[28] $\Delta E > 0$ would imply that mechanism (iii) plays a large role, hence we expect a large contribution from a C 1*s* satellite $U_c - U$ below a fully relaxed line component, if the latter exists with significant intensity. If other sources of shake-up, e.g., electron-hole pairs[29] or plasmons[30] obscure this reference due to different coupling at chemically different C-atom sites, of which there are three in K_3C_{60}, cases (ii)–(iv) become more difficult to unravel. Furthermore, we must assume there are no significant differences between the coupling to phonons and plasmons for the C 1*s* and t_{1u} levels.

With these considerations in mind, in Fig. 4 we compare the Auger to the valence PES self-convolution for all three phases. We have subtracted a polynomial from each curve, corresponding to the large, broad structure in the data, to emphasize the fine structure corresponding to particular two-hole states, in the manner of Lof *et al.*[13] To put the Auger spectrum on the proper two-hole binding-energy scale, we have subtracted the binding energy of the C 1*s* line, taken to be located at the center of the line, from the Auger kinetic energy. We have discussed the case of pure C_{60} in detail elsewhere,[31] and shown there that a PES self-convolution gives a semiquantitative description of the Auger spectrum. This indicates correlation effects are comparable for all molecular orbitals, and do not vary strongly at different length scales within a molecule, consistent with calculations.[32] The exception for pure C_{60} is a peak at about 3.3 eV, which is probably due to the decay of shake-up states from the initial core ionization, as observed in smaller molecules.[33] It is also clear from the inset of Fig. 2 that the Auger spectrum for K_3C_{60} shows noticeable structures in the raw data, which can be directly associated with those in Fig. 4.

Lof *et al.* have made extensive efforts to show that for pure C_{60} the shift ΔE between the Auger and self-convoluted valence-photoelectron spectra is the Coulomb interaction of two holes, equivalent to the Hubbard U.[13] In our prior work,[31] we gave a value of 1.1 ± 0.2 eV for U, which we now believe to be an underestimate based on newer data. The value indicated in Fig. 4, which we now report, 1.4 ± 0.2 eV, is 0.2 eV smaller than that of Lof *et al.*[13] but within experimental uncertainties. Thus we confirm their result. However, due to the low mean free path in electron spectroscopy, the experimental value of U we obtain is larger than that characteristic of a molecule in the bulk because of the less efficient screening[13,31,34] at the surface. A self-consistent model calculation, assuming that only surface molecules are probed in the experiments, indicates a difference ~0.3 eV. A similar correction has been found empirically for anthracene.[35] With this correction, our results are in good agreement with recent theoretical work.[34]

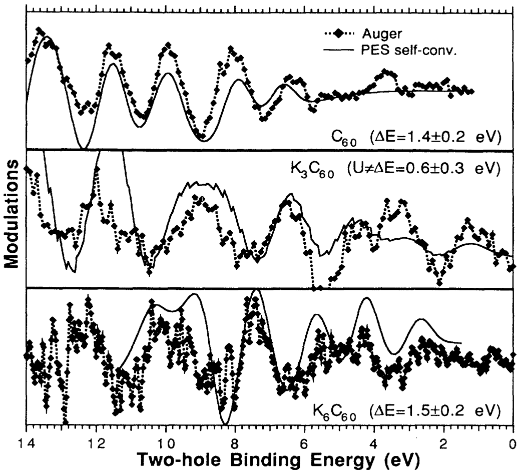

FIG. 4. Auger spectra and self-convoluted valence spectra, with smooth polynomial subtracted to emphasize modulation structure, as a function of K content. Binding energies for the Auger spectra correspond to kinetic energy with the C 1*s* binding energy subtracted, to put the spectrometer Fermi level at 0. Energy shifts indicated correspond for pure C_{60} to the Hubbard U, as shown by Lof *et al.*, and thus for K_6C_{60} as well (Ref. 13). For K_3C_{60} we conclude that the shift is less than U, as discussed in the text.

For K_3C_{60} the agreement between the Auger and self-convoluted valence-spectral modulations is also quite good, using $\Delta E = 0.6 \pm 0.3$ eV. This result is independent of which of the valence spectra we choose from Fig. 2, and implies that case (iii) described above is appropriate. We reiterate that the value of ΔE depends on our choice of the energy of the C 1*s* line. The fully relaxed line is 0.6 ± 0.3 eV to lower binding energy than the center. If the satellite dominates, $\Delta E = U_c - U$. However, if the intensities of the fully relaxed and satellite components are comparable, $\Delta E < U_c - U$. The fact that the spectral weight in the Auger is distributed similarly to that in the PES self-convolution, e.g., that the structures line up well and that no structures differ qualitatively between the two, suggests that there cannot be comparable weights for the differently screened components, and since $U_c - U \approx \Delta E$ the data are most compatible with the former scenario. It is important to note that a (defect-) doped Mott-Hubbard insulator, with a finite density of free carriers, would be expected to yield satellite and Auger spectral contributions with $\Delta E = U_c$ and/or $\Delta E = 0$ as well. Since no C 1*s* spectra for K_3C_{60} published to date show a satellite ~1.5 eV above the main line, and there is very little weight in the Auger spectra at threshold, defects appear to play a minor role in the screening of core holes in K_3C_{60}. A *small* contribution from cases (ii) and (iv) *is* compatible with our results. All of the above considerations taken in concert suggest that a screening electron is transferred between molecules with probability less than 1, much as for physisorbates,[22,23] but occurs rapidly on the scale of the core-hole lifetime, h/γ. In essence, therefore, one could most easily explain our results in terms of intrinsic, weak electronic coupling between the fulleride cages in K_3C_{60}. The removal of the intramolecular gap appears to play a pivotal role in this difference with the other two known insulating compounds.

Our result should be unaffected by contamination from small amounts of other phases, based on the agreement between our PES spectrum and that of other groups[9,11] and the lack of depth dependence in PES indicated in Fig. 2. Further evidence of a unique compositional assignment for the K_3C_{60} Auger spectrum comes from the Auger spectra themselves. For pure C_{60}, the kinetic energies of the first Auger structures are too high in binding energy to interfere with the near-threshold region of K_3C_{60}, and the structures do not agree in relative position and width. Notably, there is a strong resemblance for both the Auger and PES self-convolution of K_6C_{60} when compared to their counterparts for K_3C_{60}. This is in accord with the expectation[25] and observation[8,36] that the major differences in the electronic structure of these phases in the ground state are the extent of occupation of the t_{1u} band, and the absence or presence of a small gap. However, the shift needed to align Auger and PES self-convolution is different by 1 eV for the two cases. Moreover, the kinetic energies of the Auger spectra for the two phases differ by more than this amount. Thus, we can rule out a significant contaminant phase contribution to our result for ΔE in K_3C_{60}. The difficult problem that remains is that at good resolution no strong features in the data exist to show clearly, e.g., the positions of satellite and fully relaxed core-hole states. It is possible that broadening due to site variations represents an insurmountable barrier in this regard; certainty, higher resolution measurements with tighter photon-energy calibration would reduce the presently large error bars, which may be vital to completely unravel what may be a borderline correlated system.

To summarize, we confirm earlier results for the value of U in pure C_{60}, $U \approx 1.5$ eV, and find that this also holds true for the fully K-doped insulator, K_6C_{60}. For K_3C_{60} the energy obtained in the same way is 0.6 ± 0.3 eV, which we ascribe to the activation of a weak intermolecular screening. Thus, we tentatively attribute this value to the difference between core-valence and valence-valence correlation energies, $U_c - U$, with U of the same magnitude as for the phases at $x = 0$ and 6.

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