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Electronic structure of potassium-doped La@C_{82} metallofullerene studied with photoelectron spectroscopy

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The electronic structure of potassium-doped La@C_{82} has been studied with synchrotron-radiation photoelectron spectroscopy. Ultraviolet photoemission measurements indicate evolution of the valence-band states of La@C_{82} with increasing potassium content, but K_xLa@C_{82} remains semiconducting for all x between 0 and 6, with a band gap of at least 0.4 eV, in contrast to K-doped C_{60}. The valence-band features, including those which arise from the interactions of C_{82} cages with La and K, show oscillatory behavior of photoemission intensity with incident photon energy. The strength of the oscillations varies between the states, and we associate diminished oscillations with increased localization of electron density. Finally, although core and valence states of La@C_{82} change considerably with potassium dosage, the encapsulated La atom is well shielded from the outside chemical environment and its valency remains close to 3+.

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I. INTRODUCTION

An attractive property of fullerenes is their ability to be electron doped in a variety of ways, allowing the opportunity to engineer their electronic and physical properties. Such properties are of vital importance when considering their use in nanoelectronic applications. Previous studies of alkali-metal-doped C_{60} have shown the remarkable nature of its electronic structure, in which a full range of electronic properties from insulator to superconductor has been demonstrated.[1,2] When C_{60} is doped with potassium there is electron transfer from the metal to the molecule and occupation of the C_{60} lowest unoccupied molecular orbital (LUMO) is observed in photoemission experiments.[2,3] The electronic structure of K_xC_{60} compounds can be described in a charge-transfer picture where the LUMO of C_{60} is gradually filled as the doping level x increases from 0 to 6. Another type of doping is by means of encapsulation of one or more atoms in the fullerene cage, providing a new class of endohedral fullerenes. Nowadays, endohedral forms of the majority of lanthanide metals have been successfully produced and their properties and applications have been gradually realized. Photoemission work on lanthanide monometallofullerenes such as La@C_{82} and Ce@C_{82} has revealed a charge state close to 3+ for the encapsulated metal atom.[4–6] However, resonant photoemission measurements revealed a more detailed picture of the metal-cage interaction in endohedral fullerenes, which involves strong hybridization between the metal valence states and the molecular orbitals of the cage in addition to the charge transfer.[7]

Endohedral metallofullerenes can have a multitude of unique properties and phenomena associated with the charge-transfer interaction between the encaged metal atom and the carbon cage. Alkali intercalation of endohedral fullerenes is important for exploring new phases of fullerenes exhibiting novel electronic and transport properties. The potassium intercalation of metal-encapsulated fullerenes has so far been explored by our group on Y@C_{82} (Ref. 8) and Pichler *et al.* on Tm@C_{82} (Ref. 9). In both cases, photoemission spectroscopy reveals new spectral features near the Fermi level, which were attributed to charge transfer from potassium atoms to the unoccupied states of the carbon cage. The possibility of tuning the electronic properties of endohedral fullerenes in a similar manner to those of the bulk fullerite crystal has important implications for the study of molecular conductors. Our scanning tunneling microscopy (STM) studies of pristine La@C_{82} films have shown close-packed layers of molecules.[5] Stacking such planes will result in interstitial sites similar to those in solid C_{60}. A fundamental question to address, however, is to what extent the endohedral fullerene-potassium atoms interaction modifies the electronic properties of the molecule and the electronic state of the encapsulated metal atom. More specifically, is the same wide range of doping behavior (insulating, metallic, and superconducting) that is observed for fullerite possible for La@C_{82}? In this paper we have investigated this issue by examining the electronic structure of La@C_{82} and its encapsulated atom, through a combined photoemission spectroscopy and doping study of the fullerene. The results show that the electronic properties of K-doped La@C_{82} differ dramatically from K-doped fullerite and that the compound K_xLa@C_{82} remains semiconducting for all x between 0 and 6.

II. EXPERIMENTAL DETAILS

The experiments were carried out on beamline 4.1 of the Synchrotron Radiation Source (SRS), Daresbury Laboratory, using a standard UHV chamber equipped with a Scienta SES200 hemispherical electron analyzer (angular acceptance of ±5°). The Ag(111) crystal was prepared by argon-ion sputtering and annealing cycles at approximately 420 °C, until no impurities could be detected by photoemission. La@C_{82} (purity $>99.9\%$) was prepared and purified as described elsewhere and stored in a carbon disulphide (CS_2) solution.[10] The molecule has been previously characterized by x-ray diffraction and found to possess C_{2v} symmetry.[11] The CS_2 was allowed to evaporate in a tantalum crucible under ambient conditions before being transferred to the UHV system. Multilayer films were prepared by sublimation of purified La@C_{82} at 560 °C, while the Ag substrate was kept at 180 °C. During the fullerene evaporation the pressure in the main chamber rose from 1×10^{-10} to 4×10^{-8} mbar. Potassium was then deposited from a well-degassed SAES getter source with the fullerene film kept at 200 °C, which enables equilibrium compositions of K-doped fullerene phases. Photoemission spectra were acquired with the electron analyzer using synchrotron radiation for valence-band [ultraviolet photoemission spectroscopy (UPS)] spectra and Mg $K\alpha$ x-rays from a conventional x-ray gun for core-level [x-ray photoemission spectroscopy (XPS)] spectra. XPS surveys of the film, before and during measurements, show signals of C, La, and K elements and no other impurities. To quantify the surface stoichiometry, we used the relative intensities of the C 1*s* and K 2*p* peaks, taking into account the appropriate photoemission cross sections of these states.[12] All UPS spectra presented here were taken at normal emission and with the incoming light at 45° with respect to the surface normal.

III. RESULTS AND DISCUSSION

Analogous to alkali fullerides, C_{82}-based endofullerenes doped with an alkali metal can adopt a variety of intercalant-host-type structures,[9,13] in which an alkali-metal atom can occupy either octahedral or tetrahedral site (the interstitial sites have hard-sphere radii of 2.4 and 1.3 Å, respectively, based on a La@C_{82} radius of 5.7 Å, while the radius of a potassium ion is 1.33 Å). When studying K-doped La@C_{82} systems, it is of great concern whether the potassium atoms deposited onto the fullerene film diffuse into the film and form a uniform composition. It is possible that the deposited potassium remains largely at the film surface and its content decreases with depth. We have examined several films of K_xLa@C_{82} ($0<x<6$), which were prepared by depositing a potassium layer over the La@C_{82} film kept at 200 °C and subsequently annealed at elevated temperatures up to 320 °C. Annealing has been used commonly to achieve superconducting K-doped fullerite by accelerating the migration of potassium into the film as well as evaporating any excess potassium condensed at the film surface.[1,14] We have acquired the C 1*s*, K 2*p*, and the valence-band spectra of K-doped La@C_{82} prior and during annealing; examination of the spectra reveals no significant spectral changes upon annealing. This suggests that potassium atoms diffuse and react quickly with the La@C_{82} film at 200 °C. Another issue is the surface sensitivity of photoelectron spectra which is a well-known problem in studies of K-doped fullerenes. Due to the large sizes of fullerenes, one would expect signals from the surface layer to dominate any photoemission spectra. Schiessling *et al.*[15] reported angle dependences of photoelectron spectra of single-crystal K_3C_{60} and pointed out bulk and surface components in the spectra, while others reported little differences between bulk and surface electronic structures for K-doped C_{60} as measured by varying the incident photon energy.[16] As our samples were prepared at 200 °C where potassium ions are known to have high mobility,[17] one would expect the ions to sit far apart and be uniformly distributed throughout the film due to electrostatic interactions. Therefore, the as-prepared K-doped La@C_{82} films are believed to be significantly uniform and that, although our XPS and UPS measurements have different sampling depths (approximately 3 nm and 5 nm, respectively[15]), they are probing the same K_xLa@C_{82} film composition.

A. Comparison with La@C_{82} and C_{84}

Figure 1(a) shows the evolution of the valence-band spectra for La@C_{82} as a function of potassium intercalation together with the analogous spectrum of empty fullerene C_{84}, which has been previously shown to exhibit a similar valence-band spectrum as that of C_{82}.[14] These spectra were measured using a photon energy $h\nu=35$ eV. The largest differences between the valence-band spectra of La@C_{82} and C_{84} are found in the highest occupied levels. The spectral features of the pristine La@C_{82} valence-band are in good agreement with previous studies[4,5] and display the characteristic features of higher metallofullerenes at binding energies of 1.6 (labeled A'), 2.1 (A), and 3.2 eV (B). These features arise from states associated with Cπ bonding. The small feature close to the Fermi level, located at 0.9 eV and completely absent in the C_{84} spectrum, has been identified as a singly occupied molecular orbital (SOMO) of Cπ origin.[4] The encapsulated La ($5d^16s^2$) atom donates almost three valence electrons to the C_{82} cage to form the endohedral complex, which has the electronic structure of $La^{3+}@C_{82}{}^{3-}$. Two electrons are transferred to the C_{82} LUMO, while the remaining electron gives rise to the SOMO peak. In comparison with its empty fullerene counterpart, La@C_{82} displays a broad highest occupied (HOMO) band, consisting of two substructures (peaks A and A'). This splitting of the HOMO state results from interaction with the encapsulated La ion.[4] The spectral onsets of La@C_{82} and C_{84} are 0.4 and 1.1 eV below the Fermi level, respectively, indicating the semiconducting nature of both fullerenes. There are significant dif-

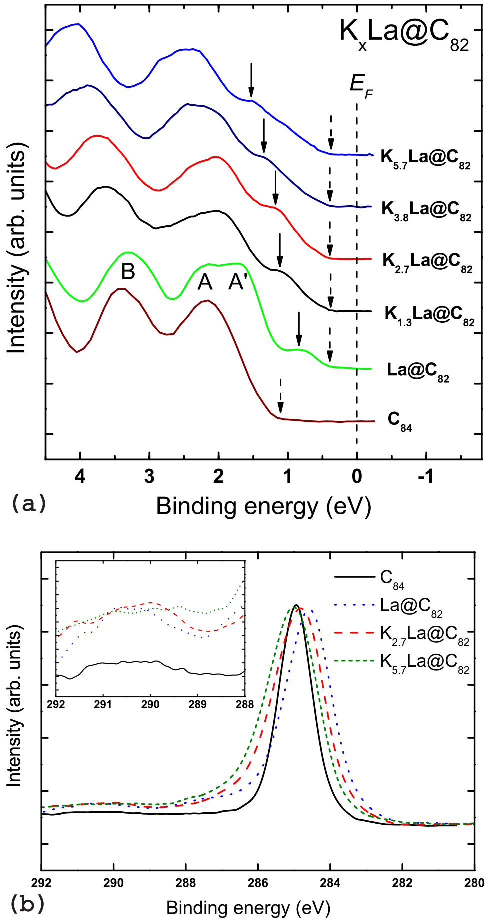

FIG. 1. (Color online) (a) Valence-band spectra of $K_xLa@C_{82}$ at several stages of potassium intercalation with the analogous spectrum of the empty fullerene C_{84} shown for comparison. The spectra were recorded using a photon energy $h\nu=35$ eV. The solid and dashed arrows indicate the SOMO structure and the onset of the spectra, respectively. (b) C 1*s* core-level spectra, taken using Mg $K\alpha$ x rays. Inset shows an enlarged view of the shake-up structures on the high-binding-energy side. The reduction in intensity and broadening of the shake-up feature upon the potassium intercalation of $La@C_{82}$ are apparent.

ferences in the overall shape of the valence-band spectra of $La@C_{82}$ and C_{84}. This is due to structural and isomeric differences between $La@C_{82}$ and C_{84} (C_{84} is a mixture of two most abundant isomers with D_2 and D_{2d} symmetry[18]).

Upon potassium intercalation, significant spectral changes occur as the potassium content x in the formula $K_xLa@C_{82}$ [indicated beside each spectrum in Fig. 1(a)] increases from 0 (pristine $La@C_{82}$) to 5.7 (near saturation). The spectra shown for various stages of intercalation are representative of the valence band of $K_xLa@C_{82}$ for $0<x<6$. At the first stage of doping ($K_{1.3}La@C_{82}$), the SOMO grows in intensity and shifts its position to a higher binding energy by 0.35 eV, while peaks A and A' of the HOMO structure broaden and merge to form a large single peak. The splitting of the HOMO state is not observed again at any stage of doping. In the spectrum of $K_{2.7}La@C_{82}$, the HOMO and peak B broaden and shift their positions farther away from the Fermi level E_F from the previous positions of $x=1.3$, and this trend continues with further intercalation. The shoulder S increases in intensity with increasing dose as a result of the occupation of the state associated with the SOMO of $La@C_{82}$ by the K 4*s* electrons. At all stages of doping the valence-band features of $La@C_{82}$ are noticeable, suggesting that the molecule does not disintegrate upon potassium intercalation. (The shake-up structure of the C 1*s* spectra remains clearly visible, although with a reduced intensity, for potassium intercalated $La@C_{82}$ [see Fig. 1(b)] supports this suggestion.) Careful inspection of the region near E_F reveals no density of states at the Fermi level and the spectral onset, indicated by a dashed arrow above each $K_xLa@C_{82}$ spectrum, remains at 0.4 eV for all x values, within the experimental uncertainty. This is in stark contrast with K-doped fullerite, in which a new LUMO-derived band appears and crosses the Fermi level for x equal or close to 3.[15] A significant feature to note is that the states that are shifted upon potassium intercalation behave in a rigid-band-like fashion: the separation between the SOMO and HOMO of $La@C_{82}$ is virtually unchanged within our resolution at 0.8 eV for all compositions other than $x=0$.

Analysis of the C 1*s* line of $K_xLa@C_{82}$ can provide useful information to explain the behavior of the valence band upon potassium intercalation. Figure 1(b) compares the C 1*s* spectra of C_{84} and $K_xLa@C_{82}$, which all exhibit a main peak and a broad satellite structure centered at about 6 eV above the main line. Both C_{84} and $La@C_{82}$ display symmetrical peaks, with a full width at half maximum (FWHM) measured at 0.96 and 1.32 eV, respectively. These peaks represent the envelope for the multitude of small differences in C 1*s* binding energies caused by the presence of the endohedral atom as well as inequivalent carbon sites in C_{82} and C_{84} (there are at least three inequivalent carbon sites in C_{82} and higher fullerenes.[19]) The C 1*s* line shape of $La@C_{82}$ only changes slightly upon doping. There is an increase in the background on the high-binding-energy side of the main line, resulting from inelastic scattering of photoelectrons due to intercalated potassium atoms. For pristine $La@C_{82}$ the C 1*s* line is centered at a binding energy of 284.6 eV, compared to 285.0 eV for C_{84}. Upon potassium intercalation, the FWHM of the C 1*s* line increases slightly to 1.40 eV for $x=2.7$, but hardly changes with further intercalation. The broadening of the C 1*s* main line at the first stage of intercalation is probably due to locally different carbon sites when the molecule is ionically bound to the potassium atoms (discussed further below). We also note that the peak of $K_xLa@C_{82}$ remains almost symmetrical at all stages of doping, similar to the case of C_{70},[20] but in contrast to C_{60}.[21] The general lack of broadening of the C 1*s* line or asymmetrical line shape can be rationalized as being due to the excellent intramolecular screening afforded by fullerenes,[22] which is apparently sufficient to reduce small potential differences due to the presence of potassium ions. In addition, and most importantly, unlike potassium intercalation of C_{60}, the C 1*s* peak position progressively shifts to a higher binding energy with increasing doping from 284.6 eV for pristine $La@C_{82}$ to 284.9 eV for $K_{5.7}La@C_{82}$. The C 1*s* shift to a higher binding energy upon potassium intercalation has been previously observed in K-doped $Y@C_{82}$ (Ref. 8) and $Sc_3N@C_{82}$ (Ref. 23). While the fairly strong shift of the SOMO peak of $La@C_{82}$ is a result of the rearrangement of electrons in the valence states, the coincidence of the valence and C 1*s* shifts to higher binding energies might appear anomalous as carbon atoms should become more negatively charged with doping level. A natural explanation is the proximity of carbon atoms to the potassium positive ions, resulting in an increase in binding energy from the Madelung potential. For K-doped La@C_{82} the Madelung potential could be larger than the potential induced by the negative charge on carbon atoms because the latter charge is partially delocalized on the fullerene cage (discussed further in Sec. III B) and on average rather distant from an individual carbon atom, while the potassium ions have a strongly localized positive charge and would be in close proximity to the cage surface. It is possible that screening of the electronic response of the molecule plays a role for changes in the C 1*s* line shape. However, given the fact that K_xLa@C_{82} remains semiconducting for all x between 0 and 6, in stark contrast with K-doped C_{60} which becomes metallic for x equal or close to 3, the extra screening effect due to potassium intercalation is likely to be small. This behavior is similar to that observed on potassium absorption on graphite,[24] but in contrast with the strong intermolecular screening in K_3C_{60}.[16]

As the symmetry of both C_{84} and La@C_{82} is considerably lower than that of C_{60}, the satellites of the C 1*s* spectra do not exhibit clear interband transition features. The only distinct peak that can be seen is the shake-up structure [shown in the inset of Fig. 1(b)], centered at about 6 eV above the C 1*s* main line. This feature is normally associated with the creation of a collective π electron plasmon. Upon potassium intercalation of La@C_{82}, the shake-up feature loses intensity and broadens, implying that there is screening of the collective electronic response of the molecule. As the shake-up feature reflects the final states in photoemission—i.e., the molecule left in an excited state—the widening of the shake-up feature also indicates a distortion of the carbon cage when the molecule is ionically bound to the potassium atoms.

Core-level photoemission can provide information on the chemical state of the encapsulated atom. Monitoring the La 3*d* spectrum can provide an indication of any changes in the electronic state of the encapsulated atom since any sign of mixed electronic states will be manifested in changes of the La 3*d* line shape. Furthermore, if there is any change in the valency of the lanthanum atom (towards La^{2+}), it will cause a clear shift in the 3*d* photoemission spectrum.[25] Figure 2 compares the La 3*d* core-level spectra of pristine La@C_{82} and the nearly-saturation-doped $K_{5.7}$La@C_{82}. To allow for a better comparison, the spectra had a linear background subtracted and were normalized to the overall peak intensities. Both spectra comprise $3d_{3/2}$-$3d_{5/2}$ spin-orbit doublets. The overall La 3*d* line shape is very similar to that of lanthanum tri-iodide,[25] with a weak shoulder on the low-binding-energy side of each peak—i.e., representative of a lanthanum atom of charge state close to 3+. Comparison of the two spectra clearly illustrates that there are only subtle changes following the potassium intercalation. The spectra are well aligned in the peak positions as well as the slope of the low-binding-energy side of each peak. Despite the formation of strong ionic bonds with nearly six potassium atoms and changes in the molecular electronic state as evidenced by the valence spectra, there is clearly no evidence of La 3*d* binding energy shifts or spectral broadening. The results are consistent with a recent x-ray absorption study of Ce@C_{82},[6] which found the absorption spectrum of cerium remains unchanged when the molecule covalently bonds to a silicon surface. This is remarkable, since it demonstrates that the encapsulated atom remains impervious to dramatic changes in molecular chemical environment. The results clearly highlight the high degree of shielding offered by the C_{82} cage to the lanthanum atom and support the concept of a "superatom,"[10] in which the electronic state of the M atom in M@C_{82} is little changed even when the molecule accepts up to six electrons.

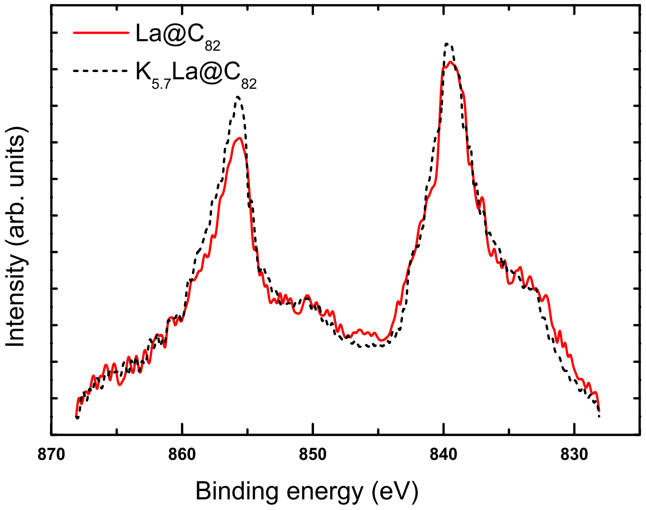

FIG. 2. (Color online) Core-level photoemission spectra of the La 3*d* from La@C_{82} and $K_{5.7}$La@C_{82}. Both spectra were normalized to the integrated intensities after subtraction of a linear background. No binding energy shift associated with K doping are observed.

B. Incident photon energy dependence

Because of the near-spherical shape of a fullerene molecule, the electronic eigenstates may be considered in terms of spherical harmonics and described by angular quantum numbers l.[26] As C_{82} contains 82 electrons involved in shallow-lying π-bonding energy levels, the state with $l=5$ is fully occupied by 22 electrons while the $l=6$ state is partially filled with 10 electrons. The electrons in the $l=6$ state contribute to form the HOMO, and those in the $l=5$ state are responsible for the next-HOMO (NHOMO); thus, a ratio of photoemission intensities, HOMO/NHOMO, is expected to be 5:11 if the photoionization cross sections of these states were identical. However, strong oscillations of the photoemission intensities with incident photon energy have been previously observed in C_{82}.[14] This interesting phenomenon, also found in other fullerenes,[8,27] has been attributed to intramolecular interference effects.[28,29] A few different models have been formulated to explain the phenomenon by considering the photoemission initial and final states. In the initial-state model[29] the oscillations arise from interference of a spherically symmetrical wave emitting from the molecule, while for the final-state model[28] scattering of photoelectrons from a shell of atoms produces a spherical standing wave. However, although the *ab initio* calculation results by Hasegawa *et al.*[28] rely on the approximation of a simplified spherical-shell-like initial state, the intensity modulations of the valence-band states were still obtained. This indicates that the oscillation is not genuinely related to the exact nature of the photoelectron initial state, but to the scattering of photoelectrons out of the unique near-spherical structure of fullerenes. The *ab initio* calculation results were subsequently confirmed by experimental data.[30,31] Since the oscillations arise from the distribution of electron density over a spherical shell with a relatively large radius,[28] one may therefore expect electronic states which are strongly localized to show weaker oscillations than those which extend across the cage. In this section, we investigate the photon-energy-dependent changes in the valence band of La@C_{82} and K-doped La@C_{82} with the aim to further elucidate metal-endofullerene interactions. It is known that doping of C_{60} with potassium leads to the formation of distinct phases. For a film with an average stoichiometry of K_xC_{60} and $0<x<6$, the film generally consists of phase-separated regions of distinct phases of C_{60}, K_3C_{60} and K_6C_{60} at 300 K.[21] A similar behavior of phase separation has been observed for potassium intercalation of C_{70} (Ref. 20) and Tm@C_{82} (Ref. 9). However, at 300 K and x approximately 1, there exists a stable phase of KC_{60}, in which only the octahedral site is occupied.[20] In light of this behavior in K-doped fullerenes and to avoid differences in valence-band photoemission from phase-separated regions, we investigated the potassium-endohedral fullerene interaction by focusing on the electronic structure of a $K_{1.1}$La@C_{82} film, which is expected to consist dominantly of the K_1La@C_{82} phase.

Figure 3 illustrates the variations of the valence band spectra of La@C_{82} and $K_{1.1}$La@C_{82} measured using photons with different energies. The oscillations of the relative intensities of the low-binding-energy features are clearly discernible. Dashed lines indicate the approximate positions of valence-band features, which deviate slightly as the incident photon energy is varied because of oscillatory intensities and a slight overlap of the peaks. As discussed above, the spectral features predominantly reflect emission from carbon-derived states: the Cπ-derived states are organized in three bands A-C and the Cσ orbitals are located above 6 eV binding energy, appearing in peak D. Comparison of the valence-band spectra for La@C_{82} and $K_{1.1}$La@C_{82} reveals that the structures are almost identical in the leading 8 eV of the valence band, but the whole spectra of $K_{1.1}$La@C_{82} shift away from the Fermi level by 0.3 eV. The shoulder S has a higher intensity in $K_{1.1}$La@C_{82}, which is a result of about one electron being transferred to the SOMO level of La@C_{82}. The spectra of $K_{1.1}$La@C_{82} show less sharp features than those of La@C_{82}, probably due to the superposition of valence bands from phases other than K_1La@C_{82}, even though the contribution from these phases should be small.

It is clearly seen in Fig. 3 that the low-binding-energy features oscillate in intensity with photon energy. Figure 4 shows variations in the intensities (measured by peak heights) of the features B, A, A', and S, which have been normalized to the sum of the B, A, and A' intensities. The reason for this normalization scheme is to highlight the peaks which exhibit strong intensity oscillations, since the sum of intensities will not vary in relative intensity as strongly as any individual peak. This is particularly true because the HOMO (A) and next-HOMO (B) states should exhibit essentially antiphase oscillations.[28] The states B, A, and A' coincide for La@C_{82} and $K_{1.1}$La@C_{82} over the entire photon energy range, indicating that the symmetry and electron occupation of these electronic states are unaffected by potassium doping. The S intensity of $K_{1.1}$La@C_{82} is approximately twice that of La@C_{82} due to the transfer of an additional electron to the SOMO level from the potassium atom. Interestingly, La@C_{82} and $K_{1.1}$La@C_{82} display similar periodic variations for the states B and A', with the maxima and minima occurring at the same energy positions, which proves that the molecule does not change shape or size upon

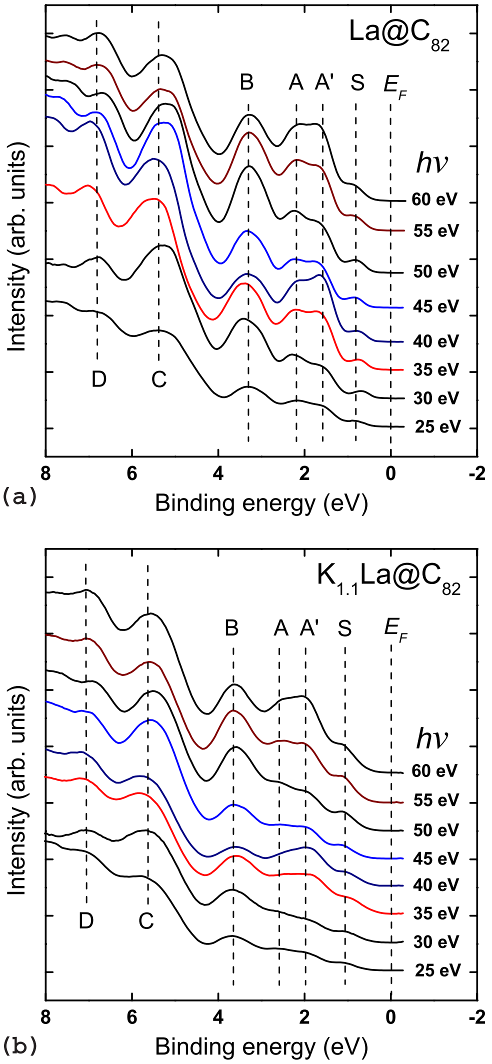

FIG. 3. (Color online) Valence-band spectra of (a) La@C_{82} and (b) $K_{1.1}$La@C_{82} acquired at different photon excitation energies in the range $h\nu = 25-60$ eV. There are seven identifiable features within the leading 8 eV range of the spectra (labeled S and $A-D$).

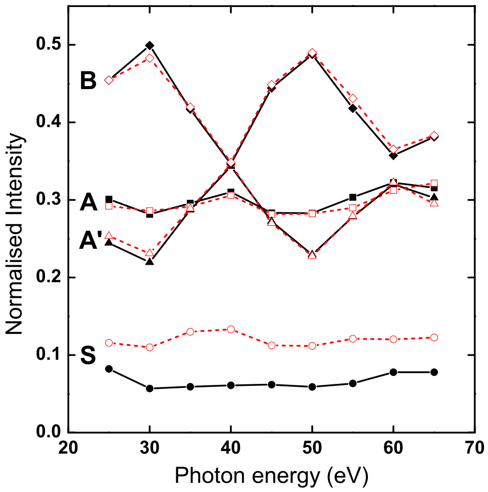

FIG. 4. (Color online) Variations in the intensities of the valence-band features *S* (circles), *A′* (triangles), *A* (squares), and *B* (diamonds) for La@C_{82} (solid symbols) and $K_{1.1}$La@C_{82} (open symbols) as a function of photon energy. All the intensities have been normalized to the sum of the *A′*, *A*, and *B* intensities. The solid and dashed lines are intended as guides to the eyes.

potassium doping. The mean value of the normalized intensity of peak *A* over the photon energy range is approximately equal to that of peak *A′*, suggesting that the *A* and *A′* states contain six electrons each.

The most remarkable observation is that states *A* and *S* clearly show reduced intensity oscillations in comparison to *A′*. It is impossible to say that their intensities do not oscillate since the intensities are normalized to a sum which itself is probably oscillatory. However, it is clear from the arguments given above that the states *A* and *S* must be more localized than the state *A′*. We rationalize this observation as follows: The interaction of La with the cage removes the degeneracy of the C_{82} HOMO state through the overlap between the cage and La orbitals. The bonding combinations will have lower energy, giving rise to the *A* state of La@C_{82}, and the electron density in these orbitals will be increased in the region of overlap. This represents a localization of electron density, and one should therefore expect a reduced intensity oscillation for peak *A*. The *A′* state is either nonbonding or antibonding, and the distribution of electron intensity across the majority of the cage is consequently unperturbed; thus, an oscillatory intensity is expected for this state. The weak oscillations of the *S* state also indicate localization. This appears to be at odds with density-functional theory calculations of La@C_{82},[32] which show that the electron density associated with the SOMO is largely delocalized on the fullerene cage, but is fully consistent with the hybridization model proposed by Kessler *et al.*[7] in which a small electron density is left in the La 5*d* orbital. This small amount of localization results in significantly reduced photon-energy dependence for photoionization and suggests that this experiment is a very sensitive probe of electron delocalization for fullerene systems.

IV. CONCLUSION

In conclusion, we have performed a complete photoemission study of K-doped La@C_{82}. UPS reveals that K_xLa@C_{82} is semiconducting for all *x* between 0 and 6, in contrast to K-doped C_{60}. Upon intercalation, the valence states of La@C_{82} broaden and shift to higher binding energies, while the state associated with the SOMO of La@C_{82} is gradually filled with electrons transferred from potassium atoms with increasing dosage but its spectral onset remains at 0.4 eV below the Fermi level. The valence-band states of K_xLa@C_{82} display variability in the strength of intensity oscillations with incident photon energy, which we associate with the electron density distribution across the cage. We argue from these results that the charge transferred from potassium is localized on the fullerene cage. The C 1*s* photoemission further testifies to the ionic bonding to the potassium atoms and distortion of the fullerene cage. The valence state of the encapsulated lanthanum has been probed by La 3*d* XPS in both pristine and nearly-saturation-doped forms; the results show that the atom remains “close to the 3+” valence state and is well screened from the outside chemical environment of its hosting cage.

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[1] A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez, and A. R. Kortan, Nature (London) **350**, 600 (1991).

[2] M. Merkel, M. Knupfer, M. S. Golden, J. Fink, R. Seemann, and R. L. Johnson, Phys. Rev. B **47**, 11470 (1993).

[3] R. Hesper, L. H. Tjeng, A. Heeres, and G. A. Sawatzky, Phys. Rev. B **62**, 16046 (2000).

[4] D. M. Poirier, M. Knupfer, J. H. Weaver, W. Andreoni, K. Laasonen, M. Parrinello, D. S. Bethune, K. Kikuchi, and Y. Achiba, Phys. Rev. B **49**, 17403 (1994).

[5] C. Ton-That, A. G. Shard, S. Egger, A. Taninaka, H. Shinohara, and M. E. Welland, Surf. Sci. **522**, L15 (2003).

[6] K. Schulte, L. Wang, P. J. Moriarty, J. Purton, S. Patel, H. Shinohara, M. Kanai, and T. J. S. Dennis, Phys. Rev. B **71**, 115437 (2005).

[7] B. Kessler, A. Bringer, S. Cramm, C. Schlebusch, W. Eberhardt, S. Suzuki, Y. Achiba, F. Esch, M. Barnaba, and D. Cocco, Phys.

Rev. Lett. **79**, 2289 (1997).

[8] C. Ton-That, A. G. Shard, V. R. Dhanak, H. Shinohara, J. S. Bendall, and M. E. Welland, Phys. Rev. B **73**, 205406 (2006).

[9] T. Pichler, J. Winter, C. Grazioli, M. S. Golden, M. Knupfer, P. Kuran, L. Dunsch, and J. Fink, Synth. Met. **103**, 2470 (1999).

[10] H. Shinohara, Rep. Prog. Phys. **63**, 843 (2000).

[11] E. Nishibori, M. Takata, M. Sakata, H. Tanaka, M. Hasegawa, and H. Shinohara, Chem. Phys. Lett. **330**, 497 (2000).

[12] J. J. Yeh and I. Lindau, At. Data Nucl. Data Tables **32**, 1 (1985).

[13] X. Liu, M. Krause, J. Wong, T. Pichler, L. Dunsch, and M. Knupfer, Phys. Rev. B **72**, 085407 (2005).

[14] S. Hino, K. Matsumoto, S. Hasegawa, K. Iwasaki, K. Yakushi, T. Morikawa, T. Takahashi, K. Seki, K. Kikuchi, S. Suzuki, I. Ikemoto, and Y. Achiba, Phys. Rev. B **48**, 8418 (1993).

[15] J. Schiessling, L. Kjeldgaard, T. Kaambre, I. Marenne, J. N. O'Shea, J. Schnadt, C. J. Glover, M. Nagasono, D. Nordlund, M. G. Garnier, L. Qian, J. E. Rubensson, P. Rudolf, N. Martensson, J. Nordgren, and P. A. Bruhwiler, Phys. Rev. B **71**, 165420 (2005).

[16] P. A. Bruhwiler, A. J. Maxwell, A. Nilsson, N. Martensson, and O. Gunnarsson, Phys. Rev. B **48**, 18296 (1993).

[17] Z. Y. Li, K. M. Hock, and R. E. Palmer, Phys. Rev. Lett. **67**, 1562 (1991).

[18] K. M. Allen, T. J. S. Dennis, M. J. Rosseinsky, and H. Shinohara, J. Am. Chem. Soc. **120**, 6681 (1998).

[19] A. Bassan, M. Nyberg, and Y. Luo, Phys. Rev. B **65**, 165402 (2002).

[20] M. Knupfer, D. M. Poirier, and J. H. Weaver, Phys. Rev. B **49**, 8464 (1994).

[21] D. M. Poirier, T. R. Ohno, G. H. Kroll, P. J. Benning, F. Stepniak, J. H. Weaver, L. P. F. Chibante, and R. E. Smalley, Phys. Rev. B **47**, 9870 (1993).

[22] E. Rotenberg, C. Enkvist, P. A. Bruhwiler, A. J. Maxwell, and N. Martensson, Phys. Rev. B **54**, R5279 (1996).

[23] L. Alvarez, T. Pichler, P. Georgi, T. Schwieger, H. Peisert, L. Dunsch, Z. Hu, M. Knupfer, J. Fink, P. Bressler, M. Mast, and M. S. Golden, Phys. Rev. B **66**, 035107 (2002).

[24] P. Bennich, C. Puglia, P. A. Bruhwiler, A. Nilsson, A. J. Maxwell, A. Sandell, N. Martensson, and P. Rudolf, Phys. Rev. B **59**, 8292 (1999).

[25] J. H. Weaver, Y. Chai, G. H. Kroll, C. Jin, T. R. Ohno, R. E. Haufler, T. Guo, J. M. Alford, J. Conceicao, L. P. F. Chibante, A. Jain, G. Palmer, and R. E. Smalley, Chem. Phys. Lett. **190**, 460 (1992).

[26] N. Troullier and J. L. Martins, Phys. Rev. B **46**, 1754 (1992).

[27] P. J. Benning, D. M. Poirier, N. Troullier, J. L. Martins, J. H. Weaver, R. E. Haufler, L. P. F. Chibante, and R. E. Smalley, Phys. Rev. B **44**, 1962 (1991).

[28] S. J. Hasegawa, T. Miyamae, K. Yakushi, K. Inokuchi, K. Seki, and N. Ueno, Phys. Rev. B **58**, 4927 (1998).

[29] Y. B. Xu, M. Q. Tan, and U. Becker, Phys. Rev. Lett. **76**, 3538 (1996).

[30] M. R. C. Hunt, T. Pichler, L. Siller, P. A. Bruhwiler, M. S. Golden, N. Tagmatarchis, K. Prassides, and P. Rudolf, Phys. Rev. B **66**, 193404 (2002).

[31] C. Ton-That, A. G. Shard, S. Egger, V. R. Dhanak, and M. E. Welland, Phys. Rev. B **67**, 155415 (2003).

[32] J. Lu, X. W. Zhang, X. G. Zhao, S. Nagase, and K. Kobayashi, Chem. Phys. Lett. **332**, 219 (2000).