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Bulk and surface charge states of K$_3$C$_{60}$

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I. INTRODUCTION

C$_{60}$ ions in condensed form have an important role in the understanding of high-temperature superconductivity. C$_{60}$-based salts with alkali metals (A) with stoichiometry A$_3$C$_{60}$ are well-known to superconduct at temperatures up to 42 K, exceeded only by the copper oxide-based materials.$^1$ The stoichiometrically neighboring compounds A$_2$C$_{60}$ are insulating, which is explained by the effects of electronic correlations, lattice symmetry, and vibronic coupling for these narrow-band systems.$^2$–$^6$ These are so-called “acceptor” compounds, in which each C$_{60}$ molecule is negatively charged as a result of virtually complete transfer of the alkali valence electrons.

A. Previous photoelectron spectroscopy studies of K$_3$C$_{60}$

K$_3$C$_{60}$ has become a primary testing ground for investigations of fulleride electronic structure, presumably because of the ease with which crystals could be prepared.$^7$–$^9$ Soon after the first studies$^7$–$^9$ establishing the existence of stable, composition-dependent phases and a metallic conduction band density-of-states (DOS) at an alkali stoichiometry of 3, however, questions regularly emerged over the complex line shapes measured using photoelectron spectroscopy (PES) for the metallic composition. It was immediately apparent that the narrow bands predicted theoretically$^{10}$ were not reflected in the spectra, which were quite broad. This conflict extended as well to the DOS at $E_F$, which was lower than found using other techniques, and in disagreement with the consensus models of superconductivity in the fullerenes.$^1$ The large size of C$_{60}$ and typical mean free path effects of electrons in condensed materials suggested right away that the presence of a surface compound could be at the root of this conflict.$^{11,12}$ Proposals there based on analysis of time-dependent doping of a pure C$_{60}$ film included the idea that the $t_{1u}$ band reflected mainly bulk properties, and that the $h_u$ and deeper bands were strongly affected by the emission from an insulating surface compound. Support for this was also found in the work functions of the samples, as compared to K$_n$C$_{60}$; the latter must have a complement of 3 K atoms per fulleride on the vacuum side of the surface fulleride layer, and has a lower work function than K$_1$C$_{60}$, consistent with a higher concentration of K on the surface.$^{12}$ At the same time, of the two phases, only K$_4$C$_{60}$ was found to be sensitive to impurities over times of the order of many hours, suggesting that K$_3$C$_{60}$ had no K layers exposed at the surface.$^{12}$ These experiments were performed on mixed-phase samples, however, and yielded at times complex, weak structures which were not duplicated by later workers.

The arguments in favor of a surface phase were countered by the lack of observation of a difference between bulk and surface electronic structure, as measured by varying the emission angle, and the degree of scattering of the electrons from subsurface layers,$^{13}$ although the existence of such angle dependencies had been asserted in the earlier work.$^{12}$ A second observation apparently favoring the similarity of bulk and surface compositions was the lack of strong photon energy dependence reported.$^{14}$ Since it was, moreover, possible to describe the broad conduction band line shape in terms of coupling to vibrations and plasmons,$^{13}$ a broad consensus along the lines of bulk-surface equivalence developed, with electron-electron correlations and electron-plasmon coupling implicated for the complex spectra observed.

After this initial group of publications, a method of quite reliably producing purified single-composition samples in vacuo for PES studies was reported.$^{15}$ It was applied to new studies of the PES of K$_3$C$_{60}$ first several years later.$^{16}$ There it was found that the line shape reported earlier$^{13,17}$ for the lowest unoccupied molecular orbital (LUMO)-derived conduction band was largely reproduced, albeit sharper for the more highly purified samples. No major angle dependence of the conduction band spectrum could be detected, supporting the earlier consensus view.$^{13,16}$ Later, similar arguments and a similar lack of visible surface effects in electron energy
loss spectra (EELS) of the same samples further strengthened this viewpoint.\textsuperscript{18}

B. Open questions on the PES of K\textsubscript{3}C\textsubscript{60}

While the lack of an observed difference between surface and subsurface (bulk) layers of K\textsubscript{3}C\textsubscript{60} can perhaps suffice to maintain that deduction as the consensus,\textsuperscript{13,14,16,18} there are a number of observations which are nontrivial to reconcile with this view, aside from those already discussed.\textsuperscript{11,12} We will list these in what follows as a critical review of the current state of the field of PES studies on the superconductor fulleride phases, which is necessary to understand how the present results unify a number of apparently conflicting interpretations of K\textsubscript{3}C\textsubscript{60} PES spectra. Readers not needing a detailed review may wish to skip to Sec. I C.

1. Temperature dependence

A strong temperature dependence in the data was detected quite early,\textsuperscript{13} which amounted to a washing-out of the DOS at $E_F$ at room temperature. No clear explanation for this was offered, but the correlation of the DOS at $E_F$ with the first portion of the highest occupied molecular orbital (HOMO)-derived band in this respect was noted.\textsuperscript{13} This observation was later duplicated and attributed to strong electron-electron correlations splitting the conduction band further than previously speculated, i.e., to a degree involving partial overlap with the HOMO-derived band.\textsuperscript{19} Given the different models of the valence spectra offered,\textsuperscript{13,19} the reason for the similar temperature-dependence of the strong portion of the LUMO-derived band with the weak portion of the HOMO-derived band remains an open question.

2. Charge-charge correlations and spectral widths

Possible roles of charge-charge correlations in the spectra have been discussed\textsuperscript{13,14,17} since the first spectral consequences were reported.\textsuperscript{14,20} The likelihood that they could be an important source of broadening, as opposed to vibrations and plasmons,\textsuperscript{13} has been implicated after the repeated observation of simpler (and narrower) spectra of K\textsubscript{3}C\textsubscript{60} monolayers adsorbed on silver substrates,\textsuperscript{21,22} thus supporting early arguments.\textsuperscript{20} This difference was thought to be connected to the added presence for a monolayer of substrate-derived image screening,\textsuperscript{23} which reduces the intramolecular charge-charge correlation energy $U$ by about half. It is not clear, however, why a reduction of the scale of correlations by a factor of about 2 should almost totally quench their broadening effects, which is implied by the fact that the spectra of the Ag-adsorbed monolayers strongly resemble those of pure C\textsubscript{60} and K\textsubscript{3}C\textsubscript{60} in width.\textsuperscript{14,21} In a model of dominant intramolecular correlations, one would expect a shift of spectral weight by the change in $U$,\textsuperscript{24,25} i.e., from about 1 eV from the main line to about 1/2 eV, which is not observed, as we reconsider in Sec. III E. In addition, the HOMO-derived band for doped monolayers has a sharp low-binding-energy onset,\textsuperscript{16,21} reminiscent of that of K\textsubscript{3}C\textsubscript{60} in keeping with the correlation of $E_F$ and this shoulder already noted above and in previous work.\textsuperscript{13,19} Perhaps the most important challenge to the idea of correlation satellites is, however, that they are not reflected similarly in the spectra of different bands; for the LUMO-derived band the low-binding-energy structure, or main line, is strongest, whereas in the remaining portion of the valence spectra and the C 1\textit{s} line the intensity of the higher-binding-energy structures, or ostensible satellites, is much greater than the main line, contrary to general expectations in such a picture.

3. K distribution at the surface

The C 1\textit{s} line of K\textsubscript{3}C\textsubscript{60} is one of the broadest measurable for an intact molecule.\textsuperscript{14,19,26} Since chemical shifts are well-known to affect core level binding energies,\textsuperscript{24} a natural explanation for such broadening is a distribution of C-atom sites. Such a distribution is established in the bulk of K\textsubscript{3}C\textsubscript{60} due to the Madelung potential exerted by the alkali ions, as well as the molecular charge distribution, which splits the degeneracy of the carbon atoms into three distinguishable sites with a ratio of 2:2:1. This was therefore adopted as an explanation of the splitting observed for the highly pure sample.\textsuperscript{26} Theoretically, however, the local charges differ only slightly, and the effects due to this are expected to be small.\textsuperscript{27} This would also require that 1.5 surface K ions per fulleride molecule adopt positions and exert fields consistent with the bulk structure, although the lack of further fulleride neighbors could be expected \textit{a priori} to induce them to approach the surface molecules more closely than in the bulk, and to exert stronger fields. This merely points out that the conditions for exactly a 2:2:1 ratio of C-atom sites are not trivially fulfilled at the surface with the given assumptions, whereas violations of the assumptions would not be surprising.

Further evidence that such a bulklike model must be re-examined comes from monolayer studies. Examining the C 1\textit{s} line in such cases,\textsuperscript{28–32} one generally finds much narrower lines, without an obvious, large substructure as for K\textsubscript{3}C\textsubscript{60}. In addition, no strongly-split, broad line has been reported for a K\textsubscript{3}C\textsubscript{60} monolayer supported on a metal substrate. These facts in themselves suggest that drastically different local chemical environments for different C atoms on a given molecule are not sufficient to explain such large chemical shifts in the bulk fulleride. On the other hand, the general lack of such shifts in verifiably asymmetric potentials can be rationalized\textsuperscript{31} as being due to the excellent intramolecular screening afforded by the fullerene,\textsuperscript{33,34} which apparently is sufficient to reduce such potential differences to small levels on the scale of the linewidth. The large width and obvious splitting\textsuperscript{26} of the C 1\textit{s} line of K\textsubscript{3}C\textsubscript{60} must therefore be considered an open question, more a challenge to the consensus model than a support.

4. Macroscopic electric fields and the possibility of a half-valence compound in the surface layer

Quite recently in the history of the field, it was pointed out that there are fundamental reasons to assume from first principles that the surface composition of K\textsubscript{3}C\textsubscript{60} could be quite different from the bulk.\textsuperscript{35} The layers of fullerene and potassium can be considered to be stacked in the (111) direction, which is also the direction exposed at single crystal
surfaces studied so far. This stacking leads to strong local fields, as is well known, they being the basis of the Madelung potential. At the surface, however, it is important to compensate these fields, since otherwise, just as at the surface of a capacitor, macroscopically (and nanoscopically) huge fields would arise, which is not observed. This allows a few possible scenarios. One involves the standard bulklike termination, but two lead to termination with fulleride charges of $-1.5$ or $-2.5$. The $-1.5$ charge state entails a structure which exposes no potassium at the surface, therefore offering a natural explanation for why $K_3C_{60}$ is very robust in standard UHV chambers for many hours, whereas $K_6C_{60}$ is relatively reactive. We return to the question of robust in standard UHV chambers for many hours, whereas $K_6C_{60}$ is relatively reactive. 

We return to the question of the surface composition below, and simply note that the electrostatic considerations brought forward there represent a significant challenge to the consensus model in their own right. Since the sample preparation approach of Ref. 35 was somewhat different than the recommended recipe, it is perhaps understandable that small differences in the spectra and interpretation of the DOS at $E_F$ arose in that study. It is, however, noteworthy that one observation was used to suggest that the heat-treated samples were underdoped in the surface layer, namely that the DOS at $E_F$ increased if those samples were exposed to fractions of a monolayer of potassium. This is intriguing because of the simultaneous growth of the low-binding-energy shoulder of the HOMO band, i.e., a correlation similar to that seen in a previous growth study, and in the temperature dependence. Indeed, this shoulder and the DOS at $E_F$ are both strongest at the same composition, above which another phase, $K_4C_{60}$, begins to form. Thus the temperature and doping dependencies require that a successful model of the system explain the excellent correlation of the strong portion of the LUMO-derived bands with the weak portion of the HOMO-derived bands.

5. The bulk intensity in the spectrum and the mean free path in $K_3C_{60}$ photoemission studies

We now want to address the question of the surface sensitivity of the PES spectra, which has thus far been characterized in terms of the electron mean free path. This is necessary due to the emphasis placed upon this point by recent proponents of the dominant consensus as well as opposing viewpoints, claiming that only the surface electronic structure is observed in the spectra. We present here, therefore, a rather in-depth examination of the previous work on this issue. The simplest way to discuss the surface sensitivity is under the assumption that a photoelectron travels from the point of origin along a straight line trajectory, with a certain probability of inelastic scattering on the way to the sample surface. The ensuing attenuation of the photoemission signal can be described by a simple exponential law, under which the average distance that photoelectrons travel along the trajectory between inelastic collisions is given by the inelastic mean free path (IMFP).

Concerning the surface sensitivity of $C_{60}$ systems, the reference cited most is the study by Wertheim et al. That work compares $C_{60}/Cu(111)$ overlayer experiments and previous results of $C_{60}$ and $K_3C_{60}$ multilayers with the calculated IMFP for amorphous carbon. Some of the experimental IMFP values were shifted downwards by about 50% to match the theoretical curve. This was explained as a correction due to an assumed nonlayerwise growth of the $C_{60}$ film on Cu(111). The corrections applied to the overlayer data were applied as a conservative estimate of the maximum possible effect of scattering, i.e., to explore the reasonable lower limit on the bulk contribution. However, there is reason to question some of the assumptions of Wertheim et al. For instance, the curve by Tanuma et al. used there is calculated for single crystal and amorphous elements. In a follow-up paper, Tanuma et al. show that the IMFP of organic compounds is generally larger than those of elements. Details on the calculation of the IMFP are given in the Appendix. There we see as well that, primarily because of its lower density, $C_{60}$ is expected to have one of the highest IMFP for condensed materials, ignoring possible structural effects such as diffraction. For the analysis in the present study photoelectrons with a kinetic energy of about 100 eV are considered rather important. For this energy Wertheim et al. report an IMFP of 6 Å.

Goldoni et al. evaluated the IMFP from PES and EELS measurements. Their values of the IMFP are displayed together with a fitted curve. This fit gives lower values than expected from the theoretical work of Tanuma et al. for amorphous carbon and for organic compounds. Their PES data are taken from an overlayer study of $C_{60}/Ag(100)$ and the coverage is estimated by the ratio of the C 1s to Ag 3d photoemission signal. They also employ EELS data taken for a wider range of excitation energies by comparing the attenuation of the intensity of the interface layer with that of the surface layer for a bilayer of $C_{60}/Au(110)$. Unfortunately, there are no structures in the interface layer EELS data in the energy interval used, which makes such intensity estimates nontrivial. The value of the IMFP at kinetic energies of 100 eV is reported to be 5 Å.

Maxwell et al. show the development of the C 1s photoemission line shape for increasing numbers of layers $C_{60}$ on Au(110). The C 1s line of the bilayer can be decomposed into contributions from surface (62%) and interface (38%) layers. Assuming a simple exponential decay of the photoemission signal, the ratio of the contributions yields an IMFP of 16.3 Å for 100 eV kinetic energy electrons.

Given the large difference between the third and previous two values, it seems necessary to consider the sensitivity of the IMFP to the determination of the bulk contribution to the spectrum. As we show in detail in the Appendix, the apparent disagreement among the results reported is due to an emphasis on expressing them in terms of the IMFP. In terms of intensity, on the other hand, the contribution from bulk molecules to PES of $C_{60}$ solids agrees within the uncertainties for all three studies and can be expected to be in the range of 20%–30% of the total photoemission signal for kinetic energies near 100 eV. This puts additional constraints on any model of the electronic structure near the surface.

C. Summary of previous work and outline of present paper

To summarize, the broadest consensus seems to be that the signal from subsurface layers is not represented in PES...
spectra, and a majority of researchers in the field have apparently assumed that bulk and surface of single-crystal K$_3$C$_{60}$ have the same composition. Furthermore, at least one plausible model for the LUMO line shape has been proposed in terms of a K$_3$C$_{60}$ surface stoichiometry, but no plausible explanation of the deeper levels, including the C 1$s$, has emerged. The idea that intramolecular correlation effects somehow lie at the root of the complex line shapes observed in PES has not been borne out by any study this far. Thus the claim that the surface signal dominates to the extent that a subsurface (bulk) signal is impossible to measure, in contrast to an early point of view, is valid only to the extent that a 20%–30% signal cannot be extracted.

We show that the substructure in the C 1$s$ and deeper valence levels have the same origin, which we attribute to different K concentrations in surface and bulk. This similarity between different spectral regions is explained by an almost universal tendency of the deeper valence and C 1$s$ levels to shift uniformly as a function of K doping level (for crystalline phases) or charge transfer in general, a tendency overlooked by previous workers. The bulk is found to be metallic, and the surface to be a largely insulating compound (perhaps weakly metallic) from the spectra alone. Assuming a surface charge of −1.5 per fulleride consistent with the field-neutralization and chemical inertness requirements, we are able to explain these observations in terms of the allowed charge states at the surface and the known intramolecular correlation energy, $V$, as well as the intramolecular term, $U$. The surface compound emerges naturally in this picture, and is explained in terms of a correlated insulator, with a gap (or pseudogap) given by $2V$.

II. EXPERIMENTAL DETAILS

The experiments were carried out at Beamline I511 at MAX-lab. A standard UHV preparation chamber with a base pressure of $2 \times 10^{-10}$ mbar was employed. A film 300 Å thick was prepared layer-by-layer in increments of approximately 30 Å in situ on a Cu(111) substrate, alternating C$_{60}$ and K deposition. C$_{60}$ was evaporated from a homebuilt crucible, and K from an SAES getter source which was activated in the UHV chamber. After each deposition cycle the sample was annealed at 600 K for 6 h to sublime excess C$_{60}$, resulting in a single phase. The sample spectra at 100 K compared well with previous studies. A (1 × 1) (111) low-energy-electron-diffraction (LEED) pattern was observed, consistent with previous work on K$_3$C$_{60}$ crystal surfaces.

The spectra were taken using linearly polarized undulator light incident at about 82° from normal; note that the direction of radiation incidence was (almost) in the plane of the sample surface. The sample holder was supported in a chamber which could rotate around this axis due to special pumping and support constructions. Hence both sample and analyzer could be rotated independently around the light incidence axis in order to change the detection direction relative to the light polarization and sample normal. We found that aligning the spectrometer to the polarization direction minimized the effects of scattered photoelectrons as observed for solid C$_{60}$, which we discuss in more detail in Sec. IV. However, the same general trends in the photoemission spectra are observed if the polarization is fixed along the sample normal. Grazing emission will be used to refer to collection of the electrons at 70° from normal. The photon energy was 402 eV for the C 1$s$ and K 2$p$ spectra, and 110 eV for the K 3$p$, valence, and LUMO-derived spectra, with total energy resolutions (analyzer acceptance angles) of 150 meV ($\pm 9^\circ$) for C 1$s$ and K 2$p$, 80 meV ($\pm 6^\circ$) for valence, and 40 meV ($\pm 4^\circ$) for LUMO-derived spectra. Combined with the kinetic energy of just over 100 eV, this implies that electrons are collected from the entire Brillouin zone. All spectra were corrected for the nonlinear transmission function of the photoelectron analyzer.

III. RESULTS AND DISCUSSION

A. C 1$s$ PES

We begin the presentation of our data with the C 1$s$ spectra, which are simpler to analyze than the valence data. C 1$s$ PES is shown in Fig. 1. There is an obvious angle dependence in the shoulder at 284.3 eV. This observation suggests that the C 1$s$ line consists of at least two components. The weaker one is located primarily at low binding energy and the stronger one at high binding energy. The component which becomes weaker at grazing emission is assigned to subsurface molecules, leaving the dominant component as a surface contribution. One observes intensity variations of at most about 20% in x-ray photoelectron diffraction on C$_{60}$ monolayers, and since such intensity variations have not been observed in valence PES for solid C$_{60}$ samples, we rule out an important role for diffraction in our observation. The angle dependence suggests, moreover, that the intensity ratio depends on the choice of emission angle, and rules out the previous analysis in terms of chemical shifts due to different carbon sites.

We would therefore like to avoid strong assumptions regarding the line shapes. The large binding energy shift deduced for the components in Fig. 1 suggests that not all molecules have the same charge, according to the discussion in Sec. I B 3, i.e., that some may not be in a metallic state. Hence the proper choice of line shapes for a reasonable a
priori decomposition of the spectrum becomes difficult. We chose an empirical approach instead. To determine an approximate empirical line shape for the surface component, the two spectra of Fig. 1 were scaled to match at the shoulder. One measure of the scaling factor is the shape of the tail in the low binding energy region in the difference spectrum, which should be similar in shape to the grazing emission spectrum. Taking this into account it is possible to scale the normal and grazing emission spectra to have similar bulk contributions, as illustrated in Fig. 2.

The difference spectrum gives an empirical profile for the high-binding-energy component, as displayed in Fig. 2. The high-energy tail is likely to be too strong due to the effects of scattered photoelectrons for grazing emission, and can probably be corrected in the manner suggested by the arrows. The dotted lines show two Gaussians and their sum. The meaning of the curves S1 and S2 will be taken up later. The resulting line shape strongly resembles the grazing emission spectrum. It can now be employed to obtain an estimate of the bulk spectral profile via a similar subtraction procedure using matching at high binding energy, as illustrated in Fig. 2(c), with the result shown in Fig. 2(d) representing the empirical bulk line shape. We surmise that this difference spectrum should be corrected as suggested by the arrows, due to the overly large scattered electron intensity at high binding energies in the spectrum of Fig. 2(b). The shape of the difference spectra turns out to be rather robust, which means that even for slightly different relative scaling of the original curves the empirical line shape does not change much, in particular the empirical bulk line shape is always asymmetric with a tail towards higher binding energies. Nevertheless, the two components give an impression of where the main intensity from the bulk and surface contributions are found in the spectra, and of their profiles. Linear combinations of the two components, scaled to match the total at each angle, are shown as solid lines in Fig. 3.

B. Valence bands

The photoemission spectrum of pure $\text{C}_{60}$ shows a clear separation between the highest occupied molecular orbital (HOMO) and the next band (HOMO-1). In contrast, the valence line shape of $\text{K}_3\text{C}_{60}$ consists of broad structures, hampering a straightforward spectroscopical identification of individual MOs. This width has been discussed in the literature in terms of plasmon excitation\cite{13} and correlation satellites.\cite{25} A plasmon excitation at 0.6 eV has been measured by different techniques,\cite{18,47} motivating its use in models of the spectra, but not ruling out possible correlation satellites.

Most studies of the $\text{K}_3\text{C}_{60}$ valence band focused on the LUMO-derived line shape. Before discussing this, we want to analyze structures in the fully occupied valence region. A typical valence spectrum is shown in Fig. 4. Similar to that...
subtle features in the K$_3$C$_{60}$ spectrum are reproduced semi-
dependence between the HOMO-derived and C$_{1s}$
preserved one-to-one correlation between the electronic
quantitatively by this method. Not only does this suggest a
mechanism modeled by summing replicas of the C$_{1s}$
noted previously for C$_{60}$, but has not been discussed more
in the literature, selected using the following criteria:
all data from charge transfer systems which we could locate
charge transfer is summarized in Table I. We have included
affected by such interactions, such as C$_{60}$/A$_{u}$
here on the HOMO, cases in which the HOMO appears un-
C$_{60}$/Ni, C$_{60}$/Pt, C$_{60}$/Si, and C$_{60}$/InP. Since we focus
in C$_{60}$ systems show a constant energy separation upon
in particular not for fullerides. That the levels
screening of a core hole in C$_{60}$, which makes the final
state charge distribution similar to that of a valence hole, and
thus the external screening contributions quite similar. The
existence of identical shifts for the valence and C$_{1s}$ levels
confirms that the small variations in charge density found
for different carbon sites in K$_3$C$_{60}$ cannot be the cause of the
splitting in the C$_{1s}$ line, consistent with the discussion in
Sec. I B 3 and in the results of Sec. III A.

As noted in Sec. I B 4 there is a clear trend that, upon
deposition of K onto C$_{60}$, the shoulder below the HOMO-
derived band and the intensity at $E_F$ behave similarly, as
shown in Fig. 1 of Ref. 17 and elsewhere. At the same
time, the main part of the HOMO-derived band and the
intensity at the higher binding energy side of $E_F$ also vary in a
coordinated manner, suggesting that the LUMO is also to be
included in the phenomenon collected here of uniform shifts.
Indeed, successive K doping of C$_{60}$/Si shows a rigid shift of
all the valence levels. In Fig. 1 of Ref. 21, the shape of the
LUMO-derived band changes, but the energy difference be-
tween the “LUMO” and “HOMO” is constant for all K
concentrations. Fig. 2 of the same reference shows that the peaks
(“LUMO,” “HOMO,” and “HOMO-1”) of ML $K_3C_{60}$ co-
incide with the shoulders and peaks of solid K$_3C_{60}$ which
assign to the metallic bulk phase, similar to C$_{60}$/Ag(100) in
Fig. 3(b) of Ref. 16. Successive intercalation, e.g., in Merkel
et al., yields a constant energy difference between the
HOMO-derived and C$_{1s}$ bands of 282.7±0.2 eV. Thus all
available data on bulk fullerides and a number of other
charge transfer fulleride systems are consistent with the
present model of a uniform shift of all levels in C$_{60}$ upon
charge transfer, as a function of charge state. This rational-
izes the excellent correlation between the fully occupied lev-
els and the C$_{1s}$ in Fig. 4(a). Hence the observed uniform

![FIG. 4. (a) Normal emission valence PES spectrum of K$_3$C$_{60}$.
The solid line is a model given by the sum of the illustrated images
of the normal emission C$_{1s}$ spectrum (dashed lines), placed ac-
cording to the peaks of pure C$_{60}$ as suggested by the vertical lines.
(b) Comparison with a pure C$_{60}$ spectrum (shifted in energy) to help
illustrate the uniform shifts. See the text for more details.]

![Table I. C 1s and HOMO-derived binding energies for the
indicated samples, illustrating the uniform shifts of these levels in
cases of charge transfer bonding.]

<table>
<thead>
<tr>
<th>Reference</th>
<th>Sample</th>
<th>C 1s (eV)</th>
<th>HOMO-derived (eV)</th>
<th>ΔE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maxwell et al.</td>
<td>$C_{60}$</td>
<td>289.6</td>
<td>6.9</td>
<td>282.7</td>
</tr>
<tr>
<td>Goldoni et al.</td>
<td>K$<em>3$C$</em>{60}$</td>
<td>285.0</td>
<td>2.3</td>
<td>282.7</td>
</tr>
<tr>
<td>Brühwiler et al.</td>
<td>K$<em>3$C$</em>{60}$</td>
<td>285.1</td>
<td>2.3</td>
<td>282.8</td>
</tr>
<tr>
<td>Goldoni et al.</td>
<td>K$<em>3$C$</em>{60}$</td>
<td>285.0</td>
<td>2.3</td>
<td>282.7</td>
</tr>
<tr>
<td>Present work</td>
<td>K$<em>3$C$</em>{60}$</td>
<td>285.0</td>
<td>2.3</td>
<td>282.7</td>
</tr>
<tr>
<td>Maxwell et al.</td>
<td>C$_{60}$/Au(110)</td>
<td>284.4</td>
<td>1.7</td>
<td>282.7</td>
</tr>
<tr>
<td>Tzeng et al.</td>
<td>C$_{60}$/Au(111)</td>
<td>284.5</td>
<td>1.8</td>
<td>282.7</td>
</tr>
<tr>
<td>Tsuei et al.</td>
<td>C$_{60}$/Cu(111)</td>
<td>284.2</td>
<td>1.6</td>
<td>282.6</td>
</tr>
<tr>
<td>Magnano et al.</td>
<td>C$_{60}$/Ag(110)</td>
<td>284.4</td>
<td>1.8</td>
<td>282.6</td>
</tr>
<tr>
<td>Pedio et al.</td>
<td>C$_{60}$/Ag(111)</td>
<td>284.5</td>
<td>1.9</td>
<td>282.6</td>
</tr>
</tbody>
</table>

*Table I. C 1s and HOMO-derived binding energies for the
indicated samples, illustrating the uniform shifts of these levels in
cases of charge transfer bonding.

$^a$Ionization potential, referred to vacuum level.
$^b$Unpublished.
shift in the present work is further and more conclusive evidence for the existence of different molecular sites near the sample surface, differentiated by their charge state and presence or lack of metallic character, as suggested above based on the C 1s spectra.

C. Photon energy dependence

After establishing the existence of distinguishable surface and bulk signals in the spectra via angle-dependent PES, we now want to turn to the photon energy dependence in the spectra to provide a cross-check of our interpretation. We will compare the present carbon and potassium data to spectra excited with Al Kα radiation. Due to the higher kinetic energy of the photoelectrons for Al Kα excitation, the signal from the bulk is expected to be increased. In Fig. 5 we compare the valence band and core level PES of K₃C₆₀ taken at 110 eV (dashed line) with high excitation energy data (circles). A version of the former is shown convoluted with a Gaussian to facilitate the comparison in a first approximation of the effects of the poorer resolution in the x-ray spectra.

For the interpretation of the comparison it is important to recall that the bulk signal in the high energy data is expected to be attenuated for two reasons: (1) the spectrum was taken at 45° emission from the surface normal and (2) the light was not strongly polarized. To estimate the IMFP at 1200 eV kinetic energy, we use the centroid of our own determination of the bulk/surface intensity ratio as the relevant measure of the IMFP at 100 eV, and extrapolate. The intensity is estimated using Eq. (A1) in the Appendix.

The core level data are shown in Fig. 5(a). The spectra have similar line shapes, especially after broadening the low-energy data. The intensity on the low binding energy side is quite similar, suggesting similar bulk contributions. Given the emission angle difference, this is consistent with a larger bulk contribution in the C 1s data at higher excitation energy. The broad line shape allows no more detailed analysis.

The high noise level hampers a detailed analysis of the LUMO-derived region in Fig. 5(b); however, the comparison shows that the apparent agreement at different photon energies is due to the small expected differences in the LUMO region, which can in turn be attributed to the relatively weak surface LUMO emission. The HOMO-derived band is difficult to assess, due to the poor statistics. This is a consequence of the much lower valence cross section at x-ray energies, and causes a sloping background in the data as well, as can be appreciated upon comparing the data of Ref. 38 with those in Fig. 4. We attempt to indicate the heights of the shoulder and peak positions (2.2 eV) of the HOMO-derived bands. Starting from the LUMO-derived backgrounds in each spectrum, the peak-to-shoulder ratios are about 2:1 in the low-energy, and perhaps 1.5:1 in the high-energy spectra, respectively. This is consistent with the C 1s data, though not quantitatively precise. It is also consistent with expectations of higher bulk intensity, modified by a reduction due to the more grazing emission angle. The bulk-to-surface ratio in both spectra is then expected to be of the same order of magnitude, as observed. The K spectra show a photon energy dependence as well, in line with our model of different surface and bulk sites, which is discussed together with its angular dependence below in Sec. III F.

D. Electrostatics and surface vs bulk structure revisited

As already discussed, the spectra are derived predominantly from the surface layer, which in addition to the observed angle dependence motivates our assignment above of the weaker, low-binding-energy component of the C 1s and valence PES to molecules in the bulk. This assignment implies that the Madelung potential due to screening and/or charge states is significantly different in the surface and bulk layers. Here we want to take up the crystal structure, based on the excellent discussion by Hesper et al., in order to motivate the implications to be drawn from our data. The basic points after considering the electrostatics of the ionic compound K₃C₆₀ were described in Sec. I B 4. There are three possible energetically stable surface configurations, with an outermost layer and charge state of either C₆₀⁻₁, K⁺, or K⁻¹. Our sample and others are quite stable against contamination over the period of preparation and measurement over tens of hours, which is not the case for K₆C₆₀, leading us to exclude the possibilities that the outermost
layer consists of reactive alkali ions. This leaves only the case in which the outermost layer of K₃C₆₀ consists of C₆₀ planes with an average molecular charge of −1.5. Figure 6 depicts the surface layer, with the C₆₀ molecules forming a hexagonal lattice as obtained by LEED and STM. As is well-known, the voids between the molecules correspond to the tetrahedral and octahedral lattice sites, located below the surface C₆₀ layer, which are occupied by potassium ions. In Fig. 6(b) the particular stacking sequence along the ⟨111⟩ direction is shown. Planes of single C₆₀ layers alternating with three planes of K layers form alternating charge planes. The slices to which the planes belong are indicated in Fig. 6(c). This structure will form the basis of discussion in what follows.

E. LUMO PES

Clearly the conduction band, derived from the lowest unoccupied molecular orbital (LUMO) of C₆₀, is generally the most interesting aspect of the electronic structure of a superconducting compound, which explains the multitude of studies aimed at this portion of the electronic structure, often to the exclusion of most of the rest of the bands. This portion of the spectrum is arranged oppositely to all others, with a maximum at low binding energy, and a minimum at higher binding energy, exposing the fundamental difficulty in explaining all portions of the spectrum simultaneously.

Figure 7 shows an expanded view of the LUMO-derived PES collected both in normal and grazing emission. The grazing emission spectrum compares well with previous data.
Defining the transport properties, since \( U \) and \( E_{\text{F}} \), tend to drive the system into a metallic state. For the terms of bulk assemble model LUMO-derived spectra for both angles in will now use the results obtained and deduced thus far to HOMO-derived and deeper valence bands, suggests that the nearest-neighbor Coulomb repulsion presents a case of a surface with half-integer doping, the charged fullerenes can in principle arrange themselves as a principle. To see this explicitly, we note that the differently singly charged sites, allowing metallic conduction in principle. To see this explicitly, we note that the differently charged fullerenes can in principle arrange themselves as a charge-density wave (CDW) as illustrated in Fig. 6.

This configuration corresponds to an insulating state with a gap of 2\( V \). To see this, it is necessary to consider the total energy in a given electron transfer process. We begin with the transfer of an electron from a molecule at \(-2\) to a site with charge \(-1\), but not a nearest-neighbor, i.e., far enough away to ignore interactions between the initial and final molecules. Underlying this approach is the assumption that, because the one-electron LUMO-derived band is quite narrow,\(^{10}\) we can ignore the slight difference in binding energy due to that aspect of the local charge state, and focus on the differences in the correlation contributions. For the initial state of the starting molecule, these amount to Coulomb energies proportional to the local charge times the nearest-neighbor charges times \( V \), or \( E_{\text{PES}}=2(2\cdot2+4\cdot1)V=16V \). The initial state correlation contribution of the target molecule in the transition is similarly derived to be \( E_{\text{PES}}=1(4\cdot2+2\cdot1)V=10V \). The local correlation-dependent energy of the starting configuration is then \( E_{\text{PES}}=E_{\text{F}}+E_{\text{I}}=26V \). After the transfer, we carry out similar calculations for the two sites, obtaining \( E_{\text{F}}=28V \). Thus the energy input to the system required for this transition is \( \Delta E=E_{\text{F}}-E_{\text{I}}=2V \), which is the minimum energy for complete separation of the transported charge from its original site, and corresponds to the fundamental gap of a correlated insulator. Transfer to a nearest-neighbor singly charged site, on the other hand, costs only \( V \) (note the need to avoid double-counting the mutual interaction), and corresponds to a charge transfer exciton for the surface layer. As we show below the CDW is not the only solution for the ground state of the half-integer-charged surface layer, but serves as a starting point for considering its properties, and we will now examine the consequences expected in PES.

Calculating the absolute binding energy in PES of this system is a task far beyond the scope of the present work. Instead, we focus on the difference in binding energy of the two surface sites, analogously to the electron transfer calculations above. PES corresponds to electron removal, and so we calculate the correlation contributions to the binding energies.

We seek, therefore, electron removal energies from singly and doubly charged sites. We have shown above that the initial state term in the former case is \( E_{\text{I}}-E_{\text{PES}}=10V \). For the doubly charged site, we need to add the on-site contribution, \( U \), which is the repulsion between the two conduction band electrons on the given molecule, to the previous calculation, giving \( E_{\text{I}}-E_{\text{PES}}=U+16V \).

The final state energies are calculated similarly. \( E_{\text{I}}-E_{\text{PES}}=0 \) and \( E_{\text{I}}-E_{\text{PES}}=8V \). These yield net changes of \( \Delta E_{\text{Net}}=E_{\text{F}}-E_{\text{I}}-E_{\text{PES}}=10V \) and \( \Delta E_{\text{Net}}=E_{\text{F}}-E_{\text{PES}}=16V \). The difference between these is then the predicted binding energy difference for PES from surface sites with the indicated net charge states, i.e., \( \Delta E_{\text{Net}}=U+2V \). Taking values of \( U=\pm1.1eV \) and \( V=\pm0.35eV \) for negatively charged molecules,\(^{43}\) we obtain \( \Delta E_{\text{Net}}=U \pm 0.4V \). This splitting is illustrated as the separation between the surface sub-peaks, \( S1 \) and \( S2 \), of the C 1s given in Fig. 2(b), that is, it has the correct magnitude to rationalize the width of the C 1s surface component peak, which we take as support for the derivation given above.

FIG. 7. LUMO-derived band of \( K_3C_{60} \) for the indicated emission angles. The light polarization is always parallel to electron emission direction. The model shown is described in the text.

At other angles\(^{13,16,35}\) the ratio of the peak height at \( E_{\text{F}} \) to the signal at 1.3 eV in the normal emission spectrum is greater than in all previous reports, however. This is due to the experimental geometry and, in particular, the use of polarized light, which we address in more detail in Sec. IV. The angle dependence shows that the intensity at \( E_{\text{F}} \) drops with increased emission angle, suggesting that the emission at \( E_{\text{F}} \) is associated with the subsurface (bulk) electronic structure. This is consistent with the results for the C 1s line. This angle dependence and the uniform shifts expected for all the levels suggest that the near-\( E_{\text{F}} \) region of the spectrum has a significant bulk component, but leaves open the question of the characteristics of the surface component, although the lack of intensity at lower binding energy of this component for the C 1s and, by implication of the analysis in Sec. III B, HOMO-derived and deeper valence bands, suggests that the surface components derive from an insulating compound. We will now use the results obtained and deduced thus far to assemble model LUMO-derived spectra for both angles in terms of bulk (B) and surface (S1,S2) contributions, as shown.

To construct a model of this spectrum, it is necessary to have a clearer view of which charge states are involved at the surface, for which we refer to Fig. 6(a). A half-integral average surface charge state of \(-1.5\) as inferred in Sec. III D corresponds to half of the molecules at a charge of \(-1\), and the other half at \(-2\), since the molecular nature of the sample requires near-integral local charges.\(^{56}\) \( K_3C_{60} \) is, as reviewed in Sec. I, a correlated material, in which the intramolecular Coulomb repulsion \( U \) tends to drive the system toward an insulating state, whereas kinetic energy terms, represented by the one-electron bandwidth \( W \), aided by Jahn-Teller coupling, tend to drive the system into a metallic state.\(^{5}\) For the present case of a surface with half-integral doping, the nearest-neighbor Coulomb repulsion \( V \) becomes important in defining the transport properties, since \( U \) no longer constitutes a barrier for transfer of an electron from doubly to singly charged sites, allowing metallic conduction in principle. To see this explicitly, we note that the differently charged fullerenes can in principle arrange themselves as a...
Unique to a quantitative understanding of the LUMO-derived band is the fact that the number of electrons occupying this band varies as a function of molecular charge state, giving population-derived intensity factors of 1:2:3 (surface:surface:bulk), based on the discussion in Sec. III D. Because all other bands are fully occupied, the intensity factor for each of their spectral components is only a function of position in the sample (attenuation due to scattering), rather than local population. This already suggests the answer to the riddle of the fundamentally different line profiles for LUMO compared to all other bands, if the bulk molecular state is $-3$, since this factor compensates for the strong attenuation expected for the bulk portion of the spectrum, and the $-1$ and $-2$ charged molecules represent each only one-half monolayer, reducing their relative intensity by an extra factor of 2.$^{69}$ To model the spectra, however, some understanding of the expected line profiles and energetics is needed.

For the line profile of the bulk component of the LUMO, we simulate the vibrational structure using the gas phase spectrum$^{57}$ of C$_{60}$, which was broadened to mimic instrumental resolution and convoluted with a plasmon loss function$^{19,47}$ in line with previous work.$^{13}$ This approach worked well as a first approximation in a recent K$_3$C$_{60}$ monolayer study.$^{22}$

The line profile of each surface component is the next issue. The analysis above and depicted in Fig. 2(b) indicates that these, S1 and S2, are contained in the broad surface line shape, which is almost symmetric if the assumed scattering tail is excluded. Since both components are equal in intensity and derived from an insulator, we expect similar line shapes. As derived above, we take the splitting of the two surface charge states to be 0.4 eV. Thus the surface component should be split into two equal subcomponents, S1 and S2, shifted by this amount, as illustrated in Fig. 2(b). The same is then expected for the LUMO, with the intensity modification determined by population; the binding energy is given by the separation observed in the C 1$s$, placing the $-2$ contribution at about $E_F - 0.6$ eV. The surface components are therefore represented by symmetric curves similar to the components in Fig. 2(c), scaled according to the assumed charge state.

The ratio between surface and bulk structure is taken from the analysis of the C 1$s$ line shape.$^{58}$ The solid lines in Figs. 7(a) and 7(b) are the sums of these three components, taking electron multiplicity and surface-to-bulk ratio into account. It is apparent that this model gives semiquantitative agreement with the measured spectra, and it serves to explain their angle dependence.

Our model does not attempt to explain all details of the photoemission line shape; it is aimed at the angle dependence, with an assumption of common bulk and surface line shapes at both angles. It can be speculated, e.g., that coupling to intramolecular vibrations, origin of the structure appearing at about 0.25 eV, could be different from the gas phase results. Correlation satellites as well as effects due to incomplete charge transfer could be responsible for intensity at energies greater than 1 eV. These and similar details remain to be worked out. Thus we have succeeded to unify the picture of the distribution of bulk and surface spectra for the C 1$s$, LUMO-derived, and deeper valence bands.

Reexamining the PES of a single layer C$_{60}$ doped to charge state $-3$ reported by Yang et al.$^{22}$ in terms of the present picture adds further insight. In Fig. 8 we compare the LUMO-derived band from that sample to our spectrum. Clearly, in the region where the surface states of solid K$_3$C$_{60}$ appear in our model, less intensity is observed in the single layer spectrum, supporting our location of the charge states C$_{60}^-$ and C$_{60}^0$ in the solid K$_3$C$_{60}$ spectrum.

It has been suggested elsewhere$^{55,57}$ that the surface layer of K$_3$C$_{60}$ should be a metal due to the possibility of non-CDW charge configurations, which are equally stable. Spectroscopically, the large difference in binding energy, and especially the lack of significant intensity at $E_F$, suggests that this is not the case. Examining the metallic configurations, one finds that zero-cost transitions from $-2$ to $-1$ sites involve transfer over separations of at least two sites, which will presumably have a relatively low probability due to the small nearest-neighbor orbital overlap, suggesting that this is the reason that the surface exhibits primarily insulator character. The width of the individual surface lines consistent with the analysis above could be due in part to a distribution of local (non-CDW) charge configurations, leading to final states with energies above and below the main candidates already discussed, but otherwise conforming to the same general description.

**F. K spectra**

The bulk signal in the K-derived spectra (2$p$ and 3$p$) is expected to show two components reflecting the tetrahedral and octahedral lattice sites occupied by the alkali atoms. K 2$p$ spectra recorded with Al Kα excitation show two components close to the theoretical intensity ratio$^{14,59}$ of 2:1. PES in the literature taken at different excitation energies, thus probing different sample depths, expose at least three components.$^{26}$ Spectra taken at lower excitation energy are shown in Fig. 9. The normal emission spectrum in Fig. 9(a) shows quite broad line shapes with several components. The components show a significant angle dependence, as shown in Fig. 9(b). This cannot be explained solely as being due to only two atomic sites. From our discussion of the surface structure it is clear that more than two bulklike components is reasonable: in principle, at least two octahedral and four tetrahedral surface components are also expected. To extract the contribution from the surface components we scale the

![FIG. 8. Comparison of the present LUMO-derived photoemission spectrum to that of a K$_3$C$_{60}$ monolayer (Ref. 22). The difference spectrum shows intensity at higher binding energy in the region of the expected surface contribution, as explained in the text.]
normal emission data to match the grazing emission data at the shoulder as shown in Fig. 9. Since the surface shows contributions from different depths, however, it is not possible to isolate the bulk contribution using this procedure. This suggests that the bulk is strong at lower binding energies (the tetrahedral component), but the octahedral component suggested by high photon energy data 14,59 is difficult to isolate in the data. Further support for this assignment is given in Fig. 10, where we compare K 3p spectra acquired at different excitation energies. Once again, the low-binding-energy component is enhanced at high excitation energies, which supports the present model. The fact that more than two components are observed is an additional challenge to the consensus model of a bulklike surface, since the placement, if not the number as suggested here, of the K ions relative to the surface fulleride layer must differ substantially from that of the bulk. The broad shape of the surface emission is also supportive of the present model with several K sites expected to contribute.

IV. INFLUENCE OF THE LIGHT POLARIZATION

Recent studies on solid C 60 have established that the photoelectron cross section is largely that of the free molecule, which for nonoriented molecules places the strongest emission along the light polarization direction.42 The same effect is observed for K 3C 60 , making it paramount to exploit when measuring the band profiles. To illustrate this, we have measured spectra in different geometries, e.g., with polarization kept normal to the surface, and observed for these cases as well a decrease of the features at the low-binding-energy side of the C 1s and valence subband as well as the signal at E F with respect to the rest of the LUMO-derived band. Our observation is that the electrons are emitted most strongly along the polarization direction, and if one holds that direction fixed (e.g., along the surface normal), then spectra taken at other angles will obtain relatively strong contributions from the electrons which were scattered out of the primary emission cone. Photoemission of the LUMO-derived band is shown for both cases in Fig. 11. The light polarization is fixed in Fig. 11(a) and is always along the emission direction in Fig. 11(b). Keeping the light polarization along the measured electron emission direction minimizes the effects of inelastically scattered photoelectrons, so that the high-energy tail changes relatively little for grazing emission. This observation is one possible explanation for the range of values reported for the “mean free path” in such samples. It also rationalizes the lack of angle dependence previously reported.

FIG. 9. (a), (b) K 2p photoemission of K 3C 60 at the indicated emission angles, taken at hν=365 eV. The contributions of inelastically scattered photoelectrons were subtracted after estimation of a Shirley background. The separation of bulk tetrahedral and octahedral sites as previously determined in Ref. 59 is indicated. (c) The difference between normal and grazing emission shown as a dashed line was determined using the illustrated rescaled spectra of (a) and (b). The difference should be a good approximation to the surface line shape. The analysis is not as straightforward as in the C 1s region, which is rationalized in the present model as due to the existence of several K surface sites.

FIG. 10. K 3p PES at the indicated excitation energies.

FIG. 11. Angle-dependent PES spectra of the K 3C 60 LUMO-derived band at the indicated angles and polarization settings.
for K₃C₆₀ using unpolarized light,¹³,¹⁶ due to the fact that the strongest emission was never in the measurement direction, and so strong contributions from scattered electrons would be expected in all measurement angles. Since we have found that the polarization direction determines the primary emission cone of the electrons for fullerene solids, the choice we have presented here is the optimal one for comparing mean free path effects on the emission intensities.

A valence spectrum taken in the condition of light polarization along the emission direction is shown in Fig. 12. The height of peaks and shoulders is indicated by braces. The ratio of peak height to shoulder intensity is 1.6 in normal emission and 3.4 in grazing emission.

FIG. 12. Valence PES of K₃C₆₀ taken at 110 eV at the indicated emission angles. The light polarization direction was parallel to the electron emission direction. The height of peaks and shoulders is indicated by braces. The ratio of peak height to shoulder intensity is 1.6 in normal emission and 3.4 in grazing emission.

We have shown thus far that the consensus picture of the surface composition and electronic structure of K₃C₆₀ being similar to the bulk is not justified, using the following observations: (1) The splitting of the C 1s level requires at least two different molecular charge states, one in the surface and one in the bulk; (2) Uniform binding energy shifts among all levels for charge transfer compounds require a common explanation for the LUMO, HOMO, and C 1s bands; in combination with the most likely surface structure, this suggests two surface valences (−1 and −2), and one bulk valence (−3), which gives a semiquantitative explanation of the observed width in the surface component, and the observed LUMO line shape; (3) The widths of the bulk and surface K₃C₆₀ spectra are now understood to be much smaller, in line with monolayer observations and with theory; and (4) The mapping dependence of the spectra, in particular the EF−HOMO-shoulder correlation, is well-understood in terms of changing molecular charge states, since those portions of the spectra belong to −3-charged molecules. This also rules out the existence of a surface superconductor, since the gap-opening at EF observed in PES experiments must be attributed to the bulk, and is therefore consistent with expectations based on transport measurements.¹⁰ There are, however, two remaining issues to consider.

V. DISCUSSION

A. Temperature effects

There is a common temperature dependence of the bulk HOMO component and the intensity at EF.¹⁹ Note that the small feature between HOMO and HOMO-1, and the small shoulder on the low-binding energy side of HOMO-2 (see Fig. 1 of Ref. 19) vanish at higher temperature in the same manner, which is an expected correspondence in our model. The C 1s line exhibits similar changes as the temperature is increased.²⁶ We propose that this can be explained as an effect of disorder at increasing temperature decreasing the intensity of the bulk relative to the surface component. These effects have in principle several possible explanations, most of which can be ruled out. Coupling to intramolecular vibrations is well-known to generally increase the level of broadening with increased temperature, but for fullerenes has no other major effect (see, e.g., Refs. 60 and 61). A change in the charge density could cause major shifts of the core and deeper valence lines as the lattice expands, or upon redistribution of K within or even out of the sample, but this would not explain the observation at EF of similar intensity decreases as for the HOMO and C 1s shoulders. In particular, the temperature effects are reversible, suggesting that K does not strongly redistribute itself; also, the sample remains largely metallic throughout most, if not all, of the observed temperature range, though there are speculations that there may be a metal-insulator transition in the higher range of temperatures studied.⁶²

A recent study on an Al surface shows similar variations in surface to bulk intensity at increasing temperature quite clearly, if one examines their Fig. 1. They show that the identifiable bulk intensity is strongly redistributed due to intrinsic phonon coupling, and can be decomposed according
to the number of phonons absorbed or emitted. This would explain how the intermolecular vibrations contribute to the broadening in the spectra, but could not explain intensity redistributions of the scale observed here, especially considering the low energy of those phonons.

We propose instead that the similarity in temperature-induced effects in C 1s, HOMO-derived, and LUMO-derived bands can be understood in terms of a decreased effective IMFP at higher temperatures. Due to the higher probability for elastic and near-elastic scattering at elevated temperatures, electrons originating from deeper layers will travel a longer path before reaching the surface, thereby increasing their chance of inelastic scattering relative to that of electrons emitted from the surface layer. Hence the effective IMFP decreases at higher temperatures. This would explain the reduced bulk signal in the spectrum. In our case, with a weak bulk signal to begin with, the surface signal will increasingly dominate as the temperature increases. This simple explanation appears to be the only one consistent with the temperature-dependent observations, and is also supportive of the present model.64

B. EELS

Using EELS Goldoni et al. conclude that the surface and bulk electronic structure of K3C60 are quite similar.18 Since the surface layer has charge states −1 and −2 in our model, a reduced plasmon loss, presumably at a much lower energy, would be expected. Studies of mixed phases do not show any signal in the energy range up to 0.6 eV from lower stoichiometries in EELS.65 In this picture the observed plasmon loss for K3C60 would then be assigned to the first and deeper bulk layers at low temperature. As the temperature is increased, electron-vibration scattering increases, thus causing the surface signal to increasingly dominate, assuming the mechanism proposed in Sec. VA applies. Considering the largely insulating character at lower charge state deduced for this layer, it is not clear which excitations should arise, but, e.g., plasmon excitation would be presumably lower in energy, perhaps dwarfed by the elastic beam. We can also assume that at elevated temperatures the Fermi-Dirac distribution will reduce the number of occupied states below EF, perhaps thereby reducing the plasmon energy itself, rationalizing the EELS observation of a slight energy decrease at higher temperature.65 Thus the EELS results of Ref. 18 appear to be reasonably reconciled with our interpretation of the photoelectron spectra in a simple manner.

VI. CONCLUSIONS

We have reported an angle dependence in the C 1s, HOMO- and LUMO-derived bands of K3C60, pointing towards an insulating surface and metallic bulk. We have summarized work in literature and found a constant separation in energy between C 1s and HOMO-derived bands in all charge transfer C60 systems. Based on the constant separation and on our observations we developed a model that identifies common features in core level and valence spectra.

This model enabled us to resolve major difficulties in previous interpretations of similar data. It explains the broad photoemission line shapes in terms of bulk and surface electronic structure consistently in the K 2p, C 1s, and valence spectra. Our analysis shows that the LUMO-derived band can be modeled as a bulk line at the Fermi level which resembles gas phase data in its vibronic structure, consistent with previous work13,16,22 plus two surface lines at higher binding energy, and with intensities scaled by mean free path and population effects. Thus our result suggests that the correlated surface of K3C60 is an insulator, or at best, a poor metal, a situation driven by the dominance of the intermolecular electron-electron correlations at the surface.

Note added in proof. Recently, we discovered an EELS study (Ref. 73) which comes to similar conclusions about the surface electronic structure based on vibrational energies. Also, some additional details relevant to the present work may be found in Ref. 74.

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APPENDIX: ADDITIONAL ASPECTS OF THE IMFP IN C60 SOLIDS

If we reexamine the published IMFP values in terms of the intensities which they imply, we find that all published results are consistent within the experimental uncertainties. Wertheim et al.,11 report 6 Å, Goldoni et al.18 4.7 Å, which gives contributions from the bulk signal of 32% and 22%, respectively. In the study by Wertheim et al. no error bars were declared; however, these can be assumed to be of the same order of magnitude as in the other study. Maxwell et al. show a contribution from the bottom layer in a two layer system of 38%. To better understand these results, we calculate the expected intensity for a given IMFP.

As a first approximation, the photoemission intensity of a system consisting of a surface layer and m subsurface layers is calculated via a sum of exponential functions with a primary intensity I0:

\[ I_{\text{surf}} = I_0 e^{-\frac{\lambda}{\lambda_{\text{surf}}}} \]
FIG. 14. Calculated IMFPs from the TPP-2M formulas for the set of materials as shown in Table II as a function of kinetic energy.

\[ I_{\text{surf}} = I_0 e^{-2(5+8n)/\lambda}, \quad (A1) \]

where the length of the path the photoelectron originating from the \( n \)th subsurface layer has to travel to the surface is given by the numerator in the exponent, \((5+8n)\) Å. The IMFP is denoted by \( \lambda \). The size of the \( C_{60} \) molecule is 10 Å. We therefore assume that the photoemission signal originates on average 5 Å below the top of a given layer. The layer separation is taken to be 8 Å, equal to the spacing in a crystal. The relative contribution of the subsurface layers is given by the ratio

\[ R_{\text{surf},m} = \frac{I_{\text{surf}}}{I_{\text{surf},m} + I_{\text{surf}}}, \quad (A2) \]

where \( m = 2 \) (\( m = \infty \)) for a bilayer (semi-infinite) system. As shown in Fig. 13, the IMFP as estimated using PES intensities diverges for larger subsurface contributions, emphasizing the importance of monitoring the uncertainties in the measured intensities. For example, for a ratio of 38% the IMFP is properly given by 16 Å, thus within the given error bars the contribution from bulk molecules in \( C_{60} \) solids can be expected to be in the range of 20%–30% of the total photoemission signal for \( h\nu = 110 \) eV.

Now we compare this result with the general case. An IMFP of the order of 16 Å at the photon energy of 100 eV is somewhat larger than expected from the “universal curve” for elements. To a first approximation the IMFP is a function of kinetic energy, whose shape is almost independent of the material. This can be understood from the argument that the cross section for inelastic electron scattering depends on the valence electron density, which is almost a constant for metals, explaining the general behavior for those systems. Calculations of the universal curve carried out by Tanuma et al. give good agreement with experimental data. A more detailed study of organic compounds, however, gives values of the IMFP larger than expected from the universal curve for metals. This deviation has its origin in the lower density and different plasmon energies for these systems.

The IMFP \( \lambda \) in solid elements and compounds at electron energies of more than 50 eV can be obtained with good accuracy with the TPP-2M equation of Tanuma et al.

\[ \lambda = E/\left[ E_p^2/2 + E_g^2 + 0.069\rho^{0.1} \right], \quad (A3) \]

\[ \beta = -0.10 + 0.944/\sqrt{E_p^2/E_g^2}, \quad (A4) \]

\[ \gamma = 0.191\rho^{-0.5}, \quad (A5) \]

\[ C = 1.97 - 0.91E_p^2/829.4, \quad (A6) \]

\[ D = 53.4 - 20.8E_p^2/829.4, \quad (A7) \]

with \( E_p \) as the free-electron plasmon energy.

\[ E_p = 28.8\sqrt{N_V\rho/M}, \quad (A8) \]

\( \rho \) is the density, \( N_V \) the number of valence electrons per atom/molecule, \( M \) the atomic/molecular weight, and \( E_g \) the energy gap.

In Fig. 14 the IMFP is calculated from Eq. (A3) for different metallic and organic systems; the parameters used are summarized in Table II. The curves for the metals display the lowest IMFP, whereas the IMFP for organic compounds can be up to a factor of 2 larger. Thus for the interpretation of photoemission results of organic compounds the universal curve for elements gives values which are too small. \( C_{60} \) in particular, is expected to show a relatively high IMFP, in contrast to earlier assumptions.

**TABLE II.** Parameters used for the TPP-2M equation. Values of the parameters \( \beta \), \( \gamma \), \( C \), and \( D \) were calculated, except for paraffin and iron, where the parameters were taken from fits of Eq. (A3) to experimental IMFP data. For cases in which \( E_p \) was calculated from the given values for \( N_V \), \( \rho \), and \( M \), the resulting value is set in parenthesis.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \beta ) (eV(^{-1}) Å(^{-1}))</th>
<th>( \gamma ) (eV(^{-1}))</th>
<th>( C ) (Å(^{-1}))</th>
<th>( D ) (eV Å(^{-1}))</th>
<th>( \rho ) (g cm(^{-3}))</th>
<th>( M )</th>
<th>( N_V )</th>
<th>( E_p ) (eV)</th>
<th>( E_g ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (amorph)</td>
<td>0.0141</td>
<td>0.135</td>
<td>1.36</td>
<td>39.5</td>
<td>2</td>
<td>12</td>
<td>4</td>
<td>(23.5)</td>
<td>1.6</td>
</tr>
<tr>
<td>graphite</td>
<td>0.0157</td>
<td>0.129</td>
<td>1.390</td>
<td>40.1</td>
<td>2.2</td>
<td>23</td>
<td>(Ref. 66)</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>diamond</td>
<td>0.0080</td>
<td>0.102</td>
<td>0.902</td>
<td>29.0</td>
<td>3.51</td>
<td>12</td>
<td>4</td>
<td>(31.17)</td>
<td>5.4</td>
</tr>
<tr>
<td>( C_{60} )</td>
<td>0.0085</td>
<td>0.146</td>
<td>1.205</td>
<td>35.9</td>
<td>1.72 (Ref. 66)</td>
<td>26.4</td>
<td>(Ref. 66)</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>26-n-Paraffin</td>
<td>0.0160</td>
<td>0.175</td>
<td>1.01</td>
<td>14.9</td>
<td></td>
<td>18.8</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.0155</td>
<td>0.0742</td>
<td>0.991</td>
<td>30.5</td>
<td></td>
<td>30.6</td>
<td></td>
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</tbody>
</table>
BULK AND SURFACE CHARGE STATES OF K₃C₆₀

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1 O. Gunnarsson, Rev. Mod. Phys. 69, 575 (1997).
47 A. I. Liechtenstein, O. Gunnarsson, M. Knupfer, J. Fink, and J. F. 165420-15


58 In Fig. 4 we have demonstrated the coincidence between the C 1s and valence line shapes. In the spectra the photoelectrons have comparable kinetic energies. Since the C 1s line shape matches that of the HOMO-derived band, the surface and bulk contributions are comparable in both cases, and we can use this information to model the LUMO-derived PES data.


64 Of course, if a metal-insulator transition occurs (Ref. 61), we would only apply this model at lower temperatures, and would need to understand the changes in line shape expected in such a phase to make sensible conclusions of the consequences, though the presently proposed mechanism would remain active to a similar extent. Such a phase is at this point speculative, and a transition temperature has not been identified.


67 To good first approximation, assuming complete charge transfer from K to C60 (Ref. 56).

68 Including the spectra from a third angle does not materially improve the line-shape determination, since the scattering effects at high binding energy also change with angle.

69 This factor of 2 is not taken up explicitly in what follows, since it is automatically included in the experimental intensity measured here, and follows naturally for the C 1s and deeper valence spectra from the separation of the surface component into two subcomponents. It serves to explain, however, how the bulk states can easily be seen in the LUMO-derived spectrum.

70 The diameter of the sphere formed by the carbon atoms of C60 is 7 Å. In addition the size of the π-electron cloud associated with the carbon atoms has to be taken into account, which gives the van der Waals diameter of approximately 10 Å (Ref. 71).


