The Influence of surfaces and interfaces on the properties of C60 compounds

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Chapter 1

Unusual aspects of C\textsubscript{60} compounds

It was but a short time after the discovery of C\textsubscript{60} molecules (Buckminsterfullerenes or “Buckyballs”) \cite{1} and the development of methods for their large scale production \cite{2} that curious results began to appear concerning their physical properties. For instance, not only do they display metallic behaviour when compounded with certain other elements like alkali metals \cite{3}, these compounds even became superconducting \cite{4} at temperatures as high as the best conventional superconductors, and were in this respect only surpassed by the cuprate superconductors, discovered just a few years before \cite{5}.

In this thesis we shall mainly concentrate on the electronic structure of these alkali fullerides, and especially on the superconducting K\textsubscript{3}C\textsubscript{60} and Rb\textsubscript{3}C\textsubscript{60} compounds. It is clear that even after almost ten years of experimental and theoretical work, the path to understanding the electronic properties of these compounds is far from straight-forward \cite{6}.

To give a complete overview here of all measured and calculated properties of C\textsubscript{60} compounds would be a substantial undertaking. Instead, the reader is referred to the many reviews, for instance Refs. \cite{7–13}, on different aspects of C\textsubscript{60} that appeared over the years. A few of the basic molecular and solid-state properties of C\textsubscript{60} and various alkali-C\textsubscript{60} compounds will be discussed here, to serve as a general introduction to the more detailed studies presented in later chapters.

1.1 Molecular and solid-state properties of C\textsubscript{60}

Topologically, the C\textsubscript{60} molecule is a truncated icosahedron (which consists of 12 pentagons and 20 hexagons) with a carbon atom at each of the identical vertices, as shown in Fig. 1.1. Together with the other members of the fullerene
family \((C_{70}, C_{76}, \ldots, \text{bucky-onions, carbon nanotubes, etc.})\) it represents the purest form of carbon known, not presenting any dangling bonds for interaction with the surroundings, unlike graphite and diamond, the other known forms of carbon. The diameter of the molecule, measured through the carbon nuclei, is about 7 Å. With 120 symmetry operations, the truncated icosahedron is of all regular polyhedra the one closest to spherical.

Pure \(C_{60}\) crystallizes in an fcc (face-centered cubic) close-packed structure, as one would expect from nearly spherical molecules that are only weakly bonded by Van der Waals forces. Indeed, above about 250 K the molecules rotate freely [15] and the lattice truly has an fcc symmetry on timescales larger than the typical rotation period, which is in the picosecond range [16]. Below 250 K, most rotational degrees of freedom freeze out and the total symmetry is lowered to simple cubic. In this phase the molecules are still able to flip between two stable positions, but below 90 K this also stops [17]. In most studies, the lowered symmetry (the so-called merohedral order) is neglected, but it may be important for some of the more subtle effects.

Figure 1.2 shows the energy levels of an isolated \(C_{60}\) molecule, obtained from Hückel calculations [19], where the labels on the right indicate the symmetry of the orbital and the number of dashes the degeneracy [20]. In the neutral state, the \(h_u\) and \(t_{1u}\) levels in the middle are the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO), respectively. Even if the molecule is not neutral these labels are often retained. The
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$g_g + h_g$ level is usually called the HOMO−1 level.

Since, electronically, the neutral C₆₀ molecule is a closed-shell system, and the interactions between the C₆₀ molecules are small, the solid is a band insulator with a band-gap of about 2.3 eV [21]. Early local-density approximation (LDA) band structure calculations greatly underestimated the gap, finding values of 1.5 eV [22] and even 1.2 eV [23]. Later, quasiparticle (GW) calculations, that include correlation effects in a more correct way than LDA only, increased the gap to 2.15 eV [24], which is much closer to the experimental value. Because of the small overlap between the electronic states of neighbouring molecules, most of the molecular-orbital character is preserved in the solid. The bands that are formed are narrow, of the order of 0.5 eV, and well-separated from each other. This is clearly observable in the photoemission spectrum in Fig. 1.3, which, at the moment, can simply be regarded as a plot of the density of states versus the binding energy.

Because of the large diameter of the C₆₀ molecules, the interstitial cavities are large enough to accommodate several species of atoms without destroying the basic C₆₀ lattice. In an fcc lattice there are three interstitial cavities per primitive unit cell, one with octahedral symmetry and two with tetrahedral symmetry, making it possible to form compounds of the general form AₓBᵧC₆₀, with A and B metal atoms. The terms *intercalation* and *doping* are frequently used to describe the process of filling the interstitial cavities, although both are somewhat inappropriate, since we are not merely introducing impurities but
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Many metal-$C_{60}$ compounds have been produced, but most emphasis has always been placed on alkali (and to a lesser degree on alkaline-earth) compounds, since these seem to have the most interesting physical properties. Whether a certain compound will form is determined for a large part by the size of the atom or ion relative to the size of the interstitial cavities. The nearest-neighbour distance in pristine $C_{60}$ is 10 Å, so if the molecules are regarded as hard spheres, it is easy to figure out that the radii of the octahedral and tetrahedral cavities are respectively 2.1 Å and 1.1 Å. From all alkali atoms, only potassium and rubidium will fit comfortably in both, to make $K_3C_{60}$ and $Rb_3C_{60}$. Caesium is too big (especially for the tetrahedral sites) to fit in without distorting the lattice, while lithium and sodium are so small that they prefer to form more complicated structures where interstitial cavities are multiply occupied. Various ternary compounds of the form $A_1B_2C_{60}$, now with $A$ and $B$ different, and even solid solutions like $A_{3-x}B_xC_{60}$ have also been made. The latter are particularly useful as they make it possible to change the average lattice constant in a continuous way.

When trying to fit more than three K or Rb atoms per buckyball into the lattice, a structural phase transition occurs, from fcc (face-centered cubic) to bcc (body-centered cubic). The bcc structure is less close-packed than the fcc structure, providing more room for interstitial atoms. Per $C_{60}$ there are now

Figure 1.3: Typical photoemision spectrum of undoped $C_{60}$. 
six identical interstitial cavities, each with a distorted tetrahedral surrounding. Completely filling those cavities with an alkali element A, we end up with $A_6C_{60}$. Incomplete filling leads, at least around room temperature, to the formation of $A_4C_{60}$, which can be seen as an ordered defect structure of $A_6C_{60}$, with the symmetry lowered to bct (body-centered tetragonal). It seems that at room temperature these two ($K_4C_{60}$ and $K_6C_{60}$) are the only stable phases above $K_3C_{60}$. If this is correct then any alkali concentration in between will lead to phase-separation into $K_4C_{60}$ and $K_6C_{60}$.

1.2 Electronic properties of $A_3C_{60}$

Of all $C_{60}$ compounds, $K_3C_{60}$ and Rb$_3$C$_{60}$ have by far attracted the most interest, because of their unexpected conducting and superconducting properties. It is mainly for their relatively low resistivity, and its positive temperature coefficient, that these compounds are commonly called “metallic”. We shall see, however, that these compounds do not behave like common metals in many respects, and that calculating parameters in the ways usually employed with metals can sometimes yield surprising results.

Although we will refer mainly to $K_3C_{60}$ (the most widely studied of the two) in the rest of this chapter, it should be implicitly understood that almost all arguments are applicable to $Rb_3C_{60}$ just as well, since they are very much alike in most respects.

It is generally accepted that the alkali atoms (at least in the case of K and Rb) are complete ionized, having all donated their outer $s$ electrons to the empty $C_{60}$ conduction band. The 1+ alkali ions left behind are electronically inert, their highest core-levels having binding energies of 15–20 eV, way below the valence band, and their lowest electron affinity states are higher than the relevant conduction band structures.

As said before, the property that first catches the eye in the $A_3C_{60}$ compounds is their good conductivity. To get some feeling on how well they compare to conventional metals it is instructive to try to determine some of the characteristic parameters, like the mean free electron path, in a simple semiclassical Drude-like model.

We can make a crude estimate [25, 26] for the electronic mean free path $l$ from the resistivity $\rho$ and the electron density $n_e$, using the Drude expression $\sigma = n_e e^2 \tau / m$, with $\sigma = 1 / \rho$ the conductivity, $\tau$ the mean scattering time, $e$ the electron charge and $m$ the electron mass. Assuming a spherical Fermi surface, the electron density is $n_e = g k_F^3 / 3 \pi^2$, with $g$ the orbital degeneracy of the conduction band (which is 3 for $C_{60}$), and $k_F$ the Fermi wavenumber. The mean free path is given by $l = v_F \tau$, where $v_F$ is the Fermi velocity $\hbar k_F / m$. 

Combining everything, we obtain the expression

\[
l = \frac{\hbar}{e^2} \left( \frac{3\pi^2}{gn_e^2} \right)^{1/3} \frac{1}{\rho}.
\]

The alkali atoms are completely ionized, so we can calculate the electron density from the lattice constant (14.24 Å in K₃C₆₀), and using the lowest resistivity values reported in the literature (about 0.5 mΩ cm just above \( T_c \) [27]), we find a mean free path of about 7 Å. This is of the order of one buckyball diameter, indicating that there is very strong intra-molecular electron-electron or electron-phonon scattering. In fact, this partially invalidates our initial assumptions that we could describe the system as an independent-electron gas with a well-defined Fermi surface. At higher temperatures, the mean free path calculated from the resistivity is even lower. At room temperature, \( l \) may have decreased by a factor of two, so that it is considerably shorter than the molecular spacing.

Although there is a large variation between samples prepared in different ways, generally, the temperature dependence of the resistivity below, say, room temperature is roughly quadratic, suggesting that electron-electron scattering is dominant. To fit this data, however, one has to assume an electron-electron coupling in the order of 1 eV [28], which is larger than the bandwidth of the material, and so again inconsistent with the assumption of a free electron gas. Other explanations for this behaviour exist, however. It was suggested [29] that the quadratic dependence is a kind of “artefact” caused by measuring the resistivity at constant pressure. When converted to constant volume, the resistivity vs. temperature relation appeared linear, although this was only investigated for a rather small temperature interval.

Above room temperature the resistivity increases roughly linear with temperature [25], as expected in the presence of electron-phonon scattering. Normally, one would expect the resistivity to saturate as function of temperature when the mean free path becomes of the order of the lattice spacing. Instead, the resistivity of K₃C₆₀ seems to continue to increase almost linearly up to the highest temperatures investigated (about 800 K), although it is reported that Rb₃C₆₀ does show some signs of saturation [30]. Very recently, Gunnarsson and Han [31] reported the results of quantum Monte Carlo calculations where they found that, contrary to what is expected in the semi-classical picture, the resistivity does not have to saturate at all when the mean free paths becomes shorter than the lattice spacing. It seems that quantum effects make the semi-classical Boltzmann equation qualitatively survive when, classically, it is supposed to break down.

Another interesting puzzle is found in the optical conductivity, where the Drude-weight at low frequencies turns out to be about an order of magnitude
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smaller than expected if A₃C₆₀ were a conventional metal [32,33]. This could indicate that the effective charge-carrier density is much lower than three per C₆₀ molecule, or that the normal-state properties like the band mass are renormalized due to strong electron-phonon or electron-electron interactions. In the case of large electron-mass renormalization, a strong coupling with low-frequency phonons is expected, which is not consistent with the observation that the superconducting state should be treated in the weak-coupling limit [32]. Also, theoretical calculations of the optical conductivity point out that the introduction of a strong electron-phonon coupling is actually not sufficient to explain the large reduction of the Drude weight [33].

A useful technique to gain insight into the character of the charge carriers is the Hall effect. In a simple Drude-like model of free charge-carriers, the Hall coefficient \( R_H \), which is the proportionality factor of the Hall voltage to the current and the applied magnetic field, has the simple form \( R_H = 1/ne \), for charge carriers with density \( n \) and charge \( e \).

In this model, the sign of the Hall effect reflects the sign of the charge carriers, which could, in a half-filled system like K₃C₆₀, either be electrons or holes. Two Hall effect studies have been published to date, one on K₃C₆₀ [34], and one on both K₃C₆₀ and Rb₃C₆₀ [35], yielding rather surprising results. Although not completely in agreement with each other, they both indicate that the charge carriers may effectively change sign as function of temperature, something that is not expected in typical metals. In both cases it is suggested that disorder may play an important role.

In summary, we can say that, although K₃C₆₀ displays some metallic characteristics, it is certainly an unusual metal. The large variety in the experimental data taken by different groups also indicates that the method of sample preparation could have a large influence, for instance because of small differences in doping concentration or sample homogeneity. It has been suggested already in an early stage [34] that the granularity of the materials, which may be intrinsic property, could play a dominating role in determining the electronic properties.

1.3 Superconductivity

One of the biggest surprises that the alkali-doped fullerides had in store was their superconductivity, the discovery of which came just after that of another class of superconductors, the high-\( T_c \) cuprates or HTC’s. Not only the occurrence of superconductivity was unexpected, also the height of the transition temperature is remarkable: 19 K for K₃C₆₀, 30 K for Rb₃C₆₀, up to 33 K for RbCs₂C₆₀ [36], and even 40 K for Cs₃C₆₀ under pressure [37]. At first, it was not clear whether the fullerides belonged to the category of the conventional
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Figure 1.4: The superconducting transition temperature $T_c$ as function of the C\textsubscript{60} valence. In (a) the different valencies were effected by changing the ratio between mono- and divalent dopants, and in (b) by electrostatically changing the electron concentration in a field-effect transistor structure built on top of a C\textsubscript{60} single crystal (where the light band approximately represents the transition). (a) from Yildirim et al. [41], (b) from Schön et al. [42].

Bardeen-Cooper-Schrieffer (BCS) superconductors or to the HTC’s, or perhaps formed a whole new class by themselves. The general consensus at the moment, based, among others, on the investigation of the carbon isotope effect [38–40], is that the electron-electron attraction responsible for the superconductivity at least is phonon-mediated, unlike what is generally accepted for the HTC’s. The normal-state resistance vs. temperature behaviour, however, is certainly more reminiscent of the HTC’s than of normal metals.

The only fullerides that display superconductivity (with just a few exceptions) are those where the C\textsubscript{60} is trivalent. An interesting question is how critical this valence is for the superconductivity. Yildirim et al. [41] conducted a study where the C\textsubscript{60} valence was varied around 3, without changing the crystal structure, by doping with a combination of monovalent and divalent cations. It was found that the superconducting transition temperature $T_c$ is sharply peaked around a doping level corresponding to three electrons per C\textsubscript{60} molecule, as shown in Fig. 1.4a. On the other hand, Schön et al. [42] recently demonstrated that, in a field-effect transistor made from a single crystal of C\textsubscript{60}, superconductivity could be induced by electrostatic doping, probably in the topmost monolayer. In this case, not only does the superconducting region turn out to be much broader (Fig. 1.4b), $T_c$ itself hardly varies over the whole range. It is not clear at the moment whether this is an effect of, for instance, the lowered symmetry or the different nature of the doping, or that it is actually an
intrinsic property of fulleride superconductors. Something that may be of importance is that, when going off-stoichiometric in a chemically doped system, the vacancies or extra alkali ions introduce impurity potentials, which may have a magnitude of several volts at the neighbouring $C_{60}$ cites. Even when they are strongly screened, these potentials will probably remain large compared to the bandwidth, and so act as charge traps, possibly prematurely destroying the superconductivity. In the Schön experiment those doping-dependent traps are not present, and as such it may be a cleaner system for demonstrating the doping dependence of $T_c$.

### 1.4 Other alkali-$C_{60}$ compounds

In contrast to $K_3C_{60}$, $K_1C_{60}$ as well as the whole range of body-centered compounds, from $K_4C_{60}$ up to $K_6C_{60}$ are non-metals. $K_4C_{60}$ is a narrow-band semiconductor with a band gap of about 0.5 eV [43], in sharp contrast to the general idea that a partially filled band should produce a metal. Also more detailed band-structure calculations [44] predict $K_4C_{60}$ to be a metal.

$K_1C_{60}$ is a semiconductor too, but much less is known about it, mainly because its structure and phase diagram are much more complex than any of the other $C_{60}$ compounds [45]. Different phases are found, ranging from simple rocksalt at high temperature (above, say, 150°C [46, 47]) to dimer [48] and polymer [49] phases at low temperature. Which low-temperature phase is formed depends strongly on the rate of cooling. At low temperatures there is also a strong tendency to phase-separate into $K_3C_{60}$ and so-called $\alpha$-$C_{60}$, which is a solid solution containing up to a few percent of potassium [47, 50–52].

When the potassium concentration reaches its largest value in $K_6C_{60}$, the $t_{1u}$ LUMO-derived band is completely filled. It is again a band insulator, and the resistivity may be close to the value of pure $C_{60}$. This is a very difficult system to study because of its extreme reactivity, making the samples deteriorate rapidly even in the best vacuum obtainable.

What happens electronically in between $K_4C_{60}$ and $K_6C_{60}$ is largely unknown. Even though the doping concentration can be varied continuously, there are no other metallic phases in this region, although there may be a shallow resistance minimum about halfway when backdoping the sample by adding more $C_{60}$ [45]. Even at a fixed doping level, the resistivity changes in time, and seems to have a large temperature hysteresis. Together with the observed difference in forward and backward doped samples, this suggests that these samples are not in equilibrium, and that phase separation (probably into $K_4C_{60}$ and $K_6C_{60}$) plays an important role.
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The failure of the bandstructure calculations to describe the various alkali-C$_{60}$ compounds led to the suggestion that, because of the weak coupling between the molecules, the intra-molecular Coulomb interaction might play a significant role in establishing the electronic structure [21]. A large Coulomb interaction may actually invalidate the assumptions made in conventional band structure theory.

In conventional band-structure theory, every electron is presumed to move independently through a periodic potential dictated by the positive ion cores that make up the lattice, and the collective potential of all the other electrons together in a mean-field manner. These effectively single-particle theories, in which the correlations between the motions of individual electrons are neglected, work actually surprisingly well to describe large classes of solids, like semiconductors and many common metals.

There are, however, other classes of solids where the assumption of non-correlated electrons proves to be partially or completely invalid, and for which Coulomb interactions must be taken into account explicitly. These materials are commonly called (strongly) correlated electron systems. For instance, many transition-metal oxides, including the high-temperature cuprate superconductors (HTC’s) and giant magnetoresistance (GMR) compounds, typically manganates, fall into this category. Both from a fundamental point of view as well as application-wise these materials are attracting a large and growing interest at the moment. Because the electrons in these materials have to be treated as a true many-body system, in contrast to the one-electron models normally used to calculate band structures, the theoretical (and mathematical) framework is much more complicated, and generally very difficult or impossible to handle even numerically, let alone analytically. For this reason, there exists, at the moment, not a single all-compassing “theory” for correlated materials. Most work is done on various model-systems, each taking into account different interactions, while leaving out others.

One of the most basic ways of accommodating many-body aspects in a model is by introducing a correlation energy $U$ in the form of a Coulomb repulsion between pairs of electrons on one atom or molecule (which we shall collectively call a “site”). The long-range character of the electrostatic Coulomb interaction is neglected here, which may later on be compensated by introducing intersite interactions like a nearest-neighbour Coulomb interaction $V$.

The pair interaction $U$ can be shown to be equivalent to the energy it costs to move an electron from one part of the system to another, over a large distance.
Consider the following ground-state system in the tight-binding limit, consisting of \( M \) sites, in which every site has \( n \) electrons, for a total of \( N \) electrons in the whole system:

\[
\begin{array}{cccccccc}
  n & n & n & n & n & n & n & n \\
\end{array}
\]

For the moment we leave out the electron spin and consider each site as consisting of a single infinitely-degenerate orbital. Moving an electron from one site to another site far away, i.e., creating a non-local electron-hole pair, leaves us with

\[
\begin{array}{cccccccc}
  n & n-1 & n & n & n & n+1 & n \\
\end{array}
\]

The total Coulomb energy in the initial state is \( M \cdot \frac{1}{2} n(n-1)U \), while in the final state it is \((M-2) \cdot \frac{1}{2} n(n-1)U + \frac{1}{2} (n-1)(n-2)U + \frac{1}{2} (n+1)nU \). It is easy to work out that, whatever the ground-state occupation \( n \) is, the difference between the initial and final state, and thus the creation energy of an electron-hole pair, is always equal to \( U \).

To determine the magnitude of \( U \), the process of creating an electron-hole pair can be split up into two independent actions, namely removing an electron (which costs the ionization energy \( E_I \)), and adding an electron somewhere else (which gains the electron affinity \( E_A \)). The pair interaction \( U \) is then equivalent to the difference \( E_I - E_A \). These two processes, which create, respectively, an \( N - 1 \) and an \( N + 1 \) electron system, are commonly called photoemission and inverse photoemission processes.

An interesting question is now whether this “correlation” energy \( U \), that is not present in one-electron theories, may completely inhibit the movement of electrons (and hence cause the system to become insulating) under certain circumstances, even in a system that is not comprised of closed-shell atoms or molecules (and so, classically, would be a metal). One of the simplest models used to address this problem, for an array of atoms with only \( s \)-orbitals, is the Hubbard model \([53–55]\), described by the Hamiltonian

\[
\mathcal{H} = -t \sum_{\langle i,j \rangle, \sigma} (c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma}) + U \sum_i n_{i\uparrow}n_{i\downarrow},
\]

where \( t \) is the hopping integral (which is assumed to be equal for all sites), \( c_{i\sigma}^\dagger \) and \( c_{i\sigma} \) are the creation and annihilation operators for an electron at site \( i \) with spin \( \sigma \) (\( \uparrow \) or \( \downarrow \)), \( n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma} \) is the number operator, and \( \langle i, j \rangle \) signifies a sum over nearest-neighbours. The general solution of this model is unknown except in one dimension, and even there it is far from trivial, so we will not go very deeply into
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it here. Note also that the simple form of the Hamiltonian as presented above is not sufficient to describe a multi-orbital system like $C_{60}$. More complicated forms exist, incorporating orbital degeneracy, nearest-neighbour Coulomb interactions, polarizability, and so on [56–59].

Whether the system is a metal or an insulator depends on the relative magnitude of $U$ and the bandwidth $W$, where $W$ includes the hopping integral $t$ and the lattice connectivity. Consider an electron-hole excitation as described above. This excitation costs an energy $U$, but after this the electron and the hole it left behind are free to propagate through the lattice basically in a one-electron way, because the total potential of the $n$-occupied sites they encounter is again periodic. An energy $W$ (the one-electron bandwidth) is thus gained. If this gain is large enough, the system is likely to be a metal. The presence of the two energy scales $U$ and $W$ suggests that the quantity that governs the metallicity of the material is the fraction $U/W$. For $U/W \gtrsim 1$, it is energetically not favourable for an electron to move, and the system will become a so-called Mott-Hubbard insulator. The point at which the metal-to-insulator changeover occurs is usually called the Mott transition.

To experimentally determine whether a system is a metal or an insulator, and to determine the magnitude of the gap in the latter case, photoemission spectroscopy (PES) and inverse photoemission spectroscopy (IPES) are very powerful techniques. In photoemission, an electron is excited from the solid into the vacuum by a photon of a specified energy $h\nu$, leaving behind an $N-1$ electron system. Because the total energy is conserved, the energy of this system can be determined by measuring the kinetic energy of the outgoing electron. By repeating this experiment many times and counting the frequency of electrons in small kinetic energy intervals, a photoemission spectrum can be constructed, depicting the probability (or spectral weight) of all $N-1$ electron states as a function of their energy. Quite similarly, inverse photoemission, where an electron at a certain energy is injected and the outgoing photon’s energy is measured, probes the probability of all $N+1$ electron states. One of the very appealing characteristics of photoemission and inverse photoemission spectroscopy is that they are closely related to the one-particle Green’s functions, providing a direct link between theoretical and experimental results [60].

Very useful diagrams for understanding correlated electron systems are obtained by plotting the photoemission and inverse photoemission spectra back-to-back, with their zero-energy points coinciding. The chemical potential $\mu$ is then by definition situated at the meeting-point, as it is the point at which the costs of both adding or removing an electron are zero. In the case that there is actually a non-zero spectral weight at the chemical potential, the system can be called a metal, and we can define the Fermi level $E_F$ as being equivalent to the chemical potential.
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Figure 1.5: Photoemission and inverse photoemission spectra as expected in a Hubbard model for different values of $U/W$. The grey shading indicates occupied states. Adapted from Morikawa et al. [61].

Figure 1.5 shows some impressions of the expected photoemission and inverse photoemission spectra of a partially-filled single-band Hubbard system for increasing $U/W$ ratio. In the limit of $U \to 0$ (top), we are right back at the single-electron picture, and the system is clearly metallic. In this case the combined PES/IPES spectrum is equivalent to the conventional density of states as described in one-electron band-structure theory. In the other limiting case, i.e., for $U \gg W$ (bottom), we are in the Mott-Hubbard insulator regime. The electronic states are split up in what are called the Upper Hubbard Band (UHB) and the Lower Hubbard Band (LHB). At the chemical potential there are no states, confirming the insulating character. Note that, although the picture looks similar to that of the density of states of a band insulator in one-electron theory, it describes a completely different system. The UHB and LHB on either side of the chemical potential represent one and the same partially-filled band, respectively in the $N+1$ and the $N-1$ electron systems. The $N$ electron system does not enter in this picture at all, and neither do electron-number-conserving (e.g., optical) excitations.

What happens in the intermediate regime, where $U \approx W$ (Fig. 1.5, middle)
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is still a focus of intensive research, both theoretically and experimentally [62]. In Hubbard’s original view [55], the bands would simply coalesce as shown in the middle plot. More recent calculations may yield quite different behaviour, like, for instance, in the Brinkman-Rice picture [63] (left), where the band is considerably narrowed with respect to the one-electron bandwidth. Even more recently, theories like dynamical mean-field theory [64] (right) predict the emergence of very narrow features near the Fermi level when $U$ and $W$ are of the same order.

![Figure 1.6](image)

**Figure 1.6:** (a) Schematic representation of an Auger process in $C_{60}$. A C 1$s$ core electron is removed, after which an electron from the HOMO-derived valence band drops into the core hole, thereby exciting another electron from the valence band into the vacuum. The final state has two holes in the valence band, localized on one site. (b) The KVV Auger spectrum of $C_{60}$ and the self-convolution of the valence-band photoemission spectrum, shifted to find a Coulomb interaction $U$ of 1.6 eV. Part (b) from Lof et al. [21].

To see where in this picture $C_{60}$ fits, the intra-molecular Coulomb interaction $U$ and the one-electron bandwidth $W$ have to be determined. This could be done directly with photoemission and inverse photoemission, but, apart from the technical difficulties of inverse photoemission, this is complicated by the fact that neutral $C_{60}$ is a closed-shell system, so that there will be an additional energy $\Delta$, the molecular orbital splitting, between the observed upper and lower Hubbard bands. Although these problems can be solved, as will be shown in Chapter 5 of this thesis, the initial determination of $U$ by Lof et al. [21] and Brühwiler et al. [65] was done in a slightly different way. Instead of comparing the photoemission $(N-1)$ and inverse photoemission $(N+1)$ spectra, they used Auger spectroscopy. In an Auger process (illustrated in Fig. 1.6a) an electron from a core-level is removed by photoemission or electron impact, after which another electron from a higher level, in this case from the valence band, drops
down into the core hole, transferring its excess energy to a third electron by exciting it into the vacuum level. The Coulomb energy $U$ is the energy difference between the resulting $N - 2$ electron final state and an $N - 2$ electron system with the holes on two different sites, as can be easily worked out by counting the number of on-site electron pairs in either situation. The energy spectrum of the latter two-hole system can be simulated by self-convoluting the normal valence-band photoemission spectrum, since that self-convolution basically is the probability of encountering two uncorrelated one-hole systems at a certain total energy, as a function of that energy. As can be seen in Fig. 1.6b, the self-convoluted photoemission spectrum turns out to coincide quite nicely with the Auger spectrum if it is shifted by about 1.6 eV, giving us the sought-after Coulomb interaction. The fact that this shift is almost identical for all peaks in the Auger spectrum indicates that the Coulomb interaction is not strongly dependent on which orbitals are involved. It should be noted that the found $U$ is the effective value in the solid state. The Coulomb interaction of the free isolated molecule (e.g., in the gas phase) can be determined directly from the ionization energy $E_I$ (7.6 eV [66]) and the electron affinity $E_A$ (2.65 eV [67]), decreased by the molecular orbital splitting $\Delta$ ($\approx 1.5$ eV), giving us a molecular $U$ of about 3.5 eV. This molecular value is screened in the solid-state to 1.6 eV by the high polarizability of the surrounding $C_{60}$ molecules (about which more in Chapter 5).

The one-electron bandwidth $W$ can be calculated with conventional (LDA) band structure theory [44], giving values of the order of 0.5 eV, which seems to be consistent with experimental values found with, for instance, photoemission on pure $C_{60}$ (Fig. 1.3). If one assumes that the hybridization between the $C_{60}$ molecules (and therefore $t$ and $W$) is not strongly modified by the presence of the alkali ions, this implies that the ratio $U/W$ for any $K_xC_{60}$ is about 3, clearly placing it into the Mott-Hubbard insulator regime.

Figure 1.7 shows schematically the expected combined photoemission and inverse photoemission spectra for pure $C_{60}$, $K_4C_{60}$, $K_4C_{60}$ and $K_6C_{60}$ in the Mott-Hubbard picture as well as in the one-electron (rigid band) picture. Contrary to the rigid-band case, where the Fermi level shifts through the LUMO-derived band as the valence of the $C_{60}$ increases, in the Mott-Hubbard system the spectral weight at the Fermi level remains zero, while the spectral weight of the upper Hubbard band is transferred to the lower Hubbard band.

If one now compares the photoemission-side of these curves to experimental photoemission spectra, shown in Fig. 1.8, a remarkable discrepancy shows up. The $C_{60}$, $K_4C_{60}$ and $K_6C_{60}$ spectra at first sight look quite similar to the Mott-Hubbard cases sketched in Fig. 1.7, apart from a small and rigid shift for $K_4C_{60}$. One of the most important observations here is that the HOMO peaks of $C_{60}$ and $K_6C_{60}$ line up exactly, demonstrating that the Fermi level did not pass
Chapter 1. Unusual aspects of $C_{60}$ compounds

通过LUMO带，清楚地展示了这些化合物的关联性质。相比之下，$K_3C_{60}$光谱有一个清晰的费米能级，并且更接近于刚性带图，而不是Mott-Hubbard图。在更仔细的检查中，还有其他的差异。在所有钾掺杂样品中，分子轨道峰的形状被修改。这可能与库伦相互作用并不完全地轨道-独立，以及可能也与碱原子势能或晶体对称性部分地提升轨道退激发有关。同样重要的是交换相互作用在HOMO和部分填充LUMO之间。这些修改尤其明显在$K_3C_{60}$中，所有峰值显著变宽，要么导致$K_3C_{60}$呈金属性。

不同的场景已被提出以解释这种差异。其中一个最新的是Gunnarsson等人[68–73]提出的，即在退激发系统如$C_{60}$中，Mott相变发生的标准条件是
1.5. Coulomb interaction and Mott-Hubbard insulators

modified from $U/W \approx 1$ to $U/W \approx \sqrt{G}$, with $G$ the orbital degeneracy. This brings the $K_xC_{60}$ compounds very close to the transition, opening the door, so to speak, for more subtle effects to come in and play important roles in determining the character of the material. These include factors like the different lattice structure and spacing, the influence of the alkali ions [70] and the precise balance between Jahn-Teller effects and Hund’s rule coupling [73]. All in all, they seem to favour $K_3C_{60}$ to be metallic, and $K_4C_{60}$ to be insulating.

A much older idea is that, although $K_3C_{60}$ may be a correlated system, it is always somewhat off-stoichiometric [21]. X-ray diffraction [74] and NMR studies [75,76] suggest that a certain percentage of vacancies is always present in (in this case) Rb$_3$C$_{60}$, making it approximately Rb$_{2.94}$C$_{60}$, although it has also been argued that the effects seen in NMR cannot be associated with alkali vacancies at all [77]. We will first briefly review the effect of non-stoichiometry on a Mott-Hubbard insulator.

Figure 1.8: Photoemission spectra of $C_{60}$, $K_3C_{60}$, $K_4C_{60}$ and $K_6C_{60}$.
1.6 Doping a Mott-Hubbard insulator

From the Hubbard model we learn that it is possible to have an insulator with a partially filled valence band. The argument only holds, however, when that band has an integer occupation. For a non-integer occupation, e.g., in a doped system, the system consists (in the tight-binding limit) of a mixture of, say, \( n \) and \( n + 1 \) electron sites. It is now always possible to perform the combined action of adding and removing an electron, effectively moving an electron from one site to another, without change in total energy, as illustrated here:

\[
\begin{array}{cccccc}
  n & n+1 & n & n+1 & n & n+1 \\
  \downarrow \text{PES} & & & & \uparrow \text{IPES} \\
  n & n & n & n+1 & n & n+1 \\
\end{array}
\]

The total energies of the initial and final states are the same, so an electron-hole excitation can be made at no cost, making the system metallic for any value of the Coulomb interaction \( U \).

The consequences for the expected photoemission and inverse photoemission spectra of \( K_xC_{60} \) are best illustrated in the limit that \( W \) is negligible compared to \( U \). This is done schematically in Fig. 1.9, with \( x \) varying between 2 and 3. More extensive theoretical treatments are given by, for instance, Eskes and Meinders [56,78,79]. The initial and final states corresponding to each peak are indicated, where \( H^n \) and \( L^n \) signify \( n \)-occupied HOMO and LUMO levels. The \( U \)'s between the different orbitals are assumed to be equal. To construct those spectra, the number of ways that an electron can be added to or removed from a given ratio of \( n \) and \( n + 1 \) electron sites is counted, and plotted as a function of the final-state energy.

As soon as any non-stoichiometry is introduced into, say, the \( K_xC_{60} \) situation at the top, the Fermi level moves into the bottom of the former upper Hubbard band \( (L^2 \to L^3) \), while new spectral weight appears on the photoemission side at \( E_F \), due to the \( L^3 \to L^2 \) transition that is now possible, and which costs the same amount of energy that is gained in the \( L^2 \to L^3 \) transition. The system is now a metal with a well-defined Fermi energy. At the same time, the former lower Hubbard band moves a distance \( U \) below \( E_F \), and at a distance \( U \) above \( E_F \) spectral weight appears in the inverse photoemission spectrum, corresponding to the \( L^3 \to L^4 \) transition, and likewise a distance \( U \) above the HOMO peak, corresponding to \( H^{10}L^3 \to H^9L^3 \). As a result, all peaks from the stoichiometric case have developed satellites a distance \( U \) to the right. Upon
1.6. Doping a Mott-Hubbard insulator

Figure 1.9: The expected photoemission and inverse photoemission spectra of the HOMO- and LUMO-derived bands of $K_xC_{60}$ as it is doped from an initially stoichiometric composition of $K_2C_{60}$ (top) to another stoichiometric composition $K_3C_{60}$ (bottom). HOMO and LUMO states with $n$-occupation are labelled $H^n$ and $L^n$. Where not indicated, the HOMO occupation remains the same. The values of $U$ and $\Delta$ are slightly modified with respect to the real $C_{60}$ values to separate out the peaks. See also [56].
further doping, more and more spectral weight is transferred from the original peaks to these satellites, and finally the original peaks vanish completely when a new stoichiometric state is reached, at which time the system is again an insulator.

In a vacancy-model of $K_xC_{60}$, the electronic structure would look similar to the one but lowest graph in Fig. 1.9. A problem with such a model, however, is that, if those vacancies are to be responsible for the metallic and superconducting behaviour, one would expect properties like resistivity and $T_c$ to depend strongly on their concentration. These properties, however, show remarkably little variation between samples prepared by different groups in sometimes completely different ways. One would have to envision some sort of intrinsic defect-producing mechanism, not subject to variations in preparation method. Also, in the study of Yildirim et al. [41], where the electron concentration $n$ is varied around 3, the highest $T_c$ is claimed to occur at precisely $n = 3.0$, and goes down sharply as soon as $n$ starts deviating from this value. Finally, in the study presented in Chapter 6 of this thesis, it is shown that the samples with the highest conductivity and $T_c$ are those that have the highest concentration of potassium possible in an fcc $C_{60}$ lattice, and so, the lowest number of vacancy sites.

Because experimental photoemission spectra of $K_xC_{60}$ do in fact look much like some of the off-stoichiometric cases in Fig. 1.9, it may be speculated that even if the bulk is very close to stoichoimetric, there may be intrinsic reasons that the surface, which is in practice the only part of the sample that is probed by photoemission, is not. In Chapter 6 we will show that these reasons indeed exist, and that the surface of $K_xC_{60}$ has to be off-stoichiometric and metallic, irrespective of the size of $U$ or the presence of vacancies in the bulk.

1.7 $K_xC_{60}$ monolayers

Before turning to the study of bulk $A_xC_{60}$ systems, we first present (in Chapters 3-5) the results of studies performed on monolayers of $C_{60}$, doped and undoped, on metal surfaces. The reason to start with monolayers is that they provide, if correctly prepared, an environment to test ideas about the effects of electron correlations that is much better defined than most “bulk” samples, which are usually complicated by things like low diffusion rates, non-equilibrium phases and phase-separation.

Because of their closeness to the metal-insulator transition, it should be clear that the properties of $K_xC_{60}$ compounds are expected to be very sensitive to modifications to the parameters responsible for that transition, like the Coulomb interaction $U$, the bandwidth $W$ (i.e., the inter-ball hybridization), and probably other contributions like the dimensionality of the system. By putting a
monolayer of C$_{60}$ molecules on top of a metal surface, we may be able to “tune” these parameters and observe the repercussions on the electronic structure.

In Chapter 3 the interaction of a C$_{60}$ monolayer with a metallic single-crystal surface is studied, showing, among other effects, a large deviation from the pattern of filling the LUMO band in a Mott-Hubbard insulator, as was sketched earlier. It seems that the metal surface effectively suppresses most of the correlation effects, resulting in large modifications in the spectral weight near the Fermi level.

The metal-C$_{60}$ interaction is studied in more detail in Chapter 4, by depositing the monolayers on different metals. The charge transfer from the metal to the C$_{60}$ turns out to depend on the species of metal, probably in a way related to its work function. By doping the monolayer with potassium, the hybridization with the metal seems to decrease, and at full doping it appears to be more or less electronically decoupled, making the element-specific modifications of the photoemission spectrum vanish.

The observation, made in Chapter 3, that the filling of the LUMO-derived band in a C$_{60}$ monolayer on a metal surface resembles more a rigid-band system than a correlated one, is quantified in Chapter 5. There, the Coulomb interaction $U$ is measured directly using photoemission and inverse photoemission spectroscopy, both for a C$_{60}$ overlayer on silver as well as for the bulk material. It turns out that the metallic substrate is capable of substantially reducing $U$ because of its high polarizability.

A very important “preparation” for the bulk measurements is to establish how surface sensitive the employed techniques actually are. If we want to study fullerides (or any other material, for that matter) with photoelectron spectroscopies, it is crucial to realize that the results of these techniques may not be representative for the electronic structure of the bulk material. Although the outgoing photoelectrons are already excited into the vacuum level, they still have to leave the solid. On their way to the surface (and even some time after they left it) they may experience all kinds of elastic and inelastic scattering. The deeper they originate, the higher the probability that they lose their kinetic energy information or do not reach the surface at all. Disregarding electron diffraction effects, the probability of reaching the surface from a depth $z$ without scattering is approximately proportional to $e^{-z/z_0}$, where $z_0$ is the so-called escape depth, which is related to the inelastic mean free path. For inverse photoemission spectroscopy similar arguments apply for the incoming electron.

An experimental photoemission spectrum will typically consist of contributions from several atomic or molecular layers, possibly having different electronic structures. To gain insight into which part of the system is actually observed, we have to know the intensity ratio of these contributions, which is governed by the escape depth. The escape depth is strongly energy and material dependent, and
it is not easy to give, \textit{a priori}, a good estimate of its value. However, by studying the photoemission spectrum from a single monolayer on a substrate that has a completely different but known spectrum, we should be able to single out the signal originating from the overlayer, and find the attenuation factor for signals coming from below. In Chapters 3 and 4 we will see that the escape depth is very small indeed, of the order of half a bucky-ball diameter, indicating that one should be very careful with linking bulk electronic structure to photoemission spectra.

References

REFERENCES

[20] For a more extensive overview of the molecular electronic structure of C_{60} see, e.g., B. Koopmans, Ph.D. thesis, University of Groningen, 1993
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