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Phil. Trans. R. Soc. Lond. A 1998 **356**, 231-247
doi: 10.1098/rsta.1998.0159

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The development of metallic behaviour in clusters on surfaces

By M. R. C. Hunt and R. E. Palmer
Nanoscale Physics Research Laboratory, School of Physics and Astronomy,
University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

The transition between metallic and insulating behaviour in three prototype nanometre scale systems, alkali metal monolayers adsorbed on graphite, C_{60} monolayers adsorbed on metal surfaces and small metal clusters on surfaces, are examined. The transition between metallic and non-metallic behaviour is shown to be governed by fundamentally different physical phenomena in each system, indicating the need to consider the precise details of individual systems. The power of the surface science techniques of electron energy loss spectroscopy (EELS) and photoemission spectroscopy (PES) for investigating metallic and insulating behaviour in nm scale systems is demonstrated via measurements made on the model systems. We also review the state-of-the-art in cluster beam deposition and show that it is now possible to create monodisperse supported cluster films, the electronic structure of which may be interrogated by EELS and PES.

Keywords: alkali-metal adsorption; cluster deposition; fullerene films; metal–non-metal transition

1. Introduction

Materials in which characteristic lengthscales are measured in nm (‘nanoscale materials’), be they clusters, thin films or large molecules (such as fullerenes or nanotubes), often display electronic properties that are radically different from those of the equivalent bulk material and which, furthermore, vary strongly with size. Clusters, for example, show strongly size-dependent properties (de Heer 1993), which can be probed by photoelectron spectroscopy (PES) (Wertheim 1990). The measurement of the response of a system to the addition or removal of charge is an important means of determining metallicity (Wertheim 1990). In the fullerenes, which are insulating in the solid phase (for a review, see Dresselhaus *et al.* 1996), changes in molecular size and symmetry significantly change electronic structure, which may be followed by a range of spectroscopic measurements.

Strong size-dependent variation in the electronic structure of nanoscale materials, if successfully exploited, should pave the way for precise control of the properties of materials assembled from these species and thus lead to a potentially huge range of applications, such as novel catalysts, gas sensors, electronic materials, etc. However, if these applications are to be realized, the effect of interaction of a nanoscale species with its supporting substrate (necessary for the fabrication of solid-state materials) must be quantified. In this paper we shall pay specific attention to metallic and insulating behaviour in three related nm scale model systems. The first, an alkali metal film adsorbed on the graphite (0001) surface, is an example of an insulator–metal transition in a two-dimensional system, driven by the interaction between the

Phil. Trans. R. Soc. Lond. A (1998) **356**, 231–247
Printed in Great Britain

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metal atoms and their supporting substrate. We then turn our attention to C_{60}, which can be regarded as the prototypical 'molecular cluster'. The interaction of C_{60} with a variety of metal surfaces and dopants is examined, and we show that it is possible to gain considerable control over the electronic structure of single C_{60} layers, once more exploiting the interaction between the adsorbed thin film and its substrate. Finally, we examine the possibilities for measuring the insulator–metal transition of supported size-selected clusters, paying particular attention to the role that electron spectroscopy can play in determining cluster electronic properties.

2. EELS and PES as probes for metallic and insulating behaviour

The two primary techniques with which the data presented in this paper were acquired are electron energy loss spectroscopy (EELS) and photoemission spectroscopy (PES). In this section, we shall briefly describe the salient features of these techniques and the information that may be furnished by them.

The basic principle of low energy EELS (Ibach & Mills 1982) is to direct a highly monochromatic, highly collimated beam of electrons at a surface and to study the energy distribution of the backscattered electrons. The small mean-free path of electrons in condensed matter results in a high degree of surface sensitivity—the backscattered electrons will have interacted only with the topmost atomic or molecular layers of the surface under investigation. A typical low energy EEL spectrometer can operate with incident beam energies in the range 0.2–300 eV and with a resolution as fine as 0.5 meV, allowing both vibrational and electronic excitations of a surface to be measured.

One of the major advantages that EELS possesses over optical techniques for the measurement of electronic excitations of nanoscale materials is that energy loss events are not limited to the excitation of dipole active transitions. Dipole forbidden transitions are also accessible and, in consequence, more complete information regarding the electronic transitions of the investigated material may be obtained. An example of the power of the EELS technique is demonstrated in figure 1, which shows a series of electronic excitation spectra from a variety of C_{60} films (Hunt *et al.* 1995, 1997). The bottom spectrum (figure 1*a*) is from a 5 monolayer (ML) film of C_{60} grown on a gold substrate. The spectrum from this film is the same as that from a bulk C_{60} sample and shows a clear region of almost zero intensity between the last vibrational excitations and the first electronic excitation. This region corresponds to the band gap of an insulating film. The small features, marked with arrows, before the onset of the strong peak at 2.2 eV correspond to excitonic transitions within the insulating film (Hunt *et al.* 1997; Cepek *et al.* 1996). The peak at 2.2 eV corresponds to the transition between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) derived bands of the solid C_{60} film. This transition is dipole inactive and, in consequence, is absent from optical spectra obtained from C_{60} films and crystals (Wang *et al.* 1992; Pichler *et al.* 1992). In the spectra shown in figures 1*b*–*e*, the films are metallic, the metallicity manifest by the absence of a band gap and the considerable broadening of electronic transitions. This broadening of electronic transitions (interband and plasmon excitations) arises due to the decay of the excitations into electron-hole pairs (Landau damping) which is only accessible in the presence of a metallic system.

Photoemission spectroscopy, particularly of the valence band region, provides another powerful technique by which information about electronic structure may

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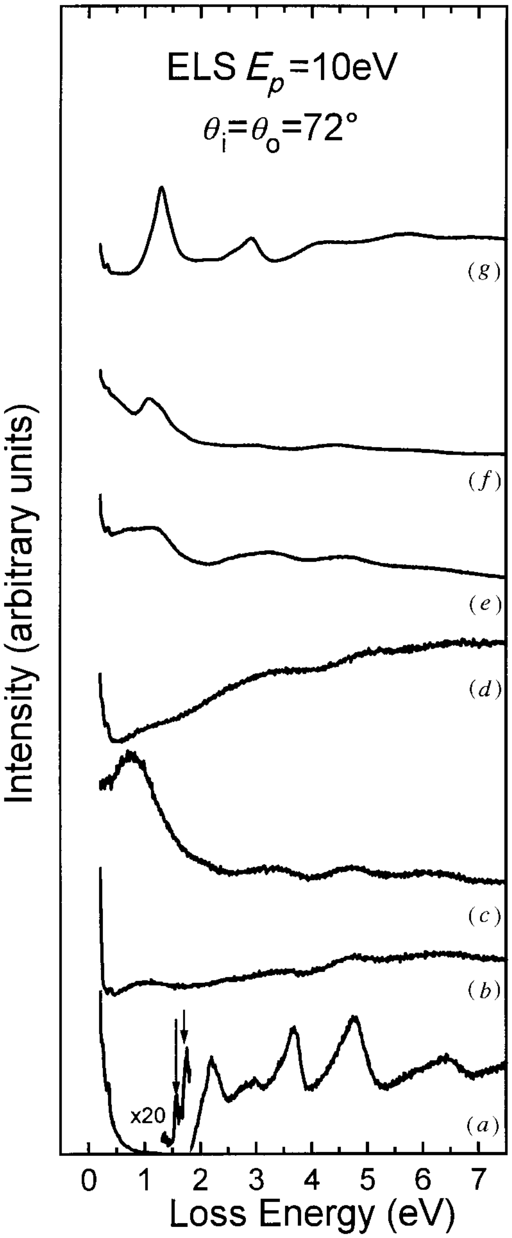

Figure 1. Electron energy loss spectra showing the electronic excitations of C_{60}. (*a*) A multilayer (5 ML) film on Au(110) and 1 ML C_{60} on (*b*) Au(110), (*c*) polycrystalline Ag, (*d*) Ni(110) and (*e*) Au(110) precovered by 1 ML Cs; (*f*) Au(110) precovered by 1.4 ML Cs; (*g*) Au(110) precovered with 2 ML Cs. The spectra were obtained in the specular geometry (angles of incidence and reflection at 72° to the sample normal) and an incident beam energy of 10 eV. (After Hunt *et al.* 1995, 1997.)

be obtained. In photoemission, a monochromatic beam of photons is directed upon the surface under investigation and electrons are emitted via the photoelectric effect. These photoelectrons are energy analysed, and their spectrum, in the absence of electron correlation effects, corresponds to the occupied density of states (DOS) of

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the surface weighted by the appropriate transition matrix elements. As in the case of electron energy loss spectroscopy, the small inelastic mean-free path of electrons in solid materials results in a high degree of surface sensitivity in this technique.

Examination of a photoemission spectrum in the region near to the Fermi energy provides useful information on the metallic or insulating nature of the material from which the spectrum is obtained. In general, if the system is not perturbed strongly from equilibrium by the incident photon beam, and there is a sharp cut-off of occupied states at the Fermi level in the spectrum, the material is ‘metallic’, although it should be noted that these states may well be spatially localized and thus not result in metallic transport properties. In this paper we shall use the term ‘metallic’ to describe a system in which there is an effective continuum of electronic states intersected by the Fermi level, and which in consequence will display a clear Fermi cut-off in PE spectra. In EEL spectra, such a system will show no band gap and will manifest Landau damping, as described above. This particular definition of metallicity is particularly appropriate as we progress through the model systems described here, for upon reaching the limit of discrete small metal clusters, the concept of metallic transport properties is no longer readily applicable.

3. Alkali metal films on graphite(0001)

The evolution of the electronic structure of alkali metal films formed by atomic vapour deposition onto graphite is of particular interest for a number of reasons. The relatively simple electronic structure of alkali metal atoms in comparison to, say, atoms of a transition metal, make them ideal candidates for the study and understanding of basic adsorption phenomena, catalytic promotion, etc. In addition to these more ‘traditional’ fields of interest, the two-dimensional close-packed alkali metal islands which form on graphite for certain coverages of alkali metal, as discussed below, represent a useful model of two-dimensional atomic clusters. The studies of alkali metal adsorption on graphite(0001), which are described in detail below, show that the electronic excitations of this substrate, in addition to those of the adsorbate, can provide useful information about the nature of the interaction between the adsorbate (or indeed cluster) and the graphite surface below.

When very small quantities (coverage less than approximately 0.02 ML†) of the alkali metals K, Rb or Cs are adsorbed on a graphite surface at temperatures low enough to inhibit intercalation (Barnard *et al.* 1993; Wu & Ignatiev 1983), a dispersed phase of the alkali metal adatoms forms (Hunt *et al.* 1996; Hock & Palmer 1991; Wu & Ignatiev 1986; White *et al.* 1992, 1994). This phase has been described as a ‘correlated liquid’ (White *et al.* 1994) in which the alkali atoms maintain maximum distance between each other. Adatom–adatoms spacings as large as 60 Å have been observed (Hunt *et al.* 1996). The electronic excitation spectrum of this surface is rather interesting, as shown in figure 2, and displays a clear, rather broad, peak which moves to higher energies as the alkali metal coverage increases. A similar energy loss peak is observed from the clean graphite surface at elevated temperature and is a result of a surface plasmon excitation due to the population of conduction band states at the Brillouin zone edge by thermally promoted electrons (Jensen *et al.* 1991). Indeed, as the temperature of the sample increases, so does the population

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† Where a 1 ML film of alkali metal on graphite contains the same number of alkali metal atoms as there are carbon atoms in the outermost layer of the graphite(0001) surface.

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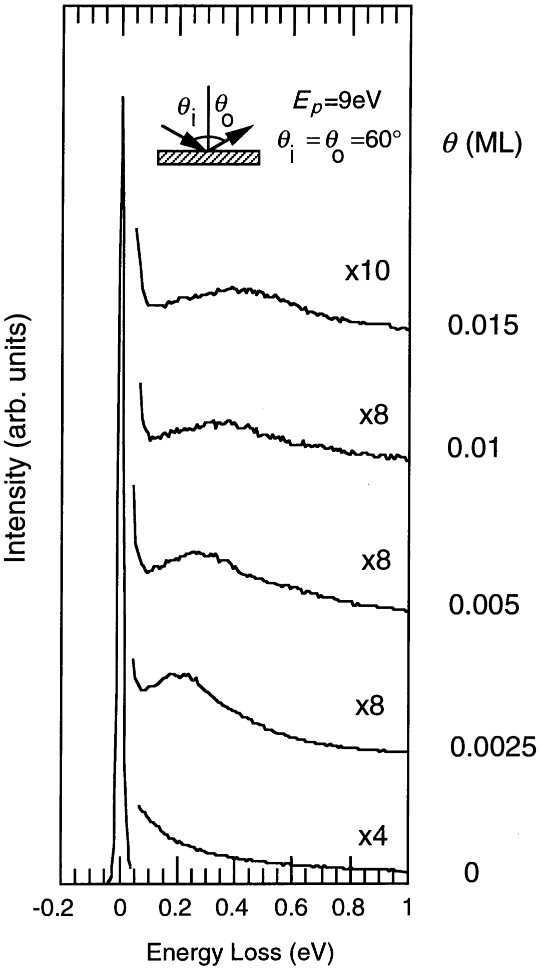

Figure 2. Electron energy loss spectra showing the evolution of the electronic structure of the Cs/graphite(0001) adsorption system. Note the appearance of a surface plasmon in the presence of adsorbed Cs, which increases in energy with Cs coverage (Hunt et 1996).

of the sparsely occupied band, resulting in a clear increase in the plasmon energy. At the low temperatures required by alkali adsorption experiments (90 K, for the spectra in figure 2), the thermal population of the 'conduction band' is rather low and in consequence the plasmon is predicted to lie at very low energy (about 40 meV) (Li *et al.* 1991). The combination of low energy and intensity results in a complete absence of this peak in the energy loss spectra (figure 2, bottom). However, when alkali metal adatoms are introduced onto the surface, a significant redistribution of charge takes place, from the alkali metal s state to the empty states of the substrate. This redistribution of charge populates the graphite conduction band with carriers, in exactly the same manner as thermal excitation, resulting in an increase in the energy of the low energy graphite surface plasmon. Increasing the coverage of alkali metal atoms results in an increase in the total charge redistributed towards the graphite surface, and therefore population of the graphite conduction band, which results in a concomitant increase in the graphite surface plasmon energy.

The increase in graphite surface plasmon energy continues with coverage until a

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maximum energy is reached. Further adsorption of alkali metal atoms leads not to a further increase in the plasmon energy of the graphite surface, as one might expect, but to the appearance of new loss features (Hunt *et al.* 1996; Li *et al.* 1991) (figure 3). The coverage at which this change in electron energy loss spectra occurs is exactly that at which a phase transition (Hunt *et al.* 1996; Li *et al.* 1991) occurs in the two-dimensional adatom liquid. When the density of the two-dimensional alkali metal liquid reaches a critical value, the adsorption of more alkali metal adatoms results in the nucleation of a new, more closely packed, phase which has a p(2×2) structure for K (Li *et al.* 1991), and a rather less well-defined structure for Cs (Hunt *et al.* 1996). These two-dimensional close-packed islands redistribute little (if any) of their charge towards the substrate: instead the s state electrons are retained within the two-dimensional alkali metal film. The two-dimensional alkali metal islands are therefore metallic, and, strikingly, behave as though they are almost decoupled from the graphite substrate. The clearest manifestation of this decoupling is the appearance, still at submonolayer coverage, of a loss peak which has exactly the same energy as the surface plasmon of a thick (bulk) alkali metal film (Hunt *et al.* 1996; Li *et al.* 1991) (figure 3). The presence of this loss indicates that the condensed two-dimensional alkali metal islands are behaving in a very similar way to the bulk metal, and, moreover, that the perturbation resulting from adsorption on the graphite surface has little impact upon the electronic excitations of the condensed alkali phase. The absence of a significant substrate induced perturbation to the electronic excitations of the condensed alkali phase demonstrates the extremely weak nature of the interaction between the condensed two-dimensional alkali metal layer and the graphite below.

When Cs is adsorbed on the graphite surface, the 'thick film' surface plasmon peak becomes visible when the Cs begins to form a $(\sqrt{7} \times \sqrt{7})$R19.11° phase (Hunt *et al.* 1996). The spacing between neighbouring Cs atoms in this phase is 6.4 Å or 122% of the bulk interatomic distance (this distance is significantly larger than that for the condensed phase of K (4.91 Å) which forms a p(2×2) overlayer (Li *et al.* 1991), the p(2×2) structure is also observed for Cs at higher coverages (Hunt *et al.* 1996; Hu *et al.* 1986)). The observation of metallicity even at the relatively large interatomic distance of 6.4 Å indicates that a significant charge overlap between neighbouring alkali metal atoms still occurs resulting in the formation of a metallic film.

This striking transition from a liquid of adatoms, spaced as far apart as possible, and which redistribute charge towards the substrate surface, to a complete close-packed metallic single layer of alkali metal, which behaves almost as a freestanding slice of the bulk, can be explained in terms of the energetics of the adsorption system (Ishida & Palmer 1992). When an alkali metal atom is adsorbed on the graphite surface, and redistributes charge towards that surface, the total energy of the system may be broken down into a number of separable components (Ishida & Palmer 1992). The total adsorption energy of an alkali metal atom has been modelled by equation (3.1), and consists of the adsorption energy for an alkali atom in the limit of zero coverage ($E_{\text{ads}}(0)$), coverage dependent electrostatic (A/r^4) and Pauli repulsion ($u(\theta)$) terms, which model adatom–adatom interactions, and a 'band energy term', $h(\theta)$:

$$E_{\text{ads}}(\theta) = E_{\text{ads}}(0) - [(A/r^4) + u(\theta) + h(\theta)]. \tag{3.1}$$

The last term plays a vital role in the observed phase transition (Hunt *et al.* 1996; Li *et al.* 1991; Ishida & Palmer 1992) and its origin can be explained as follows. Graphite

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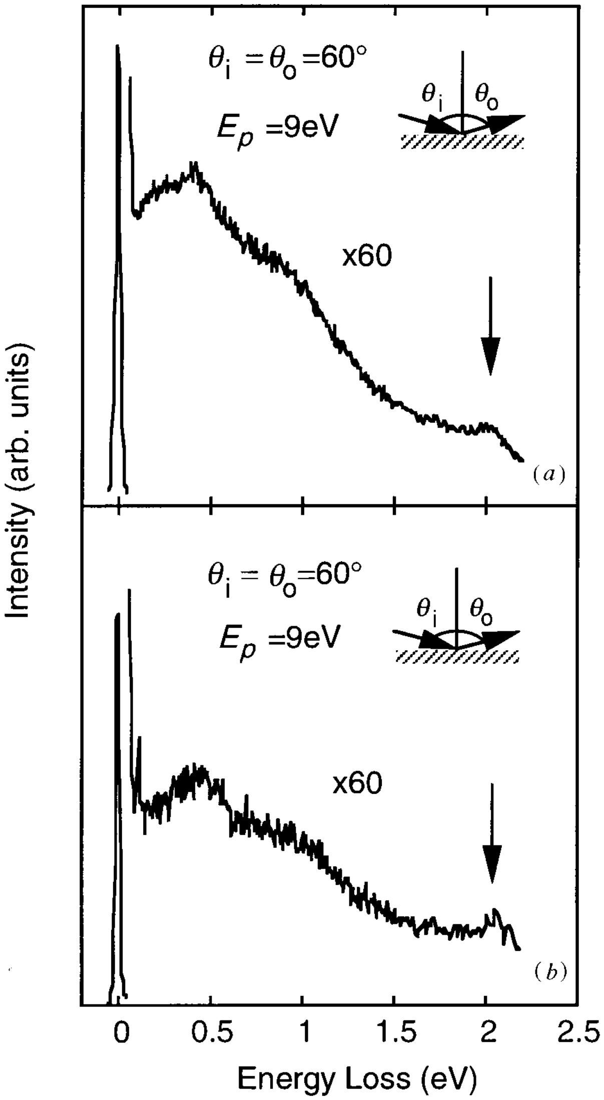

Figure 3. Electron energy loss spectra of condensed Cs layers on graphite(0001) in (*a*) the 7×7 and (*b*) co-existing 7×7 and (2×2) phases. Loss features at the same energy as the surface plasmon of a thick (bulk) Cs film are marked with arrows (Hunt et 1996).

is a semimetal and therefore is has a very low density of states (DOS) at the Fermi level. In consequence, transfer of charge from an adsorbed layer raises the local Fermi level of the near surface region quite considerably, resulting in an extra energy cost associated with adsorption and charge redistribution, which increases quite rapidly with the total amount of redistributed charge. This is in marked contrast to alkali adsorption on metal surfaces in which the substrate has a very large DOS in the vicinity of the Fermi level and can effectively soak up charge with negligible change in energy. In the alkali metal/graphite adsorption system, the band energy term rapidly becomes important, and a coverage is reached at which it is no longer energetically favourable to redistribute charge towards the substrate. At this point, a phase transition occurs, driven by the unfavourability of further charge redistri-

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bution, and further deposition of alkali metal results in the growth of close-packed metallic islands, immersed in a 'sea' of liquid adatoms, and with an electronic structure apparently rather decoupled from that of the substrate. The transition from a dispersed to a condensed alkali metal phase occurs at the same graphite surface plasmon energy (Hunt *et al.* 1996), and hence conduction band electron density, in both Cs and K which is indicative of the dominant role that the band energy term plays in determining both the electronic and the geometric structure of this system.

Whilst the transition from a dispersed to a more condensed phase occurs for the same value of the modified graphite surface plasmon energy for the adsorption of both K and Cs, it does not occur at the same coverage. This demonstrates that in the dispersed phase the the two alkali metals redistribute charge towards the surface to a different degree. By following the evolution of the energy of the graphite surface plasmon as a function of alkali metal coverage, it is possible to obtain an estimate of the degree of charge redistributed towards the graphite surface using a simplified model (Hunt *et al.* 1996; Li *et al.* 1991): it is found that, in the dispersed phase, adsorbed Cs atoms redistribute about 50% more charge to the unoccupied states of the surface than adsorbed K atoms. The sensitivity of the graphite electronic structure to charge redistribution enables the excitations of the substrate itself to be used as a probe of the electronic structure of a deposited species. It is for this reason that, as will be described below, we have chosen graphite(0001) to be the substrate for our first cluster deposition experiments.

4. C_{60} thin films

The interaction of metals with C_{60} can also lead to a transition between metallic and insulating behaviour. However, despite some superficial similarity that may appear to exist between this system and the adsorption of alkali metal on the graphite surface (predominantly sp^2 bonded carbon networks interacting with alkali metals), the metal–insulator transition occurs for somewhat different physical reasons. In this section we shall consider the growth of monolayer films of C_{60} molecules on a variety of metal surfaces. The basic physical behaviour of the fullerene–metal system is found not to be perturbed by whether the C_{60} is deposited upon a given substrate/coadsorbate or the substrate/coadsorbate material is deposited upon a C_{60} multilayer film (Hunt 1995). The major advantage offered by the adsorption of C_{60} onto a metal surface is that one can more easily obtain a smooth even interface. Many metals do not wet the C_{60} surface evenly, but form clusters upon it (Ohno *et al.* 1993), consequently giving rise to spectral features due to both perturbed and unperturbed C_{60} molecules. Flat monolayer C_{60} films may be easily grown, by taking advantage of the layer-by-layer growth mode displayed by C_{60} for a wide variety of metal surfaces (Hunt 1995; Sakurai *et al.* 1996).

The adsorption of monolayer films of C_{60} on metal surfaces, either alone or in the presence of a reactive coadsorbate, offers a unique opportunity to modify both the electronic and the geometric structure of the molecular film. A wide range of molecular oxidation states, and hence electronic structures, are observed when C_{60} is deposited on different surfaces (Hunt *et al.* 1995, 1997; Hunt 1995; Modesti *et al.* 1993) and comparison with the properties of bulk metal-C_{60} compounds enable us to gain insight into the effects of dimensionality on this class of materials. In this section we shall first consider the form of the EEL and photoemission spectra obtained from a multilayer film and then from C_{60} monolayers adsorbed on metal surfaces with

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a decreasing work function. From the shape of the spectra it will be possible to determine if the film is insulating, semiconducting or metallic. In addition to this information, the electronic spectra, taken together with vibrational spectra (which we will not discuss here), can provide us with a strong indication of the fullerene molecular oxidation state by comparison with spectra obtained from bulk materials of known stoichiometry and molecular charge state. Having demonstrated the way in which a C_{60} monolayer can be changed from a metal to a semiconductor/insulator by appropriate choice of supporting substrate, we shall finally focus upon films and solids containing C_{60} in the -4 oxidation state which display electronic properties far removed from those which would be predicted by simple band theory.

In the solid state at room temperature, C_{60} forms a molecular solid with a face centred cubic (FCC) crystalline structure. The molecules are bound primarily by van der Waals interactions resulting in weak overlap of the molecular electronic states. The molecular nature of a crystalline C_{60} film is demonstrated by the photoemission spectrum in figure 4*f*. A series of relatively sharp photoemission peaks is observed, corresponding to the molecular-orbital derived electronic bands of the C_{60} film. A multilayer C_{60} film is insulating, as evidenced by the absence of emission at the Fermi level in the PE spectrum (figure 4*f*) and the observation of a clear band gap region in an EEL spectrum from a similar film (figure 1*a*).

Adsorption of a single layer of C_{60} molecules onto a metal surface leads to a dramatic change in the electronic excitation spectrum of the film in comparison with that of the multilayer, and by inference the electronic structure of the fullerene molecules within the multilayer film. The spectra in figure 1*b*–*d* show the electronic excitation spectra for C_{60} monolayers adsorbed on Au(110), polycrystalline Ag and Ni(110), respectively (Hunt *et al.* 1995). One can immediately see that the sharp excitations which were present in the spectrum from the multilayer film are strongly broadened by the interaction between the metal surface and the monolayer of fullerene molecules, and there is no longer an observable band gap. That this change is due to a significant perturbation of the electronic structure of the C_{60} film, rather than a combination of the loss functions of substrate and film has been shown by comparison of the experimentally observed spectra with theoretical spectra of an unperturbed C_{60} film in contact with the metal surfaces generated from the measured dielectric response of the bulk materials (Hunt *et al.* 1995). Further support for this argument comes from examination of vibrational EEL and PE spectra from the monolayer films which cannot be explained by any superposition of metal and C_{60} spectra (Hunt *et al.* 1995; Modesti *et al.* 1993; Maxwell *et al.* 1994; Cepek *et al.* 1996).

The absence of a band gap in the EEL spectra of C_{60} monolayers adsorbed on the clean metal surfaces shown in figure 1 provide clear evidence for metallic behaviour in the C_{60} films induced by chemical bond formation with the substrate. Precoverage of a metal surface with a given quantity of alkali metal, effectively creating a more ‘reactive’ surface, can lead to further changes in the electronic structure of the C_{60} film (Hunt *et al.* 1997; Hunt 1995; Modesti *et al.* 1993), as seen in the EEL spectra of figures 1*e*–*g* and the photoemission spectra of figures 4*c*–*e*. These spectra clearly demonstrate dramatic changes and indicate the formation of metallic and insulating phases. Moreover, rather than a continuous evolution of C_{60} behaviour with increasing alkali metal coverage, three distinct alkali-C_{60} phases were observed (Hunt *et al.* 1997), with coexistence of these phases at intermediate Cs coverages.

Figure 1*g* shows an EEL spectrum characteristic of C_{60} monolayers adsorbed at

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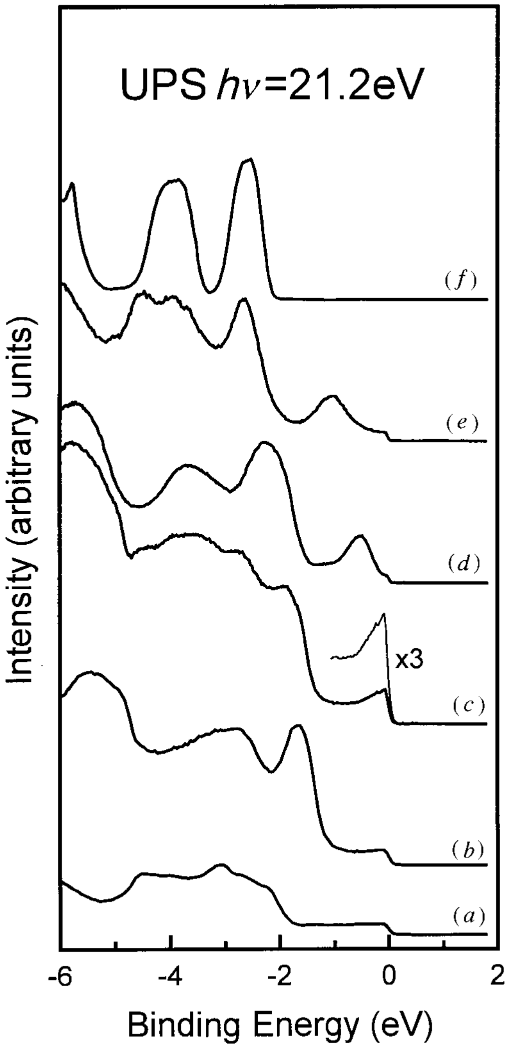

Figure 4. Photoemission spectra of C_{60} monolayers adsorbed on Au(110) and alkali metal precovered Au(110). (*a*) The clean Au(110) surface, (*b*) 1 ML C_{60} on Au(110), (*c*) 1 ML C_{60} on Au(110) precovered by 1 ML Cs, (*d*) 1 ML C_{60} on Au(110) precovered by 1.4 ML Cs, (*e*) 1 ML C_{60} on Au(110) precovered by 2 ML Cs, and (*f*) a multilayer (5 ML) C_{60} film on Au(110). The photoemission spectra were obtained with He I radiation (21.22 eV) in the normal emission geometry. The C_{60} multilayer and monolayer spectra are normalized to the highest occupied molecular orbital (HOMO) peak intensity, and an arbitrary normalization is used for the spectrum from clean Au(110) to show the photoemission features clearly. Features due to He I satellites have been removed (Hunt *et al.* 1997).

125 K on Cs precoverages of between 2 and 4 ML†; a gap of relatively low background intensity is observed extending from the vibrational energy region to an onset at about 0.7 eV. The presence of a gap in the spectrum indicates that the material is now a semiconductor. The photoemission spectrum of figure 4*e* shows emission at

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† Where 1 ML of Cs is defined as a complete close-packed $c(2 \times 2)$ layer on the Au(110) surface (an adatom density of 4.2×10^{14} cm^{-2}.

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the Fermi level, but this emission can be entirely accounted for by the underlying Cs covered gold surface, no Fermi level emission arises from the C_{60} monolayer film. A comparison of the EEL and photoemission spectra of the monolayer film with those of bulk Cs_6C_{60} (Hunt *et al.* 1997), which is known to be semiconducting (Haddon *et al.* 1994), show that they are strikingly similar, indicating that the bulk alkali fulleride and the C_{60} monolayer adsorbed on multilayer Cs behave almost identically.

When Cs precoverage is reduced to about 1.4 ML, the electronic properties of a coadsorbed C_{60} monolayer change quite considerably, as evidenced by the EEL and photoemission spectra of figures 1*f* and 4*d*, repectively, which are considerably different to those for the higher alkali precoverages. A close similarity is seen in the gross features of this spectrum when compared to transmission electron energy loss spectroscopy (TEELS) results on bulk K_4C_{60} films (Golden *et al.* 1995), which display semiconducting (Haddon *et al.* 1994) behaviour. However, there is a significant difference between the TEELS results and the EEL spectrum of figure 1*f*, namely the presence of a strong low energy continuum of losses in the latter, indicative of a metal or a semiconductor with a small band gap. The photoemission spectrum of figure 4*d* cannot, unfortunately, resolve this issue since it is impossible to determine the substrate contribution uniquely. However, subtraction of the substrate contribution using different weights strongly suggests that any emission at the Fermi level due to the C_{60} monolayer is extremely weak, indicating that the monolayer is most likely a semiconductor with a narrow gap.

Further reduction of Cs precoverage to about 1 ML, results in an adsorbed C_{60} monolayer with an EEL spectrum (figure 1*e*) which displays a strong continuum of electronic excitations. This continuum of excitations indicates that the monolayer is either weakly metallic, or is a semiconductor with a band gap which is less than about 200 meV, which would be masked by molecular vibrational modes. The photoemission spectrum of figure 4*c* resolves the issue in this case (Hunt *et al.* 1997) due to the extremely pronounced Fermi cut-off which can be observed (which is much stronger than the appropriate contribution from the substrate). Thus we can conclude that the C_{60} monolayer on Au(110) precovered with 1 ML Cs behaves in a metallic fashion.

The general evolution of the electronic structure of the C_{60} monolayer films can be accommodated by a very simple model, assuming charge transfer from the substrate and/or coadsorbate to the C_{60} film (although this is an inadequate description for C_{60} adsorbed on Ni(110)). Using the charge transfer model, a direct analogy may be drawn between the properties exhibited by the monolayer films and bulk alkali metal C_{60} salts with well-defined stoichiometry and, in consequence, C_{60} oxidation states. By analysing electronic excitation, photoemission and vibrational excitation spectra, one can determine the approximate oxidation state of the C_{60} molecules within each monolayer film, which are summarized in table 1.

The oxidation states determined for the C_{60} molecules in the monolayer films adsorbed on different surfaces can be used to explain the electronic structure of most the films: the C_{60} molecules in the monolayer adsorbed on 2 ML Cs/Au(110) are in an oxidation state of '−6', i.e. each C_{60} molecules formally possesses six extra electrons. These electrons completely fill the triply degenerate conduction band formed from the lowest unoccupied molecular orbitals (LUMOs) of the C_{60} molecules, and in consequence the film is non-metallic. The electronic structure of the C_{60} monolayer adsorbed on the Au(110) surface precoved with 1.4 ML Cs is more complex (as is that of the bulk material with the same C_{60} oxidation state) and for that reason we

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Table 1. *Formal oxidation states determined for* C_{60} *adsorbed on a variety of metal surfaces*

1 ML C_{60} adsorbed on:	formal oxidation state
Au(110)	−1
polycrystalline Ag	−1
Ni(110)	−2
1 ML Cs/Au(110)	−3
1.4 ML Cs/Au(110)	−4
2 ML Cs/Au(110)	−6

shall discuss the features of this particular 'phase' in more detail later. For a Cs precoverage of 1 ML, the molecular oxidation state is '−3' and the LUMO derived band is half filled leading to metallic behaviour. Similarly, for C_{60} monolayers adsorbed on the noble metal surfaces, Au(110) and polycrystalline Ag, the molecules have an oxidation state of −1. Single filling of the triply degenerate conduction band thus leads once more to a metallic film. A monolayer C_{60} film on Ni(110) is also metallic and this can be modelled in terms of the donation of two electrons per C_{60} molecule leading to an oxidation state of −2 (but significant hybridization between Ni d states and C_{60} π states is likely to occur complicating this simple picture). This is illustrated by the variation of formal C_{60} oxidation state with the work function of the substrate. In general, as the workfunction of the surface decreases, more charge is transferred from the surface to the C_{60} molecules. However, Ni(110) runs counter to this trend, it has a higher workfunction than polycrystalline Ag, yet formally transfers more charge per C_{60} molecule. In consequence, it can be seen that it is surface 'reactivity', of which workfunction is but a crude estimate, which determines the formal oxidation state of an adsorbed C_{60} monolayer.

We have shown above that by varying the 'reactivity' of a surface the oxidation state of C_{60} molecules in a single layer can be substantially changed, leading to monolayer films which are metallic, insulating or semiconducting, depending on the degree of interaction between the fullerene molecules and the surface beneath them. This strong variation of transport properties brought about by the chemical environment of the fullerene molecules indicates that it is possible to modulate the electronic structure of a C_{60} film by varying the concentration of a dopant material within the film, perhaps enabling the future creation of electronic devices.

Whilst the electronic structure of the C_{60} monolayer films discussed above could be understood simply in terms of the filling of the LUMO-derived conduction band of the C_{60} film, the C_{60} monolayer on Au(110) precovered by 1.4 ML Cs, and its bulk analogue, present a more intriguing problem. Comparison of electronic excitation and photoemission spectra with bulk alkali fullerides (Hunt *et al.* 1997; Golden *et al.* 1995), and analysis of vibrational spectra indicate a C_{60} oxidation state of −4. One would expect that in a simple band filling model that the triply degenerate conduction band would be two-thirds full, leading to a metallic material. However, bulk A_4C_{60} (A = K, Rb or Cs) in which the C_{60} molecules are in the −4 oxidation state is, in fact, semiconducting. Calculations (Suzuki & Nakao 1995) have indicated that it is unlikely that the crystal field alone could bring about the required conduction band splitting to give rise to a semiconducting material. Consequently, some other mechanism must be responsible. Theories divide into two groups: those which postulate that electron–electron correlation effects (Meinders 1994) drive a transition from

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a metallic to an insulating state, and those which rely on band splitting induced by a Jahn–Teller effect, either dynamic or static (Remova *et al.* 1995).

Electronic correlation effects become important in a system when the on site electron repulsion energy, U, is of the order of the conduction band width, W. In such a system, the energy change brought about by a conduction electron hopping from one site to another, occupied, site cannot be compensated by a consequent change in energy within the band. The net result is that the electrons become correlated and their intersite motion must be undertaken in concert.

The molecular nature of solid C_{60} results in a rather weak overlap between electronic states, and this retention of molecular character leads to narrow well defined peaks in photoemission spectra from the bulk material. The weak overlap between molecular states in the vicinity of the LUMO level result in electronic energy bands with rather small dispersion (Shirley & Louie 1993; Satpathy *et al.* 1992), as can be understood by consideration of a simple tight binding model as the overlap integral becomes smaller. Theoretical work (Shirley & Louie 1993; Satpathy *et al.* 1992) suggests LUMO band dispersions of the order of 0.5 eV. In contrast, Auger electron spectroscopy and photoemission have been employed to measure the intrasite Coulomb energy in pure C_{60} and some alkali fullerides finding values of the order of 1–2 eV (Lof *et al.* 1992; Brühwiler *et al.* 1992, 1993). Therefore, one would expect that alkali metal-C_{60} compounds should behave as highly correlated electron systems, and in the case of A_4C_{60} it would not be surprising if correlation effects drove the system into a semiconducting, rather than the expected metallic, state.

If the alkali-metal C_{60} salts behave as highly correlated electronic systems, calculations based on the degenerate Mott–Hubbard model in the atomic limit (Meinders 1994) indicate that stoichiometric A_3C_{60} should be a Mott–Hubbard insulator. It has therefore been suggested that the metallic behaviour of these compounds arises from a slight non-stoichiometry (Meinders 1994; Lof *et al.* 1992), effectively doping the insulating material. However, the reproducibility of A_3C_{60} film properties and clear phase separation (Poirier *et al.* 1995) amongst the alkali-metal C_{60} compounds suggests that it is also possible that the A_3C_{60} phases are stoichiometric, in which case the electronic correlation effects in this system would not be strong enough to drive it into an insulating state.

The Jahn–Teller effect involves the distortion of a system (either a lattice or molecule) containing electron(s) in a degenerate band. The molecular distortion splits the band into lower and higher energy components. The total energy of the system may be lowered if the electron(s) then occupy the lower energy split band. The energy of distortion is recouped by lowering the total electronic energy. If the lower component(s) of the split band is full, the system now becomes a semiconductor, with a band gap defined by the energy gap between the highest filled and lowest empty components of the originally degenerate electron band. It has been suggested (Wang *et al.* 1992; Pichler *et al.* 1992) that Jahn–Teller distortion of C_{60} molecules in the solid state could play a significant role in determining the electronic structure of the alkali-metal C_{60} compounds.

It is not yet clear which, if either, of the above two mechanisms is responsible for the electronic properties of bulk A_4C_{60}, and those of the monolayer C_{60} film adsorbed on the 1.4 ML Cs precovered Au(110) surface. Nor is it clear if the change of dimensionality as represented by the monolayer film of C_{60} molecules in the -4 oxidation state leads to a significant change in electronic properties. In consequence, the electronic structure of A_4C_{60} remains a subject of considerable interest.

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5. Supported metal clusters

When the metal–insulator transition is considered in clusters of elements that are metallic in the bulk, one must be careful to define exactly what metallicity means in these systems. Measurement of the metallic transport properties of a single metal cluster, such as the conductivity, is not feasible: even the act of attaching a probe will extend and perturb the system. Many of the aspects of metallic behaviour in the bulk arise through the possibility of exciting a continuum of electron hole pairs for any energy (Wertheim 1990). The finite number of atoms in a cluster lead to a finite number of conduction band states, and unless these overlap (due to their thermal width at the measurement temperature) the electron-hole pair excitation spectrum no longer spans a continuum of energy and consequently properties which we would associate with metallic behaviour are no longer manifest. This change in electronic properties as a result of the formation of discrete levels in small systems is known as the *Kubo effect* (Kubo 1962).

Although the transition from insulating to metallic behaviour will not be sharp (Wertheim 1990), even in a beam of free clusters, it is possible that adsorption of cluster materials onto surfaces will perturb the cluster electronic structure to a degree that may drive the system from metallic to non-metallic behaviour or vice versa. The behaviour of such supported clusters is of particular interest for future cluster research (Palmer 1997); thin cluster films and arrays must be supported by a substrate and this substrate may have considerable influence upon the properties of the deposited clusters.

EELS and photoemission, as demonstrated above, are extremely powerful techniques for probing the electronic structure of surfaces and thin films and can enable us to differentiate between metallic and non-metallic behaviour. Whilst surface sensitive, the electron beams used in EELS are generally of the order of 0.5 mm in diameter, and in consequence sample a large number of any nanoscale species that may be present upon the surface. The photon beams produced by most laboratory sources for photoemission are generally even broader. In consequence, to make precise studies of the variation of cluster electronic properties as a function of size, we must endeavour to create large area monodisperse cluster films. Too great a size variation could easily mask size dependent effects. In the remainder of this section we consider some of the state-of-the-art techniques of cluster deposition that are now being used in Birmingham to create the homogeneous cluster films required for spectroscopic measurements.

It is now possible to produce beams of size selected clusters by a wide variety of techniques ranging from condensation of evaporated atoms (Goldby *et al.* 1997) to the sputtering of clusters/small particles from surfaces (Hall *et al.* 1997). Cluster size distributions vary with source type and the cluster material but are typically in the range 50 to greater than 2000 atoms for a gas aggregation source and 1 to 15 atoms for a sputter source. The mass resolution can be down to a single atomic mass unit, allowing the differentiation of isotopes within the clusters.

A well-defined size distribution within a cluster beam does not necessarily translate into an equally well-defined distribution when the clusters are deposited on a surface. Temperature (and hence diffusion rate), cluster size and impact energy all play an important role in defining the final range of cluster sizes in the deposited film (Francis *et al.* 1996). Indeed, these parameters are also able to significantly influence the cluster morphology (Francis *et al.* 1996; Carroll *et al.* 1996). Figure 5 shows SEM micrographs of Ag_n clusters deposited onto graphite at room temperature with dif-

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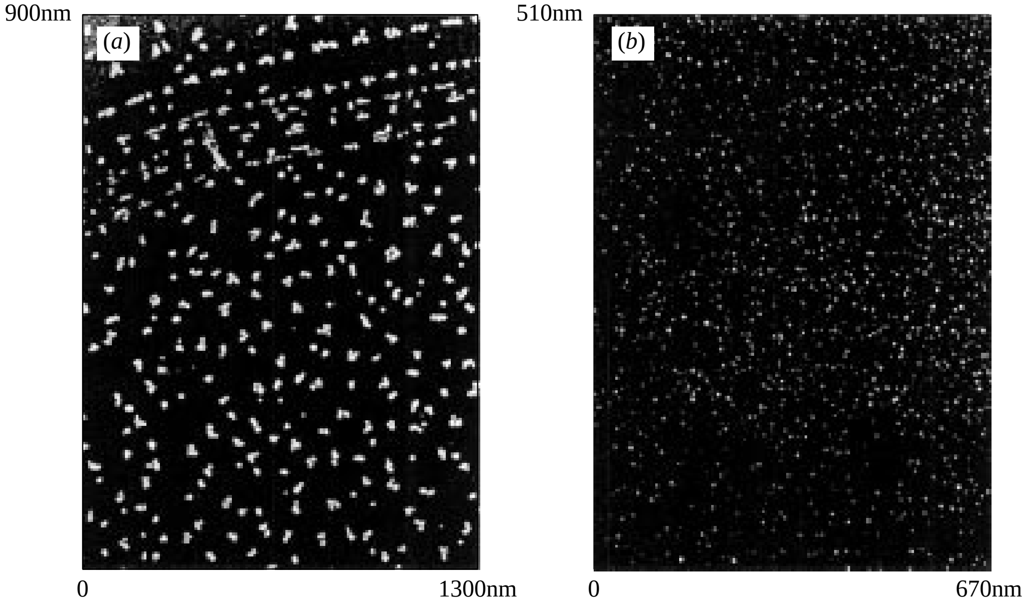

Figure 5. SEM images showing Ag_n^+ clusters (size range $n = 20$–300) deposited onto a graphite substrate at room temperature with a coverage of 0.016 clusters nm^{-2}; (*a*) at 50 eV impact energy, (*b*) 400 eV impact energy. Note the aggregation of clusters deposited at low impact energy indicating their ability to diffuse over the surface, whilst those deposited at higher energy are immobile and therefore remain separate (Goldby *et al.* 1997).

ferent impact energies. At low impact energies the clusters are clearly free to diffuse over the surface and agglomerate to form fractal structures (figure 5*a*). If the impact energy is increased, however, the resulting distribution of cluster sizes is that of the incident beam (figure 5*b*), i.e. no diffusion across the surface occurs. This inhibition of cluster diffusion arises from self-pinning (Francis *et al.* 1996; Carroll *et al.* 1996)—the highly energetic clusters damage the substrate upon impact and are trapped at the defects that they have created. Monodisperse films formed in this fashion, or by cooling a substrate to prevent diffusion, are currently being investigated by spectroscopic techniques (Hall and co-workers 1997, unpublished work) and represent the state-of-the-art in the science of supported mass-selected clusters.

It should be stressed that the cluster deposition techniques used for exploring the evolution of cluster electronic structure also have direct applications. For example, size-selected clusters deposited onto a hydrogen terminated Si(100) surface have been applied as etch masks for the formation of nanometre diameter silicon pillars (Tada *et al.* 1997). Surprisingly, significant dependence upon the cluster size has been observed even in this fabrication process, a result of the ability of a given cluster size to maintain an etch mask.

6. Summary

We have demonstrated the power of electron energy loss spectroscopy and photoemission spectroscopy in determining the electronic structure of nanometre scale systems, with particular focus on the transition between metallic and non-metallic behaviour. The electronic properties of three model systems have been considered, ultrathin alkali metal films adsorbed on a graphite surface, C_{60} monolayers adsorbed

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on metal surfaces and small metal clusters. Each type of system is capable of displaying a metal–insulator transition, but in each case the transition is driven by a different physical process.

When alkali metal atoms are adsorbed on the graphite(0001) surface, a transition from a dispersed highly polarized (or part ionized) atomic gas to a metallic film occurs in the adsorbed two-dimensional first layer of the alkali metal film as a function of the coverage (or density): beyond a critical coverage significant charge redistribution from the adsorbed metal atoms towards the substrate becomes energetically unfavourable resulting in the formation of close-packed metallic islands when more alkali atoms are deposited. Single monolayers of C_{60} molecules on metal surfaces may manifest either semiconducting or metallic behaviour depending upon the reactivity of the substrate onto which they have been adsorbed. Many of the gross features of the behaviour of the C_{60} monolayer films can be explained in terms of the filling of the LUMO derived conduction band of the film. However, a the electronic properties of a monolayer of C_{60} in an oxidation state of '-4' are, like those of its bulk analogue A_4C_{60}, somewhat more difficult to explain: it has yet to be resolved wether electron–electron correlation, the Jahn–Teller effect, or possibly even both, can explain the deviation from a simple band filling model. Finally, we have briefly considered what defines the metal–insulator transition in small metal clusters and demonstrated that current cluster beam deposition techniques are now opening up the way towards exploring the electronic properties of monodisperse cluster films. These studies will enable the relationships of cluster size and cluster–surface interaction to electronic structure and, in particular, metallic behaviour to be determined.

M.R.C.H. thanks the Leverhulme Trust for financial support. The work described in this review was supported by the Royal Society, the EPSRC and the European Community (contract number: CHRX-CT94-0580).

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