

**Well-shielded cerium atoms: Electronic structure of adsorbed Ce@C<sub>82</sub> on Si surfaces**

K. Schulte,\* L. Wang, and P. J. Moriarty

*School of Physics and Astronomy, University of Nottingham, Nottingham NG7 2RD, United Kingdom<sup>†</sup>*

J. Purton and S. Patel

*Daresbury Laboratory, Daresbury, Warrington, Cheshire WA4 4AD, United Kingdom*

H. Shinohara

*Department of Chemistry, Nagoya University, Nagoya 464-8602, Japan*

M. Kanai and T. J. S. Dennis

*Department of Chemistry, Queen Mary and Westfield College, University of London, London E1 4NS, United Kingdom*

(Received 29 October 2003; revised manuscript received 29 October 2004; published 31 March 2005)

The interaction of Ce@C<sub>82</sub> with clean and silver-terminated Si(111) surfaces has been studied with synchrotron-radiation photoemission spectroscopy and near-edge x-ray absorption fine-structure (NEXAFS) spectroscopy. Use of an Ag/Si(111)-( $\sqrt{3} \times \sqrt{3}$ )R30° surface as an initial substrate enables the molecule-substrate interaction to be progressively strengthened through controlled annealing. Although strong covalent bonding and distortion of the fullerene cage are observed following the removal of the Ag-induced reconstruction (above 550 °C), the cerium atom's valence and overall electronic structure, as probed by Ce 3*d* NEXAFS, appear to be remarkably unaffected.

DOI: 10.1103/PhysRevB.71.115437

PACS number(s): 71.20.Tx, 33.60.-q, 71.20.Eh

**I. INTRODUCTION**

One of the attractive properties of the fullerenes is their ability to be electron doped in a variety of ways, leading to a multitude of unique properties and phenomena.<sup>1-3</sup> The first well-known type of doping is by means of intercalation and has provided a new family of superconductors such as K<sub>3</sub>C<sub>60</sub>. The second method involves replacing a carbon atom by another species (e.g., azafullerene; C<sub>59</sub>N) or adding functional groups, as in phenylated C<sub>60</sub>, opening the doorway to controlling the organization of these molecules on surfaces. A third route is associated with the ever-expanding class of endohedral or *incarcerated*-fullerenes, in which one or more atoms are encapsulated by the carbon cage.<sup>4</sup>

Nowadays, incarcerated forms of the majority of the first row rare-earth metals have been successfully produced and their properties and applications are slowly being uncovered. One of the possible suggested uses is as quantum bits (qubits) in the field of quantum computing, since endofullerenes present an excellent way of isolating the spin of the encapsulated atom from its surroundings.<sup>5</sup> In order to address and read each spin, however, organized pattern formation is essential, as is knowledge about the interaction of the endohedral fullerene with the underlying substrate. The influence of the molecule-substrate interaction on the electronic structure and the chemical environment of an atom enclosed within a fullerene cage is the key motivation driving our study of Ce@C<sub>82</sub> on silicon and silver-terminated silicon. The choice for silicon as a substrate is motivated by its previous use in fullerene studies in which it was shown that silicon exhibits strong covalent bonding to fullerenes,<sup>6</sup> the strength of which can be increased by annealing,<sup>7</sup> and, by using scanning tunneling microscopy (STM), molecular manipulation and pattern formation are readily achievable.<sup>8</sup>

In choosing Ce@C<sub>82</sub> specifically, we also address the properties of one of the most studied rare-earth elements. In bulk form, cerium exhibits a fascinating first-order transition, accompanied by a 15% volume collapse, as well as antiferromagnetic, paramagnetic, and superconducting phases. It is the most reactive element of the rare-earth group, after europium, and the complex physics accompanying its single occupied 4*f* band, close to the Fermi level, has baffled scientists for many decades.<sup>9</sup>

In incarcerated form, Ce@C<sub>82</sub> provides a unique way of studying single atoms of cerium in controlled surroundings. Up to now, the endohedral cerium fullerenes have received only a modest amount of attention, focused mainly on their production and the valence of cerium, which was found to be 3+.<sup>10-13</sup> Recently, Shibata *et al.* found that Ce@C<sub>82</sub> is a mixture of two isomers in a 4:1 ratio, with the majority associated with C<sub>2v</sub> symmetry. They also confirmed the valence suggested before and conducted structural and transport studies.<sup>14</sup> We now have expanded the endohedral cerium fullerene investigation further, by taking a closer look at its electronic properties and its interaction with the surrounding world, through a combined photoemission spectroscopy (PES), near-edge x-ray absorption fine-structure (NEXAFS) spectroscopy, and annealing study of bulk and monolayer (ML) Ce@C<sub>82</sub>.

**II. EXPERIMENT**

The photoemission and x-ray absorption experiments were carried out on beamline 5U1 of the Synchrotron Radiation Source (SRS), Daresbury, U.K. 5U1 uses a monochromator which has a single 1200 l/mm grating covering the energy range 60–1000 eV. The monochromator takes

light directly from the SRS permanent magnet undulator, without an entrance slit. The exit slit was set to  $\leq 50 \mu\text{m}$ . The emitted photoelectrons were measured using a single channel hemispherical analyzer, which permitted an overall instrumental resolution varying between 0.25 eV at the lowest end to around 1.2 eV at the upper end of the energy range. The x-ray absorption measurements were performed using a partial yield detector, at photon energy resolutions between 0.1 and 0.5 eV.

Preparation of clean Si(111)-(7 $\times$ 7) surfaces involved sample degassing at 600 °C for 8–12 h, followed by brief (“flash”) annealing at 1200 °C for 15–30 s by means of direct current sample heating. The sample temperature was monitored using an infrared pyrometer, and the pressure kept below  $1.2 \times 10^{-9}$  Torr during flashing. Silver was then deposited from a thoroughly degassed Knudsen cell (*K* cell) at 780 °C, whilst the Si substrate was kept at 500 °C, forming the Ag/Si(111)-( $\sqrt{3} \times \sqrt{3}$ )R30° reconstruction. Both the clean and reconstructed Ag/Si surfaces were checked with low-energy electron diffraction, surface sensitive core-level, and valence-band photoemission for order and cleanliness.

Ce@C<sub>82</sub> molecules were prepared and purified as described elsewhere,<sup>15</sup> and stored in a CS<sub>2</sub> solution. The CS<sub>2</sub> was allowed to evaporate off at ambient pressure in a standard Knudsen cell mounted on a linear transfer arm before connecting it to the UHV system. After degassing for 24 h at 200 °C, the molecules were sublimed on to the Ag/Si surface in UHV at 450–500 °C for 20 min, during which the pressure in the main chamber rose from  $9 \times 10^{-11}$  Torr to  $2 \times 10^{-8}$  Torr. This did not corrupt the passivated Ag/Si surface, as will be shown in the next section, whereas previous attempts to deposit the molecules directly onto the Si(111)-(7 $\times$ 7) surface did show signs of unwanted oxidation. The linear transfer arm also allows us to deposit at a 1.5-cm distance to the substrate. We found such a short sample-*K*-cell distance necessary to ensure a high-enough flux for obtaining a thick multilayer, in which the Si (and Ag) PES signals are completely suppressed, even at incoming photon energies of 1000 eV. An STM measurement of a Ce@C<sub>82</sub> thick film prepared in this way showed large, well-ordered, hexagonally close-packed facets in a Stansky-Krastonov growth mode.<sup>16</sup>

### III. RESULTS AND DISCUSSION

There are several reasons for growing a thick Ce@C<sub>82</sub> film in the manner described above. First, the initial silver termination passivates the silicon surface and prevents oxidation during growth of the fullerene film. Second, in bulk Ce@C<sub>82</sub> one expects rather weak bonding between the molecules, somewhat analogous to C<sub>60</sub>, providing us with a measure of the electronic state of the pure endohedral fullerene. Third, the desorption of all Ce@C<sub>82</sub>, apart from the last monolayer, takes place at temperatures below the desorption point of silver, and thus allows us to study the screened binding of Ce@C<sub>82</sub> to Ag/Si. And finally, above 550 °C the silver desorbs from the surface, *through* the Ce@C<sub>82</sub> monolayer,<sup>17</sup> permitting us to study the effects of strong co-

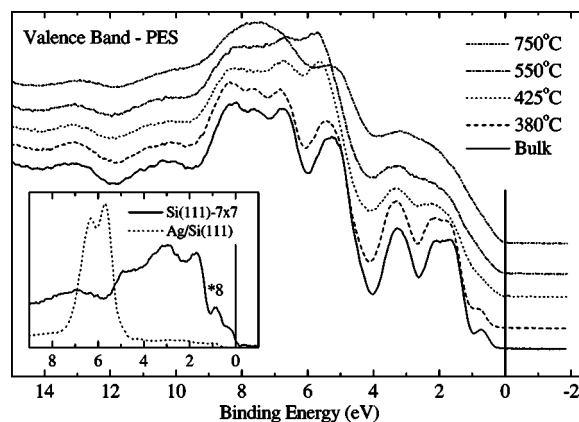


FIG. 1. Valence-band spectra of Ce@C<sub>82</sub>, taken at 60-eV incoming photon energy. Labels indicate the annealing temperature. All spectra have been normalized to the integrated intensity between 0- and 10-eV binding energy, and the annealed spectra have been shifted for clarity. The inset shows valence-band spectra of clean Si(111)-(7 $\times$ 7) (rescaled by 8), and Ag/Si(111)-( $\sqrt{3} \times \sqrt{3}$ )-30° before deposition of the fullerene.

valent bonding between the molecules and the Si(111) substrate layer, again without any oxidation.

As our objective is to follow the electronic state of the cerium atom, whilst the cage increases its interaction with the surrounding environment, we monitor the spectral changes after 10-min annealing at 380, 425, 550, and 750 °C, respectively, allowing enough time for cooling to room temperature before measurements were taken. In this way we probe the sample as we reach ML Ce@C<sub>82</sub> on Ag/Si after 425 °C, and a strongly bound (sub)-ML on Si after 750 °C. We have measured the valence band, Si 2*p*, and C 1*s* photoemission spectra, as well as C 1*s*-2*p* and Ce 3*d*-4*f* NEXAFS spectra, during the annealing process. All photoemission spectra presented here were taken at normal emission and with the incoming light at 45° with respect to the surface normal, whereas the NEXAFS spectra were recorded in normal incidence and with the detector at 45° to the surface normal.

#### A. Valence-band PES

Figure 1 shows the valence-band spectra of Ce@C<sub>82</sub>, taken after different stages of the annealing cycle. The bulk spectrum at the bottom of the figure clearly displays characteristic higher fullerene features: the C $\sigma$  related orbitals are located above 6-eV binding energy, and the C $\pi$  orbitals are organized in four distinct peaks at 1.65, 2.10, 3.26, and 5.3 eV. The small feature centered at 0.73 eV is similar to the onset seen in La@C<sub>82</sub> and was identified there as a single occupied molecular orbital (SOMO) of C $\pi$  origin, with very little La character.<sup>18</sup> Compared to La<sup>3+</sup>, Ce<sup>3+</sup> has an extra 4*f* electron, which might not be participating in the atom-cage bonding. This would give rise to an extremely narrow and weak feature in the valence band that would escape detection amidst the much stronger carbon-dominated orbitals.<sup>19</sup>

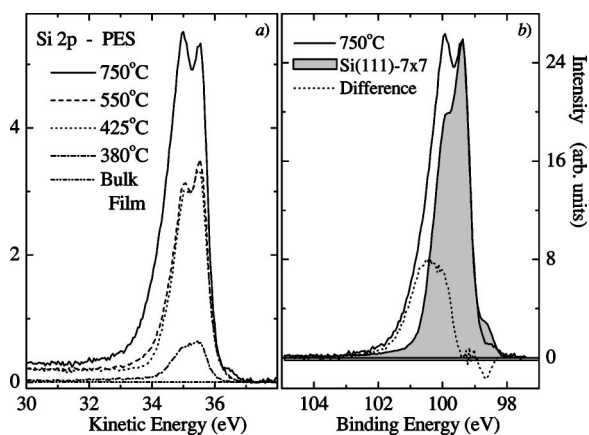


FIG. 2. Si  $2p$  core-level spectra, taken at 140-eV incoming photon energy. (a) Spectra taken after annealing at the indicated temperatures, normalized to the photon flux. (b) The 750 °C spectrum rescaled to the Si  $2p_{3/2}$  peak of the clean, reconstructed silicon surface before deposition, plus their subtraction.

After annealing at 380 °C, there is little change except from a slight increase in width of the SOMO feature, which may have its origin in the decrease of the layer thickness, allowing the signal of the underlying Ag/Si valence band to mix through. After 425 °C, however, all the  $C\pi$ -related bands below 5 eV have broadened out considerably and the band at 5.2 eV has shifted and increased in energy being influenced by the Ag  $4d$  feature sitting underneath it (see inset to Fig. 1). The increased broadening of the  $C\pi$  features is caused by the fact that previously identical carbon sites contributing to the lower binding-energy orbitals now have become distinct due to the binding of carbon atoms to the Ag/Si surface at the bottom of the fullerene cage, thereby lifting the degeneracy of the energy levels. Annealing to 550 °C spreads out the lower-lying features completely and the individual bands are hardly recognizable anymore.

The final curve shows the valence band after annealing at 750 °C. Only three distinct shapes can be seen now that the  $C\sigma$  bonds have also been affected by the strong covalent bonding to Si, and the fullerene cage must therefore be heavily distorted. The cage, however, is still intact, as will be discussed in Sec. III C. The influence of the Ag  $4d$  orbitals has now disappeared, which is reflected by the decrease in intensity and binding energy of the 5.2-eV feature.

### B. Si $2p$ PES

Monitoring surface sensitive Si  $2p$  spectra (taken at 140-eV incoming photon energy) is an excellent way of studying the formation of C-Si bonds, as the presence of C-Si bonds will manifest itself immediately in the decrease of the slope of the high binding-energy (BE) side of the Si  $2p$  peak and leads to the formation of a true tail, or even a bulge, when the number of C-Si bonds increases.<sup>20,21</sup> The spectra shown in Fig. 2 are all aligned with the Si  $2p_{3/2}$  peak position of the clean Si(111)-(7 $\times$ 7) surface. The left-hand side [Fig. 2(a)] shows the intensity, as taken, of the Si  $2p$  core level as a function of annealing temperature. What is immediately clear from these measurements is that, although Ce@C<sub>82</sub>

desorption has already started at 380 °C, allowing the Si  $2p$  signal to be recovered, the majority of the molecules are desorbed when the sample is annealed at 425 °C. In fact, the spectra indicate that a monolayer coverage is reached, because subsequent annealing at 550 °C does not significantly increase the Si  $2p$  intensity any further. It is not until the silver starts desorbing above 550 °C that another increase in Si  $2p$  signal is achieved.

In addition, apart from the intensity, the shape of the spectrum also changes when going from a monolayer of Ce@C<sub>82</sub> on Ag/Si(111) to a monolayer of Ce@C<sub>82</sub> bound directly to silicon. This can be seen in Fig. 2(a), where the intensity of the Si  $2p_{1/2}$  component appears to be higher than the Si  $2p_{3/2}$  component after the 750 °C anneal. The reason for this increase of intensity on the high binding-energy side of the Si  $2p$  peak is, as we stated at the beginning of this section, caused by C-Si bonding. In order to show that the Si  $2p$  peak has really broadened out significantly we have rescaled the 750 °C peak to match the intensity of the Si  $2p$  peak of the clean surface (after a Shirley background subtraction). This is shown in Fig. 2(b), which also shows the subtraction of the clean Si surface peak from the rescaled annealed monolayer peak. We emphasize here that we by no means expect that the surface underlying the Ce@C<sub>82</sub> molecules now is a perfect 7 $\times$ 7 reconstruction, we just merely want to point out the difference in Si  $2p$  signal of silicon subjected to carbon bonding with respect to that of an unimpaired surface. The subtraction spectrum, similarly, is also indicative, but not an exact representation, of the expected weight of the newly formed C-Si bonds. We do not present a fit of the Si  $2p$  spectrum at this point, as we believe there are too many parameters needed and too little physical constraints at hand to warrant a meaningful interpretation.

It is, nevertheless, noteworthy to point out that there is a partial recovery of the Si  $2p$  rest atom peak on the low binding-energy side of the bulk peak. From Fig. 2(b) one can see that this is, however, slightly downward shifted in binding energy. This and a reduced intensity give rise to a small negative structure in the subtraction plot. But the mere presence of a rest atom peak, and the absence of a photoemission peak at a relative binding energy of  $\sim +4$  eV, associated with silicon oxide formation, indicates that we still have a clean, nonoxidized Si surface. Attempts to follow the same evolution with regards to any C-Ag bonding failed, due to poor signal-to-noise ratios on the very weak Ag  $3d$  peaks, which only appeared in surface-sensitive spectra after the 425 and 550 °C anneals.

### C. C $1s$ PES and XAS

Instead of monitoring the Ag  $3d$  emission we can, however, follow the evolution of the C  $1s$  photoemission spectrum as depicted in Fig. 3. To allow for a better comparison, the C  $1s$  spectra were all normalized and aligned to the bulk film spectrum. The normalization factors next to the temperature labels reflect a steady decrease in the C  $1s$  intensity until the monolayer is reached at 425 °C, followed by a final decrease after the silver has desorbed. The overall trend of the higher temperatures is mirrored in the widening of the C

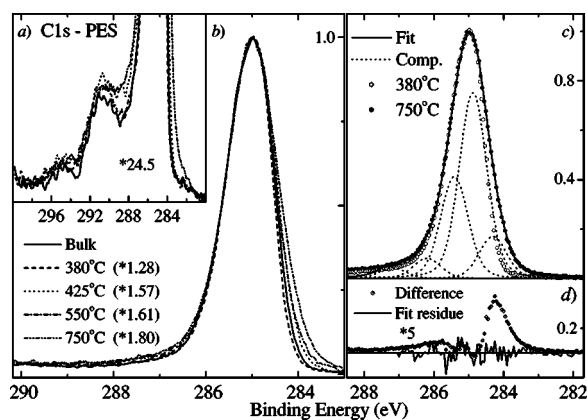


FIG. 3. All C 1s core-level spectra were taken at 400-eV incoming photon energy, normalized to the photon flux, and then aligned and normalized to the bulk C 1s (BE 285.0 eV). Annealing temperatures as indicated. In (a) an enlarged view of the shake-up structures on the high-binding-energy side. For clarity, the 550 °C spectrum is left out. In (b) the widening of the C 1s peak with annealing is apparent, especially at the low-BE side. Normalization factors as indicated. (c) depicts the 5-peak fit to the 750 °C spectrum (see text for details) and (d) depicts the 750-380 °C difference spectrum, and the rescaled residue of the 5-peak fit.

1s peak, but the narrowest spectrum is actually the one taken after the 380 °C anneal (or, in fact, in the entire range 300-340-380 °C, not shown). This suggests that the bulk film might be more disordered than the annealed multilayers. The smallest full width at half maximum (FWHM), as measured, is 1.15 eV (1.19 bulk), passes through 1.22 eV reaching the monolayer, and settles at 1.3 eV after the 750 °C anneal. Another noticeable feature is that the main change seems to occur on the low binding-energy side of the peak. We have attempted to quantify this somewhat further in Figs. 3(c) and 3(d), by showing our 5-peak fit to the 750 °C spectrum. Two peaks, separated by 0.54 eV, are needed to fit the main body of all our measured C 1s lines. We believe these two peaks represent the “envelope functions” for the multitude of small differences in C 1s binding energies caused by (a) the presence of the cerium atom and (b) the three locally different carbon sites found in C<sub>82</sub> and other higher fullerenes.<sup>22</sup> An additional two peaks are inserted on the high BE side to account for the onset of the shake-up structures and other energy losses. The fifth peak was only needed whilst fitting the 550 °C spectrum and beyond. Previous papers have shown that the formation of covalent C-Si bonds through annealing is accompanied by a new peak at approximately 1-eV below the main C 1s line.<sup>21</sup> We find a consistent fit to all five C 1s spectra with the fifth peak emerging at 0.57-eV below the main line, increasing in intensity from 9% (550 °C) to 23% (750 °C) of the main fit component. The Lorentzian linewidth of the fit components steadily increases from 0.12 to 0.20 eV throughout the annealing above 380 °C; this can be explained by the notion that the increased interaction of the cage with the substrate means that more decay channels are available. This, in turn, will decrease the lifetime and therefore increase the intrinsic Lorentzian width of the C 1s line. In Fig. 3(d) a difference spectrum of the 750 and 380 °C spectra is also plotted to

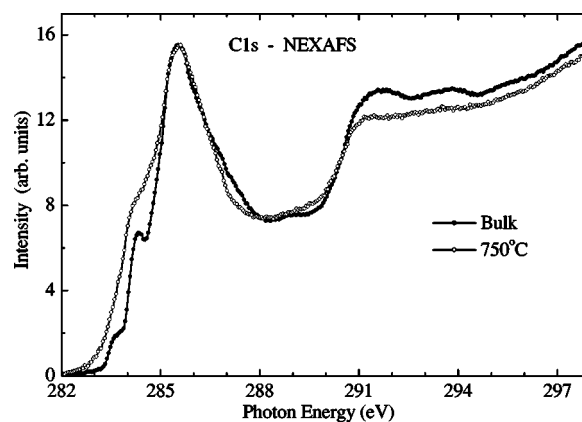


FIG. 4. C 1s NEXAFS spectra, taken in partial yield mode, normalized to the photon flux. The spectrum taken after annealing at 750 °C is scaled up by a factor of 1.1 after background subtraction.

provide an alternative illustration of the increase in width. Although the “new” peak is less than 1-eV away from the main line, it dramatically increases after removal of the Ag layer and we therefore believe it is indeed indicative of C-Si bond formation. Compared to the enormous changes in the valence band and the Si 2p spectra, the broadening of the C 1s is relatively modest. This, however, is not unusual for covalently bound fullerene systems.<sup>2</sup>

A better way of assessing the bonding strength in these cases is to examine the evolution of the shake-up structures on the high-binding-energy side of the carbon 1s peaks after normalization to the main peak intensities (see Fig. 3, inset). These structures reflect those final states of the photoemission process, where the molecule has been left in an excited state. As the symmetry of the molecule is lower than in C<sub>60</sub>, the convolution of occupied and unoccupied states does not exhibit clear interband features and the only distinct peak that can be seen is a broad structure, centered at about 6-eV above the C 1s main line, normally associated with the creation of a collective  $\pi$  electron plasmon. Upon annealing, the plasmon feature gradually loses intensity and, after annealing at 750 °C, broadens out as well. This indicates that there is increased screening of the collective electronic response of Ce@C<sub>82</sub> molecules on the Ag/Si surface and that, in addition, the cage distorts when it is strongly bound to the silicon surface after annealing at 750 °C. It is, however, *still intact* following this high-temperature anneal, since the shake-up structure remains clearly visible. In order to further convince ourselves that the majority of the Ce@C<sub>82</sub> molecules is still unimpaired we performed time-of-flight secondary ion mass spectroscopy (TOF-SIMS) on the sample and indeed found the strongest peak to be at the combined Ce@C<sub>82</sub> mass.

This picture is further corroborated by C 1s NEXAFS spectra, depicted in Fig. 4, which represent a measure of the unoccupied states of the core-ionized molecule. It has been shown that C 1s NEXAFS spectra are sensitive to the specific isomer of the fullerene cage in the case of Tm@C<sub>82</sub>, showing different energies for the lowest unoccupied molecular orbitals (LUMOs) of distinct isomers as well as

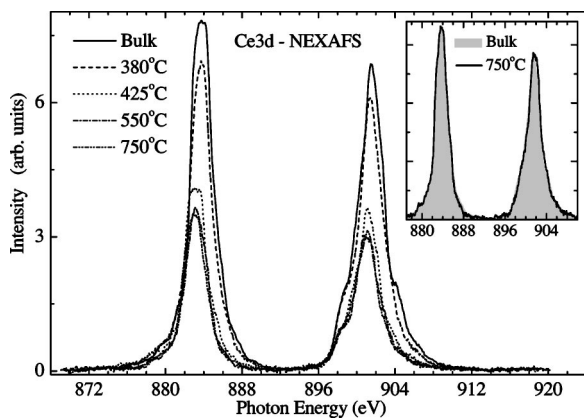


FIG. 5. Ce  $3d$  NEXAFS spectra, taken in partial yield mode, normalized to the photon flux, and background subtracted. In the inset, the spectrum taken at  $750^\circ\text{C}$  is rescaled and shifted by  $0.7\text{ eV}$  to match the bulk curve.

sharper peaks for the more symmetric isomer.<sup>23</sup> In our bulk Ce@C<sub>82</sub> NEXAFS spectrum, we can distinguish a sharp peak at  $284.3\text{ eV}$  and a weaker feature at  $283.6\text{ eV}$  in an approximate 4:1 intensity ratio. Recent work has shown the existence of two isomers in Ce@C<sub>82</sub> samples in the same ratio.<sup>14</sup> We therefore tentatively conclude that the sharper feature corresponds to the LUMO of Ce@C<sub>82</sub>-{C<sub>2v</sub>} and the weaker feature most likely corresponds to the second isomer, which should have lower symmetry, such as C<sub>s</sub>. The majority of the unfilled  $\pi^*$  orbitals overlap in energy and form the strongest peak in the NEXAFS spectrum at  $285.5\text{ eV}$ , and the onset of a  $\sigma^*$  band is at  $290\text{ eV}$ . After annealing, the isomer signatures are no longer clearly discernible, due to the distortion and strong covalent bonding of the fullerene cage to the silicon substrate. As in the case of the C  $1s$  photoemission main line, there is no striking broadening or large shift of the cluster of  $\pi^*$  orbitals at  $285.5\text{ eV}$ , consistent with a covalent type of bonding.

#### D. Ce $3d$ XAS

Having examined the effects of annealing on the cage by means of valence-band photoemission, Si  $2p$  PES, C  $1s$  PES, and C  $1s$  NEXAFS, we have ascertained that in the case of a monolayer of Ce@C<sub>82</sub> on silver-terminated silicon, annealing mainly increases the screening of the collective excitations. The fullerene cage is distorted and covalently bound to the silicon substrate after annealing at  $750^\circ\text{C}$ . In this section we will investigate the effect the substrate-cage bonding has on the encapsulated cerium atom. We chose to use NEXAFS instead of photoemission, because it is a more reliable probe of changes in the valence and electronic structure of atoms with localized levels such as  $3d$  and  $4f$  systems as it suffers far less from final-state screening effects encountered in photoemission.<sup>24</sup> The Ce  $3d$  NEXAFS spectra are depicted in Fig. 5. The general shape of the bulk spectrum is consistent with a valency of around  $3+$ , without any signs of mixed valence, as compared to Ce  $3d$  XAS measurements and calculations of CeF<sub>3</sub> and CeO<sub>2</sub>.<sup>25-27</sup> The spectrum is therefore predominantly defined by the spin-orbit splitting and the

multiplet fine structure of the Ce  $4f^2$  final state. If there is any change in the valency of the cerium atom during the annealing process, the shape will be affected in a straightforward manner, since any change towards Ce<sup>4+</sup> will cause additional peaks to rise up at  $6\text{-eV}$  above the main Ce  $4f^2$  lines, associated with admixture of the  $4f^1$  final state. However, even in the nominally Ce<sup>4+</sup> material CeO<sub>2</sub> the relative weight of the  $4f^0$  state is never more than 30%. Shifts to lower valency might be unlikely, but would cause a change in the asymmetry of the  $M_5$  peak, resembling then the spectrum of Pr<sup>3+</sup>.<sup>25</sup>

However, what actually happens is that the spectral shape does not change significantly, but the position of the whole spectrum is shifted  $0.5\text{ eV}$  to lower energy when the monolayer is reached, and a further  $0.2\text{ eV}$  when the sample is annealed to  $750^\circ\text{C}$ . This means that the potential well provided by the surrounding carbon cage is affected by its surroundings. It appears less deep to the cerium atom, when just a monolayer of Ce@C<sub>82</sub> is left on top of the semiconducting Ag/Si substrate (due to image charge screening). It might be more strongly screened by the Si(111)-(7×7), which partially emerges again after the  $750^\circ\text{C}$  anneal as reflected by a small rest atom peak in the Si  $2p$  spectra. In addition to that, the potential well should flatten out when the cage gets distorted at the final annealing stage.

#### IV. CONCLUSIONS

In conclusion, we have performed a complete photoemission and x-ray absorption study of Ce@C<sub>82</sub>, including an annealing study of a Ce@C<sub>82</sub> film on silver-terminated Si(111), starting from the thick sublimed film. After annealing at  $425^\circ\text{C}$  a monolayer coverage is obtained, as shown by the valence band and Si  $2p$  PES spectra. These do not appear to change or lose intensity further after subsequent annealing at  $550^\circ\text{C}$ . Annealing above  $600^\circ\text{C}$  causes the silver to desorb from the surface, leaving the fullerene molecules to bind directly to the silicon surface, as again evidenced by the valence band and Si  $2p$  PES spectra. Carbon  $1s$  photoemission and x-ray absorption spectra further testify to the covalent bonding on the Si substrate and distortion of the carbon cage. The valency of the imprisoned cerium atom, however, is remarkably unaffected throughout the whole annealing procedure, although it does appear to feel the change in strength of the potential well in which it is immersed. More subtle changes could occur in the cerium related orbitals of the valence band, and an experimental and theoretical resonant photoemission study to ascertain the influence of the shallow Ce  $4f$  and  $5d$  levels is now underway. The final point to make is that the carbon cage is a perfect way of shielding normally very reactive cerium from oxidation, both in CS<sub>2</sub> solution at ambient pressure, and annealing up to the strongly bound monolayers on silicon, since at no stage during or after our measurements was any evidence of oxidation found in the spectra.

#### ACKNOWLEDGMENTS

We gratefully acknowledge the Engineering and Physical Sciences Research Council (EPSRC) for financial support

under Grant No. GR/R01880/01, as well as Nanospectra under Grant No. HPRN-CT-2002-00320. T.J.S.D. thanks the Royal Society for a Joint Research Project-Japan. We also thank the Council for the Central Laboratory of the Research

Councils (CCLRC) for beam time at SRS-Daresbury, and B. Hill, G. Miller, and V. Dhanak for their help and technical assistance. Lastly, we thank Dr. Frank Rutten for performing the TOF-SIMS measurements.

\*Electronic address: karina.schulte@nottingham.ac.uk

†URL: <http://www.nottingham.ac.uk/physics/research/nano/>

- <sup>1</sup>H. Shinohara, Rep. Prog. Phys. **63**, 843 (2000).
- <sup>2</sup>P. Rudolf, M. S. Golden, and P. A. Brühwiler, J. Electron Spectrosc. Relat. Phenom. **100**, 409 (1999).
- <sup>3</sup>M. Knupfer, Solid State Ionics **42**, 42 (2001).
- <sup>4</sup>We realize that although the use of the words “endohedral fullerene” and “X@C<sub>82</sub>” has become widespread in the physics community, the correct IUPAC nomenclature is in fact “*incarceration*” and “*iCeC<sub>82</sub>*,” denoting the *incarceration* of an atom or molecule. This description is more consistent, for instance, when adducting groups to the carbon cage.
- <sup>5</sup>W. Harneit, C. Meyer, A. Weidinger, D. Suter, and J. Twamley, Phys. Status Solidi B **233**, 453 (2002); C. Meyer, W. Harneit, A. Weidinger, and K. Lips, *ibid.* **233**, 462 (2002).
- <sup>6</sup>C. Cepek, P. Schiavuta, M. Sancrotti, and M. Pedio, Phys. Rev. B **60**, 2068 (1999).
- <sup>7</sup>I. Marenne, P. Rudolf, M. R. C. Hunt, J. Schiessling, L. Kjeldgaard, P. Bruhwiler, M. S. Golden, T. Pichler, M. Inakuma, and H. Shinohara, AIP Conf. Proc. **544**, 146 (2000).
- <sup>8</sup>P. Moriarty, Y. R. Ma, M. D. Upward, and P. H. Beton, Surf. Sci. **407**, 27 (1998).
- <sup>9</sup>For an overview see, e.g., A. K. McMahan, C. Huscroft, R. T. Scalettar, and E. L. Pollock, J. Comput.-Aided Mater. Des. **5**, 131 (1998).
- <sup>10</sup>S. Nagase and K. Kobayashi, Chem. Phys. Lett. **228**, 106 (1994).
- <sup>11</sup>J. Ding, L.-T. Weng, and S. Yang, J. Phys. Chem. **100**, 11120 (1996).
- <sup>12</sup>B.-B. Liu, G.-T. Zou, H.-B. Yang, S. Yu, J.-S. Lu, Z.-Y. Liu, S.-Y. Liu, and W.-G. Xu, J. Phys. Chem. Solids **58**, 1873 (1997).
- <sup>13</sup>W. Sato, K. Sueki, K. Kikuchi, K. Kobayashi, S. Suzuki, Y. Achiba, H. Nakahara, Y. Ohkubo, F. Ambe, and K. Asai, Phys. Rev. Lett. **80**, 133 (1998).
- <sup>14</sup>K. Shibata, Y. Rikiishi, T. Hosokawa, Y. Haruyama, Y. Kubozono, S. Kashino, T. Uruga, A. Fujiwara, H. Kitagawa, T. Takano, and Y. Iwasa, Phys. Rev. B **68**, 094104 (2003).
- <sup>15</sup>M. Kanai, T. J. S. Dennis and H. Shinohara, AIP Conf. Proc. **633**, 35 (2002).
- <sup>16</sup>L. Wang, K. Schulte, R. A. J. Woolley, M. Kanai, T. J. S. Dennis, J. Purton, S. Patel, S. Gorovikov, V. R. Dhanak, E. F. Smith, B. C. C. Cowie, and P. J. Moriarty, Surf. Sci. **564**, 156 (2004).
- <sup>17</sup>G. Le Lay, M. Göthelid, V. Y. Aristov, A. Cricenti, M. C. Håkansson, C. Giammichele, P. Perfetti, J. Avila, and M. C. Ascensio, Surf. Sci. **377-379**, 1061 (1997).
- <sup>18</sup>D. M. Poirier, M. Knupfer, J. H. Weaver, W. Andreoni, K. Laasonen, M. Parrinello, D. S. Bethune, K. Kikuchi, and Y. Achiba, Phys. Rev. B **49**, 17403 (1994).
- <sup>19</sup>Preliminary results of a *4d-4f* and *3d-4f* resonant photoemission study of Ce@C<sub>82</sub> indeed show an appreciable enhancement in the low-binding-energy region of the valence band at threshold.
- <sup>20</sup>A. Pesci, L. Ferrari, C. Comicioli, M. Pedio, C. Cepek, P. Schiavuta, M. Pivetti, and M. Sancrotti, Surf. Sci. **454-456**, 832 (2000).
- <sup>21</sup>M. de Seta, N. Tomozeiu, D. Sanvitto, and F. Evangelisti, Surf. Sci. **460**, 203 (2000).
- <sup>22</sup>A. Bassan, M. Nyberg, and Y. Luo, Phys. Rev. B **65**, 165402 (2002).
- <sup>23</sup>T. Pichler, M. Knupfer, M. S. Golden, T. Böske, J. Fink, U. Kirbach, P. Kuran, L. Dunsch, and Ch. Jung, Appl. Phys. A: Mater. Sci. Process. **66**, 281 (1998).
- <sup>24</sup>T. Pichler, Z. Hu, C. Grazioli, S. Legner, M. Knupfer, M. S. Golden, J. Fink, F. M. F. de Groot, M. R. C. Hunt, P. Rudolf, R. Follath, C. Jung, L. Kjeldgaard, P. Brühwiler, M. Inakuma, and H. Shinohara, Phys. Rev. B **62**, 13196 (2000).
- <sup>25</sup>B. T. Thole, G. van der Laan, J. C. Fuggle, G. A. Sawatzky, R. C. Karnatak, and J.-M. Esteva, Phys. Rev. B **32**, 5107 (1985).
- <sup>26</sup>T. Jo and A. Kotani, Phys. Rev. B **38**, R830 (1988).
- <sup>27</sup>M. Nakazawa, S. Tanaka, T. Uozumi, and A. Kotani, J. Electron Spectrosc. Relat. Phenom. **79**, 183 (1996).