Phase coexistence of clusters and islands: europium on graphene

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Abstract. The adsorption and equilibrium surface phases of europium (Eu) on graphene on Ir(111) are investigated in the temperature range from 35 to 400 K and for coverages ranging from a small fraction of a saturated monolayer to the second layer by scanning tunnelling microscopy. Using density functional theory including 4f-shell Coulomb interactions and modelling of electronic interactions, excellent agreement with the experimental results for the equilibrium adsorbate phase, adsorbate diffusion and work function is obtained. Most remarkably, at 300 K in an intermediate coverage range a phase of uniformly distributed Eu clusters (size 10–20 atoms) coexists in two-dimensional equilibrium with large Eu-islands in a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. We argue that the formation of the cluster phase is driven by the interplay of three effects. Firstly, the metallic Eu–Eu binding leads to the local stability of $(\sqrt{3} \times \sqrt{3})R30^\circ$ structures. Secondly, electrons lower their kinetic energy by leaving the Eu clusters, thereby doping graphene. Thirdly, the Coulomb energy penalty associated with the charge transfer from Eu to graphene is strongly reduced for smaller clusters.

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1. Introduction

In recent years, it has become apparent that the properties of graphene, even if present in high structural quality, depend critically on its environment (e.g. on the type and distribution of chemical species adsorbed to graphene [1]). As an example, the enormous mobilities for charge carriers in graphene predicted from theory are often not realized for adsorbed graphene, be it on SiC [2] or for exfoliated graphene on SiO$_2$ [3]. Only for suspended graphene [4] or graphene on BN [5], mobilities come close to the theoretical values.

This critical dependence of the graphene properties on the environment may also be turned into an advantage if new compound materials are constructed that bestow graphene with novel properties while keeping the desirable features of its electronic band structure intact (e.g. its conical band structure and the Dirac cone). As an example, it was proposed to bring the ferromagnetic insulator EuO into contact with graphene in order to induce a spin split Dirac cone with the resulting option for spin filtering in graphene [6]. Due to the large magnetic moment of 7 $\mu_B$ of the europium (Eu) 4f-shell, metallic Eu is also a material with the potential to bestow magnetic properties on graphene.

As a prerequisite for future work in this direction, it is necessary to understand in detail the adsorption and growth of Eu on graphene. Moreover, we believe that a systematic study of Eu adsorption and growth as a function of coverage and temperature under controlled, clean conditions offer insight into fundamental aspects of the interaction of graphene with an entire class of materials.

In this paper, we present a temperature- and coverage-dependent study of Eu adsorption on graphene supported by Ir(111). Graphene on Ir(111) is selected, as it is readily formed in situ as monolayer flakes or as complete and dense monolayer film in excellent structural quality under...
well-defined ultra-high vacuum (UHV) conditions [7–9]. It is only marginally doped, possesses a largely preserved Dirac cone (only a tiny band gap opens above the Fermi level) [10, 11], and is physisorbed to the substrate as indicated by its large height of 3.38 Å [12] above the Ir. Despite its 25 Å moiré superperiodicity resulting from graphene’s lattice mismatch with Ir(111) [7], it can be considered as a reasonable experimental approximation to unperturbed graphene.

Adsorption of transition metals with their localized d-valence orbitals tends to induce local rehybridization of graphene on Ir(111) to diamond-like $sp^3$ carbon [13, 14]. Their localized orbitals interact with the carbon $p_z$-orbitals and thereby destroy the $\pi$-electronic system. Such a hybridization does not take place through Eu adsorption, which displays valence electrons with an isotropic charge distribution. Therefore, Ir(111) as graphene support will only have minor effects on the adsorption properties of Eu.

The demand for careful and systematic experimental adsorption studies on graphene is also underlined by the numerous first-principles calculations related to the effects of adsorbed atoms on graphene [15–26], to a large extent for transition metals. We believe it is fair to say that there is a considerable imbalance between calculations and experiments. There has been hardly any systematic experimental adsorption study of graphene and consequently the theoretical work is somewhat limited. Here, we adopt a combined theoretical–experimental approach, thoroughly investigate the adsorption properties of Eu on graphene in theory and experiment and cross link the results of both.

We combine temperature-dependent Eu growth and annealing experiments, scanning tunnelling microscopy (STM), work function measurements by $I(z)$ scanning tunnelling spectroscopy (STS), low-energy electron diffraction (LEED), density functional theory (DFT) calculations including 4f-shell Coulomb interactions and qualitative modelling of electronic interactions in order to gain an understanding of the Eu/graphene adsorbate system. While we observe clear similarities of the adsorption properties of Eu on graphene to the well-studied system of potassium adsorption on graphite [27–30] (repulsive adsorbate interactions, phase coexistence of phases with different densities and relevance of band energy effects), pronounced differences will also become apparent. Most notably, despite the presence of repulsive interactions, for small adsorbate coverages Eu forms small clusters, uniformly distributed over the graphene substrate, rather than a disperse phase of adatoms. We will show that cluster formation may be understood by analysing the interplay among Eu valence electronic structure, charge transfer to graphene and the low graphene density of states close to the Fermi level.

This paper is organized as follows. After introducing the experimental and calculational methods in section 2, we show in section 3 the experimental results for coverage-dependent Eu adsorption at 35 K (section 3.1) and 300 K (section 3.2). In section 3.3, we present annealing experiments which are key to distinguish between growth kinetics and equilibrium phase properties. The experimental section terminates with the results of the work function measurements obtained by $I(z)$ STS (section 3.4). In section 4, the DFT results for coverage-dependent adsorption energies and electronic structure (section 4.1) as well as for the work function of the adsorbed layer (section 4.2) are presented. In section 5, we analyse our results and link experiments and calculations. Section 5.1 establishes the equilibrium phases of Eu on graphene, section 5.2 explains the observed phase coexistence of clusters and islands on graphene, section 5.3 discusses the low-temperature data and section 5.4 makes a comparison to previous work.
2. Experimental and calculation methods

Experiments were performed in a UHV chamber with base pressure below $3 \times 10^{-11}$ mbar. The Ir(111) substrate crystal was prepared by repeated cycles of sputtering at 920 K and annealing to 1520 K, yielding clean Ir(111) with terrace widths of the order of 100 nm. For graphene growth, two methods were employed. To prepare graphene flakes with a typical linear dimension of 30 nm covering a fraction of 0.2 of the Ir(111) substrate, temperature programmed growth (TPG) was used. TPG consists in room temperature ethylene adsorption till saturation followed by subsequent thermal decomposition at a temperature—here 1500 K—selecting the flake size [7, 8]. To achieve a well-oriented graphene film entirely covering the substrate, the TPG method was combined with chemical vapour deposition (TPG + CVD). For the TPG + CVD graphene film, in addition to the TPG step, the flakes were grown to full coverage through exposure to a pressure of $1 \times 10^{-7}$ mbar of ethylene at 1150 K for 1200 s [9]. Such TPG + CVD films are continuous over substrate steps [31].

For Eu growth at room temperature or annealing of Eu films from low to room temperature closed TPG + CVD films were necessary; otherwise intercalation of Eu underneath graphene takes place. TPG + CVD films were used for the experiments represented by figures 1(d) and (g), figure 3, and figure 5. For Eu growth at low temperature, TPG graphene was used. The provided sufficiently large areas for structure formation and allowed us at the same time the observation of Eu on Ir(111). This was helpful for precise coverage calibration, as for small coverages Eu forms on Ir(111) only phases of separated, single adatoms [32]. Thereby, for the experiments shown in figures 1(c), (e), (f) and (h) the deposited amount of Eu was precisely evaluated by counting adatoms on STM topographs of Ir terraces adjacent to graphene flakes.

For Eu evaporation high-purity material from the Ames laboratory was evaporated from a water-cooled Knudsen cell. To ensure clean films, the pressure during growth was kept below $1 \times 10^{-10}$ mbar. To establish such conditions prolonged degassing of the Eu was conducted. Reproducibility and flux control of Eu was ensured by measuring the deposition rate with a quartz crystal microbalance moved to the precise sample growth position prior to each growth experiment. Deposited amounts are specified throughout the paper in monolayers (ML), where we define 1 ML (or 100% ML) as the amount of Eu corresponding to one adsorbed Eu atom per graphene unit cell, i.e. per two C atoms.

Imaging was performed with a home built, magnetically stabilized STM [33] at 35 K, unless stated otherwise. Due to the high mobility of Eu on graphene, low-temperature imaging was mandatory. For the same reason, only low tunnelling currents of the order of 100 pA could be used to image the dispersed phase of Eu on graphene. The sample bias voltage $U_s$ and the tunnelling current $I_t$ are given for each topograph. The images were digitally post-processed with WSxM software [34].

LEED measurements were carried out using a three-grid rear view analyser in combination with a video camera mounted on the LEED flange. For all experiments shown, the diffraction patterns were recorded over an extended energy range from 20 to 150 eV. This enables unambiguous specification of the superstructures with respect to the well-oriented graphene lattice. LEED patterns are displayed with inverted contrast to enhance the visibility of the diffraction spots.

A first-principles description of the Eu adsorption on graphene on Ir(111) is achieved by means of DFT calculations within the generalized gradient approximation (GGA) [35].

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consider both, non spin-polarized calculations with the Eu 4f-shell frozen to $f^7$ configurations and spin-polarized calculations including the Eu 4f-shell, where we account for the strong local Coulomb interactions of the Eu 4f-electrons within the GGA + U approach. Here, we use the Coulomb parameters of $U = 7$ eV and $J = 1$ eV, which have been established to be well suited

**Figure 1.** (a) STM topograph of a graphene flake grown on Ir(111) by TPG. The moiré corrugation is visible in the flake. The inset (4.1 nm × 4.1 nm) displays the moiré together with the atomically resolved graphene lattice. (b) Inverted contrast LEED pattern of Ir(111) partially covered with TPG graphene flakes at a primary electron energy of 78 eV. Red and black arrows highlight first-order Ir and graphene reflections, respectively. (c–h) STM topographs after Eu adsorption at 35 K. White lines indicate boundaries of graphene flakes. (c) 0.8% ML Eu ($U_s = −1.8$ V, $I_t = 14$ pA). (d) 1.8% ML Eu ($−0.67$ V, 11 pA). (e) 3.3% ML Eu ($−1.8$ V, 50 pA). (f) 5% ML Eu ($−2.1$ V, 25 pA). (g) 15% ML Eu ($−1.5$ V, 86 pA). (h) 25% ML Eu ($−0.65$ V, 93 pA). (i) Inverted contrast LEED pattern of the 25% ML experiment at a primary electron energy of 78 eV. Black lines indicate the unit cell of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure with respect to the graphene lattice. Red arrows indicate the primitive translations of the Ir(111) surface unit cell. The STM topograph size is always 40 nm × 40 nm.
for describing the spectral properties of rare earth systems [36, 37]. To simulate different Eu coverages, we consider hexagonal graphene supercells with sizes between $(\sqrt{3} \times \sqrt{3})R30^\circ$ supercells (6 C atoms) and $6 \times 6$ supercells (72 C atoms) containing different amounts of adsorbed Eu as well as graphene on four-layer Ir(111) slabs. Using the Vienna ab initio simulation package (VASP) [38] with the projector-augmented wave [39, 40] basis sets, we obtain relaxed adsorption geometries and calculate electronic properties including the local density of states (LDOS), work functions and dipole moments. In all calculations, the carbon atoms and Eu atoms were relaxed until forces were below 0.02 eV Å$^{-1}$. In the calculations with Ir substrate, the Ir(111) slab was forced to a perfect fcc lattice with lattice constant 3.5 Å to avoid computationally very expensive calculations involving supercells with lateral extent corresponding to the full moiré structure.

3. Experimental results

3.1. Low-temperature europium (Eu) adsorption

As a prerequisite for the presentation and discussion of the low-temperature Eu adsorption experiments, figure 1(a) displays a graphene flake on Ir(111) as obtained by the TPG method. The graphene is well oriented with respect to the substrate such that the $\langle 1\bar{1}0 \rangle$-directions of Ir(111) and the $\langle 10\bar{1}0 \rangle$-directions of graphene coincide with an angular scatter of $(0.00 \pm 0.25)^\circ$. The periodicity visible is the moiré resulting from the mismatch of the 2.461 Å of the graphene unit cell and the 2.715 Å of the Ir(111) surface unit cell, giving rise to an incommensurate $10.3 \times 10.3$ superstructure with respect to the graphene lattice (9.3 × 9.3 with respect to Ir(111)) and a pitch of 25.3 Å [7]. The relation of the moiré to the graphene lattice is visualized by the inset of figure 1(a). In a recent calculation using the van der Waals density functional (vdW-DF), the height modulation resulting from the moiré was estimated to be 35 pm [12]. The graphene is physisorbed, but with a slight chemical modulation of binding to the substrate. Figure 1(b) displays the corresponding LEED pattern, where the first-order Ir and graphene spots are surrounded by moiré reflections.

The sequence of STM topographs in figures 1(c)–(h) visualizes the evolution of the surface morphology with deposited amount $\theta$ of Eu. In figure 1(c), a graphene flake extends through the central part of the image from top to bottom. Its borders are indicated by white lines. After a dose of $\theta = 0.8$% ML Eu, dots with a rather non-uniform distribution are visible. We recalculate the Eu dot number density $\rho$ to their separation in an ideal hexagonal arrangement as $d = (\rho \cos 30^\circ)^{-1/2}$ in order to specify their average spacing. In the topograph of figure 1(c), we find $d = 13.8$ graphene unit cell repeat distances $a_C = 2.461$ Å. The dots display two distinct brightnesses with apparent heights of 3 and 5 Å, respectively. As about 60% of the dots are the brighter ones and as the average atom number $s_{av}$ in each dot is 1.6 atoms we infer that the brighter dots correspond to Eu dimers and the lower ones to single adatoms.

After deposition of $\theta = 1.8$% ML Eu in figure 1(d), the density of dots $\rho$ has roughly doubled and the dot separations are almost uniform with some hexagonal order. Comparison to figure 1(a) shows that the Eu adsorbates have locked in orientation to the graphene moiré. Indeed, we measure $d = 9.8a_C$, which is very close to the moiré repeat distance of 10.3$a_C$. Compared to figure 1(a) the average dot size increased only slightly to $s_{av} = 1.75$ atoms. This again corresponds to the proportions of brighter and darker dots assuming them to consist of dimers and monomers, respectively.
For $\theta = 3.3\%$ ML in figure 1(e), the dot density has increased by about 65% compared to figure 1(d), corresponding to a decrease in $d$ to $7.7 a_C$. While the dots still display short-range order, the apparent hexagonal order of figure 1(d) is lost. In contrast to the significant decrease in $d$, $s_{av}$ increased only slightly to $s_{av} = 1.9$ atoms. Based on the average dot size and the proportions of brighter and darker dots, we again identify them as dimers and single adatoms, respectively.

After deposition of $\theta = 5\%$ ML Eu in figure 1(f), the dot density and $d$ remained almost constant compared to figure 1(e) with $d = 7.3 a_C$. In contrast, $s_{av}$ increased significantly to $s_{av} = 2.6$ atoms. Apparently, when a critical dot separation of $d \approx 7.5 a_C$ is approached, new dimers are no longer formed. The atoms deposited additionally are integrated into existing clusters. This leads to a size increase, i.e. an increase in $s_{av}$. Adatoms are absent in figure 1(f), most clusters are still dimers and probably also some trimers are present, displaying the same brightness as dimers. A few dots in figure 1(f) display a new height level of $8 \text{Å}$. It is plausible that this level corresponds to the smallest possible two-layer clusters, a tetrahedral arrangement of Eu atoms in a tetramer.

Increasing the deposited amount to $\theta = 15\%$ ML leaves the dot density and $d$ almost unchanged at $d = 7.9 a_C$, whereas the average cluster size increases to $s_{av} = 9.3$ atoms, as shown in figure 1(g). Two height levels can clearly be distinguished in figure 1(g) which are of 5 and $8 \text{Å}$ height.

For $\theta = 25\%$ ML in figure 1(h), the cluster density has again decreased slightly through coalescence of the clusters, while they grew strongly in size compared to figure 1(g). The cluster positioning is again influenced by the moiré periodicity signified by their hexagonal arrangement and $d = 9.8 a_C$. However, their size distribution is less uniform than in figure 1(d). Their average size is $s_{av} = 24$ atoms. We note that in the first Eu layer the clusters may be partly coalesced. The atoms are arranged in a $(\sqrt{3} \times \sqrt{3})$R30° structure with respect to the graphene lattice, as visible in the LEED pattern shown in figure 1(i).

Figure 2 summarizes the evolution of $d$ and $s_{av}$ with $\theta$. It is apparent that when the minimum cluster separation of $d \approx 7.5 a_C$ is approached, cluster formation ceases and the clusters start to grow in size. When reaching the minimum separation $d$ with increasing $\theta$, the dimer appears to be the preferred, ‘magic’ cluster size, to which aggregation of additional atoms appears to be unfavourable. Noteworthy, for the same coverages on Ir(111), Eu monomers form as preferred entities. Eu monomers on Ir(111) are, for instance, visible in the surroundings of the graphene flake in figure 1(e).

For $\theta = 1.8\%$ ML, $\theta = 3.3\%$ ML and $\theta = 5\%$ ML also the most probable cluster separation $d_{prop}$ as obtained from the image self-correlation is indicated in figure 2. The values of $d$ and $d_{prop}$ agree rather well. From this agreement and with the minimal $d$ and $d_{prop}$ being considerably smaller than the moiré pitch, we conclude that the latter is not essential for the minimal cluster separation. However, when $d$ comes close to the moiré pitch the orientation order is enhanced and turned hexagonal. The observed behaviour would be consistent with a short-range attractive interaction of Eu monomers with clusters, resulting in the observed cluster growth with coverage. Moreover, the apparent initial inhibition of cluster growth beyond the dimer size and the observed short-range order indicate the presence and relevance of a repulsive interaction between adatoms and dimers. While the separation of the Eu atoms in the clusters cannot be determined directly, the observation of the $(\sqrt{3} \times \sqrt{3})$R30° structure in the larger clusters of figure 1(h) makes it plausible that Eu atoms in clusters, beginning with the dimer size, possess a characteristic distance close to the one of this structure.
Figure 2. Average cluster size $s_{\text{av}}$ in atoms (black squares), average cluster separation $d$ (blue triangles) and most probable cluster separation $d_{\text{prop}}$ (red dots) versus deposited amount $\theta$. Both distances are given in graphene unit lengths $a_C = 2.461 \, \text{Å}$. The dashed line marks the moiré repeat distance. Lines are a guide to the eyes.

A remark on the height evolution of the cluster is in place here. According to our measurements, the first layer of Eu on graphene has an apparent height of 5 Å and the second layer an apparent height of 3 Å, giving rise to 8 Å high two-layer clusters. Due to the rapid decay of the peaked LDOS of adatoms, their apparent height is considerably lower, similar to that known for adatoms on metal surfaces [41, 42]. This explains the low 3 Å apparent height of adatoms on graphene.

3.2. Room temperature Eu adsorption

Figure 3 displays the evolution of the surface morphology with increasing $\theta$ if deposited at 300 K on TPG + CVD graphene. Similar to $\theta = 3.3\%$ ML Eu deposited at 35 K, after deposition of the same amount at 300 K the sample is covered with small dispersed clusters, as shown in figure 3(a). As distinct from the low-temperature situation, the clusters are larger with $s_{\text{av}} = 14.4$ atoms instead of $s_{\text{av}} = 1.9$ atoms. Correspondingly, the average cluster separation increased from $d = 7.7 \, a_C$ to $d = 21 \, a_C$. Based on the self-correlation of the topograph shown as the inset on the lower right of figure 3(a), we conclude on a local hexagonal order, despite the apparent inhomogeneities in cluster distribution. Note also that substrate steps (more precise: locations where the graphene film bends over them) are decorated by a rim of clusters.

Upon an increase of $\theta$ to 12% ML only a slight decrease of $d$ is possible while at the same time a condensed island phase is squeezed out as visible in figure 3(b). The separation of clusters in the disperse phase has dropped to $d = 17 \, a_C$. The clusters appear larger than for $\theta = 3.3\%$ ML, but a quantitative statement is impossible due to the phase coexistence and the large scale of the structures involved. The clusters are more regularly positioned than for $\theta = 3.3\%$ ML and based on the self-correlation on the lower right of figure 3(b), we conclude on a hexagonal short-range order. Again, the substrate steps are decorated by Eu with a stripe width corresponding to the typical cluster diameter. Assuming the distance $d = 17 \, a_C$ to be the
Figure 3. (a–c) STM topographs after Eu deposition at 300 K on TPG + CVD graphene on Ir(111). (a) 3.3% ML Eu ($U_s = -1.0$ V, $I_t = 9.6$ pA, the same for the upper right inset). The inset at the lower right: two-dimensional (2D) self-correlation of a 200 nm × 200 nm image part. (b) 12% ML (−0.83 V, 87 pA, the upper right inset: −0.63 V, 4.9 pA). Inset at the lower right: 2D self-correlation of a 60 nm × 60 nm image part covered by clusters only. (c) 40% ML (−0.56 V, 0.11 nA, the same for the inset). The inset is filtered to enhance the moiré contrast. Second layer islands are encircled with blue lines. Image sizes for (a)–(c) are 320 nm × 320 nm and for the upper right insets 40 nm × 40 nm.

minimum distance of clusters achievable and assuming the clusters to possess the size observed in figure 3(a) after deposition of 3.3% ML, we estimate that beyond $\theta = 5$% ML the formation of the condensed phase sets in.

The islands of the condensed phase as well as the clusters have an apparent step height of 5 Å, consistent with our assignment for the height of the first Eu layer of clusters in the previous section. The Eu islands reflect the corrugation of the graphene moiré with Ir(111), as visible in the topographic insets of figures 3(b) and (c). While for STM imaging of graphene on Ir(111) the moiré contrast and the apparent corrugation depend strongly on tunnelling conditions, this is not the case for STM imaging of the Eu islands resting on graphene/Ir(111). We find a corrugation of $(38 \pm 2)$ pm for the voltage range $-1.6 \leq U_s \leq +0.4$ V with $I_t \approx 100$ pA. This insensitivity to the tunnelling voltage indicates that the geometric, rather than the electronic corrugation is measured. At least, the agreement of our result with the vdW-DF study is remarkable, which yields a corrugation, of $35$ pm for the graphene moiré [12].

After deposition of $\theta = 40$% ML Eu, the first Eu layer is almost perfectly closed and islands of the second layer nucleated on top, as shown in figure 3(c). The apparent height of the second layer islands is about 3.4 Å, close to the expected height for a step on the dense packed ⟨110⟩ terrace of bcc Eu. The observed height is consistent, but slightly larger than what we inferred in the previous section for the apparent height of the second layer in clusters.

The crystallographic structure of the first and second layers of condensed Eu on graphene remains to be determined. Figure 4(a) shows the LEED pattern of the 12% ML experiment. At the borders of the LEED screen the graphene spots are present, while further inside ($\sqrt{3} \times \sqrt{3}$)R30° reflections with respect to these graphene reflections are visible, together with faint moiré spots. Figure 4(b) shows an STM topograph of the same experiment, taken at the edge of an Eu island. In the upper image part graphene on Ir(111) is visible (grey), while in the
Figure 4. (a) Inverted contrast LEED pattern of the 12% ML experiment at a primary electron energy of 58 eV. (b) Corresponding STM topograph (6.6 nm × 6.6 nm, $U_s = -0.63$ V, $I_t = 18$ nA) at an Eu island edge. The white line indicates the edge of the Eu island (coloured) grown on graphene on Ir(111) (grey). The image contrast is adjusted such that the graphene and the island level are visible simultaneously. The angle between the dense-packed rows of Eu and graphene is 30°. (c) Inverted contrast LEED pattern of the 40% ML experiment at a primary electron energy of 58 eV. (d) Corresponding STM topograph (4.9 nm × 4.9 nm, $-0.04$ V, 6.7 nA) showing atomic and moiré contrast of a second layer island. The indicated $\langle 1\overline{1}00 \rangle_c$ and $\langle 1\overline{1}20 \rangle_c$ directions of the graphene lattice are also valid for (b).

lower part the Eu island grown on graphene is imaged (coloured). The angle of 30° between the dense-packed atomic rows of graphene and of the Eu islands is highlighted by thin black lines. Comparing the atomically resolved structures in the two image parts, the larger unit cell within the Eu adsorbate layer becomes obvious. We conclude that the first layer Eu islands on graphene possess a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. The nearest-neighbour distance of the Eu atoms in this hexagonal layer is 4.26 Å. This value is just in between the two Eu–Eu distances found for a (110) plane of bulk Eu, which is quasi-hexagonal with atomic distances of 3.97 and 4.58 Å along and across the $\langle 001 \rangle$-chains, respectively.

The crystallographic structure of the second layer islands is identical to that of the first layer, i.e. Eu still does not form its bcc bulk structure but is a two-layer hcp or fcc crystal. This is consistent with the LEED pattern in figure 4(c) after deposition of 40% ML Eu. The $(\sqrt{3} \times \sqrt{3})R30^\circ$ spots together with the corresponding moiré ones are intense, while other reflections are absent. The atomically resolved topograph of a second layer island in figure 4(d)
Figure 5. STM topographs of annealing sequences after deposition of 1.8% ML ((a)–(c)) and 15% ML ((d)–(f)) Eu at 35 K on graphene/Ir(111). (a) 1.8% ML Eu as grown ($U_s = -0.67$ V, $I_t = 11$ pA). (b) The same as (a), but additionally annealed to 200 K for 60 s ($-2.4$ V, 0.16 nA). (c) The same as (b), but additionally annealed to 300 K for 60 s ($-0.75$ V, 62 pA). (d) 15% ML Eu as grown ($U_s = -0.79$ V, $I_t = 15$ pA). (e) The same as (d), but additionally annealed to 300 K for 120 s ($-1.98$ V, 7 pA). (f) The same as (e), but additionally annealed to 400 K for 120 s ($-1.55$ V, 83 pA). The insets in (a) and (d) display the 2D self-correlation of the respective images. Topograph size is always 60 nm × 60 nm.

is a direct proof for the ($\sqrt{3} \times \sqrt{3}$)R30° structure and nicely displays the persistence of the moiré corrugation up to the second Eu layer.

3.3. Annealing

In order to obtain insight into the relative importance of energetic versus kinetic effects for the observed morphologies, we performed two sets of annealing experiments. Figures 5(a)–(c) represent STM topographs after deposition of 1.8% ML Eu at 35 K. Figure 5(a) displays the starting configuration, while figures 5(b) and (c) are topographs after additional annealing intervals of 60 s at 200 and 300 K, respectively. As highlighted by the image self-correlation shown in the inset of figure 5(a), the starting configuration is hexagonally ordered due to the close match of $d = 9.8 a_C$ with the moiré periodicity. Through annealing, the cluster density decreases considerably, resulting in an increase of the cluster separation starting from $d = 9.8 a_C$ at 35 K to $d = 18 a_C$ and $d = 26 a_C$ after annealing to 200 and 300 K, respectively. The average cluster size increases from $s_{av} = 1.75$ atoms at 35 K via $s_{av} = 5.9$ atoms at 200 K to $s_{av} = 12$...
atoms at 300 K. We note that the cluster separation after annealing to 300 K is close to the one that would result from direct deposition at 300 K. Although the precisely matching experiment is missing, after deposition of 3.3% ML at 300 K as in figure 3(a) we find $s_{av} = 14.4$ and $d = 21 \ a_C$.

Figures 5(d)–(f) represent STM topographs after deposition of 15% ML Eu at 35 K. Figure 5(d) displays the starting configuration, while figures 5(e) and (f) are topographs after additional annealing intervals of 120 s at 300 and 400 K, respectively. Similar to the previous annealing sequence, the image self-correlation shown in the inset of figure 5(d) underlines the hexagonal order of the brighter clusters in the starting configuration. In the initial configuration the average cluster spacing is $d = 7.9 \ a_C$. Upon annealing to 300 K the uniform cluster phase decomposes into a phase of large, compact ($\sqrt{3} \times \sqrt{3}$)R30° Eu islands which is embedded into a phase of disperse clusters with a rather uniform spacing of monolayer height. Quantitative analysis results in $d = 12 \ a_C$, a separation somewhat smaller than that of phase coexistence after deposition at 300 K without additional annealing (see figure 3(b)), which is $d = 17 \ a_C$. Upon further annealing to 400 K the coexistence of islands and clusters is destroyed. A uniform cluster phase with $d = 21 \ a_C$ and $s_{av} = 57$ atoms is re-established. The clusters display a much larger average height of $h_{av} = 1.2 \ nm$ compared to what we discussed until now (in the following briefly: 3D clusters). Given the apparent heights of 5 Å for the first Eu layer and 3–3.4 Å for the second Eu layer, we conclude that the 3D clusters are at least three atomic layers high. A very few remainders of ($\sqrt{3} \times \sqrt{3}$)R30° Eu islands are left which are bounded by 3D clusters. We take this as an indication of dewetting of the monolayer ($\sqrt{3} \times \sqrt{3}$)R30° Eu islands from graphene. LEED conducted after annealing the 15% ML sample to 400 K displays no diffraction spots other than the Ir(111) and the graphene moiré ones. Heating from 300 to 400 K apparently destroys the ($\sqrt{3} \times \sqrt{3}$)R30° structure of islands and clusters. The 3D clusters are likely to be present in bcc crystal structure of bulk Eu without a single specific orientation with respect to graphene.

### 3.4. Work function measurements

Using the Wentzel–Kramers–Brillouin approximation, the tunnelling current $I_t$ through a 1D barrier of width $z$ can be described by

$$I_t(z) \propto \exp(-k \sqrt{\Phi} z), \tag{1}$$

with the constant $k \approx 1.025 \ eV^{-\frac{1}{2}} \ Å^{-1}$ and the apparent barrier height $\tilde{\Phi}$ [43]. By $I_t(z)$ measurements $\tilde{\Phi}$ can be directly determined as

$$\tilde{\Phi} = \left( \frac{1}{k} \frac{d \ln(I_t)}{dz} \right)^2. \tag{2}$$

For a simple trapezoidal barrier we find

$$\tilde{\Phi} = \frac{1}{z} \int_0^z \left( \Phi_s - \frac{\Phi_s - \Phi_t + eU_s}{z} \cdot z' \right) \ dz' = \frac{\Phi_s + \Phi_t - eU_s}{2}, \tag{3}$$

with $\Phi_s$ and $\Phi_t$ being the work functions of the sample and the tip, $U_s$ the bias voltage and $e$ the elementary charge. Using (3), comparative measurements of the work functions $\Phi_{s1}$ and $\Phi_{s2}$ at different sample positions become possible through $I_t(z)$ measurements if the same bias voltage
Figure 6. (a) $I_t(z)$ measurements for Ir(111) (blue dots) and graphene on Ir(111) (grey triangles) taken with the same tip at $U_s = -0.5$ V. (b) $I_t(z)$ measurements for graphene on Ir(111) (grey triangles) and $(\sqrt{3} \times \sqrt{3})$ R30° Eu islands on graphene on Ir(111) (black squares) taken with the same tip at $U_s = -1.0$ V. In (a) and (b), the graphene data are shifted by 1.5 Å for better visibility; red lines indicate fits to the data.

is used and $\Phi_1$ stays constant, i.e. no tip change occurs. As can be seen from (3), then the work function difference $\Delta \Phi = \Phi_{s1} - \Phi_{s2}$ is just twice the difference of the apparent barrier heights $\bar{\Phi}_{s1} - \bar{\Phi}_{s2}$, while the unknown quantities $\Phi_1$ and $U_s$ drop out.

While the trapezoidal barrier is certainly an oversimplification to an actual tunnelling barrier, to first order the errors involved (e.g. image potential effects) cancel in $\Delta \Phi$. We therefore conducted sets of $I_t(z)$ spectra in adjacent sample areas of different structures, but with identical tip (no tip changes) and identical bias voltages. One set was obtained on Ir(111) with TPG graphene flakes. $I_t(z)$ spectra were taken on the flakes and on clean Ir(111) next to them. The other set was taken on TPG+CVD graphene with $(\sqrt{3} \times \sqrt{3})$ R30° Eu islands. $I_t(z)$ spectra were taken on the islands and next to the islands in areas without Eu clusters. Figure 6 shows examples of $I_t(z)$ spectra and their corresponding fits for (a) Ir(111) compared to graphene on Ir(111) with identical tip and (b) graphene on Ir(111) and $(\sqrt{3} \times \sqrt{3})$ R30° Eu islands on graphene on Ir(111) again taken with identical tip. Averaging over many pairs as shown in figures 6(a) and (b) results in apparent work function differences $\Delta \Phi_{Ir-Ir/C} = (1.1 \pm 0.3)$ eV and $\Delta \Phi_{Ir/C-Ir/C/Eu} = (1.4 \pm 0.3)$ eV.

While the significance of these numbers will be discussed in conjunction with the corresponding DFT calculations in section 4.2, the reduction of the work function through Eu adsorption has direct relevance for STM image interpretation. Due to the lower tunnelling barrier of Eu compared to graphene, the tip will be at a much longer distance from Eu compared to graphene to draw the same current in constant current mode imaging. Therefore the 5 Å apparent height of the first Eu layer is a convolution of the structural height and the lower work function. As the first and the second Eu layer display to first order the same work functions, the apparent height of 3–3.4 Å measured for the second layer can be considered to be much closer to the structural height.
Figure 7. Spin and orbitally resolved LDOS of a Eu adatom (left) and Eu dimer (right) on graphene. The spin-down Eu 4f-LDOS is outside the energy range shown here.

4. Density functional theory results

To understand the growth and electronic properties of Eu on graphene supported by an Ir(111) substrate, we present first-principles simulations in the following. We consider the case of single Eu adatoms and dimers as well as dense superstructures of Eu on graphene on Ir(111). The adsorption site, the adsorption energy, the LDOS and the magnetic moment are discussed for Eu on free-standing graphene (section 4.1), while the work function changes and dipole moments upon Eu adsorption are calculated for graphene on Ir(111) (section 4.2).

4.1. Structure and local density of states of Eu adatoms on graphene

Using a supercell containing 32 C atoms and one Eu atom (corresponding to $\theta = 6.3\%$ ML), we obtain relaxed structures for starting configurations with Eu at different high-symmetry sites. We find the lowest-energy configuration for Eu positioned 2.5 Å above the middle of a carbon hexagon (h-site). Eu on top of a carbon atom (t-site) or above a bridge site (b-site) is higher in energy by 0.12 and 0.11 eV, respectively.

The LDOS of a Eu adatom in its minimum energy configuration depicted in figure 7 shows that Eu is in $4f^7$-configuration with the 6s-orbital being singly occupied. With the s- and the f-electron spins coupling ferromagnetically, this leads to a total spin of $S = 4$ of Eu. Both the Eu s- and f-LDOS consist of one peak, which is characteristic for ionically bonded impurities on graphene [20]. The Eu LDOS suggests that the adatoms have approximately eight valence electrons. Hence, our calculations yield ionic bonding between Eu and graphene with Eu atoms carrying a charge of the order of $+1e$. The LDOS at the carbon sites shows that the Dirac point is at $-0.95$ eV for $\theta = 6.3\%$ ML (see below). In a rigid band model, this shift corresponds to doping of the graphene bands by $-0.85e$ per graphene unit cell, which is well in line with Eu having eight valence electrons.
Figure 8. (a) Adsorption energy $E_{ad}$ per Eu atom adsorbed to h-sites depending on the coverage $\theta$. Adsorption energies for regular superstructures of Eu adatoms as well as for Eu dimers on graphene are shown. The upper nonlinear axis marks the corresponding Eu nearest-neighbour distances $d$ in the hexagonal Eu superlattice structures. For the honeycomb lattice of Eu atoms at $\theta = 22.2\%$ ML and for Eu dimers, $d$ is recalculated to the Eu separation in an ideal hexagonal arrangement with the same density. Results of non-spin-polarized calculations with frozen Eu 4f-shell (black squares) as well as more accurate spin-polarized calculations including the Eu 4f-shell (red dots) are shown. Lines are a guide to the eye. (b–i) Calculated Eu (grey) superstructures on graphene (yellow) for coverages of 2.8, 4.0, 6.3, 11.1, 22.2, 25.0, 33.3 and 44.4\% ML.

The Eu adsorption energies shown in figure 8 depend strikingly on the Eu coverage. Here we use the convention that the adsorption energy is a negative quantity, i.e. the decrease of system free energy upon adsorption at 0 K. At a coverage of 6.3\% ML the adsorption energy exhibits a maximum. The dense ($\sqrt{3} \times \sqrt{3}$)R$30^\circ$ superstructure yields the lowest adsorption energy $E_{ad} = -1.53$ eV.

At a growth temperature of 35 K and for $\theta \leq 5\%$ ML, our STM experiments suggest that Eu dimers are formed preferentially. For Eu dimers adsorbed on graphene, our calculations yield the coverage-dependent adsorption energies shown in figure 8. At low coverages ($\theta < 12.5\%$ ML), dimer formation is energetically favoured compared to having a hexagonal lattice of isolated adatoms. In the dimers, the Eu–Eu distance is 4.0 Å $\approx 1.6a_C$, which is slightly smaller than, but similar to, the Eu–Eu distance of $\sqrt{3}(a)_C \approx 4.3$ Å in the ($\sqrt{3} \times \sqrt{3}$)R$30^\circ$ superstructure. Similar to the ($\sqrt{3} \times \sqrt{3}$)R$30^\circ$ structure, the dimer atoms are located close to h-sites, but with a small shift towards each other.

The electronic structure of the Eu dimers on graphene differs from that of the Eu monomers (figure 7) mainly in the Eu s-orbitals: in the case of the dimer, the Eu s-orbitals split into bonding and antibonding molecular orbitals (MO) visible as two peaks in the Eu s-LDOS. The bonding–antibonding splitting of the Eu 6s-orbitals ($\sim 1$ eV) is larger than the spin-splitting.
Figure 9. Spin and orbitally resolved LDOS of Eu p(2 × 2) (left) and (√3 × √3)R30° superstructures (right) on graphene. The spin-down Eu 4f-LDOS is outside the energy range shown here.

(∼0.5 eV). While the bonding Eu 6s-MO is always fully occupied, the occupation of the antibonding Eu 6s-MO is concentration dependent: at θ = 5.6% ML it is virtually empty but becomes slightly occupied at a coverage of 12.5% ML (figure 7). From the shift of the Dirac point we obtain nominal charges for the dimers of +0.76e and +0.66e per Eu atom at coverages of 5.6% ML and 12.5% ML, respectively.

This trend continues to the dense Eu superstructures on graphene: for the p(2 × 2) and (√3 × √3)R30° superstructures on graphene (figure 9) the LDOS of the Eu 6s-orbitals broadens, indicating that these orbitals further delocalize due to band formation within the Eu layer. Furthermore, the Eu 6s-orbitals are not fully spin-polarized, which results in a reduction of the magnetic moment to 7.3 µB and 7.5 µB for the p(2 × 2) and (√3 × √3)R30° superstructure, respectively. In both cases, graphene is n-doped by Eu. The Dirac point appears at −1.5 eV and −1.3 eV for p(2 × 2) and (√3 × √3)R30° corresponding to a charge transfer of 0.6e and 0.3e, respectively.

In going from the lowest calculated coverage of θ = 2.8% ML to the experimentally observed (√3 × √3)R30° superstructure at θ = 33% ML, the charge transfer per Eu atom decreases by about a factor of three, from 0.85e to 0.3e, while the magnitude of adsorption energy more than doubles. This finding can be rationalized by stating that with increasing coverage the Eu bonding shifts from a purely ionic one, between the Eu adatom and the graphene substrate, to a more metallic bonding dominated by bonds within the Eu layer. This metallic bonding is signalled by the formation of a partly occupied s-band in the (√3 × √3)R30° superstructure (compare figure 9, right panel).

An estimate of the relative strength of the two contributions to bonding is obtained by the following considerations. Linear interpolation of the low-coverage data of figure 8 to zero allows one to estimate the ionic bond strength of an isolated Eu atom to graphene to be ≈ −1 eV (spin-polarized data). At zero coverage the charge transfer will be about 1e. New Journal of Physics 14 (2012) 023022 (http://www.njp.org/)
Table 1. Comparison of the work function values measured by \( I_t(z) \) spectroscopy and calculated by DFT.

| Adsorbate on substrate | Substrate          | DFT \( \Phi_{\text{ads+sub}} \) (eV) | DFT \( \Phi_{\text{sub}} \) (eV) | DFT \( \Delta \Phi \) (eV) | Experiment \( \Delta \Phi \) (eV) |
|------------------------|--------------------|--------------------------------------|----------------------------------|---------------------------|----------------------------------|
| Graphene on Ir(111)    | Ir(111)            | 4.3                                  | 5.6                              | 1.3                       | 1.1 ± 0.3                        |
| \((\sqrt{3} \times \sqrt{3})R30^\circ\) Eu islands on graphene on Ir(111)| Graphene on Ir(111) | 2.8                                  | 4.3                              | 1.5                       | 1.4 ± 0.3                        |

For \( \theta = 33\% \) ML, according to our calculations the charge transfer per Eu atom has decreased to 0.3e. Assuming for simplicity a linear correlation between charge transfer and bond strength, the ionic contribution to the \(-1.5\) eV binding energy (spin-polarized data) at \( \theta = 33\% \) ML is therefore \(-0.3\) eV, leaving a metallic Eu–Eu binding energy of about \(-1.2\) eV per atom.

There is another important feature in figure 8, not yet explained: with increasing coverage from \( \theta = 0 \) to \( \theta \approx 10\% \) ML the Eu adatoms become less and less strongly bound. This decrease in bond strength takes place in the coverage regime where due to their large separation metallic bonds between Eu adatoms are still absent. We identify two contributions to this decrease in the magnitude of adsorption energy. (i) As pointed out by Ishida and Palmer [28], due to the small density of states of graphene, charge transfer to graphene causes an upward shift of the Fermi level. As the band energy increases with \( \theta \), the charge transfer per Eu atom is reduced. Consequently, the ionic bond strength is diminished. (ii) As charge transfer lifts neutrality, with increasing \( \theta \) an increasing Coulomb energy penalty has to be paid resulting from ion–ion repulsion and electron–electron repulsion in the graphene layer, which counteracts the attraction between positively charged Eu ions and the negatively charged screening clouds.

Both effects not only diminish the bond strength with increasing \( \theta \) (as long as direct Eu–Eu bonding is absent), but also cause a net long-range repulsive interaction between Eu ions. For illustration, assume a homogeneous adatom distribution to be replaced by a homogeneous adatom distribution with double density, but covering only half of the graphene substrate. The band energy as well as the Coulomb repulsion will increase to the values corresponding to doubled coverage and the total system energy increases. As a consequence, a force results, which tends to disperse the adatom distribution into the empty graphene area.

4.2. Work function changes

The experimentally measured work function changes upon Eu adsorption and can serve as a fingerprint of charge doping and additional surface dipoles due to Eu adsorption. Calculating these work function changes theoretically can further corroborate the experimental observations of the Eu structures adsorbed on graphene. To this end, we modelled the Ir(111) surface in DFT calculations by a slab consisting of four atomic Ir layers which was covered with graphene and Eu on one side and \( \approx 25\) Å of vacuum between the periodic images of the slabs. The work functions were then obtained by comparing the Fermi level to the vacuum levels. In the calculations with adsorbed Eu, we employed dipole corrections according to [44]. The calculated work functions are shown in table 1. The work function of the Ir(111) surface is 5.4 eV for the relaxed surface and 5.6 eV when Ir is forced to a perfect fcc lattice with lattice constant 3.5 Å. As the calculation of graphene on Ir(111) was performed for the latter geometry,
we expect a theoretical error margin of the order of 0.2 eV. Previous experimental values for the Ir(111) work function are 5.70 and 5.76 eV \cite{45,46}, in reasonable agreement with our results.

For graphene on Ir(111) our calculations find a work function of 4.3 eV. It is 1.3 eV lower than the Ir one, in good agreement with the 1.1 eV found in our experiments. A recent low-energy electron microscopy study found that the Ir(111) work function is lowered by 0.8–0.9 eV due to graphene adsorption \cite{11}, in reasonable agreement with our findings.

Upon Eu adsorption, both theory and experiment found a reduction of the work function by 1.4–1.5 eV. This is well in line with the observation of charge being transferred from the Eu s orbital to the graphene bands and corresponding dipoles being formed. We find Eu adatoms on graphene causing dipole moments of 0.07eÅ in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure. When decreasing the Eu concentration the dipole moment per atom increases, reaching 0.36eÅ for $\theta = 6.3\%$ ML. Table 1 summarizes the results of our DFT work function calculations and STM work function change measurements.

5. Discussion

In order to shed some light onto the puzzle of Eu adsorption on graphene, we first analyse the room-temperature adsorption and annealing experiments to establish the thermodynamic equilibrium Eu phases on graphene. We then investigate the mechanism for the coexistence of two phases, the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure and a phase of well-separated clusters of about 15 atoms. Finally, we will analyse in more detail the low-temperature experiments, in which kinetic limitations complicate the interpretation, and compare our result with previous work.

5.1. Equilibrium phases

As shown in figure 5(f), after annealing to 400 K we observe 3D Eu clusters on graphene, distributed uniformly. The Eu bulk cohesive energy is $-1.86$ eV \cite{47}, while the largest DFT calculated spin-polarized adsorption energy of Eu on graphene is $-1.53$ eV for the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. These numbers suggest that Eu prefers to bind to Eu rather than to graphene. Therefore, in thermodynamic equilibrium and without any kinetic restrictions, we assume Eu grows as 3D islands. In our data, we have no evidence for a specific epitaxial relation of the Eu clusters with respect to graphene, but this could change for longer or higher annealing temperatures.

At temperatures below 400 K, the formation of 3D structures is kinetically inhibited. Constraining thermodynamic considerations to two dimensions, we may analyse the resulting 2D equilibrium phases. For $\theta \leq 5\%$ ML we obtain at 300 K monolayer-high Eu clusters uniformly distributed over the sample. For a few per cent of a monolayer deposited, typical separations are $d \approx 20a_C$ and $s_{av} \approx 15$ atoms. It is plausible that increasing $\theta$ up to 5% ML will decrease $d$ to a minimum value (compare figure 3(a)) and $s_{av}$ to a maximum value, but both values will be of similar magnitude to the numbers mentioned above. This disperse cluster phase is realized for a given $\theta$ at 300 K, irrespective of the kinetic pathway: either by direct deposition at 300 K (compare figure 3(a)) or by low-temperature deposition and subsequent annealing to 300 K (compare figures 5(a)--(c)). From this independence of the kinetic pathway, we conclude that the disperse cluster phase is an equilibrium surface phase at 300 K.

Several arguments lead to the conclusions that each cluster is built from Eu atoms in a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. Firstly, our DFT calculations show that this structure has the
lowest energy and already a single dimer prefers a geometric configuration consistent with a relaxed \((\sqrt{3} \times \sqrt{3})R30^\circ\) arrangement. Secondly, we find experimentally at all temperatures the cluster height (except for the single adatom) to be similar to the height measured for large \((\sqrt{3} \times \sqrt{3})R30^\circ\) Eu islands. Finally, at low temperature and for large clusters with \(s_{av} = 24\) atoms, we observe a \((\sqrt{3} \times \sqrt{3})R30^\circ\) LEED pattern, as shown in figure 1(h). These facts leave little doubt that all 2D clusters observed—and specifically the clusters of the disperse cluster phase observed after 300 K deposition—possess internally a structure close to the \((\sqrt{3} \times \sqrt{3})R30^\circ\) one.

For \(5\% \text{ ML} \leq \theta \leq 33\% \text{ ML}\), we observe coexistence of monolayer-high Eu clusters uniformly distributed over the sample with compact \((\sqrt{3} \times \sqrt{3})R30^\circ\) Eu islands. This situation is realized for a given \(\theta\) at 300 K, again irrespective of the kinetic pathway: either by direct deposition at 300 K (compare figure 3(b)) or by low-temperature deposition and subsequent annealing to 300 K (compare figures 5(d) and (e)). The slight differences in cluster densities and sizes as well as island densities and sizes realized on the two pathways indicate that kinetic limitations are not fully lifted. Nevertheless, we conclude that the disperse cluster phase is in thermodynamic equilibrium with the \((\sqrt{3} \times \sqrt{3})R30^\circ\) island phase. The phase diagram is shown in figure 10 and discussed in more detail in section 5.2.

Since the \((\sqrt{3} \times \sqrt{3})R30^\circ\) island phase is an equilibrium phase it should fully cover graphene for \(\theta = 33.3\% \text{ ML}\). As figure 3(c) shows, even after deposition of 40\% ML, small patches of the disperse cluster phase are still left, while \((\sqrt{3} \times \sqrt{3})R30^\circ\) second layer islands nucleated. The nucleation of second layer islands prior to the closure of the first layer is a typical behaviour in epitaxial growth, even if step edge barriers are negligible [48]. This behaviour represents a kinetic limitation and the first layer would close perfectly for sufficiently small supersaturations during growth. But based on our observations we conclude that the \((\sqrt{3} \times \sqrt{3})R30^\circ\) islands are the equilibrium structures in the second layer on a Eu \((\sqrt{3} \times \sqrt{3})R30^\circ\) monolayer on graphene under the constraint of two dimensional phase formation. Note that for the second layer no disperse cluster phase is formed. This underlines the specificity of the disperse cluster phase for Eu adsorption on graphene. In conclusion, we find four equilibrium or quasi-equilibrium phases as a function of coverage and temperature: (i) the 3D cluster phase at 400 K; (ii) the disperse cluster phase at 300 K and for small coverages; (iii) the \((\sqrt{3} \times \sqrt{3})R30^\circ\) island phase, which has an extended coexistence range with the disperse cluster phase and is phase pure only for \(\theta = 33.3\% \text{ ML}\) at 300 K; (iv) eventually, again a \((\sqrt{3} \times \sqrt{3})R30^\circ\) island phase, which is the only stable condensed phase in the second Eu layer at 300 K.

5.2. Phase coexistence of clusters and \((\sqrt{3} \times \sqrt{3})R30^\circ\) islands

The most striking observation reported here is probably the disperse cluster phase at low coverage and, especially, its coexistence with the \((\sqrt{3} \times \sqrt{3})R30^\circ\) island phase at room temperature for larger coverages.

Phase coexistence implies that the free energy \(F = E - TS\) plotted as a function of coverage (or composition) must be concave in the phase coexistence range. Due to the large number \(N_{Eu}\) of atoms per cluster, the entropic contribution to the free energy \(TS\) per Eu atom arising from the possibility of distributing the clusters across the plane (estimated as \((k_BT/N_{Eu})\ln(1/\theta) \ll 0.01 \text{ eV}\)) is even at room temperature small compared to all other contributions (see below) and will therefore be neglected in the following. Consequently, we can use our DFT result for the adsorption energy per Eu atom to estimate the energy (per graphene
Figure 10. Equilibrium phase diagram and schematic plot of the change of the free energy per graphene unit cell due to the adsorption of Eu as a function of the Eu coverage $\theta$. Full black dots: adsorption energy from spin-polarized DFT calculations assuming uniform coverage (the same data as in figure 8). The average free energy can be lowered down to the red dotted line for $\theta < 1/3$ by putting all Eu atoms into one large island with a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure ($\theta = 1/3$). For $\Theta < \Theta_c$ the system can, however, gain even more energy by breaking the large island into smaller clusters (solid blue line; the corresponding energy gain is exaggerated in the schematic figure). While for $\theta < \theta^*$ the disperse cluster phase is stable, one can lower the energy down to the blue dashed line for $\theta^* < \theta < 1/3$ due to the coexistence of the cluster phase with $\theta = \theta^*$ and of an island with the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure at $\theta = 1/3$.

unit cell) as a function of the coverage $\theta$ (dots in figure 10). The concave DFT curve predicts for any coverage below 33% ML the coexistence of bare graphene with a big $(\sqrt{3} \times \sqrt{3})R30^\circ$ island taking up all deposited material. A large metallic $(\sqrt{3} \times \sqrt{3})R30^\circ$ island is preferred in the DFT calculation to isolated adatoms (and also compared to the dimer phase) by the dominant contribution of metallic Eu–Eu binding to the total adsorption energy. Here it is important to take into account that the DFT calculation assumed a uniform coverage and does, by construction, not allow for cluster formation. While Eu atoms form indeed locally a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure (as predicted by DFT), our experiments show that for low coverage extra energy can be gained by breaking up the big island into clusters.

When forming uniformly distributed clusters out of the single $(\sqrt{3} \times \sqrt{3})R30^\circ$ island, the breaking of Eu–Eu bonds will cost edge energy $E_{\text{edge}}$ per Eu atom. The electrons can, however, lower their kinetic energy by moving away from the Eu clusters into areas where graphene is not covered by Eu. In the limit of vanishing coverage and small charge transfer $\delta n$ per Eu, the energy gain per Eu can be estimated from the difference in the work function of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure and pure graphene, $\Delta E_\Phi \approx -\delta n \times 1.4 \text{ eV}$, see table 1. The redistribution of charge, however, is associated with a Coulomb energy penalty arising from the charging of the clusters. It is the interplay of these three contributions to the
total energy that determines the phase diagram and leads to cluster formation. Firstly, the edge energy $E_{\text{edge}}$ of the cluster arises because the Eu atoms locally prefer the $(\sqrt{3} \times \sqrt{3})$R30° phase where metallic binding to neighbouring Eu atoms is possible. Secondly, electrons gain energy by lowering their kinetic energy when moving away from the cluster, thereby building up a charge imbalance that, thirdly, costs Coulomb energy. The fact that this energy penalty (which limits the gain of kinetic energy) can be reduced by forming clusters is in our opinion the main driving mechanism for the formation of the disperse cluster phase. Ultimately, optimizing the energy by choosing the optimal cluster size maximizes the energy gain, thus lowering the total energy by forming clusters instead of one large $(\sqrt{3} \times \sqrt{3})$R30° island.

For an estimate of the Coulomb energy the screening from the underlying Ir substrate plays an important quantitative role. However, to get a qualitative understanding of the physics, we neglect for the following argument the underlying Ir substrate. We consider a grossly oversimplified model which mimics screening only by a relative permittivity $\epsilon_r > 1$ (valid only for insulating substrates) and also assumes that the electrons distribute uniformly on the part of graphene not covered by Eu. Approximating, furthermore, the Eu island by a uniformly charged disc, one obtains for a single island (i.e. in the limit $\theta \to 0$) an energy cost per Eu of $E_c \approx (\delta n^2 / r) \times 5.5$ eV. The Coulomb energy grows rapidly with increasing the number of Eu atoms per cluster $N_{\text{Eu}}$, implying that $\delta n = 0$ for an infinite size cluster.

Minimizing $E_c + \Delta E_{\Phi}$ we obtain an energy gain per Eu of approximately $E_{\text{gain}} = -\frac{\epsilon_r}{\sqrt{N_{\text{Eu}}}} \times 0.1$ eV. For a magic cluster with $N_{\text{Eu}} = 19$ Eu atoms (two shells around a central atom), one has 15 broken bonds (compared to 19 atoms in an infinite $(\sqrt{3} \times \sqrt{3})$R30° structure) and therefore the energy gain per broken bond is only $\epsilon_r \times 0.03$ eV. This approximation can only serve as an order of magnitude estimate. In reality the energy gain will be bigger, as the Coulomb energy can be considerably reduced by employing a non-uniform distribution of the electrons around the cluster. Furthermore, screening will also lead to a substantial increase of the energy gain as can be seen from the linear dependence of $E_{\text{gain}}$ on $\epsilon_r$. In this approximation, the two opposing energy contributions—$E_{\text{gain}}$ favouring small clusters and $E_{\text{edge}}$ favouring large islands—are both proportional to $1 / \sqrt{N_{\text{Eu}}}$. Therefore, our toy model does not predict an optimal cluster size.

To obtain the phase diagram and an optimal cluster size, two more effects have to be taken into account. Firstly, for small $N_{\text{Eu}}$ when $\delta n \propto 1 / \sqrt{N_{\text{Eu}}}$ becomes larger, nonlinear effects have to be taken into account. Probably the most important effect is that the binding of Eu to graphene becomes more ionic (according to our DFT results an Eu atom in the $(\sqrt{3} \times \sqrt{3})$R30° phase loses $\sim 0.3$ electron compared to $\sim 1$ electron for a single Eu atom). If this reduces the Eu–Eu binding energy, it could explain the existence of an optimal cluster size for small $\theta$. Furthermore, for increasing coverage $\theta$, the gain in potential energy due to cluster formation is reduced both by the Coulomb repulsion of neighbouring clusters approaching each other and by the doping of the pristine graphene, which lowers the gain of kinetic energy by Pauli blocking. It has been argued by Ishida and Palmer [28] that this effect is especially important in graphene, where due to the peculiar low density of states the Fermi energy rapidly rises with doping. As in the limit $\theta \to 1/3$ the gain in energy vanishes completely, there will necessarily be a critical coverage $\theta_c$ such that the cluster phase is not locally stable for $\theta > \theta_c$.

Figure 10 displays schematically the resulting free energy as a function of the coverage $\theta$, which is consistent with the experimental results and the theoretical arguments described above. The blue solid line describes the free energy for a phase of clusters where for each value of $\theta$ the (average) number of atoms per cluster $N_{\text{Eu}}$ has been optimized. For $\theta > \theta_c$ this optimization leads to $N_{\text{Eu}} = \infty$ and therefore to an energy which can be obtained by the usual
linear interpolation of the energies at $\theta = 0$ and $\theta = 1/3$. For $\theta < \theta_c$ the optimal clusters have a finite size and the energy is lower. As shown and discussed in figure 10 this leads to phase separation in the regime $\theta^* < \theta < 1/3$, where a cluster phase with coverage $\theta^*$ coexists with big $(\sqrt{3} \times \sqrt{3})R30^\circ$ islands. While for $\theta \to \theta_c$ the size of the optimal cluster nominally diverges, it is finite at $\theta^*$.

A full ab initio calculation of the energy of the cluster phase would certainly be highly desirable. But a direct simulation appears to be impossible at present due to the large unit cells required.

5.3. Kinetically limited growth at low $T$

All morphologies fabricated at 300 K or annealed to a temperature well above 35 K were cooled down to 35 K to freeze their high mobility for imaging. These morphologies are quite different from the ones grown and imaged at 35 K, even if one compares similar coverages. Therefore the 35 K morphologies represent to a good extent the kinetic limitations of the growth process. One might argue that part of the difference in appearance is due to the different relevance of entropy at 35 and 300 K. However, the arrangement of small clusters with $s_{av} = 1.9$ obtained after deposition of 3.3% ML (compare figure 1(e)) certainly has a larger entropy than the arrangement of clusters with $s_{av} = 14.4$ obtained for the same $\theta$ at 300 K (compare figure 3(a)). Thus the entropy argument goes in the wrong direction and appears to be largely irrelevant (consistent with the estimates given above). In the following, we analyse the 35 K data represented in figure 1 under the viewpoint of kinetic limitations and put these data into relation to our DFT calculations.

Imaging at 35 K makes it obvious that the morphology is frozen at 35 K. It is plausible that the entity with the highest mobility is the monomer, for which we calculate an activation energy $E_a = 0.11$ eV. This value is a lower bound approximation based on the difference in adsorption energy between the h-site and the b-site. Assuming a standard attempt frequency $v_0 = 1 \times 10^{12}$ Hz, we obtain at 35 K a hopping rate $v = v_0 e^{E_a/k_b T} = 1.4 \times 10^{-4}$ Hz, where $k_b$ is the Boltzmann constant. The resulting hopping period of the order of an hour is consistent with the observed frozen morphology, thereby keeping experiment and DFT calculation consistent.

Up to about $\theta \approx 5$% ML the 35 K data display clusters limited to the dimer size, causing a decreasing and rather uniform cluster–cluster separation down to a minimum value of $d = 7.3 \, a_C$. This behaviour is a clear expression for the relevance of repulsive interactions that were discussed already in section 4 and are manifested in figure 8. These are repulsive Coulomb interactions between the Eu ions and between their screening clouds in graphene. In addition, we have Pauli repulsion of the electrons in the screening clouds: due to the low density of states, the overlapping of the screening clouds will cause a local upward shift of the Fermi energy (i.e. an increase of band energy) [28]. Therefore, the screening clouds pinned to the Eu ions will avoid coming close and thus keep the Eu ions apart.

Two effects contribute to making dimers a preferred cluster size in this coverage range. Firstly, due to the single s-electron of an adatom (one s-electron is transferred to graphene), bond formation with a second adatom is associated with a large-energy gain, consistent with our DFT calculations (compared with section 4). Secondly, the long-range Coulomb repulsion between two dimers is considerably larger than that between two adatoms, thereby keeping dimers apart.

Through continued deposition therefore more and more dimers will be formed until their concentration reaches a maximum, where the screening clouds substantially overlap. At this
point, cluster growth (allowing the formation of more Eu–Eu bonds) takes place rather than the
formation of new dimers. If this description is proper, the minimum dimer distance of \( d \approx 7a_C \)
is an estimate for the extension of the delocalized screening cloud around dimers resulting from
the charge transfer of Eu s-electrons to graphene. Subsequent aggregation may also be eased
by the reduced charge transfer of the newly arriving adatoms after the Fermi level has already
shifted by about 1 eV through the already existing clusters. The reduced charge transfer implies
a reduced repulsive interaction of the adatom with the existing clusters.

The 35 K and the 300 K data display a striking similarity. In both cases, initially the
graphene is covered rather uniformly by a single phase of disperse and similar-sized clusters,
until beyond \( \theta \approx 5\% \) ML the morphology becomes more heterogeneous with different cluster
sizes or the onset of the \((\sqrt{3} \times \sqrt{3})R30^\circ\) islands. However, the selected cluster sizes and
distances for the same coverage differ significantly for the same \( \theta \) due to the presence of
repulsive interactions, which cause kinetic growth limitations at low temperature. Both values,
\( s_{av} \) and \( d \), are much larger at 300 K.

5.4. Comparison to previous work

The adsorption of Eu on graphene bears certain similarities to the adsorption of alkali metals
on graphite and metal surfaces. The basis of these similarities is the fact that in the low
coverage limit an adsorbed Eu adatom donates an s-electron to the substrate, as is observed
for alkali metal adsorption. Still the best studied system of alkali metal on graphite is the
adsorption of potassium [27–30, 49, 50]. Upon adsorption at 90 K a disperse adatom phase
was observed, giving rise to an LEED ring, which compresses continuously upon adsorption
until at a critical coverage a \((2 \times 2)\) K overlayer forms. Alkali adsorption on metals usually
leads through a sequence of adatom phases with increasing density till a dense ordered phase is
formed. However, the coexistence of phases differing in density as much as for K on graphite or
here for Eu on graphene has not been observed on metals [51, 52]. In a theoretical study [28],
Ishida and Palmer emphasize that for a semimetallic substrate with a low density of states
such as graphene, the band energy changes significantly with coverage. These authors propose
that this strong band energy change may give rise to the phase coexistence of adatoms and a
condensed phase of K on graphite.

In contrast to previously reported work, we find coexistence of a low-density phase of
uniformly distributed clusters with a condensed phase of high density. The low-density phase
is formed by clusters, which already combine at low coverage aspects of ionic and metallic
bonding. The phase separation is understood here as resulting from the requirement to donate
charge to graphene as rapidly and uniformly as possible in order to lower the electron kinetic
energy of the system under the constraint of minimal repulsive Coulomb and band energy
effects, while maintaining as much Eu–Eu bonding as possible.

For K on graphite, the adsorption energies of adatoms, dimers and \((2 \times 2)\) monolayer
structures have been calculated by DFT in [49]. The adsorption energies of a K adatom and
a dimer in a \( 4 \times 4 \) graphite supercell are \(-0.99 \) and \(-0.74 \) eV per K atom, respectively. For
the saturated K adsorbate layer forming a \((2 \times 2)\) superstructure layer an adsorption energy
of \(-0.81 \) eV per K atom was found. This is qualitatively different from the adsorption energies
obtained for Eu on graphene, where we find that isolated adatoms gain generally less energy by
adsorption than dimers or the saturate adlayer in the \((\sqrt{3} \times \sqrt{3})R30^\circ\). Eu adatoms on graphene
thus seem to form stronger adsorbate–adsorbate bonds than K adatoms. This can be understood
in two limiting cases: in the dilute limit, K on graphene or graphite has a completely empty 4s orbital, in contrast to the half-filled 6s-orbital of Eu on graphene. Thus, only for Eu, but not for K, the outer s-orbital can lead to a strong metallic adsorbate–adsorbate bond. At higher coverage, the difference between the K adsorption on graphite and Eu adsorption on graphene may also be in part due to the larger cohesive energy of Eu, making adsorbate–adsorbate bonding more important compared to adsorbate–substrate bonding.

In a recent study, Liu et al [23] deposited Eu to graphene on SiC at room temperature. They observed a layered growth of Eu on graphene, in agreement with our findings presented in figure 3(c). However, the structure of the Eu adlayer remained unknown and the initial islands with an apparent height of 7.5 Å were interpreted to be predominantly composed of three layers, while in the present study we find systematically only monolayer islands with an apparent height of 5 Å. Most interestingly, the disperse cluster phase was not observed by Liu et al. We envision two potential reasons. Firstly, the morphology was imaged at room temperature where the clusters are mobile. This might have hampered imaging and suppressed their presence in the topographs. Secondly, graphene on SiC is already n-doped and the Dirac cone is about 0.45 eV below the Fermi edge [53], whereas graphene on Ir(111) is hardly doped (at most p-doped by 0.1 eV [10]). For n-doped graphene the kinetic energy gain by delocalization of Eu s-electron is reduced, thereby favouring the formation of \((\sqrt{3} \times \sqrt{3})R30^\circ\) islands.

Liu et al [23] also calculated the adsorption energy of the Eu adatom on graphene by means of spin-polarized DFT calculations with frozen f-electrons in a \((4 \times 4)\) supercell. They obtain \(-0.90\) eV, which is close to our value of \(-0.88\) eV resulting from the non-spin-polarized calculation of the \((4 \times 4)\) Eu adatom superstructure. However, due to Coulomb repulsion and band energy effects, a single adsorbate in a \((4 \times 4)\) supercell still has a considerably higher \(E_{\text{ad}}\) than in a \((6 \times 6)\) supercell (we calculated \(E_{\text{ad}} = -0.99\) eV). Based on the data of figure 8(a), we extrapolate for the limit of \(\theta \rightarrow 0\) a value of \(E_{\text{ad}} \sim -1.1\) eV. Most importantly, adsorption energies at different coverages are required to understand the coverage-dependent phase diagram of Eu adsorbed on graphene (cf section 5.2).

5.5. Outlook

In this study, we have shown that the interplay among the peculiar band structure of graphene, Coulomb energies and the chemistry of adsorbates determines their phase diagram and can lead to new phases such as a phase of diluted Eu clusters coexisting with Eu islands.

Taking into account that adsorbates may play an important role in the functionalization of graphene, certainly more studies of such systems are desirable. An intriguing possibility is that one might be able to control the physics of adsorbates and their phases by gate voltages. Due to the delicate balance of two coexisting phases, which react sensitively to Pauli blocking and small changes in kinetic energy, Eu on graphene might be an ideal model system to study such phenomena. Furthermore, it will be interesting to investigate the magnetic properties of Eu islands and Eu clusters on graphene.

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