Large noble metal clusters: electron confinement and band structure effects

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Abstract. For the electronic properties of large clusters the interaction of the free electron gas with the ion core lattice may result in additional quantization phenomena which are well known in the area of surface and thin-film physics. We measured the geometric and electronic properties of silver and gold clusters grown in nanopits on graphite with low-temperature scanning tunnelling microscopy and spectroscopy in combination with high-resolution photoemission. With the emergence of a Shockley surface state on the top (111) facets of gold clusters with a size of about $10^4$ atoms, we observed one explicit example for the influence of the ion core lattice. The two-dimensional confinement of the surface state is set into the context of a possible one-dimensional confinement perpendicular to the surface, analogous to quantum well states in thin metal films. The basic mechanisms for the dependence of the electronic structure on the cluster size and the shape are tentatively discussed within a ‘bulk limit’, introducing the bulk band structure into the description of the clusters.

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1. Introduction

There are two possible pathways to approach the properties of clusters, being located between single atoms and the macroscopic bulk material. One can treat them as aggregates of atoms, i.e. large molecules, or one can describe them as a nanoscopic piece of bulk material, influenced by confinement in all three dimensions. For metal clusters the jellium model [1] often successfully describes the electronic properties with a free electron gas confined to the spherical or ellipsoidal shaped positive background charge [2]. The geometric structure of the ionic cores can be introduced into this model in some more detail as a perturbation to the simple jellium model [3]. For larger clusters it may be an alternative to describe them as a small piece of metal using the complete band structure of the bulk material. In particular if the clusters show a faceted shape this can contain effects known from surface or thin-film physics, with an additional lateral confinement. Here we present this approach using results measured for large faceted gold clusters on a graphite surface. They are compared with corresponding data for silver clusters on graphite. Shockley surface states confined to the cluster facets and quantum well states related to a vertical electron confinement in the cluster will be discussed.

2. Experimental details

The samples were produced and measured in a surface science facility, which combines scanning tunnelling microscopy (STM) at $T = 5$ K and high-resolution ($\Delta E = 10$ meV) ultraviolet photoelectron spectroscopy (UPS) together with means for surface preparation in a common ultrahigh vacuum (UHV) chamber [4]. The preparation of the cluster samples followed the method of [5]. We produced nanometre sized pits with a depth of one monolayer on the surface of highly oriented pyrolytic graphite (HOPG) using the parameters described in [6]. Then we deposited the metal atoms by electron beam evaporation. In previous work [6]–[8] silver was deposited at an HOPG surface temperature of 300 K. Gold could be deposited at a temperature of 620 K due to its higher sticking coefficient. With STM at $T = 300$ or 5 K we measured the cluster height distribution and we imaged the size and shape of several individual clusters.

The scanning tunnelling spectroscopy (STS) data on individual clusters, either $dI/dV$ spectra measured with varying tunnelling voltage $V$ at a single position or $dI/dV$ maps measured for fixed $V$ for varying positions $(x, y)$, were taken at $T = 5$ K under open loop conditions by
lock-in detection. For STM and STS at low temperature we used an in situ preparation of the electrochemically etched tungsten tips [9], which we found advantageous to the quality and stability of the STS data.

3. STM and STS results

In figure 1 we compare colour coded STM images and line profiles for silver and gold clusters respectively grown on HOPG. The gold clusters show a faceting in the lateral cluster shape and a flat top of the clusters in the line profiles, in contrast to the silver clusters for which neither the lateral shape nor the line profiles indicate facets. Previous measurements for these sample systems using electron diffraction [10], STM [11] or UPS [6] showed that the gold clusters have a preferential orientation with the (111) plane parallel to the HOPG surface. In contrast to this, silver clusters show a random orientation on the graphite [6]. The STM images of the silver clusters suggest that the observed random orientation is accompanied by an absence of facets on the cluster surface. This may be explained by differences in the growth process, in particular the lower substrate temperatures used for the silver deposition. But recent results for the structure of small gold clusters in the gas phase point to the fact that there is a more fundamental difference between silver or copper on the one hand and gold on the other, i.e. the more directional bonding for the latter metal, which leads to a preference for flat cluster structures [12].

The hexagonal top facets of the gold clusters become even more clearly visible in the 3D displays showing STM data measured at $T = 5$ K (figure 2). We observed quite different facet shapes for the individual clusters. Using the different surface energies in the interpretation of the Wulff construction, we would expect (111) and (100) facets on the sides of the clusters, the (111) facets being the larger ones. Some of the clusters do not have a threefold symmetry (see the left cluster in figure 2), which indicates that the cluster shape has not reached equilibrium,
3.4

**Figure 2.** 3D displays of STM images (measured at $T = 5$ K) for three individual gold clusters grown in nanopits on HOPG. The image size and the cluster height $h$ is given for each image.

but is still influenced by the growth process, e.g. the coalescence of several smaller clusters, grown at the pit edge, to one larger cluster.

We measured nearly identical data for the tunnelling current $I$ with a variation of the tunnelling gap, i.e. $I(z)$ on top of the clusters and on the HOPG respectively (not shown), which indicates that the height measured with the STM will be close to the geometric height of the clusters. In contrast to the inflation of the total lateral cluster size [5] the imaging of the flat (111) facet is not hindered by the convolution with the tip shape. We assume that the cluster side facets are formed by (111) and (100) surfaces making an angle of $70.5^\circ$ and $54.7^\circ$ respectively with the HOPG surface [13]. With this the cluster volume of the individual clusters can be calculated in good approximation using a truncated cone with an angle of $60^\circ$ to the HOPG surface and the facet as the top surface.

In figure 3 we present $dI/dV$ spectra measured for six individual gold clusters, together with the shape and the size $\Omega_1$ of the facets as well as the cluster heights $h$. The resulting number of atoms $N$ was calculated as described above. Two $dI/dV$ spectra are given for each cluster: one measured for a small area at the centre of the facet and one averaged over the whole facet area. With the spectra measured in the facet-centre we select only electron states with a certain symmetry (cf the discussion of figure 5 below). The spectra averaged over the whole facet area, less well defined, include all states. Hence, the comparison of the two curves allows a rough estimation of the spatial distribution. The facet area varies for the five larger clusters within the range of a factor of two; the same applies to the height of the six clusters. The volume of the largest cluster is about four times larger than that of the smallest one. The cluster spectra are strongly structured with peaks of several $10$ meV width, measured with a sinusoidal modulation voltage of $12$ meV$_{\text{rms}}$, which will not lead to a significant additional broadening. In contrast the spectra taken on the HOPG surface have a smooth V-shape (see [8]). We discuss the cluster spectra in the following sections in view of confined surface and volume states.

4. **Confined surface states**

First, we focus on the largest cluster with $N = 1.5 \times 10^4$ atoms in figure 3. For this cluster we observed a pronounced nodal pattern in the $dI/dV$ maps measured on the top (111) facet.
Figure 3. STS data measured at $T = 5\,\text{K}$ for six individual gold clusters grown in nanopits on HOPG. The height $h$, the top facet area $\Omega$ and the number of atoms $N$ are given for each cluster. In addition the shape of the facet is indicated with STM images (except for the smallest cluster, for which the facet area was estimated using the topographic image measured simultaneously with the $dI/dV$ data). Two $dI/dV$ spectra are displayed for each cluster: one measured in the centre of the facet and one averaged over the whole facet area. The vertical solid (dashed) lines indicate the energy positions predicted for the states with $n = 1, 4$ ($n = 2$) for the model of a hexagonal box discussed in the context of figure 5. STS measured at $T = 5\,\text{K}$ with open feedback loop; setpoint: 1.1 V, 0.1 nA; modulation: 12 mV$_{\text{rms}}$.

Together with the observation of a clear peak-structure at about $-0.5\,\text{eV}$ with photoemission close to normal emission ($\pm 3^\circ$), we were able to identify these patterns as due to an Au(111) Shockley surface state confined to the hexagonal facet area. The photoemission data and other details of this experiment are discussed in a separate paper [14]; here we summarize the data in figure 4 (animated figure). Voltage-dependent $dI/dV$ maps are shown in a 3D display, the $z$-axis is scaled in absolute units. At certain energies pronounced nodal patterns show up. The first four are marked at their corresponding voltages in the $dI/dV$ spectra in the inset.

In figure 5 we describe the experimental $dI/dV$ maps for the cluster of figure 4 and another, slightly smaller, cluster using the model calculation for a two-dimensional electron gas in a hexagonal confinement as given in [15]. The different modes are consecutively numbered with regard to their energies $E_n$, $n \geq 1$. For the minimum of the parabolic dispersion of the surface state we use the symbol $E_0$. The values of $E_n$, calculated as well as measured, are given with respect to the lowest-energy mode $E_1$ with one antinode of the state density in the centre. The energy axis is scaled in such a way that it is independent of the facet area $\Omega$. The effective mass...
Figure 4. See movie. STS data measured on the top (111) facet of a gold cluster with $N = 1.5 \times 10^4$ atoms ($h = 3.9$ nm, $\Omega = 37$ nm$^2$). The voltage-dependent $dI/dV$ map shown in the 3D display (top) can be identified with a Shockley surface state confined to the hexagonal facet area shown in the topographic STM image (bottom left). In the $dI/dV$ spectra (bottom right) extracted from figure 3 we indicate the momentary energy position with a moving vertical line. The first four detected quantized modes of the confined surface state are indicated at their corresponding voltages in the $dI/dV$ spectrum with small grey-scale patterns. STS measured at $T = 5$ K with open feedback loop; setpoint: 1.1 V, 0.1 nA; modulation: 12 mV$_{\text{rms}}$.

$m^* = 0.26m_e$ as taken from recent photoemission experiments [16] was checked with our own angle resolved photoemission measurements for a bulk Au(111) surface.

In addition the modes are compared with the eigenstates inside a 2D circular box of radius $r$. The wavefunction is given by $\psi_{m,l}(\rho, \phi) \propto J_l(k_m,l\rho)e^{il\phi}$ with the Bessel function $J_l$ and the wavenumber $k_{m,l} = z_{m,l}/r$. With given radius $r$ the $m$th zero crossing of the $l$th-order Bessel function $z_{m,l}$ defines the energy $E_{m,l} = \hbar^2k_{m,l}^2/(2m^*)$ [17]. This gives $E_{m,l} = E_0 + (\hbar^2\pi/2)z_{m,l}^2/(\Omega m^*)$ for the energies of the different modes. As can be seen in figure 5 the energy positions of the modes which were clearly observed in the experiment (cf animated figure 4) correspond nicely to the modes with angular momentum $l = 0, 1$; and the corresponding calculated energy positions in the hexagonal confinement are different only by a small amount. Consequently the energy difference between the surface state onset and the lowest-energy mode, scaled with the facet area, i.e. $(E_1 - E_0)\Omega$ is also nearly identical for the hexagonal confinement (2.725 eV nm$^2$) and the circular confinement (2.662 eV nm$^2$).
Figure 5. Left column (‘hexagon’): energies for the different quantized modes (numbered with \( n = 1 \ldots 13 \)) of a two-dimensional electron gas confined to a hexagonal box calculated using the theory from [15]. An effective mass \( m^* = 0.26 m_e \) was used for the dispersion \( E(k_{\parallel}) \). For those modes which are clearly observed in the experiment, we display in addition the corresponding calculated state densities as given in [15]. Middle column (‘experiment’): measured energies and \( dI/dV \) maps for two clusters with different facet areas \( \Omega \), heights \( h \) and the resulting number of atoms \( N \). Right column (‘circle’): energies for the modes with \( l = 0 \) and 1 of a two-dimensional electron gas confined to a circular box [17]. The vertical axis is scaled in a way, that it is independent from the hexagonal (respectively circular) area \( \Omega \).

In order to fit the absolute energetic position of the first centre antinode mode \( E_1 \), the minimum of the surface state parabolic dispersion has to be set to \( E_0 = -528 \) and \(-588 \) meV for the clusters with \( h = 3.9 \) and 2.5 nm respectively, i.e. shifted to lower energies compared with the onset of the surface state band on a macroscopic gold surface \((-487 \) meV) [16]. This can be related to the shift of the surface state to lower energy for thin metal films due to the interaction with the substrate within the decay length of the surface state [18] or with possible shifts due to film strain [19]. We use the two fixed points for \( E_0(h) \) given above together with the limiting value \( E_0(\infty) = -487 \) meV to set up a parametrization of \( E_0(h) \) as used in [18]. This results in the formula \( E_0(h) = -487 \) meV \(-491 \) meV \( \cdot \exp(-h/1.581 \) nm). Together with the model for the confinement of the two-dimensional electron gas to a hexagonal box from [15]
we can now calculate predicted energy positions for all the different clusters. The cluster height
determines the surface state onset, while the scaling for the peak positions is given by the facet
area. We have indicated the energy positions predicted for the states with \( n = 1, 4 \) (and \( n = 2 \))
in figure 3 with solid (and dashed) lines respectively.

For the three largest clusters almost all of the modes can be identified in the \( dI/dV \) spectra. The mode at \(-441 \text{ meV}\) for the \( N = 9.9 \times 10^3 \) cluster is visible as a shoulder; however, it can be clearly identified in the corresponding \( dI/dV \) maps (cf figure 5). The mode at \(-9 \text{ meV}\) for the \( N = 1.1 \times 10^4 \) cluster is suppressed by the dip at the Fermi energy, which will be discussed in section 5.

The agreement for the three smallest clusters is much worse. For the clusters with \( N = 7.2 \times 10^3 \) and \( 5.2 \times 10^3 \) one can observe a peak near the energy predicted for the \( E_2 \) mode, but the peaks for \( E_1 \) are not visible, and no agreement at all is obtained for the cluster with \( N = 4.0 \times 10^3 \).

In figure 6 we show \( dI/dV \) spectra and maps for the cluster with \( N = 5.2 \times 10^3 \) atoms. An alternation between a maximum and a minimum in the centre of the facet area is also present in this case, and the nodal pattern is still visible but much less pronounced than in the case of the larger clusters discussed in figures 4 and 5. This corresponds to the smaller differences between the \( dI/dV \) spectra measured in the centre or taken as the average over the whole facet area. The description using a confined Shockley surface state does not fit to this case, as becomes obvious for the peak at \(-0.31 \text{ eV}\) which is predicted to be a mode with \( n = 2 \), i.e. with a node in the centre of the \( dI/dV \) map, in contrast to the measured antinode in the centre. We will discuss an alternative assignment for the modes of the smaller clusters in the next section.
The difference to the larger clusters is underlined by the $dI/dV$ spectra measured for $V = -1 \ldots +1$ V shown in figure 7. Because measurements with $|V| > 0.6$ V induced the danger of a tip change, we performed only single $dI/dV$ spectra and no $dI/dV$ maps for this extended energy range. One can observe a series of peaks which starts above $-0.5$ eV for the cluster with $N = 1.5 \times 10^4$ atoms. In the limit of a very large facet this will converge to a step-like structure typical for a two-dimensional Shockley surface state [20, 21], with its energy close to the corresponding step for an Au(111) surface. On the cluster with $N = 5.2 \times 10^3$ atoms we do not observe such a pronounced step-like onset of the peaks in the $dI/dV$ spectra, near the minimum of the surface state band on a macroscopic gold surface. In this context it is remarkable that for the cluster with $N = 1.5 \times 10^4$ atoms both the energetic positions and the patterns of the different modes fit to the theory for a confined surface state (cf figure 5). In addition, the shape of the $dI/dV$ spectra measured in the centre and on the whole facet (cf figure 3) is in very good agreement with measured and calculated spectra for a slightly distorted hexagonal Ag(111) island as shown in figure 8 of [15] (of course with a different absolute energy scale). In particular this is valid for the enhancement of the first mode at $E_1$ and the almost complete suppression of the second mode at $E_2$ in the centre of the facet. Some remnant of this pattern is also visible in figure 3 for the clusters with $N = 1.1 \times 10^4$ and $9.9 \times 10^3$ atoms, but for smaller sizes the spectra are different as discussed, e.g. in the context of figure 6 above. We expect that there exists a minimum facet size or a minimum cluster height, below which the surface state disappears. This has to be checked with more STS data for clusters with a size around $N = 10^4$ atoms. But for states within the cluster volume a nodal pattern depending on the symmetry of the quantized states can also be expected, as was shown, e.g., for the case of semiconductor clusters [22]. We discuss this in the next section.
5. Electron confinement in the cluster volume

For thin metal films the confinement of the conduction electrons perpendicular to the film thickness leads to ‘quantum well states’, which basically correspond to the one-dimensional ‘particle-in-a-box’ problem. The resulting discrete energy levels were studied in the past mainly with photoelectron spectroscopy [23, 24] but recently also STS has been used for local measurements [25]. Experiments for a freestanding metal film with nanoscopic thickness were performed for small gas bubbles a few crystal monolayers below the surface [26], but most samples consist of a thin metal film grown on a substrate. In the latter case the barrier for the electron transmission into the substrate occurs, e.g. for energies within a bandgap of the substrate material, or due to different symmetries of the electron states in the film and in the substrate.

But for the Au clusters the application of such quantum well states is not straightforward. In spite of the flat (111) facets on top of the gold clusters a simple square-well potential of a width corresponding to the cluster height, similar to [27], does not give a description of the peak positions. Using this model the valence band energy level spacing close to the Fermi energy is \( \Delta E \approx \pi \hbar^2 k_F / (m^* d_z) \). With \( k_F \approx 1.2 \times 10^{10} \) m\(^{-1}\), \( m^* \approx 1 \) and \( d_z = 3 \) nm corresponding to the mean cluster heights, this results in \( \Delta E \approx 1 \) eV. Indeed this is the experimentally observed value for quantum well states, e.g. in an Ag(100) film of about this thickness [28] with \( m^* \approx 0.7 \) for the direction perpendicular to the film surface. Within this model the experimentally observed \( \Delta E \approx 0.2 \) eV for the gold clusters requires significantly altered material properties such as, e.g., an increased effective mass \( m^* \gg 1 \). But this contradicts the existence of a Shockley surface state, as was observed on the facets of the largest clusters (see section 4), which indicates an electronic structure which is already very close to the bulk properties. The interaction of the valence band electrons with the lattice of the ionic cores can have a significant effect on the energy quantization for quantum well states in thin metal films [24]. In general, they cannot be described by a simple free electron gas, but band structure effects have to be considered. Applying the bulk band structure to an Au(111) film, quantum well states in the occupied region are expected only for energies below the valence band maximum at \(-1\) eV, due to the gap in the surface-projected volume band structure [29, 30]. This region is not covered by the spectra in figure 3, for technical reasons (cf the discussion of figure 7). An energy quantization in the valence band below the gap in the (111) direction was found for Ag(111) films on HOPG [31]. In addition one observes the existence of surface states on these (111) films [18, 19], with a shifted energy position compared with the bulk surface due to the interaction with the substrate (cf section 4). This shows that the main features of the band structure for the direction perpendicular to the film surface remain, though the thickness of only a few atomic layers would suggest an ill-defined \( k_\perp \). The same observation is also made for other properties of thin metal films such as, e.g., the photon energy dependence in the normal emission photoelectron signal [23]. For the case of faceted metal clusters this corresponds to the previously discussed presence of detailed properties connected with the bulk band structure, already for clusters with a diameter of a few nanometres.

The disagreement between the calculated modes and the measured spectra for the three smaller clusters in figure 3 suggests that the surface state disappears below a critical cluster size of about \( 10^4 \) atoms. Qualitatively the series of patterns in the \( dI/dV \) maps are still visible, but the energies of the modes do not fit to the model applied for the confined surface state in section 4 (cf figure 6). For the cluster with \( N = 5.2 \times 10^3 \) atoms we can get considerably better agreement if we assume a significantly increased facet area of \( \Omega' = 41 \) nm\(^2\) instead of the measured value \( \Omega = 23 \) nm\(^2\), and if we shift the onset of the surface state to \( E'_0 = -660 \) meV.
With these modified parameters we get the energies $-592, -490, -310, -100$ and $179$ meV for the modes with $n = 1, 2, 4, 7$ and $10$, respectively (cf experimental data in figures 6 and 7). A similar identification of the peaks in the $dI/dV$ spectra together with the corresponding $dI/dV$ maps can be obtained for the cluster with $N = 7.2 \times 10^3$ atoms assuming $\Omega' = 51$ nm$^2$ and $E'_0 = -605$ meV. The model of section 4 predicts a similar $E'_0$ for clusters with $N = 5.2 \times 10^3, 7.2 \times 10^3$ and $9.9 \times 10^3$, because of their similar height. In contrast, the values of $E'_0$ for the two clusters discussed above are significantly smaller than for the cluster with $N = 9.9 \times 10^3$ ($E'_0 = -588$ meV).

Up to now the modified parameters $E'_0$ and $\Omega'$ for the smaller clusters are purely heuristic. The values for $\Omega'$ are not unreasonable, since they are in between the area of the top and the bottom facet of the clusters, but we remark that we would also get the same result by changing the effective electron mass, which would shift $m^*$ closer to $m_e$, the value for a free electron gas. On the whole, the modifications can be taken as an indication that the spectra for the smaller clusters show the transition from peaks given by confined surface states to features induced by the modification of electronic volume properties with decreasing cluster dimensions. For very small clusters the connection to different bulk phenomena will get less well defined, and the electronic structure is better described by a three-dimensional electron confinement, e.g. with the well-known jellium model [1], in which the effect of the ionic cores can be included as perturbation [3].

Finally we would like to mention the minimum which is located for all clusters in figure 3 at $V = 0$, i.e. at the Fermi energy. It can be excluded that this feature is caused by an artefact within the lock-in detection because we see it identically, only with a smaller signal-to-noise ratio, in the $I(V)$ curves after numerical differentiation. One would not expect the Fermi energy to be special, neither for surface nor for volume states, if the $dI/dV$ spectra simply represent the density for the confined and quantized states. Therefore this minimum indicates that the $dI/dV$ spectra cannot be interpreted solely as given by the local density of states. Effects like the charge transport in the tip/cluster/surface system [32], perhaps in combination with the vanishing density of states at the Fermi energy for the HOPG substrate, have to be considered as well.

6. Band structure effects in the energy quantization

In figure 8 we present a schematic illustration for the discussed ‘bulk limit’ in the description of large faceted metal clusters, focusing on a (111) facet of a noble metal cluster. Two cross sections of the bulk band structure are shown: on the left-hand side $E(k_\perp)$ for the direction perpendicular to the surface, with the parabolic maximum or minimum for the valence band below or above the gap in the (111) direction respectively; and on the right-hand side the curve $E(k_{||})$ for the Shockley surface state within the gap in the shaded projected volume band structure. In both directions a confinement will lead to an energy quantization. For a laterally extended thin metal film, quantum well states will occur below and above the gap in the (111) direction. The confinement of the Shockley surface state to a nanoscopic facet area will lead to quantized modes, too. Measuring the electronic structure of a large, faceted cluster one may observe a combination of both, as indicated in the energy spectrum in the middle. In addition quantized volume states can exist inside the bandgap, if an electron confinement occurs for other than the high-symmetry (111) direction [26].

For the actual experimental result the choice of the spectroscopic technique will be crucial. The density of states at the Fermi level is given by $m^*\Omega/(\pi\hbar^2)$ for the surface state (without
confinement) and by \((2m_e)^{3/2}(-E_V)^{1/2}V/(2\pi^2\hbar^3)\) for the volume states (for a free electron gas) with \(E_V = -5.5\ \text{eV}\) for the valence band minimum of gold with respect to the Fermi energy. Inserting the facet area \(\Omega\) and the volume \(V\) for the cluster presented in figure 4, this gives a density of states which is about 100 times larger for the volume states than for the surface states. Therefore it will be difficult to detect the surface state, e.g. for free clusters. Nevertheless, for the gold clusters on graphite here the surface state could be observed because angular selectivity in the photoemission experiment and the surface sensitivity of STS were employed. The relative contribution of the confined surface state is larger for certain energies due to the emergence of discrete modes, and it will be important to include it in the discussion, in particular for processes which are localized at the cluster surface, such as adsorption processes [33] or growth phenomena [34]–[37] for example.

The existence of Shockley surface states is expected to be restricted to large facets on the cluster surface. Up to now we have measured STS spectra for clusters without facets only for cluster sizes below about \(N = 6 \times 10^2\) atoms [8]. One reason is, that the STS measurement often leads to a displacement of larger clusters, probably due to lateral force components between the cluster and the STM tip. This in particular is the case if one cannot profit from the extremely stable tunnelling conditions on a flat top facet. Extending the STS measurements to larger clusters without facets will be of interest to test how the electronic structure depends on the cluster shape.

7. Conclusion

In the limit of large, faceted metal clusters the interaction of the free electron gas with the ionic core lattice results in additional quantization phenomena which are well known in the area of surface and thin-film physics. We have discussed this topic using experimental results for large noble metal clusters grown on HOPG. For faceted gold clusters we observed one explicit example for this kind of effect with the emergence of a Shockley surface state for clusters with a size of \(10^4\) atoms. The lateral two-dimensional confinement of the surface state within the (111) facet area leads to quantized states, which may be important for processes on the cluster.
surface due to the resulting large density of states at certain positions close to the Fermi energy. For the three-dimensional electron confinement, in particular also perpendicular to the surface, the wealth of experimental and theoretical work which exists for quantum well states in metal films on surfaces may lead to a deeper understanding for the case of large metal clusters as well. The interconnections between this kind of ‘bulk limit’, using the bulk volume and surface band structure as a starting point for the description of large clusters, and the models successfully used for the description of small metal clusters, e.g. the jellium model, are still to be explored.

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