Morphology and electron confinement properties of Co clusters deposited on Au(111)

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Abstract. We present the first measurements of both the morphology and electronic structure of preformed Co nanoclusters in the size range of a few up to several hundreds of atoms by means of low-temperature scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS). Co clusters are produced in the gas phase and deposited under controlled ultra-high vacuum conditions onto clean Au(111) with low density, well below complete coverage of the Au(111) substrate. We find that smaller clusters, which typically contain less than 20 atoms, exhibit a significant surface mobility with subsequent aggregation, whereas larger clusters turn out to be immobile. From a systematic analysis of the cluster height distribution, we infer that approximately spherical clusters experience only a restricted flattening and have a multilayered structure, which sometimes is observed to exhibit hexagonal facets, pointing to a truncated octahedral shape. Furthermore, detailed STS measurements on individual Co clusters reveal the presence of various size- and shape-dependent maxima with large energy spacings of the order of 100 meV, as well as an occupied state around $-200$ meV that originates from the Co 3d band. Our findings provide direct evidence for the existence of strong electron confinement effects in the Co clusters stemming from delocalized Co valence electrons. Our results provide an original contribution to the understanding of cluster physics and in particular of the specific electronic structure.

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1. Introduction

Controlled growth and characterization of nanostructures on surfaces is currently one of the most active research areas of solid-state physics. At the scale where small means different, nanosized particles exhibit fascinating size-dependent physical properties that differ strongly from the properties of their bulk counterpart. For a reliable investigation of the nanoworld and its novel properties, appropriate measurement tools are required: scanning tunneling microscopy (STM) combined with scanning tunneling spectroscopy (STS) offers an ideal means to study in detail both the geometrical and electronic properties of individual nanoparticles on metallic substrates.

One possible route for the creation of well-defined nanoparticles is to grow them by atomic deposition and subsequent self-organization on an atomically flat substrate. Intriguing electronic phenomena such as surface state scattering and two-dimensional electron confinement effects [1, 2] are observed for such systems. Here, we opt for the alternative route of depositing nanoparticles that are preformed in the gas phase on single-crystalline surfaces [3]–[5]. Gas-phase cluster deposition offers a high degree of freedom to fine-tune the properties of nanostructured materials by selecting the appropriate particle size, composition, kinetic energy and substrate. Transition metal clusters, and in particular Co clusters, have been investigated thoroughly during the last couple of decades. Apart from a fundamental point of view, Co clusters are also of technological interest because of their relevance as building blocks for future nanoelectronic applications, in particular magnetic data storage [6], their catalytic properties, e.g. for the growth of carbon nanotubes [7], and even in view of creating well-defined nanosized metal–semiconductor contacts [8, 9]. Information on the electronic structure of Co clusters in the gas phase has been obtained by measurements of ionization energy [10] and electron affinity [11] as a function of size. Pronounced size specificity also was found in the evolution of Co cluster magnetism [12]–[16], originating from the combined contributions of geometrical effects (shells of atoms) and electron delocalization effects (increased spin moment and enhanced orbital momentum). The importance of the interplay between geometric structure and electronic structure has urged a large number of detailed theoretical investigations with varying degrees of complexity [17]–[19]. Computationally, the electronic structure of Co clusters was found to be dominated by the 3d band, subject to small
size narrowing with respect to the bulk, and discrete energy states of mainly 4s/4p character around the Fermi level, with energies and energy intervals strongly depending on cluster size and structure [17]. The appealing magnetic properties of small Co clusters have triggered a lot of work on thin films consisting of Co clusters preformed in the gas phase as building blocks, including ferromagnetic cluster assembled films and films of Co clusters embedded in a thin antiferromagnetic matrix [20]–[22]. So far, however, such clusters have not been investigated individually in terms of morphology or electronic properties when interacting with metal surfaces.

A good control of both cluster and substrate cleanliness is of major importance for the reliable growth of films with well-defined physical–chemical properties. For example, small amounts of oxide molecules embedded into silver clusters are known to strongly modify the cluster mobility on surfaces, which in turn influences the growth of nanostructures from the clusters and the related relaxation mechanisms [23]. The role of surface contamination is also evident for Co island growth by atom deposition and subsequent self-organization onto Au(111): in situ Co atom deposition on clean Au(111) results in the formation of self-organized mono- and bilayer-high particles at specific reconstruction points on the Au(111) surface [24], while randomly spread and monolayer-high particles are observed on ex situ grown Au(111) that is polluted due to exposure to ambient conditions [25]. To avoid sample contamination and oxidation, a home-built ultra-high vacuum (UHV) transport vessel was developed and made compatible with both the cluster deposition apparatus and the UHV STM setup, allowing us to deposit the clusters onto atomically clean substrates and transport the samples under UHV conditions.

For the present study, deposition of Co clusters on clean Au(111) enabled us to systematically investigate the morphology as well as electronic properties of individual nanoclusters in the size range of a few up to several hundreds of atoms by means of STM and STS under controlled UHV conditions. We show that, except for the smallest Co clusters (monomers, dimers, trimers, etc up to about 20 atoms), the clusters have negligible mobility after deposition at room temperature on clean Au(111). The mobility of Co clusters on Au(111) turns out to be comparable to the mobility of the previously experimentally [26] and theoretically [27] studied Au clusters on Au(111). On the other hand, Au cluster mobility turns out to be much higher on graphite [28]. Furthermore, we show by an extensive height analysis that the cluster deformation upon impact on the surface appears to be rather limited, resulting in approximately hemispherical clusters. By means of high-resolution STS measurements we were able to observe an occupied state peak around $-200\text{ meV}$ for all Co clusters, similar to recent experiments on Co islands created by atomic deposition and subsequent self-organization [29]. Moreover, a number of broadened maxima are observed in the STS spectra, both below and above the Fermi level. Our findings therefore provide the first direct evidence of strong confinement of itinerant electrons in the three-dimensional Co clusters that interact with the metallic Au(111) substrate.

2. Experimental

2.1. Substrate preparation and transport

Epitaxially grown 140 nm thick Au(111) films on freshly cleaved mica were prepared ex situ by molecular beam epitaxy (MBE) at elevated temperatures [30]. After removal from the MBE growth chamber, the Au(111) surfaces are cleaned in the UHV preparation chamber that is part of the UHV STM setup by repeated cycles of Ar ion sputtering (at about 4 keV and $10^{-6}\text{ mbar}$)
Figure 1. Abundance spectra of free cationic Co clusters as a function of (a) the number of atoms in the cluster and (b) the corresponding cluster diameter. The mean cluster size was tuned to be around 200 atoms ($\simeq 1.6$ nm cluster diameter). The diameter was calculated assuming the clusters to be spherical.

and annealing (at about 720 K). Substrates are then transported under UHV conditions first to the cluster deposition apparatus and after cluster deposition back to the STM setup by means of a compatible home-built UHV transport vessel (pressure always remains below $2 \times 10^{-9}$ mbar and is most of the time in the $10^{-10}$ mbar range). The vessel consists of a small chamber provided with a long transport arm and an ion pump that can run autonomously for 24 h using a battery.

2.2. Cluster production and deposition

Cobalt clusters were produced by a laser vaporization source, which is integrated with a UHV cluster deposition chamber, onto cleaned Au(111) substrates that are kept at room temperature [30, 31]. Cluster beams with a size distribution ranging from a few atoms up to several hundreds of atoms can be produced, as recorded with time-of-flight mass spectrometry. A typical mass spectrum of the cationic free Co clusters as a function of (a) the number of atoms in the cluster and (b) the corresponding cluster diameter is presented in figure 1. The diameter was calculated assuming the clusters to be spherical and using the Wigner–Seitz radius for Co (0.138 nm). The maximum in the cluster size distribution was tuned to around 200 atoms ($\simeq 1.6$ nm cluster diameter). We note, however, that clusters larger than observed in the mass spectra may be present in the cluster beam, since the measured cluster distribution has an upper cutoff due to the decreasing efficiency of the detector for the largest clusters. The clusters were deposited with their inherent low kinetic energy ($\simeq 0.15$ eV atom$^{-1}$). This kinetic energy is small when compared to the atomic binding energy within the cluster, and consequently negligible cluster fragmentation is expected upon impact [27]. Deposition times were chosen to achieve a low cluster density, well below complete coverage of the substrate.
2.3. Low-temperature UHV STM and STS

STM and STS measurements were performed with a commercial scanning tunneling microscope (Omicron NanoTechnology). The STM operates under UHV conditions at a base pressure below $5 \times 10^{-11}$ mbar and at low temperatures, and is connected to a UHV preparation chamber with a typical base pressure of $2 \times 10^{-10}$ mbar. For maximum topography and energy resolution, all measurements were performed at liquid helium temperature ($T_{\text{sample}} \simeq 4.5$ K). Mechanically cut PtIr (10% Ir) tips were used. Tips were cleaned in situ by applying high-voltage pulses up to 10 V while being in close proximity of a clean Au(111) surface, until stable topography and spectroscopy can be achieved. The well-known electron surface state of the Au(111) surface was hereby used as a reference in the STS measurements [32]. STM topographic imaging was performed in constant current mode. Local $I(V)$ curves are measured with open feedback loop during topographic imaging. $I$ and $V$ correspond to the tunneling current and voltage, respectively. On the other hand, local spectroscopy data ($dI/dV$ versus $V$) with open feedback loop and differential conductance images ($dI/dV(x,y)$ with closed feedback loop), hereinafter referred to as local density of states (LDOS) maps, were acquired by means of harmonic detection with a lock-in amplifier at modulation frequencies in the 200–1500 Hz range and with modulation amplitudes in the 10–40 mV range. Everywhere in the text the tunneling bias voltage $V$ refers to the sample voltage, while the STM tip is virtually grounded. Image processing was performed using Nanotec WSxM [33].

3. Results and discussion

3.1. STM measurements

Figure 2(a) presents a three-dimensional visualization of a typical STM image after deposition of Co clusters, which are preformed in the gas phase, on a clean and atomically flat Au(111) surface. Particles of various sizes are routinely found on the ‘herringbone’ reconstructed Au(111) surface, with heights ranging from only one monolayer up to over 2 nm. As this height distribution is comparable to that of the cluster size distribution before deposition (see figure 1), we conclude that the Co clusters do not exhibit significant diffusion on Au(111) at room temperature. Nevertheless, two types of particles can be distinguished.

At the elbows of the surface reconstruction, exclusively one-monolayer-high islands are found, similar to the case of Co atom deposition and subsequent self-organization [24]. One such very small Co island is included in the height profile in figure 2(d). At the elbows, a single atomic point dislocation is present, which acts as a nucleation site for Co island growth [34]. The similarity to islands grown by Co atom deposition indicates that the islands result from the diffusion and aggregation of clusters that are sufficiently small (single atoms, dimers, trimers, etc) to interact with the surface in a way that is similar to that of individual atoms. It has been reported before by Chado et al [35] that Co islands grown on Au(111) by atom deposition start to form a bilayer already at sizes of about 20 atoms. This is in agreement with what is observed in the STM images. As mentioned above, the Co islands situated at the elbows are one monolayer high exclusively. The full width at half maximum of these islands is observed to be as small as 1.5–2.0 nm. Taking into account the tip convolution effects (see below), the island sizes correspond to only a few Co atoms. We may therefore assume that the upper size limit of Co clusters on Au(111) having a significant surface mobility is indeed of the order of 20 atoms,
Figure 2. STM images of deposited Co clusters on an Au(111) surface ($T = 4.5$ K). (a) The larger clusters show negligible mobility after deposition, whereas the smallest clusters (single atoms, dimers, trimers, etc) diffuse towards the elbows of the Au(111) ‘herringbone’ reconstruction and aggregate into monolayer-high islands. (b, c) The deposited Co clusters have an approximately hemispherical shape exhibiting hexagonal facets. (d) Height profile taken across the four Co clusters along the white dotted line indicated in (a).

Although the island formation (in particular the growth of a second layer) may be different when compared to [35] if small clusters are involved in the island formation.

On the other hand, higher particles, which correspond to individual deposited clusters, are randomly spread across the substrate. This can be accounted for by the strong metal–metal interaction between cluster and substrate that prevents cluster diffusion, despite the large mismatch between the lattice parameters ($0.251$ nm for Co(0001) and 0.288 nm for Au(111) [4, 36]). The different behavior we observe for the very small and the larger clusters illustrates that cluster diffusion depends on cluster size [4].

Figure 3 shows a histogram of the cluster height distribution based on STM measurements (figures 2(a) and (d)), together with a smoothed version of the diameter abundance spectrum shown in figure 1(b) (red solid line). The monolayer-high aggregates are not included in this histogram, as they do not result from single deposited clusters and their amount depends on the density of ‘elbows’ of the Au(111) reconstruction. The distribution of cluster heights corresponds well to that of the cluster diameters: the cluster height with highest abundance is found to be around 1.0 nm after deposition, compared to a mean cluster radius (diameter) of about 0.8 nm (1.6 nm) before deposition. It can be concluded from the relation $r_{after} = 2^{1/3} r_{before}$ that these values match nicely when we assume that the clusters are spherical before deposition and can be approximated as hemispheres after deposition. In view of the large spread in cluster sizes and the uncertainties involved in the used size estimates, this conclusion should be considered with care. The actual shape of the deposited clusters will be size-dependent.

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Figure 3. Height histogram of the deposited Co clusters on Au(111) as determined by STM measurements, together with the (smoothed) diameter abundance spectrum of figure 1(b) (red solid line). Clusters experience only a rather limited flattening upon impact and interaction with the Au surface, and preferentially have heights that are multiples of one Co monolayer (one monolayer = 0.205 nm). Inset: the diameter histogram of deposited Co clusters as determined by STM (gray) and the corresponding corrected histogram (black), which takes into account the broadening due to tip convolution (assuming a spherical tip apex with a radius of 8.0 nm).

Nevertheless, to a good approximation the deposited clusters can be modeled as having a shape somewhere in between a sphere and a hemisphere. The limited amount of flattening indicates that the approximately spherical Co clusters retain their shape to a large extent on the Au(111) surface. This can be attributed to the rather large mismatch between the lattice parameters of the clusters and the substrate (see above).

Additionally, we note that there appear rather pronounced maxima in figure 3 at specific cluster heights that are multiples of one monolayer of Co atoms, indicating that the clusters have a highly ordered and layered structure after deposition on Au(111) [37]. The Co clusters are, however, generally observed as ‘smooth’ hemispherical entities (see figures 2(a) and (d)), which can be largely attributed to tip convolution effects that ‘smear out’ the actual shape of the cluster. In a few exceptional cases, clusters showed hexagonal faceting on Au(111), as illustrated in figures 2(b) and (c). Together with the ‘discreteness’ of the height distribution, this points to clusters having the shape of truncated octahedra. This would be in agreement with the structure of a $\beta$-Wulff polyhedron, predicted for Co nanoparticles with sizes below 20 nm [38]. This structure has already been observed for deposited Co clusters in an Nb matrix [39] and on Ge(001) surfaces [9].
Figure 4. (a) A schematic diagram of the effect of tip convolution (gray) on a sharp step edge on the Au(111) surface (black), assuming a spherically shaped tip apex. (b) Topographic STM image of a step on the Au(111) surface. (c) Height profile along the white dotted line indicated in (b).

Figure 5. A schematic diagram of the effect of tip convolution (gray) on a hemispherical cluster (black), assuming a spherically shaped tip apex.

The histogram with the gray shaded bars in the inset of figure 3 shows the distribution of the cluster diameters (full width at half maximum) as obtained from topographic height profiles such as the one shown in figure 2(d). The average diameter is found to be around 6 nm, i.e. larger than the value around 2 nm that is expected for a hemispherical cluster shape. This discrepancy can be accounted for by tip convolution effects. Assuming a spherically shaped tip apex as schematically presented in figure 4(a), one can estimate the tip radius $R_t$ from a height profile taken at an Au(111) step edge (see figures 5(b) and (c)) with height...
Figure 6. (a) STM LDOS map of individual Co clusters on Au(111) obtained at 50 mV. The clean Au(111) surface shows complex standing wave patterns due to scattered surface state electrons. LDOS maps of a Co cluster obtained at (b) 1500 mV and (c) 2500 mV are dominated by topographic variations.

$h = 0.235 \text{nm}$ from the relation $R_t = (h^2 + w^2)/2h$. For the experimental step broadening of $w = 2 \text{nm}$, the latter relation yields a tip radius of around 8 nm, which is acceptable for a mechanically cut PtIr tip. Using this value for the tip apex radius, we have constructed a histogram of ‘deconvoluted’ cluster diameters $D = 2r_c$ (at the cluster–substrate interface) based on the experimental cluster diameters $D_{\text{FWHM}}$ measured at half maximum height (see figure 5). Assuming a hemispherically shaped cluster with radius $r_c$, the relation between $D$ and $D_{\text{FWHM}}$ is given by $D = 2\left(\sqrt{(D_{\text{FWHM}})^2/3 + 4/9 R_t^2} - 2/3 R_t\right)$, which yields the corrected histogram with the black bars in the inset of figure 3. The resulting ‘deconvoluted’ mean cluster diameter around 2 nm nicely agrees with the cluster height with highest abundance around 1 nm, assuming the formation of hemispherically shaped Co clusters after deposition on Au(111).

3.2. STS measurements

Due to the specific cluster–substrate interaction that prevents diffusion of or surface wetting by the clusters, Co clusters are immobilized on the Au(111) surface while partially retaining their initial shape. Co nanoparticles of various sizes and heights (up to 2.4 nm) can be formed. This provides additional flexibility when compared to the monolayer and bilayer Co islands grown by atomic deposition and subsequent self-organization [29]. Preformed cluster deposition therefore appears to be ideally suited for a systematic investigation of individual Co cluster properties as a function of size and interaction with the underlying substrate.

We performed detailed LDOS measurements on and around Co clusters deposited onto the Au(111) surface. Figure 6(a) shows a typical STM LDOS map obtained at 50 mV. Due to the cleanliness of the substrate, pronounced standing wave patterns are clearly visible. The interference patterns are known to arise from a quasi-two-dimensional electron gas that is confined to the Au top atomic layers, commonly referred to as surface state electrons [40].

We did not observe electron standing waves on deposited Co clusters within a bias voltage range of $-1000$ up to $+2500$ mV. This is illustrated in more detail in the cluster LDOS maps in figures 6(b) and (c): the LDOS maps reveal features that correspond to topographic variations.
Figure 7. Typical d$I$/d$V$ spectra obtained on a Co cluster, revealing a pronounced occupied state maximum around $-200\,\text{mV}$ at the center of the cluster and a featureless spectrum at the cluster edges. A d$I$/d$V$ spectrum taken on the Au(111) surface next to the Co cluster and showing the typical onset of the Au(111) surface state is added as a reference. Inset: STM image of the cluster under investigation. Marks indicate the location where the STS spectra are recorded.

of the cluster surface, independent of the applied bias voltage. Co clusters therefore differ from their atomically flat counterpart, i.e. Co islands that are grown by atomic deposition and subsequent self-organization. On the latter islands, the surface state electrons are scattered at the island edges exclusively. Since the shape of such islands is nearly perfectly hexagonal, the backward and forward scattered surface state electrons give rise to standing wave patterns consisting of only a limited number of wave vectors that depend strongly on the applied bias voltage [29]. In the case of clusters, confined electrons are scattered at all edges and facets of the cluster’s outer surface, so that scattered electrons cannot give rise to standing wave patterns that can be probed with STM and STS.

The intrinsic electronic structure of the Co clusters can however be probed by local measurements of d$I$/d$V(V)$ spectra. Figure 7 presents typical spectra as measured on the top and at the edge of a single Co cluster. The inset shows a topographic constant current image of the cluster under investigation, where we have indicated the locations where the STS spectra are recorded as well as the measured cluster height. Although only of indicative value, the number of cluster atoms can be estimated by considering either the undeformed spherical or deformed hemispherical shape. This yields values of 130–520 atoms, respectively, where the latter value is thought to be the most reliable value, as discussed above. A d$I$/d$V$ spectrum measured on the surrounding Au(111) is added as a reference, showing the typical onset of the surface state around $-480\,\text{mV}$ [32]. Each of the presented spectra was checked for its reproducibility at least three times. Spectra taken at the cluster top reveal the presence of a
pronounced occupied state peak around $-200 \text{ mV}$, independent of cluster size. Similar states were observed in earlier studies of Co islands on Au(111) that were grown by atom deposition and subsequent self-organization [41]. As is known for bulk and surface cobalt, this occupied state results from a band mainly stemming from hybridization of the Co atom 3d states with 4s–4p states. This agrees with the findings of local spin DFT calculations for Co clusters with 55 and 147 atoms [17], and is also confirmed by ab initio calculations for Co islands grown on Au(111) [41].

It appears that the method of nanoparticle production (atom versus cluster deposition) does not have a significant influence on the occupied Co state. In contrast to the top of the clusters, we did not observe the maximum in the $dI/dV$ spectra around $-200 \text{ mV}$ at the edges of the clusters. This might be attributed to the different tunneling conditions at the cluster top (vertical tunneling always occurs via the same outermost tip asperity) when compared to the cluster edge (sideward tunneling possible via different asperities and/or tunneling to the Au substrate). Tunneling via multiple tip asperities to multiple regions of the cluster and surface may possibly lead to averaging out of spectral features. This suggests that STS measurements are not able to accurately probe the cluster electronic properties at the edges, since we did not observe any distinct STS features at these edges.

Apart from the occupied state peak, many of the clusters also showed one or more additional maxima within the experimentally accessible energy window, with large energy level splittings of the order of several hundred mV (see figure 8). Next to each curve, a topographical (constant current) image of the cluster under investigation is presented and the location at which the spectrum is obtained is indicated. The cluster height is added for each of the $dI/dV$ spectra.

Similar to the cluster in figure 7, an indicative value of the number of cluster atoms can be given. The values range from 60 to 240 atoms for the smallest cluster, and from 250 to 1000 atoms for the largest cluster, where the larger values are expected to be the most reliable. Again, these maxima are observed exclusively for $dI/dV$ spectra that are measured at the top of the cluster. We note that the occupied state peak around $-200 \text{ meV}$ is somewhat broadened for the gas-phase Co clusters when compared to the case of Co islands grown by atom deposition [29]. This can be explained by the very different shape of both types of nanoparticles (truncated octahedra versus atomically flat). Therefore, less Co atoms contribute to the tunneling spectra taken on top of a Co cluster when compared to the islands obtained by atom deposition, resulting in a weaker spectroscopic signal that consequently appears more blurred/broadened. The exact energy of the additional peaks was found to vary strongly from one cluster to the other. No clear correlation with cluster size could be determined. It is not too surprising that only a very limited number of maxima are probed in the STS spectra on top of the clusters. Indeed, this is, e.g., consistent with previous STS results for Ag islands on Ag(111) [1], and for Ag clusters on graphite [42].

By combining theory and experiment it was shown that STS can only probe a fraction of the discrete energy levels within the nanoparticle and that at different locations on the particle one probes different levels. Since we are experimentally restricted to the cluster top exclusively, as discussed above, we only have access to the levels at this location. Since the STS maxima depend strongly on the surface area and shape of the outer surface of the cluster, this explains why some clusters show zero, one, two or three additional maxima. This can also explain why the curves in figures 8(b)–(c) are very different, although the spectra are registered on clusters having equal height. Therefore, it is not straightforward to unambiguously link the cluster size with the observed maxima and establishing the precise link is beyond the scope of the present work. Nevertheless, the observed pronounced maxima in the $dI/dV$ spectra clearly show that
Figure 8. $dI/dV$ spectra obtained on various Co clusters. All clusters exhibit a pronounced occupied state maxima around $-200 \text{ mV}$ and additionally show one or more broadened maxima, of which the exact energy positions vary from cluster to cluster. A constant current STM image of the cluster under investigation and the cluster height are shown for each spectrum. Marks indicate the location where the STS spectrum is recorded. Scan ranges for the images are (a) $9.1 \times 9.1 \text{ nm}^2$, (b) $10.4 \times 10.4 \text{ nm}^2$, (c) $10.8 \times 10.8 \text{ nm}^2$, (d) $8.1 \times 8.1 \text{ nm}^2$ and (e) $21.8 \times 21.8 \text{ nm}^2$ ($T = 4.5 \text{ K}$).

Itinerant Co cluster electrons experience strong confinement within the nanosize clusters, giving rise to a pronounced discretization of the electron energy levels.

Assuming in the most simple approximation a three-dimensional spherical square well potential, we can estimate the mean energy level spacing $\delta E$ expected for a cluster in the size range under study. This yields a mean energy level spacing $\delta E \sim 2\pi^2 \hbar^2 / (m_e k_F V)$, where $m_e$ is the electron mass and $k_F$ the Fermi wave vector of Co ($13.9 \text{ nm}^{-1}$) [36]. In the limit of free
spherical clusters of radius \( r_c \), an upper limit for the mean energy level splitting \( \Delta E \) can be obtained from the shell closings in a spherical jellium model given by \( \Delta E \sim \hbar^2 k_F \pi / (2.71 m_e r_c) \) \cite{43, 44}. The mean level spacing in the cluster size range of interest given by both models is plotted in figure 9. Obviously the experimentally observed peak spacings are within the broad energy range of up to 1 eV allowed by the models (spherical square well potential and shell closings) and therefore our findings are compatible with the quantum-mechanical picture of discrete energy levels. The very broad energy gap range given by both models for one specific cluster size indicates the importance of the cluster shape for the degeneracy of the electron levels of the cluster.

To fully unravel the origin of the observed maxima in the \( dI/dV \) spectra, more detailed calculations of energy-level spacings would be required, taking into account the cluster structure and symmetry. This was done, e.g., for a number of fcc and hcp Co clusters in \cite{17}, giving rise to the occurrence of multiple degenerate energy levels with significantly altered energy level spacing. This results in bunching of levels into electronic shells and in enlarged energy gaps between subsequent energy levels, a phenomenon that can become very pronounced for small clusters in the size range under investigation \cite{45}. Therefore, although the average energy-level splitting in the clusters can be quite small, the levels are grouped in band-like features with very large energy gaps in between two subsequent bands, which explains the observed large peak spacings and the fact that discrete bands are not observed for all clusters. Computations along the lines used in \cite{17} also provide more detailed information on the electronic structure of the clusters. For example, the pronounced band at \(-200\) mV is reproduced as originating from the 3d Co electrons, while the discrete states appearing around and above the Fermi level are found to have a pronounced 4s–4p character. Our spectroscopic experiments directly confirm these theoretical findings concerning the coexistence of a band originating from localized 3d Co electrons, which is hardly depending on size, with discrete electron states resulting from the confinement of itinerant cluster electrons exhibiting strong size dependence. In addition, the relatively strong intensity of the discrete states with respect to the 3d band points towards a larger spill-out of the delocalized electron states.
Apart from the intrinsic electronic properties of the Co clusters, the spectroscopic data are influenced as well by the interaction with the substrate. For a quantum electron system, such as an atom or a small cluster, in the close vicinity of a continuum spectrum, i.e. the Au metal surface, strong interactions are expected, resulting in both shifts and broadening of the energy levels of the quantum system. This has been extensively described for atoms scattering of a surface [46] or escaping from a surface [47]. In our present experiments, similar cluster–surface metal–metal interactions can account for the rather large peak broadening (full width at half maximum is of the order of 100 mV).

4. Conclusions

For the first time the morphology and electronic properties of Co clusters deposited on clean Au(111) under controlled UHV conditions have been systematically investigated by means of low-temperature STM and STS. A high mobility and subsequent aggregation is observed for the smallest clusters of up to around 20 atoms, whereas the strong metallic interaction with the underlying substrate inhibits the mobility of the larger clusters. By a systematic analysis of the experimental results we have shown that the approximately spherical Co clusters experience a limited flattening after deposition: the clusters exhibit a multilayered structure which sometimes is observed to exhibit hexagonal facets, pointing to a truncated octahedral shape. Furthermore, we have probed for the first time the electronic structure of individual Co clusters of various sizes by means of STS, thereby revealing the discrete nature of the electron structure in spherical nanoparticles. Besides the Co 3d electron band at 200 meV below the Fermi level, the STS spectra reveal the presence of multiple broadened maxima with energy spacings of the order of several hundred meV. This provides evidence for strong quantum confinement of itinerant Co electrons of mainly 4s and 4p character and is indicative of size-dependent electronic shell structures.

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