Electronic Structure of MgO-Supported Au Clusters: Quantum Dots Probed by Scanning Tunneling Microscopy

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We investigate via density functional theory (DFT) the appearance of small MgO-supported gold clusters with 8 to 20 atoms in a scanning tunneling microscope (STM) experiment. Comparison of simulations of ultrathin films on a metal support with a bulk MgO leads to similar results for the cluster properties relevant for STM. Simulated STM pictures show the delocalized states of the cluster rather than the atomic structure. This finding is due to the presence of *s*- derived delocalized states of the cluster near the Fermi energy. The properties of theses states can be understood from a jellium model for monovalent gold.

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Recent progress in the controlled growth of ultrathin (a few monolayers, ML, thick) insulating alkali-metal-halide or metal-oxide films has made it possible to fabricate well-defined templates for spectroscopic studies of insulator-supported metal particles and molecule-metal systems [1–5]. While these films are thick enough to isolate an adsorbate electronically from the metal support, they are thin enough to enable tunneling from or to the scanning tunneling microscope (STM) tip under imaging conditions. This facilitates investigations of nanoscale metal-insulator-metal systems, where new insights can be gained into (i) factors defining the electronic structure, (ii) the charge state(s) of the adsorbate, and (iii) the molecule-metal bond formation.

Since the mid-1990s, first-principles calculations have provided information about the basic interactions between an insulating surface and a metal cluster or a metal adatom [6–16]. In general, the cluster-substrate interaction is weak for a defect-free substrate and characterized as polarization type. However, substrate defects with trapped electrons greatly enhance the binding of metal adatoms or clusters. Recently, nucleation of small gold particles at surface color centers (F_s) on 3–4 ML thick MgO films grown on Ag(001) was detected via STM [4].

In this Letter, we show in detail that gold clusters with 8 to 20 atoms, bound at F_s on MgO substrate, appear as 1–2 nm particles under typical STM imaging conditions [4]. The simulated STM images have internal structures, which however do not reflect the atomic structure of the cluster but rather the symmetries of the electronic states near the Fermi energy, located in the band gap of MgO. The symmetries and energy ordering of the delocalized electron states for flat Au_{13} and Au_{20} clusters can be understood with a simple model: a planar quantum dot.

Two different density functional theory (DFT) implementations were used. The clusters adsorbed on bulk MgO with a F_s were treated by using an nonperiodic, embedded-cluster method [6,14,17], Born-Oppenheimer Molecular Dynamics [18], Perdew-Burke-Ernzerhof (PBE) generalized-gradient-corrected (GGA) functional [19] and Troullier-Martins norm-conserving pseudopotentials [20]. Reference calculations for Au_8, over a Ag(001) supported MgO film, were performed with a DACAPO code [21], which uses periodic boundary conditions together with the revised PBE (RPBE) [22] GGA functional and Vanderbilt ultrasoft pseudopotentials [23]. More details of the setups are given in Refs. [17,24,25].

Our STM analysis is based on the Tersoff-Hamann (TH) formalism [26,27], where the measured signal is proportional to the local density of single-particle states (LDOS) of the sample at the position of the tip vertex, and integrated over the energies allowed by the applied bias voltage. Unoccupied states contribute at positive bias (negative tip) and occupied ones at negative bias (positive tip). Our simulations describe STM in a constant current mode, which according to the TH approximation translates to constant density. The tunneling current I and the electron density n are related by $n(\mathrm{e}/\mathrm{\AA}^3) \approx 2 \times 10^{-4}\sqrt{I}(\mathrm{nA})$ [26]. Here, we use mainly a density of 2×10^{-5} $\mathrm{e}/\mathrm{\AA}^3$ corresponding to a current of 10 pA, which is a typical value in the experiment [4].

We start with the properties of a Au_8 cluster adsorbed at F_s on the MgO surface and on the thin Ag-supported MgO film. An initial guess for the geometry was taken from Refs. [14,17]. Figures 1(a) and 1(b) show that the relaxed structures on both supports are very similar. The overall geometry is the same, with the Au-Au bond lengths being on average 0.1 Å longer for $Au_8/F_s/\mathrm{MgO}(001)/\mathrm{Ag}(001)$. The formation energies, E_c, [28] are 2.36 eV and 2.08 eV for $Au_8/F_s/\mathrm{MgO}$ and $Au_8/F_s/\mathrm{MgO}/\mathrm{Ag}$, respectively.

Figures 1(c) and 1(d) show the LDOS plots [29], projected onto the gold cluster and the support. The following remarks can be done by comparing the supports: (i) the LDOS of the gold cluster is remarkably similar on both supports, with respect to the overall valence band width of about 6 eV and the fine details of the peak structure, (ii) the

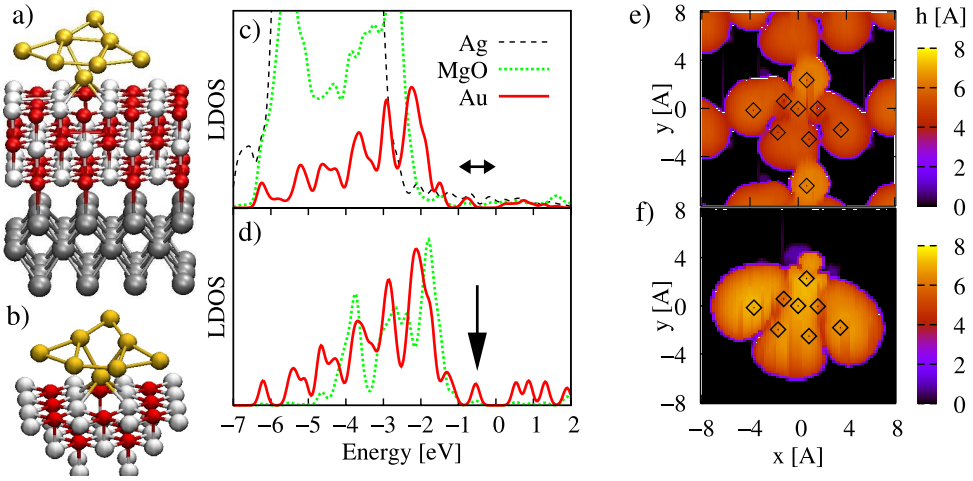

FIG. 1 (color online). (a) Au_8 at F_s on MgO(3 ML)/Ag(001) (in the order of increasing darkness: Mg white, Au yellow, Ag grey, O red). (b) The corresponding cluster adsorbed at F_s on MgO(001). (c) a LDOS plot and (e) a simulated STM image for structure (a). (d) a LDOS plot and (f) a simulated STM image for structure (b). The Fermi energy is at zero in (c) and (d). The horizontal and vertical arrows in (c) and (d) show the state(s) from which the corresponding STM images have been constructed. The positions of the Au atoms are indicated by the diamonds in (e) and (f).

MgO LDOS plots differ, because the band width and shape of the $O(p)$-derived valence band are affected by the underlying silver support in Fig. 1(c), (iii) the uppermost part of the gold LDOS lies in the band gap of MgO, and (iv) the silver support fixes the overall Fermi energy in Fig. 1(c), thereby introducing a relative shift of the gold LDOS with respect to the upper edge of the MgO valence band.

According to the TH approximation, STM probes the electronic states located within the bias voltage, V_b, from the Fermi surface. For negative bias, the highest occupied state of the $Au_8/F_s/MgO(001)$ lies at -0.8 eV in Fig. 1(d). The corresponding state is found around -0.9 eV for $Au_8/F_s/MgO(001)/Ag(001)$ in Fig. 1(c). Figures 1(e) and 1(f) show the simulated STM images at a density of 1×10^{-4} e/Å^3 corresponding to a current of 0.25 nA. Despite the slight overlap in the periodic calculation [Fig. 1(e)], the electronic density of the gold cluster appears to obey an identical symmetry in both models. However, the symmetry seen in the STM picture does *not* reflect the *atomic symmetry* of the cluster, but the symmetry of the imaged electron state. We conclude that the theoretical model with 3 ML MgO film on Ag(001) gives the same physical results as the one that describes Au_8 on a bulklike MgO(001) surface, as far as the electronic properties of MgO-supported Au_8 cluster are concerned. This finding is in line with Ref. [3], where the lower limit for the thickness of an insulating MgO film on Ag was shown to be about 3 ML.

Next, we focus on the electronic states of larger supported gold clusters by means of the computationally less demanding MgO(001) embedded-cluster model. The gold cluster containing 20 atoms is known to be electronically magic in gas phase, having a large highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap as detected by photoelectron spectroscopy [30]. Accompanying DFT calculations predicted an atomically closed, tetrahedral structure, which has been later confirmed by other theoretical work and experimentally by electron diffraction [31,32]. Au_{20} supported by MgO/Mo was reported to be an active catalyst for CO_2 production [6]. Model calculations of Au_{20} adsorbed on F_s of bulk MgO(001) [33,34] and on an ideal MgO/Mo support [8] have recently appeared.

Here, we consider an alternative structure motif for the MgO-supported Au_{20}, which we expect to be relevant particularly for experiments where gold clusters are nucleated at F_s via diffusion of preadsorbed gold adatoms. Earlier simulations have shown that gold clusters pin to the defect via one atom [6,7,14,33,34]. The remaining 19 cluster atoms can form an atomically closed-shell, near-planar layer above the pinning atom (see Fig. 2). The E_c of this structure is 2.43 eV.

Figure 3 presents the LDOS of Au_{20}/MgO, projected on the gold cluster and the support. The analysis of the spatial extent and angular-momentum symmetries of the Kohn-

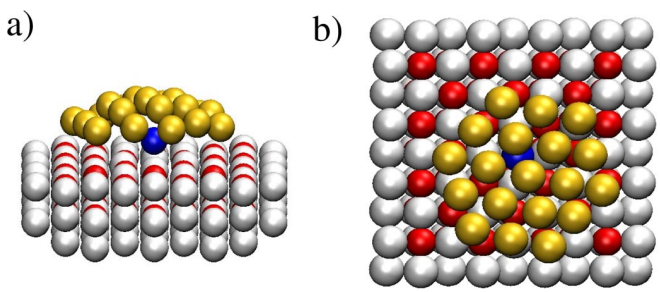

FIG. 2 (color online). A side view (a) and a top view (b) of a flat, geometrically closed-shell $Au_{20}/F_s/MgO$. The Au atom closest to the F_s is marked by dark (blue) shading.

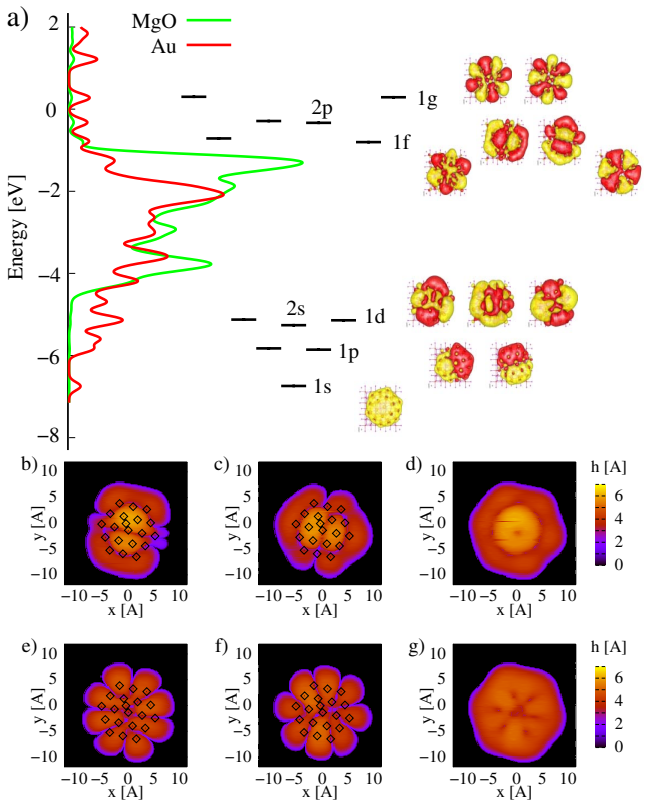

FIG. 3 (color online). (a) Left: LDOS of Au_{20} from Fig. 2. The energy levels of the Kohn-Sham states with a clear delocalized character are indicated in the middle, and the corresponding wave functions are plotted on the right. The simulated STM pictures (b) and (c) show the two occupied, $2p$-like states below the Fermi energy (d) the sum of (b) and (c). (e) and (f) show the first two empty states and (g) their sum. The atom positions are indicated by diamonds in (b), (c), (e), and (f).

Sham states on the Au cluster, analogously to gas-phase Au_{16} [35] and Au_{20} [31], shows that ten states, 20 electrons in total, (i) extend over the whole cluster and (ii) display rather clear symmetries of one major angular-momentum component with respect to the center of the cluster. The energy level structure of the states is given next to the LDOS curves and the symmetries are visualized on the right in Fig. 3. The energy ordering and symmetries of the states correspond astonishingly well to the model of delocalized "jellium" electrons in a 2D harmonic oscillator [36]. The energy levels of the model are shown schematically in Fig. 4. The eigenstates of the 2D harmonic oscillator can be characterized by their principal quantum number and the projection of their angular momentum on the normal vector of the plane m. To simplify the notation, we use the atom nomenclature for this projection; i.e., $|m| = 0, 1, 2, 3, 4$ is denoted by s, p, d, f, g. According to the model, 20 electrons form the closed-shell $(1s^2 1p^4 1d^4 2s^2 2p^4 1f^4)$ configuration. Indeed, the two-fold degenerate HOMO state of the flat cluster, Fig. 3(b)–3(d), can be described as a jelliumlike $2p$ orbital,

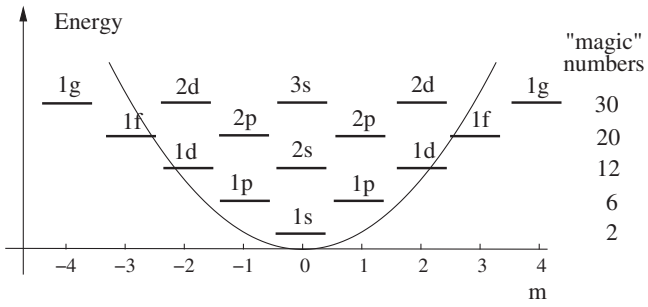

FIG. 4. Energy levels and electron shell closings of the 2D harmonic oscillator model for a planar quantum dot.

whereas the two-fold degenerate LUMO state has the character of the next jellium state $1g$ [Figs. 3(e)–3(g)] [37]. Hence, the properties of the states near to the Fermi energy fit in the simple harmonic oscillator model for monovalent gold. Note that the two electrons of the F_s do not contribute in the counting as they are localized in the vicinity of the pinning Au atom. The simulated STM images produced by these orbitals are shown in Fig. 3. The states with $|m| > 0$ have an intrinsic two-fold degeneracy as shown in Fig. 4. Therefore, STM is not expected to resolve the single states ($-m$ and m) alone but will rather see the sum of both, as shown in Figs. 3(d) and 3(g). There the angular nodal structure is completely washed out, and only the radial features are visible.

Finally, we consider a 13-atom cluster, which has a geometrically magic 12-atom configuration on top of the pinning atom and the formation energy 2.43 eV [Fig. 5(a)]. The Au_{13} cluster is interesting due to the odd number of valence electrons, thus making the cluster an electronically open-shell system. Supported by an insulating surface, this implies the localization of spin in the cluster, which we have verified in this work. Considering the 2D harmonic oscillator model for 13 electrons (Fig. 4), the highest occupied state should have either $2p$ or $1f$ character. Figures 5(b) and 5(c) display a $1f$-symmetric HOMO, which is spin split from the $1f$-symmetric LUMO by 0.17 eV. Provided that the Fermi energy sets in between these states, we predict that the *same* orbital symmetry should be visible by STM both at positive and negative bias voltages. It is interesting to note that an analogous "singly-occupied molecular orbital" (SOMO) has been

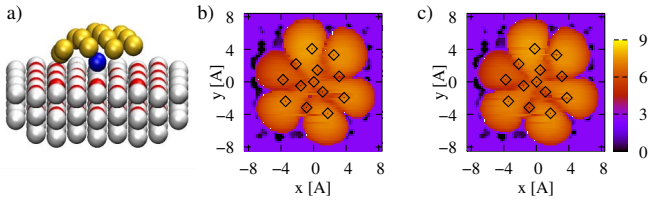

FIG. 5 (color online). (a) Au_{13}/MgO and simulated STM images for (b) HOMO, (c) LUMO. The atom positions are marked by diamonds in (b) and (c). The pinning Au atom is marked by dark (blue) shading.

imaged by STM on gold-pentacene complex adsorbed on NaCl(001)/Cu(001) [2]. Also in this case, the adsorbate has an odd number of electrons, and the unpaired electron is localized on the adsorbate by the insulating NaCl(001) film.

We have shown via DFT calculations that Au clusters with 8 to 20 atoms, adsorbed on F_s over a thin MgO(001) film or bulk MgO(001), appear as 1–2 nm particles in lateral dimensions, if imaged by STM. The main finding of this Letter is that the STM images have an internal structure, which reflects the symmetries of delocalized electron states near the Fermi energy and not the atomic structure [38]. These states lie in the band gap of MgO, and the level structure is sparse enough so that *single-electron states* could be imaged in suitable conditions. Theoretically, the energy ordering and the orbital symmetries of these states can be well understood by considering a harmonic oscillator model for a planar quantum dot. Given that the atomic structure of the adsorbed gold cluster is relatively flat, which may be enhanced by a supporting metal below the oxide film [8,25], electronic magic numbers should then correspond to 6, 12, 20, 30, 42, ... The F_s-defect does not affect the ''s-electron count'' of the delocalized ''metallic'' states of the cluster. We considered three qualitatively different cases: (i) a low-symmetry cluster (Au_8), where a single state can be imaged; (ii) a cluster with a high atomic symmetry but with an open electron shell (Au_{13}), where the unpaired electron is localized on the cluster, and the corresponding SOMO state in the MgO band gap; and (iii) a high-symmetry, electronically closed-shell cluster (Au_{20}), where individual symmetries of $|m| > 0$ states are averaged out by the STM imaging. We hope that our results will help to understand and interpret the STM data of metal clusters supported on ultrathin insulators, which are model systems regarding nanoparticle growth, low-dimensional electron physics, nanocatalysis, and molecular electronics.

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[1] J. Repp, G. Meyer, F. E. Olsson, and M. Persson, Science **305**, 493 (2004).
[2] J. Repp *et al.*, Science **312**, 1196 (2006).
[3] S. Schintke *et al.*, Phys. Rev. Lett. **87**, 276801 (2001).
[4] M. Sterrer *et al.*, Angew. Chem., Int. Ed. Engl. **45**, 2630 (2006).
[5] M. Sterrer *et al.*, Phys. Rev. Lett. **98**, 096107 (2007).
[6] A. Sanchez *et al.*, J. Phys. Chem. A **103**, 9573 (1999).
[7] B. Yoon *et al.*, Science **307**, 403 (2005).
[8] D. Ricci, A. Bongiorno, G. Pacchioni, and U. Landman, Phys. Rev. Lett. **97**, 036106 (2006).
[9] H. Häkkinen and M. Manninen, J. Chem. Phys. **105**, 10565 (1996).
[10] H. Häkkinen and M. Manninen, Phys. Rev. Lett. **76**, 1599 (1996).
[11] V. Musolino, A. Selloni, and R. Car, Phys. Rev. Lett. **83**, 3242 (1999).
[12] V. Musolino, A. D. DalCorso, and A. Selloni, Phys. Rev. Lett. **83**, 2761 (1999).
[13] M. Moseler, H. Häkkinen, and U. Landman, Phys. Rev. Lett. **89**, 176103 (2002).
[14] H. Häkkinen *et al.*, Angew. Chem., Int. Ed. Engl. **42**, 1297 (2003).
[15] G. Barcaro, A. Fortunelli, F. Nita, and R. Ferrando, Phys. Rev. Lett. **95**, 246103 (2005).
[16] G. Pacchioni and N. Rösch, J. Chem. Phys. **104**, 7329 (1996).
[17] M. Walter and H. Häkkinen, Phys. Rev. B **72**, 205440 (2005).
[18] R. N. Barnett and U. Landman, Phys. Rev. B **48**, 2081 (1993).
[19] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[20] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
[21] https://wiki.fysik.dtu.dk/dacapo.
[22] B. Hammer, L. B. Hansen, and J. K. Nørskov, Phys. Rev. B **59**, 7413 (1999).
[23] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[24] K. Honkala and H. Häkkinen, J. Phys. Chem. C **111**, 4319 (2007).
[25] P. Frondelius, H. Häkkinen, and K. Honkala, Phys. Rev. B **76**, 073406 (2007).
[26] W. A. Hofer, A. S. Foster, and A. L. Shluger, Rev. Mod. Phys. **75**, 1287 (2003).
[27] J. Tersoff and D. R. Hamann, Phys. Rev. Lett. **50**, 1998 (1983).
[28] The per-atom formation energy, $E_c(N)$, of an N-atom cluster at F_s on the support is calculated as $E_c(N) = N^{-1}[E(\mathrm{Au}_N/\mathrm{support}) - E(\mathrm{support}) - NE(\mathrm{Au})]$ where $E(\mathrm{Au})$ is the spin-polarized total energy of a gas-phase Au atom.
[29] We evaluate the LDOS by projecting Kohn-Sham states onto atom-centered s, p, d components of spherical harmonics inside a sphere, or evaluating the weights of Kohn-Sham states in Voronoi atomic volumes.
[30] J. Li, X. Li, H.-J. Zhai, and L.-S. Wang, Science **299**, 864 (2003).
[31] B. Yoon *et al.*, Chem. Phys. Chem. **8**, 157 (2007).
[32] X. Xing, B. Yoon, U. Landman, and J. H. Parks, Phys. Rev. B **74**, 165423 (2006).
[33] L. Molina and B. Hammer, J. Catal. **233**, 399 (2005).
[34] M. Walter and H. Häkkinen, Lecture Series on Computer and Computational Sciences **4**, 990 (2005).
[35] M. Walter and H. Häkkinen, Phys. Chem. Chem. Phys. **8**, 5407 (2006).
[36] S. M. Reimann and M. Manninen, Rev. Mod. Phys. **74**, 1283 (2002).
[37] The observed splitting between the occupied $2p$ and $2f$ states [Fig. 3(a)] is due to the deviation of the Kohn-Sham potential from the harmonic oscillator model.
[38] We note that the STM images shown in Fig. 1(a) of Ref. [4] seem to indicate similar nodal structures for some of the larger gold clusters.