PHYSICAL REVIEW B **67**, 085404 (2003)

Theoretical study of small two-dimensional gold clusters

Jin Zhao, Jinlong Yang,* and J. G. Hou†

Structure Research Laboratory and Laboratory of Bond Selective Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, China

(Received 16 March 2002; revised manuscript received 9 October 2002; published 7 February 2003)

The geometric and electronic properties of small two-dimensional (2D) Au_N ($N=2-20$) clusters are studied using the density-functional method. The lowest-energy geometries of a closed-packed nature are selected for 2D Au_2- Au_8 clusters. A clear odd-even oscillation is found for the stability and energy gaps of Au_N clusters with $N\leqslant 15$. The polarizabilities of the 2D clusters are calculated and found to be strongly anisotropic. In the normal direction of a 2D cluster, the polarizability is smaller than that of bulk Si, indicating a nonmetallic character. A fitting formula is proposed to estimate the polarizability of a 2D Au cluster with arbitrary size and shape in the normal direction. The behavior of a 2D Au cluster in a strong electric field is also discussed.

DOI: 10.1103/PhysRevB.67.085404 PACS number(s): 73.22.−f, 71.15.Mb, 61.46.+w

I. INTRODUCTION

Small clusters have been a subject of intense investigation in recent years. Gold clusters are of significant interest, due to their promising applications in developing new nanodevices. Experimental and theoretical studies on the structural, electronic, optical, magnetic, and other physical and chemical properties of the isolated and passivated gold clusters are at the forefront of cluster science.[1–11]

Most of the experimental and theoretical studies have been focused on three-dimensional (3D) Au clusters.[6–8,10–15] However, great interest in two-dimensional (2D) Au clusters has been developed recently.[2,16–18] The 2D Au clusters have been synthesized on the top of well-characterized insulating self-assembled monolayers (SAM's) grown on the metallic substrates.[19] By the means of a scanning tunneling microscope (STM), these 2D Au clusters have been systematically investigated.[17,18]

The capacitance of a nanojunction formed by a STM tip and a 2D Au cluster was measured through the single-electron tunneling spectroscopy of a double-barrier tunnel junction.[17] In order to have a quantitative comparison between experiment and theory, there is an urgent need to know whether a 2D Au cluster exhibits metallic behavior in the normal direction so that the cluster can be set as the central metallic electrode of a double-barrier tunnel junction. The behavior of a 2D Au cluster under an external field is also interesting because in the measurement of the STM, an external electric field is imposed on the 2D Au cluster, which may cause the deformation of structure and a nonlinear dielectric response.

In this paper, we report a theoretical study of small 2D Au_N ($N=2-20$) clusters. Our calculations are carried out by using the local density approximation (LDA) based on the density-functional theory (DFT). At the LDA level, we choose the Vosko-Wilk-Nusair (VWN) local correlation functional together with the DNP basis functions. The VWN local correlation functional is the Vosko-Wilk-Nusair[20] parametrization of Ceperley and Alder's electron gas Monte Carlo data,[21] which can be used successfully to predict the cluster structure. The DNP basis functions are the double-numerical atomic orbitals augmented by polarization functions, i.e., functions with angular momentum one higher than that of the highest occupied orbital in the free atom. For comparison, some calculations are repeated by the generalized gradient approximation (GGA) using the Becke-Lee-Yang-Parr[22,23] (BLYP) functional. The electronic structure is obtained by solving the Kohn-Sham[24,25] equations self-consistently. All-electron calculations with scalar relativistic corrections are used. Medium grid mesh points are employed for the matrix integrations. Self-consistent field procedures are done with a convergence criterion of 10^{-6} a.u. on the energy and electron density. Geometry optimizations are performed using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm,[26] with a convergence criterion of 10^{-3} a.u. on the gradient, 10^{-3} a.u. on the displacement, and 10^{-5} a.u. on the energy. All the calculations are carried out allowing for spin polarization and carried out using the molecular simulation package DMOL3.[27]

In our study, the substrate effect on 2D Au clusters can be neglected. The substrate (a monolayer of thiol) is self-assembled on a freshly Au(111) surface, and the S atoms bond with the Au(111) surface, leaving saturated C-H bonds on the top ends of the SAM. So the interaction between a 2D Au cluster and the substrate is van der Waals type, much smaller than the interaction among Au atoms of the cluster. To support the above argument, we calculated the adsorption energy of a Au_2 cluster on the SAM substrate [the $(CH_3CH_2SH)_7$ cluster model is used to mimic the substrate] using the LDA and obtained a value of 0.025 eV/atom, which is much less than the Au-Au binding energy of 1.55 eV/atom. To see the substrate effect on the structure and relative stability of 2D Au clusters, we studied hexagonal and zigzag Au_7 clusters with and without the SAM substrate. We found that the substrate has little effect on the optimized structures, and the changes of bond lengths are less than 0.01 Å. With the substrate, the binding energy difference between the 2D hexagonal and zigzag Au_7 clusters is 0.63 eV, almost the same as the value (0.62 eV) obtained without the substrate. Moreover, the calculated frequencies of 2D Au_7 clusters with and without the SAM substrate are all positive, indicating that the 2D Au_7 clusters are indeed local minima.

0163-1829/2003/67(8)/085404(6)/$20.00

In the following, we discuss the nominal low-energy geometries (NLEG's) of 2D Au_N clusters in Sec. II. In Sec. III we report their electronic structures and densities of states (DOS). We present the calculated polarizabilities of the 2D Au clusters and propose an empirical formula to estimate the polarizability of a 2D Au cluster with arbitrary size and shape in the normal direction in Sec. IV. In Sec. V, the behaviors of 2D Au clusters under external electric fields are discussed. Finally a summary is given in Sec. VI.

II. NOMINAL LOW-ENERGY GEOMETRIES

The NLEG's of 2D Au_2-Au_8 clusters are determined by maximizing the calculated binding energies for the possible geometries. Since the number of possible geometries increases quite rapidly with cluster size, it becomes impossible to determine the NLEG's of the larger clusters with this method. We only assume several probable geometries for each of the larger clusters and regard the isomer with the largest binding energy among them as the NLEG. The NLEG's we obtained for the clusters are shown in Table I. From this table, one can see that the cluster favors more close-packed geometries.

In Fig. 1, we display the calculated binding energy (E_B) of the Au clusters as well as the second differential of the binding energy: $\Delta^2 E_B(N) = 2E_B(N) - E_B(N+1) - E_B(N-1)$. $\Delta^2 E_B(N)$ exhibits strong odd-even oscillations when the number of atoms in a cluster is smaller than 15, indicating that even-numbered Au_N clusters are relatively more stable than the neighboring odd-numbered ones. The oscillations become irregular and insignificant when N is larger than 15. The increase of $E_B(N)$ with N indicates the better stability as the structure grows in size. For the large size, this increase should lead to the cohesive energy of the 2D bulk. The E_B value for 2D close-packed Au_{55} is calculated to be 3.55 eV/atom, close to the value of 3.48 eV/atom found for Au_{20}. Since the calculations using the LDA usually overestimate the binding energy, we have checked a few clusters by the GGA. The difference of binding energy between the LDA and GGA is almost a constant of 0.4 eV/atom.

III. ELECTRONIC STRUCTURE AND DENSITY OF STATES

A particularly interesting property for clusters is the energy gap (E_g) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). In Fig. 1 we plot E_g for Au_2-Au_{20} clusters with the NLEG's. Odd-even oscillations of E_g are observed. In the range of $5 \leqslant N \leqslant 15$, the E_g of an even-numbered cluster is larger than that of its odd-numbered neighbors. In the ranges of $N < 5$ and $N > 15$, a reversed relationship exists. The E_g is particularly large for Au_3, Au_6, Au_{10}, and Au_{19} clusters (3.72 eV, 1.74 eV, 1.18 eV, and 1.18 eV, respectively). This odd-even oscillation is considered to be caused by the spin-pairing effect. It is believed the E_g of odd-numbered clusters is caused by the spin polarization. For even-numbered clusters, it may be due to the crystal field splitting. The similar oscillation has been found for the 3D Au clusters.[11,15]

The DOS provides a convenient overall view of the cluster electronic structure. Figure 2 displays the total and partial DOS of the Au_4, Au_{10}, Au_{16}, and Au_{20} clusters. The DOS are obtained by a Lorentzian extension of the discrete energy levels and a summation over them. The broadening width parameter is chosen to be 0.10 eV. From the total DOS, we find that the sparse and sharp discrete spectrum of Au_4 evolves towards a continuous "bandlike" structure of Au_{20}, with Au_{10} and Au_{16} lying in some sense in between. From the partial DOS, we can see that the contribution of $6s$ and $6p$ orbitals is negligible below the Fermi energy (E_F) and the orbital hybridization is strong above the E_F.

IV. POLARIZABILITIES

In order to determine whether a 2D Au cluster exhibits metallic behavior, the polarizabilities in x, y, and z directions of the 2D Au_N ($N = 2$–20) clusters are studied. The elements of the polarizability tensor α_{ij} ($i,j = 1$, 2, and 3) are defined as

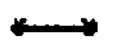
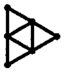
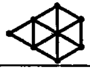
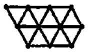
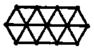
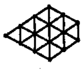
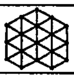
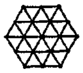
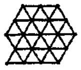
$$\alpha_{ij} = \frac{\partial \mu_i}{\partial E_j}, \tag{1}$$

where μ_i and E_j are the Cartesian components of the dipole moment and the applied electric field, respectively. In our calculation, this first-order change is estimated by the finite difference. The dipole moment is first calculated at zero external field. An external field of strength 0.001 a.u. is then imposed in the positive and negative x, y, z directions, respectively, and the change in the dipole moment is calculated and averaged to give α_{ij}. (There are a few cases in which the $|\Delta\mu|$ for the positive and negative fields differs by more than 0.01 D. In those cases we decreased the external field strength to 0.0005 a.u.) For the 2D clusters, the elements α_{i3} and α_{3i} ($i = 1$ and 2) are equal to zero. So the polarizability in the z direction (α_{zz}) can be calculated directly by $\partial\mu_z/\partial E_z$. When the 2D cluster has an axis of symmetry in the x or y direction, all the elements in the tensor except the diagonal ones are equal to zero. In these cases, the polarizability in the x and y directions (α_{xx} and α_{yy}) can be calculated directly by $\partial\mu_i/\partial E_i$ ($i = x$ and y). All the clusters except Au_{11} and Au_{20} have the symmetry axis in the x or y direction in our study. For Au_{11} and Au_{20} clusters, we have diagonalized the full polarizability tensor to obtain polarizabilities in the x and y directions.

Our calculated results for the NLEG's are presented in Table I. All the results are calculated with the LDA. We have checked the LDA calculated α_{zz} with the GGA for Au_2-Au_{10} clusters and found that the changes are very small (see Table I).

It is found that the polarizabilities of the 2D clusters in the x and y directions (the lateral directions) are much bigger than the one in the z direction (the normal direction) and that in the z direction the polarizability falls down gradually with the increase of the number of atoms in the cluster. We expect that as the cluster size goes to infinity, the polarizabilities of the 2D clusters in the lateral directions should also become

TABLE I. The geometries, binding energies (E_B), HOMO-LUMO gaps (E_g), and polarizabilities (α_{xx}, α_{yy}, and α_{zz}) for the 2D Au clusters with the NLEG's. The values in the parentheses are the GGA results.

N	Structure	E_B(eV/atom)	E_g(eV)	α_{xx}(Å^3/atom)	α_{yy}(Å^3/atom)	α_{zz}(Å^3/atom)
2		1.55 (1.11)	1.80	7.13	2.97	2.97 (3.01)
3		1.94 (1.54)	3.72	5.64	5.63	2.68 (2.71)
4		2.31 (1.93)	1.00	7.63	4.39	2.48 (2.52)
5		2.55 (2.12)	1.37	7.79	4.99	2.37 (2.40)
6		2.77 (2.35)	1.74	6.46	6.46	2.26 (2.28)
7		2.85 (2.43)	0.87	6.52	6.52	2.15 (2.19)
8		2.94 (2.53)	0.74	8.12	5.81	2.12 (2.16)
9		3.00 (2.57)	0.46	9.63	5.35	2.08 (2.11)
10		3.11 (2.73)	1.18	8.61	6.01	2.02 (2.06)
11		3.14	0.65	9.70	5.96	2.00
12		3.24	1.10	7.56	7.59	1.95
13		3.23	0.69	11.20	5.73	1.94
14		3.32	1.00	9.06	6.80	1.90
15		3.33	0.76	10.46	6.42	1.89
16		3.35	0.68	11.88	6.08	1.89
17		3.38	0.99	10.46	6.42	1.85
18		3.43	0.45	8.11	9.02	1.83
19		3.47	1.18	8.57	8.57	1.80
20		3.48	0.32	9.02	8.57	1.80

infinite, displaying metallic behavior in the cluster plane. To explain the decrease of the polarizability in the normal direction, we notice that atoms in a 2D cluster can be roughly divided into edge and core atoms. The edge atoms have bigger polarizabilities than the core atoms since the edge atoms have fewer nearest-neighbor (NN) atoms than the core atoms. When the cluster is small, the polarizability α_{zz} of a cluster reflects contributions from both the core and edge atoms, while it is dominated by the contribution from the core atoms when the cluster becomes large.

If we assume in a 2D cluster that the polarizability α_{zz} can be divided into contributions of different kinds of atoms

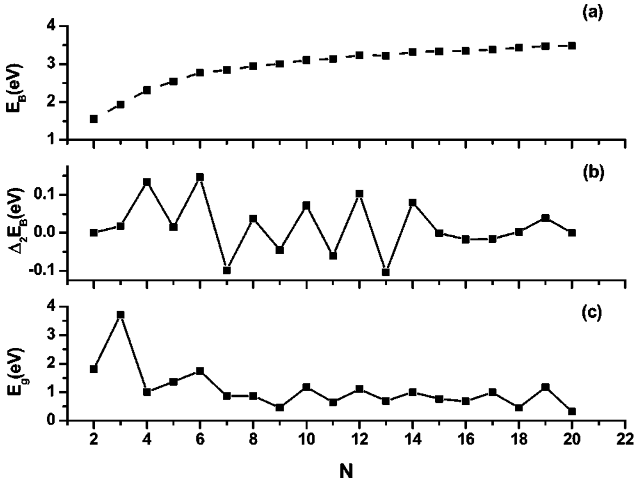


FIG. 1. Size dependence of (a) the binding energy per atom, (b) the second differential ($\Delta^2 E_B$) of E_B, and (c) the HOMO-LUMO gap (E_g) of 2D Au clusters.

which have different NN atoms, we can write down a formula to estimate it:

$$\alpha_{zz} = (\alpha_{z1}\times n_1 + \alpha_{z2}\times n_2 + \alpha_{z3}\times n_3 + \alpha_{z4}\times n_4 + \alpha_{z5}\times n_5)/n, \tag{2}$$

with

$$n = n_1 + n_2 + n_3 + n_4 + n_5, \tag{3}$$

where α_{z1}, α_{z2}, α_{z3}, α_{z4}, and α_{z5} are the contributions from the atoms with 2, 3, 4, 5, and 6 NN atoms, respectively.

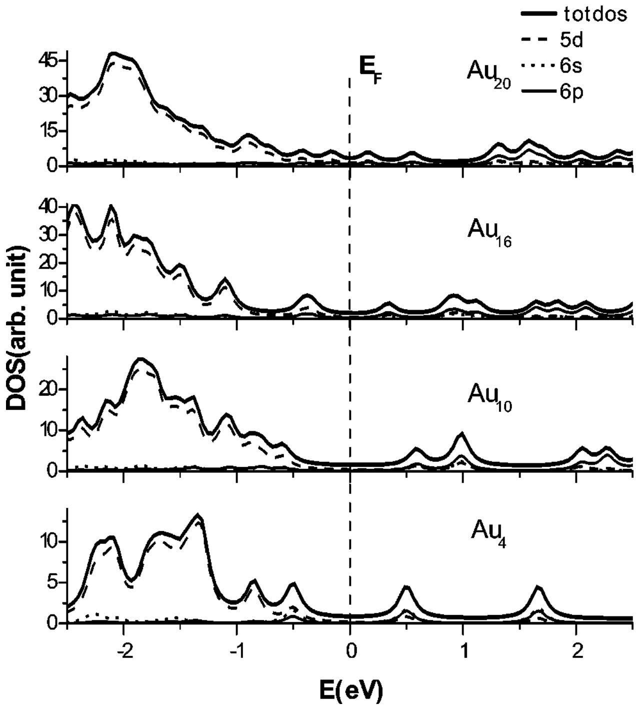


FIG. 2. The total and partial DOS of Au_4, Au_{10}, Au_{16}, and Au_{20} clusters. The thicker solid line is the total DOS, and the thinner solid line is the partial DOS of the $6p$ orbital. The dashed line is the partial DOS of the $5d$ orbital, and the dotted line is the partial DOS of the $6s$ orbital.

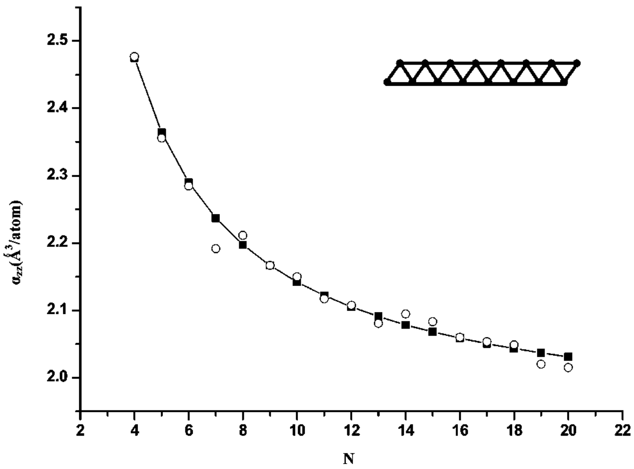


FIG. 3. The polarizabilities α_{zz} of 2D Au clusters with the zigzag structure. The open circles present the calculated polarizabilities while the solid circles present the estimated ones from the formula.

We have performed a least-squares fitting and get the estimated α_{z1}, α_{z2}, α_{z3}, α_{z4}, and α_{z5} as $\alpha_{z1} = 2.66$ Å^3/atom, $\alpha_{z2} = 2.29$ Å^3/atom, $\alpha_{z3} = 1.90$ Å^3/atom, $\alpha_{z4} = 1.43$ Å^3/atom, $\alpha_{z5} = 1.31$ Å^3/atom. The largest relative deviation for the fitting is about 1%. It is obvious that the more NN's the atom has, the smaller the contribution to the polarizability is. This can be understood by noting that with more NN atoms, the interaction among the atom and its NN atoms is stronger, and polarization by the external electric field becomes more difficult.

The formula for the polarizability α_{zz} should be independent of the form of the 2D structures. In order to check the transferability of the fitting parameters in the formula, we have calculated the α_{zz} of Au_4-Au_{20} clusters with zigzag structure by the LDA and the formula, shown in Fig. 3. From this figure, one can see that the estimated α_{zz} gives a good approximation to the LDA-calculated one, proving the transferability of the fitting parameters. Now, we can use the formula to estimate the α_{zz} of the infinite chain with zigzag structure to be 1.90 Å^3/atom (i.e., α_{z3}) and the α_{zz} of the infinite single-atom chain to be 2.66 Å^3/atom (i.e., α_{z1}).

In Fig. 4, we have plotted the estimated polarizability α_{zz} of the 2D round cluster as a function of the radius. From this we can estimate the polarizability α_{zz} of a 2D Au island easily from the size. When the cluster becomes large enough, the polarizability of the cluster will reach the bulk value of the 2D Au cluster, which is estimated as $\alpha_{z5} = 1.31$ Å^3/atom, lower than that of Si bulk.[28] We conclude that in the normal direction of a 2D Au cluster, it exhibits nonmetallic properties.

V. BEHAVIOURS OF 2D Au CLUSTERS IN ELECTRONIC FIELDS

In the measurement of the capacitance of a nanojunction formed by a STM tip and a 2D Au cluster, the capacitance is observed to first increase and then decrease at short separa-

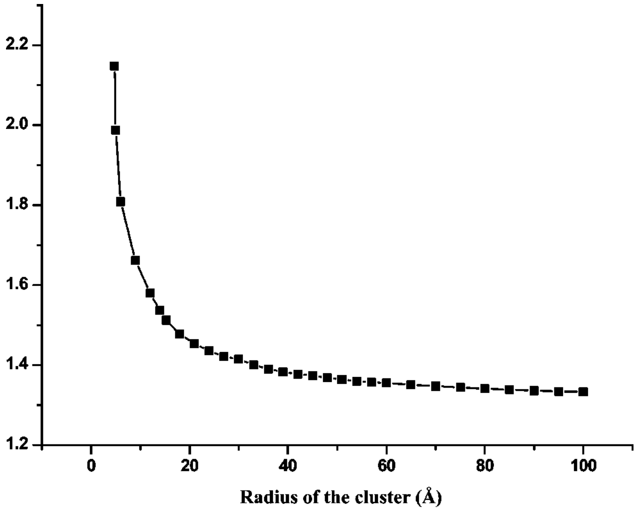


FIG. 4. Radius dependence of the polarizability α_{zz} of 2D round Au clusters.

tion by decreasing the STM tip-cluster separation.[17] One possibility is that the decrease in capacitance at very small tip-cluster separation is due to a nonlinear dielectric response. Using a heuristic simple parallel-plate capacitor model with a finite dielectric constant for the Au cluster in the field direction, we can write down an equivalent capacitance as $C=\varepsilon_0\varepsilon_{Au}A/(d_{Au}+\varepsilon_{Au}d)$, where ε_0 is the permittivity of free space, and ε_{Au}, A, and d_{Au} are the dielectric constant, area, and thickness of the Au cluster, respectively. Since ε_{Au} may not be a constant in the strong electric field, the decrease of the capacitance could be anticipated.

In the measurement of the STM, the bias voltage is about 0.01–2 V. The distance between the two electrodes is about 5–15 Å. We take the Au_{16} cluster as an example to investigate the strong external field effect on the polarizaility α_{zz} of 2D Au clusters. The structure of the Au_{16} cluster is optimized, and the average bond length expands from 2.78 Å to 2.82 Å as the electric field strength increases from 0.001 a.u. to 0.01 a.u.. The DOS almost has no change.

The dipole moment in the normal direction of the cluster as a function of the intensity of external electric field is shown in Fig. 5. The slope of the curve slightly decreases with the increase of electric-field intensity, implying that the polarizability α_{zz} decreases in the strong field. However, the decrease is very slight which verifies that the field effect of the capacitance of the nanojunction in the STM measurement may be not substantial.

Because of the electron tunneling in the STM experiment, the cluster may be charged. We investigate the relationship of dipole moments of $Au_{16}{}^{-}$, $Au_{16}{}^{2-}$, $Au_{16}{}^{+}$, and $Au_{16}{}^{2+}$ with the external electric fields, as shown in Fig. 5. From this figure, one can see that the polarizabilities of charged clusters also decrease with the increase of the intensity of the electric field and that the more electrons the cluster gains, the bigger the dipole moment is.

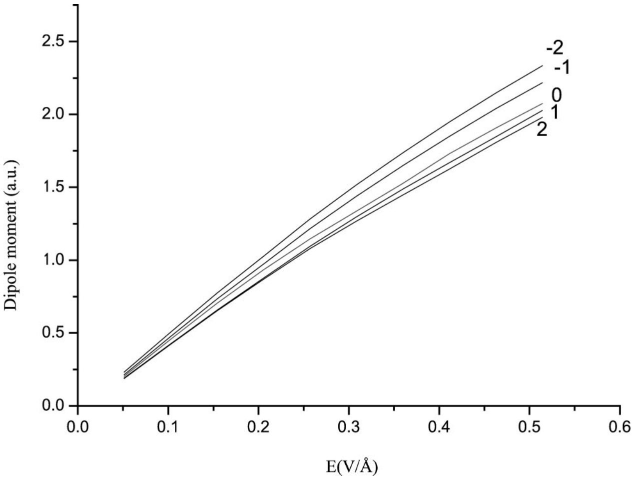


FIG. 5. The electric-field dependence of the dipole moments in the field direction of 2D Au_{16}, $Au_{16}{}^{-}$, $Au_{16}{}^{+}$, $Au_{16}{}^{2-}$, and $Au_{16}{}^{2+}$ clusters.

VI. SUMMARY

In this paper, small 2D Au clusters are theoretically studied for their NLEG's, electronic structures, and the dielectric properties using the DFT method. A series of close-packed structures is found as the NLEG's for the 2D Au clusters. The changes of the electronic structures of these clusters have been characterized by means of DOS plots and HOMO-LUMO gaps. The DOS evolves from a discrete behavior for the small clusters as Au_4 to a ''bandlike'' appearance in Au_{20}. The HOMO-LUMO gaps are found to show odd-even oscillations. The polarizabilities of the Au clusters in the x, y, and z directions with different structures have been investigated. It is found that in the lateral direction, the cluster displays metallic dielectric properties. In the normal direction, the polarizability has the same magnitude as that of a semiconductor, displaying nonmetallic properties. We have deduced one fitting formula from which the polarizability of the 2D Au cluster can be estimated without calculation. Under an external field of 0.001–0.01 a.u., the deformation of the cluster is very small. We can conclude that in the measurement of the STM, the structures of clusters will not be decomposed by the electric field. The polarizabilities of 2D Au clusters decrease slightly with the increase of the electric-field intensity.

ACKNOWLEDGMENTS

This work was partially supported by the National Project for the Development of Key Fundamental Sciences in China (Grant Nos. G1999075305 and G001CB3095), by the National Natural Science Foundation of China, by the Foundation of Ministry of Education of China, and by the Foundation of the Chinese Academy of Science.

[*] Electronic address: jlyang@ustc.edu.cn
[†] Electronic address: jghou@ustc.edu.cn

[1] R. L. Whetten, J. T. Khoury, M. M. Alvarez, S. Murthy, I. Vezmar, Z. L. Wang, P. W. Stephens, C. L. Cleveland, W. D. Luedtke, and U. Landman, Adv. Mater. **5**, 8 (1996).

[2] R. P. Andres, T. Bein, M. Dorogi, S. Feng, J. I. Henderson, C. P. Kubiak, W. Mahoney, R. G. Osifchin, and R. Reifenberger, Science **272**, 1323 (1996).

[3] C. A. Mirkin, R. L. Letsinger, R. C. Mucic, and J. J. Storhoff, Nature (London) **382**, 607 (1996).

[4] A. P. Alivisatos, K. P. Johnsson, X. G. Peng, T. E. Wilson, C. J. Loweth, M. P. Bruchez, and P. G. Schultz, Nature (London) **382**, 609 (1996).

[5] R. P. Andres, J. D. Bielefeld, J. I. Henderson, D. B. Janes, V. R. Kolagunta, C. P. Kubiak, W. J. Mahoney, and R. G. Osifchin, Science **273**, 1690 (1996).

[6] I. L. Grazón, K. Michaelian, M. R. Beltrán, A. Posada-Amarillas, P. Ordejón, E. Artacho, D. Sánchez-Portal, and J. M. Soler, Phys. Rev. Lett. **81**, 1600 (1998).

[7] I. L. Grazón, C. Rovira, K. Michaelian, M. R. Beltrán, P. Ordejón, J. Junquera, D. Sánchez-Portal, E. Artacho, and J. M. Soler, Phys. Rev. Lett. **85**, 5250 (2000).

[8] K. Michaelian, N. Rendán, and I. L. Garzón, Phys. Rev. B **60**, 2000 (1999).

[9] T. G. Schaaff and R. L. Whetten, J. Phys. Chem. B **104**, 2630 (2000).

[10] Hannu Häkkinen, Michael Moseler, and U. Landman, Phys. Rev. Lett. **89**, 033401 (2002).

[11] Jinlan Wang, Guanghou Wang, and Jijunzhao , Phys. Rev. B **66**, 035418 (2002).

[12] Oliver D. Häberien, Sai-cheong Chung, Mauro Stener, and Noker Rösch, J. Phys. Chem. **106**, 5189 (1997).

[13] C. L. Cleveland, Uzi Landman, Thomas G. Schaaff, Marat N. Shafigullin, Peter W. Stephens, and R. L. Whetten, Phys. Rev. Lett. **79**, 1873 (1997).

[14] C. L. Cleveland, U. Landman, M. N. Shafigullin, P. W. Stephens, and R. L. Whetten, Z. Phys. D: At., Mol. Clusters **40**, 503 (1997).

[15] Hannu Häkkinen and U. Landman, Phys. Rev. B **62**, R2287 (2000).

[16] C. J. Kiely, J. Fink, M. Brust, D. Bethell, and D. J. Schiffrin, Nature (London) **396**, 444 (1998).

[17] J. G. Hou, Bing Wang, Jinlong Yang, X. R. Wang, H. Q. Wang, Qingshi Zhu, and Xudong Xiao, Phys. Rev. Lett. **86**, 5321 (2001).

[18] Bing Wang, Xudong Xiao, Xianxiang Huang, Ping Sheng, and J. G. Hou, Appl. Phys. Lett. **77**, 1179 (2000).

[19] Bing Wang, Xudong Xiao, and Ping Sheng, J. Vac. Sci. Technol. B **18**, 2351 (2000).

[20] S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Chem. **58**, 1200 (1980).

[21] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[22] A. D. Becke, J. Chem. Phys. **88**, 1053 (1988).

[23] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).

[24] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[25] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[26] R. Fletcher, *Practical Methods of Optimization* (Wiley, New York, 1980), Vol. 1.

[27] DMOL3 is a density-functional-theory-based package with atomic basis distributed by Accelrys [B. Delley, J. Chem. Phys. **92**, 508 (1990)].

[28] Ke Deng, Jinlong Yang, and C. T. Chan, Phys. Rev. A **61**, 025201 (2000).