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Electronic Structure of a Gold Nanotube

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Abstract—The electronic structure of a gold nanotube has been studied by quantum-chemical methods. The energy dependences of total and partial densities of states of a nanotube with 16 atoms in a translational unit cell have been calculated by the linearized augmented-cylindrical-wave method. It has been demonstrated that the nanotube has a metal-like band structure. The *s*(Au) states are located completely in the valence band and are not involved in electron transport. The Fermi level is located at the peak of the total and partial *d*(Au) densities of states, which should contribute to the high electron tunneling conductance of the system. The valence band width is 11 eV.

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Gold nanoparticles have chemical properties that noticeably differ from the characteristics of the bulk material and depend on their size and geometry [1]. Gold nanoparticles are better catalysts than the bulk material, for example, in reactions of selective hydrocarbon oxidation [2], can be used in design of complex functional clusters [3], and exhibit quantum properties related to their small size [4]. The Au–Au chemical bonds in nanoparticles essentially differ from the bonds in the bulk phase [5]. In particular, it has been shown by spectroscopy that, on average, the shortest distances between the atoms in gold nanoparticles are 0.042 Å longer than in the metal [1, 6].

Until recently, the known gold nanoparticles were clusters containing from a few atoms to several tens of atoms and ordered nanocrystalline structures in the form of decahedra containing up to 250 gold atoms [1]. Later, linear one atom thick nanowires [7], nanotubes with different wall thickness [8–10], nanorods [11], and bundles of nanorods up to 250 nm long [5, 12] have been fabricated. Interest is such one-dimensional gold nanomaterials is caused, in particular, by the fact that they are very promising candidates for use as contacts between the elements of molecular electronics.

The electronic structure of monoatomic chains, clusters, and fragments of nanocrystalline structures of gold atoms has been comprehensively studied by quantum-chemical methods and compared with electronic spectroscopy data [13–31]. Recently, the band structure of gold nanorods has been calculated [11], whereas nanotubes have not been theoretically studied thus far.

The aim of this study is to fill this gap and calculate the band structure of the simplest gold nanotube by the linearized augmented-cylindrical-wave method (LACW), which has been previously used for studying pure, doped, and intercalated carbon nanotubes [32–37].

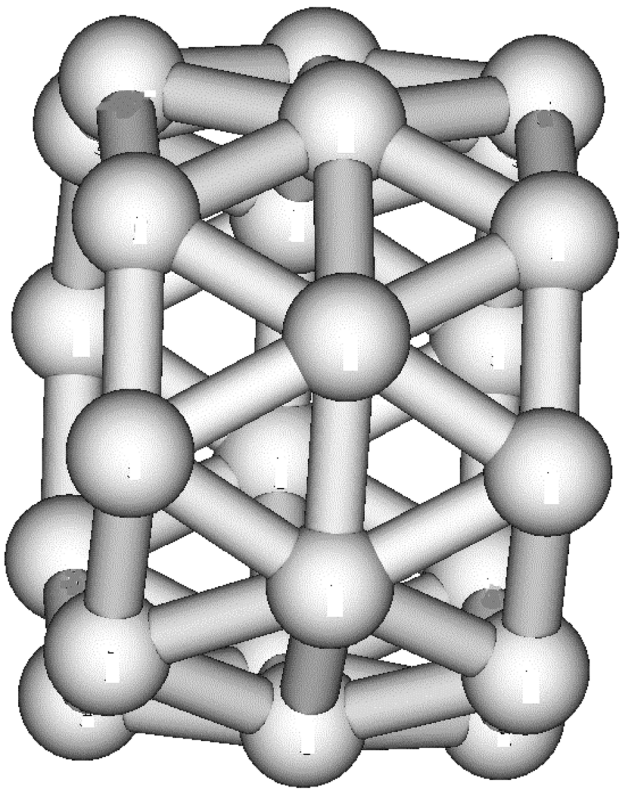

Fig. 1. Fragment of the Au_{16} nanotube.

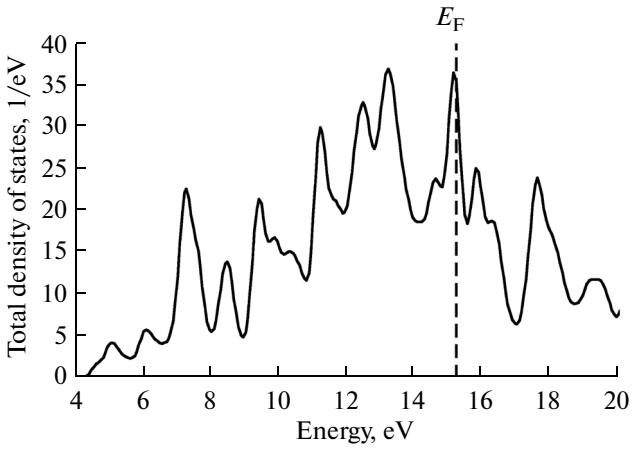

Fig. 2. Total density of states of electrons in the Au_{16} nanotube normalized to the total number of valence electrons in the unit cell.

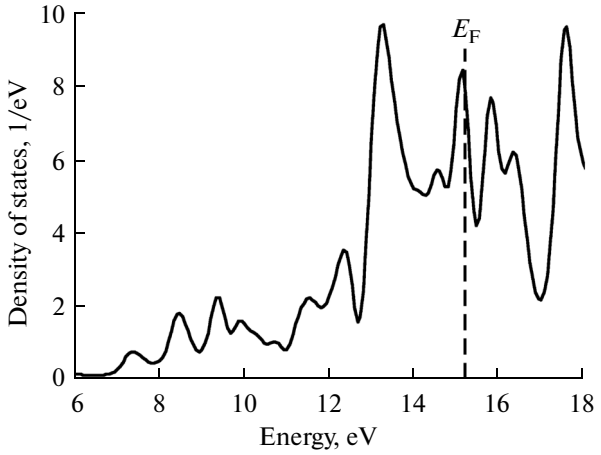

Fig. 3. Partial densities of *d*(Au) states in the Au_{16} nanotube.

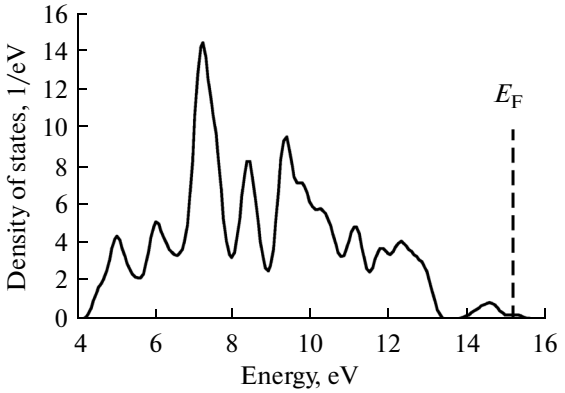

Fig. 4. Partial densities of *s*(Au) states in the Au_{16} nanotube.

COMPUTATIONAL METHOD

In the LACW method, we consider a one-electron model, and the problem of calculation of electronic levels is reduced to the solution of the one-electron Schrödinger equation. For constructing the electron potential, the local density functional approximation for exchange interaction is used. Each atom of the system is surrounded by a sphere where the potential is taken to be spherically symmetric, and in the interspherical space, the potential is assumed to be constant between two impenetrable cylindrical barriers—the outer barrier of radius a and the inner barrier of radius b—separating the nanotube region from the outer and inner vacuum regions. The electronic spectrum of the system is determined by the free electron motion in the interatomic space of the nanotube, electron scattering on atom centers, and reflection of electrons from the barriers [4–6].

The translational unit cell of the nanotube consists of two parallel planes each of which contains eight gold atoms so that the entire tube is generated by translation of two layers, i.e., 16 gold atoms. Each next layer is rotated by an angle of $\pi/16$ around the nanotube axis with respect to the previous layer. Figure 1 shows three layers, the first layer being translationally equivalent to the third layer. Information on the structure of the Au_{16} nanotube was obtained by molecular dynamics methods and was kindly supplied by Prof. E.S. Kryachko, Bogolyubov Institute of Theoretical Physics, National Academy of Sciences of Ukraine. This system is represented by a stable nanotube with a minimal number of atoms in the unit cell and a minimal diameter. The average Au–Au bond length is 2.53 Å, and the nanotube radius R_{NT} is 3.84 Å. The radii of the potential barriers were determined as follows: $a = R_{NT} + \delta$ and $b = R_{NT} - \delta$, where δ is the arithmetic mean of the covalent and van der Waals radii of the gold atom.

COMPUTATION RESULTS

Figures 2–4 show the total and partial *d*(Au) and *s*(Au) densities of states of electrons in the nanotube. The figures demonstrate that nanotube have a metallike electronic structure; the band gap is absent. The Fermi level is located at the peak of the total density of states, which should contribute to the high electron tunneling conductance of the system. The valence band width is 11 eV. The *s*(Au) states are located completely in the valence band and should not be involved in electron transport. The top of the valence band and the conduction band are made of the *d*(Au) states and, thus, electron transport in the nanotube should involve only the *d*(Au) electrons. Near the Fermi level, the curves of total and partial *d*(Au) density of states are qualitatively coincident.

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REFERENCES

1. V. G. Yarzhemsky and C. Battocchio, Russ. J. Inorg. Chem. **56**, 1 (2011).
2. M. Haruta, Nature **437**, 1098 (2005).
3. M. C. Daniel and D. Astruc, Chem. Rev. **104**, 293 (2004).
4. C. Burda, X. B. Chen, R. Narayanan, et al., Chem. Rev. **105**, 5562 (2005).
5. G. J. Hutchings and A. S. K. Hashmi, Angew. Chem., Int. Ed. Engl. **45**, 7896 (2006).
6. W. Szczerba, M. Radtke, U. Reinholz, et al., Radiat. Phys. Chem. (2011). doi:10.1016/j.radphyschem.2011.02.003.
7. A. I. Yanson, R. G. Bollinger, H. E. Brom, et al., Nature **395**, 783 (1998).
8. Y. Kondo and K. Takayanagi, Science **289**, 606 (2000).
9. C. R. Bridges, P. M. DiCarmine, A. Fokina, et al., J. Mater. Chem. A **1**, 1127 (2013).
10. Y. Bi, Nanotecnology **19**, 275306 (2008).
11. A. Roy, T. Pandey, N. Ravishankar, et al., AIP Adv. **3**, 032131 (2013).
12. S. Bulusu and X. C. Zeng, J. Chem. Phys. **125**, 154303 (2006).
13. H. Hakkinen, M. Moseler, and U. Landman, Phys. Rev. Lett. **89**, 033401 (2002).
14. H. Hakkinen, M. Moseler, and U. Landman, Phys. Rev. B **62**, R2287 (2002).
15. S. Gilb, K. Jacobsen, D. Schooss, et al., J. Chem. Phys. **121**, 4619 (2004).
16. S. Lecoultre, A. Rydlo, C. Felix, et al., J. Chem. Phys. **134**, 074302 (2011).
17. A. Sekiyama, J. Yamaguchi, M. Higashiya, et al., New J. Phys. **12**, 043045 (2010).
18. C. Cleveland and U. Landman, J. Chem. Phys. **94**, 7376 (1991).
19. L. D. Marks, Philos. Mag. **49**, 81 (1984).
20. P. D. Jadzinsky, G. Calero, C. J. Ackerson, et al., Science **318**, 430 (2007).
21. F. Vitale, R. Vitaliano, C. Battocchio, et al., Nanoscale Res. Lett. **3**, 461 (2008).
22. J. Li, X. Li, H. J. Zhai, et al., Science **299**, 864 (2003).
23. V. G. Yarzhemsky, Yu. V. Norov, S. V. Murashov, et al., Inorg. Mater. **46**, 924 (2010).
24. J. Oviedo and R. E. Palmer, J. Chem. Phys. **117**, 9548 (2002).
25. P. Pyykko and N. Runeberg, Angew. Chem., Int. Ed. Engl. **41**, 2174 (2002).
26. X. Li, B. Kiran, J. Li, et al., Angew. Chem., Int. Ed. **41**, 4786 (2002).
27. M. P. Johansson, D. Sudholm, and J. Vaara, Angew. Chem., Int. Ed. Engl. **43**, 2678 (2004).
28. A. Karttunen, M. Linnolahti, T. A. Pakkanen, et al., Chem. Commun., 465 (2008).
29. V. G. Yarzhemsky, G. Polzonetti, M. V. Russo, et al., Sci. Technol. Ind. **1**, 66 (2011).
30. F. Tielens and E. Santos, J. Phys. Chem. C **114**, 9452 (2010).
31. A. H. Pakiari and Z. Jamshidi, J. Phys. Chem. A **114**, 9212 (2010).
32. E. P. D'yachkov, L. O. Khoroshavin and I. A. Bochkov, et al., Russ. J. Inorg. Chem. **59**, 683 (2014).
33. I. A. Bochkov, E. P. D'yachkov, and P. N. D'yachkov, Russ. J. Inorg. Chem. **59**, 1454 (2014).
34. P. D'yachkov and D. Kutlubaev, Mater. Sci. Eng. **38**, 012003 (2012).
35. P. N. D'yachkov, D. Z. Kutlubaev, and D. V. Makaev, Phys. Rev. **82**, 035426.
36. P. N. D'yachkov and D. V. Makaev, Phys. Rev. B **76**, 195411 (2007).
37. P. N. D'yachkov and V. A. Zaluev, J. Phys. Chem. C **118**, 2799 (2014).

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