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Electronic states and stability of selenium clusters

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Electronic structures and stability of Se_n ($n=3,4,5,6,7,8$) clusters have been studied by using the discrete variational method in the framework of the local-density approximation. Binding energy, ionization potential, affinity energy, and other electronic properties using the structure models of Hohl *et al.* [Chem. Phys. Lett. **139**, 540 (1987)] are presented and compared with the available experiments. In addition, a rectangular lattice arrangement of selenium clusters has been fabricated on highly oriented pyrolytic graphite, and examined by the scanning tunnel microscope image which was found to consist of a $0.72 \times 0.85 \text{ nm}^2$ lattice spacing with individual molecules of $0.53 \pm 0.05 \text{ nm}$ in diameter. Theoretical calculations reproduce well the experimental observations.

The use of selenium in the xerographic process stimulated experimental as well as theoretical research on the structural, optical, and electrophotographic properties of the solid phase of selenium.^{1,2} Selenium clusters occur in the vapor phase, in crystalline modifications, and as major constituents of the liquids.^{3,4} In the vapor state, the main constituents of selenium gas at about 800 K are Se_5 , Se_6 , and Se_8 rings, with only a minute amount of smaller molecules. Therefore, it is very important to study the properties of selenium clusters.

Mesoscopic systems composed of metallic or nonmetallic clusters, as well as artificially created low-dimensional materials, have attracted much attention due to their properties and application perspectives.⁵ It is expected that the ring-type selenium clusters may create two-dimensional ordered arrays at the early stage of deposition onto some substrates,⁶ though the lattice-matching condition has been a strong limitation in creating the artificially stacked layered structures. However, this difficulty can be overcome if the interface bonding between the constituent materials has a van der Waals nature.

Experimental work on the structure and electronic properties of selenium clusters has been reported.^{6,7} The ionization potentials have been determined by the UV photoelectronic spectra with relevance to their geometrical structures. Hohl *et al.*⁸ have calculated the structures of the Se_n ($n=3-8$) clusters by the local spin-density approximation method combined with molecular dynamics and simulated annealing. However, the electronic states of the selenium clusters have not been reported to our knowledge, which are very important for understanding and analyzing the experimental observations.

In this paper, we present studies on the electronic structure and stability of small selenium clusters by first-principles calculations. The calculated electronic properties are compared with the available experimental results and the theoretical studies are correlated with our scan-

ning tunneling microscopy (STM) observations of selenium clusters fabricated onto the graphite crystals.

The calculations are based on the density-functional theory within the local-density approximation,⁹ and the linear combination of atomic orbitals. This method, which has been discussed in detail elsewhere,^{10,11} has been used successfully in physics and chemistry of condensed matter and molecules.¹³ The basis set is chosen to be the numerical form of the orbital solutions of the self-consistent-field Kohn-Sham equation for the selenium atom.

The main point is to solve the secular equation

$$(\mathbf{H} - E\mathbf{S})\mathbf{C} = 0 \quad (1)$$

self-consistently to obtain the energy levels E_i and the coefficient C_{ij} , where \mathbf{H} is the Hamiltonian matrix and \mathbf{S} is the matrix of overlap integrals.

According to the standard local-density approximation, the total energy is evaluated by¹²

$$\begin{aligned} E_{\text{tot}} &= \sum_i n_i \epsilon_i - \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\ &\quad + \sum \int \rho(\mathbf{r}) [\epsilon_{\text{xc}}(\mathbf{r}) - v_{\text{xc}}(\mathbf{r})] d\mathbf{r} \\ &\quad + \frac{1}{2} \sum_{\mu} \sum_{\nu} \frac{Z_{\mu} Z_{\nu}}{R_{\mu\nu}} \\ &\equiv \int e(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \sum_{\mu} \sum_{\nu} \frac{Z_{\mu} Z_{\nu}}{R_{\mu\nu}}, \end{aligned} \quad (2)$$

where ϵ_i, n_i are the eigenvalue and occupation number of the i th molecular orbital, respectively. ϵ_{xc} is the exchange-correlation energy density, $R_{\mu\nu}$ the distance between μ and ν atoms. $e(\mathbf{r})$ is an energy density. The von Barth-Hedin exchange-correlation function is used in the calculations.¹⁴ The binding energy of the cluster is then defined with respect to a reference system, say the dissociated atoms, as

$$E_b = -(E_{\text{tot}} - E_{\text{tot}}^{\text{ref}}). \quad (3)$$

In this method, the numerical error of E_b is minimized with the point-by-point error-cancellation technique. In this technique, the reference system energy is computed with the same sampling grid as in the self-consistent field and the cluster energy procedures by freezing the atoms at their respective lattice sites and they are now assumed to be noninteracting, so that the numerical error of E_b can be partly canceled out via point-by-point subtraction.

We chose $4s^2$, $4p^4$, and $4d^0$ as the valent basis set for the calculations, while keeping the inner orbitals frozen. To satisfy us with the choice of the basis set and other input parameters, we calculated the selenium dimer as a test. The binding energy and interatomic distance we get are 3.75 eV and 2.2 Å, respectively, in good agreement with the experimental results of 3.410 eV and 2.17 Å.¹⁶

The stable structures of Se_n ($n=3-8$) have been reported by Hohl *et al.*⁸ using the *ab initio* molecular-dynamics studies. For the Se_3 cluster, they get C_{2v} , see Fig. 1, as the most stable structure. We have also checked our result for Se_3 and found the C_{2v} structure has a little larger binding energy (5.28 eV) than the D_{3h} structure (5.14 eV). For the C_{2v} structure, the bond length and bond angle are 4.25 Å and 119°, respectively, which are consistent with the results of Hohl *et al.*⁸ The bond length is 4.20 Å in the D_{3h} structure. We use the models of Hohl *et al.* for other larger clusters.

The calculated binding energies, ionization potentials, affinity energies, and the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are tabulated in Table I. The ionization potential (IP) and affinity energy (AE) are calculated by employing the transition-state method developed by Slater¹⁷ assuming that ionization does not change the structure of clusters. Ionization potentials obtained from photoelectron spectra⁷ are also listed in the table for comparison.

It is noted from Table I that the calculated IP's are in good agreement with the experimental results. However, the IP's and AE's do not show obvious relation with the cluster size. It is well known that the IP of the cluster represents the energy needed to ionize one electron in the HOMO orbital and the AE is the energy for LUMO to accept one electron. Therefore, they should be related to the characters of the HOMO and LUMO orbitals, respectively. Table II gives the composition of the HOMO and LUMO for the selenium clusters obtained by Mulliken population¹⁵ analysis. We find that clusters with more 4s components in the HOMO orbital have higher

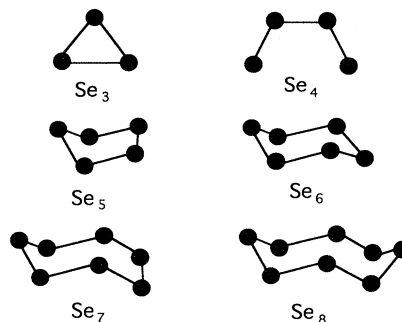


FIG. 1. Assumed structures of selenium clusters from Ref. 8.

IP's and clusters with more 4s components in the LUMO orbital have higher AE's. The reason is that the 4s atomic orbital has lower energy than that of the 4p. Therefore, the IP's and AE's are associated with the hybridization of the 4s and 4p orbitals. A similar conclusion is also found for the small sulfur clusters.¹⁸

The binding energy increases as the cluster size increases on the whole and Se_6 and Se_8 clusters have larger binding energies compared with adjacent molecules. The stability of the clusters can be understood in terms of the second derivative of the binding energy. In Fig. 2, we reproduce the results from the calculated binding energies,

$$\Delta E_N = E_{N+1} + E_{N-1} - 2E_N, \quad (4)$$

as a function of N for selenium clusters. Note the prominent peaks for Se_3 , Se_6 , and probably Se_8 clusters (which is not included in the figure because we lack the value of Se_9), which indicate the increased stability of the clusters. From the point of view of the electronic structure, Se_6 and Se_8 clusters have a quite large energy gap between HOMO and LUMO and their HOMO's are fully occupied single a_{1g} states which are composed of the 4p electronic state of selenium; these are required for the high electronic stability.

The density of states (DOS) of Se_5 and Se_6 molecules, which are obtained by Lorentz broadening (0.2 eV in this study) of the discrete energy levels, is given in Figs. 3 and 4. From these figures, we can see that s states are far below the Fermi level while d states are above, and p states are near the Fermi level.

Becker, Rademann, and Hensel,⁶ reported the 10.0-eV photoelectron spectra of Se_n ($n=2,5,6,7,8$) clusters. The prominent feature is that while the spectra obtained for Se_6 and Se_8 show one single band, two or three peaks

TABLE I. Binding energy (E_b) per atom, ionization potential (IP), affinity energy (AE), Fermi energy (FE), and energy gap between HOMO and LUMO (E_g) of selenium clusters, units in eV.

| | Se_3 | Se_4 | Se_5 | Se_6 | Se_7 | Se_8 |
|------------|--------|--------|--------|--------|--------|--------|
| E_b | 2.64 | 2.72 | 2.95 | 3.12 | 3.07 | 3.34 |
| IP | 10.02 | 9.48 | 8.84 | 8.67 | 8.87 | 8.86 |
| AE | 3.05 | 3.13 | 1.84 | 4.64 | 2.34 | 2.85 |
| FE | 6.75 | 6.12 | 5.17 | 5.09 | 5.65 | 5.79 |
| E_g | 2.26 | 0.82 | 2.17 | 2.86 | 2.16 | 2.32 |
| IP (expt.) | 9.2 | 9.1 | 8.3 | 8.4 | 8.2 | 8.4 |

TABLE II. Compositions of the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO), units in percentage.

| | HOMO | LUMO |
|-----------------|-----------------|-----------------|
| Se ₃ | 15% 4s + 82% 4p | 7% 4s + 90% 4p |
| Se ₄ | 12% 4s + 86% 4p | 9% 4s + 89% 4p |
| Se ₅ | 95% 4p | 100% 4p |
| Se ₆ | 6% 4s + 93% 4p | 10% 4s + 82% 4p |
| Se ₇ | 95% 4p | 95% 4p |
| Se ₈ | 5% 4s + 94% 4p | 7% 4s + 88% 4p |

with different intensities are observed for Se₅ and Se₇ clusters. For the explanation of the spectra, it is ascribed to their different symmetric groups of the geometrics. Se₆ and Se₈ clusters are highly symmetric rings (*D*_{3d} and *D*_{4d}). In contrast, Se₅ and Se₇ show a lower symmetry (*C*_{1h}) and the spectra show split bands.

Compared with our theoretical calculations, the energy of the ionizing light is so small that only the lone pair 4p- π electrons can be torn out of the molecule. By analyzing the composition of the molecular orbitals near the HOMO level, we find the first peak below the Fermi level in Figs. 3 and 4 is composed of the 4p- π orbitals. This means that only these electrons have been excited in the experiments. It is noted that the DOS of Se₆ has one sharp peak for the 4p- π orbitals while that of Se₇ really shows splitting of the band due to the lower symmetry.

From above theoretical studies, we conclude that Se₆ and Se₈ clusters have closed-shell electronic structures and their binding energies are larger than the adjacent species and we expect that the interactions between these clusters should be van der Waals-like. These clusters may be used as building blocks to assemble new materials due to their exceptional stable electronic structure.

We have fabricated a rectangular lattice arrangement of Se_n clusters on the C plane of a graphite crystal and examined by STM images. Details of the experiment have been reported elsewhere;¹⁹ only the main points of the observations are discussed below.

Figures 5(a) and 5(b) show the geometrical model of selenium six- and eight-membered molecule arrays on graphite, as deduced from our STM data. The molecule's

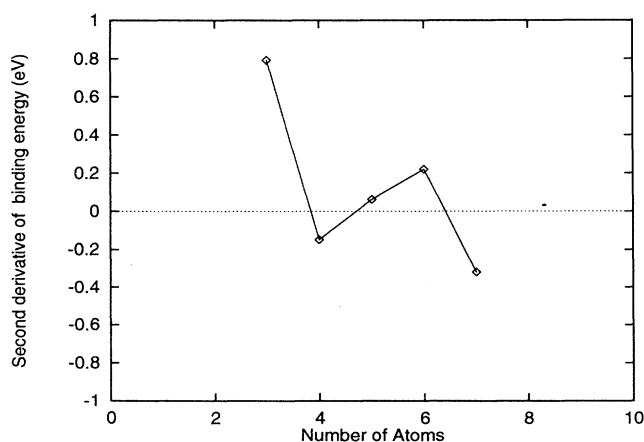


FIG. 2. Second energy derivatives of selenium clusters.

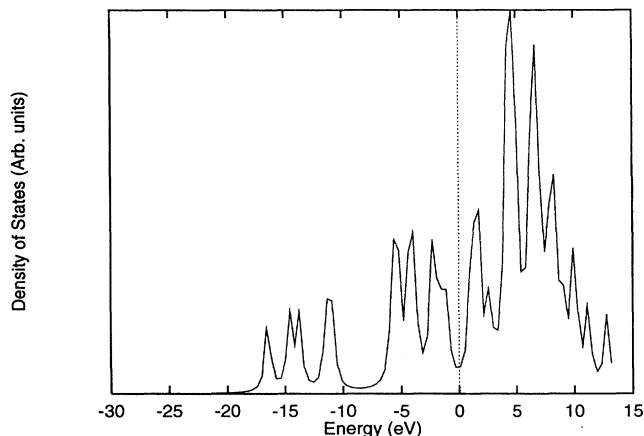


FIG. 3. Total density of states of Se₅ cluster.

average diameter is 0.53 ± 0.05 nm and the height is about 0.28 ± 0.04 nm. The diameter of individual objects (0.53 nm) is comparable to 0.526 nm found for Se₈ rings in a monoclinic crystal. The lattice constants (0.72 and 0.85 nm) coincide with three times the binary and bisectric distances of the hexagon in graphite. We do not expect that the arrays consist of compact selenium clusters, because the only known form of Se is a ring molecule or chain in all states of aggregation as gas, liquid, and solid. It is rather unlikely that the structure changes to other forms on graphite that is chemically inactive, and Se₆ and Se₈ molecules are electronically very stable.

No steps were observed at the grain boundaries or inside the grains. We therefore identified these structures as being due to two-dimensional arrays of clusters. In short, we have observed one monolayer of selenium ring-type molecules on the C plane of graphite. They are bound by weak van der Waals forces. With the STM data error, 0.05 nm, it is impossible to decide which type of ring has been observed on the basis of the geometrical data. However, the six- and eight-membered rings should be dominant because of their stable electronic structures.

The stability of these structures is studied by changing the bias voltage from +0.7 to -0.7 eV. Different types of modifications of the molecular arrangements were ob-

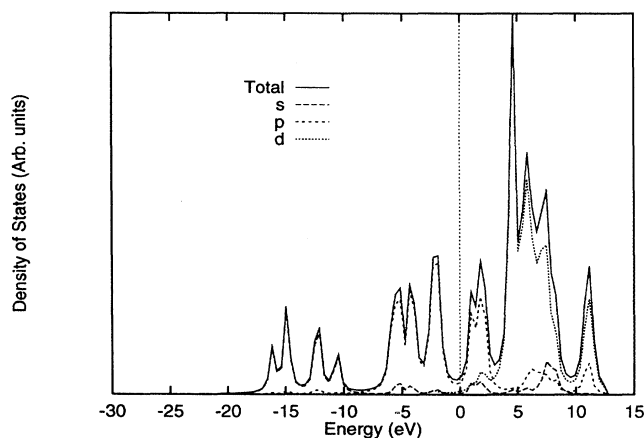


FIG. 4. Total and partial density of states of Se₆ cluster.

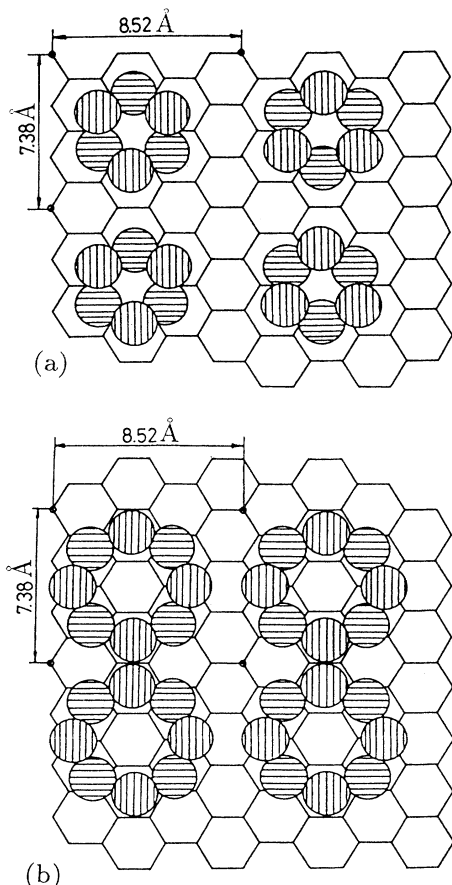


FIG. 5. Geometrical model of the configuration for (a) the six-membered and (b) the eight-membered Se rings on graphite surface. (Se molecules are crown type.)

served. At about -0.7 V (minus on the sample relative to the probe), the regular arrangement suddenly collapses to a random distribution of larger clusters due to the break of the ring-type clusters and the process of the phase change in the lattice system is not reversible with respect to the bias voltage.

From the present theoretical calculations, we can understand better the reason for the structural transforma-

tion as the bias voltage changes. There are six valence electrons per Se atom, and these electrons are highly localized, as indicated by the partial DOS. The amount of the energy increase ΔE in the electric field of $V_T=0.7$ V is 4.2 eV; it is larger than the binding energy of 3.13 and 3.34 for Se_6 and Se_8 molecules, which are the dominant species in the two-dimensional molecular crystal. Therefore, Se clusters are broken and the two-dimensional molecular crystal disappears under the voltage of 0.7 eV. In fact, if the Se_6 molecule gets 3.12 eV energy, it should be broken. The critical voltage for the transformation might be $3/12/6=0.502$ V, instead of 0.7 V. However, since there exists the tunnel current and the nonlocalized electrons in the two-dimensional lattice, the number of localized electrons per atom should be less than six. From this point of view, the localized electron number per atom of Se_6 molecule should be $3.12/0.7=4.5$.

In summary, the electronic structures Se_n ($n=3,4,5,6,7,8$) clusters have been studied by first-principles local-density-functional calculations. The IP's and AE's of the clusters are found associated with the hybridization of the 4s and 4p wave functions in their HOMO and LUMO. From the calculated binding energies, the second energy derivative, and other electronic properties we find that the Se_6 and Se_8 clusters are electronically more stable than their adjacent molecules, and those clusters could be used as building blocks to assemble various new materials as shown by our fabrication of selenium clusters onto the C plane of the graphite crystal. Because of the large value of the HOMO-LUMO gap, both cluster-cluster and cluster-substrate interactions are van der Waals interactions, which are important for forming monomolecular nanocluster lattice systems.

The nanometer-scale modification on those structures may be realized by changing both internal structures of cluster and their arrangement on the substrate by applying appropriate voltages of the STM probe.

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- ¹R. A. Zingaro and W. Cooper, *Selenium* (Van Nostrand Reinhold, London, 1964).
- ²J. Struke, *The Physics of Selenium and Tellurium* (Pergamon, Oxford, 1969).
- ³R. Steudel and E. M. Strauss, *Adv. Inorg. Chem. Radiochem.* **135**, 35 (1984).
- ⁴R. Steudel, *Z. Anorg. Allg. Chem.* **139**, 478 (1981).
- ⁵A. Aoki, M. Tsukada, and M. Schlütter, *New Horizons in Low-Dimensional Electron Systems* (Kluwer Academics, Dordrecht, 1992).
- ⁶J. Becker, K. Rademann, and F. Hensel, *Z. Phys. D* **19**, 229 (1991); **19**, 233 (1991); *Z. Naturforsch. Teil A* **46**, 453 (1991).
- ⁷B. Tribottet, A. Benamar, D. Rayane, P. Melinon, and M. Broyer, *Z. Phys. D* **23**, 352 (1993).
- ⁸D. Hohl, R. O. Jones, R. Car, and M. Parrinello, *Chem. Phys. Lett.* **139**, 540 (1987).
- ⁹W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- ¹⁰Z. Q. Li and B. L. Gu, *Phys. Rev. B* **47**, 13 611 (1993); Z. Q.

- Li, B. L. Gu, and R. S. Han, *Chem. Phys. Lett.* **207**, 41 (1993).
- ¹¹D. E. Ellis and G. P. Painter, *Phys. Rev. B* **2**, 2887 (1970).
- ¹²B. Delley, D. E. Ellis, A. J. Freeman, and D. Post, *Phys. Rev. B* **27**, 2132 (1983).
- ¹³Z. Q. Li, J. Z. Yu, K. Ohno, and Y. Kawazoe, *J. Phys. Condens. Matter* **7**, 47 (1995).
- ¹⁴U. von Barth and L. Hedin, *J. Phys. C* **5**, 1629 (1972).
- ¹⁵R. S. Mulliken, *Phys. Rev.* **45**, 87 (1933).
- ¹⁶*American Institute of Physics Handbook* (McGraw-Hill, New York, 1982), pp. 7-181.
- ¹⁷J. C. Slater, *Phys. Rev.* **81**, 385 (1951).
- ¹⁸B. Pan, C. Duan, S. Xia, and C. Xiao, *Phys. Rev. B* **50**, 17 556 (1994).
- ¹⁹B. Czajka, B. L. Gu, J. Z. Yu, K. Ohno, Y. Kawazoe, A. Kasuya, and Y. Nishina, *Sci. Rep. Res. Inst. Tohoku Univ. Ser. A* **39**, 57 (1994).