THE JOURNAL OF PHYSICAL CHEMISTRY A LETTERS

2006, *110,* 12073−12076
Published on Web 10/19/2006

Experimental and Theoretical Characterization of Aluminum-Based Binary Superatoms of $Al_{12}X$ and Their Cluster Salts

Minoru Akutsu,[†] Kiichirou Koyasu,[†] Junko Atobe,[†] Natsuki Hosoya,[†] Ken Miyajima,[†] Masaaki Mitsui,[†] and Atsushi Nakajima*,[†,‡]

Department of Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan, and CREST, Japan Science and Technology Agency (JST), c/o Department of Chemistry, Keio University, Yokohama 223-8522, Japan

Received: August 10, 2006; In Final Form: September 30, 2006

The geometric and electronic structures of aluminum binary clusters, Al_nX (X = Si and P), have been investigated, using mass spectrometry, anion photoelectron spectroscopy, photoionization spectroscopy, and theoretical calculations. Both experimental and theoretical results show that $Al_{12}Si$ has a high ionization energy and low electron affinity and $Al_{12}P$ has a low ionization energy, both with the icosahedral structure having a central Si or P atom, revealing that $Al_{12}Si$ and $Al_{12}P$ exhibit rare-gas-like and alkali superatoms, respectively. Experiments confirmed the possibility that the change in the total number of valence electrons on substitution could produce ionically bound binary superatom complexes, the binary cluster salts $Al_{12}P^+F^-$ and $Al_{12}B^-Cs^+$.

Nanostructured materials assembled from finite-sized stable clusters have been extensively sought after since the discovery of C_{60}.[1] One critical guiding principle for cluster-assembled materials has been the electron shell model,[2] which predicts that metal clusters having 8, 20, 40, ..., electrons would acquire an electronic stability. From this viewpoint, investigators have focused much attention on aluminum (Al) clusters as building blocks for Al-based materials. In particular, Al_{13}^- is a cluster known for a pronounced stability due to coincident closures of electronic (40*e*) shells and its high-symmetry geometry (13-atom icosahedral).[3] Al_{13} has a high electron affinity (EA) of 3.6 eV, and Al_{13}^- is a very stable cluster anion,[4,5] having superhalogen character;[6] Al_{13} has been the subject of many theoretical efforts.[7−11]

Efforts to examine the superatom behavior involved in electronic and geometric shell closings have focused on substituting the central atom in Al_{13}. Since the icosahedral structure of 13 homogeneous atoms forces a configuration in which 12 surface atoms extend to encapsulate one central atom, the bond length between the surface atoms is stretched by about 5% compared to that between a surface and a central atom.[12] The doping of a central atom having a smaller diameter, therefore, might produce closed-shell electronic and geometric structures that would lead to more stable species.[8,10,13,14]

We have intensively studied the electronic and geometric structures of binary Al clusters by mass spectrometry (MS), anion photoelectron spectroscopy (PES), photoionization spectroscopy (PIS), and theoretical calculations. An improved ability to produce cold mixed clusters has enabled us to form Al-based binary superatoms of rare-gas-like or alkali characters with a silicon (Si) atom having four valence electrons or a phosphorus (P) atom having five valence electrons. Furthermore, these changes provided the possibility of producing an ionically bound, binary superatom complex—the binary cluster salt $PAl_{12}F$—and, with the substitution of P by trivalent boron (B), the complex $Al_{12}BCs$.

The details of our apparatus have been described elsewhere.[13] Binary Al clusters were produced via dual laser vaporization of a pure Si or P and pure Al targets with a He carrier gas and were mass-analyzed with time-of-flight MS. Neutral binary Al clusters were photoionized with an ArF (193 nm) or F_2 laser (157 nm), while charged binary Al clusters were directly mass-analyzed. The photoionization mass spectrum of neutral species exhibits the spectrum of ions formed from photoionized neutrals, because charged clusters were deflected prior to photoionization. Figure 1 shows the mass spectra of the Al−Si anions, neutrals, cations, and the Al−P cations. As shown on the right side of Figure 1, the intensity distributions show a systematic change of local maxima; they display distinctive peaks at the masses of the $Al_{12}Si$ neutral and the $Al_{12}P^+$ cation, as well as those of Al_{13}^- and $Al_{11}Si_2^+$.

The fact that the magic number behavior for $Al_{12}X^{+/0/-}$ exhibits a charging state dependence suggests that the principle of double shell closings of 40*e* and an icosahedral configuration could work in favor of substitution of Si or P atoms. All $Al_{12}Si$, $Al_{12}P^+$, and $Al_{11}Si_2^+$ clusters possess 40*e*, if we assume that Al, Si, and P atoms have three, four, and five valence electrons, respectively. As reported previously,[15] a chemical probe method is useful in deducing the chemical stability of Al_nX. In particular, susceptibility to oxidation would be a good test of inertness, and then, O_2 was used as a reactant gas. In fact, the reactivity of Al_nX toward O_2 reactant gas can reveal chemical inertness: none of the $Al_{12}Si$ and $Al_{12}P^+$ clusters exhibit adsorption reactivity, although the plots of the reactivity are not shown.

---

* To whom correspondence should be addressed. E-mail: nakajima@chem.keio.ac.jp.
[†] Faculty of Science and Technology, Keio University.
[‡] Japan Science and Technology Agency (JST).

10.1021/jp065161p CCC: $33.50

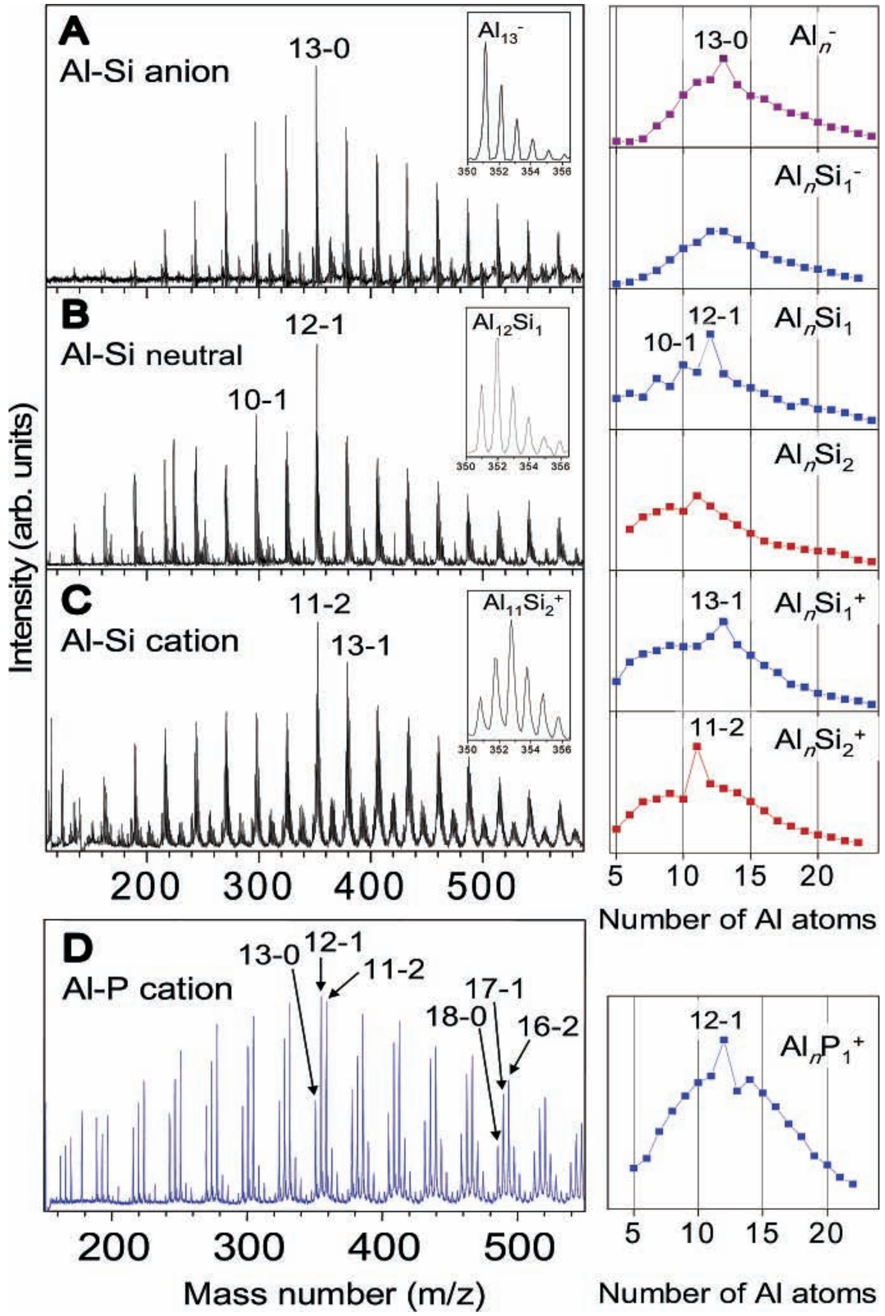

Figure 1. Mass spectra of (A) Al−Si anions, (B) Al−Si neutrals, (C) Al−Si cations, and (D) Al−P cations. On the right side of the figure, the intensity distributions obtained from the mass spectra are shown against the number of Al atoms, where they display distinctive peaks at the masses of the $Al_{12}Si$ neutral and the $Al_{12}P^+$ cation, as well as those of Al_{13}^- and $Al_{11}Si_2^+$.

Thus, $Al_{12}X$ is favored electronically as well as from geometric packing; the electron configuration of Al_nX must actually be closed when X is Si and P^+. A plausible explanation is that $Al_{12}X$ assumes a closed electron configuration when a Si (P^+) dopant having four valence electrons completes the shell of 40*e*.[8,11b]

The electronic states were probed by anion PES and neutral PIS. Although the mass of Si (28 u) is very close to that of Al (27 u), a modified acceleration stage for the MS makes it possible to separate $Al_{12}Si^-$ from Al_{13}^-.[16] Figure 2 shows the PES spectra of $Al_{12}Si^-$ and $Al_{12}SiF^-$ at 213 nm (5.82 eV) as well as those reported for $Al_{12}B^-$ and $Al_{13}Cs^-$ for comparison, in which photoelectrons were analyzed with a magnetic bottle-type photoelectron spectrometer calibrated using the known spectrum of Au^-. Here, the F-atom adduct was formed by the adsorption reaction with F_2 gas,[15] whereas the Cs-atom adduct was formed by the reaction with Cs vapor produced with the high-temperature pulsed valve (≈440 K).[17] The PES spectrum of $Al_{12}Si^-$ (Figure 2A) displays a hump around 2.1 eV (labeled X), followed by a large energy gap and more transitions at higher energies, a vertical detachment energy (VDE) of 2.16 ± 0.05 eV, and an adiabatic detachment energy of 1.69 ± 0.07 eV for $Al_{12}Si^-$. The latter is the electron affinity (EA) of $Al_{12}Si$.

The spectrum of $Al_{12}Si^-$ is very different from those of Al_{13}^-, $Al_{12}B^-$, and $Al_{12}P^-$ in which the detachment peaks start in the higher energy region without a separate peak. Experimental verification for a singly occupied molecular orbital (MO) has been achieved by the technique of halogen-atom doping.[15] As shown in Figure 2B, the spectrum of $Al_{12}SiF^-$ lacks the peak X in Figure 2A, while the other spectral features are more or less maintained. The gap of the A−X separation (1.53 eV)

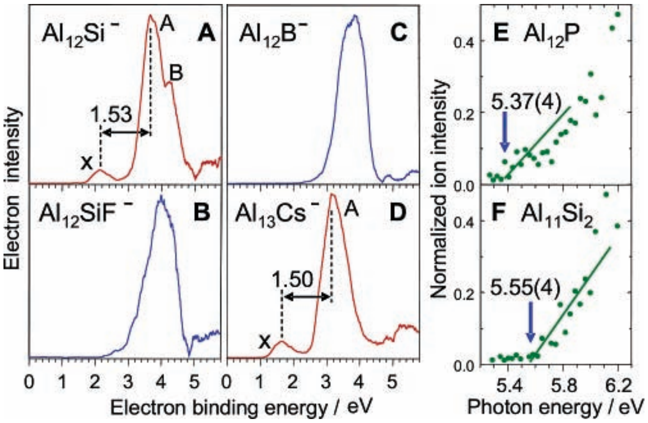

Figure 2. Photoelectron spectra of (A) $Al_{12}Si^-$, (B) $Al_{12}SiF^-$, (C) $Al_{12}B^-$, and (D) $Al_{13}Cs^-$ at 213 nm (5.82 eV) and PIE curves for (E) $Al_{12}P$ and (F) $Al_{11}Si_2$.

in $Al_{12}Si$ is large, almost the same as that in C_{60} (1.57 eV).[18] Interestingly, the spectral features of $Al_{12}Si^-$ and $Al_{12}SiF^-$ are closely similar to those for $Al_{13}Cs^-$ and $Al_{12}B^-$ (Figure 2C,D),[13b,17] a resemblance consistent with the idea that they both are isoelectronic. The large gap suggests that $Al_{12}Si$ should be very inert and may possess a highly symmetric geometry. As discussed below, it has been theoretically proposed that $Al_{12}X$ assumes the doped atom-encapsulated structure of an icosahedron.

PIS has been applied for neutral binary Al clusters using the output of an OPO laser (340−193 nm). The ionization energy (E_i) was evaluated by the photoionization efficiency (PIE) curve. For the E_i's of Al_nP and Al_nSi_2, the $Al_{12}P$ and $Al_{11}Si_2$ clusters exhibit local minima at 5.37 ± 0.04 and 5.55 ± 0.04 eV (Figure 2E,F) against a cluster size n, while the E_i of $Al_{12}Si$ is high in the range 6.42 eV $< E_i <$ 7.90 eV. This result of low E_i's for $Al_{12}P$ and $Al_{11}Si_2$ is consistent with a total of 41e.

All of the calculations of equilibrium geometries and vibrational frequencies of the clusters were performed at the density functional theory (DFT) level of theory, using the B3LYP functionals[19a] built into the Gaussian 03 program package,[19b] and the 6-31G* basis set for Al, Si, and F. The total energies and relative energies of all optimized structures were refined using single-point B3LYP/6-311+G* calculations. For Cs, the basis set used was the Los Alamos ECP including an outermost core orbital.[19c] With our DFT calculations for all of the $Al_{12}B^-$

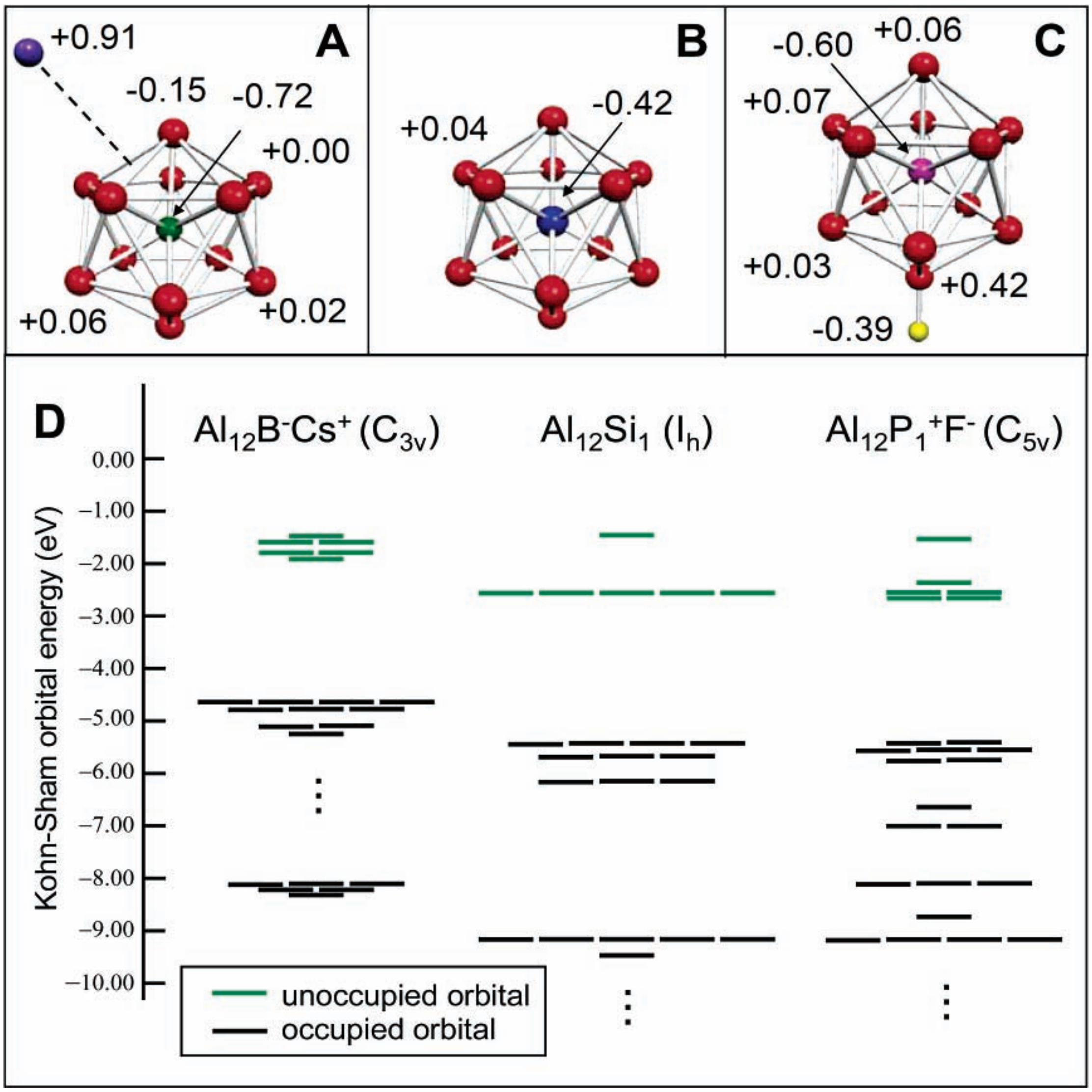

Figure 3. Theoretically optimized (A) $Al_{12}BCs$, (B) $Al_{12}Si$, and (C) $Al_{12}PF$ structures with Mulliken atomic population as well as (D) calculated orbital diagrams of $Al_{12}Si$, $Al_{12}PF$, and $Al_{12}BCs$. A large gap between the HOMO and the LUMO (more than 2.5 eV) exists in common, which exhibits an electronically closed configuration. It is well demonstrated that the change in the total number of valence electrons on substitution could produce ionically bound binary superatom complexes, the binary cluster salts $Al_{12}P^+F^-$ and $Al_{12}B^-Cs^+$.

anions, $Al_{12}Si$ neutrals, and $Al_{12}P^+$ cations, the most stable structures without any imaginary vibrational frequencies were obtained for the icosahedral structure (I_h symmetry) having a central dopant atom (Figure 3B). For $Al_{12}Si^-$, the stable structure without any imaginary vibrational frequencies was obtained for the slightly distorted icosahedral structure (C_{2h} symmetry) having a central Si atom. For the most stable structure, the calculated VDE value was derived to be 2.10 eV, which is in good agreement with our experimental results of 2.16 eV. Furthermore, the highest occupied molecular orbital (HOMO)−lowest unoccupied molecular orbital (LUMO) gap of $Al_{12}Si$ (C_{2h} symmetry) was estimated to be 1.26 eV from the calculated gap between the first HOMO (a_g) and the second HOMO (a_u) of $Al_{12}Si^-$, which is also in good agreement with our experimental result of 1.53 eV. It is noteworthy that the gap is consistent with that of hydrogen atom or alkali metal atom doped Al_{13} found by experiments[17,20] and calculations.[21]

As shown in Figure 3, the Mulliken atomic charges of the Si atom and the Al atoms are −0.42 and +0.04, implying that $Al_{12}Si$ has substantial contribution from a $[Si^{\delta-}Al_{12}{}^{\delta+}]$ charge distribution. Geometrically, the calculated bond distance between surface Al−Al atoms is slightly shortened to 0.280 nm in $Al_{12}Si$ and 0.281 nm in $Al_{12}P^+$ from 0.282 nm in $Al_{13}{}^-$, suggesting that the substitution of the central atoms leads to geometric relaxations. The $Al_{12}Si$ and $Al_{12}P$ clusters of icosahedral binary Al can be viewed as a rare-gas-like and alkali superatoms, respectively, because $Al_{12}Si$ has a high E_i value and a low EA, whereas $Al_{12}P$ has a low E_i value. When the reactivity of $Al_{12}P$ toward F_2 was examined, $Al_{12}P$ neutral was converted to the product of $Al_{12}PF$ (Figure 3C), while the $Al_{12}P^+$ cation and the $Al_{12}Si$ neutral are nonreactive toward F_2 or O_2. The formation of $Al_{12}PF$ suggests that $Al_{12}P$ has superalkali character. In fact, the measured E_i value of $Al_{12}PF$ is high, in the range $6.42 \text{ eV} < E_i < 7.90 \text{ eV}$, in agreement with the calculated adiabatic E_i value of 6.55 eV. Similarly, when the Al-based binary superatom of $Al_{12}B$ is exposed to the vapor of the alkali atom cesium (Cs), the oppositely charged cluster salts of $Al_{12}BCs$ (Figure 3A) are preferentially formed, and the experimental E_i's of $Al_{12}BCs$ (5.97 ± 0.04 eV) and $Al_{13}Cs$ (5.99 ± 0.03 eV) are well reproduced theoretically. Note that both $Al_{12}PF$ and $Al_{12}BCs$ are electronically closed as salts, as shown in calculated orbital diagrams (Figure 3D).

As well as the known superhalogen Al_{13}, the existence of the binary superatom family of $Al_{12}Si$, $Al_{12}P$, and $Al_{12}B$ suggests that it should be possible to create Al-based cluster-assembled materials. Current studies involving the reaction of binary Al clusters with halogen or alkali atoms suggest that it is possible to synthesize "binary cluster-salt crystals".[7,22]

Acknowledgment. This work is partly supported by the Ministry of Education, Culture, Sports, Science, and Technology, Grant-in-Aid for the 21st Century COE "Keio LCC". K.K. and N.H. are grateful to Research Fellowship of JSPS for Young Scientists.

References and Notes

(1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature (London)* **1985**, *318*, 162.

(2) Knight W. D.; Clemenger, K.; de Heer, W. A.; Saunders: W. A.; Chou, M. Y.; Cohen, M. L. *Phys. Rev. Lett.* **1984**, *52*, 2141.

(3) Leuchtner, R. E.; Harms, A. C.; Castleman, A. W., Jr. *J. Chem. Phys.* **1989**, *91*, 2753.

(4) Cha, C.-Y.; Ganteför, G.; Eberhardt, W. *J. Chem. Phys.* **1994**, *100*, 995.

(5) Li, X.; Wu, H.; Wang, X. B.; Wang, L.-S. *Phys. Rev. Lett.* **1994**, *81*, 1909.

(6) (a) Bergeron, D. E.; Castleman, A. W., Jr.; Morisato, T.; Khanna, S. N. *Science* **2004**, *304*, 84. (b) Bergeron, D. E.; Roach, P. J.; Castleman, A. W., Jr.; Jones, N. O.; Khanna, S. N. *Science* **2005**, *307*, 231.

(7) Khanna, S. N.; Jena, P. *Phys. Rev. Lett.* **1992**, *69*, 1664.

(8) (a) Gong, X. G.; Kumar, V. *Phys. Rev. Lett.* **1993**, *70*, 2078. (b) Gong, X. G. *Phys. Rev. B* **1997**, *56*, 1091. (c) Kumar, V.; Sundararajan, V. *Phys. Rev. B* **1998**, *57*, 4939. (d) Ashman, C.; Khanna, S. N.; Liu, F.; Jena, P.; Kaplan, T.; Mostoller, M. *Phys. Rev. B* **1997**, *55*, 15868.

(9) (a) Seitsonen, A. P.; Puska, M. J.; Alatalo, M.; Nieminen, R. M.; Milan, V.; Payne, M. C. *Phys. Rev. B* **1993**, *48*, 1981. (b) Ekardt, W. *Z. Phys. B* **1997**, *103*, 305. (c) Akola, J.; Manninen, M.; Hakkinen, H.; Landman, U.; Li, X.; Wang, L.-S. *Phys. Rev. B* **1999**, *60*, 11297. (d) Rao, B. K.; Khanna, S. N.; Jena, P. *Phys. Rev. B* **2000**, *62*, 4666.

(10) Kumar, V.; Bhattacharjee, S.; Kawazoe, Y. *Phys. Rev. B* **2000**, *61*, 8541.

(11) (a) Alonso, J. A.; Lopez, M. J.; Molina, L. M.; Duque, F.; Mananes, A.; *Nanotechnology* **2002**, *13*, 253. (b) Charkin, O. P.; Charkin, D. O.; Klimenko, N. M.; Mebel, A. M. *Chem. Phys. Lett.* **2002**, *365*, 494.

(12) Mackay, A. L. *Acta Crystallogr.* **1962**, *15*, 916.

(13) (a) Nakajima, A.; Kishi, T.; Sugioka, T.; Kaya, K. *Chem. Phys. Lett.* **1991**, *187*, 239. (b) Kawamata, H.; Negishi, Y.; Nakajima, A.; Kaya, K. *Chem. Phys. Lett.* **2001**, *337*, 255.

(14) Li, X.; Wang, L.-S. *Phys. Rev. B* **2002**, *65*, 153404.

(15) Koyasu, K.; Akutsu, M.; Mitsui, M.; Nakajima, A. *J. Am. Chem. Soc.* **2005**, *127*, 4998.

(16) Even, U.; Dick, B. *Rev. Sci. Instrum.* **2000**, *71*, 4415.

(17) Koyasu, K.; Akutsu, M.; Atobe, J.; Mitsui, M.; Nakajima A. *Chem. Phys. Lett.* **2006**, *421*, 534.

(18) Wang, X.-B.; Ding, C.-F.; Wang, L.-S. *J. Chem. Phys.* **1999**, *110*, 8217.

(19) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Frisch M. J.; et al. *Gaussian 03*, revision C.02; Gaussian Inc.: Wallingford, CT, 2004. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(20) (a) Bukart, S.; Blessing, N.; Klipp, B.; Müller, J.; Ganteför, G.; Seifert, G. *Chem. Phys. Lett.* **1999**, *301*, 546. (b) Thomas, O. C.; Zheng, W.-J.; Lippa, T. P.; Xu, S.-J.; Lyapustina, S. A.; Bowen, K. H., Jr. *J. Chem. Phys.* **2001**, *114*, 9895. (c) Zheng, W.-J.; Thomas, O. C.; Lippa, T. P.; Xu, S.-J.; Bowen, K. H., Jr. *J. Chem. Phys.* **2006**, *124*, 144304.

(21) Khanna, S. N.; Rao, B. K.; Jena, P. *Phys. Rev. B* **2002**, *65*, 125105.

(22) Khanna, S. N.; Jena, P. *Chem. Phys. Lett.* **1994**, *219*, 479.