RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 41, NUMBER 2 15 JANUARY 1990-I

Ab initio study of the geometry and electronic structure of lead iodide semiconductor clusters

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(Received 16 October 1989)

Layered anisotropic semiconductor clusters of the type Pb_xI_{2x} are studied in *ab initio* Hartree-Fock calculations that include relativistic effects. Total energies, internuclear distances, and net atomic charges are calculated. Large increases in the equilibrium iodine-lead interlayer distance result in as much as a 10% reduction of the in-plane internuclear separations and blueshifts in the electronic spectra, which are attributed to quantum size effects observed in recent experimental studies.

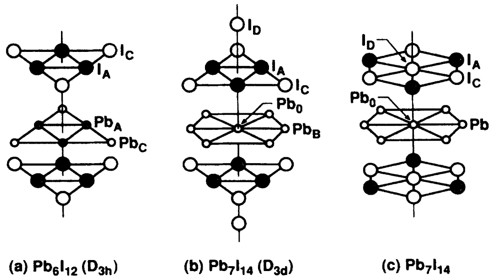
The properties of clusters are attracting increased attention because they represent an intermediate physical regime where neither atomic nor solid-state descriptions seem totally adequate.[1-3] Besides interest in fundamental questions such as how electronic structure evolves as a function of size, there is also the possibility of using finite-size effects to create new materials having unique electronic and optical properties.[4,5] In modern semiconductor research, for example, it is commonplace to fabricate structures whose physical dimensions are considerably smaller than carrier wavelengths, which leads to physical phenomena that cannot be observed in bulk matter.[6] Clusters containing from about 10 to 1000 atoms are particularly noteworthy because their properties set the ultimate limits on the use of physical size to alter the behavior of matter.

Many experimental techniques are now available to synthesize clusters both in gas and condensed phases,[7-12] but as yet there is no generally available experimental procedure to determine the structure and spectra of the clusters produced. Hence, theoretical insight into cluster structure as a function of cluster size takes on a major role. The computational difficulty inherent in treating large systems comprised of heavy elements, however, has precluded rigorous *ab initio* studies on such clusters. Up to now, theoretical treatments on systems of this type have largely neglected relativistic effects, as well as certain exchange interactions among electrons.[13] Consequently, the majority of *ab initio* work in semiconductor systems has appeared on small clusters of light elements such as silicon.[14,15] In such strongly covalent systems, it is found that small isolated clusters tend to reconstruct and to form tightly bound symmetrical structures with a high degree of coordination. Moreover, this tendency to minimize the number of exposed dangling bonds has the consequence that the bulk silicon structure is recovered only for very large clusters.

In this Rapid Communication, we report the results of rigorous *ab initio* quantum-mechanical calculations on semiconductor clusters containing as many as 21 heavy atoms. All of the theoretical results presented here were calculated using fully *ab initio* procedures; that is, no experimental parameters were used and all of the terms in the Hamiltonian were retained. Since no integrals were approximated or disregarded, all Coulomb and exchange interactions among electrons were explicitly evaluated for each cluster. Furthermore, relativistic effects, which are significant in these heavy-element systems,[16] were also included in the calculations.

The structures of the layered semiconductors investigated here exhibit a radically different dependence on cluster size than do those of isotropic silicon. Unlike clusters of Si, layered semiconductors of the type Pb_xI_{2x} essentially retain the structure of the bulk crystalline lattice in the lateral direction for the range of geometries studied. We find, however, that there can be significant electronic coupling between interlayer perturbations and intralayer lattice constants in these clusters. Indeed, for very large increases in the Pb-I interlayer spacings, we see in-plane lattice constants decrease by as much as 20%. With these results, it might be possible to explain recent compelling scanning tunneling images of structurally related BiI_3 clusters.[17]

Two cluster models are studied, one of Pb_6I_{12} and two of Pb_7I_{14} stoichiometry. These are shown in Fig. 1. Each has the layer symmetry of the bulk crystal and is comprised of a plane of lead atoms above which are situated two triangular layers of iodine atoms. Pb_6I_{12} has D_{3h} point-group symmetry (hexagonal close packing), while both Pb_7I_{14} clusters have D_{3d} point-group symmetry (cubic close packing). All three represent fragments of the bulk crystalline solid (one unit cell thick) having iodine layers slightly perturbed from the bulk arrangement to preserve the symmetry of each cluster. Pb-Pb, I-I, and



(a) Pb_6I_{12} (D_{3h}) (b) Pb_7I_{14} (D_{3d}) (c) Pb_7I_{14}

FIG. 1. Pb_xI_{2x} clusters ($x=6,7$).

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Pb-I internuclear distances were initially determined from the lattice constants of crystalline PbI_2.[18] All internuclear distances were then optimized in *ab initio* Hartree-Fock calculations, consistent with the variation principle and within the symmetry constraints. Self-consistent field (SCF) energies for the lowest-lying molecular-orbital electron configurations were calculated for each geometric orientation of the clusters. SCF calculations on heavy-element systems based on relativistic effective core potentials (REP's) have been shown to yield reliable geometric parameters.[16] In addition, this method yields fully optimized molecular orbitals for each electronic state treated, in contrast to many standard methods based on band theory. REP's (Ref. 19) were used to represent the $1s$-$4s$ $2p$-$4p$, and $3d$-$4d$ core electrons in I [Ref. 20(a)] and the $1s$-$5s$, $2p$-$5p$, $3d$-$5d$, and $4f$ core electrons in Pb.[20(b)] Relativistic effects cannot be ignored for systems containing heavy elements such as Pb and I.[16] Basis sets of contracted Gaussian-type functions were used to represent the valence orbitals of Pb and I.[20] Calculations were accomplished on a Cray X-MP supercomputer using programs based on the "equal contribution theorem" for two-electron symmetry orbital integrals.[21] These *ab initio* restricted closed-shell and restricted open-shell Hartree-Fock linear combination of atomic-orbital–molecular-orbital (LCAO-MO) calculations consumed approximately 20 min of Cray X-MP time for each nuclear configuration. The geometry optimizations required a minimum of ten orientations per cluster.

Energy-optimized interlayer and intralayer distances of Pb_6I_{12} were found to be 11% expanded and 1% contracted, respectively, relative to bulk PbI_2. This swollen interlayer distance is not unexpected for a Pb_6I_{12} cluster having D_{3h} point-group symmetry because the electron-rich I atoms of the top layer are arranged in "head-on" positions relative to those in the bottom layer. This is in contrast to bulk PbI_2, where each iodine atom in a top layer is positioned directly above the midpoint between two iodine atoms located in a bottom layer. This system tends to contract laterally as the interlayer separations expand. For example, expansion of the interlayer separation by 40% results in a 7% contraction in metal-layer lateral dimensions.

A total of five MO electron configurations were studied for neutral Pb_6I_{12}. Four of these states were nearly degenerate and lay 1.6 eV higher in energy than the ground state. The electronic excitations involved orbitals associated with both iodine and lead atoms. Furthermore, five of the six lowest unoccupied MO's (LUMO's) for each electron configuration have energies lower than -2.7 eV, indicating that the neutral system is electron deficient. This conclusion is supported by means of Koopmans' theorem.[22]

If the cluster wave function $\Psi(2N)$, a $2N$-electron antisymmetrized product of MO's $\{\phi_m\}$, is stationary and ϕ_m is an eigenfunction of the Fock operator, then $\Psi(2N+1)$, whereby an electron is added to ϕ_m, is also stationary with respect to any further variations in the orbitals. This means that the orbital energy ε_m corresponds to the electron affinity of the neutral system, providing that ε_m is unoccupied. Therefore, systems possessing very low-lying LUMO's are electron deficient; i.e., the addition of one or more electrons to these orbitals will increase the overall stability of the system.

To satisfy this electron deficiency, we studied a doubly charged anionic Pb_6I_{12} cluster. We also believe that the anion is the most natural cluster to consider from the experimental point of view since clusters of this type are prepared in solution as colloidal particles in the presence of excess iodide ions.[23] The total energy of $Pb_6I_{12}{}^{2-}$ is more than 6 eV lower than the corresponding neutral species. In this case, nearly all of the LUMO's have energies greater than zero (~ 2.7 eV), indicating a quenching of the system's electrophilicity.

A geometry optimization was also carried out for $Pb_6I_{12}{}^{2-}$. The equilibrium interlayer and intralayer distances were found to be expanded by 14% and 1%, respectively, relative to bulk PbI_2. This cluster is also slightly swollen with respect to neutral Pb_6I_{12}, but this is expected due to the increased ionicity. As with the neutral cluster, expansion of the interlayer separation results in a contraction of intralayer distances, although not as pronounced as for the neutral system; that is, a 40% expansion in interlayer separation results in a 3% contraction in lateral dimensions relative to the bulk crystal. As previously mentioned, results of SCF calculations on heavy-element systems have been shown to be reliable, with the accuracy of the method increasing as the number of electrons treated explicitly increases.[16] Therefore, SCF results for $Pb_6I_{12}{}^{2-}$, a 110-valence-electron system, are expected to be reliable, and any structural differences between our models and those of bulk PbI_2 are attributable to cluster effects.

A total of ten low-lying electron configurations of the cluster were studied at both the calculated equilibrium interatomic distances and at a geometry corresponding to a 60% expansion in the interlayer distance and a 10% contraction in lateral dimensions. These percentages were chosen from the results of a series of calculations at geometries ranging from 30% contraction to 100% expansion of the lattice constants in the vertical direction and 30% contraction to 20% expansion in the lateral direction. All of the open-shell configurations were treated as pure spin triplet states; i.e., the cluster wave functions are spin eigenfunctions having total spin quantum number $S=1$. Excitation energies relative to the lowest state found are given in Table I, while Table II reports electron charge/atom values calculated based on a Mulliken population analysis[24] for the lowest-lying state at each of the aforementioned two geometries.

The energy separations for equilibrium $Pb_6I_{12}{}^{2-}$ listed in Table I are clearly bandlike, with the two lowest-lying states nearly degenerate in energy and states 3 through 8 lying at or near the band gap of bulk crystalline PbI_2 at 2.5 eV.[25] The last state corresponding to $Pb_6I_{12}{}^{2-}$ listed in Table I is considerably blueshifted relative to the band gap of the bulk. The same type of energy separations occur at an expanded interlayer distance, the only exception being for state 4, which has an energy value between three essentially degenerate low-lying states and four states grouped near the band gap of the bulk solid. A total of 45 electron transitions among the ten lowest-lying states found were examined. The density of states shown in Fig. 2 indicates that these transitions are peaked at 0.2,

TABLE I. Electronic states of $\mathrm{Pb}_x\mathrm{I}_{2x}$ clusters (eV).

Cluster	State No.	ΔE (Equil.)[a]	ΔE (Expanded Z)[a]
$\mathrm{Pb_6I_{12}}^{2-}$ [b]	1	0.00	0.00
	2	0.03	0.14
	3	2.14[c]	0.47
	4	2.21	1.19[c]
	5	2.25	1.31
	6	2.36	2.05
	7	2.41	2.12
	8	2.49	2.39
	9	2.53	2.47
	10	4.84	3.06
$\mathrm{Pb_7I_{14}}^{2-}$ [d]	1	0.00	0.00
	2	0.26	0.35
(five layers)	3	0.28	0.76
	4	0.35	0.95
	5	0.59	1.11
	6	0.63	2.14
	7	0.75	2.71
	8	0.76	2.90
	9	0.99	3.29
	10	1.01	3.49
	11	1.26	3.99
$\mathrm{Pb_7I_{14}}^{2-}$ [e]	1	0.00	0.00
	2	0.68	1.71
(three layers)	3	1.54	1.99
	4	1.80	2.39
	5	1.83	3.17
	6	2.19	4.29
	7	2.39	4.67
	8	3.27	4.75
	9	3.31	. . .
	10	4.97	. . .

[a] See text.
[b] See Fig. 1(a).
[c] Lowest-lying closed-shell singlet state.
[d] See Fig. 1(b).
[e] See Fig. 1(c).

2.5, and 4.9 eV, with the second peak lying near the experimental bulk band gap of $\mathrm{PbI_2}$ and the third blueshifted relative to the band gap by 2.3 eV.

Charge/atom values appearing in Table II indicate that the predominant interlayer interactions occur between the atoms comprising the smaller Pb and I triangles [Pb_A and I_A in Fig. 1(a)] for the lowest-energy state of $\mathrm{Pb_6I_{12}}^{2-}$ at both geometries treated. This is also the case for the other eight-electron configurations of $\mathrm{Pb_6I_{12}}^{2-}$ listed in Table I, with the exception of the highest-energy state (state 10). Comparison between charge/atom values for this state at the equilibrium geometry and at an expanded interlayer separation shows that the interlayer interactions predominantly involve both types of Pb and I atoms [Fig. 1(a)]. No differences are seen between charge/atom values for the ground state and the corresponding values for each of the higher-energy states (states 2–9 in Table I) at both geometries treated, indicating that the electronic transitions are predominantly intralayer and occur among symmetry-related atoms. A more detailed analysis of the Mulliken populations reveals that these electron excitations correspond to metal-metal transitions. Differences in charge/atom values between the highest-energy state of $\mathrm{Pb_6I_{12}}^{2-}$ (state 10) listed in Table I and the ground state are as high as 0.2 (compared to ~0.02 for states 2–9). In this case, the transition involves both Pb and I atoms.

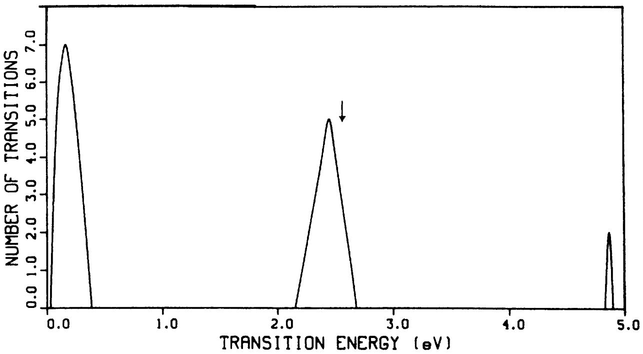

FIG. 2. Density of calculated $\mathrm{Pb_6I_{12}}^{2-}$ states. The arrow marks the position of the bulk band gap.

As noted above, two cluster orientations were studied for $\mathrm{Pb_7I_{14}}$ [Figs. 1(b) and 1(c)]. Since the neutral system was found to be electron deficient, analogous to $\mathrm{Pb_6I_{12}}$, two electrons were added to the cluster. A geometry and electronic state optimization of the first [Fig. 1(b)] resulted in a 20% contraction and 10% expansion of interlayer and intralayer distances, respectively, relative to bulk $\mathrm{PbI_2}$. The lowest 11 states (the energy for each of which corresponds to the weighted mean of the energies of all the pure spin multiplets for that particular electron configuration) are nearly monotonically distributed for the five-layered cluster, as shown in Table I. On the other hand, bandlike behavior is observed when the interlayer distances are expanded by 60% and lateral dimensions are contracted by 10% relative to the bulk crystal. Energy gaps of 2.7 eV and higher may be attributed to quantum

TABLE II. Population analysis for the lowest-energy states of $\mathrm{Pb}_x\mathrm{I}_{2x}$ clusters (Ref. 22).

Cluster	Atom	Charge/atom[a] (Equil.)	Charge/atom[a] (Expanded Z)
$\mathrm{Pb_6I_{12}}^{2-}$ [b]	Pb_A	0.81	0.57
	Pb_C	0.69	0.67
	I_A	−0.44	−0.33
	I_C	−0.64	−0.62
$\mathrm{Pb_7I_{14}}^{2-}$ [c]	Pb_0	1.01	−0.29
(five layers)	Pb_B	0.80	0.55
	I_A	−0.41	−0.15
	I_C	−0.59	−0.51
	I_D	−0.93	−0.53
$\mathrm{Pb_7I_{14}}^{2-}$ [d]	Pb_0	0.08	−0.49
(three layers)	Pb_B	0.80	0.67
	I_A	−0.53	−0.45
	I_C	−0.53	−0.45
	I_D	−0.26	−0.05

[a] Electron units.
[b] See Fig. 1(a).
[c] See Fig. 1(b).
[d] See Fig. 1(c).

size effects, which are responsible for blueshifts in the spectrum. The predominant interlayer interactions occur among the Pb layer, I_A and I_D [Table II and Fig. 1(b)], and a comparison of charge/atom values for the ground state and the corresponding values for each of the excited states at both geometries indicates that all of the transitions involve both Pb and I orbitals.

The second Pb_7I_{14} cluster studied, which contains three layers [Fig. 1(c)], was also found to be electron deficient. Consequently, a doubly charged anion was investigated. Initial intralayer atomic distances for this cluster corresponded to those in the bulk crystal,[18] although interlayer atomic distances differed from those of the bulk due to the positioning of the hexagonal layers. Upon optimization it was found that the lowest-energy geometry of $Pb_7I_{14}{}^{2-}$ corresponds to a 2.2% lateral contraction and a 38.7% vertical expansion relative to the bulk lattice constants. The cluster was also studied at a geometry corresponding to a 60% vertical elongation and a 20% lateral contraction. These percentages were chosen from a series of calculations analogous to those on $Pb_6I_{12}{}^{2-}$. A total of ten electron configurations were studied for the anion at both the equilibrium geometry and at an expanded interlayer separation. The energies of these states appear in Table I (dashed lines indicate energies greater than 5 eV). As for the five-layered cluster, the states correspond to the weighted mean of all the multiplets for a particular electron configuration. Clearly, the system exhibits a bandlike behavior (Table I). The first excited state at 0.68 eV corresponds to a single electron transition. The next three states (1.54–1.83 eV) are double excitations from the ground state, while states 6 and 7 (2.19–2.39) correspond to single excitations. The remaining states (3.29 eV and higher), which are higher lying than the bulk-energy band gap, correspond to double excitations from the ground state. It is noteworthy that elongated $Pb_7I_{14}{}^{2-}$ exhibits energy gaps of 3.17, 4.67, and 4.75 eV, which may be attributed to quantum size effects, as suggested by Sandroff, Hwang, and Chung (3.42, 3.95, and 4.80 eV).[23]

Charge/atom values for all Pb_7I_{14} clusters studied (Table II) indicate that the interlayer interactions involve both types of Pb and I atoms in each layer [Figs. 1(b) and 1(c)]. The center lead (Pb_0) and the center iodines (I_D) are especially affected by interlayer perturbations since the charge on these shifts by as much as 1.3 electrons (for Pb_0) in the case of five-layered $Pb_7I_{14}{}^{2-}$. The largest perturbations are expected for these atoms, however, since they lie along a symmetry axis and therefore experience the greatest number of nearest-neighbor interactions. Pb_0, in fact, is positioned at the center of symmetry. Although not tabulated, there are also significant differences (as large as 0.6) between charge/atom values for the lowest-energy state and the corresponding values for each of the higher-energy states of the Pb_7I_{14} anionic cluster at the two geometries listed in Table II, further indicating that the electron excitations in these clusters involve both the Pb and I layers.

Our findings regarding the reduction of in-plane lattice constants when interlayer distances are expanded from their equilibrium values aid in the understanding of recent scanning tunneling microscope (STM) images of layered BiI_3 clusters.[17] (These layered semiconductors are very similar chemically to those of PbI_2 and both systems have been studied experimentally.[11]) In that study, atomically resolved images showed structures having honeycombed symmetry after colloidal suspensions of BiI_3 were evaporated onto graphite surfaces. Since the central bismuth plane in BiI_3 has honeycombed symmetry (in contrast to the hexagonal symmetry of the iodine planes), the STM images are most likely individual bismuth atoms. Interestingly, the lattice constant of these putative $Bi_{10}I_{30}$ clusters was measured to be 0.65 nm, roughly 20% smaller than the bulk in-plane lattice constant. Hence, these STM images could be revealing clusters whose topmost layer of iodine has been removed or displaced from its underlying bismuth plane. Chemical oxidation or cluster-tip interactions could be responsible for these large perturbations.

The research at Stevens was supported in part by Bellcore, the National Science Foundation under Grant No. CHE-8912674, an allocation of supercomputer time at the Pittsburgh Supercomputing Center, and the Air Force Office of Scientific Research.

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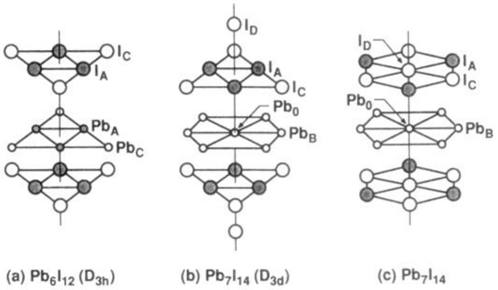

FIG. 1. Pb_xI_{2x} clusters ($x=6,7$).