The structural and electronic properties of germanium clathrates

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The structural and electronic properties of germanium clathrates \( \text{Ge}_{46} \) and \( \text{K}_{8}\text{Ge}_{46} \) are studied by first principles calculations within the local density approximation. The equilibrium structures are obtained by \textit{ab initio} pseudopotential calculation combined with dynamic minimizations. The clathrate structure is found as a low energy phase for germanium. The electronic band structures for \( \text{Ge}_{46} \) clathrates are calculated and the band gap is found to be considerably larger than that of the diamond phase. Due to the effect of pentagonal rings, strong similarity in electronic properties between clathrate and \( \text{Ge}_{24} \) fullerene structure are found. The effect of doping clathrate cages with metal atoms are examined. The \( \text{K}_{8}\text{Ge}_{46} \) clathrate is found to be metallic with the conduction bands only slightly modified by K dopants.

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I. INTRODUCTION

The Si and Ge clathrates can be viewed as covalent fullerene solids which is composed of three-dimensional networks of fullerene cages connected by face sharing. The silicon clathrate compounds \( \text{M}_{x}\text{Si}_{46} \) and \( \text{M}_{x}\text{Si}_{136} \) (\( \text{M}=\text{Na}, \text{K}, \text{Rb}, \text{and Cs} \)) were first synthesized in 1965.\(^1\) The structures of semiconductor clathrates can be classified into two cubic structural types with 46 atoms or 136 atoms per unit cell.\(^1\) As shown in Fig.1, the type I clathrate (Clathrate-46) is formed by two smaller 14-face pentagonal dodecahedra (12 five-fold rings, \( I_h \)) and six larger 16-face tetrakaidecahedra (12 five-fold rings and 2 six-fold rings, \( D_{6d} \)). The structure of type II clathrate (Clathrate-136) consists of sixteen smaller pentagonal dodecahedra (12 five-fold rings, \( I_h \)) and eight larger hexakaidecahedra (12 five-fold rings and 4 six-fold rings, \( T_d \)). Electronic structure calculations based on different methods have shown that these two open network structures have similar electronic properties.\(^2\)

The research interests of semiconductor clathrates come from several aspects: (1) possible alteration of electronic structures and energy gap from standard diamond form,\(^2\)\(^3\)\(^4\)\(^5\), (2) metal-insulator transition in \( \text{M}_{x}\text{Si}_{136} \) with different concentration of metallic impurity,\(^6\)\(^7\)\(^8\)\(^9\)\(^10\), (3) the finding of superconductivity behavior in \( \text{Na}_{x}\text{Ba}_{y}\text{Si}_{46x} \), (4) candidate for thermoelectric applications,\(^11\)\(^12\)\(^13\)\(^14\)\(^15\) (5) template to from three dimensional arrays of nanosized clusters,\(^16\) (6) similarity in structural and electronic properties between semiconductor clathrates and nanoclusters,\(^17\)\(^18\)\(^19\)\(^20\)\(^21\).

There are lots of the experimental and theoretical studies on \( \text{Si}_{46} \) and \( \text{Si}_{136} \) clathrates and their compounds.\(^1\)\(^2\) The structural, electronic and vibrational properties of Si clathrates are investigated through various theoretical levels ranging from \textit{ab initio} to tight-binding and empirical potential.\(^1\)\(^2\)\(^3\)\(^4\)\(^5\)\(^6\)\(^7\)\(^8\)\(^9\)\(^10\) The most interesting result from those calculations is that the band gap is about 0.7 eV higher than that of diamond phase. Experimental works on Si clathrates include resistivity and magnetization\(^1\)\(^2\)\(^3\)\(^4\)\(^5\), transport properties\(^1\)\(^2\)\(^3\)\(^4\)\(^5\), photoemission spectroscopy\(^4\)\(^5\)\(^6\), NMR\(^7\)\(^8\)\(^9\)\(^10\), Raman\(^11\)\(^12\)\(^13\)\(^14\)\(^15\), ESR\(^20\)\(^21\), neutron scattering\(^21\), etc.

In contrast to the intensive studies on silicon clathrates, our current knowledge on germanium clathrates is rather limited. Recently, the germa-
nium clathrate compounds such as $K_8Ge_{46}$, $Rb_xGe_{46}$, $Na_xGe_{136}$, $Cs_8Na_{16}$ have been synthesized and their structures are analyzed with X-ray diffraction. An empirical potential calculation has been performed on pure germanium clathrates. However, there is no first principles electronic structure calculation and their fundamental electronic properties are still unclear theoretically. In this work, we report results of first principles study on the structures and electronic properties of $Ge_{46}$ and $K_8Ge_{46}$ clathrates. The equilibrium structure, electronic band and band gap, electronic density of states and electron density distribution are obtained and discussed.

II. COMPUTATIONAL METHODS

First principles SCF pseudopotential method is used to perform static calculation on the electronic structures and total energy of $Ge_{46}$ and $K_8Ge_{46}$ in ideal clathrate structures with different lattice constants. The ion-electron interaction is modeled by numerical BHS norm-conserving nonlocal pseudopotential in the Kleinman-Bylander form. The Ceperley-Alder’s exchange-correlation parameterized by Perdew and Zunger is used for the LDA in our program. The kinetic energy cutoff for plane-wave basis is chosen as 12 Ryd. Ten symmetric $k$ points generated in Monkhorst-Pack spirit are employed to sample the Brillouin zone.

From the static calculation, the equation of states with ideal crystal structures and the equilibrium lattice constants are obtained. These ideal structures are further optimized by using structural minimization via conjugate gradient technique (CASTEP). The CASTEP program is based on plane-wave pseudopotential technique. It can relax the atomic position by computing the force acting on atoms from electronic calculation and moving atoms efficiently in a numerical way.

III. THE STRUCTURES AND BAND GAPS OF $Ge_{46}$

In Fig.2, we present the equation of states for both $Ge_{46}$ clathrate and diamond phase that is obtained from first principles static calculations. We find that the $Ge_{46}$ clathrate is a locally stable structure and its energy is only about 0.08 eV per atom higher than that of diamond phase. For comparison, the $\beta$-tin phase of germanium is about 0.25 eV higher in energy than the diamond phase. The low energy feature of clathrate phase is a natural consequence of its four coordinate characteristics and may be partially attributed to the softness of the bond-bending distortion modes. As compared to diamond structure, the volume per atom in the clathrate phase is increased by about 14.8%. All of these results are very close to the previous empirical potential simulation on $Ge_{46}$, in which the change of atomic volume in type I clathrate is 15.3 % and its energy is 0.071 eV per atom higher than diamond.
In previous theoretical study on bulk silicon and germanium of various phases, \cite{24} considerable similarity in the bonding behavior and phase diagram are found between silicon and germanium. In Table I, we summarize our results on the structural properties and band gaps for perfect and relaxed \( \text{Ge}_{46} \) and \( K_8 \text{Ge}_{46} \) clathrate and compare them with the previous LDA and tight-binding calculations on \( \text{Si}_{46} \) clathrate \cite{2,3,9}. We find the difference of volume and energy between clathrate and diamond phase for germanium and silicon are comparable.

The ideal clathrate structure for the \( \text{Ge}_{46} \) at equilibrium lattice constant is further optimized with CASTEP plane-wave pseudopotential calculation. Both atomic positions and unit cell parameters are allowed to relax. The SCF pseudopotential code used in static calculation has also been used to test the total energy for the initial and final structure and the results agree with CASTEP calculations. After optimization, the lattice constant of simple cubic unit cell decreases from 10.43 \( \text{Å} \) to 10.37 \( \text{Å} \). The relative atomic positions are only slightly relaxed from their initial configuration. The range of bond length distribution has also been narrowed, i.e., from the 2.375 \( \text{Å} \) \( \sim \) 2.540 \( \text{Å} \) in ideal clathrate structure to 2.38 \( \text{Å} \) \( \sim \) 2.433 \( \text{Å} \).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.pdf}
\caption{Energy per atom of diamond and \text{Ge}_{46} clathrate as a function of atomic volume.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.pdf}
\caption{(a) Electronic band structure for \( \text{Ge}_{46} \), (b) \( K_8 \text{Ge}_{46} \) clathrate near Fermi level.}
\end{figure}

The electronic band structure calculations are carried
out for Ge$_{46}$ clathrate with the equilibrium structure. The near band-gap band structures for the minimum energy configurations of Ge$_{46}$ clathrates are plotted in Fig.3(a). Both the valence band maximum and conduction band minimum are located on the $\Gamma$ to $X$ line and they are very close in $k$ space. An indirect gap of 1.46 eV is found. As for bulk germanium in diamond phase, our calculations have yielded an indirect band gap of 0.40 eV between $L$ and $\Gamma$ points. The underestimation of band gap is a common feature of LDA calculations. Nevertheless, our current results suggest that the band gap of Ge$_{46}$ phase is about 1 eV higher than that of the diamond phase, which is similar to the 0.7 eV increment in band gap found for Si$_{24}$ and Si$_{34}$ clathrates. Furthermore, the electronic band structure of Ge$_{46}$ clathrate is calculated independently via a simple tight-binding model. The tight-binding hopping parameters for germanium are taken from Ref.[32] and the parameters for nearest neighboring atoms in clathrate structure is assumed to be the same as that in diamond. According to tight-binding calculation, the band gap of diamond is 1.13 eV and the gap for relaxed clathrate Ge$_{46}$ is 2.93 eV. Although the tight-binding method usually overestimate the band gap of a system, the increment of 1.80 eV in the band gap from tight-binding model is in reasonable agreement with ab initio calculation. Therefore, we expect that the true increase of band gap $\Delta$ from diamond to Ge$_{46}$ clathrate phase might be between the LDA and TB prediction, i.e., $1.06 \text{ eV} \leq \Delta \leq 1.80 \text{ eV}$. This result suggests that the clathrate materials might be useful in the new electronic and optical application in the future.

Since the Ge$_{46}$ clathrate structure is essentially a 3D network composed by Ge$_{20}$ and Ge$_{24}$ cages with face sharing, it is interesting to compare the electronic properties of the individual Ge$_{20}$ and Ge$_{24}$ cages with that of the clathrate. SCF pseudopotential electronic structure calculations on isolated Ge$_{20}$ and Ge$_{24}$ clusters in fullerene cages are performed. The clusters are placed in a large simple cubic supercell with length of 28 a.u. In Fig.4, we present the calculated electronic density of states (DOS) for Ge$_{20}$ and Ge$_{24}$ cages along with DOS for diamond and Ge$_{46}$. The detailed analysis are given in the following.

**FIG. 4.** Electronic density of states (DOS) of Ge$_{20}$, Ge$_{24}$ fullerene, bulk germanium in Ge$_{46}$ clathrate and diamond phases Gaussian broadening of 0.136 eV is used.

Firstly, we find that most of the peaks in the DOS of Ge$_{46}$ can be assigned to Ge$_{24}$, while the DOS of Ge$_{20}$ also show some similarity with Ge$_{46}$. The DOS of Ge$_{24}$ is closer to that of clathrate because most atoms in clathrate are associated with Ge$_{24}$ cage. The presence of s-p gap in due to the large number of five-member rings in the cage and clathrate structure. This remarkable similarity implies that the Ge$_{46}$ clathrate can be taken as the small Ge fullerene assembled solid with both geometrical and electronic hierarchy. However, both the Ge$_{24}$ and Ge$_{20}$ cages are not semiconductor systems and do not have open band gaps like Ge$_{46}$ clathrates. The band splitting in Ge$_{46}$ can be attributed to the sharing of face atoms by Ge$_{20}$ and Ge$_{24}$ and the interaction between neighboring fullerene cages.

On the other hand, we can compare the DOS of clathrate and diamond in Fig.4. Several significant differences can be found. Besides the improvement of band gap in clathrate upon diamond phase, the total width of valence band of Ge$_{46}$ (about 12 eV) is narrower than that of diamond (about 13 eV). This phenomenon has been also predicted in Si$_{16}$ clathrate and observed experimentally. We also found a gap opening between the s-like and p-like states in the case of Ge$_{46}$ clathrates as well as Ge$_{20}$, Ge$_{24}$ clusters, while s and p states are overlapped in the DOS of diamond. These remarkable differences in the electronic structure of clathrate and diamond can be understood by the large portion of five-
fold ring in clathrate structure. In the diamond lattice consisting of 100% six-fold ring, the 4s orbital can form complete antibonding states, which can distribute to high energy and overlap with the lower 4p-like states. In contrast to diamond, the Ge46 clathrate is composed of 87% five-fold rings and 13% six-fold rings. In the five-fold ring, 4s orbital cannot form complete antibonding states so that the top of 4s-like states is still lower in energy than the bottom of 4p-like and a gap between s and p states inside valence band opens. The similar effect of five-fold ring on the 4p bonding orbitals will induce the incompleteness of 4p-like states. As a consequence, the valence band top of Ge46 is lower than that of diamond, which corresponds to the narrowing of valence band width and broadening of fundamental gap between valence and conduction band. The novel electronic properties caused by five-fold ring and the similarity between clathrate and fullerene cages may be explored for future electronic and optical applications.

IV. ELECTRONIC STRUCTURES OF K8GE46 CLATHRATE

Although the pure silicon and germanium semiconductor clathrates are predicted to be locally stable, experiments have only synthesized the metal-doped clathrate compounds of Si and Ge. The metallic impurity atoms inside the clathrate might influence the electronic properties of clathrate due to the interaction between the metal atoms and semiconductor skeleton. Here we have chosen the K8Ge46 clathrate as such a model system to study the doping effect on germanium clathrate.

The structural properties of K8Ge46 are studied with the same procedure we have applied on Ge46 clathrate: a static calculation of equation of states followed by a full relaxation. The minimized structure of K8Ge46 clathrate is shown in Fig.1 and the structural parameters of this minimum energy configuration is given in Table I. It is natural to find that the lattice constant of cubic unit cell for K8Ge46 is larger than pure Ge46 in both ideal and relaxed structure because of the K atoms inside the fullerene cage. We also find a decrease of lattice constant from 10.79 Å to 10.45 Å after structure minimization. The minimized lattice constant (10.45 Å) for the K8Ge46 is in good agreement with experimental value (10.66 Å)\textsuperscript{22}. During the minimization, the geometries of K8Ge46 relax from the perfect clathrate network a little more than that happened in the Ge46.

First principles SCF pseudopotential electronic structure calculation has been performed on the relaxed K8Ge46 clathrate. In Fig.3(b), we presented the electronic band structure of K8Ge46 near Fermi level. The system is found as metallic due to the K dopants. We can further examine the highest valence bands and lowest conduction bands of Ge46 and K8Ge46 shown in Fig.3(a) and (b) in detail. The valence bands of K8Ge46 are very closed to the original bands in Ge46, while the conduction band structures have been slightly modified upon the inclusion of K atoms.

![FIG. 5. Electronic density of states (DOS) of Ge46 and K8Ge46 clathrate. Gaussian broadening of 0.136 eV is used. Note the similarity in the two DOS.](image)

We also study the difference of the electronic properties between the pure and doped systems by comparing their the electronic density of states (DOS). The density of states for Ge46 and K8Ge46 clathrate are compared in Fig.5. The DOS of valence electrons in K8Ge46 is very close to that in Ge46 while the DOS for conduction electrons of K8Ge46 are somewhat different from that in Ge46. On the other hand, the gap between valence and conduction band is 0.23 eV narrower in the case of K8Ge46.
The analysis on the charge transfer and chemical bonding effects have been presented in the contour plots of the electron densities of $K_8Ge_{46}$ on the (100) plane in Fig. 6. We have also calculated the charge density distribution of $Ge_{46}$ and find it is very close to that of $K_8Ge_{46}$. As shown in Fig. 6, there is almost no charge sitting on K sites. This result is consistent with previous calculation on Na$_2$Ba$_6$Ge$_{46}$ which found a rather simple charge transfer from Na to the Si skeleton. In their calculation, some hybridization are found between Ba and Si since Ba atoms has some low lying 5$d$ orbitals. This difference also corresponds to the DOS and other electronic properties. A high DOS peak at Fermi energy is found for Na$_2$Ba$_6$Ge$_{46}$ and this material is superconducting. In comparison, the DOS at Fermi level for $K_8Ge_{46}$ is moderate and it is not superconducting.

**V. CONCLUSIONS**

We have used first principles SCF pseudopotential method to investigate the structural and electronic properties of $Ge_{46}$ and $K_8Ge_{46}$ clathrates. The main conclusion of this work can be made as follows:

1. Germanium clathrate $Ge_{46}$ is found to be a locally stable structure with its energy only slight higher than that of diamond phase, and its atomic volume is about 13% larger than diamond phase.

2. $Ge_{46}$ clathrate shows an indirect band gap along $\Gamma$-X direction that is about 1 eV higher than the band gap of diamond phase. The pentagonal rings in the clathrate structure cause the valence band structure of $Ge_{46}$ clathrate to be similar to that of $Ge_{24}$ fullerene cage. The open covalent network structures contribute to the large band gaps.

3. The $K_8Ge_{46}$ clathrate is metallic with a moderate density of states. The valence band structures and DOS are similar to those of the pure $Ge_{46}$, while the conduction bands are modified due to the K dopants. Almost complete charge transfer from K sites to Ge frames is found in the $K_8Ge_{46}$ clathrate.

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