Predictive study of thermodynamic properties of GeC

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Abstract. We present in this paper a molecular dynamics simulation of structural and thermodynamic properties of the hypothetical IV–IV compound GeC in the zinc-blende structure. This study is performed with the use of the well-tested Tersoff potential. Various physical quantities including elastic constants, Debye temperature, thermal expansion coefficient, heat capacity, and Grüneisen parameter are predicted. The comparison with the corresponding results for SiC is also discussed.

1. Introduction

Despite their technological promise, the IV–IV compounds such as SiC, SiGe, and GeC have received considerably less attention than the elemental group IV materials C, Si, and Ge. The complexity of these ‘exotic’ new materials poses a challenge to the theorist aiming to compute the most fundamental of their properties: lattice constants, bulk modulus, cohesive energy, and band gaps.

Several studies of SiC have been reported. The recent growing scientific and technological interest in silicon carbide arises from its peculiar physical properties, i.e., its mechanical, chemical, and thermal stability. In the last few years, the electronic properties of some SiC polytypes have been calculated [1]–[4]. Further studies went deep into the elastic [5] and the optical properties [6], and the high-pressure behaviour [7, 8]. Furthermore, molecular dynamics simulations have been carried out to study the thermomechanical properties of SiC [9].

On the other hand, SiGe does not normally form an ordered compound, but can exist as a random alloy in a cubic structure [10]. Dünweg and Landau [11] have studied the phase

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transition of \( \text{Si}_{1-x}\text{Ge}_x \) alloy using an extensive constant-pressure, semi-grand-canonical Monte Carlo simulation.

Another possible IV–IV compound is \( \text{GeC} \). The existence of this material in its zinc-blende form has not been reported. First \textit{ab initio} investigation \cite{12} shows that \( \text{GeC} \), like \( \text{SiC} \), is a wide-gap semiconductor with an indirect band gap. It is also unstable with respect to decomposition into the bulk forms of its separate constituents. However, amorphous \( \text{Ge}_{1-x}\text{C}_x \) films have been grown with and without hydrogen \cite{13}–\cite{15}. It is believed that these films may have important photovoltaic properties.

The aim of this work is the calculation of the structural and thermodynamics properties of \( \text{GeC} \). We use the new formulation of the Tersoff potential \cite{16} which is well adapted for multicomponent semiconductors with tetrahedral bonds. This model has previously been the most successful one for reproducing many of the elemental semiconductor properties, particularly for silicon \cite{17} and carbon \cite{18}. Our study is also extended to \( \text{SiC} \) in order to check the validity of the approach used.

\section{Simulation details}

Among the many empirical model potentials that have been developed for tetrahedral semiconductors, that of Tersoff has been the most successful as regards reproducing many of elemental semiconductor properties, particularly for silicon \cite{17} and carbon \cite{18}. Another form was developed for multicomponent systems \cite{16} to treat mixtures of these elements. The form of the energy \( E \), between two neighbouring atoms \( i \) and \( j \), is taken to be \cite{16}

\begin{equation}
E = \sum_i E_i = \frac{1}{2} \sum_{i \neq j} V_{ij},
\end{equation}

with

\begin{align*}
V_{ij} &= f_C(r_{ij})[a_{ij}f_R(r_{ij}) + b_{ij}f_A(r_{ij})], \\
f_R(r_{ij}) &= A_{ij} \exp(-\lambda_{ij} r_{ij}), \\
f_A(r_{ij}) &= -B_{ij} \exp(-\mu_{ij} r_{ij}), \\
V_{ij} &= \begin{cases} 
1 & r_{ij} < R_{ij} - D_{ij} \\
\frac{1}{2} - \frac{1}{2} \sin \left[ \frac{\pi}{2} \frac{(r_{ij} - R_{ij})}{D_{ij}} \right] & R_{ij} - D_{ij} < r_{ij} < R_{ij} + D_{ij} \\
0 & r_{ij} > R_{ij} + D_{ij}.
\end{cases}
\end{align*}

\( b_{ij} \) is the many-body order parameter describing how the bond-formation energy is affected by the local atomic arrangement due to the presence of other neighbouring atoms (the \( k \)-atoms). It is a many-body function of the positions of the atoms \( i, j, \) and \( k \). It has the form

\begin{equation}
b_{ij} = \chi_{ij} (1 + \beta^n_{ij} \zeta_{ij})^{-1/2n},
\end{equation}

with

\begin{align*}
\zeta_{ij} &= \sum_{k \neq i,j} f_C(r_{ik}) g(\theta_{ijk}) \exp[\lambda^3_{ij} (r_{ij} - r_{ik})^3] \\
g(\theta_{ijk}) &= 1 + \frac{c_i^2}{d_i^2} - \frac{c_i^2}{d_i^2} + (h_i - \cos \theta_{ijk})^2 \\
a_{ij} &= (1 + \alpha^n \eta_{ij})^{-1/2n},
\end{align*}

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Table 1. The adjusted Tersoff parameters for SiC and GeC in the zinc-blende structure.

|        | SiC          | GeC          |
|--------|--------------|--------------|
| $A$ (eV) | 1597.31      | 1570.12      |
| $B$ (eV) | 404.17       | 381.24       |
| $\lambda$ (Å$^{-1}$) | 2.983 90     | 2.9665       |
| $\mu$ (Å$^{-1}$) | 1.972 05     | 1.9583       |
| $n$    | 0.757 425    | 0.741 89     |
| $\beta$ | $-0.584 415$ | $-0.504 71$ |
| $c$    | 69 219.5     | 72 239.5     |
| $d$    | 10.3005      | 10.018       |
| $R$ (Å) | 2.33         | 2.41         |
| $D$ (Å) | 0.15         | 0.15         |
| $\chi$ | 0.97         | 0.94         |

$\eta_{ij} = \sum_{k(\neq ij)} f_C(r_{ik}) \exp[\lambda_3^3(r_{ij} - r_{ik})^3]$  

$\lambda_{ij} = \frac{(\lambda_i + \lambda_j)}{2}$  \hspace{1cm} (4)  

$\mu_{ij} = \frac{(\mu_i + \mu_j)}{2}$  \hspace{1cm} (5)  

$A_{ij} = (A_iA_j)^{1/2}$  \hspace{1cm} (6)  

$B_{ij} = (B_iB_j)^{1/2}$.  \hspace{1cm} (7)

$\zeta$ is called the effective coordination number and $g(\theta_{ijk})$ is a function of the angle between $r_{ij}$ and $r_{ik}$ that has been fitted to stabilize the tetrahedral structure. We note that $\lambda_3$ and $\alpha$ are put equal to zero [18].

$\chi$ is a parameter which strengthens or weakens the heteropolar bonds, relative to the value obtained by simple interpolation. In the case of GeC, this parameter is fitted to the heat of formation.

Using the above equations (4)–(7), we have calculated the potential parameters for GeC and SiC which are summarized in Table 1. This comparative study is performed in order to test the accuracy of this approach. We then carry out MD simulations within the canonical NVT ensemble. We simulate 216 atoms in a simple cubic simulation cell with periodic boundary conditions. To integrate the Newtonian equations of motion, we use the fifth-order predictor–corrector algorithm with a time step of $2.81 \times 10^{-15}$ s. After 20 000 iterations ($\approx 56$ ps), different average properties are calculated. This method have been extensively used to investigate equilibrium and nonequilibrium properties [19] of GeC. Several studies for the properties of fluids [20, 21], the crystal-to-amorphous transition [22], melting [23], growth mechanisms [24], and radiation damage [25] have been made using molecular dynamics simulations.

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Figure 1. The pair correlation function for GeC in the zinc-blende structure.

Table 2. Peak distances and numbers of pairs for cubic GeC in the zinc-blende structure.

| Peak | Distance (Å) | Number of pairs |
|------|--------------|----------------|
| 1st  | 1.918\textsuperscript{a}, 1.944\textsuperscript{b} | 4.00\textsuperscript{a} |
| 2nd  | 3.131\textsuperscript{a}, 3.174\textsuperscript{b} | 12.04\textsuperscript{a} |
| 3rd  | 3.677\textsuperscript{a}, 3.722\textsuperscript{b} | 12.04\textsuperscript{a} |
| 4th  | 4.437\textsuperscript{a}, 4.490\textsuperscript{b} | 6.02\textsuperscript{a} |

\textsuperscript{a} Present work.
\textsuperscript{b} Calculated from the \textit{ab initio} result taken from [12].

3. Numerical results

3.1. Structural properties

The first step of our study is to examine the structural properties of cubic GeC at $T = 300$ K using the potential parameters obtained, listed in table 1. We calculate the pair distribution function $g(r)$ for cubic GeC in the zinc-blende structure. The fourth peaks appear at 1.918, 3.131, 3.677, and 4.437 Å (see figure 1) which is in good agreement with \textit{ab initio} results[12]. These results are summarized in table 2.
Figure 2. Cohesive energy as a function of volume for the zinc-blende structures of GeC and SiC.

Figure 2 displays the cohesive energy versus volume for GeC and SiC in the zinc-blende structure. The curves are fitted to the equation of state of Murnaghan [26] from which we obtain the equilibrium lattice parameter, the bulk modulus, its derivative, and the cohesive energy. The results are given in table 3 along with the experimental measurements [5, 27], ab initio calculations [12, 28, 38], and results of atomistic simulations using the molecular dynamics method [9]. We notice that the lattice parameter for the zinc-blende structure for both SiC and GeC is in excellent agreement with other results [9, 12, 27, 28] (with an accuracy of 0.4–1.3% for SiC and 1–2% for GeC). For the cohesive energy, the accuracy is about 0.3%. From figure 2, we notice that SiC is more stable than GeC. In order to consider the structural stability of the zinc-blende GeC compound, we calculate the excess energy per atom $\Delta E(AB)$ of the compound AB:

$$
\Delta E(AB) = E(AB) - \frac{(E(A) + E(B))}{2}
$$

where $E(AB)$ is the energy per atom for the compound, and $E(A)$ and $E(B)$ are the energies per atom of the elemental solids. For SiC, $\Delta E(\text{SiC})$ is negative and is equal to $-0.32$ eV, indicating that the compound SiC is stable against decomposition into elemental solids. However, for GeC, $\Delta E(\text{GeC})$ is positive and is equal to $+0.16$ eV, which means that GeC is unstable against decomposition into its separate components. We notice that our results agree well with the ab initio calculations of Sankey et al [12]. They found that $\Delta E(\text{SiC}) = -0.30$ eV and $\Delta E(\text{GeC}) = +0.18$ eV.
Table 3. Equilibrium properties of SiC and GeC in the zinc-blende and rock-salt phases.

|                | SiC            |                                  | GeC            |                                  |
|----------------|----------------|----------------------------------|----------------|----------------------------------|
|                | Zinc-blende    | Rock-salt                        | Zinc-blende    | Rock-salt                        |
|                | Present | Calc. | Expt | Present | Calc. | Present | Calc. | Present |
| Lattice constant (Å) | 4.30  | 4.32<sup>c</sup> | 4.36<sup>a</sup> | 4.13  | 4.25<sup>f</sup> | 4.03<sup>h</sup> | 4.431 | 4.526<sup>d</sup> | 4.49<sup>e</sup> | 4.25  |
|                | 4.33<sup>d</sup> | 4.35<sup>i</sup> |                | 4.25<sup>b</sup> | 4.25  | 1.62  |                | 1.88  | 1.88<sup>d</sup> | 2.18<sup>e</sup> | 1.33  |
|                | 2.29<sup>d</sup> | 2.22<sup>i</sup> |                | 2.25<sup>b</sup> | 1.62  |                | 3.45  |                | 4.42  |          |
|                | 3.90<sup>c</sup> | 3.94<sup>e</sup> | 4.11<sup>c</sup> | 4.36  | 3.45  |                |        |                |          |          |
|                | 3.80<sup>i</sup> |                |                |        |        |                |          |                |          |          |
| Cohesive energy (eV/atom) | −6.32 | −6.18<sup>c</sup> | −6.34<sup>a</sup> | −5.16 | −5.4626 | −4.3977 |        |                |          |          |
|                | 3.29  | 4.36<sup>c</sup> | 3.60<sup>b</sup> | 2.97  |        |                |          |                |          |          |
|                | 4.20<sup>f</sup> |                |                |        |        |                |          |                |          |          |
|                | 1.65  | 1.20<sup>c</sup> | 1.50<sup>b</sup> | 1.24  |        |                |          |                |          |          |
|                | 1.63  | 2.55<sup>c</sup> | 1.50<sup>b</sup> | 1.41  |        |                |          |                |          |          |
|                | 2.6<sup>f</sup> |                |                |        |        |                |          |                |          |          |

<sup>a</sup> Reference [27].  
<sup>b</sup> Reference [5].  
<sup>c</sup> Reference [9].  
<sup>d</sup> Reference [28].  
<sup>e</sup> Reference [12].  
<sup>f</sup> Reference [16].  
<sup>g</sup> Reference [30].  
<sup>h</sup> Reference [7].  
<sup>i</sup> Reference [38].

On the other hand, we have determined the elastic constants ($C_{11}$, $C_{12}$, and $C_{44}$) using the method discussed in detail in [29]. Results are presented in table 3. A good agreement is obtained between the present results for SiC and experimental data [5]—better than that between other calculations using the same model based on other approaches [9]–[16, 30].

In order to test the transferability of the Tersoff potential, our study is extended to simulate both SiC and GeC under the application of high pressure. We display in figure 3 the curves representing the cohesive energy versus volume for SiC and GeC in the high-pressure NaCl phase, obtained using the same set of parameters. The calculated equilibrium lattice constant for...
the SiC compound is 4.13 Å. This is in agreement with the value of 4.03 Å from the first-principles work of Chang and Cohen [7]. The discrepancy is 2%, which is less than the one found from the Tersoff’s results (5%) [16]. The equilibrium energy of the rock-salt phase is 1.1 eV/atom higher than for the zinc-blende structure, compared to 0.7 from LDA calculation. Our results give an error of 6% for the cohesive energy compared to 12% for Tersoff’s calculations [16]. For GeC, a lattice parameter of 4.25 Å and the bulk modulus equal to 1.33 Mbar are obtained. The equilibrium energy is equal to 1.07 eV/atom, which is higher than that for the zinc-blende structure and is close to the value found for SiC. As a first conclusion, we can say that GeC may have interesting elastic properties which are close to those found for the SiC compound under pressure.

3.2. Thermodynamic properties

In this section, we will focus on the calculation of some thermodynamics quantities not known for GeC, such as the thermal expansion, specific heat, and Debye temperature. Since the molecular dynamics method treats the motion of the atoms classically, it will correctly determine the thermal expansion coefficient ($\alpha$) and the specific heat ($C_v$) only above the Debye temperature, where quantum effects can be neglected. The quantum mechanics corrections will be important for thermodynamic quantities such as specific heat and thermal...
expansion below the Debye temperature $\theta_D$. To the best of our knowledge, there are no measurements or calculations of the Debye temperature in the literature. Therefore, using the empirical equation taken from [35] which relates the Debye temperature to the bulk modulus $B$:

$$\theta_D = 24.0062 + 0.42939 B$$ (9)

we calculate $\theta_D = 990.13$ K for SiC, which is in good agreement with the measured value of 1080 K [36] with an accuracy of 5%, and then we obtain that $\theta_D = 831$ K for GeC.

The linear thermal expansion coefficient $\alpha_l$ can be computed directly from the slopes of the following equations; a molecular dynamics simulation was performed in an $NVT$ ensemble at each temperature to equilibrate the system and then to determine the corresponding zero-pressure lattice constant:

$$a(T) (\text{Å}) = 4.3035 + 3 \times 10^{-5} \times T \quad \text{for SiC}$$ (10)

$$a(T) (\text{Å}) = 4.3001 + 4 \times 10^{-5} \times T \quad \text{for GeC.}$$ (11)

The linear thermal coefficient $\alpha_l$ determined from equation (10) is $6.9 \times 10^{-6}$ K$^{-1}$ for SiC at $T = 1200$ K. This value is in reasonable agreement with experimental results [37] and the results obtained by Karch et al from first-principles calculations [38]. They found that $\alpha_l$ is of the order of $6 \times 10^{-6}$ K$^{-1}$ at high temperature (above 1200 K). For GeC, we found from equation (11) that $\alpha_l = 8 \times 10^{-6}$ K$^{-1}$ above 1000 K. We point out that the thermal expansion coefficient of SiC is smaller than those of GeC and other semiconductors such as AlN, BP, GaP, Si, and Ge; only diamond and BN have (slightly) smaller values [39, 40].

From the slope of the energy versus temperature curve, we estimate the specific heat of the system to be $C_v \approx 3.1k_B$ at high temperatures. This constant value corresponds to the classical Dulong–Petit prediction ($3k_B$), which is followed at high temperatures for all solids.

The thermal expansion coefficient $\alpha$ and the specific heat at constant volume $C_v$ are related by

$$\alpha = \frac{\gamma C_v}{3BV}$$ (12)

where $\gamma$ is a weighted-average Grüneisen parameter which measures the variation of pressure with internal energy at constant volume $V$. For temperatures above the Debye temperature, $\gamma$ is constant. From equation (12), we calculate the Grüneisen parameter, which is equal to 1.08 for SiC and 1.1 for GeC. These results are close to that found for carbon [41] rather than those for silicon [42] or germanium [43] at high temperatures. This means that the carbon atoms influence the physical properties of SiC and GeC much more strongly than silicon or germanium atoms.

### 4. Conclusions

In conclusion, we have presented a molecular dynamics study carried out to investigate the structural properties of GeC using a Tersoff potential, for the first time. Our calculations show that GeC is unstable against decomposition into its separate components, and that this model is transferable. Various unknown thermodynamical quantities have been predicted, such as the Debye temperature, thermal expansion coefficient, heat capacity, and Grüneisen parameter.
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