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First-principles analysis of electronic, vibrational and thermodynamic properties of type II SiGe alloy clathrates

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We have performed electronic, vibrational and thermodynamic studies of Type-II silicon-germanium clathrate alloys, namely, Si\(_{136}\)Ge\(_x\) (0 < x ≤ 128), using periodic density functional theory (DFT) computations. Our calculated lattice constant for various stoichiometric amount, namely, x, of Ge shows similar agreement with the observed X-ray diffraction (XRD) data, along with monotonically increasing dependence on x. According to our bandgap energy calculation via Vienna \textit{ab initio} simulation package (VASP), Si\(_{136}\)Ge\(_x\) has an optical “quasi-direct” bandgap of approximately 1.27 eV, which agrees well with our previous DFT result (≈1.23 eV), which was obtained using the Cambridge sequential simulation total energy package (CASTEP) code. Most of our first-principles calculations focus on exploring the low-energy transverse acoustic (TA) phonons that contribute dominantly to the induction of negative thermal expansion (NTE) behavior. Moreover, our theoretical work has predicted that the Si\(_{110}\)Ge\(_{32}\) framework exhibits NTE in the temperature range of 3 – 80 K, compared to the temperature regime (10 – 140 K) of NTE observed in “guest-free” Si\(_{136}\). It is posited that the increased number of Ge-Ge bonds may weaken the NTE effect substantially, as the composition, which is denoted x, in Si\(_{136-x}\)Ge\(_x\), is elevated from 32 (or 40) to 96 (or 104).

Recently, clathrate alloys have attracted wide research attention, which are a class of materials that possess a crystalline framework that is composed of more than one Group IV element (e.g., Si, Ge and Sn). In this paper, the study of “guest-free” clathrates that are based on a mixture of Si and Ge is of great importance. Our calculational work is centered on these semiconducting compounds, which have technological potential in both optical and electrical applications.\(^{13-26}\) The SiGe binary clathrate compounds that contain metallic fillers in the endohedral sites of the polyhedron cage have been experimentally studied by Herrmann et al.\(^{27}\) In addition, K. Moriguchi et al. has investigated the energetics and electronic properties of the Si\(_{136-x}\)Ge\(_x\) (0 ≤ x ≤ 136) system via first-principle codes.\(^{28}\) Their work predicts direct and “quasi-direct” wide band gap whose value ranges from 1.2 to 2.0 eV according to the Ge content. We adopted their atomic compositions of Si\(_{136}\)Ge\(_0\) to consider a full symmetry structure with equivalent Wyckoff sites, thereby facilitating the smooth initiation of our DFT calculations. Moreover, the physical origin of the low-temperature negative thermal expansion in Si\(_{136}\)Ge\(_x\) (0 ≤ x ≤ 128) remains ambiguous and is under discussion.\(^{29,30}\) To the best of our knowledge, one primitive model that has been applied to theoretically survey anharmonic thermodynamics that correspond to NTE behavior exploits the volume-dependent mode Grüneisen parameter, which quantifies the deviation of the collective vibration of the lattice structure from simple harmonic oscillations. The measured shift of Raman lines under varied pressure also provides an experimental approach for examining the Grüneisen parameters when they are related to low-lying optical and acoustic modes of Na\(_{136}\)Si\(_{32}\).\(^{12}\)

In this work, we present an \textit{ab initio} computational study on vibrational and thermal properties and their intrinsic relations to the finite-\(T\) NTE phenomenon based on the optimized geometry of Si\(_{136}\)Ge\(_x\) with respect to various stoichiometric compositions. The quasi-harmonic approximation (QHA) method is the most effective tool, which considers only the volume dependence of phonon anharmonicity and assumes that the temperature has a negligible effect on the phonon vibrational frequencies in the case of thermal expansion. Our calculated negative mode Grüneisen parameters, which are calculated according to \(\gamma = -\beta\ln\theta/\partial\ln\theta^2\) and derived predominantly from heat-carrying transverse acoustic (TA) phonons that are located within the Brillouin zone (BZ), indirectly demonstrate the occurrence of NTE behavior. Here, vibrational mode frequencies \(\omega_\alpha\) depends on volume \(V\) according to QHA. Furthermore, these first-principles results on \(\gamma\) remain to be comparable to the experimental Raman data.\(^{31,32}\) The finite difference method

INTRODUCTION

In contrast to the diamond phase of silicon (\(d\)-Si), there are two forms of crystalline clathrate: Si\(_6\) (Type I) and Si\(_8\) (Type II). Each of these pure materials consists of a covalently bonded framework that is composed of polyhedron cage elements. The enlarged unit cell of the Type II clathrate framework contains 136 atoms, exhibits a face-centered cubic (FCC) lattice structure and contains 20- and 28-atom cages that are connected periodically in a 4:2 ratio.\(^{1}\) Growing interest in this expanded-volume silicon has arisen for two main reasons: the confirmed existence of superconductivity in metal-doped clathrate, namely, Ba\(_{38}\)Na\(_{58}\)Si\(_{136}\),\(^{2-4}\) and the massive studies that have been conducted on efficient thermoelectric (TE) performance with guest-filled Si clathrates, which display glass-like thermal conductivity while behaving as a crystalline-cubic material.\(^{5,6}\) Specifically, the efficiency of a TE device is manifested by material’s figure-of-merit, \(ZT = \sigma^2S^2T/\kappa\), where \(\sigma\) denotes the electrical conductivity, \(T\) is the absolute temperature, and \(\kappa\) is the thermal conductivity. An effective way of enhancing \(ZT\) is through reducing the phonon thermal conductivity by nanostructuring,\(^{7,8}\) alloying,\(^{9,10}\) or introducing cage-like configuration that encapsulates rattling atoms, such as Si\(_8\) or Ge-based clathrate compounds.

At present, many reports have discussed the electronic and thermodynamic properties of Si- and Ge-based Type II clathrate compounds,\(^{11-16}\) with the objectives of identifying prominent TE materials and gaining insight into interesting properties such as anomalous thermal expansion. One characteristic of the ideal TE candidate is minimal “glass-like” lattice thermal conductivity, which can originate from the scattering of acoustic phonons by the guest atoms\(^{17,18}\) while satisfying the “Phonon Glass Electron Crystal” (PGEC) paradigm, which was proposed by G. A. Slack.\(^{19,20}\) Motivated by this concept, work on the Si-based Type II materials, namely, Cs\(_6\)Ga\(_{28}\)Si\(_{136}\) (Rb\(_6\)Ga\(_{28}\)Si\(_{136}\)) and Ge-based Type I materials, namely, Ba\(_{38}\)Ga\(_{28}\)Ge\(_{32}\) (Ba\(_{38}\)Ga\(_{28}\)Si\(_{25}\)), has been presented by K. Biswas et al., in which the existence of the very low frequency rattling modes of guests, which contribute to the suppression of the phonon thermal conductivity, are demonstrated.\(^{11,12}\) In addition, using density functional theory (DFT) within the local density approximation (LDA) approach, X. Tang et al. examined the thermal properties of the pure Si\(_{136}\) framework (which is sometimes denoted as Si\(_{3136}\)) and reported the negative thermal expansion (NTE) phenomenon in the temperature range of 10 – 140 K in experimental as well as theoretical manner.\(^{21}\)
(FDM) is utilized to estimate the above lattice dynamics quantities at $T = 0$, which explain how volume dilation results in varied dynamical matrix elements of phonons that are subjected to different bands. For instance, contraction of our supercell model yields larger mode frequencies of the longitudinal acoustic (LA) phonon and transverse optic (TO) phonon, which are located at the BZ boundary (X or L point). In addition, we report a theoretical analysis of the electronic properties of Si$_{136}$Ge$_x$ clathrates. Our calculated lattice constant values, along with the optical band gap as a function of the Ge concentration which was normalized, correlate well with data that were recently obtained using an X-ray diffraction (XRD) instrument.

**COMPUTATIONAL APPROACH**

Our first-principles calculations are conducted using the Vienna *ab initio* simulation package (VASP), which exploits the Ceperley-Alder exchange-correlation potential and pseudopotentials that are obtained via the projector augmented wave (PAW) method. The energy cutoff parameter that accounts for the plane-wave basis was selected as 150 eV when initiating the phonon calculations, which helps provide insight into the vibrational frequency of the Γ-point normal mode. Moreover, using 245.7 eV as a default value for the Si$_{136}$Ge$_x$ alloy system yields no appreciable difference in the acoustic phonon speed. A 4x4x4 Monkhorst-Pack $k$-point grid is selected for Brillouin zone integration.

The procedure of extracting electronic, vibrational and thermodynamic properties of the SiGe alloy clathrate from the periodic density functional theory computation is described as follows: The first step of geometry optimization is to relax the internal coordinates of the atoms, which are confined in a fixed unit cell of the materials. Then, the ground-state structural and electronic properties, such as the cohesive energy, were determined within the local density functional formalism. Next, a limited number of energy-volume ($E$, $V$) pairs were fitted to a 3$rd$-order Birch-Murnaghan equation of state (EOS), thereby enabling the calculation of the global minimum energy and the equilibrium lattice parameter. In addition to optimizing the geometry of each of the studied alloy clathrates, electronic properties, including the Fermi energy level ($E_F$), the electronic band structure (BS) and the electronic density of states (EDOS), are calculated in the framework of consistent structural settings.

To investigate the lattice dynamics of these Si-based clathrate compounds, a 2x2x2 Monkhorst-Pack $k$-point was applied to obtain Γ-point vibration frequencies and dispersive relations, which are derived from the harmonic force constant matrix. In addition, the thermodynamic properties that are related to phonon anharmonicity were evaluated with the aid of the QHA method: The fractional change in volume, namely, $\Delta V/V$, which governs structural dilation or contraction, and the fractional change in the mode frequency are inspected to determine the microscopic Grüneisen parameter $\gamma$. For this purpose, phonon calculations are repeated at three corresponding volume points that contain one equilibrium volume and two additional volumes that are slightly larger and smaller. Using the Feynman-Hellmann theorem, which is based on the FDM, the mode Grüneisen parameter of each phonon is evaluated by approximating the volume derivatives of dynamical matrix elements ($D_{ij}(q)$) as $\Delta D_{ij}(q) / \Delta V$.

**RESULTS AND DISCUSSION**

Electronic properties

We performed the *ab initio* computation to determine various electronic properties of Type II SiGe alloy clathrates, which are structurally formulated in covalently bonding configurations and exhibit sp$^3$-hybridized configurations. Previously, in synthesis work on Si$_{136}$Ge$_x$ ($0 \leq x \leq 136$) by L. L. Baranowski *et al.*, their phase diagrams were classified into two categories according to the guest composition, which is denoted as $x$. Their study determined that the stoichiometric amount ($\chi$) of Ge for amorphous formation ranges from approximately 20.4 to 68. The amorphous region is likely caused by a miscibility gap. Analogous to those experimental results, the following figures present the results of our first-principles work on the composition-dependence of the lattice parameter and the optical bandgap for semiconducting [Si$_1$, Ge$_x$]$_{136}$ (0 $\leq x \leq 1$). Here, it is noticed that $x'$ appearing in redefined chemical notation [Si$_{1-x'}$Ge$_{x'}$]$_{136}$ remains equivalent to the ratio of Ge composition ($\chi$) to 136.

![FIG. 1. LDA-determined lattice parameter trend (red squares) as a function of the Ge mole fraction for [Si$_{1-x}$Ge$_x$]$_{136}$ in comparison with XRD data (open circles). The dashed line that is drawn for the LDA data was obtained via a linear fitting procedure and acts as a guide for the eye. The unit 10$^{-10}$ m is equal to 1 Å.](image)

In FIG. 1, the lattice parameter increases with the Ge content; a similar trend is observed between XRD data and our LDA work in the absence of an amorphous region ($0.15 \leq x' \leq 0.5$). At various compositions of added Ge atoms (e.g., $x' = 0.15$ and $x' = 0.5$), the SiGe clathrate alloy exhibits a mostly crystalline phase with a small amount of amorphous background. This demonstrates that the alloyed clathrate structures expand because of substitutional host atoms (Ge), in comparison with the pure Si$_{136}$ framework. In addition, for $x' \leq 0.77$, our equilibrium lattice constant is 15.05 Å, which is approximately 0.3% smaller than the XRD value. In analogy to this, the previously calculated lattice constant of Si$_{136}$ (14.56 Å) is approximately 0.7% smaller than its experimental counterpart (14.63 Å).
A lower calculated optical bandgap compared to the experiment result in FIG. 2 is expected for \( x' \sim 0.77 \) of \([\text{Si}_{136-8}\text{Ge}_8]\) because the use of LDA formalism always causes the fundamental bandgap energy to be underestimated. All optical band gap energies computed here are measured from the top of the valence band at L, the zero of which remains stably fixed and independent of the Ge concentration. However, we found that degeneracy of the lowest conduction band at L and \( \Gamma \) points is not noticeably distinguished in the presence of \([\text{Si}_{136-8}\text{Ge}_8]\) (see FIG 3.), although eigenenergy of the conduction band edge at L is slightly higher (100 meV larger) than eigenenergy of the conduction band edge at \( \Gamma \) point. Therefore, this depicted band structure provided in FIG. 3 shows that \([\text{Si}_{136-8}\text{Ge}_8]\) \((x' = 8)\) exhibits the “quasi-direct” behavior regarding to band gap definition. The calculated optical band gap value turns out to be approximately 1.27 eV for \([\text{Si}_{128}\text{Ge}_8]\), which well agrees with previous DFT result \((-1.23\text{ eV})\), which was obtained via the Cambridge sequential simulation total energy package (CASTEP) code.

Furthermore, the dispersion spectrum for \([\text{Si}_{128}\text{Ge}_{104}]\), which is displayed in FIG. 4, shows its compressed optical band region \((71\text{ cm}^{-1} - 390\text{ cm}^{-1})\), for which the maximum frequency is reduced by approximately 21% compared to \([\text{Si}_{128}\text{Ge}_8]\) and \([\text{Si}_{96}\text{Ge}_{40}]\) near the top of the optical bands, an extremely flat and dense phonon mode region is observed for Ge-dominant alloy \([\text{Si}_{128}\text{Ge}_{104}]\). This apparent reduction of the highest optical band in \([\text{Si}_{128}\text{Ge}_{104}]\) might be attributable to the raising number of loose Ge-Ge bond which force constant was previously reported to be around 10 eV/Å² according to Dong’s work, compared to the “rigid” Si-Si bond, for which the effective force constant is approximately 24 eV/A² in [\text{Si}_{136-8}]. Consequently, the existence of comparably weak coupling in the Ge-Ge bond might help suppress the sound speed of lattice phonons in \([\text{Si}_{136-8}\text{Ge}_8]\) when \( x \) abruptly jumps from 8 to 104.

We postulate that the collective motion of the framework atoms at each optimized geometry of \([\text{Si}_{136-8}\text{Ge}_8]\) is affected by the number of Ge-Ge bonds, from both vibrational and transport points of view. The models that were considered here for the composition of the \([\text{Si}_{136-8}\text{Ge}_8]\) system were suggested by K. Moriguchi et al., who stated that host atoms reside at three inequivalent sites \((8a, 32e, \& \text{96g})\).

Vibrational and thermodynamic properties

The low-lying acoustic and optic mode regions are of greater importance than other portions of the predicted phonon-dispersion curves in FIG. 4. Six phonon branches are discussed here for each studied \([\text{Si}_{136-8}\text{Ge}_8]\) \((x = 8, 40, 104)\): the longitudinal acoustic (LA), transverse acoustic (TA (1) \& TA(2)) with double degeneracy along the specified direction, longitudinal optical (LO) and transverse optical TO(1) \& TO(2)) branches, which might coincide at various \(q\) points. The low-frequency portions \((0 - 75\text{ cm}^{-1})\) of the dispersion relations for \([\text{Si}_{128}\text{Ge}_8]\) and \([\text{Si}_{96}\text{Ge}_{40}]\) are quantitatively similar to each other, thereby demonstrating that the acoustic phonon speed is nearly unchanged.
Grüneisen parameter along with the macroscopic Grüneisen parameter is given in the following.

According to the DFT-determined diagram (FIG. 5), we see how the number of Ge-Ge bonds that are formed relates to the Si-fraction-dependent mode Grüneisen parameter of TA (1) and LA phonons at various high-symmetry points in $[\text{Si}_x\text{Ge}_{1-x}]_{136}$ ($0 < x^* < 1$). Here, $\gamma_i$ is computed theoretically via $\gamma_i = -\frac{V}{\alpha_i}(\Delta\omega_i/\Delta V)$ using the finite different method. Despite the almost constant calculated value of $\gamma_i$ of an LA phonon that is located near the gamma point, the remaining mode Grüneisen parameters of the same phonon confined to the BZ boundary (L and X points) are positive in sign and exhibit approximately decreasing trends as the number of Ge-Ge bonds decreases from 36 to 8. In addition, the negative value of $\gamma_1$ for an acoustic phonon at the zone center or boundary also approximately decreases with increasing Si fraction. The determined ratio of $\gamma_{TA(1)}(L)$ representing $\gamma_1$ of a TA(1) phonon at L-point for Si$_{128}$Ge$_{64}$ to $\gamma_{TA(1)}(L)$ for Si$_{16}$Ge$_{128}$ is approximately 0.72; hence, the lattice framework exhibits a weak vibrational response upon geometry dilation when the Ge fraction dominates.

The results of the following first-principles calculations (FIG. 6) demonstrate the low-energy ($0 - 125$ cm$^{-1}$) band structures of the phonon dispersions along the L-$\Gamma$-$X$ line for Si$_{128}$Ge$_{68}$ and Si$_x$Ge$_{136}$, respectively. To illustrate the dilation geometry effect on the lattice framework anharmonicity, for our plotted phonon spectrum (dashed line), we consider expanded unit cell that is +6% larger than the material’s optimized structure (see “opt. system” in FIG. 6(a)) in Si$_{128}$Ge$_{68}$ to facilitate comparison. Similarly, in Si$_x$Ge$_{136}$, the expanded unit cell remains about +5.9% larger than the material’s “+2% system” (2% times larger than optimized volume geometry) in FIG. 6(b). The reason why we select these expanded configurations for each material is that, the extremely low resolution of the variation on the wave-vector-dependent phonon mode renders the spectrum difficult to identify if the fractional change in volume deviates from zero to less than 4% in the low-frequency $\omega(q)$ regime, such as, $0 - 100$ cm$^{-1}$. The red shift of the peak of the vibrational density of states (VDOS) at approximately 76 cm$^{-1}$ in the “+2% system” of Si$_{128}$Ge$_{68}$ is attributable to suppression of its lowest-optic phonon mode (TO branch). A similar red shift of VDOS in optimized Si$_{128}$Ge$_{68}$ is observed for optic phonons, which is in the range of 100 cm$^{-1}$ and 110 cm$^{-1}$.

Thus, the apparent reduction of the mode frequency values for the degenerate TO branch in the “+8% system” (FIG. 6(b)), in which the wave-vector spans over the Brillouin zone, results in the existence of positive mode Grüneisen parameters. On the other hand, the phonon frequency for TA branch is elevated in both materials for enlarged geometry, relative to its counterpart (“opt. system” in Si$_{128}$Ge$_{68}$ and “+2% system” in Si$_x$Ge$_{136}$). Hence, the value of $\gamma_i(q)$ is negative, which is anticipated to contribute efficiently and dominantly to inducing the low-temperature negative thermal expansion (NTE) phenomenon to occur.

The exact mode Grüneisen parameters ($\gamma_i$) of the specified phonon that are obtained via LDA are listed in TABLE I. The measured or theoretically estimated values are obtained at high-symmetry points $\Gamma$, X, and L of BZ in two directions ([111] and [100]). It is noted that Wei et al. has reported some predictions$^{33}$ on $\gamma_i$ of d-Si before. All transverse acoustic phonons considered here have $\gamma_i$ values that are below zero. The calculated values of $\gamma_i$ at the X and L points for Si$_{128}$Ge$_{68}$ are similar to the experimentally determined values of $\gamma_i$ for diamond-phase silicon (see Ref. 33). The mode Grüneisen parameter of the LA phonon at the $\Gamma$ point lies between 0.90 and 1.03 for a series of Si$_{128}$Ge$_{68}$, thereby resulting in fair comparison with the value of 1.18 that was determined for Na$_3$Si$_{136}$ via Raman-scattering experiments. These calculated
results also correlate to the γT value of 1.1 that was obtained experimentally for diamond-phase silicon.

**TABLE I.** Comparison of mode Grüneisen parameters between experimentally studied NaSi,Ge32 clathrate along with diamond-phase silicon and theoretically explored Si136,Ge8 (8 ≤ x ≤ 128), along the Γ-L line ([111]) direction.

<table>
<thead>
<tr>
<th>Material</th>
<th>Mode</th>
<th>L</th>
<th>Γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si104Ge32</td>
<td>TA (1)</td>
<td>-0.76</td>
<td>-1.04</td>
</tr>
<tr>
<td>Si104Ge40</td>
<td>LA</td>
<td>2.18</td>
<td>0.98</td>
</tr>
<tr>
<td>Si104Ge96</td>
<td>LA</td>
<td>-0.85</td>
<td>-1.01</td>
</tr>
<tr>
<td>Si104Ge104</td>
<td>TA (1)</td>
<td>-1.16</td>
<td>1.32</td>
</tr>
<tr>
<td>TA (1)</td>
<td>LA</td>
<td>0.87</td>
<td>0.96</td>
</tr>
<tr>
<td>Si104Ge128</td>
<td>TA (1)</td>
<td>-1.20</td>
<td>-1.35</td>
</tr>
<tr>
<td>LA</td>
<td>0.90</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td>Si132Ge32</td>
<td>TA (1)</td>
<td>-1.43</td>
<td>-1.51</td>
</tr>
<tr>
<td>LA</td>
<td>0.71</td>
<td>0.93</td>
<td></td>
</tr>
<tr>
<td>d-Si (Exp.)</td>
<td>TA (1)</td>
<td>-1.30</td>
<td>0.05</td>
</tr>
<tr>
<td>LA</td>
<td>0.9</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>Na3Si136</td>
<td>TA (1)</td>
<td>--</td>
<td>1.18</td>
</tr>
</tbody>
</table>

In addition to anharmonicity exploration on the low-lying acoustic modes of phonons, our computations demonstrate that the γT values for most of the optical phonon modes are positive. Guided by the quasi-harmonic approximation method, our theoretically derived overall Grüneisen parameter, namely, γ(T), is the weighted average of mode Grüneisen parameter γi, which is expressed as γ(T) = 1 / Σ γiCv,i, where Cv,i is the partial vibrational mode contribution to the heat capacity. In other words, γ(T) is related to the anharmonicity of the lattice vibrations and describes how the vibrational frequencies (phonons) change as the volume is varied through T.

![FIG. 7. DFT-predicted Grüneisen parameters of Si104Ge32, Si104Ge40, Si104Ge96, and Si104Ge104.](image)

In addition, γ(T) also serves as an indirect tool for surveying anomalous thermal expansion because γ(T) = αT(T)K / Cρ,\(^{16,43}\) where αT(T) denotes the volumetric thermal expansion coefficient. The sign of αT(T) depends directly on whether γ(T) is negative or positive since the bulk modulus at the specified temperature KT and heat capacity Cρ along with material’s density ρ, always remains positive. The results of our first-principles calculation of the overall Grüneisen parameter for Si136,Ge32 (x = 32, 40, 96, and 104) is shown in FIG. 7, where the axis of abscissa gives rise to a temperature that is limited from 3 K to 99 K. The values of the Grüneisen parameter γ(T) for Si104Ge32 and Si104Ge96 have similar temperature profiles and are always negative from 3 K to approximately 80 K under the scenario of null formation of Ge-Ge bonding. These results on predicting NTE effect can be compared to the reported work of Tang et al., who experimentally and theoretically investigated the thermal properties of Si136 and pointed out an NTE region exists between in the 10-140 K temperature range.\(^{23}\) However, increased numbers of Ge-Ge bonds in Si40,Ge96 and Si32,Ge104 may weaken the NTE effect substantially; the predicted Grüneisen parameters for Si40,Ge96 and Si32,Ge104 remain negative from 3 K to the reduced upper temperature limit, which is approximately 20 K. Further exploration of how the bonding geometry of the Ge-Ge covalent bond (including the bond angle and bond-bond length) impacts the NTE behavior in Si136,Ge32, is beyond the scope of this study.

![FIG. 8. Predicted weighted Grüneisen parameter for transverse acoustic phonons (γTA(T)) and the contribution of all phonon modes (γ(T)) as functions of temperature for (a) Si104Ge32 and (b) Si104Ge40.](image)

We decouple the effect of the lowest-lying phonon branches, which contribute to the production of negative mode-dependent Grüneisen parameters, from the contribution of all other phonon modes along all possible high-symmetry directions (see FIG. 8 (a) and (b)). The two lowest phonon bands (transverse acoustic branches), rather than the remaining 100 branches, which are confined to a unit cell of the clathrate system, are anticipated to play a substantial role in producing the NTE phenomenon. Hence, the macroscopic γ(T) can be calculated primarily from the TA mode contribution via γTA(T) = γ(T) - γLA(T), where γLA(T), which is relatively small, describes the weighted average of the overall Grüneisen parameter over all optical branches, plus the LA phonon mode contribution. In FIG. 8, γTA(T) dominates γ(T). There exist soft, lowest-lying acoustic phonons, for instance, whose wave-
vectors begin at the Γ point and end at approximately 2/3 in the Γ-X (or Γ-L) direction, as shown in FIG. 6. These phonons are interesting because their approximate frequency (~ 50 cm⁻¹ in Si₁₀₄Ge₃₂ and ~ 22 cm⁻¹ in Si₁₆Ge₁₀₄) can be comparable in magnitude to the upper limits of the temperature range beyond which NTE vanishes (~ 80 K for Si₁₀₄Ge₃₂ and ~ 20K for Si₁₆Ge₁₀₄), as shown in FIG. 7.

CONCLUSIONS

We have employed the ab initio DFT method to conduct systematic investigations on the electronic, vibrational and thermodynamic properties of the Si₁₆Ge₈ clathrates. We found that low-frequency transverse acoustic phonons, which have an unusual anharmonic vibration response (negative γₚ) to slight structural expansion, are primarily responsible for the occurrence of the NTE phenomenon. In addition, the reduction of the maximum optic band spectrum and the suppression of the acoustic phonon band width are accompanied by an increase in the number of Ge-Ge bonds that are formed, from 0 (or 8) to 36. Moreover, the number of Ge-Ge bonds is expected to affect the upper limit of the temperature range beyond which NTE vanishes, thereby making it possible to have a strongly weakened NTE effect when x changes from 32 (or 40) to 96 (or 104) in Si₁₆ₓGe₈₋ₓ. Our structural investigation of Si₁₆-xGe₈ (0 ≤ x ≤ 128) serves as the fundamental step for initiating our entire first-principles work, since all vibrational and thermodynamic properties are extracted, in addition to the optimized geometry of each alloy. Our LDA-determined lattice parameter agrees well with XRD data: both show almost monotonically increasing behavior as the Ge composition, namely, x, increases. Regarding the electronic properties, the previous DFT results, which were obtained using the CASTEP code, reveal an optical band gap of Si₁₆Ge₈ of 1.23 eV, which agrees extremely well with the result of our calculation via VASP (~ 1.27 eV).

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