

# Electronic and vibrational properties of framework-substituted type-II silicon clathrates

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Framework substitution has not been widely reported among the type-II group-IV clathrates. We have performed a theoretical study of the  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$  and  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$  clathrates, using the local-density approximation (LDA) to density-functional theory. In  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$  and  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$ , eight Si atoms are substituted by Ga at the  $8a$  crystallographic sites of the framework. We predict that both  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$  and  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$  are semiconductors with LDA indirect band gaps in the range of 0.73–0.77 eV. Similar substitution with Ge (instead of Ga) rendered the materials metallic. We have compared the electronic and vibrational properties of these Ga-substituted materials with those of the partially filled  $\text{Rb}_8\text{Si}_{136}$  and completely filled  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$  clathrates. The phonon-dispersion curves show low-frequency guest “rattling” modes for each material. We have used these results to estimate the temperature-dependent values of the isotropic mean-square displacement amplitude ( $U_{\text{iso}}$ ) for the various guest atoms in  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$ ,  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$ , and  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$ . Our estimates for Na and Rb in  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$  are in good agreement with experiment. We predict that the Rb guests will have low-frequency vibrational modes and higher values of  $U_{\text{iso}}$  than the Cs guests. The large values of  $U_{\text{iso}}$ , the localized low-frequency modes, and the semiconducting properties of  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$  indicate that this type of framework-substituted type-II clathrate may be potentially useful for thermoelectric applications.

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## I. INTRODUCTION

Compounds having the type-II group-IV clathrate lattice structure have been the subject of considerable interest in recent years.<sup>1,2</sup> This is due both to their very good electrical properties (metallic or semiconducting)<sup>3–5</sup> and their glasslike thermal conductivities.<sup>6–9</sup> Materials which simultaneously have very good electrical transport and poor or glasslike thermal transport are not very common. Simultaneously satisfying both criteria means that such materials have potential applications as thermoelectrics. Some of the recent interest in these materials is also due to their potential applications as semiconductors and superconductors.<sup>10,11</sup>

A unique structural feature of a type-II clathrate is that the unit cell has two different sized cages (dodecahedra and hexakaidecahedra) which can host guests, mainly alkali or alkaline-earth metal atoms. These guest atoms, also known as “rattlers,” due to their low-frequency local vibrations, are loosely bound inside the cages. Their localized vibrations may scatter the heat-carrying phonons of the host framework,<sup>12–14</sup> which may contribute to a reduction in the lattice thermal conductivity. However, most filled type-II clathrates are metallic.<sup>15,16</sup> This means that the electronic contribution to the thermal conductivity could be large and hence such materials are not very useful as thermoelectrics.

Here, we report a theoretical study of the electronic and vibrational properties of the framework-substituted  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$  and  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$  clathrates. In these materials, the eight framework Si atoms at the  $8a$  crystallographic sites are replaced by Ga. We compare their properties with those of non-framework-substituted type-II clathrates such as  $\text{Rb}_8\text{Si}_{136}$  and  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$ . Unlike most non-framework-substituted filled clathrates,<sup>15,16</sup> we find that the Ga-substituted clathrates are semiconductors with local-density approximation (LDA) band gaps in the range 0.73–0.77 eV. Because these compounds are semiconductors, the electronic

contribution to the total thermal conductivity should be reduced in comparison to that of the metallic compounds. Using a harmonic-oscillator model and our LDA-calculated rattler frequencies, we have estimated the effective force constants of some of the guest atoms. Using those force constant values, we have predicted the temperature-dependent isotropic mean-square displacement amplitudes ( $U_{\text{iso}}$ ) and the Einstein temperatures ( $\theta_E$ ) of the various guest atoms.

## II. COMPUTATIONAL APPROACH

Our calculations are based on the LDA to density-functional theory, and use a plane-wave basis with ultrasoft pseudopotentials.<sup>17</sup> The Vienna *ab initio* simulation package<sup>18</sup> (VASP) has been used to carry out the calculations. The Ceperly-Alder functional was used to approximate the exchange-correlation term.<sup>19</sup> First, using VASP, we optimize the geometry by relaxing the internal coordinates, while keeping the lattice constant fixed. Brillouin-zone integrations are performed using a  $4 \times 4 \times 4$  Monkhorst-Pack  $k$ -point grid,<sup>20</sup> with a cutoff energy of 300 eV. The accuracy of the total-energy convergence was set at  $10^{-7}$  eV. This process is repeated for several different lattice constants until the global minimum energy is found. The resulting LDA energy versus volume curve is fitted to the Birch-Murnaghan equation of state (EOS).<sup>21,22</sup> This fitting determines the minimum binding energy, the corresponding volume, and the equilibrium bulk modulus. Electronic band structures are calculated for the material at the optimized geometry, along several high-symmetry directions in the Brillouin zone.

The vibrational dispersion relations are calculated by obtaining the dynamical matrix,  $D(q)$ . Using VASP, we calculate the dynamical matrix by moving each atom in the optimized structure by a small finite displacement,  $U_0$  (0.02 Å). We use a  $2 \times 2 \times 2$   $k$ -point grid and 150 eV cutoff energy to calculate the  $\Gamma$ -point phonon modes. Calculations repeated

with a  $4 \times 4 \times 4$   $k$ -point grid did not result in any appreciable difference in the frequencies. A complete row of the force-constant matrix is obtained for each move. Each atom is moved by  $\pm U_0$  and the average value of the force constant is obtained from the second derivative of the energy. The dynamical matrix is obtained from the Fourier transform of the force-constant matrix. The dynamical matrix at nonzero wave vector is obtained by introducing an approximation which assumes that the force constant matrix elements vanish for atoms that are separated by a distance that is greater than the third nearest neighbor. Details of this method may be found in Ref. 23. Once the  $D(q)$  is constructed, its diagonalization gives the eigenvalues (squared frequencies) and eigenvectors.

### III. RESULTS AND DISCUSSION

#### A. Structural and electronic properties

After the structural optimization, we have obtained a lattice constant of about 14.63 Å for  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$ . This is slightly higher than our calculated value of the lattice constant of  $\text{Si}_{136}$  (14.56 Å),<sup>24</sup> indicating that the framework structure expands as expected upon inclusion of the guest atoms. However, the calculated lattice constant of  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$  remained at 14.56 Å. The bulk moduli, obtained from a fit of the Birch-Murnaghan equation of state,<sup>22</sup> were 81.26 and 80.33 GPa for  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$  and  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$ , respectively. Compared to  $\text{Si}_{136}$ ,<sup>24</sup> we find a decrease in the bulk modulus of  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$  with a corresponding increase in its lattice parameter, indicating the material becomes softer upon inclusion of the guest atom.  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$  also has a similar decrease in its bulk modulus compared to  $\text{Si}_{136}$ . It is unclear why its calculated lattice parameter remains the same as that of  $\text{Si}_{136}$ . We speculate that this may be due to the local-density approximation. Energetically LDA favors higher density. Even though the Cs atom is larger than Rb, the LDA does not reflect the expansion of the Cs-containing cages.<sup>25</sup> The Rb and Cs atoms in  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$  and  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$  are located inside the large (hexakaidecahedra) cages.

The electronic properties of  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$  have been discussed elsewhere.<sup>24</sup> Figures 1(a) and 1(b) show the predicted electronic band structures of  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$  and  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$  respectively. The Ga atoms are substituted at the  $8a$  crystallographic sites of the framework. This ensures an energetically favored configuration with no Ga–Ga bond.<sup>26</sup> The band structures in Figs. 1(a) and 1(b) can be qualitatively described in the context of the rigid-band model. This rigid-band character of the band structure means that the guest-to-framework interactions are predominantly ionic in nature and that the guest atoms act as electron donors.<sup>27</sup> It also indicates that the Ga atoms, with their  $s^2p^1$  valence electronic configuration, accept electrons from the guest atoms and form covalent bonds with the neighboring Si atoms.

Our band-structure calculations show that  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$  and  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$  are semiconducting with predicted indirect band gaps of approximately 0.73 and 0.77 eV, respectively. This is in contrast to the predicted band structure for  $\text{Rb}_8\text{Si}_{136}$  (not shown) and  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$ ,<sup>24</sup> which were found

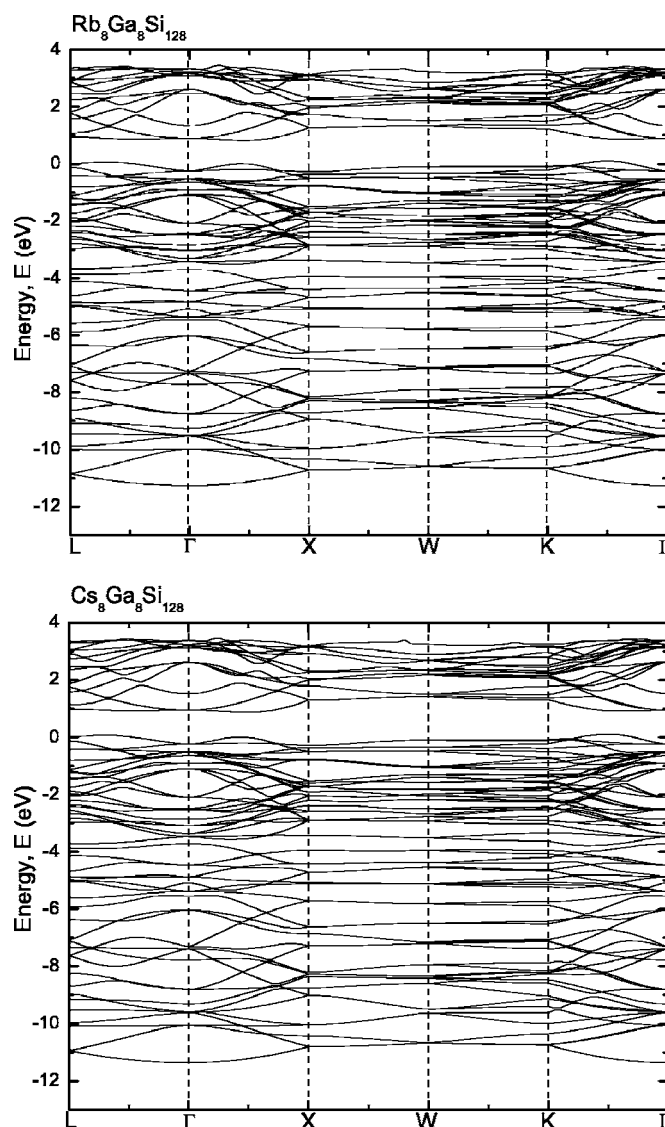


FIG. 1. Electronic band structures of (a)  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$  and (b)  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$ . The top of the valence band is taken as the zero of energy. In (a) and (b) there is an indirect band gap of  $\approx 0.73$  and 0.77 eV, respectively.

to be metallic with a “pseudogap” of about 1.0 and 0.75 eV, respectively. The reason for this is that all host Si–Si bonds in  $\text{Rb}_8\text{Si}_{136}$  and  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$  are satisfied by the Si valence electrons. Therefore in those materials, electrons from the guest atoms occupy the host conduction-band states, making the materials metallic. This is not the case in  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$  and  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$  due to the unpaired  $p$  electrons in the Ga atoms.

In order to emphasize the effect of Ga substitution, we show in Fig. 2 the total electronic density of states (DOS) of  $\text{Rb}_8\text{Si}_{136}$ ,  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$ ,  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$ , and  $\text{Ga}_8\text{Si}_{128}$ .  $\text{Ga}_8\text{Si}_{128}$  has no guest atoms inside the cages and the eight Ga atoms are substituted at the  $8a$  sites. For each material, we have chosen the zero of energy at the top of the valence band. Unlike the Ga-substituted clathrates, the Fermi level ( $E_F$ ) of  $\text{Rb}_8\text{Si}_{136}$  was found to lie inside the conduction band and is predicted to have a metallic or semimetallic property. Similar

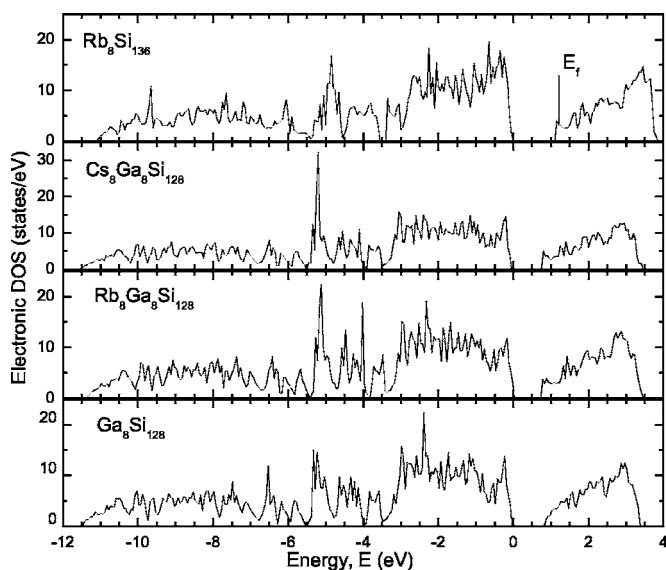


FIG. 2. Total electronic density of states of  $\text{Rb}_8\text{Si}_{136}$ ,  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$ ,  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$ , and  $\text{Ga}_8\text{Si}_{128}$ . The Fermi level of  $\text{Rb}_8\text{Si}_{136}$  lies at the bottom of the conduction band as shown by a vertical line.

results were also obtained for the completely filled  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$  clathrate.<sup>24</sup>

Figures 3(a) and 3(b) show the *s*- and *p*-orbital projected density of states (*p*-DOS) for the guest Rb and substitutional Ga atoms in  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$ . Figure 3(c) shows the *s*- and *p*-orbital projected density of states of the Ga atoms in  $\text{Ga}_8\text{Si}_{128}$ . The figures show the Ga *p* states near the top of the valence band in both  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$  and  $\text{Ga}_8\text{Si}_{128}$ . Those *p* states in  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$  are likely responsible for the semiconducting nature of this material. The unpaired valence electronic configuration of Ga and the absence of guest atoms in  $\text{Ga}_8\text{Si}_{128}$  should make it similar to a *p*-type semiconductor

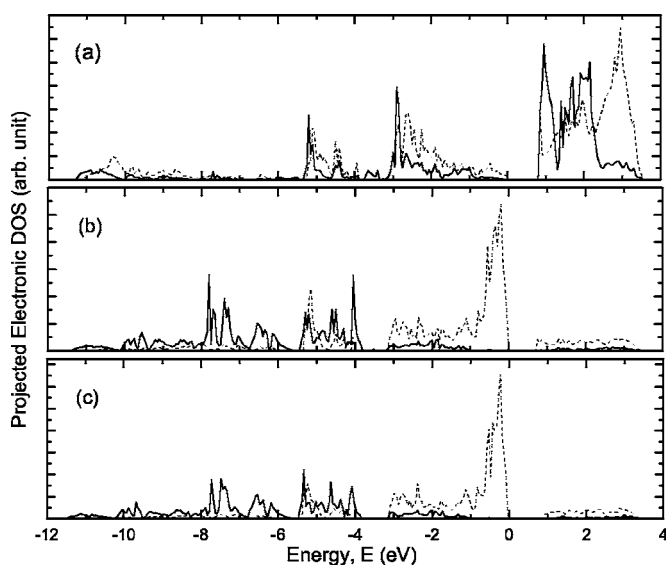


FIG. 3. *s*- (solid curve) and *p*-orbital (dashed curve) projected density of states for (a) Rb, (b) Ga in  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$ , and (c) Ga in  $\text{Ga}_8\text{Si}_{128}$ .

material.  $\text{Ga}_8\text{Si}_{128}$  was found to be semiconducting with an indirect band gap of about 0.8 eV.

The gap between the valence and conduction bands is considerably reduced in the filled clathrates, when compared to the calculated LDA band gap of about 1.24 eV in pristine  $\text{Si}_{136}$ .<sup>24,28</sup> The band gap in the empty but framework-substituted  $\text{Ga}_8\text{Si}_{128}$  is also reduced ( $\sim 0.8$  eV). Figure 3 shows the Ga *p* states at the top of the valence band in  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$  and  $\text{Ga}_8\text{Si}_{128}$ . Additionally, there are Rb *s* states near the bottom of the conduction band in  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$ . These substitutional and guest atom states may be the cause for the reduction in the overall gap between the valence and conduction bands in these clathrates.

It has been shown that the total thermal conductivity for filled type-II clathrates is high even though their lattice thermal conductivity is low.<sup>16</sup> This is because of their metallic character, which increases the electronic contribution to the total thermal conductivity. The semiconducting nature of  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$  and  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$  may help to reduce this electronic contribution.

## B. Vibrational properties

Figure 4 shows the predicted phonon-dispersion curves and the vibrational density of states (VDOS) of  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$ ,  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$ ,  $\text{Rb}_8\text{Si}_{136}$ , and  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$ , respectively. The figures are qualitatively similar to each other and they all share some common features. The acoustic modes are located below about  $50\text{ cm}^{-1}$  and the optic modes lie above that range. The optical modes are mostly flat, except for a few in the range  $200\text{--}280\text{ cm}^{-1}$ . These flat optical modes should contribute little toward heat transport. The notable feature in the dispersion curves of each material is the compression of the bandwidth of the highly dispersive heat-carrying acoustic phonons from about  $100\text{ cm}^{-1}$  in  $\text{Si}_{136}$ ,<sup>23,29</sup> to about  $50\text{ cm}^{-1}$  or lower in  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$ ,  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$ ,  $\text{Rb}_8\text{Si}_{136}$ , and  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$ . This is due to the very flat localized modes of the Rb or Cs atoms, which lie approximately at the middle of the host acoustic-mode region. Due to an avoided crossing effect, there is a strong interaction between localized rattler modes and the framework acoustic branches, resulting in a “bending” of these acoustic branches below the guest rattler modes. This should increase the probability of resonant scattering of the host acoustic phonons, and thus should suppress the lattice thermal conductivity.

There is an increased VDOS in  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$  at the bottom of the optic band, in the range of  $120\text{--}200\text{ cm}^{-1}$ . This is due to the additional modes coming from the Na vibrations, which are absent in  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$ ,  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$ , and  $\text{Rb}_8\text{Si}_{136}$ . We also find a “redshift” of the highest optical modes in  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$ . This downshift is about  $25\text{ cm}^{-1}$  with respect to those of  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$ . The higher-frequency optic bands are mainly due to the bond-stretching modes.

In the rigid-band picture, the donated electrons from Na and Rb in  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$  primarily occupy the Si framework antibonding states. These electrons reduce the Si–Si bond order and, therefore, diminish the stretching force of the Si–Si bonds.<sup>25</sup> This reduces the frequency of the bond-stretching modes in  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$ . By contrast,  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$

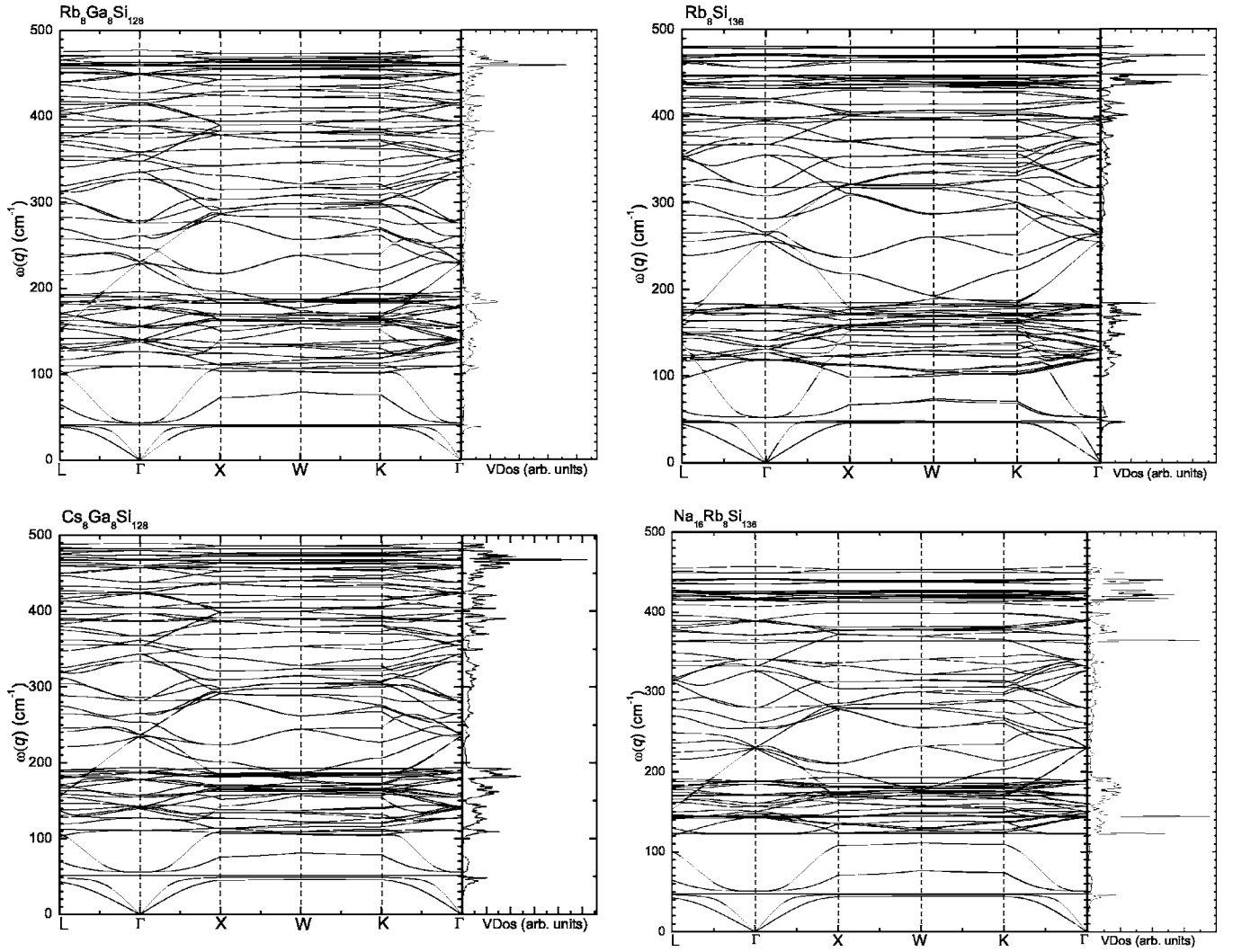


FIG. 4. Phonon-dispersion relations and vibrational density of states (VDOS) of (a)  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$ , (b)  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$ , (c)  $\text{Rb}_8\text{Si}_{136}$ , and (d)  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$ .

and  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$  are semiconductors. In those materials, the donated electrons from Rb or Cs primarily occupy the bonding states of the substituted Ga atoms, in order to facilitate their covalent bonding with Si neighbors. Our LDA-calculated average Si-Ga distances are about 2.37 and 2.38 Å in  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$  and  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$ , respectively. These are similar to the average Si-Si distances in the two clathrates (see Table I). The slightly larger bond length between Si and Ga may be due to the larger atomic radius of the Ga atom. This implies that the Si-Ga bonds are not altered appreciably

in comparison to the Si-Si bonds. Therefore, the high-frequency stretch modes should not be greatly affected in  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$  and  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$ , which is consistent with our results.

It has also been shown in Raman-scattering experiments,<sup>30</sup> that low guest content does not produce a frequency downshift in  $\text{Si}_{136}$  clathrates. Consistent with experimental observation, we see no such frequency downshift of the optical modes in  $\text{Rb}_8\text{Si}_{136}$ . There are less delocalized guest atom states in the partially filled  $\text{Rb}_8\text{Si}_{136}$  compared to

TABLE I. LDA-calculated nearest-neighbor distances in  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$ ,  $\text{Rb}_8\text{Si}_{136}$ ,  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$ , and  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$ .

Clathrate	Si-Si (Å)	Si-Rb (Å)	Si-Ga (Å)	Si-Na (Å)	Si-Cs (Å)
$\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$	2.35–2.38	3.90–3.98		3.17–3.35	
$\text{Rb}_8\text{Si}_{136}$	2.32–2.37	3.88–3.95			
$\text{Rb}_8\text{Ga}_8\text{Si}_{128}$	2.34–2.40	3.92–3.98	2.38		
$\text{Cs}_8\text{Ga}_8\text{Si}_{128}$	2.33–2.39		2.37		3.89–3.96



the completely filled  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$ . Hence, the high-frequency stretch modes in that material are not as much affected as those in  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$ , probably resulting in no observable frequency downshift for  $\text{Rb}_8\text{Si}_{136}$ .

It is also worth comparing the predicted rattler frequencies for  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$  and  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$ . The Rb guests are predicted to have frequencies in the range  $40\text{--}42\text{ cm}^{-1}$ , while the Cs frequencies lie within the  $50\text{--}52\text{ cm}^{-1}$  range. The Rb modes are thus considerably lower than the Cs modes, although the Cs atom is about 1.5 times heavier than the Rb atom. This indicates that Cs is less loosely bound than Rb in the hexakaidecahedra cages. This may be due to the larger size of the Cs in comparison with Rb. We have found a similar trend when we compared the predicted guest atom frequencies in  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$  with those in  $\text{Na}_{16}\text{Cs}_8\text{Si}_{136}$ .<sup>14</sup> Both of these materials show localized Na modes at about  $120\text{ cm}^{-1}$ . The striking differences between the two compounds are the localized modes due to Rb and Cs. In earlier work, we predicted that the Cs atoms vibrate at frequencies in the range  $65\text{--}67\text{ cm}^{-1}$ .<sup>14</sup> The present study shows that the Rb modes in  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$  lie at about  $49\text{ cm}^{-1}$ . It is conceivable that the Cs atom, because of its larger size, interacts more strongly with its neighbors, causing it to be more “strongly” bound than Rb. The stronger guest atom-host atom interaction for Cs in  $\text{Na}_{16}\text{Cs}_8\text{Si}_{136}$  is also evident from the lower experimental values of its atomic displacement parameter, in comparison to that of Rb in  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$  in the temperature region  $150\text{--}300\text{ K}$ .<sup>16</sup>

At high temperature ( $\hbar\omega < 2k_B T$ ), an estimate of the mean-square displacement amplitude for a rattler can be obtained in the Einstein model, by using the classical expression  $U_{\text{iso}} \approx k_B T / K$ , where  $K$  is the force constant of the oscillator and  $k_B$  is the Boltzmann constant. The value of  $U_{\text{iso}}$  is particularly useful in determining the amount of dynamic disorder of the various guest atoms inside the cages. Higher values of  $U_{\text{iso}}$  may lead to lower thermal conductivity.

From our calculated rattler frequencies, we can estimate the effective force constant using  $\omega = \sqrt{K/M}$ , where  $M$  is the mass of the guest atom. Our estimated values of  $K$  for Rb and Na in  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$  are  $0.76$  and  $1.26\text{ eV/\AA}^2$ , respectively. The values of  $K$  for Rb and Cs in  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$  and  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$  are  $0.55$  and  $1.275\text{ eV/\AA}^2$ , respectively. These low values of  $K$ , when compared to a similarly computed  $K$  for Si–Si bonds in the clathrates ( $\sim 10\text{ eV/\AA}^2$ ),<sup>13</sup> show the weakly bounded nature of the guest atoms inside the cages.

Using our calculated values of the effective force constants, we show in Fig. 5 (discrete symbols) the estimated values of  $U_{\text{iso}}$  for Na and Rb in  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$  at different temperatures ( $T = 150\text{--}300\text{ K}$ ). In the quantized harmonic-oscillator model,<sup>31</sup>

$$U_{\text{iso}} = \langle u^2 \rangle = \frac{h}{8\pi^2 m \nu} \coth\left(\frac{h\nu}{2k_B T}\right),$$

where  $\nu$  is the frequency of vibration of the oscillator,  $m$  is its reduced mass, and  $h$  is the Planck constant. The solid curves in Fig. 5 show plots of the above equation for the Na and Rb atoms in  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$ . Considering that the clathrate cages are quite rigid, we have assumed that the reduced mass

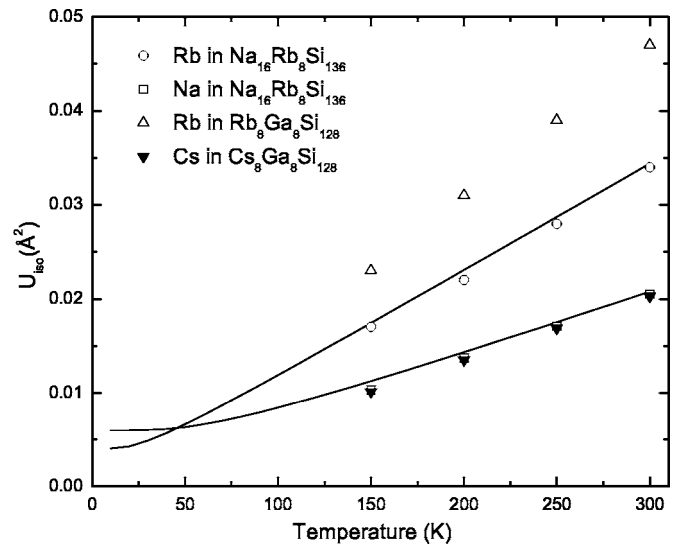


FIG. 5. Estimated values (discrete symbols) of the isotropic mean-square displacement amplitude ( $U_{\text{iso}}$ ) of the various guest atoms at different temperatures. The solid curves are plots of  $U_{\text{iso}}$  for Rb and Na in  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$ , based on the quantized harmonic-oscillator model.

of the oscillator is equal to the guest atom mass.

As seen in Fig. 5, one expects a close resemblance between the quantized and classical models in the limit  $\hbar\omega < 2k_B T$ . Our estimated values of  $U_{\text{iso}}$  obtained from the classical expression ( $U_{\text{iso}} \approx k_B T / K$ ) and our predicted frequencies ( $\omega$ ) are in good agreement with experiment.<sup>16</sup> Of course, our rattler frequencies are calculated at  $T = 0\text{ K}$ . This agreement between experiment and theory indicates that the harmonic-oscillator model is a good approximation for predicting the  $U_{\text{iso}}$  of the rattlers at finite temperatures. In other words, anharmonic effects are probably small at least up to  $300\text{ K}$ .

Figure 5 also shows our estimated values of  $U_{\text{iso}}$  (using the classical expression) for Rb and Cs in  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$  and  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$ , in the temperature range  $150\text{--}300\text{ K}$ . It is interesting that Rb has much higher values of  $U_{\text{iso}}$  than Cs in the temperature range considered. This is due to the larger values of  $K$  for Cs than for Rb. Cs is heavier and has a higher vibrational frequency, resulting in a smaller  $U_{\text{iso}}$ . This result is consistent with the experimentally obtained values of  $U_{\text{iso}}$  for Cs and Rb in  $\text{Na}_{16}\text{Cs}_8\text{Si}_{136}$  and  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$ , where it has been shown that Cs has much lower values compared to Rb.<sup>16</sup> The predicted  $U_{\text{iso}}$  values for Na in  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$  and those for Cs in  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$  are very close to each other. Thus the discrete symbols for the two cases nearly overlap each other in Fig. 5.

We have used the estimated values of  $U_{\text{iso}}$  to predict the Einstein temperatures ( $\theta_E$ ) of the various guest atoms.<sup>32</sup> These are shown in Table II. Our values of  $U_{\text{iso}}$  at  $300\text{ K}$  were used to predict  $\theta_E$ . The high value of  $\theta_E$  for Na in  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$  is consistent with its lower  $U_{\text{iso}}$  and its smaller mass. In a recent paper,<sup>33</sup> it has been suggested that the glasslike thermal conductivity in clathrates is a consequence of three different phonon-scattering mechanisms. It was shown, based on empirical evidence, that the phonons scat-

TABLE II. Predicted Einstein temperatures ( $\theta_E$ ) of the various guest atoms in  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$ ,  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$ , and  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$ .

Clathrate	$\theta_{E,\text{Na}}$ (K)	$\theta_{E,\text{Rb}}$ (K)	$\theta_{E,\text{Cs}}$ (K)
$\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$	175	70.5	
$\text{Rb}_8\text{Ga}_8\text{Si}_{128}$		60	
$\text{Cs}_8\text{Ga}_8\text{Si}_{128}$			73

tered from free charge carriers and bound/localized charge carriers were the dominant scattering mechanisms at temperatures below 50 K, and that the resonant scattering of host phonons by guest atoms occurred at temperatures above 50–70 K.<sup>33</sup> It is interesting that each estimated value of  $\theta_E$  of the various guests is above 50 K. This may also imply that the resonant scattering of host phonons would be dominant at temperatures above 50 K.

#### IV. CONCLUSIONS

We have used the LDA to study the electronic and vibrational properties of the  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$  and  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$  clathrates. We predict that both  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$  and  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$  are semiconducting, with smaller indirect band gaps than guest-

free  $\text{Si}_{136}$ . A comparison of the DOS of  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$  with those of  $\text{Rb}_8\text{Si}_{136}$  and  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$  emphasizes the role of Ga substitution. All materials considered are predicted to have low-frequency guest vibrational modes that are near the middle of the host acoustic band, which effectively compresses the acoustic-mode bandwidth. This could lead to an efficient scattering of the host acoustic phonons. Even though Cs is heavier than Rb, we predict that Rb has a lower vibrational frequency than Cs. This could mean a more efficient phonon-scattering mechanism for Rb than Cs. Our estimated temperature-dependent values of  $U_{\text{iso}}$  for Rb and Na in  $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$  agree well with experiment, implying that there is only a small anharmonic contribution at temperatures up to 300 K. As expected from our calculated frequencies, we predict higher values of  $U_{\text{iso}}$  for Rb in  $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$  than Cs in  $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$ .

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