

Rattling “guest” impurities in Si and Ge clathrate semiconductors

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Abstract

In addition to their ground state, diamond structure, Si, Ge and Sn can form crystalline solids called clathrates. As in the diamond structure, in the clathrates, the Group IV atoms are tetrahedrally coordinated and sp^3 covalently bonded to their neighbors. However, the clathrates contain pentagonal atomic rings and have open-framework lattices containing 20-, 24- and 28-atom “cages”. There are two clathrate lattices: Type I, a SC lattice with 46 atoms per unit cell and Type II, a FCC lattice with 136 atoms per cubic cell. The pure clathrates are semiconductors.

The cages can contain weakly bound impurities (“guests”), usually alkali or alkaline earth atoms. The choice of guest may be used to tune the material properties. The guests are electronic donors, but because of their weak bonding, they have small effects on the electronic band structures. However, they can produce low frequency vibrational (“rattling”) modes which can strongly affect the vibrational properties. Some guest-containing clathrates have been shown to be excellent candidates for thermoelectric applications *precisely because* the guests only perturb the electronic properties weakly, while strongly affecting the vibrational (heat transport) properties. For thermoelectric applications, semiconductor materials are needed. When all cages are filled, the clathrates become semi-metallic due to the excess valence electrons of the guests. To compensate for this, Group III atoms (usually Ga or In) are substituted on the framework sites.

After an introduction to clathrates, the results of calculations of the vibrational properties of some experimentally relevant Si- and Ge-based Type I and Type II clathrates are presented. The calculations were carried out using a first-principles, planewave, pseudopotential method. Results for the Si-based Type II materials $Cs_8Ga_8Si_{128}$ and $Rb_8Ga_8Si_{128}$, and for the Ge-based Type I materials $Ba_8Ga_{16}Ge_{30}$ and $Ba_8Ga_{16}Si_5Ge_{25}$ will be discussed with an emphasis on the very low frequency rattling modes of the guest impurities.

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1. Introduction

In addition to their ground state, diamond lattice structure, Si, Ge, and Sn can also form zeolite-like, expanded volume phases called clathrates. These are open-framework structures in which the lattice contains large (20-, 24-, and 28-atom) cages, and in which all framework atoms are in a four-fold-coordinated sp^3 bonding configuration. The local bonding in the framework of the clathrates is thus similar to that in the diamond structure. However, these lattices contain pentagonal rings, making their topology very different from that in the diamond lattice. Further, the “cages” formed by the Group IV atoms can house “guest” impurity atoms, and the

choice of guest may be used to tune the material properties. Most clathrates which have been realized in the laboratory have been guest-containing compounds.

The clathrate materials are of interest due to their unique transport properties. Specifically, they have potential thermoelectric [1–4], superconducting [5–8] and electro-optic [9,10] applications. Among the interesting properties they possess is their low thermal conductivity. This originates in the weak bonding of the guests inside the host atom cages. This results in low frequency, localized (“rattler”) vibrational modes which couple to the lattice modes by resonantly scattering the acoustic-mode, heat-carrying phonons of the host framework material [1], thereby lowering the thermal conductivity.

Of the two clathrate lattices types, compounds with the Type I crystal structure have been the more thoroughly investigated experimentally and theoretically. The pure

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framework Type I materials have a SC lattice with 46 atoms per unit cell and are denoted as X_{46} ($X = \text{Si, Ge, Sn}$). Many experimental studies of compounds based on the Type I materials (with various guests in the cages) have been carried out. The low thermal conductivity measured in these compounds is due to the weak guest–host electronic interactions, which leads to strong coupling between the localized guest rattler vibrations and the host acoustic modes. This interpretation is consistent with transport [11–18], Raman scattering [19] and acoustic measurements [20,21] as well as with theoretical calculations [22,23]. Several theoretical studies of the electronic, structural, and vibrational properties of the pure Type I clathrates and various compounds based on the Type I lattice have been carried out [24–34].

There have been fewer experimental and theoretical studies of the Type II clathrates than for the Type I materials. The pure Type II materials are denoted as X_{136} ($X = \text{Si, Ge, Sn}$) and they have a FCC lattice with 136 atoms per cubic cell. The vibrational modes of the Type II “empty” clathrates Si_{136} [29,35,36] and Ge_{136} [26] and of the filled, metallic Type II materials $\text{Na}_{16}\text{Cs}_8\text{Si}_{136}$ and $\text{Na}_{16}\text{Cs}_8\text{Ge}_{136}$ [37] have been theoretically investigated. We have earlier reported a theoretical study of the electronic structure [38] of the filled, metallic Type II materials $\text{Na}_{16}\text{Rb}_8\text{Si}_{136}$ and $\text{K}_{16}\text{Rb}_8\text{Si}_{136}$ and have found qualitative agreement with observed NMR Knight shifts. Recently, we have also reported calculations of the properties [39] of the Type II framework-substituted clathrates $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$ and $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$. Here, we report the results of a density functional-based theoretical study of the vibrational modes of the Type II framework substituted clathrate semiconductors $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$ and $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$ and of the Type I metallic clathrate materials $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ and $\text{Ba}_8\text{Ga}_{16}\text{Si}_5\text{Ge}_{25}$. The latter two materials can be thought of as two in a series of Ge–Si clathrate “alloys” which are of interest [40] for their possible thermoelectric applications. The results presented will have an emphasis on the very low frequency rattling modes of the guest impurities and the effects of these modes on the vibrational spectrum of the host framework material.

2. Computational details

Our calculations are based on density functional theory (DFT) and they use a planewave basis with ultrasoft pseudopotentials [41,42]. Our results for $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$ and $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$ were obtained in the local density approximation (LDA) and those for $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ and $\text{Ba}_8\text{Ga}_{16}\text{Si}_5\text{Ge}_{25}$ used the generalized gradient approximation (GGA).

The Vienna Ab-initio Simulation Package (VASP) [43,44] has been used with the Ceperley–Alder functional [45] to approximate the exchange–correlation energy. The implementation we use is particularly efficient for the large clathrate unit cells. This technique has been used in previous studies of Si [29,46] and Ge [26,30] and Sn [24,25] clathrates and the calculated structural and vibrational properties

were found to be in good agreement with experimental data [47–49].

Using VASP, the geometry is first optimized by relaxing the internal coordinates, while keeping the volume fixed. This procedure is discussed elsewhere [39]. The vibrational dispersion relations, $\omega(q)$, are then calculated by first obtaining the dynamical matrix, $D(q)$. Using VASP, $D(q)$ is calculated by moving each atom in the optimized structure by a small finite displacement, $U_0 = 0.02 \text{ \AA}$. A $2 \times 2 \times 2$ k -point grid and 150 eV cutoff energy were used to calculate the Γ -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 elsewhere [31]. Once $D(q)$ is constructed, its diagonalization gives the eigenvalues and eigenvectors.

3. Results and discussion

3.1. $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$ and $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$

Fig. 1 shows the predicted phonon–dispersion curves and the vibrational densities of states (VDOS) of $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$ (Fig. 1a) and $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$ (Fig. 1b). The two figures are qualitatively similar and share some common features. The acoustic modes are located below about 50 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. Comparison of these results with the vibrational spectrum of Si_{136} [31] shows a large compression of the bandwidth of the highly dispersive heat carrying acoustic phonons from about 100 cm^{-1} in Si_{136} to about 50 cm^{-1} or lower in $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$ and $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$. This is due to the very flat localized modes of the Cs or Rb guest impurities, which lie approximately at the middle of the host acoustic-mode region. Due to an avoided crossing effect, there is a strong interaction between these localized rattler modes and the framework acoustic branches, resulting in a “bending” of the 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.

It is also worth comparing the predicted rattler frequencies of $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$ and $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$. The Cs frequencies lie within the $50\text{--}52 \text{ cm}^{-1}$ range, while the predicted Rb frequencies are in the range $40\text{--}42 \text{ cm}^{-1}$. The Rb modes are thus lower than the Cs modes, although

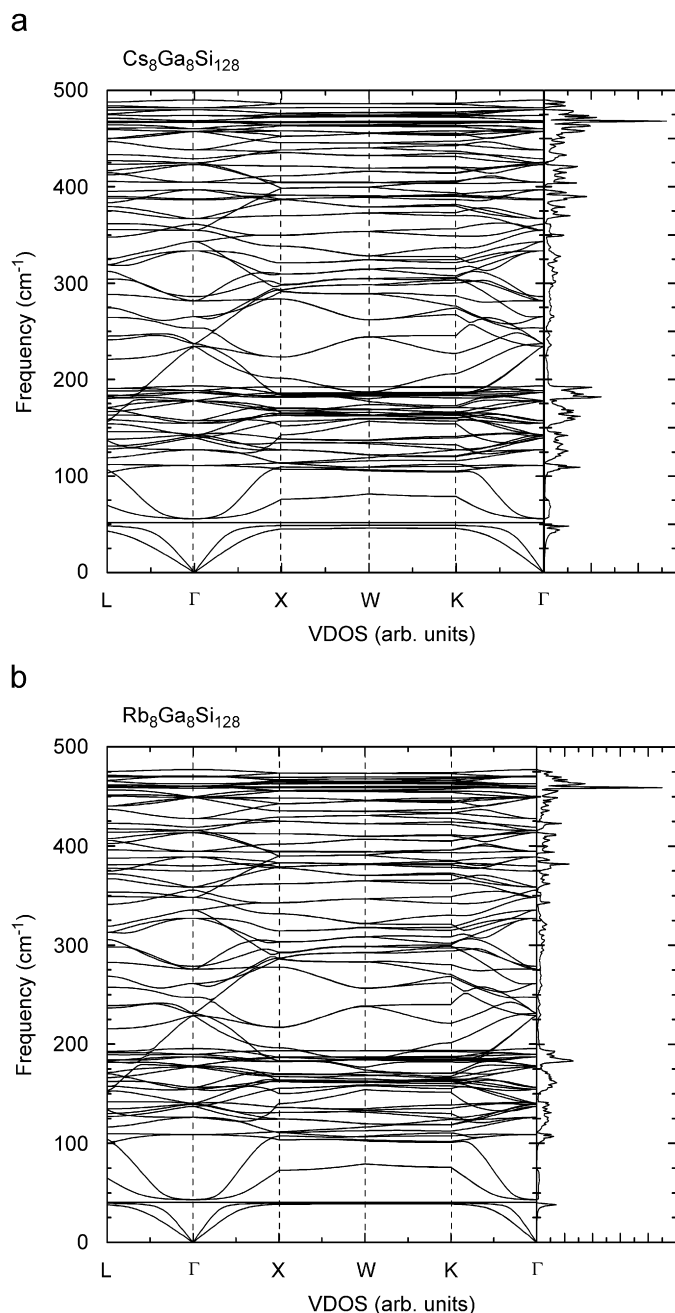


Fig. 1. Phonon-dispersion relations and vibrational densities of states (VDOS) for (a) $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$ and (b) $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$.

the Cs atom is about 1.5 times heavier than the Rb atom. This is an indication that the Cs is more strongly bound in the hexakaidecahedra cages than Rb. This may be due to the larger size of the Cs in comparison with Rb. 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.

3.2. $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ and $\text{Ba}_8\text{Ga}_{16}\text{Si}_5\text{Ge}_{25}$

Fig. 2 shows our preliminary results for the predicted phonon-dispersion curves of $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ (Fig. 2a) and

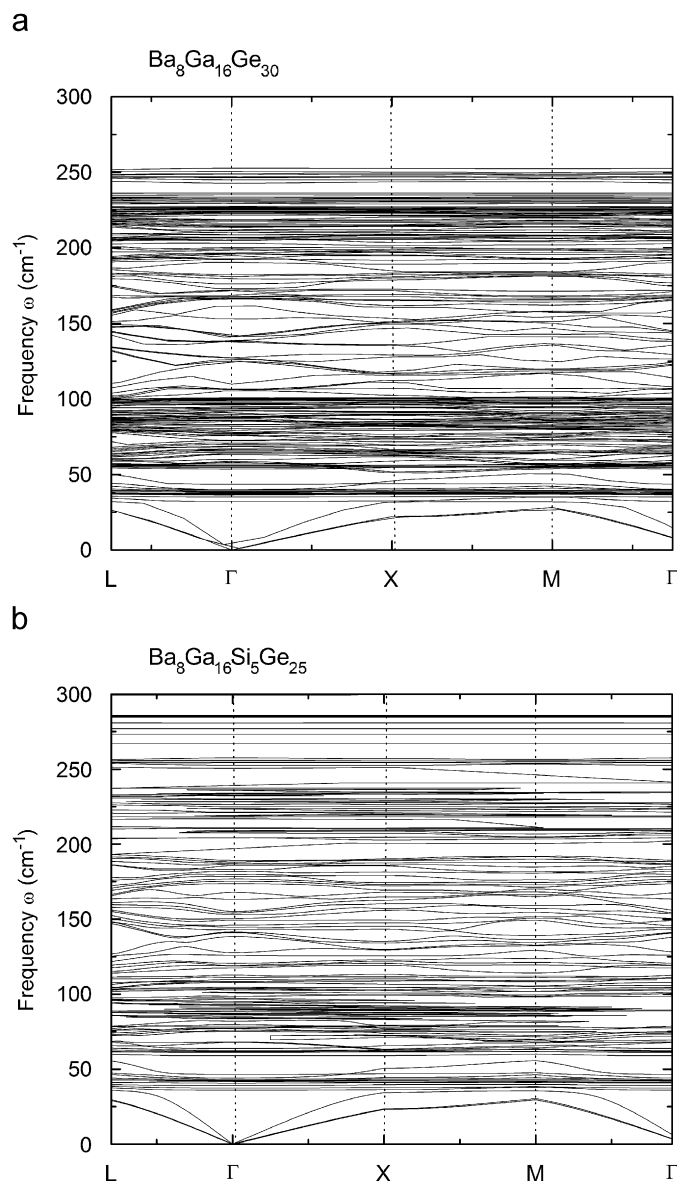


Fig. 2. Phonon-dispersion relations for (a) $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ and (b) $\text{Ba}_8\text{Ga}_{16}\text{Si}_5\text{Ge}_{25}$.

$\text{Ba}_8\text{Ga}_{16}\text{Si}_5\text{Ge}_{25}$ (Fig. 2b). The acoustic modes of both materials are predicted to lie below about $30\text{--}35\text{ cm}^{-1}$. Most of the optic modes are very flat and very closely spaced, as is typical of these modes in the clathrates. These flat optic modes are expected to contribute little to heat transport. However, some optic modes in the range $100\text{--}190\text{ cm}^{-1}$ for $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ and in the range $110\text{--}175\text{ cm}^{-1}$ for $\text{Ba}_8\text{Ga}_{16}\text{Si}_5\text{Ge}_{25}$ display significant dispersion.

Comparing our results with the vibrational spectrum of Ge_{136} [26] shows that the presence of the rattlers serves to compress the bandwidth of the highly dispersive heat carrying acoustic phonons from about 60 cm^{-1} in Ge_{136} to about 30 cm^{-1} and below in $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ and $\text{Ba}_8\text{Ga}_{16}\text{Si}_5\text{Ge}_{25}$. This is again caused by the very flat localized modes of the Ba guest impurities in the latter materials. These are predicted to occur at very low frequencies, in the

approximate range $37\text{--}42\text{ cm}^{-1}$. This should again result in a strong interaction between these localized modes and the framework acoustic branches, increasing the probability of resonant scattering of the host acoustic phonons, and thus should suppress the lattice thermal conductivity.

4. Conclusions

We have used first-principles, DFT-based calculations to study the vibrational (phonon) modes for the Si-based Type II framework-substituted clathrate materials $\text{Cs}_8\text{Ga}_8\text{Si}_{128}$ and $\text{Rb}_8\text{Ga}_8\text{Si}_{128}$, and for the Ge-based Type I Ge–Si “alloy” materials $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ and $\text{Ba}_8\text{Ga}_{16}\text{Si}_5\text{Ge}_{25}$. These materials are each of interest for their potential technological applications, especially in the field of thermoelectrics. For each material, we predict that, as expected, the localized vibrational (rattling) modes of the each of the guest impurities (Cs, Rb and Ba) inside the clathrate framework cages occur at very low frequencies. These originate in the weak bonding of the guests inside the host atom cages. Further, these rattler modes should couple to the host framework clathrate lattice modes by resonantly scattering the acoustic-mode, host material heat-carrying phonons [1], potentially suppressing the thermal conductivity and increasing the potential thermoelectric applications of each material.

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