Phonon Band Structures and Resonant Scattering in $\text{Na}_8\text{Si}_{46}$ and $\text{Cs}_8\text{Sn}_{44}$ Clathrates

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The low and glasslike thermal conductivity of metal doped semiconductor clathrate compounds makes them potentially high efficiency thermoelectric materials. The cause of this unique and remarkable property has been postulated to be due to resonant scattering of lattice phonons by localized vibrations of the dopants. We present theoretical evidence in support of this hypothesis through the analysis of electronic and vibrational interactions between dopant atoms with the host framework. In particular, the contrasting behavior of two clathrates: the *glasslike* thermal conductivity in $\text{Na}_8\text{Si}_{46}$ and the *normal* behavior in $\text{Cs}_8\text{Sn}_{44}$ can be rationalized.

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1. Introduction

The search for high mobility semiconductors with glasslike thermal conductivities as high efficiency thermoelectric materials is currently a subject of intense research. The measure for a good candidate material is given by the dimensionless quantity, $ZT = TS^2\sigma/\kappa$, where T is temperature, S is the Seebeck coefficient, σ and κ are the electrical and thermal conductivity, respectively.¹⁾ Several schemes have been proposed to satisfy these criteria. One of the recent foci has been the exploitation of materials with low thermal conductivity *via* the interactions between low frequency localized vibrations with the lattice phonons.^{2,3)} A particularly promising class of material is metal doped semi-conductors with a clathrate structure.⁴⁾ These materials have been shown to have very low and glasslike thermal properties and offer the possibility of altering the electrical conductivity by varying the nature and concentration of the metal dopants.³⁾ There is already abundant information in the literature on the experimental and theoretical characterization of the stability, electronic structure⁵⁻⁷⁾ and vibrational properties⁸⁾ of pure and doped Si and selected clathrate compounds. In spite of previous studies, the mechanism for the thermal conductivity anomaly has not been addressed. This unusual behavior was attributed to resonant scattering of the acoustic phonons by the localized vibrations of the dopants.^{3,9)} It would then suggest that the heavier the dopant atoms, the lower would be the localized vibrations and the better the phonon scattering. This conclusion, however, seems to be at variance with recently measured thermal conductivity of $\text{Na}_8\text{Si}_{46}$ ¹⁰⁾ and $\text{Cs}_8\text{Sn}_{44}$.³⁾ In the former compound, the glasslike thermal conductivity is realized¹⁰⁾ but the latter compound behaves as a *normal* crystalline solid (*i.e.* in the high temperature region, the thermal conductivity shows a T^{-1} temperature dependence).³⁾ These conflicting observations cast doubt on the applicability of the resonant scattering model. The objective of this study is to characterize the vibrations and phonon coupling mechanisms in metal-doped semi-conductor clathrates with the type-I structure. As will be shown below, the resonant scattering model is valid for this system and the apparent contraction can be resolved.

2. Method

The electronic and phonon band structures for $\text{Na}_8\text{Si}_{46}$ and $\text{Cs}_8\text{Sn}_{46}$.¹¹⁾ have been calculated with First Principles gradient corrected Local Density Functional (GC-LDA) methods. Details of the calculations have been reported elsewhere.¹⁰⁾ In essence, all-electron electronic band structures were computed with the Full Potential Linearized Augmented Plane Wave method (FLAPW).¹²⁾ The phonon band structures were calculated by a direct method¹³⁾ with the total energies and Hellmann-Feynman forces were computed from pseudopotential plane wave method within the LDA.¹⁴⁾ The theoretical results are summarized in Fig. 1 to Fig. 3.

3. Results and Discussion

The electronic band structure of $\text{Na}_8\text{Si}_{46}$ has been studied many times.^{5,6,10)} The present results agree with all the previous findings. No significant difference was found for the optimized unit cell parameter (*ca.* 1.010 nm) for both pure Si_{46} and $\text{Na}_8\text{Si}_{46}$. The salient feature is that enclathrated Na atoms do not affect the electronic band structures of the “empty” host framework.^{6,10)} The electronic structure of $\text{Na}_8\text{Si}_{46}$ can be reasonably well described by a rigid band model.^{6,10,15)} This indicates the Na–Na and Na–Si interactions are predominantly ionic and that Na atoms act primarily as electron donors. The mostly ionic nature of the Na atoms has a dramatic effect on the vibrational spectrum. The phonon band structure of $\text{Na}_8\text{Si}_{46}$ is shown in Fig. 1(a). Several flat vibrational bands can be clearly identified in the low frequency region near 70 cm^{-1} and 100 cm^{-1} . Inspection of eigenvectors shows that these bands are primarily due to the motions of the Na atoms. The non-dispersive nature of these bands (optic modes) indicates significant localization characters. The phonon band structure fully substantiates the description of the electronic band structure, showing that the Na atoms have no significant covalent interaction with the framework Si atoms. These localized vibrations “intersect” the longitudinal (LA) and transverse (TA) acoustic branches of the framework at various places inside the Brillouin zone (BZ). It

Fig. 1 Phonon band structure and (b) Partial Vibrational Density of States (PVDOS) for Si, Na in the small (S) and large (L) cages of $\text{Na}_8\text{Si}_{46}$.

is important to observe that although occasionally the acoustic branches cut across the localized bands, there are strong interactions between the phonon bands leading to the “bending” of the acoustic branches at several places. For example, these crossings occur for the 70 cm^{-1} flat along the $\Gamma \rightarrow X$ direction near the X point for the TA and at about halfway for the LA modes and about $1/3$ and $2/3$ along the $\Gamma \rightarrow M$ for the LA and TA modes, respectively. This kind of interaction extends into higher energy optic vibrational regions for the LA modes (e.g. with the localized Na vibrations at 100 cm^{-1}). These *resonant* interactions are due to “avoided crossings” of phonon modes with the same symmetry. Crystal factor group analysis at Γ gives the symmetry of the “enclathrated” Na atoms’ vibrations as $A_{2g} + E_g + T_{1g} + 3T_{1u} + 2T_{2u} + T_{2g}$,¹⁶⁾ and the framework acoustic modes as T_{1u} . Phonon branches of Na and the Si framework of the same symmetry will meet and avoid each other within the BZ. The symmetries of the lowest energy Na localized bands at Γ , in increasing energy, are T_{1g} , T_{2g} , T_{2u} and T_{1u} . Along $\Gamma \rightarrow A$, the framework acoustic modes split into the longitudinal (LA) and transverse (TA) branches with symmetry A_{2u} and E_u respectively. Symmetry forbidden avoided crossings occur when the acoustic bands ($A_{2u} + E_u$) meet the E_u component of the T_{2u} (split into $B_{2u} + E_u$) Na vibrational bands. Successive symmetry-avoided crossings of the LA branch with higher energy Na vi-

brational bands are clearly visible along the $\Gamma \rightarrow X$, $\Gamma \rightarrow R$ and $\Gamma \rightarrow M$ directions (see Fig. 1(a)). A consequence of symmetry avoided crossings is the mixing (coupling) of phonon modes¹⁷⁾ that helps to dissipate efficiently the thermal energy carried by the acoustic phonons to the localized rattling vibrations of the Na atoms. This is the basic premise of the resonant scattering model for the rationalization of the glasslike thermal conductivity in clathrates.¹⁸⁾

Except in the symmetry forbidden crossing regions, there is only very weak mixing between the Na and Si framework vibrations as depicted in the partial vibrational density of states (PVDOS) (Fig. 1(b)). Three sharp features at 72 , 98 and 135 cm^{-1} are identified as localized Na vibrations. Similar to clathrate hydrate,¹⁶⁾ the guests (Na) vibrations in the crystallographically distinct small and large cages are clearly separated.⁴⁾ The peaks at 72 and 98 cm^{-1} can be assigned to vibrations in the large cages due to the asymmetry (ellipsoidal shape) of the cage. The Na vibrations in the symmetric small cages show only one peak at 135 cm^{-1} . A detail examination of the PVDOS indicates that, in the acoustic mode region below 140 cm^{-1} , apart from the usual parabolic (Debye-like) distribution of the acoustic phonon branches, the Si framework atoms also exhibit small peaks that overlap with the Na vibrations. This observation corroborates the mixing (coupling) of the acoustic modes with the localized vibrations through resonant coupling (*vide supra*).

The phonon density of states of $\text{Na}_8\text{Si}_{46}$ has been measured by inelastic neutron scattering.¹⁹⁾ Owing to the large neutron scattering cross section for Na as compare to Si, the deduced phonon density of states is dominated by the Na vibrations. In the low frequency acoustic vibration region, a sharp feature at 83 was observed.¹⁹⁾ This feature may be correlated to the calculated Na localized vibrations at 98 cm^{-1} . Two broad bands at 300 and 435 cm^{-1} due to the Si framework vibrations were observed in the experiment.¹⁹⁾ These two bands can be assigned to strong features calculated at 330 and 425 cm^{-1} respectively. The mismatch in intensities between the observed and calculated features may be explained by the neglect of anharmonic effects. A similar effect has been observed and analyzed in the calculated and measured VDOS of ice Ih.²⁰⁾

Enclathration of Cs in the Sn_{46} framework has a strong effect on the unit cell size. The theoretically optimized unit cell for the hypothetical empty Sn_{46} is 1.203 nm . This is to be compared with the optimized unit cell parameter for $\text{Cs}_8\text{Sn}_{46}$ of 1.223 nm . The calculated cell parameter is in reasonable agreement with the experimental value of $1.2096(1) \text{ nm}$.²¹⁾ The electronic band structure of $\text{Cs}_8\text{Sn}_{46}$ is compared to the hypothetical pure Sn_{46} ($\square_8\text{Sn}_{46}$) in Fig. 2. We found a high degree of electron transfer from Cs to the Sn network. However, a rigid band description of the electronic structure is not entirely satisfactory here. Even though the band profiles for the empty Sn_{46} and $\text{Cs}_8\text{Sn}_{46}$ are broadly similar, they differ in detail. The largest discrepancies are found near the Γ and M points. At the M point the energy splitting between the two lowest bands immediately above the *pseudo*-bandgap is much larger in the doped clathrate (Figs. 2(a) and (b)). Furthermore, the involvement of Cs in the lower energy bands near the Fermi level is significant and the conduction band is modified by the Cs states. The electronic density of states (DOS) for $\text{Cs}_8\text{Sn}_{46}$ and pure Sn_{46} are compared in Figs. 2(c)

Fig. 2 Electronic band structure for (a) pure $\square_8\text{Sn}_{46}$ and (b) $\text{Cs}_8\text{Sn}_{46}$. The sizes of the filled circles reflect relative Cs contributions to the electronic band. Electronic density of states (DOS) for (c) $\square_8\text{Sn}_{46}$ (a semiconductor) and (d) $\text{Cs}_8\text{Sn}_{46}$. Notice the sharp feature below the Fermi level in $\text{Cs}_8\text{Sn}_{46}$ (dashed line).

and (d). In $\text{Cs}_8\text{Sn}_{46}$, a sharp band of Cs character that was not present in the conduction bands of $\square_8\text{Sn}_{46}$ is observed just below the Fermi surface. A comparison of the total density of states (DOS) with the partial density of states for Sn and Cs shows the profiles are very similar and they share many characteristic features. This strongly suggests that the Sn and Cs atoms rehybridize and interact with each other. The involvement of Cs in the valence band is a unique feature distinct from the Na in $\text{Na}_8\text{Si}_{46}$ but it is similar to that observed in $\text{Ba}_8\text{Si}_{46}$.⁶⁾

The phonon band structure for $\text{Cs}_8\text{Sn}_{46}$ is shown in Fig. 3(a). The lowest optic phonon branch is located at 12 cm^{-1} at Γ . This vibrational frequency is much lower than the estimate based on simple scaling of the atomic masses of Na and Cs^{22,23)} ($\sqrt{(22.99/132.91)} \times 72\text{ cm}^{-1} \approx 30\text{ cm}^{-1}$). The dispersions of phonon bands in the low frequency acoustic region differ from that of $\text{Na}_8\text{Si}_{46}$. Instead of flat localized bands, the dopant and framework mixed vibrational

bands of T_{1g} symmetry at *ca.* 12 cm^{-1} (at Γ) are highly dispersive along $\Gamma \rightarrow \text{X}$. Very strong dispersion interactions of the framework acoustic vibrations are also evident in the $\Gamma \rightarrow \text{M}$ direction. No symmetry-avoided crossing is observed for the TA and LA bands with the Cs–Sn T_{1g} vibration bands. Moreover, the maximum of the TA acoustic branch at the X point is *lower* in energy than the predominantly Cs vibrational bands. The LA mode intersects the Cs band halfway along $\Gamma \rightarrow \text{X}$ but there is no sign of avoided crossing since the symmetry of the two modes are different. Successive avoided crossings, however, are observed for the LA branch extended into the optic modes region. Another distinct difference between the phonon band structure of $\text{Na}_8\text{Si}_{46}$ and $\text{Cs}_8\text{Sn}_{46}$ is the strong dispersion of the lowest energy bands of the latter along $\text{X} \rightarrow \text{M} \rightarrow \text{R} \rightarrow \Gamma$. The phonon band structure strongly indicates that Cs atoms are part of the crystalline structure and cannot be treated as independent entities. Consequently, there is no possibility for

Fig. 3 Phonon band structure and (b) PVDOS for Cs₈Sn₄₆.

resonant scattering. The calculated carrier concentration²⁴⁾ in Cs₈Sn₄₆ of 1.4×10^{28} electron/m³ is similar to that in Na₈Si₄₆ (6.6×10^{28} electron/m³) but substantially lower than a good metal, such as Nb (1.0×10^{30} electron/m³). Therefore, Cs₈Sn₄₆ is a poor metal. If the lattice contribution is dominant, it should behave like a normal Debye solid. The thermal conductivity increases with decreasing temperature due to lower anharmonicity and vanishes abruptly when close to absolute zero temperature. This behavior is exactly as observed in the experiment.³⁾ The calculated PVDOS (Fig. 3(b)) supports the involvement of Cs in the bonding to the Sn framework. The vibrations of the Cs in the small (31 cm⁻¹) and large cages (19 and 27 cm⁻¹) are clearly separated. In comparison to Na₈Si₄₆, it is obvious that the framework atoms participate more significantly in the low frequency vibrations.

The contrasting vibrational behavior of Na₈Si₄₆ and Cs₈Sn₄₆ clathrates can be rationalized on the basis of the stiffness of the clathrate framework. As indicated by the large difference in the on-site force constants between Si–Si and Sn–Sn, the framework Si–Si covalent bonding is substantially stronger than that of Sn–Sn. In a simplified description, the Na atoms in Na₈Si₄₆ may be viewed as being trapped in square well potentials with a large barrier. The Na motions are therefore not coupled with the framework vibrations. In contrast, the Cs atoms in Cs₈Sn₄₆ are trapped in a soft harmonic potential thus, the vibrations of the Cs and the Sn are inter-mixed.

It is useful to comment on the implication of vacancies in the Sn framework on the theoretical results presented here. In

the case of Cs₈Sn₄₄, two Sn atoms are removed from the framework. This leads to eight Sn atoms with three coordination. To saturate the coordinate, it is conceivable that the Cs atoms will donate electrons to fill the unpaired orbitals of Sn. If this is the case, the Cs atoms are significantly coupled with the three-bonded Sn atoms, and no longer be regarded as localized resonant scatterers. This will have substantial effect on the thermal conductivity.

4. Conclusions

The theoretical phonon band structures presented here together with the experimental measurements of the thermal conductivity of Na₈Si₄₆ and Cs₈Sn₄₆ provide strong evidences suggesting that the glasslike thermal conductivity is due to the scattering of thermal phonon due to avoid-crossing of localized phonon bands of the metal with the framework TA acoustic branch of the same symmetry. It appears that resonant interactions of higher energy localized vibrations with the LA modes have little effect on the thermal conductivity (*cf.* Figs. 1(b) and 3(b)). These results are important for the systematic improvement of the thermoelectric property of clathrate-based materials.²⁵⁾ Dopant metal atoms must be chosen not to be too light such that the localized vibrational frequency is higher than the maximum frequency of the framework TA modes, or too heavy such that direct interactions with the framework atoms prohibit the possibility of phonon resonant scattering.

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