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Fundamental investigations on open-framework intermetallic materials of group 14

Matthew K. Beekman
University of South Florida

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Fundamental Investigations on Open-framework Intermetallic Materials of Group 14

by

Matthew K. Beekman

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy
Department of Physics
College of Arts and Sciences
University of South Florida

Major Professor: George S. Nolas, Ph.D.
Lilia Woods, Ph.D.
Sarath Witanachchi, Ph.D.
Garret Matthews, Ph.D.

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To my parents, Linda and Frank Beekman, who have always given me support and encouragement in all that I have endeavored to do.
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Fundamental Investigations on
Open-Framework Intermetallic Materials of Group 14

Matt Beekman

ABSTRACT

Crystalline open-framework intermetallics have long attracted the attention of chemists, physicists, and materials scientists. The intriguing structures such materials exhibit are often intimately related to the unique physical properties they possess. The present work is focused on the preparation and characterization of open-framework intermetallic materials based on group 14 elements, in particular those crystallizing in clathrate and related structures such as the clathrate-II phases. Materials possessing the clathrate-II crystal structure have received increased attention in recent years, as a result of both the unique properties they exhibit as well as potential for use in technologically important applications such as thermoelectrics, photovoltaics, and optoelectronics. However, in comparison with other clathrate structure types, characterization of clathrate-II materials has in general been far less extensive. Moreover, many conceivable compositions have yet to be realized.

The purpose of this work is to expand the current knowledge of the structural, chemical, and physical properties of these materials, while simultaneously exploring new compositions and synthetic routes to clathrate-II phases. One of the unique and promising aspects of clathrate-II materials is the ability to vary the guest concentration, which is shown to have significant implications for the structural and physical properties of Na$_x$Si$_{136}$ ($0 < x < 24$) materials. It is demonstrated that new compositions can be explored by novel approaches to chemical design. Framework substitution in clathrate-II compounds is explored in an effort to assess possibilities for influencing the physical properties of these materials. A novel zeolite-like framework phase, Na$_{1-x}$Ge$_{3+x}$, has been
discovered, and is shown to be a new low-thermal conductivity crystalline solid, suggesting a new approach to the design of crystalline intermetallic materials with low thermal conductivity. New directions in synthesis of intermetallics are identified, with emphasis on unconventional preparative methods and the opportunities they offer. Processing of reactive precursors by spark plasma sintering is demonstrated as a new preparative tool for crystal growth, identifying the first method for preparation of clathrate-II Na$_{24}$Si$_{136}$ single-crystals since the discovery of these compounds more than four decades ago.
1 Introduction

The chemistry and physics of group 14 elements such as silicon and germanium have been extensively studied, largely due to their fundamental importance in the development of semiconductor electronics. In addition to their ground state configurations (e.g. the diamond structure for $\alpha$-Si and $\alpha$-Ge), these elements can also exist as metastable expanded framework allotropes\textsuperscript{1,2} as well as highly stable binary,\textsuperscript{2-6} ternary,\textsuperscript{8,9} and higher order compounds\textsuperscript{10,11} known collectively as clathrates. Prior to the discovery of intermetallic clathrates based upon elements of group 14, the analogous crystal structures had been known in the gas and liquid hydrates, which constitute expanded forms of ice.\textsuperscript{12-14} The existence and crystal structure of the first intermetallic clathrates were first reported by Kasper et al.\textsuperscript{3} Systematic investigations were undertaken by Cros et al. soon thereafter.\textsuperscript{15-18} The common structural feature of all clathrate materials is an open-structured host framework that has the ability to encage guest atoms or molecules. The relationship between the structure of these and related materials, and the properties they display is of scientific and technological importance.

In the past ten years there has been a surge in interest in intermetallic clathrates. The impetus behind the increased attention given to these materials is predominantly two-fold. First, from a chemical and physical viewpoint, these materials allow for the study of the physics of compounds possessing isomorphic structures but with greatly varying properties, ranging from metals\textsuperscript{9} to semiconductors\textsuperscript{19} to superconductors,\textsuperscript{20,21} and magnetic materials as well. Intriguing and unconventional properties displayed by these materials, such as glasslike thermal conductivity\textsuperscript{19} and heavy atom tunnelling in the crystalline state,\textsuperscript{26-28} comprise novel physical phenomena in crystalline solids. Second, is the promise they hold for useful applications, ranging from thermoelectrics\textsuperscript{29-32} to photovoltaics and optoelectronics\textsuperscript{33-36} to potentially ultra-hard materials.\textsuperscript{37} It is important to recognize that these two motivations are intimately connected, since a fundamental
understanding of their chemistry and physics, as motivated by the first point, can be crucial in assessing their potential for use in applications, as given in the second.

There are several structural types that constitute the family of intermetallic clathrate materials. Of these, those with the clathrate-I crystal structure have been studied extensively and have received the most attention of all of the intermetallic clathrate types. As several excellent reviews are available, only a brief discussion of clathrate-I materials will be given in the present chapter. More attention will be paid here to a review of previous work on the synthesis and characterization of another emerging class of open-structured materials, those crystallizing with the clathrate-II* structure. The focus will be primarily on the experimental results, though theoretical work will also be discussed where pertinent. A rich collection of theoretical treatments of clathrate-II materials may be found in the literature.

1.1 Clathrate-I compounds

Two of the most significant findings that have stimulated so much research effort on intermetallic clathrates were the identification of clathrate-I materials as candidates for thermoelectric applications and the related discovery of rather unconventional heat transport for a crystalline solid, observed for a number of semiconducting clathrate-I variants. Since the original suggestion that intermetallic clathrates would be of interest for thermoelectrics, a number of promising advances and innovations have been made, further fueling interest in these materials. The very low lattice thermal conductivities that have been observed in clathrates such as Sr8Ga16Ge30 and Eu8Ga16Ge30, and which follow a literally glasslike temperature dependence, have resulted in an immense amount of effort being focused on understanding the lattice dynamics in these and related compounds. Various explanations have been proposed to elucidate the mechanisms behind this unusual thermal transport behavior, with the current prevailing understanding being in terms of a strong interaction (i.e. scattering) between localized phonons (i.e. with negligible group velocity), associated with the guest

*The synonymous terms clathrate-II and type II clathrate will be used interchangeably throughout this work, as both terms are in common use in the literature.
species, and the heat carrying acoustic phonons of the clathrate.\textsuperscript{19,69-75} This area continues to be an active field of research.

The promise these materials hold for thermoelectrics stems from the relatively good electrical properties (reasonably high Seebeck coefficients and electrical conductivities) that a number of semiconducting clathrates possess, in addition to their very low thermal conductivities. This fortuitous combination of properties has resulted in thermoelectric figures of merit $ZT$\textsuperscript{†} on the order of unity for several clathrate-I compounds,\textsuperscript{76} values comparable with current state-of-the-art materials. Considering the diversity in as yet uninvestigated compositions (cf. Chapter 2), progress toward enhanced thermoelectric properties in these compounds can be expected.

1.2 Structure, bonding, and crystal chemistry in clathrate-II materials

As with other inorganic clathrates, the clathrate-II crystal structure can be visualized in terms of face-sharing polyhedral cages resembling fullerene-like building blocks of silicon, germanium, or tin. However, an important difference between the clathrate-II structure and other fullerene solids (e.g. crystallized $C_{60}$; Ref. 77) is the tetrahedrally coordinated $sp^3$-like bonding found in the clathrates. This can be viewed as a direct consequence of the preference of silicon and germanium (and sometimes tin) in forming $sp^3$ bonds, whereas carbon readily forms both $sp^3$- (e.g. diamond) and $sp^2$-like bonds (e.g. graphite).\textsuperscript{78,79} The possibility as to whether carbon can crystallize in the clathrate-II structure remains an open experimental question.\textsuperscript{54}

The clathrate-II framework can be perceived in terms of the coordination polyhedra for the guest species: eight 28-membered hexacaidecahedra ($E_{28}$, point symmetry $Td$), and sixteen 20-membered pentagonal dodecahedra ($E_{20}$, point symmetry $Ih$) per conventional unit cell, as shown in Figure 1.1. The guest atoms reside inside these polyhedra formed by the framework. There are three crystallographic sites (space group $Fd\bar{3}m$) in the framework, $96g$, $32e$, and $8a$ in the Wyckoff notation. The guest species

\begin{footnotesize}
\textsuperscript{†} For a given material, the dimensionless thermoelectric figure of merit is defined as $ZT = S^2T/\rho\kappa$, where $Z = S^2/\rho\kappa$ is the thermoelectric figure of merit, $S$ is the Seebeck coefficient, $\rho$ is the electrical resistivity, $\kappa$ is the total thermal conductivity, and $T$ is the absolute temperature. The product $ZT$ originates in the thermodynamic analysis of the efficiency for a thermoelectric module, and to maximize efficiency it is desirable to maximize $ZT$ for the device constituent materials.
\end{footnotesize}
Figure 1.1 Sixteen pentagonal dodecahedra ($E_{20}$) and eight hexacaidecahedra ($E_{28}$) share faces to form the clathrate-II crystal structure. The occupancy of the polyhedral cages in the clathrate-II structure may be either completely filled or completely empty, or varied between the two extremes. M. Beekman and G.S. Nolas, *J. Mater. Chem.* 18, 842 (2008). Reproduced by permission of The Royal Society of Chemistry.

reside at the $8b$ and $16c$ sites, inside the $E_{28}$ and $E_{20}$ cages, respectively. The resulting structure is face-centered cubic (see Figure 1.1), and the general chemical formula can be written as $A_{8}B_{16}E_{136}$ ($A =$ guest in $E_{28}$, $B =$ guest in $E_{20}$, and $E =$ Si, Ge, Sn or substituents) in the conventional unit cell. Although qualitative similarities exist between the clathrate-II structure and other clathrate types, at least one important difference should be emphasized. This is the ability to fully vary the guest concentration in the clathrate-II materials,\textsuperscript{4} whereas the guest content is empirically fixed at full occupation in, for example, clathrate-I compounds, with very few exceptions. As discussed below, this feature has significant implications for the physical properties of these materials.

As evident from Figure 1.1, the clathrate-II framework is composed of 5-membered and 6-membered rings, corresponding to the faces of the $E_{20}$ and $E_{28}$ polyhedra. This is in contrast to the diamond structured $\alpha$ phases of the Group 14 elements, which exhibit exclusively 6-membered rings. Indeed, the average number of atoms per ring in the clathrate-II structure is 5.064, and is the smallest for any known
structure. Some of the interesting properties of these materials have been attributed to this large concentration of 5-membered rings.80,81

Structural analogies exist between the clathrate-II structure and other known compounds and structures. For example, the guest atom positions ($8b$ sites) inside the larger $E_{28}$ polyhedra form an enlarged “diamond lattice.” The $E_{28}$ polyhedra are centered on these sites, with the $E_{20}$ polyhedra being formed in the space between the $E_{28}$ cages. The clathrate-II structure may also be considered as dual to the MgCu$_2$ structure, in the sense that the constituent guest atom positions in the clathrate-II structure (centers of the polyhedra) correspond to the positions of the atoms in the MgCu$_2$ structure (i.e., $E_{20} \rightarrow$ Cu, $E_{28} \rightarrow$ Mg). The interested reader can find in the literature a number of useful discussions of the various interesting structural and geometric relationships found in clathrate materials.38,47,82-84

In Figure 1.2 a plot of the ratio of the free cavity diameter ($D$) to cage-atom diameter ($d$) for several cage-like materials is shown as a function of the square root of

![Figure 1.2](image)

**Figure 1.2** Free cavity diameter to cage-member diameter ratio versus the square root of coordination number (CN) of the interior (i.e. guest) site, for several cage-like materials.39 Si$_{24}$ corresponds to the “flattened” clathrate-I tetrakaidecahedra, which has two characteristic dimensions. M. Beekman and G.S. Nolas, *J. Mater. Chem.* **18**, 842 (2008). Reproduced by permission of The Royal Society of Chemistry.
the number of atoms in the cage, i.e. the coordination number (CN). We see that a straight line fits the data quite well indicating an empirical dependence on the coordination number of \( D/d \sim \sqrt{\text{CN}} \). The figure allows an estimate as to which atoms or molecules might be entrapped in a particular host material. From the figure, we can see that the clathrate-II \( E_{20} \) and \( E_{28} \) polyhedra fall in the intermediate range for this ratio, with the smallest and largest values shown being for the tetrahedron and the fullerene \( C_{60} \), respectively.

The clathrates can also be considered as expanded forms of silicon, germanium, and tin, and as a result of their cage-like structure they can be viewed as “naturally” nano-porous crystalline solids. As a consequence of their open structure, the volume per framework atom is as much as 15 to 20% larger in the clathrate relative to the diamond structure. However, the average \( E-E \) bond lengths for the guest-free \( \text{Si}_{136} \) (2.34 Å)\textsuperscript{1} and \( \text{Ge}_{136} \) (2.45 Å)\textsuperscript{2} clathrates are not significantly different from the “ideal” bond lengths for the corresponding diamond structures.\textsuperscript{85} In addition, the clathrate-II bond angles average close to the ideal 109.47° expected for tetrahedral coordination. As such, the free energies for the clathrate structures are found to be only slightly higher in energy than for the corresponding ground-state diamond structures (e.g. for \( \alpha \)-Si).\textsuperscript{33} The incorporation of guests into the empty structure typically results in a small but significant expansion of the structure.\textsuperscript{9,86-88}

Although the clathrate-II allotropes such as the empty \( \text{Si}_{136} \) and \( \text{Ge}_{136} \) are energetically metastable with respect to the diamond structured phases, the energy difference is apparently quite small\textsuperscript{33,47,48} and a significant energy and/or kinetic barrier must exist allowing the clathrate structure to endure. San-Miguel et al.\textsuperscript{89} and Ramachandran et al.\textsuperscript{90} have independently shown that the \( \text{Si}_{136} \) framework is stable under pressure up to 11 GPa. Moreover, no transition towards the diamond phase is observed, rather the \( \text{Si}_{136} \) framework undergoes an irreversible transition to the \( \beta \)-Sn structure of silicon at 11.5 GPa, accompanied by a large volume reduction of more than 30%.\textsuperscript{89,90} Further discussion of the high pressure properties and stability of clathrates may be found in the literature.\textsuperscript{42,43,89-92}
Some of the most interesting structural aspects of clathrate-II materials are related to the relatively weak bonding between the guest atoms and the host framework. Nolas et al. have reported on temperature dependent single crystal X-ray diffraction studies on several clathrate-II silicon and germanium compounds. Figure 1.3 shows the temperature dependence of the isotropic atomic displacement parameters (ADP or $U_{iso}$) for the framework atoms in these compounds, as well as for the guest atoms inside the larger $E_{28}$ cage. For all of the guests, the ADPs are considerably larger than those of the framework sites. Moreover, there is much stronger temperature dependence for the guest ADPs relative to the framework. The magnitude and temperature dependence of the guest ADPs is indicative of relatively large amplitude thermal motion, and is a consequence of both the significant “space” inside the hexacairodecahedra, as well as relatively weak bonding between guest and framework. Bobev and Sevov have estimated the relative size of...
Figure 1.4 Dimer formation between the Na guests in the Na$_x$Si$_{136}$ clathrates. (a) In the ideal $Fd\bar{3}m$ symmetry the guests occupy the centers of the Si$_{28}$ polyhedra. (b) EXAFS measurements indicate the formation of a weak dimer between Na guests in adjacent Si$_{28}$ cages, with the guests moving toward the shared hexagonal face of the polyhedra.$^{95,96}$ M. Beekman and G.S. Nolas, J. Mater. Chem. 18, 842 (2008). Reproduced by permission of The Royal Society of Chemistry.

guest and cage by subtracting framework atomic radii from the shortest guest-framework distances, compared to the estimated ionic radii of the guests. It is interesting to note that in general the larger the difference in size between guest relative to its $E_{28}$ cage, the larger the ADP, as evidenced in Figure 1.3. The relationship of the guest thermal motion to the thermal properties of these materials is discussed in more detail below.

Assuming the highest symmetry arrangement within the $Fd\bar{3}m$ space group, the guest atoms in the clathrate-II structure are located at the centers of their respective polyhedral cages. However, in the case of the Na$_4$Si$_{136}$ clathrate it was originally suggested by Demkov et al.,$^{44}$ who used quantum molecular dynamics simulations, that the Na guest inside the Si$_{28}$ cage could in fact move off-center, thus lowering the site symmetry from $T_d$ to $C_{3v}$. This was interpreted in terms of a Jahn-Teller distortion, and accompanying energy-lowering lifting of the degeneracy of the lowest conduction band.$^{44}$ Electron spin resonance measurements reported$^{94}$ soon after gave experimental evidence for this guest displacement in Na$_3$Si$_{136}$. More recently, analysis of extended X-ray absorption fine structure (EXAFS) measurements$^{95,96}$ and accompanying theoretical studies indicate that the Na guests in the Si$_{28}$ polyhedra can indeed move off-center in the Na$_x$Si$_{136}$ clathrates ($x = 8$ and $\sim 24$), toward the shared hexagonal faces by as much as 1
Å. Those results were interpreted in terms of the formation of a dimer between Na guests in adjacent Si$_{28}$ cages, shown schematically in Figure 1.4. This effect may be akin to the well known Peierls distortion$^{97}$ associated with the hypothetical one-dimensional monatomic lattice. As suggested by temperature dependent NMR data, a similar dimerization may also occur between Cs guests in Cs$_8$Ge$_{136}$. The off-center nature of guest atoms in clathrate-I compounds such as Sr$_8$Ga$_{16}$Ge$_{30}$ and Eu$_8$Ga$_{16}$Ge$_{30}$ has been shown$^{70,71,99,100}$ to be intimately linked to their unique physical properties, and such phenomena remain an aspect warranting further study in clathrate-II compounds.

1.3 Synthetic routes to clathrate-II materials

There are various synthetic methods that have been used to prepare clathrate-II materials, and some compositions can be produced by more than one method. Arguably the most straightforward method is direct synthesis from the elements. Guided by the observation that stabilization of the clathrate-II structure is facilitated through matching relative sizes of guest and cage, Bobev and Sevov first synthesized$^{9,86}$ the $A_8Na_{16}E_{136}$ clathrates ($A = \text{Cs, Rb}; E = \text{Si, Ge}$) by reaction of the high purity elements inside sealed niobium capsules. The mixtures were held at 650°C for three weeks, and then slowly cooled to room temperature. Later, Nolas et al.$^{93,101,102}$ used a similar method to synthesize these compounds for further characterization. The products were well-formed small crystals (~ 1 to 3 mm in size), typically along with coarse polycrystalline powders. An important consideration in the synthesis of these alkali-containing clathrates is the relatively high vapor pressure of the alkali metals and their ability to react easily with silica ampoules if used, so that reactions must be carried out within sealed, metal vessels. The synthesis of a Sn clathrate-II compound has also been reported$^{103}$ by reaction of a mixture of K:Ba:Ga:Sn in the ratio 8:16:32:104, with no K incorporated into the end compound Ba$_{16}$Ga$_{32}$Sn$_{104}$. This is the only Sn clathrate-II compound reported to date. Semiconducting clathrate-II compounds are expected to have promising thermoelectric properties. Novel routes to preparing such compositions, some of which will be given in the present work, could provide an important path to the discovery of new thermoelectric clathrate materials.
Novel compositions may be prepared from those synthesized directly from the elements. This follows from the fact that, in contrast to other clathrate types, the guest concentration in the clathrate-II may be varied while still maintaining the integrity of the structure. In our previous work, we have synthesized the new clathrate composition Cs₈Ge₁₃₆, in which Cs solely occupies the eight larger Ge₂₈ cages in the structure. This was achieved by first starting with stoichiometric Cs₈Na₁₆Ge₁₃₆, prepared from the elements as discussed above. The Na content was then reduced by successively heating Cs₈NaₓGe₁₃₆ (x < 16) under high vacuum, causing the Na to “degas” from the clathrate, while Cs remained incorporated in the structure. Using this procedure, the Na content can be reduced to less than 600 ppm. Similarly, Rb₈Ge₁₃₆ can also be prepared in this manner.

Although direct synthesis may be the most straightforward synthesis route, this method has to date been unsuccessful for preparation of a number of compositions. Conspicuous examples include the NaₓSi₁₃₆ (0 < x < 24) clathrates. These were of the first inorganic clathrates to be discovered by Kasper et al., followed shortly thereafter by a systematic study originally undertaken by Cros et al. Until the present work (cf. Chapter 5), NaₓSi₁₃₆ have only been prepared via thermal decomposition of the Zintl compound Na₄Si₄. Na₄Si₄ is prepared from the elements by reaction at 650°C or higher under inert atmosphere, though the product is extremely air and moisture

---

**Figure 1.5** Polyatomic Zintl anions (a) [E₄]⁴⁻ and (b) [E₉]⁴⁻ that act as precursor constituents in the synthesis of clathrates-II materials via thermal decomposition of silicides or germanides, as well as reaction in ionic liquids. M. Beekman and G.S. Nolas, *J. Mater. Chem.* 18, 842 (2008). Reproduced by permission of The Royal Society of Chemistry.
sensitive and handling must be performed in a N$_2$ or Ar glove-box. Na$_x$Si$_{136}$ is formed upon heating Na$_4$Si$_4$ under vacuum ($< 10^{-5}$ torr) to temperatures above ~ 350$^\circ$C. The structure$^{106-108}$ of Na$_4$Si$_4$ is monoclinic (space group C2/c) and consists of Na$^+$ and [Si$_4$]$^{4-}$ Zintl ions (cf. Figure 1.5a).$^{109}$ During thermal decomposition, most of the Na$^+$ ions are reduced and are removed as vapor, with the remaining Na acting as a template for the Si$_{136}$ framework formed by reconstruction of the [Si$_4$]$^{4-}$ cluster ions. The sodium content $x$ is controlled by varying both the temperature and time for which the specimen is heated, with higher temperatures and longer times leading to lower sodium contents. The relative intensities of several reflections from powder X-ray diffraction exhibit a strong dependence upon the Na content,$^{87,88}$ thus allowing for the determination of the Na content (and therefore composition) from Rietveld$^{110,111}$ structure refinement. The relative occupancy of the cages can also be determined in this way (cf. §4.2).

In addition to Na$_x$Si$_{136}$, the clathrate-I Na$_8$Si$_{46}$ is also commonly present in specimens prepared from decomposition of Na$_4$Si$_4$, constituting as much as 45 wt% in as prepared specimens.$^{87,88}$ This poses a challenge to producing Na$_x$Si$_{136}$ specimens of high purity for further characterization of their physical properties. Ramachandran et al.$^{87}$ utilized the difference in densities between the two phases in order to separate them. However, this technique can be quite difficult to employ, as the crystallites of the two phases are often inter-grown.$^{112}$ Preparation of phase pure Na$_x$Si$_{136}$ specimens (i.e. with negligible Na$_8$Si$_{46}$ fraction) continued to be a challenge until the present work, an aspect that will be discussed in later chapters (cf. §4.1 and Chapter 5).

Unlike the case for Na$_x$Si$_{136}$, thermal decomposition of binary phases under vacuum is not as successful in producing the Ge analogue Na$_x$Ge$_{136}$ from Na$_4$Ge$_4$. Although Na$_x$Ge$_{136}$ can be prepared from Na$_4$Ge$_4$,$^4$ a systematic study has shown that the yield is typically small, and Na$_x$Ge$_{136}$ only forms in a narrow range of synthesis temperatures.$^{104,113}$ Rather, a novel hexagonal zeolite-like framework phase Na$_{1-x}$Ge$_{3+z}$ (cf. Chapter 6) forms as the majority phase.$^{114}$ The reason may be linked to the crystal structures of the precursor compounds Na$_4$Si$_4$ and Na$_4$Ge$_4$: although both are monoclinic and are composed of Na$^+$ and [E$_4$]$^{4-}$ Zintl ions, the structures are not identical.$^{106,107}$ Thus
the subtle morphological differences in Na₄Ge₄ (space group $P2_1/c$) and Na₄Si₄ (space group $C2/c$) may promote differing structures for the decomposition products.

Other clathrate-II compositions have also been prepared by the thermal decomposition of mixed alkali or alkali/alkaline earth silicides. Ramachandran et al.$^{115}$ synthesized Cs₈Na₁₆Si₁₃₆ by thermal decomposition of Cs₈Na₁₋ₓSi, while similarly Latturner et al.$^{116}$ synthesized Rb₈Na₁₆Si₁₃₆ from RbₓNa₁₋ₓSi. The synthesis of Ba₈Na₁₆Si₁₃₆ via thermal decomposition of Na₂BaSi₄ has also been reported,$^{117}$ though the products consisted of a mixture of several phases. It is interesting to note that all precursors used thus far to prepare inorganic clathrates via thermal decomposition (and also more recently chemical oxidation$^{2,118,119}$) contain cluster $[E_n]^{m-} \ (n, m \ \text{integers})$ anions, an aspect clearly linked to their ability to promote the clathrate structure upon reaction.

One of the original questions concerning clathrate-II materials was the stability of the structure upon complete removal of the guests. Gryko et al.$^1$ showed that the clathrate-II framework is indeed stable when emptied (Na content less than 600 ppm Si),
and prepared the guest-free silicon clathrate Si$_{136}$ by means of repeated degassing of Na$_x$Si$_{136}$ and treatment with concentrated acids. Ammar et al.$^{120}$ later also prepared Si$_{136}$ using a similar technique, but reduced the residual Na content even further by reaction of the clathrate with iodine (final residual Na content ~ 35 ppm Si). The crystalline clathrate Si$_{136}$ in essence constitutes a new allotropic of silicon.

Although preparing a guest-free Ge$_{136}$ clathrate by the above described process of degassing Na$_x$Ge$_{136}$ is not feasible,$^{104,113,114}$ a new method has recently been developed by Guloy et al.$^{2,121}$ in order to circumvent this difficulty. The investigations were motivated by previous studies indicating ionic liquids are effective in polymerizing [Ge$_9$]$^{4-}$ (Fig. 1.5b) from solution. The reaction was regarded as a solvation of Na$_{12}$Ge$_{17}$ in a 1:1 molar ratio melt of AlCl$_3$ and dodecyltrimethylammonium chloride (DTAC). Specimens with Ge$_{136}$ as the major phase could be prepared by heating the reaction mixture at 300°C while sealed under inert atmosphere. This reaction was explained in terms of the reaction of the [Ge$_9$]$^{4-}$ with DTAC according to$^2$

$$4[\text{CH}_3(\text{CH}_2)_{11}\text{N(CH}_3)_3]^+ + [\text{Ge}_9]^{4-} \rightarrow 9\text{Ge}^0 + 4\text{CH}_3(\text{CH}_2)_9\text{CH}=\text{CH}_2 + 4\text{N(CH}_3)_3 + 2\text{H}_2$$

The synthesis of Ge$_{136}$ was reproduced by the author using Na$_4$Ge$_4$ as a precursor, but solvation of the precursor was not observed, indicating the reaction may in fact be heterogeneous in nature.$^{122}$ This new open-structured allotropic of Ge deserves further characterization. Using similar procedures, but with the precursor K$_4$Ge$_9$, the authors also have successfully prepared the clathrate-II K$_8$Ge$_{136}$.$^{2,123}$

Table 1.1 lists clathrate-II compositions that have been reported to date. By comparison with the extensive number of known intermetallic clathrate-I compounds,$^{38-43}$ one can quickly conclude that the conceivable clathrate-II compositions still to be investigated is quite significant. The synthesis of new compositions, in addition to those listed in Table 1.1, is important for the study of their physical and chemical properties, and to develop a fundamental understanding of structure-property relationships in open-framework and guest-host materials. Some previous work toward this understanding is outlined in the remainder of this chapter.
1.4 Electronic properties of clathrate-II materials

Since the observation of unique optical properties in porous silicon,124 low-density forms of this technologically important semiconductor have continued to be investigated for their interesting electronic properties, in comparison with the bulk crystalline diamond structured state (α-Si). An important discovery regarding the electronic properties of clathrate-II materials was the theoretical prediction33 and later experimental verification1 that the band gap of the empty clathrate Si$_{136}$ is expanded by approximately 0.7 eV relative to that for diamond structured silicon ($E_{\text{gap}}$ of α-Si ~ 1.2 eV). Thus the Si$_{136}$ allotrope constitutes a novel wide-band gap semiconductor. However, whereas the interesting optical properties of materials such as porous silicon have been attributed to quantum confinement effects, the widening of the gap in Si$_{136}$ (relative to diamond structured Si) can be understood in terms of the slight distortion in the clathrate of the ideal tetrahedral bonding found in α-Si, as well as the high density of 5-membered rings in the Si$_{136}$ structure.33 Recent theoretical work36 has discussed the importance of

<table>
<thead>
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<th>Composition</th>
<th>Synthesis Method</th>
<th>Lattice Parameter $a$ (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si$_{136}$</td>
<td>Degassing of Na$<em>x$Si$</em>{136}$</td>
<td>14.62601(9)</td>
<td>1</td>
</tr>
<tr>
<td>Na$<em>x$Si$</em>{136}$</td>
<td>Decomposition of NaSi</td>
<td>14.62601(9) ≤ $a$ ≤ 14.70704(1)</td>
<td>1,4</td>
</tr>
<tr>
<td>Cs$<em>2$Si$</em>{136}$</td>
<td>Decomposition of CsSi</td>
<td>14.64</td>
<td>4</td>
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<td>Rb$<em>x$Na$</em>{16}$Si$_{136}$</td>
<td>Direct reaction of elements</td>
<td>14.7400(4)</td>
<td>9</td>
</tr>
<tr>
<td>Cs$<em>8$Na$</em>{16}$Si$_{136}$</td>
<td>Direct reaction of elements</td>
<td>14.7560(4)</td>
<td>9</td>
</tr>
<tr>
<td>Ba$<em>8$Na$</em>{16}$Si$_{136}$</td>
<td>Decomposition of Na$_x$BaSi$_4$</td>
<td>Not reported</td>
<td>117</td>
</tr>
<tr>
<td>Ge$_{136}$</td>
<td>Reaction of [Ge$_9$]$^{3-}$ in DTAC/AlCl$_3$</td>
<td>15.2115(1)</td>
<td>2</td>
</tr>
<tr>
<td>Na$<em>x$Ge$</em>{136}$</td>
<td>Decomposition of NaGe</td>
<td>15.4</td>
<td>4</td>
</tr>
<tr>
<td>Cs$<em>8$Ge$</em>{136}$</td>
<td>Degassing of Cs$<em>8$Na$</em>{16}$Ge$_{136}$</td>
<td>15.329</td>
<td>98</td>
</tr>
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<td>Rb$<em>x$Na$</em>{16}$Ge$_{136}$</td>
<td>Direct reaction of elements</td>
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<td>9</td>
</tr>
<tr>
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<td>15.4805(6)</td>
<td>9</td>
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<tr>
<td>Ba$<em>{16}$Ga$</em>{32}$Sn$_{104}$</td>
<td>Direct reaction of elements</td>
<td>17.054(1)</td>
<td>103</td>
</tr>
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</table>

$^a$ Selected references.
Figure 1.7 Seebeck coefficient (round symbols) and resistivity (triangular symbols) as a function of temperature for polycrystalline Cs$_8$Na$_{16}$Si$_{136}$ (open symbols) and Cs$_8$Na$_{16}$Ge$_{136}$ (filled symbols). Inset: DFT computed electronic density of states for Cs$_8$Na$_{16}$Si$_{136}$ (lower) and Cs$_8$Na$_{16}$Ge$_{136}$ (upper) the dashed line indicates the Fermi level, which is well within the conduction band for both materials. M. Beekman and G.S. Nolas, *J. Mater. Chem.* 18, 842 (2008). Reproduced by permission of The Royal Society of Chemistry.

symmetry considerations for the optical properties of silicon clathrate-II materials, as well as the potential for intercalation of guests with electronegativities that are higher than that of silicon.

A promising aspect of these open-framework Si and Ge semiconductors is the potential for band-gap engineering with composition. Moriguchi et al.$^{34}$ have explored the electronic structure of clathrate-II silicon-germanium alloys, Si$_{136-x}$Ge$_x$, using density functional techniques. These authors found that the effect of alloying silicon and germanium on the clathrate framework can not only allow for varying the size of the $\sim 2$ eV band gap of Si$_{136}$, but also that Si$_{136-x}$Ge$_x$ clathrates should possess a direct band gap for a range of values of $x$. Their results indicate the band gap of Si$_{136-x}$Ge$_x$ alloys could be
continuously “tuned” from approximately 1.2 to 2 eV, in the visible range of the electromagnetic spectrum. This band-gap dependence can be contrasted to that observed in the diamond structured Si$_{1-x}$Ge$_x$ alloys (0.7 to 1.1 eV). Although the synthesis of Si$_{136-x}$Ge$_x$ clathrates has yet to be achieved, such predicted properties make these materials of particular interest for potential use in optoelectronic or photovoltaic applications.

The electronic properties of the filled group 14 clathrates can be discussed in terms of a rigid band model, in which the electropositive guests donate their valence electrons to the host framework. Within this model, the “empty” clathrate framework electronic band structure (e.g. that of Si$_{136}$ or Ge$_{136}$) is only minimally modified by introduction of the guests into the framework cages, and the donated electrons occupy the framework conduction band levels (i.e. states with “anti-bonding” character). For compounds such as Cs$_8$Na$_{16}$Si$_{136}$ and Cs$_8$Na$_{16}$Ge$_{136}$, the result is a high density of charge carriers (> $10^{21}$ cm$^{-3}$) in a partially filled band and metallic properties. This is exemplified in Figure 1.7, which shows experimental results from temperature dependent electrical transport measurements, corroborated by theoretical calculations of the electronic density of states (DOS) for these two compounds. For both compounds, the resistivities increase monotonically with temperature (typical metallic behavior), while the Seebeck coefficients remain relatively small, the (negative) sign indicating electrons are the majority carriers. It should be noted that the rigid band approximation is, strictly speaking, a simplified model, and there is evidence that the introduction of the guests can indeed modify the band structure of these materials. Nevertheless, it remains a useful model for the qualitative understanding of the electronic properties of these materials. To date, the only semiconducting clathrate-II phases for which electrical transport properties have been reported are the guest-free Si$_{136}$ and Ge$_{136}$, and the lower Na content Na$_8$Si$_{136}$. However, the ability to substitute other species for the framework atoms discussed in Chapter 3 of the present work may allow for the synthesis and characterization of new semiconducting clathrate-II variants.

The ability to adjust the guest content in clathrate-II materials offers a unique opportunity to study the effects of guest content and type on the physical properties of
inorganic clathrates. It has been observed that the electrical properties of Na$_x$Si$_{136}$ ($0 < x < 24$) clathrates depend strongly on the Na content, in that increasing the guest content considerably reduces the electrical resistivity.\textsuperscript{4,126} Moreover, high Na content Na$_x$Si$_{136}$ specimens exhibit metallic behavior whereas lower Na content specimens show semiconducting or insulating behaviour.\textsuperscript{4,126,127} Transport,\textsuperscript{4,126} NMR,\textsuperscript{128} and magnetic susceptibility measurements,\textsuperscript{129} as well as theoretical calculations,\textsuperscript{44,125} indicate a metal to insulator transition occurs at $7 < x < 12$, though the precise value of $x$ at which this occurs has yet to be determined unequivocally and could also conceivably depend on the relative occupation of the two different caged Na sites in the structure. In analogy with the superconducting fullerenes\textsuperscript{130} and also some clathrate-I compounds\textsuperscript{20,21} the possibility of superconductivity in clathrate-II Na$_x$Si$_{136}$\textsuperscript{129} and Ba$_8$Na$_{16}$Si$_{136}$\textsuperscript{117} has been explored, but with negative results. Superconductivity has as yet not been observed in clathrate-II phases.

The electronic structure of several clathrate-II phases has been studied employing nuclear magnetic resonance techniques.\textsuperscript{1,98,115,128,131-134} Common to several clathrate-II materials are the relatively large NMR shifts for both the guest and framework species. These shifts have been interpreted as akin to the Knight shifts in metals, originating in the hyperfine interactions between the NMR nuclei and the delocalized conduction electrons.\textsuperscript{135} Indeed, the Knight shifts for $^{23}$Na in the Na$_x$Si$_{136}$ clathrates (1600 to 2000 ppm as referenced to 1 mol NaCl at 0 ppm) are larger than in metallic sodium (1123 ppm).\textsuperscript{132,133} Moreover, in contrast to the behavior associated with Knight shifts in metals, which are typically found to be approximately temperature independent,\textsuperscript{135} the Knight shifts in Rb$_8$Na$_{16}$Si$_{136}$,\textsuperscript{116} Na$_x$Si$_{136}$,\textsuperscript{132,133} and Cs$_8$Ge$_{136}$\textsuperscript{98} are found to exhibit strong temperature dependences, increasing as the temperature is decreased. As originally suggested by Gryko et al.,\textsuperscript{132,133} this phenomenon appears to be related to distinct features, such as a sharply peaked structure, in the electronic density of states near the Fermi level in these materials.\textsuperscript{61}
1.5 Thermal and vibrational properties of clathrate-II materials

Of the most conspicuous aspects of intermetallic clathrates (as well as hydrate and other clathrates) are their thermal, lattice dynamical, and vibrational properties, which continue to be intensely studied.\(^{19,48,49,57,93,136-144}\) The relatively large number of atoms in the clathrate-II unit cell, as well as the presence or absence of the guests, results in distinctive thermal properties for these materials. As discussed above, the relatively large difference in size and weak bonding between guest and cage in many filled clathrates promotes localized guest vibration modes, a phenomenon which has been termed as “rattling.” This is reflected in the magnitude and temperature dependence of the guest atom ADPs determined from single crystal XRD, as discussed above (Figure 1.3).\(^{93}\)

Previous studies have shown\(^{145-147}\) that ADPs determined from crystallographic analysis can be used to estimate the frequencies of the localized vibrations undergone by guest atoms such as those in the clathrate-II materials, and also to estimate other pertinent physical quantities for the solid. With the assumption that the guest acts as a three dimensional “Einstein” oscillator,\(^{148}\) the “rattler” frequency can be estimated from the simple relation \(U_{\text{iso}} = k_B T/m (2\pi\nu)^2\), where \(k_B\) is Boltzmann’s constant, \(m\) is the mass of the “rattler,” and \(\nu\) is the frequency of vibration. Vibration frequencies determined using this approach for \(\text{Cs}_8\text{Na}_{16}\text{Si}_{136}\) and \(\text{Cs}_8\text{Na}_{16}\text{Ge}_{136}\) are given in Table 1.2.\(^{93}\)

Table 1.2 Vibrational frequencies for the guest atoms in \(\text{Cs}_8\text{Na}_{16}\text{Si}_{136}\) and \(\text{Cs}_8\text{Na}_{16}\text{Ge}_{136}\), as determined from temperature dependent single crystal XRD (ADP data),\(^{93}\) Raman scattering,\(^{101}\) and density functional theory calculations.\(^{57,101}\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu_{\text{ADP}})</th>
<th>(\nu_{\text{Raman}})</th>
<th>(\nu_{\text{theory}})</th>
</tr>
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<tr>
<td></td>
<td>Cs</td>
<td>Na</td>
<td>Cs</td>
</tr>
<tr>
<td>(\text{Cs}<em>8\text{Na}</em>{16}\text{Si}_{136})</td>
<td>53.4</td>
<td>141</td>
<td>57</td>
</tr>
<tr>
<td>(\text{Cs}<em>8\text{Na}</em>{16}\text{Ge}_{136})</td>
<td>41.8</td>
<td>117</td>
<td>18</td>
</tr>
</tbody>
</table>

\(^a\)N.A. = Not Raman Active
The “rattling” motions of the guest atom, or soft phonon modes, in the $A_8B_{16}E_{136}$ clathrates have also been studied by Raman scattering experiments. From group theoretic analysis, it is found that the guest atoms in the larger $E_{28}$ hexacaidecahedra contribute a Raman-active optic mode ($T_{2g}$ symmetry), while the guest atoms in the smaller $E_{20}$ dodecahedra do not contribute any Raman-active modes. Figure 1.8 shows room temperature Raman scattering spectra obtained on polycrystalline $Si_{136}$ and single-crystal $Cs_8Na_{16}Si_{136}$. The low-frequency Cs “rattle” mode at $57 \text{ cm}^{-1}$ is clearly discernable, and this observed Raman shift is in qualitative agreement with the frequency of $64 \text{ cm}^{-1}$ predicted for this mode by density functional theory computations. A similar

**Figure 1.8** Stokes Raman scattering spectra for $Si_{136}$ and $Cs_8Na_{16}Si_{136}$. The Cs “rattle” mode at $\sim 57 \text{ cm}^{-1}$ is indicated. Reprinted with permission from G.S. Nolas, C.A. Kendziora, J. Gryko, J.J. Dong, C.W. Myles, A. Poddar, and O.F. Sankey, *J. Appl. Phys.*, 2002, 92, 7225, Copyright 2002, American Institute of Physics.
Figure 1.9 Computed phonon dispersion relations along selected directions in reciprocal space for Cs$_8$Na$_{16}$Ge$_{136}$. The Na and Cs “rattle” modes are labeled. The frequency of the Cs mode is well within the range of the host Ge$_{136}$ framework modes. Reproduced with permission from Ref. 57.

Cs optic mode was observed for Cs$_8$Na$_{16}$Ge$_{136}$, and the majority of the other Raman-active vibrational modes, largely due to framework optical phonons, for Si$_{136}$, Cs$_8$Na$_{16}$Si$_{136}$, and Cs$_8$Na$_{16}$Ge$_{136}$ were also identified. A comparison of the guest vibration frequencies determined from the ADPs, Raman scattering, and theoretical calculations are given in Table 1.2. Further theoretical calculations concerning the vibrational properties of filled $A_8B_{16}E_{136}$ clathrates have been reported by Myles et al., who used density functional techniques. Figure 1.9 shows the calculated phonon dispersion curves for one of the compounds studied in that work, Cs$_8$Na$_{16}$Ge$_{136}$. For the most part, the phonon dispersion is very similar in character to that calculated for the parent Ge$_{136}$ clathrate. The important difference, however, is the appearance of flat, nearly dispersionless modes corresponding to the localized motion of the Na and Cs guests (labeled in Figure 1.9). In particular, the Cs guest modes are found well within the frequency range of the host acoustic phonons, which are responsible for the dominant heat carrying contribution to the lattice thermal conductivity.

The above results indicate the potential for strong scattering of these acoustic phonons. Such phenomena have been observed and extensively studied in clathrate-I.
materials (§1.1) as well as clathrate hydrates,\textsuperscript{149} wherein localized guest vibrational modes can efficiently scatter heat-carrying acoustic phonons resulting in very low thermal conductivities.\textsuperscript{19} Our preliminary experimental results\textsuperscript{104,126} from thermal conductivity measurements on polycrystalline Na\textsubscript{x}Si\textsubscript{136} specimens have suggested this resonant scattering effect may indeed be present in some semiconducting clathrate-II variants. We note that although there is clear evidence for the localized guest mode in materials such as Cs\textsubscript{8}Na\textsubscript{16}Ge\textsubscript{136} or Cs\textsubscript{8}Na\textsubscript{16}Si\textsubscript{136},\textsuperscript{57,101} the thermal conductivity appears to be dominated by the electronic component in these metallic compounds.\textsuperscript{93,150} The synthesis of new filled semiconducting clathrate-II variants will allow further study of their expected interesting thermal transport properties.

In addition to vibrational phenomenon related to the caged guest motions, the open-structured framework of clathrate-II phases results in unique thermal properties in its own right. Nolas et al. reported\textsuperscript{143} on the thermal properties of the empty clathrate Si\textsubscript{136}, and found that this crystalline material has a very low thermal conductivity, an order of magnitude lower than that of diamond-structure silicon and comparable in magnitude with amorphous SiO\textsubscript{2}. This is observed even in the absence of the phonon scattering mechanisms found in filled clathrates.\textsuperscript{19} The low thermal conductivity of Si\textsubscript{136} relative to diamond silicon can be understood in terms of the combined increase in unit cell size and open-framework structure of the former with respect to the latter.\textsuperscript{81,151} The results of theoretical studies\textsuperscript{81} point to distinct features in the phonon structure which are related to the relative increase in unit cell size. These include gaps in the phonon dispersion relations as well as zone-boundary folding, to which the very low thermal conductivity in the Si\textsubscript{136} allotrope can be attributed. These results suggest additional approaches to the design of low thermal conductivity crystalline solids.

\textit{1.6 Remarks on the present work}

As evidenced in this chapter, the unique structural and physical properties of novel intermetallic clathrate materials, in addition to their potential for use in technologically relevant applications, form the impetus for the need for a more detailed understanding of these material systems, in particular the clathrate-II materials. What
opportunities in terms of thermoelectrics still exist in the clathrate-I system? What is the available composition space for the clathrate-II material system, and how can we access new compositions? What opportunities lie in novel synthetic routes to clathrate and related compounds? What are the structure-property relationships in clathrate-II systems? What other types of open-framework intermetallics may be of interest? The fundamental investigations into the synthesis, structural, and physical properties of open framework intermetallic materials of group 14 described in the pages that follow is an attempt to address these questions. This work is also intended to provide insight and establish the groundwork for future research into these intriguing and technologically promising material systems.
2 Preparation and physical properties of the binary clathrate-I

\[ \text{K}_8\text{Ge}_{44}\square_2 \]

As noted in Chapter 1, phases with the clathrate-I crystal structure have been the most studied of the intermetallic clathrates. However, the majority of work to date has concentrated on the ternary compounds. With the exception of the unconventional superconductor \( \text{Ba}_8\text{Si}_{46} \),\(^{21,152-168}\) less attention has been paid to the binary type I clathrates, in particular with regard to their thermoelectric properties. Table 2.1 presents a compilation of known binary type I compositions, as well as corresponding references from the literature. Of the binary type I clathrate compositions listed in Table 2.1, several of these compounds have not been well characterized with respect to their thermoelectric properties, and one can imagine other hitherto unrealized compositions are possible.

The clathrate-I crystal structure is characterized by face sharing coordination polyhedra, which form a covalently bonded \( E_{46} \) framework through \( sp^3 \)-like bonding of \( E = \text{Si, Ge, or Sn} \). There are three crystallographically distinct framework sites in this cubic structure (space group \( Pm\bar{3}n \)), 6c, 16i, and 24k. There are two guest atom sites, 2a and 6d, corresponding to the centers of two dodecahedral and six tetracaidecahdral cages per unit cell. A fragment of the clathrate-I unit cell is illustrated in Figure 2.1.

The crystal chemistry of type I clathrates has often been discussed within the context of the Zintl-Klemm concepts.\(^{109,196,197}\) Within this description, electropositive guest atoms (e.g. the alkali metals) are treated formally as electron donors, which donate their valence electrons to the host framework, within a rigid band approximation.\(^{174,193,198,199}\) Since the \( sp^3 \) bonding in the clathrate results in an intrinsic semiconductor in the absence of guests, these donated electrons will, in binary clathrates, occupy the framework conduction bands, or remain localized at framework vacancies if the formation of such vacancies is energetically favorable.\(^{175,189,193}\) Thus electron-rich
Table 2.1 Examples of known binary type I clathrate compositions with selected references given. In the chemical formulas, the symbol “□” represents a framework vacancy.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Synthesis Method</th>
<th>Lattice Parameter (Å)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₈Si₄₆</td>
<td>Decomposition of NaSi</td>
<td>10.19648(2)³⁷</td>
<td>3,4,5,2,87,88,134,169-174</td>
</tr>
<tr>
<td>K₈Si₄₆</td>
<td>Decomposition of KSi</td>
<td>10.27518(5)¹⁷⁵</td>
<td>4,174-177</td>
</tr>
<tr>
<td>Rb₂Si₄₆</td>
<td>Decomposition of RbSi</td>
<td>10.27188(6)¹⁷⁵</td>
<td>4,175</td>
</tr>
<tr>
<td>Cs₈Si₄₆</td>
<td>HPHT³⁹</td>
<td>10.4176(4)¹⁷⁸</td>
<td>178</td>
</tr>
<tr>
<td>Ba₈Si₄₆</td>
<td>HPHT³⁹</td>
<td>10.328(2)¹⁵²</td>
<td>21,152-168</td>
</tr>
<tr>
<td>I₈Si₄₆xIₓ</td>
<td>HPHT³⁹</td>
<td>10.4195(7)¹⁷⁹</td>
<td>179-182</td>
</tr>
<tr>
<td>K₈Ge₄₄□₂</td>
<td>Decomposition of KGe</td>
<td>10.66771(1)¹⁷⁵</td>
<td>4,175,183,184</td>
</tr>
<tr>
<td>Rb₈Ge₄₆</td>
<td>Decomposition of RbGe</td>
<td>10.70⁴</td>
<td>4</td>
</tr>
<tr>
<td>Ba₈Ge₄₃□₃</td>
<td>From the elements</td>
<td>10.65615(5)¹⁸⁵,⁶</td>
<td>168,185-187</td>
</tr>
<tr>
<td>I₈Ge₄₆xIx</td>
<td>Decomposition of GeI</td>
<td>10.814¹⁸⁸</td>
<td>188</td>
</tr>
<tr>
<td>Rb₈Sn₄₄□₂</td>
<td>From the elements</td>
<td>12.0581(3)¹⁸⁹,⁶</td>
<td>189,190</td>
</tr>
<tr>
<td>Cs₈Sn₄₄□₂</td>
<td>From the elements</td>
<td>12.1054(4)¹⁹²,⁶</td>
<td>191-195</td>
</tr>
</tbody>
</table>

³⁹High-pressure/high-temperature synthesis.

⁶These type I clathrates can be described by larger unit cells of lower symmetry, with a’ = 2a, due to the ordering of the framework vacancies.

³¹At 120 K.

Figure 2.1 Partial crystal structure of K₈Ge₄₄□₂. The large, red spheres represent the K guests, while the smaller blue spheres represent the Ge framework. The 6c sites are indicated by the smaller, white spheres.
compositions such as Na$_8$Si$_{46}$ and K$_8$Si$_{46}$ exhibit metallic properties.\cite{4,152,170,172} The formation of two vacancies per unit cell in clathrates such as K$_8$Ge$_{44}$\,\square, Rb$_8$Sn$_{44}$\,\square, and Cs$_8$Sn$_{44}$\,\square (\square = framework vacancy) can be rationalized by the accommodation of the eight electrons per unit cell donated by the guests. Since each framework vacancy will be surrounded by four framework atoms that are only 3-bonded, each of these atoms can accommodate one electron each in a non-bonding orbital; a schematic illustrating this is shown in Figure 2.2. Several detailed crystallographic studies\cite{175,183,189-192} indicate that the vacancies in these clathrates are found at the 6\,c sites (indicated in Figure 2.1), which are the most symmetric of the three framework sites. As a result of the vacancy formation, the composition is charge-balanced, and the chemical formula may be explained as $A_8E_{44}\square$ ($A$ = guest, $E$ = framework). A similar rationale can be used in the case of the halogen substituted and filled clathrates, although in this case the guests are electronegative and the guest-host polarity is reversed.\cite{179,188} This simple electron counting model is useful as a qualitative description of structure and bonding in these vacancy bearing clathrates.\cite{175,189-192}

\textbf{Figure 2.2} Simple schematic illustrating the presumed local electronic environment of a framework vacancy in K$_8$Ge$_{44}$\,\square, after Ramachandran et al.\cite{175}
In the search for novel clathrate materials with enhanced thermoelectric properties, the binary type I clathrates remain a subset that deserves further study. In this chapter, a study on the preparation and electrical and thermal transport properties of polycrystalline binary clathrate-I K$_8$Ge$_{44}$ is reported. In comparison with prior work, the importance of specimen preparation in the observed properties of clathrate compounds is emphasized. Thermal conductivity data for this compound, presented for the first time, reveal the binary clathrate-I K$_8$Ge$_{44}$ is a low thermal conductivity crystalline solid.

The binary clathrate K$_8$Ge$_{44}$ was synthesized using a procedure analogous to that which has been previously reported. The monosilicide precursor K$_4$Ge$_4$ (cubic, space group $P43n$) was first synthesized from the high purity elements. This was accomplished by reacting a mixture of K metal and Ge powder (ground to 325 mesh) at 650°C in tungsten crucibles, sealed under nitrogen inside a stainless steel reaction vessel. The resulting K$_4$Ge$_4$ compound is extremely air and moisture sensitive, thus all handling was carried out inside a nitrogen filled glove box. The K$_4$Ge$_4$ compound was then ground by mortar and pestle to fine powder, placed in a quartz tube closed at one end, and the quartz tube attached to a high vacuum apparatus. The K$_4$Ge$_4$ powder was then heated at 440°C under vacuum (10$^{-5}$ torr) for 24 hours. The specimen was then removed from the vacuum apparatus, vented in a nitrogen atmosphere, and washed with ethanol and distilled water under flowing nitrogen to remove any unreacted K$_4$Ge$_4$ or residual K metal. Although the precursor K$_4$Ge$_4$ (which exhibits ionic bonding between K$^+$ and [Ge$_4$]$^{4-}$ units) is very sensitive to air and moisture, the clathrate K$_8$Ge$_{44}$ is stable as a result of the strong covalent Ge bonding of the framework, and the encapsulation of K within the framework polyhedra. The specimen was in turn dried by heating under vacuum overnight. The synthesis products were very fine, grayish polycrystalline powders, which were further ground and then compacted into an 83% dense pellet by hot pressing at 380°C under flowing nitrogen. A parallelepiped specimen for transport measurements of approximate dimensions 2 mm × 2 mm × 5 mm was then cut from the pellet using a wire saw.
Figure 2.3 Powder X-ray diffraction patterns for K₈Ge₄₄. (a) PXRD pattern calculated for exactly two vacancies per unit cell on the 6c site, with all other sites fully occupied. (b) Experimental, measured pattern using powder ground from the hot-pressed pellet.

Table 2.2 Selected data at 300 K for the K₈Ge₄₄ specimen of the present work.

<table>
<thead>
<tr>
<th>Composition (EDS)</th>
<th>a (Å)</th>
<th>Relative Density (%)</th>
<th>ρ (mOhm-cm)</th>
<th>S (μV/K)</th>
<th>κ (W/m-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₈Ge₄₃ (9)</td>
<td>10.667(5)</td>
<td>83</td>
<td>30.5</td>
<td>−77</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Structure and crystallinity were confirmed by powder X-ray diffraction (XRD) using Cu Kα radiation. Diffraction data were collected using powder ground from the pellet after hot pressing. Microstructure and chemical composition were analyzed using a JOEL scanning electron microscope (SEM) and Oxford energy dispersive spectroscopy (EDS). Thermal analysis was performed using a TA Instruments SDT Q600.

Four-probe electrical resistivity (ρ) and steady state Seebeck coefficient (S) and thermal conductivity (κ) were carried out on the same specimen in a radiation shielded cryostat. Voltage contacts were made by soldering electrical leads to nickel plated dots.
0.5 mm in diameter, while the temperature difference and specimen temperature were measured by thermocouples attached to the specimen by Stycast™ epoxy. Figure 2.3 shows a powder XRD pattern collected from powder ground from the pellet post-hot pressing, and indicates the phase purity of the specimen. Also shown in Figure 2.3 (bottom) is a simulated powder XRD pattern for \(\text{K}_8\text{Ge}_{44}\square_2\), calculated assuming exactly 2 vacancies per unit cell on the 6c site. This calculated pattern corroborates the experimental diffraction pattern very well. The cubic lattice parameter \(a = 10.667(5) \, \text{Å}\) was calculated from the positions of high angle reflections using NIST SRM silicon as an internal standard, and is in agreement with the value 10.66771(1) Å previously reported.\(^{175}\) Scanning electron microscopy (SEM) analysis indicated typical grain size in the range of 1 to 10 μm, though both larger and smaller grains were observed. Energy dispersive spectroscopy (EDS) measurements taken on 11 separate grains yielded an average chemical composition in reasonable agreement with the expected composition of \(\text{K}_8\text{Ge}_{44}\square_2\), and confirmed the presence of vacancies on the Ge framework (Table 2.2). We have assumed the guest sites to be fully occupied, as is the case in the majority of type I clathrates.

Results from differential thermal analysis (DTA) measurements on the \(\text{K}_8\text{Ge}_{44}\square_2\) specimen are shown in Figure 2.4. The large endothermic transition at high temperature is the melt of \(\alpha\)-Ge (diamond structure), which is present after the complete decomposition of the K-Ge specimen. The curve shows at least two exothermic events between 400 and 600°C (inset), the first of which occurs just above 480°C. This indicates that \(\text{K}_8\text{Ge}_{44}\square_2\) is a meta-stable phase. The presence of multiple exothermic peaks in the curve suggests phase transitions to other K-Ge phases. von Schnering et al,\(^{184}\) have studied the thermal decomposition of \(\text{K}_4\text{Ge}_4\) underdynamic vacuum, and found evidence for several other binary K-Ge phases, in addition to \(\text{K}_8\text{Ge}_{44}\square_2\). Several of these proposed compounds have not yet been further characterized.

Figure 2.5 shows the temperature dependence of \(\rho\) and \(S\) from 12 to 300 K. The sign of \(S\) is negative in the entire temperature range shown, and increases in magnitude monotonically with temperature with essentially constant slope. These data indicate the
Figure 2.4 Differential thermal analysis (DTA) for K₈Ge₄₄ for K₈Ge₄₄. An enlargement of the curve in the range 400 to 700°C is shown in the inset, showing the multi-peak nature of the decomposition. M. Beekman and G.S. Nolas, “Physical Properties of Hot-pressed K₈Ge₄₄,” Advances in Electronic Ceramics, Ceram. Eng. Sci. Proc. 28 (8), 233 (2007). Reprinted with permission of The American Ceramic Society, www.ceramics.org (2007). All rights reserved.

majority carriers in K₈Ge₄₄ are electrons, and S reaches a moderate value of – 77 μV/K at 300 K. With the exception of very low temperature activated behavior below 40 K, ρ increases monotonically with temperature, behavior typical of a metallic or heavily doped semiconductor material. This result contrasts appreciably with previously reported measurements of Ramachandran et al.,¹⁷⁵ who reported the electrical conductivity (replotted as ρ in mOhm-cm in the inset of Figure 2.5) of a cold-pressed pellet of K₈Ge₄₄ (synthesized at a temperature between 350 and 380°C) exhibiting an activated temperature dependence. As both the synthesis and consolidation procedures (hot-pressing vs. cold-pressing) differed between these two works, we suggest that specimen preparation can have a significant effect on the measured transport properties of this material. In particular, although the specimens studied in Ref. 175 were reported to be 85-90% of the theoretical density, we emphasize that electrical measurements will be more reliable when obtained on hot-pressed rather than cold-pressed materials, since the former better ensures good electrical contact between the polycrystalline grains, which
Figure 2.5 Electrical transport for K₈Ge₄₄□₂. (a) Temperature dependence of the Seebeck coefficient for K₈Ge₄₄□₂. (b) Temperature dependent electrical resistivity of K₈Ge₄₄□₂. Inset to (b): Resistivity data from Ramachandran et al., re-plotted from Ref. 175 in mOhm-cm vs. T (K) for comparison (same units as main plot).

cannot be guaranteed with the latter. The metallic-like temperature dependence of ρ shown in Figure 2.5 suggests that K₈Ge₄₄□₂ might be included in the class of metallic Zintl phases, but may also indicate significant contributions to conduction from impurity levels, as observed previously for the Cs₈Sn₄₄□₂ analogue.

Figure 2.6 shows κ of K₈Ge₄₄□₂ in the range 12 to 300 K. For comparison, the thermal conductivities of two other type I clathrates, Cs₈Sn₄₄□₂ and Sr₈Ga₁₆Ge₃₀ are also shown. Our measurements reveal that K₈Ge₄₄□₂ is a very low thermal conductivity crystalline solid, with κ ~ 1 W/m-K at room temperature. Although the thermal conductivities of the three clathrates are all comparable at room temperature,
they differ somewhat in both magnitude and temperature dependence at lower temperatures. It has been shown previously \cite{192,194} that for Cs₈Sn₄₄\(\square_2\) the guest atom vibrations have a much smaller significance in the scattering of the heat carrying acoustic phonons than for Sr₈Ga₁₆Ge₃₀, and the latter exhibits a much lower \(\kappa\), attributed to strong phonon scattering via a resonant interaction with the localized Sr vibrations. \cite{19,30} Below 200 K, K₈Ge₄₄\(\square_2\) displays a thermal conductivity intermediate between that of Cs₈Sn₄₄\(\square_2\) and Sr₈Ga₁₆Ge₃₀, with a relatively flat temperature dependence as compared to the other two clathrates, over entire range of measurement. Although we expect that there will be point defect scattering of phonons present in K₈Ge₄₄\(\square_2\) due to the presence of vacancies on the Ge framework, it is unlikely that this alone explains the very low thermal conductivity. Therefore we suggest that K vibrations inside the Ge cages of the
framework are able to scatter phonons in $\text{K}_8\text{Ge}_{44}\square_2$ as is the case with other type I clathrates. However, it is clear from Figure 2.6 that this effect is not as prominent as in $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$. Theoretical calculations by Dong et al.\textsuperscript{203} have predicted a much stronger interaction between alkaline earth guests (e.g., Sr or Ba) and the framework acoustic modes in germanium clathrates as compared to alkali guests (e.g., K). This is in agreement with the results shown in Figure 2.6. More detailed crystallographic study, in combination with inelastic scattering experiments (e.g. Raman scattering) should help to elucidate the extent of the effects of the K guest vibrations on the vibrational properties of $\text{K}_8\text{Ge}_{44}\square_2$.

To summarize, we have presented here the results from a study of the temperature dependent transport properties of the binary clathrate-I $\text{K}_8\text{Ge}_{44}\square_2$. This intermetallic clathrate exhibits a metallic-like $\rho$, and a relatively high Seebeck coefficient of $-77 \mu\text{V/K}$ at room temperature. A comparison of the electrical properties with previous work indicates the dependence of specimen properties on preparation, and we emphasize the importance of specimen preparation as key in the proper evaluation of thermoelectric materials. In particular, of interest for future work is a comprehensive investigation into the possible influence of synthesis conditions on the composition and physical properties in this K-Ge clathrate-I system. The thermal conductivity of $\text{K}_8\text{Ge}_{44}\square_2$, presented for the first time, is shown to be very low, comparable in magnitude to other type I clathrates. The resistivity of $\text{K}_8\text{Ge}_{44}\square_2$ is relatively high, but the moderate room temperature Seebeck coefficient and very low thermal conductivity suggests that the binary type I clathrates are a class of materials which deserve further evaluation in the search for new thermoelectric materials.
3 Framework substitution in germanium clathrate-II

An important aspect regarding the clathrate-II intermetallics pertains to the diversity in compositions that are in principle possible within this material system (cf. §1.3). To date, only a small subset of these conceivable compositions has been experimentally realized. This raises the question, what approaches are promising to explore novel compositions, while simultaneously allowing for the study of the influence of composition on physical properties? Substitution on the group 14 framework by other atomic species provides such an opportunity, and may also facilitate preparation of semiconducting clathrate-II compositions, which are expected to possess favourable thermoelectric properties (cf. §1.5). As such, we have initiated the first study of framework substitution in clathrate-II materials through the synthesis and characterization of novel germanium-based compositions. Since it is known that noble metals substitute on the group 14 frameworks in clathrate-I compounds,8 the substitution of Ag and Cu for Ge in Cs8Na16Ge136 was investigated, through synthetic study, single-crystal and powder X-ray diffraction, energy dispersive spectroscopy (EDS), extended X-ray absorption fine structure (EXAFS) analysis, and transport properties measurements.

3.1 Synthesis

The synthesis104 of Cs8Na16MxGe136-y (M = Ag and Cu) specimens studied in this work was performed as follows. High purity Cs metal (99.98%), Na metal (99.95%), Ag or Cu powder (99.9%), and Ge powder (ground to 325 mesh from intrinsic crystalline Ge), were combined in tungsten crucibles, after thoroughly premixing the Ag (or Cu) and Ge powders. The crucibles and mixtures were then sealed under nitrogen inside steel canisters, which were in turn sealed in quartz ampoules. The mixtures were held at 800°C for two days, then at 650°C for seven days. Specimens with nominal transition metal contents of y = 5, 8, and 10 were prepared. The products consisted of small (~ 0.5 mm in
size) crystals possessing a metallic lustre that are stable toward both air and water. Portions of the entire sample were ground for powder X-ray diffraction. The compositions of the small crystals were also analyzed using energy dispersive spectroscopy (EDS). EDS analysis on hot-pressed Cs$_8$Na$_{16}$Cu$_5$Ge$_{131}$ showed a uniform Cu:Ge ratio of 4.7:131.3 within the polycrystalline grains, very close to the nominal ratio 5:131. For optimal comparison, specimens of the parent compound Cs$_8$Na$_{16}$Ge$_{136}$ (i.e. non-substituted) were also prepared, according to the same procedure as for Cs$_8$Na$_{16}$M$_y$Ge$_{136-y}$.

The attempt to prepare a specimen with composition Cs$_8$Na$_{16}$Cu$_{10}$Ge$_{126}$ according to the above procedure resulted in a type II clathrate with a lattice parameter only marginally larger than that for Cs$_8$Na$_{16}$Cu$_5$Ge$_{131}$, and the appearance of a small amount of the additional Cu$_5$Ge phase, as detected by X-ray powder diffraction. This suggests the solubility limit for Cu in the structure has been exceeded. Similar results were observed for Ag substitution as discussed below.

3.2 Single crystal X-ray diffraction studies of Cs$_8$Na$_{16}$Ag$_y$Ge$_{136-y}$

Three Cs$_8$Na$_{16}$Ag$_y$Ge$_{136-y}$ specimens were studied by single crystal XRD, and are denoted according to their nominal compositions as I ($y = 0$), II ($y = 5$), and III ($y = 8$). Single crystal X-ray diffraction measurements and structural refinements were carried out by Dr. Winnie Wong-Ng of the National Institute of Standards and Technology. Small (< 0.1 mm in size) single crystals were cut from the larger aggregates for single crystal X-ray diffraction (XRD) measurements. The structures of the Cs$_8$Na$_{16}$Ag$_y$Ge$_{136-y}$ crystals were determined using single crystals mounted on Lindemann type glass fibres in random orientations. Data collection was performed at 298 K with Mo K$_\alpha$ radiation on a computer-controlled $\kappa$-axis diffractometer equipped with a graphite crystal incident beam monochromator. Mo K$_\alpha$ radiation (0.71073 Å) and a Zr filter were used. Preliminary cell constants and orientation matrices for data collection were obtained from least-squares refinements using setting angles of 25 reflections (18° < $\theta$ < 25°). The final lattice parameters of the three Cs$_8$Na$_{16}$Ag$_y$Ge$_{136-y}$ samples were obtained from X-ray powder diffraction using the Rietveld refinement method (see Appendix A). The GSAS software
### Table 3.1 Summary of data collection for the three compositions of Cs₈Na₁₆Ag₆Ge₁₃₆₋ₙ

<table>
<thead>
<tr>
<th>y = 0</th>
<th>y = 5.9</th>
<th>y = 6.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>gray (metallic)</td>
<td>gray (metallic)</td>
</tr>
<tr>
<td>Radiation, graphite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monochromator</td>
<td>Mo, 0.7107 Å</td>
<td>Mo, 0.7107 Å</td>
</tr>
<tr>
<td>Data collection</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Standard reflections</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intensity monitor</td>
<td>8 8 8</td>
<td>–3 –13 –3</td>
</tr>
<tr>
<td></td>
<td>10 10 0</td>
<td>8 8 –8</td>
</tr>
<tr>
<td></td>
<td>10 6 0</td>
<td>10 10 0</td>
</tr>
<tr>
<td>Orientation monitor</td>
<td>8 8 8</td>
<td>10 10 0</td>
</tr>
<tr>
<td></td>
<td>16 4 0</td>
<td>4 0 16</td>
</tr>
<tr>
<td></td>
<td>10 6 0</td>
<td>5 15 5</td>
</tr>
<tr>
<td># Reflections measured</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
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<td>2252</td>
</tr>
<tr>
<td>Independent</td>
<td>352</td>
<td>474</td>
</tr>
<tr>
<td>Refinement</td>
<td>311 (&gt; 4σ)</td>
<td>403 (&gt; 4σ)</td>
</tr>
<tr>
<td>2θ range (°)</td>
<td>2° - 64°</td>
<td>2° - 72°</td>
</tr>
<tr>
<td>Range of h,k,ℓ</td>
<td>0 &lt; h, k, l &lt; 23</td>
<td>0 &lt; h, k, l &lt; 25</td>
</tr>
<tr>
<td>Range of transmission factors</td>
<td>0.15 - 0.23</td>
<td>0.11 - 0.25</td>
</tr>
</tbody>
</table>

was used for analysis of the powder XRD data. The reported structure of Cs₈Na₁₆Ge₁₃₆ was employed as a starting model.

Table 3.1 gives details of the experimental and structural solution for the three crystals. The ω/2θ scan method was used for data collection. During the data collection process, 3 reflections were used to monitor the stability of the crystal, and another three to monitor the orientation. All three crystals were found to be stable chemically and mechanically with respect to X-ray. Lorentz and polarization corrections (CAD4 manual) were applied. At the end of data collection, 3 reflections with χ angles near 90° were measured as a function of the φ angle in order to obtain the empirical absorption correction curve.
The data were reduced and the structures were refined using the PC version of SHELXTL.\textsuperscript{208} The initial model used for least-squares refinements was that of \( \text{Cs}_8\text{Na}_{16}\text{Ag}_y\text{Ge}_{136-x} \).\textsuperscript{9} The cell parameters obtained from the powder diffraction data were then used during structure refinements. Full matrix least-squares refinements on structure factors (\( F^2 \)) were carried out. Atomic scattering factors were taken from the International Tables of Crystallography.\textsuperscript{209} A summary of data collection details is given in Table 3.1.

X-ray powder diffraction patterns for the three \( \text{Cs}_8\text{Na}_{16}\text{Ag}_y\text{Ge}_{136-x} \) samples are presented in Figure 3.1. All patterns exhibit reflections characteristic of the type II clathrate crystal structure, and indicate the phase purity of the samples. As shown in the
Table 3.2 Crystal data and structure refinement for Cs$_8$Na$_{16}$Ag$_y$Ge$_{136-y}$ (at 25 °C)

<table>
<thead>
<tr>
<th></th>
<th>Sample I ($y = 0$)</th>
<th>Sample II ($y = 5.9$)</th>
<th>Sample III ($y = 6.7$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Crystal data</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Space group</td>
<td>$Fd\bar{3}m$ (No. 227)</td>
<td>$Fd\bar{3}m$ (No. 227)</td>
<td>$Fd\bar{3}m$ (No. 227)</td>
</tr>
<tr>
<td>Cell constant</td>
<td>$a$ (powder)</td>
<td>$a$ (powder)</td>
<td>$a$ (powder)</td>
</tr>
<tr>
<td></td>
<td>15.49262(9) Å</td>
<td>15.51605(6) Å</td>
<td>15.51618(9) Å</td>
</tr>
<tr>
<td></td>
<td>$V$</td>
<td>$V$</td>
<td>$V$</td>
</tr>
<tr>
<td></td>
<td>3718.56(4) Å$^3$</td>
<td>3735.46(2) Å$^3$</td>
<td>3735.55(3) Å$^3$</td>
</tr>
<tr>
<td></td>
<td>$Z$</td>
<td>$Z$</td>
<td>$Z$</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td><strong>Least-squares refinements</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$wR(F^2)$</td>
<td>0.0571</td>
<td>0.070</td>
<td>0.064</td>
</tr>
<tr>
<td>$R1$</td>
<td>0.024 (311 refl.)</td>
<td>0.027 (403 refl.)</td>
<td>0.029 (397 refl.)</td>
</tr>
<tr>
<td>$R2$</td>
<td>0.031 (352 refl.)</td>
<td>0.036 (474 refl.)</td>
<td>0.044 (505 refl.)</td>
</tr>
<tr>
<td>Goodness of Fit</td>
<td>1.159</td>
<td>1.060</td>
<td>1.130</td>
</tr>
</tbody>
</table>

inset of Figure 3.1, a very small amount of elemental Ag was found to be present in Sample III. This is consistent with single-crystal XRD and EDS measurements discussed below, which found the value of $y$ for Sample III to be less than the target value of 8. This indicates the solubility limit for Ag in the structure has likely been exceeded. As confirmed by single crystal and powder XRD measurements, all three samples crystallized with the cubic type II clathrate crystal structure (space group $Fd\bar{3}m$). Summaries of the single crystal XRD data collection and refinement results are given in Tables 3.1 and 3.2. The refined atomic positions, occupancies, and thermal parameters are given in Table 3.3. The Na atoms were found to exclusively occupy the smaller Ge$_{20}$ dodecahedra, while the Cs atoms occupy the larger Ge$_{28}$ hexacaidecahedra. No mixing of the cation guests was observed at these sites, both of which were also found to be fully occupied from the single crystal structural refinement. As was originally observed by Bobev and Sevov, stabilization of the clathrate structure appears to be facilitated by “matching” cation and cage sizes, thus the smaller Na and larger Cs reside in the smaller Ge$_{20}$ and larger Ge$_{28}$ polyhedra, respectively.
### Table 3.3

Atomic coordinates of the three Cs$_8$Na$_{16}$Ag$_x$Ge$_{136-y}$ compositions ($Fd\bar{5}m$, No. 227; origin chosen at center ($\bar{3}m$)).

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>Symm.</th>
<th>Occupancy</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U_{\text{iso}}$(Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs</td>
<td>8b</td>
<td>$\bar{4}3m$</td>
<td>1.0</td>
<td>3/8</td>
<td>3/8</td>
<td>3/8</td>
<td>0.0352(3)</td>
</tr>
<tr>
<td>Na</td>
<td>16c</td>
<td>$\bar{3}m$</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.036(1)</td>
</tr>
<tr>
<td>Ge1</td>
<td>96g</td>
<td>$m$</td>
<td>1.0</td>
<td>0.06783(2)</td>
<td>0.06783(2)</td>
<td>0.37033(2)</td>
<td>0.0116(2)</td>
</tr>
<tr>
<td>Ge2</td>
<td>32e</td>
<td>$3m$</td>
<td>1.0</td>
<td>0.21761(2)</td>
<td>0.21761(2)</td>
<td>0.21761(2)</td>
<td>0.0110(1)</td>
</tr>
<tr>
<td>Ge3</td>
<td>8a</td>
<td>$\bar{4}3m$</td>
<td>1.0</td>
<td>1/8</td>
<td>1/8</td>
<td>1/8</td>
<td>0.0103(3)</td>
</tr>
<tr>
<td>Cs</td>
<td>8b</td>
<td>$\bar{4}3m$</td>
<td>1.0</td>
<td>3/8</td>
<td>3/8</td>
<td>3/8</td>
<td>0.0402(4)</td>
</tr>
<tr>
<td>Na</td>
<td>16c</td>
<td>$\bar{3}m$</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.041(1)</td>
</tr>
<tr>
<td>Ge1/</td>
<td>96g</td>
<td>$m$</td>
<td>0.94(1)</td>
<td>0.06771(2)</td>
<td>0.06771(2)</td>
<td>0.37045(2)</td>
<td>0.0095(1)</td>
</tr>
<tr>
<td>Ag1</td>
<td></td>
<td></td>
<td>0.06(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge2</td>
<td>32e</td>
<td>$3m$</td>
<td>1.0</td>
<td>0.21755(2)</td>
<td>0.21755(2)</td>
<td>0.21755(2)</td>
<td>0.0092(2)</td>
</tr>
<tr>
<td>Ge3</td>
<td>8a</td>
<td>$\bar{4}3m$</td>
<td>1.0</td>
<td>1/8</td>
<td>1/8</td>
<td>1/8</td>
<td>0.0092(3)</td>
</tr>
<tr>
<td>Cs</td>
<td>8b</td>
<td>$\bar{4}3m$</td>
<td>1.0</td>
<td>3/8</td>
<td>3/8</td>
<td>3/8</td>
<td>0.0335(4)</td>
</tr>
<tr>
<td>Na</td>
<td>16c</td>
<td>$\bar{3}m$</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.035(2)</td>
</tr>
<tr>
<td>Ge1/</td>
<td>96g</td>
<td>$m$</td>
<td>0.952(8)</td>
<td>0.06767(2)</td>
<td>0.06767(2)</td>
<td>0.37043(2)</td>
<td>0.0029(2)</td>
</tr>
<tr>
<td>Ag1</td>
<td></td>
<td></td>
<td>0.048(8)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge2/</td>
<td>32e</td>
<td>$3m$</td>
<td>0.94(1)</td>
<td>0.21751(3)</td>
<td>0.21751(3)</td>
<td>0.21751(3)</td>
<td>0.0037(2)</td>
</tr>
<tr>
<td>Ag2</td>
<td></td>
<td></td>
<td>0.06(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge3</td>
<td>8a</td>
<td>$\bar{4}3m$</td>
<td>1.0</td>
<td>1/8</td>
<td>1/8</td>
<td>1/8</td>
<td>0.0021(3)</td>
</tr>
</tbody>
</table>

Empirically, in type I clathrates, transition metals have only been observed to occupy framework positions.\(^8\) For completeness, the possibility of Ag substitution at the guest positions of the type II clathrates in the present study was systematically ruled out during preliminary structural refinements, and the single crystal X-ray diffraction data indicate Ag substitutes exclusively for Ge on the Ge framework. All Ge/Ag sites in the present study of the Cs$_8$Na$_{16}$Ag$_x$Ge$_{136-y}$ clathrates were refined with a total occupancy constrained to unity. As indicated by the site occupancies in Table 3.3, Ag shows a
preference for substitution on the 96g site. For Sample II ($y = 5.9(1.0)$), substitution is found exclusively on the E1 (96g) site. For Sample III ($y = 6.7(1.1)$), the majority of the Ag again substitutes on this site ($\approx 70\%$ of the total Ag content), though 4.8% and 6.5% of the 96g and 32e sites, respectively, are occupied by Ag. Preferential occupation of substituting species has also been observed in type I clathrates, and several structural studies have revealed a preference for the 6c site (space group $Pm\bar{3}n$) in these compounds.\textsuperscript{7,8,210} In particular, transition metals substituting for silicon and germanium were found to preferentially occupy the 6c site,\textsuperscript{8} which is the most symmetric of the type I clathrate framework sites. The 6c sites in the type I clathrates are located on hexagonal six-member rings of framework atoms. The E1 (96g) sites in the type II clathrate structure, which the Ag atoms are found to preferentially occupy, in fact constitute all of the hexagonal six-member sites (cf. Figure 1.1), whereas the clathrate-I 6c sites comprise one third of the hexagonal ring sites. In contrast to the 6c sites of the type I clathrates, the 96g sites are the least symmetric site of the framework in the clathrate-II structure, but they also bear the most strain of all of the sites in the structure, as with the 6c site in clathrate-I.

We next offer a qualitative discussion of the cage environments of the alkali guests in the Cs$_8$Na$_{16}$Ag$_y$Ge$_{136-y}$ samples. The relevant bond distances in Cs$_8$Na$_{16}$Ag$_y$Ge$_{136-y}$ are given in Table 3.4. In Cs$_8$Na$_{16}$Ag$_y$Ge$_{136-y}$, Na resides in the smaller 20-membered cage with Na-Ge distances ranging from 3.3543(0) Å to 3.5419(2) Å for Sample I; from 3.3593(0) Å to 3.5492(2) Å for Sample II; and from 3.3594(0) Å to 3.5493(3) Å for Sample III. The larger Cs were found to reside inside the larger 28-membered cage, with Cs-Ge distances ranging from 3.3543(0) Å to 3.5419(2) Å for Sample I; from 3.3593(0) Å to 3.5492(2) Å for Sample II; and from 3.3594(0) Å to 3.5493(3) Å for Sample III. The shortest Cs-Ge and Na-Ge distances in the three compounds are 4.1395(4) Å and 3.3543(0) Å, respectively, and both were found in the non-substituted Cs$_8$Na$_{16}$Ge$_{136}$ sample. Subtracting from these distances the single-bond radius of Ge (1.225 Å),\textsuperscript{211} the difference values become 2.915 Å and 2.129 Å for Cs-Ge and Na-Ge, respectively. This provides a rough measure of the amount of “space” inside the respective cages. If we instead subtract the single-bond radius for Ag (1.412 Å)\textsuperscript{211} from
these guest-framework distances, we obtain 2.728 Å and 1.942 Å for Cs-Ag and Na-Ag, respectively. Assuming the alkali guests to be singly ionized (i.e. Na⁺ and Cs⁺), we may take the approximate ionic radii for Cs and Na to be 1.70 Å and 1.3 Å, respectively.\(^{212}\) Using this simple estimate of the available space inside the framework polyhedra, these alkali metals can “fit” into the type II cavities quite easily, with some excess space. As shown in Table 3.3, the refined atomic displacement parameters (\(U_{iso}\)) for the Cs and Na guests in the Cs\(_8\)Na\(_{16}\)Ag\(_y\)Ge\(_{136-y}\) specimens are both significantly larger than those for the

**Table 3.4** Selected inter-atomic distances (Å) in Cs\(_8\)Na\(_{16}\)Ag\(_y\)Ge\(_{136-y}\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>x</th>
<th>Atoms</th>
<th>Distance</th>
<th>Atoms</th>
<th>Distance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0</td>
<td>Cs-Ge1</td>
<td>4.139(4) × 12</td>
<td>Ge1-Ge1</td>
<td>2.5006(4) × 2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cs-Ge1</td>
<td>4.226(1) × 12</td>
<td>Ge1-Ge1</td>
<td>2.5051(9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cs-Ge2</td>
<td>4.224(1) × 4</td>
<td>Ge1-Ge2</td>
<td>2.4902(4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Na-Ge1</td>
<td>3.5419(2) × 12</td>
<td>Ge2-Ge1</td>
<td>2.4903(4) × 3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Na-Ge2</td>
<td>3.4452(3) × 6</td>
<td>Ge2-Ge3</td>
<td>2.4850(6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Na-Ge3</td>
<td>3.3543(0) × 2</td>
<td>Ge3-Ge2</td>
<td>2.4850(5) × 4</td>
</tr>
<tr>
<td></td>
<td>5.9(1.0)</td>
<td>Cs-Ge1/Ag1</td>
<td>4.1448(3) × 12</td>
<td>Ge/Ag1-Ge/Ag1</td>
<td>12.5013(4) × 2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ge1/Ag1-Cs</td>
<td>4.2293(4) × 12</td>
<td>GeAg1-Ge/Ag1</td>
<td>2.5142(8)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ge2-Cs</td>
<td>4.2315(6) × 4</td>
<td>Ge/Ag1-Ge2</td>
<td>2.4955(4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Na-Ge1/Ag1</td>
<td>3.5492(2) × 12</td>
<td>Ge2-Ge/Ag1</td>
<td>2.4955(4) × 3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Na-Ge2</td>
<td>3.4497(2) × 6</td>
<td>Ge2-Ge3</td>
<td>2.4871(6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Na-Ge3</td>
<td>3.3593(0) × 2</td>
<td>Ge3-Ge2</td>
<td>2.4871(6) × 4</td>
</tr>
<tr>
<td></td>
<td>6.7(1.1)</td>
<td>Cs-Ge1/Ag1</td>
<td>4.1454(4) × 12</td>
<td>Ge/Ag1</td>
<td>2.5010(4) × 2</td>
</tr>
<tr>
<td></td>
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<td>Ge1/Ag1-Cs</td>
<td>4.2285(5) × 12</td>
<td>Ge1/Ag1</td>
<td>2.515(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ge2/Ag2-Cs</td>
<td>4.2326(7) × 4</td>
<td>Ge/Ag1-Ge/Ag2</td>
<td>2.4952(5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ge1/Ag1-Na</td>
<td>3.5493(3) × 12</td>
<td>Ge/Ag2-Ge/Ag1</td>
<td>2.4952(5) × 3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Na-Ge2/Ag2</td>
<td>3.4494(3) × 6</td>
<td>Ge/Ag2-Ge3</td>
<td>2.4861(7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Na-Ge3</td>
<td>3.3594(0) × 2</td>
<td>Ge3/Ge/Ag2</td>
<td>2.4861(7) × 4</td>
</tr>
</tbody>
</table>
framework Ge/Ag atoms, in agreement with those previously reported for Cs$_8$Na$_{16}$Ge$_{136}$. The larger U$_{iso}$ for Cs and Na can be attributed to the weaker bonding between guest and framework, allowing for relatively large thermal motion of the guest atoms inside their framework cages (cf. §1.2 and 1.4). Indeed, the thermal motion associated with Cs in the larger cage of these clathrates corresponds to an optic phonon mode. The presence of such loosely bound guest atoms in type I clathrate materials results in the very low lattice thermal conductivities some clathrates possess, which can be attributed to the scattering of the heat carrying acoustic phonons by the localized, incoherent guest vibration modes. Recent experimental and theoretical results suggest a similar effect may occur in type II clathrates, and from the large U$_{iso}$ values for the alkali guests we postulate that the lattice thermal conductivities of Cs$_8$Na$_{16}$Ag$_y$Ge$_{136-y}$ clathrates should be quite low.

The Ge-Ge distances in the three Cs$_8$Na$_{16}$Ag$_y$Ge$_{136-y}$ compounds (in the range of 2.4850(4) Å to 2.5159(10) Å) are somewhat longer than that in elemental α-Ge (2.445 Å), where strong tetrahedral bonds are expected. As one compares the corresponding bond lengths in the three Cs$_8$Na$_{16}$Ag$_y$Ge$_{136-y}$ compositions (Table 3.4), one observes that in general the compositions with Ag substitution give rise to longer bond lengths as compared to those of Cs$_8$Na$_{16}$Ge$_{136}$. However, the corresponding bond distances in compositions II and III are not significantly different (consistent with their somewhat similar lattice parameters).

Table 3.5 gives the selected bond angles surrounding the Ge/Ag sites. In Cs$_8$Na$_{16}$Ge$_{136}$, each Ge is bonded to four other Ge atoms; schematics showing the local bonding environments of the Ge1 (96g), Ge2 (32e), and Ge3 (8a) sites are given in Figure 3.2. The Ge3 (8a) site has four equal bonds and six equal bond angles and therefore it is the most symmetric site (and also has the strongest Ge-Ge bond among the three Ge sites). The Ge2 (32e) site has two different sets of angles, and by comparison with the Ge3 (8a) site it is relatively more distorted (or more strained). Around Ge1 (96g), the angles show the most pronounced deviation from ideal tetrahedral symmetry, with an angle of 120° corresponding to the internal angle of the hexagonal face of the E$_{28}$
Table 3.5 Selected bond angles for Cs₈Na₁₆AgₓGe₁₃₆₋ₓ (°)

<table>
<thead>
<tr>
<th>Central atom</th>
<th>Sample I (y = 0)</th>
<th>Sample II (y = 5.9(1.0))</th>
<th>Sample III (y = 6.7(1.1))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge1</td>
<td>105.26(2) × 2</td>
<td>105.34(2) × 2</td>
<td>105.40(2) × 2</td>
</tr>
<tr>
<td></td>
<td>108.17(2) × 1</td>
<td>108.06(2) × 1</td>
<td>108.02(2) × 1</td>
</tr>
<tr>
<td></td>
<td>108.87(2) × 2</td>
<td>108.83(1) × 2</td>
<td>108.80(2) × 2</td>
</tr>
<tr>
<td></td>
<td>119.82(0) × 1</td>
<td>119.83(0) × 1</td>
<td>119.83(0) × 2</td>
</tr>
<tr>
<td>Ge2</td>
<td>107.10(2) × 3</td>
<td>107.20(2) × 3</td>
<td>107.24(2) × 3</td>
</tr>
<tr>
<td></td>
<td>111.74(2) × 3</td>
<td>111.64(1) × 3</td>
<td>111.60(2) × 3</td>
</tr>
<tr>
<td>Ge3</td>
<td>109.47(2) × 6</td>
<td>109.47(0) × 6</td>
<td>109.47(0) × 6</td>
</tr>
</tbody>
</table>

Figure 3.2 Local tetrahedral bonding environments of the (a) Ge1 (96g), (b) Ge2(32e), and (c) Ge3 (8a) sites in Cs₈Na₁₆Ge₁₃₆, with bond angles given. The Ge1 site in (a) is the least symmetric, and is the center for the ~120° interior angle of the hexagonal face of the hexacaidecahedra. Ag substitutes preferentially at this site. Reprinted from A.N. Mansour, et al., “Local Structure of Cu in Cs₈Na₁₆Cu₅Ge₁₃₁ Type II Clathrate,” *J. Solid State Chem.* **182**, 107-114, Copyright 2009, with permission from Elsevier.
cage. (Recall six Ge1 link together to form the hexagonal face of the polyhedra in the Cs8Na16Ge136 structure.) Therefore the local bonding environment around the Ge1 (96g) site is the most “distorted” of the three framework sites, and is expected to be the most susceptible for substitution. Our single crystal XRD refinement results support this conclusion, as preference is found for substitution at the Ge1 (96g) site. Also, from Table 3.4, we note that the bond distances surrounding the Ge1 site are slightly larger that the others in the structure, indicating slightly weaker bonding around this site. Although the presence of the d-orbitals of Ag may also affect the bonding geometry, our results indicate that the substitution of Ag does not have a significant effect on the geometry around the Ge/Ag sites (Table 2.5).

Results of SEM/EDS analysis also confirmed the presence of Ag within the clathrate crystals. Severe overlap of the Na K (1.041 KeV) and Ge L (1.096 KeV) excitations makes accurate measurements of the Na composition extremely difficult, thus it has been assumed that the Na contribution to the compositions is ~ 10 atomic % in all compounds, an assumption that is supported by the structure determination results that there are no vacancies observed for any site in the structure. The composition of Sample II as determined from EDS was Cs7.0Na15.7Ag4.4Ge131.6, in reasonable agreement with the expected value for Sample II, whereas the Ag content \( y \) was determined from single crystal X-ray refinement to be 5.9(1.0). For sample III the composition was determined from EDS to be Cs7.4Na15.7Ag4.8Ge131.2, whereas the Ag content \( y \) was determined to be 6.7(1.1) from XRD structure refinements, notably less than the nominal value of \( y = 8 \). As determined from both X-ray diffraction and EDS measurements, the Ag content in Samples II and III are only marginally different, and both less than \( y = 8 \). These results suggest that the value of \( y \) for the solid solubility of Ag in the Cs8Na16AgyGe136-y compounds is approximately 7. The small difference in the Ag content between Samples II and III is consistent with the fact that the lattice parameter of Sample III is only marginally larger than that of Sample II.
3.3 Structural characterization of $\text{Cs}_8\text{Na}_{16}\text{Cu}_5\text{Ge}_{131}$: Powder X-ray diffraction and EXAFS

Powder X-ray diffraction patterns were collected by Dr. James Kaduk of Innovene on a Bruker D8 Advance using Cu Kα radiation, with Rietveld structure refinements carried out using the GSAS suite.\textsuperscript{205,206} Rietveld refinements (\textit{vide infra}) indicated the 8\textit{b} and 16\textit{c} sites to be fully occupied by Cs and Na, respectively, with no mixing on the two sites. Due to the lack of X-ray scattering contrast between Cu and Ge, determination of Cu/Ge relative occupancies using either single crystal or powder X-ray diffraction for the Cu substituted samples is exceedingly difficult. This aspect is further addressed by EXAFS studies below.

Figure 3.3 shows Rietveld refinement powder XRD plots for both $\text{Cs}_8\text{Na}_{16}\text{Ge}_{136}$ and $\text{Cs}_8\text{Na}_{16}\text{Cu}_5\text{Ge}_{131}$. Details of the refinement results are given in Table 3.6. The type II clathrate crystal structure was confirmed for both specimens. As shown in Figure 3.3b, a trace amount ($\sim$ 1 wt%) of elemental Ge was detected in the $\text{Cs}_8\text{Na}_{16}\text{Cu}_5\text{Ge}_{131}$ specimen. As noted from Table 3.6, the unit cell constant $a$ shrinks
Table 3.6 Selected crystallographic data and Rietveld refinement results for Cs8Na16Ge136 and Cs8Na16Cu5Ge131

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Cs8Na16Ge136</th>
<th>Cs8Na16Cu5Ge131</th>
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</thead>
<tbody>
<tr>
<td>Crystal system</td>
<td>Cubic</td>
<td>Cubic</td>
</tr>
<tr>
<td>Space group</td>
<td>Fd3m</td>
<td>Fd3m</td>
</tr>
<tr>
<td>Cell constant a (Å)</td>
<td>15.49263(10)</td>
<td>15.42000(9)</td>
</tr>
<tr>
<td>Cell Volume</td>
<td>3718.56(7)</td>
<td>3666.52(6)</td>
</tr>
<tr>
<td>Z</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Radiation</td>
<td>Cu Kα</td>
<td>Cu Kα</td>
</tr>
<tr>
<td>Impurity phases (wt %)</td>
<td>None</td>
<td>Elemental Ge (1.4 %)</td>
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<tr>
<td>Rp</td>
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<td>wRp</td>
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<td>R(F2)</td>
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<td>0.05399</td>
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<td>χ²</td>
<td>1.67</td>
<td>1.38</td>
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Table 3.7 Atomic coordinates for Cs8Na16Ge136 and Cs8Na16Cu5Ge131

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<tr>
<th>Atom</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Frac.</th>
<th>Uiso (Å²)</th>
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<tr>
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<td></td>
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<tr>
<td>Cs</td>
<td>8b</td>
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<td>0.375</td>
<td>0.375</td>
<td>1.0</td>
<td>0.0505(5)</td>
</tr>
<tr>
<td>Na</td>
<td>16c</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.0</td>
<td>0.0453(20)</td>
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<tr>
<td>Ge3</td>
<td>8a</td>
<td>0.125</td>
<td>0.125</td>
<td>0.125</td>
<td>1.0</td>
<td>0.0223(2)</td>
</tr>
<tr>
<td>Ge2</td>
<td>32e</td>
<td>0.21825(6)</td>
<td>0.21825(6)</td>
<td>0.21825(6)</td>
<td>1.0</td>
<td>0.0223(2)</td>
</tr>
<tr>
<td>Ge1</td>
<td>96g</td>
<td>0.067284(27)</td>
<td>0.067284(27)</td>
<td>0.37126(5)</td>
<td>1.0</td>
<td>0.0223(2)</td>
</tr>
<tr>
<td>Cs8Na16Cu5Ge131</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td>8b</td>
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<td>0.375</td>
<td>0.375</td>
<td>1.0</td>
<td>0.0564(5)</td>
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<tr>
<td>Na</td>
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<td>0</td>
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<td>0.0596(20)</td>
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<tr>
<td>Ge3/</td>
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<td>0.125</td>
<td>0.125</td>
<td>0.9893(24)/</td>
<td>0.0214(1)</td>
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<td>0.011(1)</td>
</tr>
<tr>
<td>Ge2</td>
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<td>0.21830(5)</td>
<td>0.21830(5)</td>
<td>0.21830(5)</td>
<td>1.0</td>
<td>0.0214(1)</td>
</tr>
<tr>
<td>Ge1/</td>
<td>96g</td>
<td>0.067298(23)</td>
<td>0.067298(23)</td>
<td>0.37163(4)</td>
<td>0.9264(10)/</td>
<td>0.0214(1)</td>
</tr>
<tr>
<td>Cu1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.074(1)</td>
</tr>
</tbody>
</table>
slightly but significantly from 15.49263(10) for Cs$_8$Na$_{16}$Ge$_{136}$ to 15.42000(9) for Cs$_8$Na$_{16}$Cu$_5$Ge$_{131}$, due to substitution of Cu for Ge on the framework. Analogous behaviour was observed in Ba$_8$Cu$_{46-x}$Ge$_{46-x}$ type I clathrates.\textsuperscript{213,214} Table 3.7 gives site occupancies, atomic positions, and isotropic atomic displacement parameters (U$_{\text{iso}}$) for both specimens as determined from Rietveld refinement. The structural refinements indicate all crystallographic sites are fully occupied in both specimens.

During the structural refinements the Cu content was allowed to refine, though it is not possible to determine the Cu content accurately using conventional X-ray diffraction, since the X-ray scattering powers of Cu and Ge are very similar as noted above. As such, the accurate determination of any site occupation preference for Cu in Cs$_8$Na$_{16}$Cu$_5$Ge$_{131}$ is also unattainable from the powder X-ray diffraction data. In the single crystal XRD work discussed above, it was found that Ag substitutes preferentially for Ge at the 96g framework site, which is the most distorted or “strained” site of the framework. Presumably Cu is likely to substitute preferentially at this site in Cs$_8$Na$_{16}$Cu$_5$Ge$_{131}$ as well. In order to gain insight into the local structure and site preference for Cu in Cs$_8$Na$_{16}$Cu$_5$Ge$_{131}$, EXAFS experiments were performed.

EXAFS data collection and analysis were carried out by Dr. Azzam Mansour of the Naval Surface Warfare Center, West Bethesda, MD. Experiments were conducted at room temperature (RT) and liquid nitrogen temperature (LNT) on the bending magnet station X-11A of the National Synchrotron Light Source. A brief summary of the principles and analysis underlying EXAFS are given in the Appendix; further details of the data collection, experimental procedure, and methods of analysis can be found in Ref. 215. All fits were made using the curve fitting code FEFFIT (version 2.984) of the University of Washington XAFS (UWXAFS) software package.\textsuperscript{216} The data were fitted using theoretical standards calculated based on the curved-wave scattering formalism of the FEFF Code (version 8.2).\textsuperscript{217,218}

The FEFF calculations were performed using established structural models for elemental Ge\textsuperscript{220} and the Cs$_8$Na$_{16}$Ge$_{136}$.\textsuperscript{9} The local structure parameters for the first few coordination spheres around Ge in Cs$_8$Na$_{16}$Ge$_{136}$ are listed in Table 3.8. In accordance with the convention used above, the three non-equivalent sites are labeled as Ge1 (96g),
Ge2 (32e), and Ge3 (8a); the nearest neighbor coordination environments and site symmetries for the three sites can be recalled from Figure 3.2. Due to the high degree of symmetry of the Ge3 site, it was used in the FEFF code to calculate the backscattering amplitudes and phase shifts for Ge-Ge interactions. The phase shift for the central Cu atom was calculated using the same cluster data for the Ge3 site while placing a Cu atom at the origin of the cluster. For comparison purposes, local structure parameters for the first two coordination spheres of elemental Ge can be found in Ref. 215.

A comparison of the raw and normalized Cu and Ge K-edge XAFS spectra collected near the liquid nitrogen temperature for Cs8Na16Cu5Ge131 are displayed in Figure 3.4. As noted from the raw data, the Ge K-edge jump is significantly larger than the Cu K-edge jump due to the higher Ge concentration relative to the Cu concentration in the specimen. The absorption edge jumps are 0.092 and 3.18 for Cu and Ge respectively. Taking into account the theoretical edge jumps for Cu and Ge of 26485 and 20068 Barns/atom,220 respectively, the atomic ratio of Ge to Cu in the specimen is determined to be 26.19. This value compares very well with the nominal value of 26.20, which is calculated on the basis of the nominal composition of the specimen. Once the spectra are normalized per Cu or Ge atom, the EXAFS oscillations are clearly prominent in the XAFS spectra for both Cu and Ge. These oscillations extend several hundred eV above the edge energy for both Cu and Ge.

Shown in Figure 3.4 are comparisons of the RT and near LNT Ge K-edge EXAFS spectra and the corresponding k-weighted Fourier transforms. It is important to note that the EXAFS spectra and Fourier transforms represent an ensemble average of the local structure of three non-equivalent sites of Ge, namely, Ge1, Ge2 and Ge3. Furthermore, the distances of various coordination spheres in the Fourier transforms are shifted lower by about 0.2-0.3 Å relative to real distances due to the phase shifts of the central and back scattering atoms. The apparent contractions in the Fourier transforms distances are accounted for during the quantitative analysis of the EXAFS spectra. As anticipated, the amplitude of the EXAFS oscillations as well as the amplitude of the Fourier transforms increased when the specimen temperature decreased from RT to the LNT due to the quenching of the thermal motion of the atoms. The Fourier transforms display a major
Figure 3.4 EXAFS data for Cs$_8$Na$_{16}$Cu$_5$Ge$_{131}$ near the Cu and Ge K-edges. (a) Raw Cu and Ge K-edge XAS data near liquid nitrogen temperature (LNT). (b) Normalized LN Cu and Ge K-edge XAS data. (c) Room temperature (RT) and LNT EXAFS spectra for Ge. (d) Fourier transformed EXAFS spectra at RT and LNT for Ge. (e) RT and LNT EXAFS spectra for Cu. (f) Fourier transformed EXAFS spectra at RT and LNT for Cu. Reprinted from A.N. Mansour, et al., “Local Structure of Cu in Cs$_8$Na$_{16}$Cu$_5$Ge$_{131}$ Type II Clathrate,” *J. Solid State Chem.* 182, 107-114, Copyright 2009, with permission from Elsevier.
peak centered around 2.2 Å, which corresponds to the first coordination sphere of the tetrahedral coordination of framework Ge atoms, while the peak centered near 3.7 Å corresponds to the more distant Ge-Ge coordination spheres. Due to the rattling behavior of the Cs and Na atoms (c.f §1.4), these guest atoms possess high degrees of thermal disorder and, therefore, the contributions of the Ge-Na and Ge-Cs interactions are very small and can effectively be ignored. As shown below, the total disorder for each of the Ge-Na and Ge-Cs pair interactions was estimated to be greater than 0.02 Å². The high degree of disorders for Ge-Na and Ge-Cs were necessary in order for the simulated Fourier transforms derived on the basis of local structure parameters from XRD data to closely resemble the Fourier transforms of the experimentally measured EXAFS spectra.

A comparison of the RT and the near LNT Cu K-edge EXAFS spectra and the corresponding k-weighted Fourier transforms are also shown in Figure 3.4. Again, as anticipated, the amplitude of the EXAFS oscillations as well as the amplitude of the Fourier transforms increased when the specimen temperature decreased from RT to the LNT due to the quenching of the thermal motion of the atoms. These Fourier transforms display a major peak centered around 2.1 Å, which corresponds to the first coordination sphere of Cu-Ge interactions and a minor peak centered around 3.7 Å, which corresponds to more distant Cu-Ge interactions.

A comparison of the Fourier transforms of RT Cu and Ge EXAFS spectra and the LNT Cu and Ge EXAFS spectra are shown in Figure 3.5. The high degree of similarity between the features of the Fourier transforms for Cu and Ge at each particular temperature is clear. As discussed earlier, both sets of Fourier transforms display a major and a minor peak corresponding to the first and second coordination spheres, respectively. This confirms that Cu substitutes for the framework Ge atoms in the structure. However, the position of the first peak in the Fourier transforms for Cu is shifted to a lower distance relative to that in the Fourier transforms for Ge. As confirmed from quantitative analysis of the spectra, the Cu-Ge distance is significantly shorter than the Ge-Ge distance.
Figure 3.5 Comparisons of Fourier transforms of the EXAFS spectra for the Cu and Ge K-edges. (a) RT and (b) LNT. The data indicate shorter Cu-Ce contacts than those for Ge-Ge. Reprinted from A.N. Mansour, et al., “Local Structure of Cu in Cs$_8$Na$_{16}$Cu$_5$Ge$_{131}$ Type II Clathrate,” J. Solid State Chem. 182, 107-114, Copyright 2009, with permission from Elsevier.

The local structure parameters of Cu and Ge in Cs$_8$Na$_{16}$Cu$_5$Ge$_{131}$ are summarized in Table 3.8. Also included in this table are the local structure parameters of elemental Ge for comparison purposes. Comparisons of Fourier transforms of experimental spectra and simulation (fit data) are shown in Figure 3.6. Within the uncertainty in the data, the many body amplitude reduction factor, $S_0^2$, for Cu is similar to that for Ge in the clathrate specimen. The value of $S_0^2$ for elemental Ge is slightly outside the range obtained for Ge in the clathrate specimen but this is likely due to the higher degree of correlation between $S_0^2$ and the disorder in the case of elemental Ge since, in this case, the XAFS measurements were made only at RT.

Our analysis for elemental $\alpha$-Ge reveals a RT first shell Ge-Ge distance of 2.444 Å, which is in excellent agreement with the well-established value of 2.450 Å.$^{219}$ The RT first shell Ge-Ge distance of 2.486 Å for the clathrate is also in excellent agreement with the weighted average distance of the three Ge sites, which is calculated to be also 2.486 Å. The RT Cu-Ge distance of 2.354 Å, however, is significantly smaller than the RT Ge-Ge distance of 2.486 Å. The Cu-Ge distance is also significantly smaller than the well
Table 3.8 Summary of local structure parameters as determined from analysis of XAFS spectra. $S_0^2$ is the many body amplitude reduction factor which accounts for inelastic losses within the central absorbing atom, R is the coordination distance, $\sigma^2$ mean square relative displacement for the given X-Y pair of atoms, which includes both thermal and static disorder, and the R-factor is the measure of the goodness of fit for the model used to fit the experimental data.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>T</th>
<th>X-Y pair</th>
<th>$S_0^2$</th>
<th>R, Å</th>
<th>$\sigma^2$, $10^{-3}$Å²</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs$<em>8$Na$</em>{16}$Cu$<em>5$Ge$</em>{131}$</td>
<td>RT</td>
<td>Cu-Ge</td>
<td>0.74±0.03</td>
<td>2.354±0.004</td>
<td>4.34±0.46</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td>LN</td>
<td>Cu-Ge</td>
<td>0.74±0.03</td>
<td>2.349±0.003</td>
<td>2.32±0.29</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>RT</td>
<td>Ge-Ge/Cu</td>
<td>0.80±0.05</td>
<td>2.486±0.007</td>
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<tr>
<td></td>
<td>LN</td>
<td>Ge-Ge/Cu</td>
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<td>2.82±0.42</td>
<td>0.015</td>
</tr>
<tr>
<td>Ge Powder</td>
<td>RT</td>
<td>Ge-Ge</td>
<td>0.70±0.04</td>
<td>2.444±0.003</td>
<td>3.46±0.37</td>
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</table>

Figure 3.6 Comparisons of Fourier transforms of experimental spectra (solid blue lines) and simulation (fit, dashed lines). (a) RT data for Ge K-edge for elemental $\alpha$-Ge. (b) LNT data for Ge K-edge for Cs$_8$Na$_{16}$Cu$_5$Ge$_{131}$. (c) LNT data for the Cu K-edge for Cs$_8$Na$_{16}$Cu$_5$Ge$_{131}$. Reprinted from A.N. Mansour, et al., “Local Structure of Cu in Cs$_8$Na$_{16}$Cu$_5$Ge$_{131}$ Type II Clathrate,” J. Solid State Chem. 182, 107-114, Copyright 2009, with permission from Elsevier.
established elemental Cu-Cu first shell distance of 2.556 Å.\textsuperscript{219} The Cu-Ge distance is smaller by 0.132 Å from the Ge-Ge distance in Cs\textsubscript{8}Na\textsubscript{16}Cu\textsubscript{5}Ge\textsubscript{131} and by 0.202 Å from the elemental Cu-Cu distance. This shorter Cu-Ge distance is consistent with the small reduction in the lattice parameter for Cs\textsubscript{8}Na\textsubscript{16}Cu\textsubscript{5}Ge\textsubscript{131} (\(a = 15.42000\) Å) relative to the parent compound Cs\textsubscript{8}Na\textsubscript{16}Ge\textsubscript{136} (\(a = 15.49263\) Å) as discussed above. On the basis of these results, we conclude that a local distortion in the Ge framework of the clathrate is created in the proximity of the Cu atoms. In spite of such a local distortion, the RT as well as the LNT disorders for the Cu-Ge pair are essentially the same as those for the Ge-Ge pair within the uncertainty in our results. The total disorder consists of a temperature independent static term and a temperature dependent thermal term, which can be extracted separately by appropriately analyzing the temperature dependence of XAFS spectra. The microscopic Debye and Einstein temperatures for the Cu-Ge and Ge-Ge interactions are determined by modeling the temperature dependence of the thermal term using the Debye and Einstein models for lattice vibrations, respectively.\textsuperscript{221} Accordingly, our results for the static disorder, thermal disorder, and total disorder for the Cu-Ge and Ge-Ge pairs are summarized in Table 3.9. The large uncertainties in the Debye and Einstein temperatures are due to the limited number of temperature dependent EXAFS data sets (RT and LNT) we used in modeling the thermal disorder. The Debye temperatures for both Cu and Ge are similar to those observed for Ge and Ga in Eu\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30} and Sr\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30} and are characteristic of a stiff lattice.\textsuperscript{100} The similarities in the degree of static disorder, Debye temperature, and Einstein temperature for the Cu-Ge and Ge-Ge pairs indicate that the local bonding environment for Cu is very similar to that for Ge.

To address the issue of site preference for Cu substitution noted above, theoretical EXAFS spectra and Fourier transforms for each of the three Ge sites were calculated. In addition, we calculated the theoretical EXAFS spectra and Fourier transforms of the weighted average for the three Ge sites. These calculations were made using all of the local structure parameters given in Ref. 215, in which further details concerning the calculations may also be found. In these calculations, the many body amplitude reduction factor, \(S_0^2\), was set to the experimentally determined value of 0.80 for Ge. The disorders
were set to 0.005 Å² for the first shell of tetrahedrally coordinated Ge-Ge interactions, 0.010 Å² for the more distant second shell of Ge-Ge interactions, and 0.020 Å² for both the Ge-Na and Ge-Cs interactions. The disorders were primarily selected to bring qualitative resemblance with the Fourier transforms of the experimentally measured EXAFS spectra. The higher degree of disorder for the Ge-Na and Ge-Cs interactions relative to the Ge-Ge interactions is consistent with the rattling behavior of the Na and Cs guest atoms inside the framework polyhedral cages. Such a high degree of disorder was also observed for the rattling Eu and Sr atoms in Eu$_8$Ga$_{16}$Ge$_{30}$ and Sr$_8$Ga$_{16}$Ge$_{30}$, respectively.\textsuperscript{100}

Comparisons of the Fourier transforms of the theoretical EXAFS spectra simulated using single scattering (SS) contributions for each of the Ge sites with those simulated including multiple contributions (MS) are shown in Figure 3.7. It is clear from the figure that the relative trends observed in the amplitudes of the first and second shells in the case of the single scattering simulation are similar to those observed in the case of the simulation which also included the MS contributions. As evident from Fourier

### Table 3.9 Summary of the static disorder ($\sigma_{\text{static}}^2$), thermal disorder ($\sigma_{\text{thermal}}^2$), total disorder ($\sigma_{\text{total}}^2$), Debye temperature ($\theta_D$), and Einstein temperature ($\theta_E$) for the Cu-Ge and Ge-Ge pairs in Cs$_8$Na$_{16}$Cu$_5$Ge$_{131}$.

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<thead>
<tr>
<th>Model</th>
<th>X-Y pair</th>
<th>$\sigma_{\text{static}}^2$ (10$^{-3}$ Å$^2$)</th>
<th>$\sigma_{\text{thermal}}^2$ (10$^{-3}$ Å$^2$)</th>
<th>$\sigma_{\text{total}}^2$ (10$^{-3}$ Å$^2$)</th>
<th>$\theta_D$ or $\theta_E$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Debye model</td>
<td>Cu-Ge (RT)</td>
<td>0.36±0.35</td>
<td>3.99</td>
<td>4.35</td>
<td>427±32</td>
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<tr>
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<td>Cu-Ge (LN)</td>
<td>1.97</td>
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<td></td>
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</tr>
<tr>
<td>Debye model</td>
<td>Ge-Ge (RT)</td>
<td>0.80±0.47</td>
<td>3.74</td>
<td>4.54</td>
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<td>Ge-Ge (LN)</td>
<td>1.84</td>
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<tr>
<td>Einstein model</td>
<td>Cu-Ge (RT)</td>
<td>0.11±0.35</td>
<td>4.23</td>
<td>4.34</td>
<td>333±24</td>
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<td>Ge-Ge (RT)</td>
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<td>3.94</td>
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<td></td>
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</tbody>
</table>
transformed data, it is extremely difficult to distinguish between the three Ge sites on the basis of the first peak in the Fourier transforms due to the high degree of similarity in local structure parameters of the tetrahedral coordination of the three Ge sites. However, it is possible to qualitatively differentiate between the three Ge sites on the basis of the amplitude of the second peak in the Fourier transforms and its relative magnitude in comparison to the first peak. The amplitude of this peak increases upon going from the Ge1 site, to the Ge2 site, to the Ge3 site, due to a gradual decrease in the degree of effective static “disorder” resulting from an increase in site symmetry for the three Ge sites in the same respective order (i.e., Ge1, to Ge2, to Ge3, as indicated in Figure 3.2). Due to the significantly higher multiplicity of the Ge1 site and its large contribution to the weighted average EXAFS signal, the amplitude of the second peak in the Fourier transform for the weighted average of the three Ge sites is closer to that of the Ge1 site than that of the Ge2 or Ge3 site.

Figure 3.7 Fourier transforms of the theoretical EXAFS spectra simulated using (a) single scattering (SS) contributions and (b) multiple scattering (MS) contributions, for each of the Ge sites in Cs$_8$Na$_{16}$Ge$_{136}$. Reprinted from A.N. Mansour, et al., “Local Structure of Cu in Cs$_8$Na$_{16}$Cu$_8$Ge$_{131}$ Type II Clathrate,” J. Solid State Chem. 182, 107-114, Copyright 2009, with permission from Elsevier.
On the basis of the experimentally measured spectra (Figure 3.4), the amplitude of the second peak in the Fourier transform for Cu is qualitatively quite similar to that of the second peak in the Fourier transform for Ge, which again is a weighted average dominated by the contribution from the 96g site. This qualitatively suggests that Cu is either (i) randomly substituting for Ge or (ii) preferentially substituting in the Ge1 site. In other words, preferential substitution of Cu in the Ge2 site or the Ge3 site can be excluded from consideration. These results are consistent with the single crystal X-ray diffraction results presented above that showed preference for Ag and substitution on the 96g (Ge1) site in Cs$_8$Na$_{16}$Ag$_y$Ge$_{136-y}$.

3.4 Electrical and thermal transport in Cs$_8$Na$_{16}$Cu$_5$Ge$_{131}$

Polycrystalline Cs$_8$Na$_{16}$Cu$_5$Ge$_{131}$ and Cs$_8$Na$_{16}$Ge$_{136}$ specimens were prepared for transport measurements as follows. The specimens were ground and sieved to 325 mesh inside a nitrogen-filled glove box, and then consolidated by hot-pressing at 400°C. From the consolidated pellets, parallelepipeds of approximate dimensions 2 mm × 2 mm × 5 mm were cut for transport measurements using a wire saw. Details on the measurement of electrical and thermal transport properties are given in Appendix B.

The temperature dependence of $\rho$, $S$, and $\kappa$ from 12 to 300 K are shown in Figures 3.8 and 3.9. The transport data for the Cs$_8$Na$_{16}$Ge$_{136}$ specimen in the present study agree well in both magnitude and temperature dependence with those reported previously. As shown in Figure 3.9, $\rho$ for both specimens increases monotonically with temperature, indicative of behavior typical for a metallic or heavily doped semiconductor material. This can be qualitatively understood in terms of a simplified “rigid band” picture, in which the alkali guests (Cs and Na) donate electrons to the Ge and Ge-Cu framework conduction bands resulting in a relatively high concentration of carriers (cf. §1.3). The sign of $S$ is negative for both specimens, indicating electrons are the majority carriers. For Cs$_8$Na$_{16}$Cu$_5$Ge$_{131}$, we see that $\rho$(300 K) is significantly larger than for Cs$_8$Na$_{16}$Ge$_{136}$. As shown in the bottom of Figure 3.8, $S$ also increased significantly in magnitude (by a factor of ~ 2) for Cs$_8$Na$_{16}$Cu$_5$Ge$_{131}$ relative to Cs$_8$Na$_{16}$Ge$_{136}$, and displays somewhat different temperature dependence. The four-coordinated covalent bonding in the Ge$_{136}$
framework is analogous to the $sp^3$ bonding found in elemental diamond structure Ge, in which substitutional Cu has been shown to behave as an electronic acceptor. The observed increased magnitudes of both $\rho$ and $S$ for Cs$_8$Na$_{16}$Cu$_5$Ge$_{131}$ relative to Cs$_8$Na$_{16}$Ge$_{136}$ are consistent with a decrease in the available number of electrons participating in the conduction processes, indicating partial charge compensation as a result of Cu substitution on the Ge framework.
The thermal conductivities of the two specimens show very similar temperature dependences as presented in Figure 3.9. Since both Cs$_8$Na$_{16}$Ge$_{136}$ and Cs$_8$Na$_{16}$Cu$_5$Ge$_{131}$ exhibit metallic-like electrical conductivities (Figure 3.8), a considerable electronic contribution to the thermal conductivities shown in Figure 3.9 is expected. As the mass difference between Cu and Ge is relatively small (along with the concentration of Cu), significant mass fluctuation effects with respect to the lattice thermal conductivity are unlikely. From the EXAFS modeling presented above, similarities in the degree of static disorder, Debye temperature, and Einstein temperature for the Cu-Ge and Ge-Ge pairs indicate that the local bonding environment for Cu is very similar to that for Ge. Thus significant strain field effects on the lattice thermal conductivity are also not expected. Indeed, upon correction of the measured thermal conductivities for porosity, and subtracting the estimated electronic contribution $\kappa_e = L_0 T / \rho$ ($L_0 = 2.45 \times 10^{-8}$ $\text{V}^2\text{K}^{-2}$, $\rho$ obtained from the data of Figure 3.8), $\kappa_L$ for the two specimens are the same within experimental uncertainties ($\kappa_L(300 \text{ K}) = 2.7 \text{ Wm}^{-1}\text{K}^{-1}$ and 2.6 Wm$^{-1}$K$^{-1}$ for Cs$_8$Na$_{16}$Ge$_{136}$ and Cs$_8$Na$_{16}$Cu$_5$Ge$_{131}$, respectively). Thus reduction in $\kappa$ for Cs$_8$Na$_{16}$Cu$_5$Ge$_{131}$ relative to
Cs$_8$Na$_{16}$Ge$_{136}$ is most likely due to a decrease in the electronic contribution to κ in the former, consistent with the increase in electrical resistivity for Cs$_8$Na$_{16}$Cu$_5$Ge$_{131}$. We note that semiconducting filled type II clathrates are in general expected to possess relatively low lattice thermal conductivities, due to their enlarged unit cell and potential phonon scattering as a result of large amplitude anharmonic guest atom vibrations.

3.5 Concluding remarks and future directions

The synthesis and characterization of framework-substituted clathrate-II intermetallics was reported for the first time in this chapter. The Cu and Ag substituted compositions studied show response to framework substitution in both structure and physical properties. It should in principle be possible to substitute other species as well, thus the approach demonstrated herein can allow a variety of clathrate-II compositions to be explored. A preliminary investigation into group 13 substitution was also initiated as a part of the present work. Figure 3.10 shows an X-ray powder diffraction pattern for Cs$_8$Na$_{16}$In$_8$Ge$_{128}$ (Rietveld refined composition of the specimen is Cs$_8$Na$_{16}$In$_{7.8}$Ge$_{128.2}$). The pattern shows no discernable impurities or secondary phases. Refinement of the unit cell parameter $a$ yielded the value 15.6263(2) Å, which is significantly larger (by almost

![Figure 3.10](image.png)

**Figure 3.10** Powder X-ray diffraction pattern (observed, calculated, and difference) for a Cs$_8$Na$_{16}$In$_8$Ge$_{128}$ specimen. No impurity phases are discernable.
1 \%) than 15.4926(1) Å for non-substituted Cs₈Na₁₆Ge₁₃₆, also corroborating that the larger In has substituted for Ge on the type II framework.

The ability to vary the guest concentration in type II clathrates also offers the opportunity to synthesize additional new compositions. For example, we have shown previously⁹⁸,¹⁰⁴ that compositions such as Cs₈Ge₁₃₆ and Rb₈Ge₁₃₆ can be prepared by degassing Na from the stoichiometric compounds Cs₈Na₁₆Ge₁₃₆ and Rb₈Na₁₆Ge₁₃₆. The possibility of degassing framework substituted type II clathrates, to produce compositions such as Cs₈In₈Ge₁₂₈ from Cs₈Na₁₆In₈Ge₁₂₈ above is an area of future interest. Very recent electronic structure calculations by Biswas and Myles⁶² indicated that the clathrate-II composition Rb₈Ga₈Si₁₂₈ should be a semiconductor with an indirect gap, thus this synthetic route has the potential to produce filled, semiconducting type II clathrates, of interest as potential thermoelectric materials.
4 Synthesis and Characterization of $\text{Na}_x\text{Si}_{136}$ ($0 < x < 24$)

As noted in Chapter 1, one of the most conspicuous aspects of the clathrate-II phases is the ability to vary the guest content in these materials. The prototypical examples are the $\text{Na}_x\text{Si}_{136}$ clathrates, where the guest concentration may be varied between empty\(^1\) ($x \rightarrow 0$ for the Si\(_{136}\) allotrope) and fully filled ($x = 24$, cf. Chapter 5). Although some structural and physical properties for the $\text{Na}_x\text{Si}_{136}$ clathrates have been studied for selected compositions (cf. Chapter 1), a comprehensive understanding of these properties has yet to be established for this system, in particular with regard to the influence of guest content. This is in large part due to the challenges inherent in the preparation of $\text{Na}_x\text{Si}_{136}$ specimens of high phase purity needed for such study. This problem was addressed in the present work. A series of $\text{Na}_x\text{Si}_{136}$ clathrates was prepared covering a comprehensive range of Na contents. The crystal structures for the entire range of compositions were refined against powder X-ray diffraction. A non-monotonic structural response to filling was discovered, which can be attributed to the preferentially occupation of the distinct polyhedral cages by Na. Transport properties are presented for polycrystalline $\text{Na}_{22}\text{Si}_{136}$, for which consolidation by spark plasma sintering was found to be effective in achieving improved electrical contact between the polycrystalline grains.

4.1 Synthesis of $\text{Na}_x\text{Si}_{136}$ ($0 < x < 24$)

The $\text{Na}_x\text{Si}_{136}$ specimens were synthesized by thermal decomposition of the binary monosilicide $\text{Na}_4\text{Si}_4$.\(^{106-108}\) The crystal structure of the $\text{Na}_4\text{Si}_4$ precursor is composed of $\text{Si}_4^{4-}$ polyanions and $\text{Na}^+$ cations arranged in a monoclinic unit cell, as shown in Figure 4.1. Presumably, the $\text{Si}_4^{4-}$ polyanions are oxidized and $\text{Na}^+$ reduced during decomposition:

$$34[\text{Na}^+][\text{Si}_4]^{4-}(s) \rightarrow [\text{Na}^+]_x[\text{Si}_{136}]^{x-}(s) + (136 - x)\text{Na}(g)$$
Figure 4.1 Decomposition of Na$_4$Si$_4$ (top) to form the intermetallic clathrates Na$_x$Si$_{136}$ (bottom left) and Na$_8$Si$_{46}$ (bottom right). Na and Si atoms are colored blue and green, respectively.

The synthesis of Na$_x$Si$_{136}$ by thermal decomposition of Na$_4$Si$_4$ is complicated by the simultaneous formation of the clathrate-I Na$_8$Si$_{46}$ which can be present as an impurity phase inasmuch as 50 wt% in as-synthesized specimens. In order for the physical properties of the Na$_x$Si$_{136}$ clathrates to be thoroughly characterized, a reproducible and higher yield synthesis method is needed. For example, specimens for transport measurements should (i) contain no more than a few wt% impurity phases and (ii) ideally be obtainable in a single synthesis, as opposed to the mixing of several smaller samples from several syntheses which can lead to specimen inhomogeneity. One of the goals of the present work was to optimize the synthesis by thermal decomposition in order to minimize the Na$_8$Si$_{46}$ impurity fraction.

A schematic of the apparatus used for thermal decomposition of silicides and germinides is shown in Figure 4.2. The design and construction of the apparatus is
Figure 4.2 Schematic of the apparatus designed for thermal decomposition of Na₄Si₄ in the synthesis of NaₓSi₁₃₆ clathrates.

described by the author in Ref. 104. This apparatus employs a high vacuum system equipped with a turbomolecular pump, to which fused quartz ampoules can be attached. As the Na₄Si₄ precursor is extremely air and moisture sensitive, all handling was performed in a nitrogen-filled glove box. A vacuum valve and coupling was employed for transfer of the ampoule containing the specimen from the glove box to the apparatus. The ampoule containing the specimen, once evacuated, can then be inserted into a tubular furnace to initiate the reaction.

We have used a modified version of the procedure of “flash degassing” originally developed by Gryko,¹⁰⁵ in which Na₄Si₄ is rapidly heated through the decomposition temperature (~ 360°C) at the rate of several hundred °C/min. This is achieved by inserting the quartz ampoule containing the sample into a tube furnace preheated to 800°C (see Fig. 4.2), but then removing the sample before decomposition of the clathrate ensues (at ~ 450°C under vacuum). Though the exact local temperature of the specimen is not measured, the monitored temperature directly outside of the ampoule was calibrated using a “trial and error” procedure. The result from this modified “flash decomposition”
Figure 4.3 Powder X-ray diffraction patterns for several Na$_x$Si$_{136}$ specimens. The red arrow indicates the most intense reflection contributed by the Na$_8$Si$_{46}$ impurity phase.

step is a Na$_x$Si$_{136}$ clathrate with $x \sim 24$. The Na content is then varied by further heating under vacuum at 360°C to 425°C, with the time and temperature controlling the final composition (higher temperatures and longer heating times leading to specimens with a lower Na content).

Using the above described procedure, Na$_x$Si$_{136}$ clathrates typically containing less than 3 wt% Na$_8$Si$_{46}$ are reproducibly synthesized. In addition, by scaling up to larger crucible and ampoule sizes, as much as 500 mg of high quality Na$_x$Si$_{136}$ (as opposed to ~100 mg previously$^{104}$) is produced in a single synthesis run. Figure 4.3 shows powder X-ray diffraction (PXRD) patterns for representative Na$_x$Si$_{136}$ specimens prepared using the above described method. The most intense reflection contributed by Na$_8$Si$_{46}$ is indicated by an arrow in the figure. The effectiveness of this “flash decomposition” technique to
minimize the Na$_8$Si$_{46}$ fraction suggests the reaction kinetics and/or formation temperatures for the two clathrate phases may be slightly different, allowing preferential formation of one phase over the other depending on the synthesis conditions.

The products obtained from the thermal decomposition are fine polycrystalline powders, dark in color with a bluish pigment. In order to remove any residual Na$_4$Si$_4$ and/or elemental Na, the specimens were vented from vacuum in a nitrogen filled glove bag, and then washed with ethanol and then distilled water to hydrolyze the remaining residues. The specimen was then sonicated, decanted, and dried.

4.2 Structural characterization of Na$_x$Si$_{136}$ (0 < x < 24) clathrates

As the products from thermal decomposition are microcrystalline powders, structural characterization was performed using Rietveld analysis. An overview of the basic principles and application of the Rietveld method are outlined in the Appendix. pXRD patterns were collected using a Bruker D8 diffractometer in Bragg-Brentano geometry. Sample preparation and data collection are two important considerations for obtaining an accurate Rietveld structure refinement. A custom-made specimen holder was used, allowing back loading of the powder which results in a flat, planar specimen surface. The orifice of the specimen holder was constructed to be large enough to achieve a constant specimen illumination condition with no X-ray beam spill-over onto the holder. This aspect is crucial for obtaining correct intensities at low angles when beam divergence is significant. Overnight data collection was performed at 0.02$^\circ$ steps in $2\theta$, for 8 seconds per step, in the range 7 to 145$^\circ$. Rietveld structure refinements were carried out using the GSAS software package. The EXPGUI graphical user interface to GSAS was also used.

The initial model used for Rietveld refinement was taken assuming the framework Si atoms at the 96g, 32e, and 8a sites, and the Na atoms at the centers of the Si$_{20}$ and Si$_{28}$ cages at the 16c and 8b sites, respectively. However, the isotropic atomic displacement parameters ($U_{iso}$) for Na at the 8b site (fractional coordinates: 3/8, 3/8, 3/8) were found to be unreasonably large: greater than 0.1 Å$^2$, several times larger than any other site in the structure. The ADP is interpreted as the mean square atomic
displacement of an atom about its assigned crystallographic site, and can be attributed to static and/or thermal (i.e. dynamic) displacement. Although strong thermal motion is expected for this caged guest, especially considering the relatively large difference between the size of the Na guest and effective free space of the cage interior, the unusually large $U_{\text{iso}}$ suggests, in addition, significant static disorder may be present. Difference Fourier maps computed using the calculated structure factors for the model with Na at the 8$b$ site completely unoccupied, indicate significantly non-spherical residual electron density in the vicinity of the 8$b$ site, and typically with lobes directed toward the hexagonal faces of the Si$_{28}$ cage. For lower Na content specimens, the maxima in density are observed not on-center at the 8$b$ site, but rather at four nearby sites within the Si$_{28}$ cage ($3/8 + \delta$, $3/8 + \delta$, $3/8 + \delta$). Therefore, further refinement was carried out using a split-site model with Na at the corresponding nearby 32$e$ site (still space group $Fd\bar{5}m$).

Stable refinement convergence, with no damping of parameter shifts, was achieved with final simultaneous refinement of Na occupancy, $U_{\text{iso}}$, and 32$e$ positional parameter for this site. The refined off-center shifts for the sodium atoms were found to be typically near 0.4 Å. Moreover, the occupancies for the Na@32$e$ split site model consistently refined to be ¼ of the corresponding single site (i.e., Na@8$b$ model) occupancies, consistent with the four-fold increase in site multiplicity from 8$a$ to 32$e$, and the physical expectation of only one Na atom per cage. These results lend support to the interpretation of recent EXAFS experiments (cf. §1.2), which indicated significant displacement of Na from the center of the hexacaidecahedra in Na$_8$Si$_{136}$ and Na$_{x-24}$Si$_{136}$. The value we obtain of ~ 0.4 Å for the Na off-center shift is similar to that observed for guests in the Ge$_{24}$ tetracaidecahedra cage in type I clathrates such as Sr$_8$Ga$_{16}$Ge$_{30}$ and Eu$_8$Ge$_{16}$Ge$_{30}$. Ellipsoidal depictions of the ADPs for Na2 and its surrounding Si$_{28}$ cage for Na$_{22}$Si$_{136}$ are shown in Figure 4.4 for the single- and split-site models. The refined Na@32$e$ $U_{\text{iso}}$ value is reduced to more physically reasonable values for the split site model, yet still remains relatively large compared to the other sites in the structure. As mentioned above, this reflects pronounced thermal disorder for Na in the larger cage.
This feature may have important implications regarding the thermal conduction in these materials, also suggested from our thermal conductivity data for a Na$_8$Si$_{136}$ specimen.\textsuperscript{104,126} We note that in our refinements strong correlations exist between the Na $U_{iso}$ and 32e position parameter, thus it is difficult to obtain precise values for the position and $U_{iso}$ from our data. As the refinement quality of fit (see Figure 1 and Table) are the same for the on-center and off-center models, preference for one model over the other cannot be based on these factors alone. However, the physically more reasonable $U_{iso}$ are obtained in the off-center model. Similar results and conclusions were obtained in structural studies of type I clathrates,\textsuperscript{71,100,185,226,227} for which single and split site models both result in similar refinement quality. The off-centering of the guest atoms in type I clathrates results in unique phenomena in these compounds.\textsuperscript{19,27,99}

Figure 4.5 shows refinement plots (observed, calculated, and difference) for four representative specimens with compositions Na$_{1.2}$Si$_{136}$, Na$_{6.5}$Si$_{136}$, Na$_{12.2}$Si$_{136}$, and Na$_{21.6}$Si$_{136}$. A small but significant improvement in the fits was achieved by refining terms in the peak shape function corresponding to anisotropic broadening of the peaks. This type of peak broadening has been attributed to the presence of planar defects,\textsuperscript{228} and indicates such defects may be present in our Na$_x$Si$_{136}$ specimens in small concentrations. Such planar defects have been observed in transmission electron microscope (TEM) studies on Na$_x$Si$_{136}$.\textsuperscript{229} All silicon framework sites were found to be fully occupied for all
Figure 4.5 Rietveld plots of powder XRD patterns for (a) Na$_{1.2}$Si$_{136}$, (b) Na$_{6.5}$Si$_{136}$, (c) Na$_{12.2}$Si$_{136}$, and (d) Na$_{21.6}$Si$_{136}$. Observed (crosses), calculated (solid curve) and difference (lower curve) patterns are shown. Bottom set of tick marks indicate reflection positions for Na$_x$Si$_{136}$, while upper tick marks indicate those of Na$_8$Si$_{46}$. A trace amount (< 1 wt %) of α-Si was also refined in (c). Refinement residuals in each case are also given.
compositions, in agreement with previous studies\textsuperscript{87,88} that have shown that framework vacancies are not present in the Na\textsubscript{x}Si\textsubscript{136} clathrates. As shown in Figure 4.5, relatively good fits to the experimental data are achieved for all compositions, as represented by the difference patterns. An important feature to note from Figure 4.5 is the pronounced influence of the Na content on the relative intensities of a number of reflections in the patterns. This feature allows for accurate determination of the individual occupancies of the two crystallographically independent Na sites in the structure, and therefore also the total Na content in the composition.

Refinement of the crystal structures for the entire range of Na contents revealed an intriguing structural response to Na filling in Na\textsubscript{x}Si\textsubscript{136}. The relative occupancies for the two Na sites as well as the lattice parameters as a function of the total Na content are shown in Figure 4.6. The first aspect to note is that as the Na content is increased, Na preferentially occupies the larger Si\textsubscript{28} cages first. Not until these sites are almost entirely filled do the smaller Si\textsubscript{20} begin to be occupied. This indicates that Na is preferentially removed from the Si\textsubscript{20} cages first during synthesis, in general agreement with previous reports.\textsuperscript{87,88,129}

The preferential occupation of the larger Si\textsubscript{28} cages has a pronounced effect on the lattice. As shown in the top portion of Figure 4.6, the lattice parameter first decreases as Na is incorporated in the Si\textsubscript{28} cages, but then increases as the Si\textsubscript{20} cages are filled. Thus filling the two distinct cages in the Si\textsubscript{136} framework has distinctly opposite effects on the lattice. This non-monotonic response to filling, predicted qualitatively by Conesa et al.\textsuperscript{35} who used density functional theory calculations, is observed here experimentally for the first time in a guest-host system.

The extent of charge transfer from Na to the Si framework in the Na\textsubscript{x}Si\textsubscript{136} system has not yet been determined unequivocally, but is likely to play an important role in the behavior shown in Figure 4.6. Preliminary results from density functional theory (DFT) calculations carried out in collaboration with Mr. Emanuel Nenghabi and Prof. Charles Myles of Texas Tech University offer insight. Initial optimization of the unit cell for \( x = 0, 4, 8, 12, 16, 20 \) and 24, filling the Si\textsubscript{28} cages first and assuming Na on-center, revealed a trend qualitatively in agreement with that observed in Figure 4.6. The calculations can
Figure 4.6 Normalized cage occupancies (bottom) and lattice parameters (top) as a function of the total Na content, as determined from Rietveld refinement. A cage occupancy value of 1 means all cages of this type in the structure are occupied. The $32e$ spit-site occupancies for Na in the Si$_{28}$ cage (where 1/4 corresponds to full occupation of all Si$_{28}$ cages) were not fixed during refinement, which results in the scatter about 1 for $x > 8$ due to correlations with the the $U_{iso}$ for this site. The Si$_{28}$ cage can therefore be considered as fully occupied for $x > 8$ with high confidence.

Therefore reproduce the essential features of the phenomenon. An estimate of the charge transfer was made using Bader analysis.$^{230,231}$ For the seven compositions investigated, essentially complete transfer of the Na 1$s$ electron to the Si$_{136}$ framework is predicted. Such transfer suggests that the conduction band states (either in a rigid band
approximation, or due to Si-Na orbital mixing) will be increasingly occupied as the Na content is increased, in agreement with previous electronic structure calculations.$^{35,44,125}$

With this in mind, there are several conceivable interactions that could be responsible for the trend observed in Figure 4.6. These include (i) steric (repulsive) interactions resulting from the relative size of guest and cage, (ii) bonding (attractive) interactions resulting from the redistribution of charge and/or transfer from Na to the Si framework, and (iii) the increasing occupation of the conduction band states as the Na content is increased. The “interaction” noted in (iii) would be expected to increase the lattice parameter, since the conduction band states are generally of “anti-bonding” character and reduce the Si-Si bond order. While it is likely that to some extent all three of these possibilities are at play in the present case, we infer from the arguments that follow that (ii) is predominant for $x < 8$ as the Si$_{28}$ cages are filled, while (i) and/or (iii) are predominant for $x > 8$ as the Si$_{20}$ cages are filled.

Examination of subtle but significant evolution in framework atomic coordinates, interatomic distances, and bond angles obtained from Rietveld refinement reveal that the framework is not contracting and expanding uniformly. Figure 4.7 shows the interior volumes of the Si$_{28}$ and Si$_{20}$ coordination polyhedra, calculated using the atomic coordinates and lattice parameters obtained from Rietveld structure refinements for the series of specimens. A change in the volume of the polyhedra will occur due to either a change in the lattice parameter, a change in the framework atomic coordinates (specifically, the $32e$ and $96g$ sites which are not fixed by the $Fd\bar{3}m$ symmetry), or a combination of these two factors. The red and blue curves in Figure 4.7 show the “expected” trends if the atomic coordinates were fixed at the values for Na$_{7.9}$Si$_{136}$, i.e. the trend if the volume changes for $x < 8$ and $x > 8$ were due solely to the experimentally determined lattice parameter changes. The black lines are linear least squares fits to the actually observed values. These data illustrate that as the Na content increases from $x \sim 1$ to $x \sim 8$ (i.e. as the Si$_{28}$ cages are first filled), the Si$_{28}$ cage generally shows a more pronounced contraction than expected from the lattice parameter change alone, while the Si$_{20}$ cage shows a less pronounced contraction. Conversely, as the Na content is increased above $x \sim 8$ (i.e. as the Si$_{20}$ cages are filled), the Si$_{28}$ cages show a less pronounced
Figure 4.7 Si$_{28}$ and Si$_{20}$ cage volumes as a function of Na content. The volumes were calculated from the refined lattice parameters and atomic coordinates for each corresponding composition. The solid red and blue curves are the trends that would result if the atomic coordinates were fixed at the values for Na$_{7.9}$Si$_{136}$, and thus the volume changes resulted solely from the lattice parameter changes. The black lines are linear fits to the actual observed volumes, for $x \leq 8$ and $x \geq 8$.

expansion than expected from the lattice parameter change alone, while the Si$_{20}$ cages show a more pronounced expansion. These trends serve to illustrate that the contraction of the lattice for $x < 8$ is driven by the contraction of the Si$_{28}$ cage as it is filled, while the expansion of the lattice is driven by the expansion of the Si$_{20}$ cage as it is filled.$^8$

The simplest interpretation of these observations is made in terms of the relative sizes of Na guest and Si cage, and the above mentioned charge transfer. The “free space,”

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$^8$ We note that the crystallographic information obtained in a diffraction experiment is representative of the average structure. Thus as some cages are filled and others not, the local structure will differ. However, the average structure is indicative of the overall structural response to filling the respective cages.
$d_{\text{free}}$, available in the respective cages can be roughly estimated from the shortest cage center to Si distance, $r_{\text{cage}}$, and the Si covalent radius, $r_{\text{Si}} = 1.2 \, \text{Å}$, as $d_{\text{free}} = r_{\text{cage}} - r_{\text{Si}}$.

For Na$_{7.9}$Si$_{136}$, this results in values for $d_{\text{free}}$ of 2.6 Å and 2.0 Å for the Si$_{28}$ and Si$_{20}$ cages, respectively. From the estimated values of $d_{\text{free}}$ we can conclude there is up to 70% more available volume (which is proportional to $d_{\text{free}}^2$) in the Si$_{28}$ cage relative to Si$_{20}$. This is reflected in the significantly larger ADP obtained for Na@Si$_{28}$ as compared to Na@Si$_{20}$.

As tabulated by Shannon, the ionic radius of Na$^+$ for coordination number (CN) of nine is approximately 1.3 Å; the Na$^+$ ionic radius in Na$_x$Si$_{136}$ may in principle be larger due to the higher CNs in clathrate-II. Considering also that the average Si radius will effectively increase as more charge is transferred to the framework with increasing Na content, it is apparent that Na does not as readily “fit” inside the smaller Si$_{20}$ as compared to Si$_{28}$, thus may an expansion of this cage due to steric effects, and in turn the lattice as a whole also expands. For Na in Si$_{28}$, on the other hand, the large available volume allows significantly more free space. A bonding interaction appears to cause the inclusion of Na to “pull” this cage in, resulting in the apparent contraction of the lattice in contrast to the expected expansion induced by occupation of “anti-bonding” states due to charge transfer from Na.

Our results demonstrate that the clathrate-II Na$_x$Si$_{136}$ offers a relatively simple system in which the effects of relative guest/cage size can be studied. In particular, these results demonstrate that the Na-Si guest-framework is distinctly different for the two different cage environments, a finding that warrants further experimental and theoretical investigations.

4.3 Thermal stability of Na$_x$Si$_{136}$ clathrates

The thermal stability of several Na$_x$Si$_{136}$ compositions was investigated by differential thermal analysis (DTA). DTA curves, collected under flowing N$_2$ in open alumina pans, for temperatures between 250°C and 700°C are shown in Figure 4.8. The Na$_x$Si$_{136}$ clathrates all decompose exothermically near 600°C, with a slight shift in the decomposition temperature toward lower values observed as the Na content is increased above $x \sim 8$. α-Si is the only phase identified in the post-DTA powder XRD patterns. The
exothermic decomposition suggests these clathrates are metastable with respect to the elements under the above conditions. However, the relatively high decomposition temperatures suggest that the free energy difference is small, in agreement with theoretical calculations for Si$_{136}$.

4.4 Transport properties of Na$_{22}$Si$_{136}$

Another challenge inherent in a study of the transport properties of the Na$_{x}$Si$_{136}$ clathrates is preparation of sufficiently dense microcrystalline samples with good inter-grain electrical contact. Analogous to silicon in the diamond structure, an insulating oxide layer can readily form on the grains of the polycrystalline specimens. This oxide layer has been directly observed in the Na$_{x}$Si$_{136}$ clathrates, and can present difficulties in both densification and interpretation of the measured transport properties.
Although this point will be further addressed by the preparation of Na$_x$Si$_{136}$ ($x = 24$) single crystals in Chapter 5, we have also investigated the feasibility of consolidating microcrystalline Na$_x$Si$_{136}$ specimens for transport properties investigations. Both conventional hot-pressing as well as spark plasma sintering (SPS) methods were used.

Preliminary investigations into the transport properties of Na$_1$Si$_{136}$ and Na$_8$Si$_{136}$ specimens consolidated by hot-pressing were reported by the author previously. The measured electrical resistivities revealed a clear influence from the Na content, but suggested large contributions due to the porosity and/or poor inter-grain contact, a result of the low relative densities on the order of 70% that are achieved by hot-pressing. Further investigations on hot-pressed Na$_{22}$Si$_{136}$, which as noted in §1.4 is expected to exhibit metallic conduction, revealed room temperature resistivity of 300 mOhm-cm, and a negative temperature coefficient ($d\rho/dt < 0$). These observations confirm the large contribution of “extrinsic” specimen-dependent effects, and illustrate the challenges inherent in preparing specimens for transport measurements by conventional hot-pressing techniques. In collaboration with Prof. Yuri Grin and coworkers at Max Planck Institut für Chemische Physik fester Stoffe (MPI-CPfS), in Dresden, Germany, consolidation of a Na$_{22}$Si$_{136}$ specimen by SPS was also investigated. After a systematic study of the effects of heating rate, sintering temperature, and pressure, a consolidated specimen exhibiting a relative density of 83% was obtained. This is a substantial improvement as compared to hot-pressed specimens.

The measured $\rho$, $S$, and $\kappa$ in the temperature range 60 to 300 K for the Na$_{22}$Si$_{136}$ specimen consolidated using SPS are shown in Figure 4.9. $\rho$ increases monotonically with temperature, and remains less than 1 mOhm-cm in the entire temperature range. The value 0.7 mOhm-cm at 300 K is very close to that reported for the stoichiometric clathrate Cs$_8$Na$_{16}$Si$_{136}$ (cf. Figure 1.7). The values for $S$ remain relatively low, and the magnitude also increases monotonically with temperature. The negative sign of $S$ suggests that electrons are the majority carriers. The observed magnitude and temperature dependence of both $\rho$ and $S$ for Na$_{22}$Si$_{136}$ is indicative of metallic or very heavily doped semiconductor behavior.
As discussed in §1.4, metal-insulator transition has been reported to occur in Na$_x$Si$_{136}$ near 7 < $x$ < 11, though the precise value of $x$ at which this occurs, as well as the nature of this transition, has yet to be determined unequivocally. For the high Na content of Na$_{22}$Si$_{136}$, the electronic properties can be qualitatively understood in terms of a simplified rigid-band model, wherein electronic charge is transferred from the Na guests to the framework, therefore resulting in the occupation of the framework conduction bands, and the observed metallic properties. This qualitatively explains the observed behavior in Figure 4.9. Our transport measurements confirm that inter-grain sintering and relatively good electrical contact between the grains is achieved for this composition.

![Figure 4.9](image)

**Figure 4.9** Transport properties of polycrystalline Na$_{22}$Si$_{136}$. (a) Electrical resistivity (filled symbols) and Seebeck coefficient (open symbols). (b) Total measured thermal conductivity.
using the SPS method, indicating the promise of SPS consolidation for future study of the transport properties of these and related materials.

The total measured thermal conductivity (κ) for the Na$_{22}$Si$_{136}$ specimen is shown in Figure 4.9 (bottom). These data have not been corrected for the ~ 17% porosity in this specimen, which may have a non-negligible effect on the perceived κ. The temperature dependence of κ is similar to that reported for Cs$_8$Na$_{16}$Si$_{136}$ and also the type I Na$_8$Si$_{46}$.κ achieves a modest value of ~ 5.5 Wm$^{-1}$K$^{-1}$ at 300 K. Our previous investigation into the thermal conductivity of hot-pressed Na$_x$Si$_{136}$ (x = 0, 1, and 8) clathrates suggests the semiconducting variants possess relatively low thermal conductivities.
5 Single-crystals of intermetallic clathrates by spark plasma sintering: preparation, crystal structure, and transport properties of Na$_{24}$Si$_{136}$

The synthesis of many intermetallic clathrates presents formidable challenges and a number of clathrate compositions have to date only been obtained as microcrystalline powders. In such cases care must be taken in interpretation of measured structural, chemical, and physical properties for which grain boundary effects, surface composition and chemistry, and impurity phases can directly affect the observed properties. The preparation of high-quality single crystals, for structural and physical properties characterization, can be especially challenging for materials in which the elemental constituents have greatly differing melting points and/or vapour pressures, when the desired compound is thermodynamically metastable, or where growth with participation of the melt is generally not possible. This is particularly the case for alkali-silicon clathrates, for which conventional crystal growth techniques are generally inapplicable. Exploration of novel synthetic routes is necessary for realization of new compositions, but also for the preparation of high-quality single-crystals for these and other materials of interest. Herein we demonstrate the effectiveness of spark plasma sintering$^{233-235}$ (SPS) for redox preparation and crystal growth of clathrate silicides of alkali metals, in particular for the clathrate-II Na$_{24}$Si$_{136}$ which has evaded single crystal growth for more than four decades since its initial discovery.$^4$ The synthesis by SPS described in this chapter was carried out by the author during a three month independent research visitation at the Max Planck Institut für Chemische Physik fester Stoffe (MPI-CPfS), in Dresden, Germany, under the guidance of Institute Director, Prof. Yuri Grin. Transport measurements were conducted by the author using our in-house measurement system. These results reveal significant opportunities this method offers for preparation and crystal growth of materials. Structural and transport properties for bulk crystalline
Na$_{24}$Si$_{136}$ are presented, constituting the first measurements of “intrinsic” transport for any member of the Na$_x$Si$_{136}$ system.

5.1 Preparation of Na$_{24}$Si$_{136}$ by spark plasma sintering

The spark plasma sintering (SPS) technique, a variant of field assisted sintering, has in little more than a decade become an established consolidation method for preparation of dense polycrystalline specimens. The SPS technique possesses significant advantages over conventional consolidation techniques, in particular for intermetallic compounds. The defining characteristic of the SPS process is the pulsed DC electrical current, typically on the order of several hundred Amperes, that is sourced through the powder specimen and die assembly while they are simultaneously held under applied uniaxial pressure. Thus the specimen is heated internally, via resistive Joule heating, as opposed to externally as in conventional hot-pressing. The resulting high heating and cooling rates as well as short sintering times needed have proven ideal in the consolidation of ceramic, intermetallic, and nanostructured materials, especially where avoidance of grain coarsening is desired. Although a complete understanding of the role of the electric field and the beneficial mechanisms involved in this process is developing, and the existence or nature of the inter-grain plasma is still under investigation, the importance of the SPS method is evidenced by the rapidly growing number of materials investigations utilizing this technique. However, application of SPS as a method for synthesis of materials is still in its infancy, in particular regarding bulk crystal growth by this processing technique.

Sodium monosilicide, Na$_4$Si$_4$, was chosen as the reaction precursor in our experiments for its known high reactivity in promoting the formation of the intermetallic clathrates Na$_x$Si$_{46}$ (7 < $x$ < 8) and Na$_x$Si$_{136}$ (0 < $x$ < 24), as evidenced from both thermal decomposition (cf. Chapter 4) and chemical oxidation studies. This also comprises an ideal system for our study, since although the Na$_x$Si$_{136}$ variants were the first intermetallic clathrates to be reported more than four decades ago, and they are of considerable interest due to their intriguing structural and physical properties discussed in Chapter 1, until now
no method for single-crystal growth has been identified. As was illustrated in Figure 4.1, the crystal structure of Na₄Si₄ is composed of Si₄⁴⁻ polyanions and Na⁺ cations arranged in a monoclinic unit cell. Upon oxidation of Na₄Si₄, the silicon clathrate frameworks are formed, while simultaneously encapsulating sodium in the resulting Si₂₀ and Si₂₈ cage-like coordination polyhedra, as shown in Figure 4.1.
Figure 5.1a shows a schematic of the SPS system used in this study. Pulsed DC electrical current (with a possible range of 0 to 1,500 Amperes, depending upon the temperature to be achieved) is sourced through the specimen and die from the bottom (higher potential) electrode to the top (lower potential) electrode, which simultaneously act as the means for application of uniaxial pressure to the powder specimen. The specimen, die, punches, and electrodes are enclosed inside a vacuum chamber and maintained under dynamic vacuum ($10^{-2}$ torr) throughout the experiment.

Alkali metal silicide precursors were prepared from the high purity elements by reaction at 650°C in tungsten or tantalum crucibles sealed under inert atmosphere for 36 hours, as described in Chapter 4. Improved crystal morphology of the clathrate specimens synthesized by SPS was obtained when a small excess of alkali (10 wt%) was added to the initial precursor reaction mixture. The resulting precursor was ground to fine powder in an Ar filled glove box, and loaded into graphite dies of inner diameter 10 mm. Tantalum foil was used to surround the powder specimen on all sides, isolating the specimen from contact with the graphite die and punches during the SPS experiments. SPS experiments were performed using a Sumitomo Dr. Sinter SPS system. The temperature during the SPS experiments was monitored by a thermocouple inserted into a small hole drilled into the side of the SPS die (positioned approximately 1 mm from the specimen). It is important to note that the exact local temperature of the specimen is typically not known during the SPS process. In the present experiments we have measured the temperature by the standard technique and estimate the offset in the actual sample temperature to be less than ±50°C during any given stage of the experiment. Polarity of the applied voltage was determined in situ during the experiment. The system pulse cycle condition of 12 ON pulses, 2 OFF, was used for all experiments.

Effects of applied uniaxial pressure, temperature, and reaction time were studied. Crystal growth of phase pure $Na_{24}Si_{136}$ was reproducibly achieved by the following temperature schedule: heating to 450°C at 25°C/min, then to 600°C at 10°C/min, holding at 600°C for 3 hours, and then cooled to room temperature. Typical electrical current and applied voltage (across input leads to SPS apparatus) at 600°C were 267 A and 1.4 V, respectively. Uniaxial applied pressure of 100 MPa produced the best crystalline clathrate
product. Products from reactions at 550°C were found to contain a fraction (estimated to be 5 to 10 wt% from powder X-ray diffraction (p-XRD)) of the clathrate-I \( \text{Na}_8\text{Si}_{46} \), while those from reactions performed at 700°C were found to contain similar fractions of \( \alpha \)-Si. A very thin film of Na was observed to condense on the upper electrode (above the punch/die assembly), indicating preferential evaporation of Na exiting from the top of the die assembly (illustrated schematically in Figure 5.1a).

The growth of the \( \text{Na}_{24}\text{Si}_{136} \) crystalline specimens is completely reproducible. Figure 5.1b shows cross-sections of selected fractured compacts after SPS processing at 600°C and 100 MPa for differing reaction times, illustrating that the crystal growth initiates from the bottom electrode and progresses toward the top. The bluish crystalline \( \text{Na}_{24}\text{Si}_{136} \) discernable in the lower portion of the compact increases in fraction as the reaction is allowed to progress for longer durations of time. The remaining \( \text{Na}_4\text{Si}_4 \) precursor, spatially occupying the top portion of the SPS compact, is readily removed from the products by careful washing with ethanol and distilled water under flowing...
argin, allowing isolation of single phase Na$_{24}$Si$_{136}$ crystalline product, shown in Figure 5.1c and Figure 5.2. As is apparent from Figures 5.1c and 5.2, high quality crystalline product is obtained, with sizable (as broad as 500 $\mu$m along the longest dimension) crystals formed. Energy dispersive X-ray analysis detected only Na and Si in the crystals, with the inferred composition Na$_{22(1)}$Si$_{136}$ in qualitative agreement with Na$_{24}$Si$_{136}$ determined from single crystal XRD (vide infra). While a detailed understanding of the reaction kinetics and mechanisms behind the growth process has yet to be developed, the observations of Figure 5.1b clearly suggest an influence of the DC electrical current. As such, we propose that the Na$_{24}$Si$_{136}$ crystal growth is initiated from oxidation of the Na$_4$Si$_4$ precursor at the anode (bottom electrode), whereas sodium is reduced at the cathode (top electrode):

\[
34 [\text{Si}_4]^4^- \rightarrow [\text{Si}_{136}]^{24-} + 112 \text{e}^- \quad \text{(anode)}
\]

\[
112 \text{Na}^+ + 112 \text{e}^- \rightarrow 112 \text{Na} \quad \text{(cathode)}
\]

These processes are driven by the electric field that is present during the SPS experiment and the formation and evaporation of Na at the cathode.

The PXRD pattern (collected with a STOE STADI P diffractometer (Ge (111) monochromator, zero-background holder, Bragg-Brentano geometry) for a specimen ground from the Na$_{24}$Si$_{136}$ product is shown in Figure 5.3, corroborating the phase purity of the specimen. All reflections are indexed with the clathrate-II crystal structure (space group $Fd \overline{3}m$). The demonstrated growth of Na$_{24}$Si$_{136}$ by SPS therefore also constitutes a solution to a long standing challenge in the preparation of Na$_x$Si$_{136}$ clathrates: the previously known Na$_x$Si$_{136}$ synthetic routes, such as thermal decomposition$^{87,88}$ or chemical oxidation$^{118}$ of Na$_4$Si$_4$, typically produce the Na$_6$Si$_{46}$ clathrate as well in significant amounts, and this secondary phase is very difficult to avoid in the products from these synthetic routes. $\alpha$-Si is a common impurity phase in such specimens as

**Na$_4$Si$_4$ reacts with protic acids such as H$_2$O or alcohols to form SiH$_4$, which can be explosive in air. Thus washing is carried out by slow, controlled addition of ethanol and then distilled water, only under streaming argon. Under argon atmosphere, the specimen should be loaded in the vessel and sealed, then transferred to the safety hood were washing can be performed. Wearing of protective equipment is strongly recommended.**

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Figure 5.3 Powder X-ray diffraction pattern for a phase pure Na$_{24}$Si$_{136}$ specimen grown at 600°C, collected after removal of residual Na$_4$Si$_4$. All reflections correspond to Na$_{24}$Si$_{136}$. The most intense reflection corresponding to Na$_8$Si$_{46}$ which would be found just below 33° 2θ is completely unobservable.

The present work demonstrates that Na$_{24}$Si$_{136}$ is reproducibly prepared by SPS free of these impurity phases.

DSC measurements were performed on a Na$_{24}$Si$_{136}$ specimen using a Netzsch DSC 404 C calorimeter from room temperature to 1173 K with 5 K min$^{-1}$ heating rate. 7.5 mg of substance was sealed in welded Nb ampoules (Ø 5 mm, 600 mg) under argon atmosphere for measurement. No thermal events were observed on heating until 759°C, whereupon an endothermic event was observed corresponding to decomposition of Na$_{24}$Si$_{136}$.

5.2 Single-crystal X-ray diffraction studies on Na$_{24}$Si$_{136}$

Single crystal X-ray diffraction and investigations were carried out on Na$_{24}$Si$_{136}$ by Dr. Horst Bormann, Dr. Michael Baitinger, and Prof. Dr. Yuri Grin of MPI-CPfS. Data collection was performed with a rotating anode diffractometer (RIGAKU Spider,
### Table 5.1 Crystallographic data for Na$_{24}$Si$_{136}$, single crystal XRD

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula; molar mass</td>
<td>Na$<em>{24}$Si$</em>{136}$; 4372 g mol$^{-1}$</td>
</tr>
<tr>
<td>Crystal system; space group</td>
<td>cubic; Fd$ar{3}$m (No. 227), 2nd choice of origin</td>
</tr>
<tr>
<td>$a$ / Å</td>
<td>14.7157(2); Guiner powder XRD, LaB$_6$ standard</td>
</tr>
<tr>
<td>Unit cell volume</td>
<td>3186.71(8) Å$^3$</td>
</tr>
<tr>
<td>$Z$; $\rho_{calc}$/(g cm$^{-3}$)</td>
<td>1; 2.2779(1)</td>
</tr>
<tr>
<td>Diffractometer</td>
<td>RIGAKU Spider</td>
</tr>
<tr>
<td>Wave length $\lambda$ / Å; monochromator</td>
<td>0.71073; multilayer-optics</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.2 mm $\times$ 0.2 mm $\times$ 0.2 mm</td>
</tr>
<tr>
<td>$T$ / K</td>
<td>295(2)</td>
</tr>
<tr>
<td>$\theta$ range</td>
<td>2.77$^\circ$ to 33.53$^\circ$</td>
</tr>
<tr>
<td>Indexes ranges</td>
<td>$-16 \leq h \leq 12, -11 \leq k \leq 22, -10 \leq l \leq 22$</td>
</tr>
<tr>
<td>$\mu$ / mm$^{-1}$</td>
<td>1.41</td>
</tr>
<tr>
<td>$F$(000) / e</td>
<td>2168</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Multi-scan</td>
</tr>
<tr>
<td>Reflections collected; independent</td>
<td>4957; 326 [$R_{int} = 0.018$]</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on $F^2$</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>0.00035(4)</td>
</tr>
</tbody>
</table>

#### a. Single Site Model

- Refined parameters: 15
- Residuals [I > 4$\sigma$(I)]: $R_1 = 0.015$, $wR_2 = 0.024$
- Residuals (all data): $R_1 = 0.016$, $wR_2 = 0.024$

#### b. Split Site Model

- Refined parameters: 25
- Residuals [I > 4$\sigma$(I)]: $R_1 = 0.015$, $wR_2 = 0.024$
- Residuals (all data): $R_1 = 0.017$, $wR_2 = 0.025$
**Table 5.2** Atomic parameters for Na$_2$Si$_{136}$ (single site model)

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x/a$</th>
<th>$y/a$</th>
<th>$z/a$</th>
<th>$U_{eq}$ (Å$^2$)</th>
<th>Occ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0215(2)</td>
<td>1</td>
</tr>
<tr>
<td>Na2</td>
<td>3/8</td>
<td>3/8</td>
<td>3/8</td>
<td>0.119(1)</td>
<td>1</td>
</tr>
<tr>
<td>Si3</td>
<td>1/8</td>
<td>1/8</td>
<td>1/8</td>
<td>0.0087(1)</td>
<td>1</td>
</tr>
<tr>
<td>Si2</td>
<td>0.21797(1)</td>
<td>x</td>
<td>x</td>
<td>0.0089(1)</td>
<td>1</td>
</tr>
<tr>
<td>Si1</td>
<td>0.06735(1)</td>
<td>x</td>
<td>0.37129(1)</td>
<td>0.00876(9)</td>
<td>1</td>
</tr>
</tbody>
</table>

* $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor, appearing in the Debye-Waller factor $\exp(-2\pi^2 [h^2 a^* U_{11} + ... + 2 h k a^* b^* U_{12}])$.

**Table 5.3** Anisotropic displacement parameters for Na$_2$Si$_{136}$ (single site model)

<table>
<thead>
<tr>
<th>Atom</th>
<th>$U_{11}$</th>
<th>$U_{22}$</th>
<th>$U_{33}$</th>
<th>$U_{12}$</th>
<th>$U_{13}$</th>
<th>$U_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na1</td>
<td>0.0215(2)</td>
<td></td>
<td></td>
<td>-0.0018(2)</td>
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<td></td>
</tr>
<tr>
<td>Na2</td>
<td>0.119(1)</td>
<td></td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Si3</td>
<td>0.0087(1)</td>
<td></td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Si2</td>
<td>0.0089(1)</td>
<td></td>
<td></td>
<td>0.00021(6)</td>
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</tr>
<tr>
<td>Si1</td>
<td>0.0086(1)</td>
<td></td>
<td>0.0090(1)</td>
<td>0.00062(6)</td>
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</tbody>
</table>

**Table 5.4** Atomic parameters for Na$_2$Si$_{136}$ (split site model)

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x/a$</th>
<th>$y/a$</th>
<th>$z/a$</th>
<th>$U_{eq}$ (Å$^2$)</th>
<th>Occ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0214(2)</td>
<td>1</td>
</tr>
<tr>
<td>Na21</td>
<td>3/8</td>
<td>3/8</td>
<td>3/8</td>
<td>0.013(2)</td>
<td>0.19(1)</td>
</tr>
<tr>
<td>Na22</td>
<td>0.1058(8)</td>
<td>0.1249(5)</td>
<td>0.6363(7)</td>
<td>0.016(4)</td>
<td>0.032(1)</td>
</tr>
<tr>
<td>Si3</td>
<td>1/8</td>
<td>1/8</td>
<td>1/8</td>
<td>0.0085(2)</td>
<td>1</td>
</tr>
<tr>
<td>Si2</td>
<td>0.21798(3)</td>
<td>x</td>
<td>x</td>
<td>0.0088(1)</td>
<td>1</td>
</tr>
<tr>
<td>Si1</td>
<td>0.06735(2)</td>
<td>x</td>
<td>0.37134(3)</td>
<td>0.00864(8)</td>
<td>1</td>
</tr>
</tbody>
</table>

* $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor, appearing in the Debye-Waller factor, $\exp(-2\pi^2 [h^2 a^* U_{11} + ... + 2 h k a^* b^* U_{12}])$.

**Table 5.5** Anisotropic displacement parameters for Na$_2$Si$_{136}$ (split site model)

<table>
<thead>
<tr>
<th>Atom</th>
<th>$U_{11}$</th>
<th>$U_{22}$</th>
<th>$U_{33}$</th>
<th>$U_{12}$</th>
<th>$U_{13}$</th>
<th>$U_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na1</td>
<td>0.0214(3)</td>
<td></td>
<td></td>
<td>-0.0016(4)</td>
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</tr>
<tr>
<td>Na21</td>
<td>0.013(2)</td>
<td></td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Na22</td>
<td>0.011(9)</td>
<td>0.019(6)</td>
<td>0.018(7)</td>
<td>0.000(4)</td>
<td>0.002(3)</td>
<td>0.001(4)</td>
</tr>
<tr>
<td>Si3</td>
<td>0.0085(2)</td>
<td></td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Si2</td>
<td>0.0088(1)</td>
<td></td>
<td></td>
<td>0.00013(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si1</td>
<td>0.0085(1)</td>
<td></td>
<td>0.0089(2)</td>
<td>0.00054(1)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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Figure 5.4 Difference Fourier map calculated with the Na2 atom removed from the structure model. Centered at the 8b site, scaling in fractional coordinates. Despite a large displacement parameter for this site, the difference map shows on average an essentially spherical residual density, with a maximum at the center of the cage (3/8, 3/8, 3/8).

Varimax optical system, Mo Kα radiation $\lambda = 0.710747$ Å). Absorption correction was performed with a multi-scan procedure and the crystal structure refinement by employing a full-matrix least-squares procedure. Structure refinements were performed using SHELX.208 Details concerning the data collection and structure refinement are given in Table 5.1. The low residuals (for $I > 4\sigma(I)$: $R1 = 0.014$, $wR2 = 0.035$, GOF on $F^2 = 1.241$) of the structure refinement (Table 5.1) are indicative of both the quality of the acquired data and the crystallinity of the prepared crystal. Unit cell parameters were calculated from least squares refinement, using reflection positions obtained by single-profile fit of X-ray Guinier powder diffraction data (Cu Kα1 radiation, $\lambda = 1.540598$ Å, graphite monochromator, Huber 670 camera, $5^\circ \leq 2\theta \leq 100^\circ$, $\Delta 2\theta = 0.005^\circ$; LaB6 NIST standard with $a = 4.1569162(97)$ Å). Data analysis was performed with the WinCSD program.237 The cubic unit cell parameter (PXRD) $a = 14.716(1)$ Å is in general agreement with the previously reported87,88 trend for Na$_x$Si$_{136}$ extrapolated to $x = 24$. We note that a direct comparison of lattice parameters is not possible as full occupation of Na ($x = 24$) has not been previously achieved. In our single crystal specimens, all silicon framework sites are found to be completely occupied, and both sodium sites show full occupation within the
standard deviations, in accordance with the chemical composition Na$_{24}$Si$_{136}$. In light of a very large atomic displacement parameter ($U_{iso}$) observed for Na2 at the 8b site (Table 5.2), and previous EXAFS studies$^{95,96}$ indicating off-centering of Na in the large oversized Si$_{28}$ cage, split site models were refined against the single crystal data (Table 5.4). However, no improvement in the residuals was obtained (Table 5.4), and a difference Fourier map calculated with Na in the Si$_{28}$ cage removed from the model (Figure 5.4) shows only a broadly smeared, essentially spherical residual density with a clear maximum at the 8b site. It is conceivable that freezing out of thermal motion at low temperature$^{95,96}$ may cause the Na to lock into off-center positions and/or allow off-centering to become more clearly discernable. These possibilities are of interest for future investigations.

5.3 Transport properties of Na$_{24}$Si$_{136}$

As noted in §1.3, the transport properties of the Na$_x$Si$_{136}$ clathrates are of considerable interest. However, preparation of specimens of sufficient quality for accurate transport properties determination has previously been highly challenging for reasons stated above, but also due to difficulties in preparation of dense polycrystalline compacts from microcrystalline powders, as discussed in Chapter 4. Our preparation of Na$_{24}$Si$_{136}$ crystals offers the opportunity for the first investigation of the electrical and thermal transport properties of these silicon clathrates, free from interfacial and grain boundary effects associated with consolidated microcrystalline specimens.

Due to the small size of the Na$_{24}$Si$_{136}$ crystal specimens, it was necessary to modify the standard mounting procedure for our transport properties measurement system. A photograph of a Na$_{24}$Si$_{136}$ specimen mounted in this manner is shown in Figure 5.5a. Thermal bridges between the heat source (resistive heater, at top) and specimen, and heat sink and specimen, were made by bare Cu wire. Silver filled epoxy was used for thermal contact between the specimen and Cu wire thermal bridges, as well as electrical contacts for voltage probes. Thermocouples were attached with Stycast™ epoxy. The transport measurements were then conducted according to the procedures outlined in the Appendix. The difficulty in the determination of the cross-sectional area of the irregularly
shaped crystal results in a relatively large uncertainty in the electrical resistivity and thermal conductivity, which we estimate to be on the order of 40%. Regardless of this loss in precision, the obtained values can be interpreted as more accurately representative of the intrinsic properties of the material relative to the same measurements on polycrystalline specimens in this system, for which grain boundary effects can dominate.4,104,126,128

Data from temperature dependent electrical resistivity, Seebeck coefficient (S), and thermal conductivity (κ) on as-grown Na$_{24}$Si$_{136}$ crystal specimens are shown in Figure 5.5. The temperature dependence and magnitude of the resistivity data clearly indicate metallic behaviour for Na$_{24}$Si$_{136}$. Indeed, the observed magnitude of $\rho$ (29.3 $\mu$Ohm-cm at room temperature) is, to the best of our knowledge, lower than for any other intermetallic clathrate reported in the literature to date (with, of course, the exception of

Figure 5.5 Temperature dependent transport properties measurements on Na$_{24}$Si$_{136}$ crystal specimens grown by SPS. (a) Photograph (optical microscope) of a Na$_{24}$Si$_{136}$ crystal specimen mounted for transport properties measurements. (b) Electrical resistivity (triangles) and Seebeck coefficient (circles, solid curve to guide the eye). (c) Thermal conductivity of Na$_{24}$Si$_{136}$: total measured $\kappa$, along with $\kappa_e$ estimated from the measured electrical resistivity using the Wiedemann-Franz law.
the superconducting variants below their transition temperatures). This is an indication of both the unequivocal metallic conduction for this composition and the high quality of the crystals. The quality and crystallinity of the Na$_{24}$Si$_{136}$ specimen is also characterized by the calculated “residual resistance ratio” [RRR = R(300 K)/R(12 K)] value of approximately 14. We note that at the lowest temperature of our measurement (12 K), $d\rho/dt > 0$, indicating the residual resistance has still not yet been reached. A comparison with typical RRR values taken from the literature for other intermetallic clathrates is given in Table 5.6. The value for the Na$_{24}$Si$_{136}$ specimen of the present work is significantly higher than for any other intermetallic clathrate specimen reported in the literature. The magnitude of the Seebeck coefficient remains very small over the entire temperature range, corroborating the metallic conduction for this compound. The negative sign of $S$ indicates electrons are the majority carriers.

The electronic structures of Na$_x$Si$_{136}$ ($0 < x < 24$) have been investigated in several density functional theory studies.\textsuperscript{35,44,125} The inclusion of Na into the Si coordination polyhedra (Si$_{28}$ and Si$_{20}$) has significant effects on the electronic band structure, indicating a simple rigid band model strictly speaking does not apply to this system. However, as would be expected in a rigid band approximation, as Na is incorporated conduction band states progressively become more and more occupied. For the fully filled end member, Na$_{24}$Si$_{136}$, pronounced metallic conduction is expected with a relatively high concentration of carriers, which is precisely what is confirmed experimentally for the first time in the data of Figure 5.5.

The thermal conductivity $\kappa$ of Na$_{24}$Si$_{136}$ is shown in Figure 5.5c. The slight increase in $\kappa$ just below room temperature is likely due to minor radiation losses. This can be expected in the present case due to the small cross-sectional area of the specimen as compared to the surface area of the heater, specimen, and copper bridge. The thermal conductivity of Na$_{24}$Si$_{136}$ is found to be quite high, which is also consistent with the metallic behavior observed in the electrical transport properties.

The thermal conductivity of a solid can typically be expressed as simple sum of a lattice contribution ($\kappa_L$) due to phonon transport and an electronic contribution ($\kappa_e$) due to the charge carriers, so that $\kappa = \kappa_L + \kappa_e$. As a first approximation, $\kappa_e$ can be estimated from
Table 5.6 Comparison of the room temperature electrical resistivities and residual resistance ratios (RRR), $R(300 \text{ K})/R(T_0)$, for the Na$_{24}$Si$_{136}$ specimen of the present work and several intermetallic clathrate specimens from the literature showing metallic or “metallic-like” resistivities (i.e. $d\rho/dt$ is positive definite over the entire range of measurement). $T_0$ is the lowest temperature at which the corresponding resistivity was reported.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Structure Type</th>
<th>Form</th>
<th>Synthesis Method</th>
<th>Carrier Type</th>
<th>$\rho(300 \text{ K})$ (mOhm-cm)</th>
<th>$T_0$ (K)</th>
<th>RRR</th>
<th>Ref.</th>
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<tr>
<td>Na$<em>{24}$Si$</em>{136}$</td>
<td>clathrate-II</td>
<td>single crystal</td>
<td>SPS</td>
<td>$n$</td>
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<td>12</td>
<td>14</td>
<td>This work</td>
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<td>Eu$<em>8$Ga$</em>{16}$Ge$_{30}$</td>
<td>clathrate-VII</td>
<td>polycrystalline, as-synthesized</td>
<td>direct reaction of stoichiometric mixture</td>
<td>$n$</td>
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<td>2</td>
<td>3.0$^b$</td>
<td>238</td>
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<td>Cs$<em>8$Na$</em>{16}$Si$_{136}$</td>
<td>clathrate-II</td>
<td>polycrystalline, consolidated</td>
<td>direct reaction of stoichiometric mixture</td>
<td>$n$</td>
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<td>9</td>
<td>2.4</td>
<td>93</td>
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<tr>
<td>Ba$<em>8$Ga$</em>{16}$Sn$_{30}$</td>
<td>clathrate-VIII</td>
<td>single crystal</td>
<td>Ga flux growth</td>
<td>$p$</td>
<td>2.6</td>
<td>6</td>
<td>2.3</td>
<td>239</td>
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<td>Ba$<em>8$Ga$</em>{16}$Ge$_{30}$</td>
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<td>single crystal</td>
<td>slow cooling of stoichiometric melt</td>
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<td>Sr$<em>8$Ga$</em>{16}$Ge$_{30}$</td>
<td>clathrate-I</td>
<td>polycrystalline, consolidated</td>
<td>direct reaction of stoichiometric mixture</td>
<td>$n$</td>
<td>2.0</td>
<td>6</td>
<td>2.1</td>
<td>30</td>
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<tr>
<td>Na$<em>8$Si$</em>{46}$</td>
<td>clathrate-I</td>
<td>polycrystalline, consolidated</td>
<td>thermal decomposition of Na$_4$Si$_4$</td>
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<td>8</td>
<td>1.9</td>
<td>172</td>
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<tr>
<td>Cs$<em>8$Ge$</em>{136}$</td>
<td>clathrate-II</td>
<td>polycrystalline, consolidated</td>
<td>degassing Na from Cs$<em>8$Na$</em>{16}$Ge$_{136}$</td>
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<td>6</td>
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<td>Ba$<em>8$Al$</em>{14}$Si$_{31}$</td>
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<td>single crystal</td>
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<td>0.45</td>
<td>20</td>
<td>1.4</td>
<td>240</td>
</tr>
</tbody>
</table>

$^a$ At 400 K
$^b$ RRR $= R(400 \text{ K})/R(2 \text{ K})$
the Wiedemann-Franz relation $\kappa_e = L_0 T / \rho$, where $L_0 = 2.45 \times 10^{-8} \, \text{V}^2/\text{K}^2$ is the (temperature independent) Lorenz number, $T$ is the absolute temperature, and $\rho$ is the electrical resistivity. Also plotted in Figure 5.5c is the estimated $\kappa_e$, calculated from the Wiedemann-Franz relation using the measured $\rho$ shown in Figure 5.5c. It is clear that the Wiedemann-Franz relation overestimates $\kappa_e$ somewhat, which may signify that this model is not completely valid here, perhaps due to inequality of the electron relaxation times appropriate to thermal and electrical conduction; the use of the temperature independent $L_0$ may also contribute. We note however that the two data sets agree over most of the temperature range within the uncertainty of the measurement, and in general the estimation qualitatively reproduces both the magnitude and temperature dependence of the measured thermal conductivity. This is an indication that the thermal conductivity of Na$_{24}$Si$_{136}$ is dominated by the electronic contribution in this metallic compound.

Although quantitative values for $\kappa_L$ cannot be calculated from the data of Figure 5.5c, the estimation serves to suggest that the lattice contribution to $\kappa$ is small. This is consistent with our previous measurements$^{104,126}$ on consolidated polycrystalline Na$_x$Si$_{136}$ ($x = 0, 1, \text{and} 8$) specimens which all exhibited very low lattice thermal conductivities. The reasons for the low lattice thermal conductivity can made clearer by consideration of the mechanisms that are expected to significantly impede the heat transport by phonons in these materials. It is known that the lattice thermal conductivity in solids typically scales with the number of atoms in the primitive unit cell.$^{151}$ For the relatively large number of 30 atoms per primitive unit cell in Na$_{24}$Si$_{136}$, a comparatively low thermal conductivity (compared to $\alpha$-Si, for example, which contains 2 atoms per primitive unit cell and exhibits analogous bonding to the Si$_{136}$ framework) can be expected. The related increase in the unit cell volume for the silicon allotrope Si$_{136}$ results in conspicuous features in the phonon dispersion relations (and the corresponding phonon group velocities), which are modified by the relative decrease in the first Brillouin zone boundary (relative to $\alpha$-Si).$^{81}$

In addition, the strong static and/or dynamic disorder reflected in the large atomic displacement parameter for Na in the Si$_{28}$ cage also indicates potential mechanisms for impeding thermal transport in Na$_{24}$Si$_{136}$. The phenomenon of resonant scattering of heat
carrying acoustic phonons by local modes associated with the large amplitude thermal motion of guest atoms in intermetallic clathrates is well established (cf. §1.1). Several studies have suggested that off-centering of the guest ion enhances the effects of resonant scattering in these materials. Though the contributions remain to be determined unequivocally, both of these mechanisms are believed to be present in Na$_{24}$Si$_{136}$.

5.4 SPS processing as a general preparative tool

An important implication of the present work is that the SPS process holds significant promise as a general method for crystal growth of materials in cases where reactive precursors can be utilized. We have also applied the SPS method in processing of K$_4$Si$_4$ and Rb$_4$Si$_4$ precursors, using similar conditions to those described above. Single phase crystal growth of the respective clathrate-I compounds K$_{7.8(1)}$Si$_{46}$ ($a = 10.281(1)$ Å) and Rb$_{6.1(1)}$Si$_{46}$ ($a = 10.286(1)$ Å) was also successfully achieved in these cases (see Figure 5.6). We expect the method demonstrated herein of crystal growth via SPS processing of appropriate reactive precursors can be applied to the preparation of a

![Figure 5.6](image.png)

**Figure 5.6** Preparation of Rb$_6$Si$_{46}$ by SPS. PXRD (Gunier image plate) shows only reflections from the Rb$_6$Si$_{46}$ clathrate-I phase. As in Na$_{24}$Si$_{136}$, growth initiates from the bottom of the compact (inset), indicating the reaction mechanism is the same.
broader range of materials, and reveals a new preparative tool for the crystal growth and synthesis of materials where other conventional methods are unsuccessful. Analogous behaviour may in principle be common amongst the various $A_nE_m$ ($A = \text{alkali metal}, E = \text{group 14 element}, n, m \text{ integers}$) Zintl phases, since all contain similar structural and bonding motifs, and suggests direction for future studies.
6 Synthesis and characterization of a novel zeolite-like binary phase: \( \text{Na}_{1-x}\text{Ge}_{3+z} \)

In this chapter, the discovery of a novel binary phase in the Na-Ge system is reported. Showing qualitative structural characteristics analogous to some aluminum-silicate zeolites, the crystal structure of this new phase exhibits an unconventional covalently bonded tunnel-like Ge framework, accommodating Na in channels of two different sizes. Specimens were characterized by conventional and synchrotron powder X-ray diffraction, neutron powder diffraction, nuclear magnetic resonance (NMR) spectroscopy, and electrical and thermal transport measurements. The thermal conductivity of the new \( \text{Na}_{1-x}\text{Ge}_{3+z} \) phase was found to be very low, near 1 Wm\(^{-1}\)K\(^{-1}\) near room temperature.

6.1 Synthesis

The new Na-Ge phase was prepared in an analogous manner to that described for \( \text{Na}_{x}\text{Si}_{136} \) above. \( \text{Na}_4\text{Ge}_4 \) precursor (monoclinic, space group \( P2_1/c \))\(^{106,107} \) was first synthesized by direct reaction of the high purity elements at 650\(^\circ\)C. This reaction was carried out in a tungsten crucible, sealed under ultra high purity nitrogen inside a stainless steel canister, which was in turn sealed inside a fused quartz ampoule. As with the other alkali-tetrelide precursors, the resulting \( \text{Na}_4\text{Ge}_4 \) product is highly reactive with moisture and air, thus all handling was performed inside a nitrogen-filled glove box. The \( \text{Na}_{1-x}\text{Ge}_{3+z} \) phase is synthesized by thermal decomposition of \( \text{Na}_4\text{Ge}_4 \) through heating under vacuum (\( \approx 1.33 \times 10^{-4} \) Pa) at temperatures between 350 to 360\(^\circ\)C for several days. Results from a systematic investigation into the thermal decomposition of \( \text{Na}_4\text{Ge}_4 \) were presented previously by the author in Ref. 104.

The resulting thermal decomposition products are typically fine, grayish microcrystalline powders that, upon removal of any unreacted \( \text{Na}_4\text{Ge}_4 \) by washing with
water and ethanol, are stable in air and moisture. It was eventually found that amorphous fractions typically present in the as-synthesized specimens can be removed by repeated brief sonications in distilled water followed by immediate decanting of the resulting impurity-containing suspension, leaving the essentially single phase Na$_{1-x}$Ge$_{3+z}$ product which more quickly settles to the bottom of the container. After an extensive search of available crystallographic and chemical databases and literature, the new phase initially remained unidentifiable. This included reference to the available Na-Ge binary phase diagram.\textsuperscript{241} We note that some of the reported Na-Ge phases (including some not represented in phase diagram\textsuperscript{242}) have later been disputed,\textsuperscript{243} and this system remains to be well-characterized. As such, the crystal structure of the new phase was solved and refined as discussed below.

![Figure 6.1](image.png)

**Figure 6.1** Differential thermal analysis (DTA) data (exothermic up) for Na$_{1-x}$Ge$_{3+z}$ (bottom) indicating decomposition near 400°C. The prominent endothermic event at ~940°C corresponds to the melting of α-Ge. Upper left: pre-DTA PXRD pattern. Upper right: post-DTA p-XRD pattern after DTA to 500°C, indicating decomposition products contain α-Ge as the majority phase, with trace amounts of the title phase remaining.
Figure 6.1 shows data from differential thermal analysis on a specimen of the new binary, acquired under flowing nitrogen in open alumina pans. These thermal analysis measurements revealed the new phase decomposes exothermically above 400°C, whereas decomposition begins under vacuum (10^-4 Pa) at the lower temperature of 370°C. The exothermic nature of the decomposition suggests the phase is thermodynamically metastable with respect to the individual elements under the above conditions.

6.2 Crystal structure solution and refinement

As single-crystal specimens were unavailable, it was necessary to solve the crystal structure from powder diffraction data. Data collection, structure solution, and initial refinements were carried out by Dr. James Kaduk of INEOS Technologies. Synchrotron X-ray powder diffraction data were collected (Specimen I), with the help of Dr. Peter L. Lee, from 2-43.7° 2θ in 0.001° steps on the 32ID beamline of the Advanced Photon Source at Argonne National Laboratory (APS). The wavelength of 0.4958 Å (25 keV) was used. The pattern was indexed on a primitive hexagonal unit cell (Figures of merit of M(25) = 270, F(25) = 1503) using DICVOL04. A significant fraction of amorphous material in this first specimen under study precluded bulk analysis for experimental determination of the chemical composition. Therefore, an expected composition (i.e. unit cell contents), based on an empirical relation between compositions of the known Na-Ge phases and their mass densities, and the initial indexed unit cell parameters of the unknown phases, was derived as a starting point for structure solution. Attempts to solve the structure by applying single crystal techniques to extracted structure factors were unsuccessful, as were attempts to solve the structure in an orthorhombic sub-cell. Several space groups yielded essentially the same structure. The lowest residual was obtained in space group \( P6 \), but eventual analysis of the refined structure suggested that \( P6/m \) (No. 175) was the correct space group. The structure was solved using Monte Carlo simulated annealing techniques as implemented in the program Endeavour 1.3 (Crystal Impact). Rietveld refinements were carried out using the GSAS suite. The refined hexagonal unit cell parameters (Table 6.2) for the preliminary structure, as determined from
Rietveld refinement against the synchrotron XRD data, are $a = 15.05399(5)$ Å and $c = 3.96845(2)$ Å.

Neutron powder diffraction intensity data were collected (Specimen II) using the BT-1 high-resolution powder diffractometer at the National Institute for Standards and Technology Center for Neutron Research. Data collection and structure refinements were carried out by Drs. Winnie Wong-Ng, Qing Huang, and Zhi Yang. A Cu (311) monochromator was employed to produce a monochromatic neutron beam of wavelength 1.5403 Å. Collimators with horizontal divergences of 15’, 20’, and 7’ arc were used before and after the monochromator, and after the sample, respectively. The intensities were measured in steps of 0.05° in the 2θ range 3°-168°. Data were collected at 295 K and at 4 K. All data processing and Rietveld structural refinements were carried out using the GSAS suite.205,206 The neutron scattering amplitudes used in the refinements were

![Figure 6.2](image)

**Figure 6.2** Observed, calculated, and difference patterns (plotted on the same scale) obtained from Rietveld refinement using neutron diffraction data collected at 4 K. Lower tick marks indicate calculated reflections for Na$_{1-x}$Ge$_{3+z}$. Upper tick marks indicate calculated reflections for elemental Ge, which was present in the sample as a minor impurity. Refinement results are given in Table 6.1. M. Beekman, J.A. Kaduk, Q. Huang, W. Wong-Ng, Z. Yang, D. Wang, and G.S. Nolas, “Synthesis and crystal structure of Na$_{1-x}$Ge$_{3+z}$: A novel zeolite-like framework phase in the Na-Ge system,” *Chem. Commun.* 837 (2007). Reproduced by permission of The Royal Society of Chemistry.
Table 6.1 Refinement results for Specimens I and II.

<table>
<thead>
<tr>
<th>Specimen I (synchrotron)</th>
<th>Specimen II (neutron)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>300K</td>
</tr>
<tr>
<td>$R$ values</td>
<td></td>
</tr>
<tr>
<td>$wR_p$</td>
<td>0.0445</td>
</tr>
<tr>
<td>$R_p$</td>
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<tr>
<td>$\chi^2$</td>
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<tr>
<td>No. variables</td>
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</tr>
<tr>
<td>Total # data points</td>
<td>40699</td>
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<tr>
<td>Impurity phases</td>
<td>amorphous</td>
</tr>
</tbody>
</table>

Table 6.2 Lattice parameters for Specimens I and II (space group $P6/m$).

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<tr>
<th>Specimen</th>
<th>$a$(Å)</th>
<th>$c$(Å)</th>
<th>$V$(Å$^3$)</th>
</tr>
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<tbody>
<tr>
<td>I (synchrotron)</td>
<td>15.05399(5)</td>
<td>3.96845(2)</td>
<td>778.852(5)</td>
</tr>
<tr>
<td>II (neutron) @ 300K</td>
<td>15.0640(3)</td>
<td>3.9673(1)</td>
<td>779.66(3)</td>
</tr>
<tr>
<td>II (neutron) @ 4K</td>
<td>15.0052(4)</td>
<td>3.9546(1)</td>
<td>771.10(4)</td>
</tr>
</tbody>
</table>

0.363 and 0.818 ($\times 10^{12}$ cm) for Na and Ge, respectively. The preliminary structure as determined from synchrotron experiments was confirmed and the structural model was refined against neutron diffraction data at 295 and 4 K. The neutron powder diffraction pattern (observed, calculated, and difference obtained from Rietvled refinement) collected at 4 K is shown in Figure 6.2.

6.3 Crystal structure and crystal chemistry of Na$_{1-x}$Ge$_{3+z}$

The structure determination revealed that the new Na-Ge phase crystallizes in a complex zeolite-like structure. Depictions of the crystal structure are shown in Figures 6.3 and 6.4. Atomic coordinates, atomic displacement parameters, and site occupancies determined
from the structure refinements against the three data sets are given in Table 6.3. The most conspicuous aspect of the unusual crystal structure is a covalently bonded framework of Ge atoms, all of which are arranged in distorted tetrahedral (i.e. 4-bonded; see Figure 6.4) configurations with the exception of Ge1, which is only bonded to three other Ge atoms. As illustrated in Figure 6.3, the framework forms large and small channels, akin to the channels found in some oxide zeolites (cf. qualitative similarities to the AFI aluminium phosphate zeolite type\textsuperscript{246}). The present structure, however, does not correspond to any of the known zeolite structure types.\textsuperscript{246} The large and small channels in the framework both run along the \textit{c}-direction. The four crystallographically independent Ge framework sites (denoted by Ge1, Ge2, Ge3, and Ge4 in Figure 6.4) were all found to be fully occupied in refinements against both synchrotron and neutron diffraction data. From neutron

**Figure 6.3** Crystal structure of Na\textsubscript{1-x}Ge\textsubscript{3+z}, as viewed down the \textit{c}-axis. Na atoms are shown in blue, while the framework Ge atoms are shown in turquoise. The Ge7 site, which is partially occupied, is shown in white. The hexagonal unit cell is outlined in the upper right. M. Beekman, J.A. Kaduk, Q. Huang, W. Wong-Ng, Z. Yang, D. Wang, and G.S. Nolas, “Synthesis and crystal structure of Na\textsubscript{1-x}Ge\textsubscript{3+z}: A novel zeolite-like framework phase in the Na-Ge system,” \textit{Chem. Commun.} 837 (2007). Reproduced by permission of The Royal Society of Chemistry.

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diffraction at 295 K, the Ge—Ge distances in the framework range from 2.438(8) Å to 2.527(6) Å, as compared to the ‘ideal’ 2.45 Å for elemental Ge in the diamond structure. The open-framework configuration of Ge in Na$_{1-x}$Ge$_{3+z}$ results in a rather large volume per Ge atom of 32.5 Å$^3$/atom. This can be compared to 22.6 Å$^3$/atom for α-Ge and 25.8 Å$^3$/atom for the guest-free clathrate-II Ge$_{136}$, and indicates the pronounced “openness” of the framework in Na$_{1-x}$Ge$_{3+z}$.

As noted above, several crystalline binary compounds have been reported previously in the Na-Ge system. Of these, Na$_4$Ge$_4$ and Na$_{12}$Ge$_{17}$ have been characterized in the most detail. The crystal chemistry of phases such as Na$_4$Ge$_4$ and Na$_{12}$Ge$_{17}$ is understood in terms of Zintl-Klemm concepts. These compounds are composed of [Ge$_4$]$^+$ (e.g. Na$_4$Ge$_4$ and Na$_{12}$Ge$_{17}$) or [Ge$_9$]$^+$ (e.g. Na$_{12}$Ge$_{17}$) cluster anions and Na$^+$ cations. In Na$_4$Ge$_4$, for example, the Na atoms formally transfer

![Figure 6.4](image_url)

Figure 6.4 Structure of Na$_{1-x}$Ge$_{3+z}$, in the vicinity of the broad channel as viewed along the c-axis at a slight tilt. Na atoms in the smaller channels are shown in blue, while the framework Ge atoms are shown in turquoise. The variable occupancy Na6 and Ge7 sites in the larger channel are shown in grey and white, respectively. Tetrahedral coordination of Ge3 is shown, while other tetrahedral arrangements are omitted for clarity. M. Beekman, J.A. Kaduk, Q. Huang, W. Wong-Ng, Z. Yang, D. Wang, and G.S. Nolas, “Synthesis and crystal structure of Na$_{1-x}$Ge$_{3+z}$: A novel zeolite-like framework phase in the Na-Ge system,” Chem. Commun. 837 (2007). Reproduced by permission of The Royal Society of Chemistry.
Table 6.3: Crystallographic data for Na$_{1.5}$Ge$_{1.5}$ from Rietveld refinement against synchrotron X-ray and neutron powder diffraction.

<table>
<thead>
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<th>Atom</th>
<th>Wyckoff Position</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U_{iso}$ or $U_{eq}$ (Å$^2$)</th>
<th>Occupancy</th>
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<tr>
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<td>6j</td>
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<td>0.26958(8)</td>
<td>0</td>
<td>0.0115(4)</td>
<td>1</td>
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<tr>
<td>Ge2</td>
<td>6j</td>
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<td>0.44914(8)</td>
<td>0</td>
<td>0.0106(4)</td>
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</tr>
<tr>
<td>Ge3</td>
<td>6k</td>
<td>0.52012(9)</td>
<td>0.15164(9)</td>
<td>1/2</td>
<td>0.0052(3)</td>
<td>1</td>
</tr>
<tr>
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<td>0.0071(3)</td>
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<td>0</td>
<td>0.02</td>
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<td>6k</td>
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<td>Neutron diffraction data at 295 K</td>
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<tr>
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his single s electron to the Ge polyanion clusters, allowing closed shell configurations and an electronically balanced composition. The covalent Ge framework of Na$_{1-x}$Ge$_{3+z}$ is in stark contrast to the polyanionic [Ge$_4$$]^{4-}$ or [Ge$_9$$]^{4-}$ cluster units found in other Na-Ge compounds such as Na$_4$Ge$_4$ and Na$_{12}$Ge$_{17}$.

Figure 6.5 shows two perspectives of the small and large framework channels in the structure. Na atoms are situated inside the small channels (Na5), as well as in the broad channels (Na6). The broad channel consists of alternating Ge and Na, which can be interpreted as connected via Na–Ge bonds. The Ge forming this channel may also be described as a 24-ring. Inside the broad channel, a maximum of six Na can occupy the Na6 sites that are related to each other by a 6-fold symmetry. The initial synchrotron experiments and corresponding structure refinements suggested that additional Ge atoms are disordered in the middle of the broad channel. The nature of the contents in the larger channel were therefore of particular interest for the neutron diffraction investigation. In refinements against neutron diffraction data collected at both 295 K and 4 K, the

Figure 6.5 Perspectives of the two distinct Ge (green atoms) channels in Na$_{1-x}$Ge$_{3+z}$, viewed perpendicular to the c-axis. At left is shown the large channel, with the 24-ring highlighted at the top (Ge7 omitted). At right is shown the smaller channel, where Na (blue atoms) are coordinated in an 18-membered Ge cage.
additional nuclear density in the broad channel could be modeled by assigning Ge to additional sites (Ge7 in Figure 6.4) which in fact possess a 6-fold symmetry much like the Na atoms in this channel (Na6), yet reside closer to the center. These Ge sites were not found to be fully occupied, however, in contrast to the connected Ge framework. Rather the Ge7 site was found to have occupancy of 1/6, so that the Ge atoms are disordered on one Ge7 site per larger channel, per layer progressing along the c-axis. It was observed that the content of both species in the larger channel (Ge7 and Na6) can vary depending on the synthesis conditions. In particular, repeated grinding under nitrogen atmosphere and then “degassing” (i.e. heating the Na$_{1-x}$Ge$_{3+z}$ specimen under vacuum at 350°C) was found to reduce the Na content in the larger channel. This suggests a significant mobility of Na in the larger channel facilitating removal from the structure when heated under vacuum, as also observed in the Na$_x$Si$_{136}$ clathrates (see §4.2). The Ge content inside the broad channel (Ge7 position) can be varied as well. With the Ge

![Figure 6.6](image.png)

**Figure 6.6** Atomic displacement parameters for Na$_{1-x}$Ge$_{3+z}$. (a) Ellipsoid representations$^{225}$ of ADPs in the vicinity of the large channel. (b) ADPs extracted from data collected at 295 K and 4 K (lines are to guide the eye).
framework, Na5, and Na6 sites all fully occupied the chemical formula of this new phase is NaGe3. However, since the Na6 and Ge7 occupancies inside the larger channel can vary, the general formula for this non-stoichiometric phase is Na$_{1-x}$Ge$_{3+z}$.

Examination of the atomic displacement parameters (ADPs) for Na6 in the larger channel revealed significant disorder. Ellipsoid representations, depicted in the vicinity of the larger channel are shown in Figure 6.6a, while the values for the ADPs at both 295 and 4 K are plotted in Figure 6.6b. The pronounced elongation of the Na6 ellipsoid suggests substantial static disorder for this site. As shown in Figure 6.7b, the U$_{11}$ component of the ADP tensor remains very large even at 4 K. At the same time U$_{22}$ and U$_{33}$ both exhibit rather large values and stronger temperature dependence, indicating significant thermal motion for Na6 as well. The observed static and thermal disorder suggested by the ADPs for this site can be understood in terms of the rather poor bonding environment of the large channel, as well as the presence or absence of the nearby Ge7 in its fractionally occupied site.

Magic angle spinning solid-state $^{23}$Na NMR data were collected at 300 K by Prof. Russell Bowers and co-workers of the University of Florida in Gainesville, FL, and the National High Magnetic Field Laboratory in Tallahassee, FL. The $^{23}$Na NMR spectrum is shown in Figure 6.7. The NMR shifts are referenced to 1 M NaCl at 0 ppm. The spectrum reveals two resonances, at approximately 4 ppm and 23 ppm, respectively. The observation of two resonances is consistent with the two distinct crystallographic environments for Na (Na5 and Na6 above) in Na$_{1-x}$Ge$_{3+z}$. Since the integrated intensity of the NMR peak is proportional to the multiplicity of the site in the crystal structure, we can assign the higher intensity peak at approximately 23 ppm to Na in the larger channel (multiplicity of 6) and the lower intensity peak at approximately 4 ppm to Na in the smaller channel (multiplicity of 2). The magnitudes of the shifts are relatively small (i.e. close to that for Na$^{+}$ in NaCl), providing evidence that both Na are in an essentially ionic state in this phase. Large $^{23}$Na paramagnetic and/or “Knight” shifts observed for the Na$_8$Si$_{136}$ clathrates are not observed in Na$_{1-x}$Ge$_{3+z}$.
Na$_{1-x}$Ge$_{3+z}$ constitutes the first example in which an exclusively germanium framework crystallizes in a tunnel configuration, reminiscent of those found in the microporous zeolites. A structurally similar compound, the orthorhombic phase Na$_5$Sn$_{13}$, has been previously reported$^{249}$ by Vaughney and Corbett to exist in the Na-Sn system. This compound also exhibits an open-framework of covalently bonded Sn atoms, all of which are 4-bonded with the exception of one site on the interior of the larger channel in this structure which is 3-bonded. Na atoms in Na$_5$Sn$_{13}$ also occupy two different channels in the structure. The existence of these two phases exemplifies that novel structural architectures can be obtained in simple binary systems between the alkali and group 14 elements.

6.4 Transport properties of Na$_{1-x}$Ge$_{3+z}$

To investigate the transport properties of the new phase, a consolidated specimen was prepared by hot-pressing. Achieving high relative densities in the compact was found to be challenging, due to the metastable nature of the phase (see §5.1 above) which precluded the use of high sintering temperatures typically needed to produce a pellet of
relatively high density. A pellet exhibiting 62% of the expected (XRD) density was obtained by hot-pressing at 250°C, and 130 MPa for 1 hour. The powder XRD pattern obtained after hot-pressing, shown in Figure 6.8a, confirmed that the crystallinity of the specimen was maintained and decomposition did not occur during consolidation. Room temperature Seebeck coefficient and resistivity, and temperature dependent thermal conductivity were then investigated.

Room temperature Seebeck measurements yielded the value – 330 μV/K. This relatively large magnitude for the Seebeck coefficient is typical for an undoped compound semiconductor. We were unable to obtain reliable room temperature electrical resistivity data on the specimen due to difficulties in achieving adequate electrical contacts, but our measurements indicate a resistivity on the order of 10^5 mOhm-cm. The large apparent resistivity is consistent with the large magnitude for S (and the difficulty in making good electrical contacts to the specimen), and also the relatively small Na solid state NMR shifts discussed above.

Figure 6.8b shows the thermal conductivity of a Na_{1-x}Ge_{3+z} specimen at four temperatures between 150 K and 300 K. We note that since the crystal structure of Na_{1-x}Ge_{3+z} is hexagonal, the transport properties may not be isotropic in this material, and
therefore this data should be interpreted as an average of the transport along the different
crystallographic directions. Also shown in Figure 6.8b are the thermal conductivities for
single crystal $\alpha$-Ge,$^{251}$ as well as for polycrystalline and amorphous Ge films.$^{252}$ As the
porosity of the Na$_{1-x}$Ge$_{3+z}$ specimen was considerable ($\sim$ 38%), the data shown in Figure
6.8 have been corrected accordingly. It is known that porosity in polycrystalline
specimens can significantly reduce the observed thermal conductivity.$^{223,253-255}$ However,
methods have been developed in order to account for these effects.$^{223,253-255}$ Particularly
useful discussions on the effects of porosity on the thermal conductivity of solids have
been given by Klemens et al.$^{223,255}$ As detailed in Ref. 255, the thermal conductivity of
the “fully dense” material, $\kappa_{\text{dense}}$, can be estimated from the observed thermal
conductivity of a porous specimen, $\kappa_{\text{porous}}$, using the relation
$\kappa_{\text{porous}}/\kappa_{\text{dense}} \approx 1 – 3\varphi/2$,
where $\varphi$ is the relative porosity in the porous specimen. This approach was shown to be
successful in modelling the effects of porosity on the thermal conductivity of yttrium
stabilized zirconia.$^{255}$ The data for Na$_{1-x}$Ge$_{3+z}$ in Figure 6.8b are the adjusted data using
this approach. The thermal conductivity of Na$_{1-x}$Ge$_{3+z}$ is found to be very low, near 1.4
Wm$^{-1}$K$^{-1}$ in the temperature range investigated. From the large resistivity discussed
above, we can infer that the electronic contribution to $\kappa$ is negligible, and thus the
measured thermal conductivity of Na$_{1-x}$Ge$_{3+z}$ can be attributed essentially to the lattice
component entirely.

As the bonding in the Ge framework of Na$_{1-x}$Ge$_{3+z}$ is akin to that in $\alpha$-Ge, it is
useful to compare with the thermal conductivities shown for the other forms of elemental
Ge in 6.8. We see that the thermal conductivity of the Na$_{1-x}$Ge$_{3+z}$ phase shows a
pronounced reduction as compared to single or polycrystalline Ge, approaching that of
amorphous Ge in magnitude. The reasons for the low thermal conductivity of this
material can be attributed to the unusual features of its unique crystal structure. Low
thermal conductivities typically observed$^{256,257}$ for the structurally analogous oxide
zeolites are due to the openness of their framework crystal structures, as well
contributions (e.g. point-defect and resonant scattering) from non-framework cations
residing in the tunnels and cages in these structures.$^{257}$ Our observation of very low
thermal conductivity for Na$_{1-x}$Ge$_{3+z}$ illustrates that these factors can also play a role in
impeding thermal transport in non-oxide, intermetallic materials with similar structural architectures. The strong static disorder and thermal motion present in the large channel of the crystal structure may play a significant role in the scattering of the heat-carrying acoustic phonons in Na$_{1-x}$Ge$_{3+y}$.

Although the very high electrical resistivity would preclude the use of this material for thermoelectric applications, the very large $S$ and very low $\kappa$ observed for this novel structure suggests a potential approach to the design of open-framework compounds that may show promising thermoelectric properties. Moreover, the non-stoichiometry and phase width implied by the synchrotron X-ray and neutron powder diffraction experiments above suggests that the composition of Na$_{1-x}$Ge$_{3+y}$ can be varied. It is therefore of interest for future study to determine if the physical properties, and in particular the electrical properties, can in turn be influenced by varying the composition of this intriguing material.
References


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Bibliography


Appendix
Appendix: Characterization Techniques

In this appendix, some basic and brief introductory comments are made concerning some of the characterization techniques used in this work. The intent is to provide the reader unfamiliar with these techniques with a basic introduction, such that the results presented in the text may perhaps be clearer. No attempt at a comprehensive treatment is made; rather references are given where the reader may find more detailed information.

A.1 Rietveld crystal structure refinement

Many materials of scientific and technological interest are obtained as microcrystalline powders, which precludes the use of single-crystal techniques for crystal structure refinement. Moreover, information contained in a powder diffraction pattern can in some cases be more representative of a bulk specimen than a selected single-crystal. It was the pioneering work of Hugo Rietveld (Refs. A1 and A2) that showed that powder diffraction data can be systematically employed (in nontrivial cases) in the solution and refinement of the crystal structure of a material. Detailed overviews of the Rietveld methods can be found in Refs. A3 and A4.

One of the most important considerations in a powder diffraction experiment is that the 3-dimensional diffraction information is projected onto a single dimension ($2\theta$), thus information is inevitably lost due to reflection overlap. Rietveld analysis approaches this problem by fitting the entire observed powder diffraction pattern to a calculated pattern using a structural model. It is important to note that Rietveld refinement is precisely that: a crystal structure refinement technique, and cannot be used for structure solution. Rather, a starting structural model is always needed before proceeding with Rietveld refinement.

The basic principle behind the Rietveld method is that for each step in a powder diffraction experiment, $2\theta$, the observed diffracted intensity, $I_{oi}$, can be fit to a calculated intensity, $I_{ci}$, which is given by (see Ref. A4, for example)
\[ I_{ci} = s \sum_{hkl} L_{hkl} |F_{hkl}|^2 \phi(2\theta_i - 2\theta_{hkl})P_{hkl}A + I_{hkl} \]  

(A1)

where the \( hkl \) values indicate the Miller indices for the Bragg reflection under consideration, \( 2\theta_{hkl} \) indicates the position of the Bragg reflection corresponding to \( hkl \), \( s \) is the scale factor, \( L_{hkl} \) contains the Lorentz, polarization, and multiplicity factors, \( \phi \) is the reflection profile function (due to both instrumental and sample-dependent effects), \( P_{hkl} \) is a preferred orientation function, \( A \) is an absorption factor, \( F_{hkl} \) is the structure factor, \( I_{ib} \) is a contribution from the background, and the sum is over all reflections contributing to \( I_{ci} \) at \( 2\theta_i \). During Rietveld refinement, these quantities are systematically varied employing a least squares refinement algorithm which minimizes the quantity

\[ S_i = \sum_i w_i (I_i - I_{ci})^2 \]  

(A2)

where \( w_i = 1/I_i \) is a weighting factor. In other words, the algorithm aims to minimize the overall difference between the powder diffraction pattern calculated from the structural model and the pattern that is experimentally observed. This is achieved by systematically varying the structural aspects from the crystal structure model and specimen-related quantities (e.g. lattice parameters, atomic coordinates, atomic displacement parameters, site occupancies, specimen related peak profile parameters, etc.), as well as instrument/experiment related contributions (e.g., scale factor, specimen displacement, experiment related peak profile parameters, etc.), both of which contribute to the calculated intensity given by Eq. A1. In most cases, it is, of course, the information about the crystal structure that is desired.

The quality of a Rietveld refinement is judged by the refinement residuals (see Refs. A3 and A4), but more importantly by the graphical display of the fit. The standard practice for displaying this is shown in Figure A.1. The refinement profile plot has four main components: the experimentally observed diffraction pattern, the calculated pattern from the structural model, the difference pattern (equal to \( I_{oi} - I_{ci} \)), and tick marks indicating the positions for the calculated reflections for each refined phase. The
important indicator of the quality of fit is the difference pattern, which in the best case scenario should approach a flat line.

In addition to the contribution of his refinement method to the crystallography community, Rietveld also made freely and widely available his computer program which implemented the refinement algorithm. This tradition continues to the present day, as a number of Rietveld refinement programs and software are available for download via the internet free of charge.

**Figure A.1** Rietveld profile fit for a Na$_2$Si$_{136}$ specimen. (a) indicates the different components of the profile plot, while (b) shows a blown-up section from (a), showing the quality of the peak fitting in the region displayed.
charge (Ref. A5). In the present work, the General Structure Analysis System (GSAS) software suite developed (Ref. A6) by A.C. Larson and R. von Dreele and was used, along with the EXPGUI graphical user interface to GSAS, developed by Dr. Brian Toby (Ref. A7).

A.2 Extended X-ray absorption fine structure (EXAFS)

EXAFS has in the last several decades become an increasingly employed technique for gleaning useful information about local structure in a material. As opposed to a diffraction experiment, which yields averaged microscopic structural information, EXAFS is an element selective technique that yields local structural information about the environment of the atomic species whose absorption edge is being investigated. An introduction to the principles as well as approaches to modeling of EXAFS spectra can be found in Ref. A8.

In an X-ray absorption spectroscopy (XAS) experiment, the energy of an incident beam of monochromatic X-rays (e.g. from a synchrotron source) is varied, while the transmission through the specimen is monitored. As an absorption edge for a particular atomic species in the material is transversed, the absorption coefficient \( \mu \) of the material containing that species will exhibit a sharp rise, due to electronic ionization (i.e. the photoelectric effect) from the associated core energy level. As the incident photon energy is further increased above the edge, characteristic oscillations are observed; these are the XAS features of interest, the “fine structure.”

An essential principle behind the mechanisms responsible for the EXAFS oscillations observed in the absorption coefficient is the effect of scattering on the excited photoelectron. The excited photoelectron (due to its wave nature) is scattered by neighboring atoms (shown schematically in Figure A.2), resulting in interference between outgoing and scattered waves at the source (i.e. the absorbing atom). This interference can be constructive or destructive depending and the electron wavelength and nearest neighbor distances. Thus the EXAFS signal contains information about these distances around the central absorbing atom. As a result of considerable theoretical efforts in recent
decades, a well developed theory of the processes underling EXAFS has emerged (Ref. A8). As such, established computer programs are available which allow for fitting the EXAFS data using structural models, and can in turn allow very useful information concerning the local environment of the absorbing atom to be obtained.

A.3 Transport properties measurements

All transport properties measurements reported in this work were measured on our custom designed measurement system. The details of the design and implementation of this system, as well as the typical specimen mounting procedure, are found in Refs. A9 and A10. A closed cycle helium cryostat allows measurement of electrical resistivity ($\rho$), Seebeck coefficient ($S$), and thermal conductivity ($\kappa$) from 12 K to 320 K, on a single specimen, in a single measurement cycle. The transport system was extensively tested by measurement of several Standard Reference Materials (SRM) obtained from the National Institute of Standards and Technology (NIST), as well as inter-laboratory verification of measurements through comparison with other established measurement systems in industrial and university labs.
Schematics illustrating the measurement of the three transport coefficients are given in Figure A.4. Electrical resistivity is measured by a four-probe method. A small known current (typically ~ 5 mA) is passed through the specimen, and the voltage difference ($\Delta V$) measured between two points a known distance apart. $\rho$ is then determined from Ohm’s Law and the geometry of the sample as shown in Figure A.4a. To eliminate possible thermoelectric contributions to $\Delta V$, data is acquired with current sourced in both directions, with fast switching of the current direction, and the results are averaged. Temperature gradients for measurement of $S$ and $\kappa$ are applied by a small chip resistor attached to one end of the specimen, which acts as a heat source. $S$ is measured by sweeping the temperature gradient, and measuring the voltage difference ($\Delta V$) and temperature difference ($\Delta T$) at two points in a plane perpendicular to the axis of the specimen. $S$ is then determined from the slope of a plot of $\Delta V$ vs. $\Delta T$, i.e. $S = dV/dT$ as shown in Figure A.4b. For the case of measuring $\kappa$, several temperature gradients are applied to the specimen, and the slope of a plot of the power vs. the measured $\Delta T$ yields the thermal conductance. $\kappa$ is then determined from this conductance and the geometry of

\[ R = \frac{\Delta V}{I} = \rho \frac{\ell}{A} \]

\[ S = \frac{dV}{dT} \]

\[ P = \kappa A \frac{\Delta T}{\ell} \]

Figure A.4 Schematics illustrating the measurement of transport properties: (a) Four-probe resistivity, $\rho$, (b) Seebeck coefficient, $S$, and (c) thermal conductivity, $\kappa$. 
the sample. The power (\(P\)) passing through the specimen is assumed to be equal to the power generated by the heater (\(P_{heater}\)), which is calculated from \(P_{heater} = I_{heater}V_{heater}\).

The total measurement relative uncertainty at room temperature for \(\rho\), \(S\), and \(\kappa\), are estimated to be 4\%, 6\%, and 8\%, respectively (Ref. A10).

### Appendix References


A5. See http://www.ccp14.ac.uk/ for an extensive repository.


About the Author

Matt Beekman received his B.S. and M.S. degrees in Physics in 2003 and 2006, respectively, from the University of South Florida. Mr. Beekman entered the Ph.D. program in Applied Physics as a USF Presidential Fellow in 2003. While in the Ph.D. program at USF, he has authored or co-authored more than seventeen peer reviewed journal publications and twelve conference proceedings, and has given several presentations on his research at meetings of the MRS, ITS, ACS, and ACerS. In recognition of his research accomplishments, Mr. Beekman has received the 2008 ITS Goldsmid Award for Excellence in Research in Thermoelectrics by a Graduate Student, the 2006 USF Outstanding Master’s Thesis Award, and several student presentation awards at international scientific conferences.