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Synthesis and physical properties investigations of open-framework intermetallic clathrates

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Synthesis and Physical Properties Investigations of Intermetallic Clathrates

by

Stevce Stefanoski

A thesis submitted in partial fulfillment of the requirements for the degree of
Master of Science
Department of Physics
College of Arts and Sciences
University of South Florida

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Dedication

I dedicate this work to my parents, Angele and Vera Stefanoski
for their support and love that gives me a strength to accomplish my goals.
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I thank Dr. Winnie Wong-Ng from NIST for doing the single-crystal diffraction on the Na$_8$Si$_{46}$ and Na$_{24}$Si$_{136}$ single crystals. My gratitude also goes to Dr. Andrei V. Shevelkov from the Moscow State University for providing me the materials for Chapter 4, as well as for the many insights I got during our communication. I thank Dr. Phan and Dr. Hariharan for performing the measurements on the Eu$_8$Ga$_{16}$Ge$_{30}$ in Chapter 5 of this work and the constructive discussions on magnetic properties of the materials.

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Synthesis and Physical Properties Investigations of Intermetallic Clathrates

Stevce Stefanoski

ABSTRACT

Intermetallic clathrates have long been of interest for materials science research. The promise these materials hold for useful applications ranges from thermoelectrics to photovoltaics and optoelectronics to potentially ultra-hard materials and magnetic cooling applications. Their unique physical properties are intimately related to their intriguing structural properties. Thus a fundamental understanding of the chemistry and physics of inorganic clathrates offers the possibility to assess their potential for use in the various applications mentioned above.

The purpose of the current work is to expand the current knowledge of the synthetic routes for obtaining clathrate materials, their structural, chemical, and physical properties, particularly those that from in the type I, II and VIII crystal structures. New synthesis routes are presented and used for preparation of single crystals of Na₈Si₄₆ and Na₂₄Si₁₃₆. Single-crystal X-ray analysis, and resistivity, Seebeck coefficient and thermal conductivity measurements are presented. In addition, two "inverse" clathrates with compositions Sn₂₄P₁₉.₃Br₈ and Sn₁₇Zn₇P₂₂Br₈ have been characterized in terms of their transport properties. Since the magnetic refrigeration based on the magnetocaloric effect is a topic of great interest, type VIII Eu₈Ga₁₆Ge₃₀ clathrates are also explored in terms of their application for magnetic cooling.
1. Introduction

The term *clathrate* is derived from the Latin word “clathratus” meaning “furnished with a lattice”. Clathrates are compounds formed by inclusion of atoms or molecules of one type into cavities of a sequestering crystal lattice of another. The first known clathrate compound, the chlorine-water molecule, was discovered by Humphry Davy in 1811\(^1\) and, together with the analogous compounds discovered later, were termed “gas hydrates” because they entrap gas molecules in ice. Research undertaken by Kasper et al.\(^2\) reported the existence of the clathrate phase Na\(_8\)Si\(_{46}\) which was isomorphic with that of the gas hydrates. Further investigations by Cross et al.\(^3\) and Gallmeier et al.\(^4\) revealed new structures with frameworks composed of Ge, Si or Sn atoms encapsulating alkaline atoms. Einsmann et al.\(^4\) synthesized the ternary compounds A\(_8\)B\(_{16}\)E\(_{30}\) (A=alkaline metal; B=Ga, Al; E=Si, Ge, Sn). In the early 1990s, the U.S. Department of Defense (DoD) initiated a program to search for new materials with potential for thermoelectric applications. One approach taken by the scientific community was to discover novel bulk-materials that comply with the “Phonon-Glass Electron-Single Crystal” (PGEC) concept introduced by Slack.\(^5\) According to this concept, a good thermoelectric material would possess a low (“glasslike”) thermal conductivity, \(\kappa\), typical of amorphous materials, high electrical conductivity, \(\sigma\), similar to metals, and high Seebeck coefficient, \(S\), akin to semiconductors. Certain clathrates are materials that exhibit such properties.\(^6\text{-}^8\) They possess atomic-sizes voids that can encapsulate heavy-ions that undergo large anharmonic vibrations (“rattling”) and scatter phonons effectively, while their electrical properties vary with doping.

The first transport characterization on Si and Ge clathrate compounds was made by Nolas et al.\(^6\). They reported \(\kappa\) on these materials to have temperature dependences and amplitudes similar to amorphous materials, pure amorphous Ge in particular. Besides having a low \(\kappa\), these materials possess other interesting properties\(^9\) that are of interest for a range of applications. Most of the known clathrates to date are composed of group 14 elements.\(^6\text{-}^8\) In addition to their ground state configuration, there is a variety of highly stable binary,\(^2\text{-}^4\text{,}^10\text{-}^11\) ternary,\(^4\text{-}^12\text{-}^13\) and quaternary clathrates.\(^14\text{-}^15\)
From a chemical and physical viewpoint, clathrate materials allow for the study of compounds possessing isomorphic structures with greatly varying properties, ranging from metals\textsuperscript{13} to semiconductors\textsuperscript{16} to superconductors\textsuperscript{17,18}, while other compositions have been studied for their magnetic properties\textsuperscript{19,20} (cf. Chapter 5). The unconventional properties displayed by these materials, such as the aforementioned glass-like $\kappa$\textsuperscript{16} and the heavy atom tunneling in the crystalline state\textsuperscript{21-23}, comprise novel physical phenomena in crystalline solids. The promise these materials hold for useful applications ranges from thermoelectrics\textsuperscript{24,25} to photovoltaics and optoelectronics\textsuperscript{26-29} to potentially ultra-hard materials\textsuperscript{30} and magnetic cooling applications.\textsuperscript{19,20} All of these unique physical properties are intimately related to their intriguing structural properties. Thus a fundamental understanding of the chemistry and physics of inorganic clathrates offers the possibility to assess their potential for use in the various applications mentioned above.

1.1 Type I, II and VIII clathrates

The term “clathrate” refers to inclusion compounds in general, though there is a variety of crystal structure types amongst the known clathrate materials. There exist nine distinctive types of clathrate structure types,\textsuperscript{9} of which types I, II and VIII are considered in this work. Clathrates generally consist of a covalently-bonded framework composed of a group-14 elements (Si, Ge and Sn)\textsuperscript{6,31-33} encapsulating alkaline metals (Na, K, Rb, Cs)\textsuperscript{34,35}, alkaline earth metals (Ba, Sr)\textsuperscript{36} or Lanthanides (Eu).\textsuperscript{19,20} The framework of the various types of clathrates can be thought of being built by different polyhedral “cages”. Type I clathrates form in the $Pm\bar{3}m$ space group and consist of two types of polyhedra, dodecahedra ($E_{20}$) and tetrakaidecahedra ($E_{24}$).\textsuperscript{9} The frameworks of the type II clathrates are comprised of dodecahedra ($E_{20}$) and hexakaidecahedra ($E_{28}$),\textsuperscript{38} and their crystal structure is $Fd\bar{3}m$. Type VIII clathrates form only one (distorted) pentagonal dodecahedra with the space group $I\bar{4}3m$.\textsuperscript{14}
1.2 Synthesis and crystal structure of type I clathrates

The type I clathrate structure is represented by the general formula \(A_8E_{46}\), where \(A\) are alkali metals or alkali-earth atoms, and \(E\) are the group 14 elements Si, Ge or Sn. Type I ternary compounds with general formula \(A_8B_{16}E_{30}\) where \(B\) is Zn, Cd, Al, Ga, In, As, Sb or Bi\(^4,12,13\) also exist. For these compounds, the bonding is analogous to that of Zintl-phases\(^38\), where the more electropositive guest atoms donates their valence electrons to the more electronegative host atoms resulting in a closed-valence shell. These valence electrons form the covalently bonded face-sharing host framework. The type I clathrate crystal structure comprises two 20-membered pentagonal dodecahedra \(E_{20}\), each formed by twelve pentagonal faces (Figure 1.1) creating a void with \(\bar{3}m\) symmetry, and six 24-membered tetrakaidecahedra \(E_{24}\), formed by twelve pentagonal and two hexagonal faces, each creating a void with \(4m2\) symmetry.\(^4,31\) The corresponding unit cell is cubic with space group \(Pm\bar{3}n\). The group 14 framework atoms reside at three distinctive sites, 6\(c\), 16\(i\) and 24\(k\), while the “guest” atoms are encapsulated at 2\(a\) and 6\(d\) sites inside the \(E_{20}\) and \(E_{24}\), respectively. Analogous to their diamond structured compounds,\(^39\) the \(E-E-E\) bonds range from \(105^\circ\) to \(126^\circ\), averaging the ideal \(sp^3\) hybridization angle\(^9\) of \(109.5^\circ\). The clathrate structure deviates from the diamond structured counterpart in their larger average interatomic distances and larger (~15%) volume per group 14 atom, demonstrating the “openness” of the clathrate crystal structure.\(^9\)
Figure 1.1 Crystal structure of type I clathrates. The cubic unit cell is composed of two pentagonal dodecahedra ($E_{20}$) and six tetrakaidecahedra ($E_{24}$).

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Type I clathrates have been the most studied clathrate type to date. There are a few excellent reviews on the structure and the properties of these materials. In this work we are going to outline some of the most conspicuous aspects of the type I clathrates, regarding their structure, their relevance for thermoelectric applications and the related discovery of the rather unconventional heat transport, for a crystalline solid.

Cross et al. first reported the synthesis of type I clathrates with a structure similar to that of the gas hydrates. They synthesized Na$_8$Si$_{46}$ by thermal decomposition of alkali silicides under high vacuum. Einsmann et al. first synthesized ternary compounds A$_8$B$_{16}$E$_{30}$ (A=alkaline metal; B=Ga, Al; E=Si, Ge, Sn) by mixing stoichiometric quantities of the pure elements in alumina crucibles. The mixtures were slowly heated under argon atmosphere at a rate 2°C/min up to a maximum temperature of 1150°C for
Si, 1050°C for Ge and 850°C for Sn mixtures and kept there for an hour before slow cooling to room temperature.

Some stoichiometric mixtures melt congruently at certain temperatures. This was used in the direct synthesis of certain type I clathrates. Phan et al. synthesized type I Eu₈Ga₁₆Ge₃₀ by reacting stoichiometric ratios of the high purity elements in boron nitride (BN) crucible, sealed under nitrogen in a quartz tube, in an induction furnace at 1100 °C followed by rapid water quenching. Single crystals of the halogen-filled clathrate I₈As₈Ge₃₈ were grown by Chu et al. by vapor deposition in a two-zone furnace. The stoichiometric mixtures were enclosed in a sealed fused silica tube. Ge was kept at a temperature between 720 and 730 °C, and As at a temperature between 600 and 610 °C. Nolas et al. grew single crystals of Sr₈Ga₁₆Ge₃₀ and Eu₈Ga₁₆Ge₃₀ by mixing and reacting stoichiometric quantities of the high purity elements and holding them for 3 days at 950°C inside a BN crucible that was itself sealed in a fused quartz ampoule that was evacuated and back filled with argon. The ampoule was then slowly cooled to 700°C where it was left for 4 days. It was then slowly cooled to room temperature. The crystals of various Sn clathrates were synthesized by Nolas et al. by mixing and reacting the constituent elements for 2 weeks at 550°C inside a tungsten crucible that was itself sealed inside a stainless steel canister, after the canister was evacuated and backfilled with high-purity argon. The resulting Sn clathrates consisted of small octahedral shaped crystals with a shiny, somewhat blackish, metallic luster. Chakoumakos et al. grew single crystals of Sr₈Ga₁₆Ge₃₀ by first arc-melting high purity Sr and Ge together in an argon atmosphere to form SrGe₂. Then they loaded stoichiometric amounts of SrGe₂, Ga shot and Ge in a helium dry box into a carbonized silica tube. The constituents were then heated to 1050°C at 2°C/min, held at 1050°C for 20 hours, and then slowly cooled to 650°C, where they were held for several days, and finally cooled down to room temperature. Single crystals 5-10 mm in length were obtained. Reny et al. synthesized the type I clathrate I₈Si₄₆₋ₓIXₓ, the first clathrate to be filled with an electronegative element. Another interesting aspect of this material is that the iodine can be found both on the framework site and as the interstitial atom.
1.3 Electronic and thermal properties of type I clathrates

Inorganic clathrates show a rich variation in their electric properties. In a simplified model, the valence electrons from the guest atoms are donated to the framework conduction bands. If charge compensation is not accomplished by substitution on the framework sites, metallic transport is expected.\textsuperscript{49,50} Maudryk et al.\textsuperscript{50} has characterized a series of Ba and Eu substituted type I clathrates, including Cu-stabilized variants, with various framework substitutions. These include Al, Ga or In atoms occupying Si or Ge host sites. The temperature dependence of the electrical resistivity, $\rho$, is typical for metallic materials. The negative $S$ throughout the entire temperature range may be an indication that the majority carriers in these compounds are electrons.

A number of type I clathrates have been found to have semiconducting properties.\textsuperscript{6,9,40,51} Nolas et al.\textsuperscript{6} measured $\rho$ (Figure 1.2a) and $S$ (Figure 1.2b) of $\text{Sr}_x\text{Ga}_{16+x}\text{Ge}_{30-x}$, where $x$ is varied slightly.
The ability to vary the doping level of these semiconductor compounds by varying the chemical composition is one reason why they are of interest for thermoelectric applications. Ga shows a strong preference for the 6c site and a weaker preference for the 24k site. The observed Ga distribution has implications for the bonding in these materials, suggesting some Ga(6c)-Ga(24k) bonds. The doping level of this series of specimens was varied by changing the Ga-to-Ge ratio while maintaining a fixed Sr concentration. $S$ decreases with increasing the carrier concentration, as shown in Figure 1.3b, and also decreases with decreasing temperature as expected in heavily doped semiconductors with negligible phonon drag. This form of substitution didn’t produce $p$-type conduction, however substituting Zn for Ge does produce $p$-type semiconductors. The mobility in these specimens is relatively high, ranging from 730 to 2200 cm$^2$/V. Blake et al. estimated the bang gaps for Sr$_8$Ga$_{16}$Ge$_{30}$ and Ba$_8$Ga$_{16}$Ge$_{30}$ to be 0.3 eV and 0.6 eV, respectively, and the larger band gap for Ba$_8$Ga$_{16}$Ge$_{30}$ resulting in and better thermoelectric performance.
The guest-host interaction in clathrate materials directly determines the unique properties in these materials. The guest atom is weakly bonded to the framework and can “rattle” creating a strong phonon scattering center, which has a dramatic effect on the thermal conductivity of the clathrate materials. Figure 1.3a demonstrates the difference in temperature dependent lattice thermal conductivity, $\kappa_L$, for several type I clathrates.

![Figure 1.3](image)

Figure 1.3 a) $\kappa_L$ for several representative type I clathrates b) “Glass-like” $\kappa$ for Sr$_8$Ga$_{16}$Ge$_{30}$

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A comparison of guest atom’s radii (1.17 Å for Eu$^{2+}$ and 1.18 Å for Sr$^{2+}$) with polyhedra size suggest that smaller ions may “rattle” more effectively within their cages and thus scatter phonons and suppress the thermal conductivity. It is apparent from Figure 1.3a that Eu$_8$Ga$_{16}$Ge$_{30}$ possesses an amorphous-like $\kappa_L$ lower than Sr$_8$Ga$_{16}$Ge$_{30}$, due to the smaller atomic radius for Eu$^{2+}$ and the larger mass (almost twice as massive). The difference in $\kappa_L$ of Eu$_8$Ga$_{16}$Ge$_{30}$ and Cs$_8$Sn$_{44}$ is even more pronounced due to the much larger atomic radius of Cs$^{+}$ (1.70 Å). $\kappa_L$ for Cs$_8$Sn$_{44}$ varies as $T^{-1}$ and is typical of a crystalline semiconductor dominated by umklapp-scattering. Additional bonding is introduced between Cs and Sn atoms neighboring the vacancies in Cs$_8$Sn$_{44}$ such that it
constrains the Cs atoms. In the case of \( \text{Sr}_4\text{Eu}_4\text{Ga}_{16}\text{Ge}_{30} \) there are two different atoms enclosed inside the polyhedra that introduce six different scattering frequencies, three for each atom. This compound exhibits the lowest \( \kappa_L \) in the temperature range shown, tracking the temperature dependence of \( \alpha\text{-SiO}_2 \) very closely. \( \kappa_L \) of \( \text{Ba}_8\text{Ga}_{16}\text{Si}_{30} \) is relatively low, however with temperature dependence different from the one of the Ge-clathrates. Even though \( \text{Ba}^{2+} \) is more massive than \( \text{Ga} \) and \( \text{Si} \), it is similar in size with \( \text{Si}_{20} \) and \( \text{Si}_{24} \) cages, whereas \( \text{Sr}^{2+} \) and \( \text{Eu}^{2+} \) are smaller than the Ge cages. Thus the temperature dependence is similar to that of a crystalline solid, exhibiting a mass-fluctuation scattering.\(^9\)

One of the most interesting and important discoveries in terms of thermoelectrics was the magnitude and the temperature dependence of \( \kappa_L \) of Ge clathrates. Figure 1.3b shows the temperature dependence of \( \kappa \) for \( \text{Sr}_8\text{Ga}_{16}\text{Ge}_{30} \).\(^57\) The magnitude and temperature dependence are similar to that of amorphous material. The low temperature (<1 K) data indicates a \( T^2 \) temperature dependence, as shown by the straight-line fit to the data in Figure 1.4b. Although the \( \kappa \) values exceed those of amorphous Ge (\( \alpha\text{-Ge} \)) at room temperature, they are smaller than amorphous quartz (\( \alpha\text{-SiO}_2 \)) above 100 K. The low-frequency acoustic phonons have the highest group velocity\(^54\) and contribute most to \( \kappa \).

Temperature dependent single crystal and powder neutron diffraction experiments have been used by Nolas et al.\(^46\) and Chakoumakos et al.\(^47\) and the isotropic atomic displacement parameters (ADPs) were reported (Figure 1.4).
Cs1 and Cs2 represent the filler atoms that occupy the 2a and 6d sites. As shown in the figure the Cs2 atoms have much larger ADPs than those of the framework atoms. In addition to this, the temperature dependence of the ADPs for the Cs2 atoms is greater than that of the framework atoms.

Nolas et al.\textsuperscript{58} have also employed Raman scattering to study type I clathrates (Figure 1.5). From crystal symmetry considerations and group theory, the Raman active modes can be determined for both the framework and the guest atoms in the clathrates. It was found that the guest atom at the 6d site contributes two Raman active modes.
Figure 1.5 Stokes Raman scattering spectra for selected type I clathrates. The vibrational modes of the filler atoms are indicated by arrows.\textsuperscript{58}

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A theoretical investigation of the “rattling” guest atoms in type I clathrates, offered by Dong et al.,\textsuperscript{59} supports the idea of strong interaction between the localized modes of the guest atoms and the heat-carrying phonons, resulting in a low $\kappa$ in the semiconducting clathrates.
1.4 Synthesis and crystal structure of type II clathrates

The crystal structure of the type II clathrates is face-centered cubic, with the $Fd\bar{3}m$ space group. Two types of face-sharing polyhedra participate in the structure of the type II clathrates, sixteen 20-membered pentagonal dodecahedra ($E_{20}$, point symmetry $I_h$) and eight 28-membered hexacaidecahedra ($E_{28}$, point symmetry $T_d$) per unit cell (Figure 1.6). The pentagonal dodecahedra contain twelve pentagonal faces, whereas the hexacaidecahedra contain twelve pentagonal and four hexagonal faces. All of the atoms participating in the structure of the type II clathrates are tetrahedrally ($sp^3$) coordinated. The average number of atoms per ring is 5.064 and is the smallest for any known structure. There are five distinct crystallographic sites: 96$g$, 32$e$ and 8$a$ (in the Wyckoff notation) for the framework atoms, and 8$b$ and 16$c$ at which the host atoms reside inside the polyhedra. The general formula for the type II clathrates is $A_8B_{16}E_{136}$ ($A$ = guest in $E_{28}$, $B$ = guest in $E_{20}$, and $E$ = Si, Ge, Sn or substituents). The crystal structure of the type II clathrates can be viewed as dual to the MgCu$_2$ structure, if the 16$c$ sites in the $E_{20}$ cages are substituted by Cu atoms, and the 8$b$ sites in the $E_{28}$ cages are substituted by Mg atoms. We may think of the type II clathrates as of expanded forms of Si, Ge or Sn. The volume per framework atom is as much as 20% larger in the clathrate structure relative to the diamond structure, although the bond lengths, in both the diamond and the type-II clathrates, are relatively close. This open structure is responsible for some of the unique properties of these materials, as demonstrated in the next section.
The first of the inorganic clathrates discovered by far are Na$_x$Si$_{136}$ ($0 < x < 24$). Kasper et al.$^2$ prepared these compositions via thermal decomposition of the Zintl compound Na$_4$Si$_4$. Na$_4$Si$_4$, which is monoclinic with space group $C2/c$, was synthesized by direct reaction of the elements mixed in stoichiometric ratio. The final product is grayish polycrystalline material that is extremely air and moisture sensitive, thus the handling must be performed in N$_2$ or Ar-glove box. The sodium content $x$ is controlled by varying both the temperature and time, longer times and higher temperature yielding lower sodium contents. Several reflections from the X-ray diffraction exhibit strong dependence upon sodium content, thus allowing for determination of the sodium content and the relative cage occupancy by the Rietveld method.$^{66,67}$ Gryko et al.$^40$ showed that after repeated degassing of the Na$_x$Si$_{136}$ and treatment with concentrated acids, it is possible to synthesize and “empty cage” of Si$_{136}$, with sodium content less than 600 ppm Si. Further reduction of the sodium content was achieved by Ammar et al.$^{71}$ by reaction of the clathrate with iodine, resulting in sodium content less than 35 ppm Si.
Experimental observations\textsuperscript{72,73} have shown that the Si\textsubscript{136} framework is stable under pressure up to 11 GPa. No transition to the diamond phase is observed, but an irreversible transition to the $\beta$-Sn structure of silicon was observed at 11.5 GPa, accompanied by a volume reduction of more than 30%.

A challenge in the preparation of phase pure Na\textsubscript{x}Si\textsubscript{136} through degassing is the presence of the type-I Na\textsubscript{8}Si\textsubscript{46} clathrate as an impurity phase with as much as 45 wt\% in the prepared type II products.\textsuperscript{31,74} Efforts have been made to separated the two phases using the difference in densities of the two phases, however the two phases appear to be inter-grown and their physical separation seems to be a rather formidable task. This problem however, has now been resolved (cf. Chapter 3).

Cross et al.\textsuperscript{10} derived Na\textsubscript{x}Ge\textsubscript{136} from the Zintl precursor Na\textsubscript{4}Ge\textsubscript{4}, but in very small quantities since Na\textsubscript{x}Ge\textsubscript{136} forms in a very narrow range of temperatures.\textsuperscript{75,76} Instead, a novel zeolite-like phase Na\textsubscript{1-x}Ge\textsubscript{3+}z with hexagonal crystal structure forms as a majority phase.\textsuperscript{77} It seems that the subtle structural differences of the two precursors Na\textsubscript{4}Si\textsubscript{4} (space group C\textsubscript{2}/c) and Na\textsubscript{4}Ge\textsubscript{4} (space group P\textsubscript{2}1/c) promote different structures upon the degassing process. Preparation of a guest free Ge\textsubscript{136} allotrope is feasible through a chemical process described by Guloy et al.\textsuperscript{78} Three-dimensional network of four-bonded Ge atoms forms from the polymerization and oxidation of Ge\textsuperscript{4-} anions, followed by soft oxidation at 300 °C in eutectic mixture of dodecyltrimethylammonium chloride and aluminium trichloride (1:1 molar ratio).

Thermal decomposition of mixed alkali and alkali/alkaline earth silicides also forms of type-II clathrate compositions. Cs\textsubscript{8}Na\textsubscript{16}Ge\textsubscript{136} has been synthesized by thermal decomposition of Cs\textsubscript{4}Na\textsubscript{1-x}Si.\textsuperscript{79} Rb\textsubscript{8}Na\textsubscript{16}Ge\textsubscript{136} has been synthesized by thermal decomposition of Rb\textsubscript{4}Na\textsubscript{1-x}Si.\textsuperscript{80} Although the product consist of several different phases, synthesis of Ba\textsubscript{8}Na\textsubscript{16}Ge\textsubscript{136} via thermal decomposition of Na\textsubscript{2}BaGe\textsubscript{4}, has also been reported.\textsuperscript{81}

Probably the most straight-forward way of synthesizing clathrates is by direct synthesis of the pure elements mixed in the desired stoichiometric ratio. Two aspects that have to be taken into consideration are, first, the final product does not necessarily reflect the initial stoichiometry, and second, due to the high vapor pressure of the alkaline metals
and their reaction with quartz glass, reactions have to be performed in sealed metal vessels. Noting that the formation of type II clathrates is facilitated when the relative sizes of the guest and the “cage” are matched, Bobev and Sevov\textsuperscript{13,82} first synthesized A\textsubscript{8}Na\textsubscript{16}E\textsubscript{136} clathrates (A = Cs, Rb; E = 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.\textsuperscript{83-85} used similar method to synthesize these compounds for further characterization. The only Sn clathrate-II compound reported to date, Ba\textsubscript{16}Ga\textsubscript{32}Sn\textsubscript{104}, has been synthesized\textsuperscript{86} by reaction of a mixture of K:Ba:Ga:Sn in the ratio 8:16:32:104, with no K present in the final compound.

The compositions synthesized by the method described above can be used as precursors for synthesizing new compositions. For example, Gryko et al.\textsuperscript{68} synthesized the new clathrate composition Cs\textsubscript{8}Ge\textsubscript{136} by continuous heating of Cs\textsubscript{8}Na\textsubscript{16}Ge\textsubscript{13} (x < 16) under high vacuum causing sodium to “degas” from the clathrate, leaving Cs incorporated in the structure. Rb\textsubscript{8}Ge\textsubscript{136} can be prepared in a similar manner.\textsuperscript{75} Recently Beekman et al.\textsuperscript{87} reported a novel route for the synthesis of type-II Na\textsubscript{24}Si\textsubscript{136} crystals, using Spark Plasma Sintering (SPS) technique. Na\textsubscript{4}Si\textsubscript{4} was used as a precursor in the SPS system, and reacted at 600°C for desired amount of time, yielding bluish crystals with composition Na\textsubscript{24}Si\textsubscript{136}.

Table 1.1 summarizes the type-II clathrates reported to date. From Table 1.1 it is clear that significant scientific effort remains in order to further investigate type II clathrates, the methods of their synthesis, and their physical and structural characterization.
Table 1.1 Type-II clathrates, synthesis methods and lattice parameters

<table>
<thead>
<tr>
<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>39</td>
</tr>
<tr>
<td>Na$<em>x$Si$</em>{136}$</td>
<td>Decomposition of NaSi</td>
<td>$14.62601(9) \leq a &lt; 14.70704(1)$</td>
<td>10,39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0 $\leq x &lt; 24$)</td>
<td></td>
</tr>
<tr>
<td>Na$<em>{24}$Si$</em>{136}$</td>
<td>SPS</td>
<td>14.7157(2)</td>
<td>87</td>
</tr>
<tr>
<td>Ge$_{136}$</td>
<td>Chemical reaction</td>
<td>15.2115(1)</td>
<td>83</td>
</tr>
<tr>
<td>Na$<em>x$Ge$</em>{136}$</td>
<td>Decomposition of NaGe</td>
<td>15.4*</td>
<td>10</td>
</tr>
<tr>
<td>Rb$<em>8$Ge$</em>{136}$</td>
<td>Degassing of Rb$<em>8$Na$</em>{16}$Ge$_{136}$</td>
<td>15.3</td>
<td>75</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>65</td>
</tr>
<tr>
<td>Cs$<em>2$Si$</em>{136}$</td>
<td>Decomposition of CsSi</td>
<td>14.64</td>
<td>10</td>
</tr>
<tr>
<td>Rb$<em>8$Na$</em>{16}$Si$_{136}$</td>
<td>Direct reaction of elements</td>
<td>14.7400(4)</td>
<td>13</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>13</td>
</tr>
<tr>
<td>Ba$<em>8$Na$</em>{16}$Si$_{136}$</td>
<td>Decomposition of Na$_2$BaSi$_4$</td>
<td>(Not reported)</td>
<td>76</td>
</tr>
<tr>
<td>Rb$<em>8$Na$</em>{16}$Ge$_{136}$</td>
<td>Direct reaction of elements</td>
<td>15.4858(6)</td>
<td>13</td>
</tr>
<tr>
<td>Cs$<em>8$Na$</em>{16}$Ge$_{136}$</td>
<td>Direct reaction of elements</td>
<td>15.4805(6)</td>
<td>13</td>
</tr>
<tr>
<td>Ba$<em>{16}$Ga$</em>{32}$Sn$_{104}$</td>
<td>Direct reaction of elements</td>
<td>17.054(1)</td>
<td>81</td>
</tr>
</tbody>
</table>

* Note that $x$ for Na$_x$Ge$_{136}$ is not reported in Cross et al.10
1.5 Electronic and thermal properties of type II clathrates

The observation of unique optical properties in porous Si\textsuperscript{88} initiated further investigations of the electronic properties of Si clathrates. Experimental observations\textsuperscript{42} verified that the band gap of Si\textsubscript{136} allotrope is expanded by approximately 0.9 eV relative to the diamond structured \(\alpha\)-Si (band gap of approximately 1.1 eV), promoting this material as a novel wide-band gap semiconductor. This widening of the band gap has been attributed\textsuperscript{26} to a slight distortion of the ideal tetrahedral coordination observed in \(\alpha\)-Si, as well as the high density of 5-membered rings in the structure of the Si\textsubscript{136} allotrope. Theoretical investigations\textsuperscript{27} of the type II Si\textsubscript{136-x}Ge\textsubscript{x} alloys, that have as yet not been experimentally synthesized, show a direct band gap for a range of \(x\). In addition varying \(x\) can also tune this range from 1.2 to 2 eV making them promising materials for optoelectronic and photovoltaic applications.

Figure 1.7 shows experimental data from temperature dependent \(\rho\) and \(S\) measurements\textsuperscript{83} corroborated by theoretical calculations\textsuperscript{68,77} for Cs\textsubscript{8}Na\textsubscript{16}Si\textsubscript{136} and Cs\textsubscript{8}Na\textsubscript{16}Ge\textsubscript{136}. For both compounds \(\rho\) increases monotonically with the temperature, as is typical for metals. The high carrier concentration (>10\textsuperscript{21} cm\textsuperscript{-3}) corresponds to this kind of behavior for \(\rho\). The only semiconducting type II clathrates synthesized so far for which transport properties have been reported are guest free Si\textsubscript{136}\textsuperscript{42} and Ge\textsubscript{136}\textsuperscript{78} and the lower Na content Na\textsubscript{x}Si\textsubscript{136}.\textsuperscript{32,10} It is important to note that the rigid-band model was employed in the calculations, where the electropositive guests atoms donate their electrons to the electronegative host atoms. The donated electrons occupy the framework conduction band levels. The metallic behavior of \(\rho\) has been corroborated by Nuclear Magnetic Resonance (NMR) measurements.\textsuperscript{68,77,90-94} The observed Knight-shifts in these materials originate in the hyperfine interactions between the nuclei and the delocalized conduction electrons. In most metallic materials, the Knight-shifts are observed to be temperature independent, however for certain type II clathrates, for example Na\textsubscript{x}Si\textsubscript{136},\textsuperscript{92,93} Cs\textsubscript{8}Ge\textsubscript{136}\textsuperscript{68} and Rb\textsubscript{8}Na\textsubscript{16}Si\textsubscript{136},\textsuperscript{78} these shifts show a significant temperature dependence. The sharp peaks in the electronic density of states (EDOS) near the Fermi level are responsible for
this type of behavior.\textsuperscript{92} It has been observed that the electrical properties of Na\textsubscript{x}Si\textsubscript{136} are strongly dependent upon the Na content, the bigger the \( x \) the lower \( \rho \) is.

![Figure 1.7](image)

**Figure 1.7** \( S \) (round symbols) and \( \rho \) (triangular symbols) as a function of temperature for polycrystalline Cs\textsubscript{8}Na\textsubscript{16}Si\textsubscript{136} (open symbols) and Cs\textsubscript{8}Na\textsubscript{16}Ge\textsubscript{136} (filled symbols).\textsuperscript{82} Inset: DFT computed EDOS for Cs\textsubscript{8}Na\textsubscript{16}Si\textsubscript{136} (lower)\textsuperscript{72} and Cs\textsubscript{8}Na\textsubscript{16}Ge\textsubscript{136} (upper).\textsuperscript{68} The dashed line indicates the Fermi level, which is well within the conduction band for both materials.

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Clathrates meet the phonon-glass part of the criterion for the PGEC concept in part because of the oversized cages encapsulating loosely bound atoms. This offers a promising perspective for the thermal properties of these materials. Nolas et al.\textsuperscript{83} have shown the temperature dependence of the isotropic atomic displacement parameters (ADP or \( U_{iso} \)) of the host atoms for A\textsubscript{8}Na\textsubscript{16}E\textsubscript{136} (A = Rb, Cs; E = Si, Ge). It is evident from Figure 1.8 that the larger the size-difference between the cage and the guest atoms, the larger the ADP. Bobev and Sevov\textsuperscript{13} have estimated the relative size of the guest and
cage by subtracting framework atomic radii from the shortest guest-framework atom distances, compared to the ionic radii of the guests. The cages are “oversized” compared to the guest atoms, leaving them a lot of “room” to “rattle”. This rattling combined with the complex structure of these materials contributes to the effective scattering of phonons, thus lowering the thermal conductivity and promoting these materials for thermoelectric applications.

Figure 1.8 Temperature dependent isotropic atomic displacement parameters ($U_{\text{iso}}$) for the $E_{28}$ guest as well as framework sites in $A_{8}Na_{16}E_{136}$ ($A = \text{Rb, Cs}; E = \text{Si, Ge}$). Reprinted with permission from Ref. 83 Copyright [2002], American Institute of Physics.

Hermann et al. proposed a model in which the guest atoms can be considered a 3D-“Einstein” oscillators whose frequency of oscillation can be estimated from the simple relation $U_{\text{iso}} = k_B T/m(2\pi v)^2$, where $k_B$ is the Boltzmann’s constant, $m$ is the mass of the “rattler”, $T$ is the absolute temperature and $v$ is the frequency of vibration. Because of the metallic nature of $Cs_{8}Na_{16}Si_{136}$ and $Cs_{8}Na_{16}Ge_{136}$ their $\kappa$ appears to be dominated by the electronic component of the total thermal conductivity, $\kappa_e$. Figure 1.9 shows the temperature dependence of $\kappa$ for the semiconducting allotrope $Si_{136}$ from Nolas et al. As shown in the figure $Si_{136}$ has a very low $\kappa$, an order of magnitude lower than that of
diamond-structure Si and comparable in magnitude with amorphous SiO₂. The low κ of Si₁₃₆ 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.⁹⁸,⁹⁹

![Figure 1.9](image.png)

**Figure 1.9** κ as a function of temperature for polycrystalline Si₁₃₆ and a-SiO₂.⁹⁷ The solid line⁹ indicates a temperature dependence of T³.
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1.6 Clathrates for thermoelectric applications

The World’s increased energy consumption in the past few decades raises the question of how much longer will fossil fuel sources last? This motivates the scientific community to quest for new, renewable sources, such as solar, wind, geothermal, biomass, and thermoelectric. The discovery of new materials is necessary in order to increase the efficiency and decrease the cost associated with our natural sources. Our focus here is on thermoelectric materials. There is an ongoing debate within the scientific community whether thermoelectrics can be considered a viable alternative energy source. Although it is clear that thermoelectrics cannot be used for large scale energy-production¹⁰⁰, their perspective for small-scale energy production and distributed energy...
delivery is quite promising. A variety of thermoelectric materials\textsuperscript{101} is currently under scientific investigation, of which much attention is paid to clathrates.

The thermoelectric effect couples thermal and electrical phenomena, allowing a solid state conversion of energy. An imposed thermal gradient $\Delta T$ on a specimen will result in a voltage $\Delta V$ across that specimen (Seebeck effect).\textsuperscript{102-104} The Seebeck Coefficient, $S$, is defined as $S = \Delta V / \Delta T$. This type of power generation from heat produced by radioactive plutonium is widely used in deep-space applications.\textsuperscript{103} On the other hand, an electric current passing through a thermoelectric material provides a temperature gradient with heat being absorbed on the cold side of the thermoelectric device and rejected at the heat sink, thus thermoelectric devices provide a refrigeration capability (Peltier effect).\textsuperscript{104,105}

The “goodness” of a thermoelectric material is assessed through the dimensionless figure of merit,\textsuperscript{9,100} $ZT = S^2 \sigma T / \kappa$, where $\kappa = \kappa_L + \kappa_e$, and $T$ is the absolute temperature. To achieve a maximum efficiency, one needs to optimize $ZT$ by maximizing $S$ and $\sigma$, but at the same time reducing $\kappa$. Since the most promising materials for thermoelectric applications typically have carrier concentrations of approximately $10^{19}$ carriers/cm$^3$, Ioffe\textsuperscript{106} suggested searching for good thermoelectrics within the mixed semiconductors comprised of heavy atoms. Theoretical models\textsuperscript{107} suggest that energy gaps of about $10 k_BT$ are desirable for best thermoelectrics. One approach to identify potential thermoelectric materials is the PGEC proposed by Slack.\textsuperscript{5} One material system that fulfills the PGEC requirements is the clathrate material system. Clathrates possess weakly bonded atoms or molecules encaged in a host framework that can scatter phonons effectively\textsuperscript{6} resulting in a low thermal conductivity, which combined with the possibility of varying the carrier concentration\textsuperscript{6} and framework substitution\textsuperscript{108} in these materials, offers a “tuning” mechanism for optimizing the figure of merit $ZT$.

Due to an accelerated research in the past decade there is significant progress in obtaining $ZT$ values higher than the long standing limit of $ZT$=1. Figure 1.10 shows $ZT$ versus temperature for two type-I clathrates. A Czochralski grown Ba$_8$Ga$_{16}$Ge$_{30}$ clathrate crystals show $ZT$ of 1.35 at 900 K without passing a maximum\textsuperscript{100}. Sr$_8$Ga$_{16}$Ge$_{30}$ shows $ZT$
of 0.2 at room temperature, although theoretical calculations\cite{52} suggest that optimized compositions of Ba$_8$In$_{16}$Sn$_{30}$ and Sr$_8$Ga$_{16}$Ge$_{30}$ could reach $ZT$ of 1.7 at 800 K.

![Figure 1.10 ZT as a function of temperature for two type-I clathrates](image)

**Figure 1.10** $ZT$ as a function of temperature for two type-I clathrates

Clathrates are potentially relevant for the high-temperature applications, Bi-based tellurides and selenides still remain the best materials in terms of $ZT$ values in the low-temperature region. Current research on clathrates is focused on optimizing the power factor, $S^2\sigma$, and $\kappa$ as “tuning knobs” for achieving high $ZT$-values.
2.1 Synthesis and structural characterization of Na$_8$Si$_{46}$

Compounds with the type I crystal structure continue to be of scientific as well as of technological interest due to their broad range of promising properties, such as semiconducting behavior,$^6$ superconductivity,$^{24,25}$ and glass-like thermal conductivity.$^{23}$ These properties are a direct result of the nature of the structure and bonding in these materials. Na$_8$Si$_{46}$ was first synthesized by Kasper et al.$^2$, and was the first reported synthesis of a material with crystal structure similar to that of the gas-hydrates. Thermal decomposition of the Zintl phases MSi ($M=$Na, K, Rb, Cs) under vacuum or inert atmosphere leads to the formation of clathrates.$^2,15,17,59$ The synthesis of these intermetallic clathrates presents a formidable challenge, where the final product consists of type I or II clathrate as a majority phase, with the other phase present as an impurity. A number of compositions to date have only been obtained as polycrystalline powders.$^{13}$ No synthesis attempt to date reports on formation of single crystals of the type I Na$_8$Si$_{46}$ clathrate. In densified polycrystals care must be taken in the interpretation of the explored properties, for which grain-boundary and surface effects, as well as impurity phases, can be of significant importance.

The preparation of high-quality single crystals for structural and physical characterization can be especially challenging for compositions in which the elemental constituents have greatly differing melting points and vapor pressures, when the desired compound is thermodynamically unstable, or where the growth from a melt is generally not possible. This is particularly the case with alkali-silicon clathrates, for which conventional crystal growth techniques are inapplicable.

Na$_8$Si$_{46}$ is perhaps the most studied of all the type I clathrate compounds.$^{9,10,109-111}$ Nolas et al.$^{112}$ has synthesized this clathrate by thermal decomposition of sodium silicide Na$_4$Si$_4$,$^{103-105}$ at 385°C under argon at low pressure. Similarly with other synthesis methods,$^6$ the final product was a polycrystalline powder that consists mainly of the type I clathrate, and contains a small amount of the type-II Na$_8$Si$_{136}$ clathrate. Herein we report on the synthesis of single crystals of Na$_8$Si$_{46}$, grown via a Novel technique$^{113}$ for which a patent is pending, thus details are not going to be disclosed. The Zintl phase Na$_4$Si$_4$ was
used as a precursor and it was synthesized by direct reaction of the high purity elements at 650°C. The reaction was carried out inside a tungsten crucible, sealed under ultra high purity nitrogen inside a stainless steel canister, which was in turn sealed inside a fused quartz ampoule. The resulting product was Na₄Si₄, which is highly reactive with moisture and air, thus all handling was performed inside a nitrogen-filled glove box. Na₄Si₄ is a Zintl phase which crystal structure is composed of Si⁴⁺ polyanions and Na⁺ cations arranged in a monoclinic unit cell, as shown in Figure 2.1a. After washing with water and ethanol to remove the unreacted precursor, the final product Na₈Si₄₆ consisted of gray truncated cubes with average size of 0.2 mm (Figure 2.1b) and average yield ~5%. The crystals of Na₈Si₄₆ are stable in air and water.

Figure 2.1 a) The structure of the Zintl precursor Na₄Si₄
b) An SEM image of a Na₈Si₄₆ single crystal synthesized by the Novel technique³¹³
The quality of the sample was confirmed by powder X-ray analysis. All of the peaks were assigned to the type I clathrate structure of Na$_8$Si$_{46}$ (Figure 2.2).

![Powder X-ray diffraction pattern for the type I Na$_8$Si$_{46}$ clathrate.](image)

**Figure 2.2** Powder X-ray diffraction pattern for the type I Na$_8$Si$_{46}$ clathrate. Miller indices were assigned to every reflection.

The silicon host lattice of the type I Na$_8$Si$_{46}$ clathrate is simple cubic, composed of two pentagonal dodecahedra, Si$_{20}$, and six tetrakaidecahedra, Si$_{24}$ (Figure 2.3). The corresponding unit cell is cubic, with lattice parameter $a=10.19$ Å and space group $Pm\bar{3}n$. The Na atoms reside at the 2$a$ and 6$d$ crystallographic positions, and the Si(1)-Si(3) atoms forming the framework reside at three distinct crystallographic positions, 24$k$, 6$c$ and 16$i$, respectively. The maximum number of alkali metal atoms in the type I clathrate is eight, two atoms inside the smaller pentagonal dodecahedra and six inside the large tetrakaidecahedra. Each Si atom in Si$_{20}$ forms four bonds of which three are with atoms in the same dodecahedron and the fourth bond may be one of the two types: connecting one Si$_{20}$ with another or connect to atoms on four different dodecahedrons.$^{26}$
Single crystal X-ray crystallographic analysis was done by Dr. Wong-Ng at the National Institute for Standards and Technologies (NIST). A single crystal of Na$_8$Si$_{46}$ with approximate dimensions $0.18 \times 0.20 \times 0.20$ mm$^3$, was used. The X-ray intensity data were measured at 200(2) K on a three-circle diffractometer system equipped with Bruker Smart Apex II CCD area detector using a graphite monochromator and a MoK$\alpha$ fine-focus sealed tube ($\lambda = 0.71073$ Å). The detector was placed at a distance of 5.000 cm from the crystal. A total of 1280 frames were collected with a scan width of 0.30° in $\omega$ and an exposure time of 8 sec/frame using Apex2 (Bruker, 2005). The total data collection time was 5.0 hours. The final cell dimensions of $a = 10.1973(1)$ Å, $b = 10.1973(1)$ Å, $c = 10.1973(1)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 1060.366(18)$ Å$^3$, are based upon the refinement of the XYZ-centroids of 6336 reflections with $2.8 < \theta < 32.2^\circ$ using Apex2. Analysis of the data showed 0 % decay during data collection. Data were corrected for absorption effects with the Semi-empirical from equivalents method using SADABS (Sheldrick, 1996). The minimum and maximum transmission coefficients were 0.698 and 0.773, respectively.

The structure was solved and refined using the SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997) software in the space group $Pm\bar{3}n$ with $Z = 2$ for the
formula unit Na₄Si₂₃. The final anisotropic full-matrix least-squares refinement on F² with 16 variables converged at R₁=1.10% for the observed data and wR²=2.54% for all data. The goodness-of-fit was 1.000. On the basis of the final model, the calculated density was 2.312 g/cm³. The details of the single crystal refinement are given in Table 2.1.

The isotropic atomic displacement parameters Uₑq (Table 2.2) for both Na1 and Na2 atoms, positioned at the 2a and 6d sites, respectively, are much larger than those of the atoms constituting the framework, showing the relative stiffness of the framework with respect to the more “rattling” behavior of the guest atoms. The anisotropic displacement parameters (ADPs) for the atoms in the structure of Na₈Si₄₆ are listed in Table 2.3, and the bond lengths for the respective atoms are listed in Table 2.4. The results for the bond lengths are in agreement with a previous reported data by Cross et al.⁷⁴
Table 2.1 Crystal data and structure refinement for Na₈Si₄₆, single crystal XRD

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight</td>
<td>738.03</td>
</tr>
<tr>
<td>Temperature</td>
<td>200(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.20 × 0.20 × 0.18 mm³</td>
</tr>
<tr>
<td>Crystal habit</td>
<td>gray cube</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Cubic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pm3n</td>
</tr>
<tr>
<td>Unit cell dimension</td>
<td>a = 10.1973(1) Å</td>
</tr>
<tr>
<td>Volume</td>
<td>1060.366(18) Å</td>
</tr>
<tr>
<td>Z</td>
<td>2 (for empirical formula Na₄Si₂₃)</td>
</tr>
<tr>
<td>Density, ρ.calc</td>
<td>2.312 g/cm³</td>
</tr>
<tr>
<td>Absorption coefficient, μ</td>
<td>1.432 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>732</td>
</tr>
<tr>
<td>Diffractometer</td>
<td>Bruker Smart Apex II CCD area detector</td>
</tr>
<tr>
<td>Radiation source</td>
<td>fine-focus sealed tube, MoKα</td>
</tr>
<tr>
<td>Detector distance</td>
<td>5.000 cm</td>
</tr>
<tr>
<td>Detector resolution</td>
<td>11.198 pixels/mm</td>
</tr>
<tr>
<td>Total frames</td>
<td>1280</td>
</tr>
<tr>
<td>Frame size</td>
<td>512 pixels</td>
</tr>
<tr>
<td>Frame width</td>
<td>0.30°</td>
</tr>
<tr>
<td>Exposure per frame</td>
<td>8 sec</td>
</tr>
<tr>
<td>Total measurement time</td>
<td>5.0 hours</td>
</tr>
<tr>
<td>Data collection method</td>
<td>ω scans</td>
</tr>
</tbody>
</table>

θ range for data collection 2.82 to 29.93°

Index ranges
-14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -14 ≤ l ≤ 14

Reflections collected 7652
Independent reflections 305
Observed reflection, I>2σ(I) 303
Coverage of independent reflections 100.0 %
Variation in check reflections 0 %
Absorption correction Semi-empirical from equivalents SADABS (Sheldrick, 1996)

Max. and min. transmission 0.773 and 0.698
Structure solution technique direct method
Structure solution program SHELXS-97 (Sheldrick, 1990)
Refinement technique Full-matrix least-squares on F²
Refinement program SHELXL-97 (Sheldrick, 1997)
Function minimized Σw(F₀² - F_c²)²
Data / restraints / parameters 305 / 0 / 16
Goodness-of-fit on F² 1.000
Δ/σₘₐₓ 0.000

Final R indices: R₁, I>2σ(I) 0.0110
wR₂, all data 0.0254
Rₚₒₚₒ 0.0148
Rₛᵣₒ 0.0046

Weighting scheme w = 1/[(σ²(F₀²)+0.01P)²+0.746P], P = [max(F₀², 0)+2F₀²]/3
Extinction coefficient 0.0052(5)

Largest diff. peak and hole 0.215 and -0.120 e/Å³

\[ R₁ = \Sigma |F₀| - |F_c| / \Sigma |F₀|, \quad wR₂ = \left[ \Sigma w(F₀² - F_c²)² / \Sigma w(F₀²)² \right]^{1/2} \]
Table 2.2 Atomic coordinates and equivalent* isotropic atomic displacement parameters (Å²) for Na₈Si₄₆.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>Ueq</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na1</td>
<td>2a</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0145(3)</td>
</tr>
<tr>
<td>Na2</td>
<td>6d</td>
<td>0.5000</td>
<td>0.0000</td>
<td>0.2500</td>
<td>0.0296(3)</td>
</tr>
<tr>
<td>Si1</td>
<td>24k</td>
<td>0.30782(3)</td>
<td>0.11728(3)</td>
<td>0.0000</td>
<td>0.00637(9)</td>
</tr>
<tr>
<td>Si2</td>
<td>6c</td>
<td>0.5000</td>
<td>0.2500</td>
<td>0.0000</td>
<td>0.00621(12)</td>
</tr>
<tr>
<td>Si3</td>
<td>16i</td>
<td>0.184101(18)</td>
<td>0.184101(18)</td>
<td>0.184101(18)</td>
<td>0.00638(9)</td>
</tr>
</tbody>
</table>

* Ueq is defined as one third of the trace of the orthogonalized Uij tensor.

Table 2.3 Anisotropic atomic displacement parameters* (Å²) for Na₈Si₄₆

<table>
<thead>
<tr>
<th>Atom</th>
<th>U₁₁</th>
<th>U₂₂</th>
<th>U₃₃</th>
<th>U₁₂</th>
<th>U₁₃</th>
<th>U₂₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na1</td>
<td>0.0145(3)</td>
<td>0.0145(3)</td>
<td>0.0145(3)</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>Na2</td>
<td>0.0346(4)</td>
<td>0.0346(4)</td>
<td>0.0196(6)</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>Si1</td>
<td>0.00635(13)</td>
<td>0.00613(13)</td>
<td>0.00662(13)</td>
<td>0.0000</td>
<td>0.0000</td>
<td>-0.00025(9)</td>
</tr>
<tr>
<td>Si2</td>
<td>0.00603(15)</td>
<td>0.0066(3)</td>
<td>0.00603(15)</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>Si3</td>
<td>0.00638(9)</td>
<td>0.00638(9)</td>
<td>0.00638(9)</td>
<td>-0.00013(6)</td>
<td>-0.00013(6)</td>
<td>-0.00013(6)</td>
</tr>
</tbody>
</table>

* The anisotropic atomic displacement factor exponent takes the form: \(-2\pi^2 [h^2 a^2 U_{11} + \ldots + 2hka b U_{12}]\)

Table 2.4 Bond lengths (Å) for Na₈Si₄₆

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na1-Si1</td>
<td>3.3590(3)×12</td>
</tr>
<tr>
<td>Na1-Si3</td>
<td>3.2516(2)×8</td>
</tr>
<tr>
<td>Na2-Si1</td>
<td>3.4307(2)×8</td>
</tr>
<tr>
<td>Na2-Si1</td>
<td>3.9470(3)×4</td>
</tr>
<tr>
<td>Na2-Si2</td>
<td>3.6053(1)×4</td>
</tr>
<tr>
<td>Na2-Si3</td>
<td>3.7885(3)×8</td>
</tr>
<tr>
<td>Si1-Si1</td>
<td>2.3919(6)</td>
</tr>
<tr>
<td>Si1-Si2</td>
<td>2.3816(3)</td>
</tr>
<tr>
<td>Si1-Si3</td>
<td>2.3623(2)×2</td>
</tr>
<tr>
<td>Si2-Si1</td>
<td>2.3816(3)×4</td>
</tr>
<tr>
<td>Si3-Si1</td>
<td>2.3623(2)×3</td>
</tr>
<tr>
<td>Si3-Si3</td>
<td>2.3279(7)</td>
</tr>
</tbody>
</table>
2.2 Transport properties of Na$_8$Si$_{46}$

Our preparation of Na$_8$Si$_{46}$ single crystals offers the opportunity for the first investigation of the electrical and thermal transport properties on this material, free from grain boundary and interfacial effects associated with the consolidated polycrystalline specimens. The standard mounting procedure for our transport properties measurement system$^{114}$ was modified because of the small size of the crystal specimens. The new mounting configuration is depicted in Figure 2.4. Thermal bridges made by 0.76 mm diameter Cu wire were put across the sample with the voltage leads $V^+$ and $V^-$ attached on one side, and the differential thermocouple leads $T_1$ and $T_2$ attached on the other side, respectively. For the thermal contact between the Cu wire and the specimen, as well as electrical contacts for the voltage probes, a Silver filled epoxy was used. The heater and the thermocouples were attached with Stycast™ epoxy.

![Figure 2.4 Measuring the transport properties on a single crystal of Na$_8$Si$_{46}$](image)

Measurements of $S$, $\sigma$ and $\kappa$ were performed on a custom-designed closed cycle refrigerator$^{115}$ from 12 K to 300 K. $\sigma$ is measured by a four-probe method. A small current $I=I^+=I^-$ (Figure 2.4, typically 5mA) is passed through the single crystal.
specimen, and the voltage difference $\Delta V = V^+ - V^- \, \text{is measured between two points a}
\text{distance } l \text{ apart. } \sigma \text{ is then determined from the Ohm’s Law, } \sigma = I / \Delta V A, \text{ where } A \text{ is the}
cross-sectional area of the crystal. Fast switching of the current direction and measuring
the voltage in both directions eliminates possible thermoelectric contributions to $\Delta V$.

Temperature gradients for $S$ and $\kappa$ measurements are applied by 100 $\Omega$ chip resistor
attached to the top of the specimen (Figure 2.4). Using the thermal bridges in the
configuration shown in Figure 2.4 allows $\Delta V$ and the temperature gradient $\Delta T = T_1 - T_2$ to
be measured between the same two points on the specimen, thus reducing the error in the
measurement. $S$ is then calculated from the slope of a plot of $\Delta V$ versus $\Delta T$, i.e $S = \Delta V / \Delta T$.

To measure $S$, several temperature gradients are applied and the power $P$ across the
heater measured. From the slope of $P$ versus $\Delta T$ and the geometry of the specimen, using
the Fourier law we can determine the thermal conductivity $\kappa = (l / A)(P / \Delta T)$. The relative
uncertainties at room temperature for $\rho$, $S$ and $\kappa$ are estimated to be 4%, 6% and 8%,
respectively.\textsuperscript{114,115}

Figure 2.5 shows the temperature dependence of $\rho$ (empty circles) and $S$ (filled
circles) for a single crystal of type-I Na$_8$Si$_{46}$ clathrate. The positive $d\rho / dT$ and the
magnitude clearly indicate a metallic behavior, which should be expected for Na$_8$Si$_{46}$ due
to the excess of electrons coming from the Na atom. It reaches a value of 0.098 m$\Omega$/cm
at 300 K, and is lower than any other type-I clathrate reported in the literature (Table
2.5). A comparison between $\rho$ measured on a consolidated polycrystalline specimen and
a single crystal of type-I Na$_8$Si$_{46}$ clathrate clearly shows that the single crystal exhibits
nearly two orders of magnitude lower $\rho$ than the polycrystalline material. This is an
indication of the intrinsic metallic transport in the single crystal, whereas in the
polycrystalline material the inter-grain contacts, impurities surrounding these contacts, as
well as defects that might occur during the densification process,\textsuperscript{112} affect the measured
values.
Another indicator of the quality of the single crystals is the ‘Residual Resistance Ratio (RRR)’, defined as RRR=\(R(300\text{K})/R(T_0)\), with \(T_0=12\text{ K}\) being the lowest temperature of our measurements. To the best of our knowledge, the single crystals of Na₈Si₄₆ have the lowest RRR compared with other type-I clathrates reported in the literature (Table 2.5). We note that at the lowest temperature of our measurement (12 K), \(d\rho/dT>0\) which indicates that the residual resistivity has still not yet been reached.
Table 2.5 Comparison of the room temperature resistivities and residual resistance ratios $\text{RRR} = R(300 \text{ K})/R(T_0)$ for the Na$_8$Si$_{46}$ specimen of the present work and several intermetallic clathrate specimens of type I showing metallic or “metallic-like” resistivities (i.e. $d\rho/dT$ is positive definite over the entire temperature interval of measurement). $T_0$ is the lowest temperature at which the corresponding resistivity was reported.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Form</th>
<th>Synthesis Method</th>
<th>Carrier Type</th>
<th>$\rho(300 \text{ K})$ (mΩ·cm)</th>
<th>$T_0$ (K)</th>
<th>RRR</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$<em>8$Si$</em>{46}$</td>
<td>single crystal</td>
<td>novel method</td>
<td>$n$</td>
<td>0.098</td>
<td>12</td>
<td>36</td>
<td>Present Work</td>
</tr>
<tr>
<td>Na$<em>8$Si$</em>{46}$</td>
<td>polycrystalline</td>
<td>thermal decomposition of Na$_4$Si$_4$</td>
<td>$n$</td>
<td>9.7</td>
<td>8</td>
<td>1.9</td>
<td>Nolas</td>
</tr>
<tr>
<td>Eu$<em>8$Ga$</em>{16}$Ge$_{30}$</td>
<td>polycrystalline</td>
<td>direct reaction of stoichiometric mixture</td>
<td>$n$</td>
<td>0.87</td>
<td>2</td>
<td>3.0</td>
<td>Bentien</td>
</tr>
<tr>
<td>Ba$<em>8$Ga$</em>{16}$Sn$_{30}$</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>Avila</td>
</tr>
<tr>
<td>Ba$<em>8$Ga$</em>{16}$Ge$_{30}$</td>
<td>single crystal</td>
<td>slow cooling of stoichiometric mixture</td>
<td>$n$</td>
<td>0.82</td>
<td>2</td>
<td>2.2</td>
<td>Sales</td>
</tr>
<tr>
<td>Sr$<em>8$Ga$</em>{16}$Ge$_{30}$</td>
<td>polycrystalline</td>
<td>direct reaction of stoichiometric mixture</td>
<td>$n$</td>
<td>2.0</td>
<td>6</td>
<td>2.1</td>
<td>Avila</td>
</tr>
<tr>
<td>Ba$<em>8$Al$</em>{14}$Si$_{31}$</td>
<td>single crystal</td>
<td>Al flux growth</td>
<td>$n$</td>
<td>0.45</td>
<td>20</td>
<td>1.4</td>
<td>Avila</td>
</tr>
</tbody>
</table>

$^a$Type VIII at with $\rho(400)$ K
$S$ for the single crystals of Na$_8$Si$_{46}$ is negative throughout the entire temperature range (filled circles in Figure 2.5), presumably indicating that electrons are the majority carriers, as expected. It reaches a maximum value of nearly -6 $\mu$V/K at 170 K and remains very small over the entire temperature range, corroborating the metallic conduction for this compound. $S$ is similar in temperature dependence as that reported on polycrystalline Na$_8$Si$_{46}$,\textsuperscript{112} however with a lower magnitudes which coincides with the lower resistivity discussed above. The position of the peak for $S$ at relatively high temperature indicates that phonon-drag effects may not be causing this temperature dependence behavior, although phonon-electron scattering could still be the reason why the electrons are excited across the Fermi level and yield higher Seebeck coefficient.

Figure 2.6 shows the temperature dependence of $\kappa$ for a single crystal of Na$_8$Si$_{46}$ (filled circles). It increases below 40 K and then is relatively temperature independent up to room temperature. It reaches a maximum value of 28 W/m-K at 40 K, and remains relatively high in the entire temperature range, because of the contribution from the electronic thermal conduction in crystalline Na$_8$Si$_{46}$. It is higher compared to a polycrystalline compound\textsuperscript{112} (empty circles in Figure 2.6) presumably due to the additional phonon scattering from the grain boundaries and higher $\rho$ values in the polycrystalline specimen.
The temperature dependence of the heat capacity $C_p$ is shown in Figure 2.7. The room temperature value is slightly lower than that expected from the classical Dulong-Petit law. The inset in Figure 2.7 illustrates the low-temperature dependence of the heat capacity plotted as $C_p/T$ versus $T^2$. The data was fitted with a straight line between 5 K and 7 K according to the formula $C_p/T = \gamma + \beta T$, where $\gamma$ is the Sommerfeld coefficient of the electronic contribution and $\beta$ is the coefficient of the lattice contribution to the heat capacity.\textsuperscript{116,117} From this fit we obtain $\gamma = 65 \text{ mJ mol}^{-1} \text{ K}^{-2}$ and $\beta = 1.63 \text{ mJ mol}^{-1} \text{ K}^{-4}$. 

Figure 2.6 Thermal conductivity for Na$_8$Si$_{46}$ single crystals (filled circles) and microcrystalline powder (empty circles)\textsuperscript{112}
Figure 2.7 Heat capacity for single crystal Na₈Si₄₆. The inset shows $C_p (T)$ versus $T^2$ below $T=7$ K.

From the above value of $\gamma$ we have estimated the density of states at the Fermi level for both spin direction $N(E_F)$ using the relation\textsuperscript{117,118}

$$\gamma = \frac{\pi^2 k_B^2}{3} N(E_F)(1 + \lambda_{e-ph}),$$

(2.1)

where $\lambda_{e-ph}$ is the electron-phonon coupling constant set to zero as a first approximation, and obtain the value $N(E_F)=27.2$ states eV\textsuperscript{-1} per formula unit. This value is comparable to that reported by theoretical calculations\textsuperscript{119} for Na₈Si₄₆, yet slightly higher, which is another indicator of the quality of the single crystals presumably with no defects present.

To get a better insight into the lattice dynamics of the Na₈Si₄₆ clathrate, we can represent the total $C_p$ as a sum of the three contributions\textsuperscript{116}: the electronic contribution, $C_{el} = \gamma T$, coming from the electrons as heat carriers, the Debye contribution, $C_D$, originating from the cage-like structure, and the Einstein contribution, $C_E$, arising from the localized vibrations of the Na atoms inside the oversized cages, i.e.
\[ C_p = C_{el} + C_D + C_E, \]  

The Debye term is given as \(^{120}\)

\[ C_D = 9N_D R \left( \frac{T}{\theta_D} \right)^3 \int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} \, dx, \]  

where \(N_D\) is the number of Debye oscillators per formula unit (\(N_D=46\) for \(Na_8Si_{46}\)), \(\theta_D\) is the Debye temperature, and \(x = \frac{\hbar \omega}{k_B T}\), with \(\omega\) being the phonon-angular frequency.

The Einstein term is given as \(^{116}\)

\[ C_E = \sum_{i=1}^N p_i N_{Ei} R \left( \frac{\theta_{Ei}}{T} \right)^2 \frac{e^{\theta_{Ei}/T}}{(e^{\theta_{Ei}/T} - 1)^2}, \]  

where \(p_i\) are the degrees of freedom, \(N_{Ei}\) are the number of Einstein oscillators (\(N_{E1}=2\) and \(N_{E2}=6\) for the Na atoms inside the dodecahedra and tetrakaidecahedra, respectively), and \(\theta_{Ei}\) are the Einstein temperatures associated with the \(i\)th vibrational mode.

Figure 2.8 shows the plot \((C_p-C_D)/T^3\) vs \(T\) (filled circles) fitted with a solid line according to the theoretical model represented by Equation (2.2), employing Equations (2.3) and (2.4), respectively. Fitting parameters corresponding to two different models are listed in Table 2.6, with the free parameters for each model indicated. The Einstein temperatures for the Na atoms inside the dodecahedra are denoted by \(\theta_{E1}\), and for those inside the tetrakaidecahedra, \(\theta_{E2}\), respectively. Furthermore, the Einstein temperatures for the in-plane vibrations of the Na atoms inside the tetrakaidecahedra are denoted by \(\theta_{E2}||\) and for the out-of-plane (along the vertical z-axis) by \(\theta_{E2\perp}\).

**Table 2.6** Fitting parameters for the \((C_p-C_D)/T^3\) curve, according to two different models. The free parameters in each model are shown in brackets. The Debye temperature was fixed to \(\theta_D=590\) K. \(^{112}\)

| Model (free parameters) | \(\gamma\) (J mol\(^{-1}\) K\(^{-2}\)) | \(\theta_{E1}\) (K) | \(\theta_{E2}\) (K) | \(\theta_{E2\perp}\) (K) | \(\theta_{E2||}\) (K) |
|------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| I (\(\gamma, \theta_{E1}, \theta_{E2}\)) | 0.0690 | 143 | 82 | N/A | N/A |
| II (\(\gamma, \theta_{E1\perp}, \theta_{E2||}\)) | 0.0691 | 164 | N/A | 163 | 95 |
For the first model we allowed $\gamma$, $\theta_{E1}$ and $\theta_{E2}$ to be free parameters. The value obtained for $\gamma$ from the fit is in an excellent agreement with the value calculated from the linear fit to the low-temperature $C_p$ data in Figure 2.7.

The pronounced peak centered around 25 K comes from the contribution of the localized vibrations of the Na atoms inside the cages in the structure of Na$_8$Si$_{46}$. This ‘rattling’ behavior appears as a ‘dip’ in the lattice thermal conductivity (shown in the inset in Fig. 2.8) for a single crystal Na$_8$Si$_{46}$, which was obtained by subtracting $\kappa_e=\frac{L_0 T}{\rho}$ from the total $\kappa$ (Figure 2.6), where $L_0=2.45\times10^{-8}$ W $\Omega$ K$^{-2}$ is the Lorenz number. Theoretical investigations of the phonon band structure and resonant scattering$^{121}$ and Raman scattering$^{122}$ in Na$_8$Si$_{46}$ confirm that the contribution of the localized vibrations to $\kappa$ and $C_p$ appears near this temperature. The higher ADPs for the Na atoms at 6$d$ site inside the
tetrakaidecahedron (Figure 2.3) is consistent with the lower $\theta_{E2}$ compared to the $\theta_{E1}$ for the Na atom at $2a$ position inside the smaller dodecahedron. This can be corroborated by a different approach to calculating $\theta_{E1}$ and $\theta_{E2}$. From the isotropic ADPs, $U_{eq}$, for Na@2$a$ and Na@6$d$ sites, respectively, employing the relations $U_{eq}=k_B T/m(2\pi \nu)^2$, where $m$ is the mass of the Na “rattler” and $\nu$ is the “rattling” frequency, and $\theta_{E}=h \nu/k_B$, we estimate the respective Einstein temperatures to be $\theta_{E1} \approx 170$ K and $\theta_{E2} \approx 120$ K.

In the second model the asymmetry of the tetrakaidecahedron requires the vibrational modes of the Na atoms to be described by two-dimensional in-plane motions (characterized by $\theta_{E2}^{||}$ and $p^{||} \times N_{E2}^{=} = 2 \times 6$) and one-dimensional out-of-plane motions ($\theta_{E2}^{\perp}, p^{\perp} \times N_{E2}^{\perp} = 1 \times 6$), whereas the more symmetric dodecahedron can still be described with an isotropic $\theta_{E1}$. The results from the fitting $\theta_{E2}^{\perp} = 162.27$ K and $\theta_{E2}^{||} = 95.48$ K are consistent with the larger in-plane vibrational amplitudes (lower $\theta_{E2}^{||}$).

From the simple crystal chemistry formulation $[\text{Na}^+]_8 \times [(4b)\text{Si}_0]_{136}$, assuming a formal charge of $+1$ for each Na-ion and the room temperature unit cell volume $V=1060.366$ Å$^3$ (Table 2.5) we estimate the carrier concentration $n$ for the single crystal Na$_8$Si$_{46}$ to be $n=7.5 \times 10^{21}$ cm$^{-3}$, an indication of the metallic behavior for this compound. In the single band approximation, assuming $\mu=(ne\rho)^{-1}$, where $e$ is the elementary charge, we estimate the room temperature electron mobility to be $\mu=8.5$ cm$^2$ V$^{-1}$ s$^{-1}$. The inferred electron relaxation time $\tau=m/\rho ne^2=0.51 \times 10^{-14}$ s, where $m$ is the free electron mass is comparable to the room temperature values for metals.$^{123}$

Figure 2.9 shows the temperature dependence of the mean free path of the heat carriers, estimated from the $\kappa$ values (Figure 2.6), the heat capacity (2.7) of single crystal Na$_8$Si$_{46}$ and the sound velocity estimated from the elastic constants$^{124}$ for Na$_8$Si$_{46}$.\pagebreak
At room temperature the mean free path of the phonons is approximately 3.6 \( \mu \text{m} \) and increases dramatically as the temperature is lowered. This value is nearly two orders of magnitude higher than that reported\textsuperscript{112} on a polycrystalline Na\textsubscript{8}Si\textsubscript{46} clathrate which is not surprising taking into consideration that the inter-grain boundary scattering of acoustic phonons, which is a dominant effect in the polycrystalline Na\textsubscript{8}Si\textsubscript{46} clathrate at low temperatures, is not present in single crystals. At the lowest temperature of our measurements (12 K) the mean free path is comparable to the size of the single crystals, which may be an indication that the ‘rattling’ of the Na atoms ‘freezes out’ as the temperature is lowered.

Since this is the first time anyone has investigated the transport properties of single crystal Na\textsubscript{8}Si\textsubscript{46}, it is impossible to compare the results with other respective analyses. However the comparison between the measurements on a single crystal and a polycrystalline specimen clearly confirms that the single crystals offer a better opportunity to investigate the intrinsic properties of the composition Na\textsubscript{8}Si\textsubscript{46}. 

\textbf{Figure 2.9} Temperature dependence of the lattice contribution to the specific heat \( C_{ph} \) plotted as \( C_{ph}/T^3 \) vs \( T \) b) Temperature dependence of the mean free path for single crystal Na\textsubscript{8}Si\textsubscript{46}.
3.1 Synthesis and structural characterization of Na$_{24}$Si$_{136}$

In this chapter structural and physical properties of single crystal type-II Na$_{24}$Si$_{136}$ clathrates are investigated. Even though polycrystalline specimens with composition Na$_x$Si$_{136}$ (0<$x$<24) have been known for a long time$^{46,77}$ a comprehensive understanding of their physical properties is still needed, mainly due to the fact that it is still a formidable task to obtain phase pure specimens.

The first success in synthesizing single crystals of Na$_{24}$Si$_{136}$ was made by Beekman et al.$^{87}$ using the SPS technique. In this work single crystals of Na$_{24}$Si$_{136}$ clathrates were grown by the Novel method.$^{113}$ The final product with an average yield $\sim$5% consisted of bluish-tetrahedral crystals with smooth triangular faces (Figure 3.1) and average size of 0.5 mm. The quality of the product material was confirmed by X-ray analysis on powdered specimen, where all peaks were assigned to the type II Na$_{24}$Si$_{136}$ structure (Figure 3.1), and SEM analysis on a single crystal, illustrated in Figure 3.2.
Figure 3.1 Powder X-ray diffraction pattern of powdered single crystal of type II Na$_{24}$Si$_{136}$ clathrate specimens. Miller indices are assigned to every reflection.
The starting material is the Zintl Phase Na₄Si₄ which was annealed at different temperatures and pressures, for various times. Our approach was to hold the pressure constant and vary the annealing temperature and time. Figure 3.3 shows details on the dependence of temperature in the formation of single crystals of Na₈Si₄₆ and Na₂₄Si₁₃₆. In all cases the annealing time was 8 hrs. Annealing Na₄Si₄ at 585°C results in a formation of single crystals of Na₈Si₄₆ with the purity of the product material confirmed by X-ray analysis on powdered specimens (Figure 3.1). When the annealing temperature was increased to 600°C, peaks (indicated by * in Figure 3.3) of the type-II Na₂₄Si₁₃₆ phase started appearing. This may indicated that at higher temperatures the type-II phase is the more stable phase. Indeed, at temperatures of 665°C it was found that only crystals of Na₂₄Si₁₃₆ form. The purity of the product material was confirmed by X-ray analysis on powdered specimens. No peaks due to Na₈Si₄₆ were observed in the XRD spectrum, which has been a problem in synthesizing the type-II Na₂₄Si₁₃₆ clathrate. Annealing at 700°C leads to the decomposition of the type-II phase to elemental Si (the respective Si peaks in the XRD spectrum are indicated by ∇ in Figure 3.3).
Another set of experiments was performed to analyze the formation of different phases for different times, resulting in different yield of the product material, with the respective phases still being observed at the appropriate temperatures according to Figure 3.3. We found that the highest yield was achieved at approximately 8 hours, with longer times giving smaller yield, and eventually after annealing the precursor for more than 24 hours the clathrates decompose to elemental Si.

The Si host lattice for \( \text{Na}_{24}\text{Si}_{136} \) consists of sixteen pentagonal dodecahedra and eight hexacaidecahedra (Figure 3.4), in a face-centered cubic unit cell with lattice parameter \( a=14.62 \text{ Å} \) with the space group \( Fd\overline{3}m \). Unlike the \( \text{Na}_{8}\text{Si}_{46} \), \( \text{Na}_{24}\text{Si}_{136} \) is a non-stoichiometric phase with all the cages not necessarily occupied. The maximum number of alkali metal atoms occupying the polyhedral cages is \( x=24 \), with sixteen atoms inside.
the pentagonal dodecahedra, and eight atoms inside the hexakaidecahedra. The framework atoms reside at three distinctive crystallographic sites $8a$, $32e$ and $96g$, and the guest atoms reside at $8b$ and $16c$ sites. There are 24 Na atoms and 136 Si atoms per unit cell. The structure contains 5-membered and 6-membered rings and the high proportion of 5-membered rings makes the structure energetically competitive with diamond.$^{26}$

![Schematic diagram of the two building polyhedral cages in the Na$_{24}$Si$_{136}$ structure.](image)

**Figure 3.4** Schematic diagram of the two building polyhedral cages in the Na$_{24}$Si$_{136}$ structure.

A single crystal of Na$_{24}$Si$_{136}$ with approximate dimensions $0.13 \times 0.22 \times 0.27$ mm$^3$, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 200(2) K, in the same way described in chapter 2.2. A total of 3030 frames were collected with a scan width of 0.30° in $\omega$ and an exposure time of 12 sec/frame using Apex2 (Bruker, 2005). The total data collection time was 15.00 hours. The frames were integrated with Apex2 software package using a narrow-frame integration algorithm. The integration of the data using a Cubic unit cell yielded a total of 12553 reflections to a maximum $\theta$ angle of 29.98°, of which 262 were independent (completeness = 100.0%, $R_{int} = 1.83\%$, $R_{sig} = 0.40\%$) and 260 were greater than $2\sigma(I)$. The final cell dimensions of $a = 14.7121(1)$ Å, $b = 14.7121(1)$ Å, $c = 14.7121(1)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 3184.37(4)$ Å$^3$, are based upon the refinement of the XYZ-centroids of 11765 reflections with $2.4 < \theta < 32.4°$ using Apex2. Analysis of the data
showed 0 % decay during data collection. Data were corrected for absorption effects with the Semi-empirical from equivalents method using SADABS (Sheldrick, 1996). The minimum and maximum transmission coefficients were 0.746 and 0.832.

The structure was solved and refined using the SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997) software in the space group $Fd\bar{3}m$ with $Z = 8$ for the formula unit Na$_3$Si$_{17}$. The final anisotropic full-matrix least-squares refinement on $F^2$ with 18 variables converged at $R_1=1.15$ % for the observed data and $wR_2=2.90$ % for all data. The goodness-of-fit was 1.000. The largest peak on the final difference map was 0.203 $e/\text{Å}^3$ and the largest hole was -0.122 $e/\text{Å}^3$. On the basis of the final model, the calculated density was 2.280 g/cm$^3$ and $F(000)$, 2168 $e$. The details of the single crystal refinement are given in Table 3.1.

Similarly to the case of Na$_8$Si$_{46}$ the isotropic atomic displacement parameters $U_{eq}$ (Table 3.2) for both Na1 and Na2 atoms, positioned at 2$a$ and 6$d$ sites, respectively, are much larger than those of the atoms constituting the framework, showing the relative stiffness of the framework with respect to the more “rattling” behavior of the guest atoms. The anisotropic displacement parameters (ADPs) for the atoms in the structure of Na$_{24}$Si$_{136}$ are listed in Table 3.3, and the bond lengths for the respective atoms are listed in Table 3.4. Comparison between the bond lengths for Na$_{24}$Si$_{136}$ of the present work with the bond lengths for Na$_x$Si$_{136}$ ($x=1, 20.5$) from Cross et al. agrees with the general tendency of the Si-Si bond lengths to decrease upon removal of Na atoms from the polyhedral cages. The Na-Si bond lengths on the other hand show both tendencies, to increase and decrease when additional Na atoms are introduced in the polyhedral cages.
Table 3.1 Crystal data and structure refinement for Na$_{24}$Si$_{136}$, single crystal XRD.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight</td>
<td>546.50</td>
</tr>
<tr>
<td>Temperature</td>
<td>200(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.27 × 0.22 × 0.13 mm$^3$</td>
</tr>
<tr>
<td>Crystal habit</td>
<td>blue prism</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Cubic</td>
</tr>
<tr>
<td>Space group</td>
<td>Fd3m</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>$a$ = 14.7121(1) Å</td>
<td>$\alpha = 90^\circ$</td>
</tr>
<tr>
<td>$b$ = 14.7121(1) Å</td>
<td>$\beta = 90^\circ$</td>
</tr>
<tr>
<td>$c$ = 14.7121(1) Å</td>
<td>$\gamma = 90^\circ$</td>
</tr>
<tr>
<td>Volume</td>
<td>3184.37(4) Å$^3$</td>
</tr>
<tr>
<td>Z</td>
<td>8 (empirical formula Na$<em>3$Si$</em>{17}$)</td>
</tr>
<tr>
<td>Density, $\rho_{calc}$</td>
<td>2.280 g/cm$^3$</td>
</tr>
<tr>
<td>Absorption coefficient, $\mu$</td>
<td>1.411 mm$^{-1}$</td>
</tr>
<tr>
<td>$F(000)$</td>
<td>2168 $\bar{e}$</td>
</tr>
<tr>
<td>Diffractometer</td>
<td>Bruker Smart Apex II CCD area detector</td>
</tr>
<tr>
<td>Radiation source</td>
<td>fine-focus sealed tube, MoK$\alpha$</td>
</tr>
<tr>
<td>Detector distance</td>
<td>5.000 cm</td>
</tr>
<tr>
<td>Detector resolution</td>
<td>8.333 pixels/mm</td>
</tr>
<tr>
<td>Total frames</td>
<td>3030</td>
</tr>
<tr>
<td>Frame size</td>
<td>512 pixels</td>
</tr>
<tr>
<td>Frame width</td>
<td>-0.30°</td>
</tr>
<tr>
<td>Exposure per frame</td>
<td>12 sec</td>
</tr>
<tr>
<td>Total measurement time</td>
<td>15.00 hours</td>
</tr>
<tr>
<td>Data collection method</td>
<td>$\omega$ and $\phi$ scans</td>
</tr>
</tbody>
</table>

- $\theta$ range for data collection: 2.40 to 29.98°
- Index ranges: $-20 \leq h \leq 20$, $-20 \leq k \leq 20$, $-20 \leq l \leq 20$
- Reflections collected: 12553
- Independent reflections: 262
- Observed reflection, $F$ $>$ $2\sigma(F)$: 260
- Coverage of independent reflections: 100.0%
- Variation in check reflections: 0%
- Absorption correction: Semi-empirical from equivalents SADABS (Sheldrick, 1996)
- Max. and min. transmission: 0.832 and 0.746
- Structure solution technique: direct
- Structure solution program: SHELXS-97 (Sheldrick, 1990)
- Refinement technique: Full-matrix least-squares on $F^2$
- Refinement program: SHEXL-97 (Sheldrick, 1997)
- Function minimized: $\sum w(F_o^2 - F_c^2)^2$
- Data / restraints / parameters: 262 / 0 / 18
- Goodness-of-fit on $F^2$: 1.000
- $\Delta/\sigma_{max}$: 0.001

Final R indices: $R_1$, $I$ $>$ $2\sigma(I)$
- $R_1$: 0.0115
- $wR_2$, all data: 0.0290
- $R_{int}$: 0.0183
- $R_{sig}$: 0.0040

Weighting scheme: $w = 1 / [\sigma^2(F_o^2) + (0.01P)^2 + 12P]$, $P = [\max(F_o^2, 0) + 2F_c^2]/3$

Extinction coefficient: 0.00031(4)

Largest diff. peak and hole: 0.203 and -0.122 $\bar{e}$/Å$^3$

$R_1$ = $\Sigma||F_o|| - |F_c||/\Sigma|F_o||$, $wR^2 = [\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]^{1/2}$
Table 3.2 Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for Na$_2$Si$_{136}$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>$x/a$</th>
<th>$y/b$</th>
<th>$z/c$</th>
<th>$U_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na1*</td>
<td>8b</td>
<td>0.1250</td>
<td>0.1250</td>
<td>0.1466(7)</td>
<td>0.049(3)</td>
</tr>
<tr>
<td>Na2</td>
<td>16c</td>
<td>0.5000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0152(2)</td>
</tr>
<tr>
<td>Si1</td>
<td>2a</td>
<td>0.6250</td>
<td>0.1250</td>
<td>0.1250</td>
<td>0.00613(18)</td>
</tr>
<tr>
<td>Si2</td>
<td>32c</td>
<td>0.871284(19)</td>
<td>0.067382(13)</td>
<td>0.067382(13)</td>
<td>0.00649(8)</td>
</tr>
<tr>
<td>Si3</td>
<td>96g</td>
<td>0.717951(19)</td>
<td>0.032049(19)</td>
<td>0.032049(19)</td>
<td>0.00636(10)</td>
</tr>
</tbody>
</table>

* $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.
* Na1 occupation factor = $\frac{1}{6}$.

Table 3.3 Anisotropic atomic displacement parameters (Å²) for Na$_2$Si$_{136}$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$U_{11}$</th>
<th>$U_{22}$</th>
<th>$U_{33}$</th>
<th>$U_{23}$</th>
<th>$U_{13}$</th>
<th>$U_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na1</td>
<td>0.056(4)</td>
<td>0.056(4)</td>
<td>0.034(4)</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Na2</td>
<td>0.0152(2)</td>
<td>0.0152(2)</td>
<td>0.0152(2)</td>
<td>-0.0011(3)</td>
<td>-0.0011(3)</td>
<td>-0.0011(3)</td>
</tr>
<tr>
<td>Si1</td>
<td>0.00613(18)</td>
<td>0.00613(18)</td>
<td>0.00613(18)</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Si2</td>
<td>0.00683(13)</td>
<td>0.00632(9)</td>
<td>0.00632(9)</td>
<td>0.00040(9)</td>
<td>0.00002(6)</td>
<td>0.00002(6)</td>
</tr>
<tr>
<td>Si3</td>
<td>0.00636(10)</td>
<td>0.00636(10)</td>
<td>0.00636(10)</td>
<td>-0.00001(9)</td>
<td>0.00001(9)</td>
<td>0.00001(9)</td>
</tr>
</tbody>
</table>

* The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2 [ h^2 a^*^2 U_{11} + ... + 2hka^*b^*U_{12} ]$

Table 3.4 Bond lengths (Å) for Na$_2$Si$_{136}$.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na1-Si2</td>
<td>3.619(10)×2</td>
</tr>
<tr>
<td>Na1-Si2</td>
<td>3.785(7)×4</td>
</tr>
<tr>
<td>Na1-Si2</td>
<td>3.8642(15)×4</td>
</tr>
<tr>
<td>Na1-Si2</td>
<td>4.001(3)×4</td>
</tr>
<tr>
<td>Na1-Si2</td>
<td>4.0114(7)×2</td>
</tr>
<tr>
<td>Na1-Si2</td>
<td>4.0201(10)×2</td>
</tr>
<tr>
<td>Na1-Si2</td>
<td>4.225(10)×2</td>
</tr>
<tr>
<td>Na1-Si2</td>
<td>4.234(8)×4</td>
</tr>
<tr>
<td>Na1-Si3</td>
<td>3.827(5)×2</td>
</tr>
<tr>
<td>Na1-Si3</td>
<td>4.194(7)×2</td>
</tr>
<tr>
<td>Na2-Si1</td>
<td>3.1853(1)×2</td>
</tr>
<tr>
<td>Na2-Si2</td>
<td>3.3742(2)×12</td>
</tr>
<tr>
<td>Na2-Si3</td>
<td>3.2751(3)×6</td>
</tr>
<tr>
<td>Si1-Si3</td>
<td>2.3685(5)×4</td>
</tr>
<tr>
<td>Si2-Si2</td>
<td>2.3578(3)×2</td>
</tr>
<tr>
<td>Si2-Si2</td>
<td>2.3976(6)</td>
</tr>
<tr>
<td>Si2-Si3</td>
<td>2.3726(3)</td>
</tr>
<tr>
<td>Si3-Si1</td>
<td>2.3686(5)</td>
</tr>
<tr>
<td>Si3-Si2</td>
<td>2.3726(3)×3</td>
</tr>
</tbody>
</table>
3.2 Transport properties of Na$_{24}$Si$_{136}$ single crystals

The only data reported to date on transport properties of single crystals of Na$_{24}$Si$_{136}$ is from Beekman et al.\textsuperscript{120} on single crystal obtained by SPS. Here we report on $S$, $\rho$ and $\kappa$ measurements on single crystals obtained by the Novel method. The mounting configuration for measuring the transport properties on single crystals shown in Figure 2.5 was also employed in the case of Na$_{24}$Si$_{136}$ single crystals. A crystal with size ~0.5 mm was mounted as shown in Figure 3.5.

![Figure 3.5 A photograph of a mounted single crystal Na$_{24}$Si$_{136}$ for transport properties measurements.](image)

The temperature dependences and magnitudes of $\rho$ (empty circles) and $S$ (filled circles) are shown in Figure 3.6. They clearly indicate metallic behavior. The observed value of $\rho$ (45 $\mu$Ω-cm at room temperature) is, to the best of our knowledge, lower than any other intermetallic clathrate reported to date, with the exception of SPS grown\textsuperscript{87} Na$_{24}$Si$_{136}$ (Table 3.5). This is an indication of both the metallic conduction of this composition and the high quality of the single crystals. Another indicator of the quality and the crystallinity of Na$_{24}$Si$_{136}$ is the RRR value of approximately 17, which is higher than any other polycrystalline intermetallic clathrate and comparable to the RRR for
Na$_{24}$Si$_{136}$ grown by SPS. We note that at the lowest temperature of our measurement (12 K), $dho/dT>0$ which indicates that the residual resistivity has still not yet been reached.

![Graph showing resistivity and Seebeck coefficient vs. temperature](image)

**Figure 3.6** $\rho$ (empty circles) and $S$ (filled circles) for a single crystal of Na$_{24}$Si$_{136}$.

$S$ remains low in the entire temperature range and approaches zero value at low temperatures as expected for a metallic material. The negative sign of $S$ is consistent with the fact that electrons are the majority carriers.

The thermal conductivity $\kappa$ of Na$_{24}$Si$_{136}$ is shown in Figure 3.7. It is compared with $\kappa$ of several polycrystalline semiconductors (Figure 3.7) and found to be high, consistent with the metallic behavior observed in the electrical properties. The Sn clathrate exhibits temperature dependence typical of crystalline insulators$^{16}$, with $\kappa$ decreasing with increasing $T$ approximately as $1/T$, a signature of Umklapp-processes. The two Ge clathrates have more than an order of magnitude lower $\kappa$ at low temperatures with magnitudes similar to that of amorphous material.
Table 3.5 Comparison of the room temperature resistivities and residual resistance ratios RRR=R(300 K)/R(T₀) for the Na$_{24}$Si$_{136}$ specimen of the present work and several intermetallic clathrate specimens of type II showing metallic or “metallic-like” resistivities (i.e. $d\rho/dt$ is positive definite over the entire temperature interval of measurement). $T₀$ is the lowest temperature at which the corresponding resistivity was reported.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Form</th>
<th>Synthesis Method</th>
<th>Carrier Type</th>
<th>$\rho$(300 K) (mΩ-cm)</th>
<th>$T₀$ (K)</th>
<th>RRR</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$<em>{24}$Si$</em>{136}$</td>
<td>single crystal</td>
<td>novel method</td>
<td>$n$</td>
<td>0.045</td>
<td>12</td>
<td>17</td>
<td>Present Work</td>
</tr>
<tr>
<td>Na$<em>{24}$Si$</em>{136}$</td>
<td>single crystal</td>
<td>SPS</td>
<td>$n$</td>
<td>0.029</td>
<td>12</td>
<td>14</td>
<td>Beekman</td>
</tr>
<tr>
<td>Cs$<em>8$Na$</em>{16}$Si$_{136}$</td>
<td>polycrystalline</td>
<td>direct reaction of stoichiometric mixture</td>
<td>$n$</td>
<td>0.68</td>
<td>9</td>
<td>2.4</td>
<td>Nolas</td>
</tr>
<tr>
<td>Cs$<em>8$Ge$</em>{136}$</td>
<td>polycrystalline</td>
<td>degassing of Cs$<em>8$Na$</em>{16}$Ge$_{136}$</td>
<td>$n$</td>
<td>9.2</td>
<td>6</td>
<td>1.8</td>
<td>Gryko</td>
</tr>
</tbody>
</table>

51
Na$_{24}$Si$_{136}$ has unequivocally much higher $\kappa$ compared to these clathrates due to its electronic contribution, which is small in semiconductor materials. The resonant scattering of acoustic phonons because of the ‘rattling’ of the guest atoms is present in all materials shown in Figure 3.7 and this is clearly not the reason of the high thermal conductivity for Na$_{24}$Si$_{136}$. 

**Figure 3.7** Thermal conductivity $\kappa$ of Na$_{24}$Si$_{136}$ single crystals in comparison with polycrystalline clathrate materials.
It is important to notice that the relative uncertainty in the measurements of \( \rho \) and \( \kappa \) is quite high (we estimate it to be on the order of 30%), due to the difficulty in determination of the cross-sectional area of the irregularly shaped crystals. However, the obtained results can be interpreted as more accurate representation of the intrinsic properties in this material relative to the same measurements on a polycrystalline specimens, for which grain boundary effects can dominate. \(^{17,67,86}\)
4. Resistivity, Seebeck Coefficient and Thermal Conductivity of Sn$_{24}$P$_{19.3}$Br$_8$ and Sn$_{17}$Zn$_7$P$_{22}$Br$_8$

Much less is known about the thermoelectric properties of tin clathrates with cationic framework encapsulating anionic guests. In this chapter the transport properties of two Sn-clathrates with type I hydrate crystal structure with Br guests, Sn$_{24}$P$_{19.3}$Br$_8$ and Sn$_{17}$Zn$_7$P$_{22}$Br$_8$, were investigated. The results are discussed in terms of the potential for thermoelectric applications. The two specimens Sn$_{24}$P$_{19.3}$Br$_8$ and Sn$_{17}$Zn$_7$P$_{22}$Br$_8$ were prepared by Dr. A.V. Shevelkov.$^{125,126}$ Tin, zinc, red phosphorus, and tin bromide were used as starting materials. Their stoichiometric mixtures were reacted in sealed under vacuum silica tubes at 450°C for 5 days. The resulting material was ground to fine powder and annealed for 14 days at a 550°C and 300°C for Sn$_{24}$P$_{19.3}$Br$_8$ and Sn$_{17}$Zn$_7$P$_{22}$Br$_8$, respectively. Powder x-ray diffraction data was indexed to the type I clathrate structure (Pm$\overline{3}$n). The type I clathrate crystal structure can be described as a three-dimensional framework composed of tetrahedrally-bonded phosphorus and metal atoms. The framework can be thought of as being formed by six tetrakaidecahedra and two dodecahedra, formed by the pnicogen atoms, with bromine atoms residing inside polyhedra, as shown in Figure 4.1.
Although in general similar, the lattice structures of Sn$_{24}$P$_{19.3}$Br$_8$ and Sn$_{17}$Zn$_7$P$_{22}$Br$_8$ have important differences. The idealized type I clathrate framework is defined by three independent crystallographic positions, 6$c$, 16$i$, and 24$k$. In Sn$_{24}$P$_{19.3}$Br$_8$ the Sn(3) (24$k$) position is split into two sites Sn(31) (6$c$) and Sn(32) (16$i$) while the 6$c$ and 16$i$ positions remain tetrahedrally bonded. Sn(32) forms two short covalent bonds with P(2) (16$i$), and one covalent bond with tin atom, Sn(31), and completes its coordination by three relatively distant (3.16 Å to 3.31 Å) Sn(32) atoms (Figure 4.2).

Figure 4.1: Crystal structure of type I clathrate. The open circles represent the guest Br atoms occupying the polyhedra formed by Sn, P, and Zn. The filled circles are the 6$c$ and 16$i$ crystallographic positions and the gray circles represent the 24$k$ crystallographic position.

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In Sn$_{17}$Zn$_7$P$_{22}$Br$_8$ the Sn(3) site is split into three closely lying positions, two of which are occupied by tin, Sn(31) and Sn(32), and the third occupied by zinc, Zn(33).
Each metal atom is bound to two P(2) atoms and one P(1) atom and forms one covalent bond, Sn(31)–Sn(31) or Sn(32)–Zn(33) (Figure 4.3). The phosphorus atoms have very similar coordination in both structures. The P(2) atom forms one homonuclear P–P bond and is surrounded by three (Sn,P) atoms forming a distorted tetrahedron. The P(1) (16c) atom is surrounded by four (Sn,P) atoms forming an almost regular tetrahedron. In both structures, the separation between the P(2) atoms is 2.18 Å, typical for P–P bonding. The P-Sn separations range from 2.46 Å to 2.69 Å in both compounds, while the P–Zn separations in Sn17Zn7P22Br8 are shorter, ranging from 2.34 Å to 2.47 Å. The framework of Sn24P19.3Br8 contains fewer than 46 atoms, thus there are vacancies (on the 6c crystallographic sites). This is not the case for Sn17Zn7P22Br8. A detailed analysis of the structural characteristics of Sn24P19.3Br8 and Sn17Zn7P22Br8 is reported in Refs.125 and 126.

Densification for transport measurements was achieved by hot-pressing the powdered specimens at 450°C and 189 MPa for 2 h. A small amount of Sn4P3, estimated to be ~4 vol.%, was observed with XRD analysis after hot-pressing. The polycrystalline pellets were cut into parallelepipeds of dimensions 2 mm × 2 mm × 5 mm using a wire saw to reduce surface damage. Measurements of $S$, $\rho$ and $\kappa$ were performed using a radiation-shielded vacuum probe in a custom-designed closed-cycle refrigerator.127

The temperature dependence of $\ln \sigma$ for Sn24P19.3Br8 and Sn17Zn7P22Br8 is shown in Figure 4.4.
For Sn$_{24}$P$_{19.3}$Br$_8$ $\sigma$ decreases rapidly with decreasing temperature from room temperature to approximately 55 K, and is not strongly temperature dependent from 55 K to 12 K. For Sn$_{17}$Zn$_7$P$_{22}$Br$_8$ $\sigma$ decreases with decreasing temperature in the interval 300 K to 200 K, then continues to increase below 200 K. The band gap, $E_g$, for Sn$_{17}$Zn$_7$P$_{22}$Br$_8$ was estimated to be 0.11 eV from a linear fit to the data (Fig. 4.4b). This value is close to that reported previously.$^{126}$

Figure 4.5 shows the temperature dependence of $S$ from room temperature to 12 K for the two clathrates. For Sn$_{17}$Zn$_7$P$_{22}$Br$_8$ $S$ increases slowly in the entire temperature range,
reaching a room-temperature value of 40 µV/K. For Sn$_{24}$P$_{19.3}$Br$_8$, $S$ is relatively temperature independent from room temperature to 125 K, then decreases sharply to approximately zero.

![Figure 4.5 $S$ for Sn$_{24}$P$_{19.3}$Br$_8$ (black circles) and Sn$_{17}$Zn$_7$P$_{22}$Br$_8$ (open squares).](image)

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The sharp decrease in $S$ with decreasing temperature occurs at approximately the same temperature as an abrupt change in $\sigma$. This may be an indication of the onset of minority-carrier conduction at this lower temperature range. Hall measurements on both specimens yielded positive but strongly field-dependent Hall coefficients, suggesting contributions from multiple bands. The difference in the electrical transport for Sn$_{24}$P$_{19.3}$Br$_8$ and Sn$_{17}$Zn$_7$P$_{22}$Br$_8$ may be attributed to the fine yet important difference in the crystal structure of these two clathrates. In the latter, all tin atoms have tetrahedral coordination made of one metal, Sn or Zn, and three phosphorus atoms. In the former, a part of the tin framework is surrounded by three covalently bonded atoms forming a trigonal pyramid and is further linked to three rather distant (3.2 Å to 3.4 Å) tin atoms. In such a way a 3 + 3 distorted octahedral coordination is formed for the Sn(2) atoms. On average, 10.8 out of 24 tin atoms in the unit cell have this type of coordination. The remaining 13.2 tin
atoms, Sn(1), possess ‘normal’ tetrahedral coordination made of three P and one Sn atom. This structural difference adds complexity that may result in added carrier scattering. Shaturk et al.\textsuperscript{128} showed that the states just below the Fermi level are mainly composed of the orbitals of the 3 + 3 bonded Sn atoms. In addition, cationic Sn-clathrates with 3 + 3 bonded Sn atoms are narrow-gap semiconductors and display relatively high values of $\sigma$ and $S$,\textsuperscript{125} whereas those with only four-bonded tin atoms have much lower electrical conductivities.\textsuperscript{129} This results in a relatively high power factor ($S^2\sigma = 130$ W/m K\textsuperscript{2} at room temperature) for Sn\textsubscript{24}P\textsubscript{19.3}Br\textsubscript{8}, higher than any other Sn-clathrate,\textsuperscript{9,130,131} and near the values of other type I clathrates. The relatively high power factor resulted in a room-temperature ZT of 0.03. Although very low, this ZT value is higher than any other Sn-clathrate reported thus far.\textsuperscript{45}

From the measured values of $\kappa$ and $\rho$ the Wiedemann–Franz relation was employed to estimate and subtract the electronic component $\kappa_e = L_0 T/\rho$ (with Lorenz number $L_0 = 2.44 \times 10^{-8}$ V\textsuperscript{2}/K\textsuperscript{2}), thus estimating the lattice contribution $\kappa_L = \kappa - \kappa_e$. Figure 4.6 shows $\kappa_L$ for the polycrystalline Sn\textsubscript{24}P\textsubscript{19.3}Br\textsubscript{8} and Sn\textsubscript{17}Zn\textsubscript{7}P\textsubscript{22}Br\textsubscript{8} specimens. Sn\textsubscript{24}P\textsubscript{19.3}Br\textsubscript{8} exhibits a nearly $1/T$ temperature dependence between 50 K and 100 K, which is typical of crystalline dielectric materials dominated by phonon–phonon scattering.\textsuperscript{132} The low $\kappa_L$ values are due to the complex crystal structure, i.e., 56 atoms per unit cell, in these materials. The additional bonding induced between the Br and framework atoms neighboring the vacancies apparently constrains the Br atoms, thus resulting in higher $\kappa_L$ values at lower temperatures. This has also been observed in Cs\textsubscript{8}Sn\textsubscript{44}.\textsuperscript{4} In the case of Sn\textsubscript{17}Zn\textsubscript{7}P\textsubscript{22}Br\textsubscript{8} $\kappa_L$ slowly increases with decreasing temperature. It may be that the ‘rattle’ vibrational modes, although more prominent than for Sn\textsubscript{24}P\textsubscript{19.3}Br\textsubscript{8}, are not within the range of the acoustic phonons. This has also been observed\textsuperscript{46,127} for Cs\textsubscript{8}Zn\textsubscript{4}Sn\textsubscript{42} and Cs\textsubscript{8}Ga\textsubscript{8}Sn\textsubscript{38}. The Zn and P atoms in Sn\textsubscript{17}Zn\textsubscript{7}P\textsubscript{22}Br\textsubscript{8} may also produce additional alloy scattering which further suppresses $\kappa_L$. The structural difference between these two compositions, therefore, appears to be the source of their differing thermal conductivities.
The solid lines in Figure 4.6 are theoretical fits to the experimental data using the Debye approximation.\cite{126,132,133}

\[
\kappa_L = \frac{k_B}{2\pi\nu} \left(\frac{k_B T}{\hbar}\right)^3 \frac{\theta_D}{T} \int_0^1 \frac{x^4 e^x}{\tau_C^2 (e^x - 1)^2} dx
\]

where the dimensionless quantity \( x = \hbar \omega/k_B T \), \( \omega \) is the phonon frequency, \( k_B \) is the Boltzmann constant, \( \hbar \) is the reduced Planck constant, \( \theta_D \) is the Debye temperature, \( \nu \) is the speed of sound, and \( \tau_C \) is the phonon-scattering relaxation time. The phonon-scattering relaxation rate can be written as

\[
\tau_C^{-1} = \frac{\nu}{L} + A\omega^4 + B\omega^2 T \exp\left(-\frac{\theta_D}{3T}\right) + \frac{C\omega^2}{(\omega_0^2 - \omega^2)^2}
\]

where \( L \) is the grain size, \( \omega_0 \) is the resonance frequency, and \( A, B, \) and \( C \) are fitting parameters, listed in Table 4.1. The four scattering mechanisms on the right-hand side of
Eq. 4.2 represent grain boundary, point defect, phonon-phonon umklapp, and phonon resonant scattering, respectively. $\theta_D$ and $\nu$ values used in the fitting are 238 K and 2,505 m/s, respectively.\textsuperscript{134}

**Table 4.1** Fit Parameters for the Two Polycrystalline Sn-Clathrates

<table>
<thead>
<tr>
<th>Composition</th>
<th>$L$ (µm)</th>
<th>$A$ ($10^4$ s$^3$)</th>
<th>$B$ ($10^5$ s K$^{-1}$)</th>
<th>$C$ (s$^{-3}$)</th>
<th>$\omega_0$ (THz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn$<em>{24}$P$</em>{19.3}$Br$_8$</td>
<td>9.58</td>
<td>1.406</td>
<td>2.067</td>
<td>0.1</td>
<td>13.364</td>
</tr>
<tr>
<td>Sn$_{17}$Zn$<em>7$P$</em>{22}$Br$_8$</td>
<td>3.58</td>
<td>2.221</td>
<td>0.824</td>
<td>$6.72 \times 10^9$</td>
<td>4.768</td>
</tr>
</tbody>
</table>

The values for $L$ are similar to average grain size estimates using metallographic analysis. The $A$ prefactor is larger for Sn$_{17}$Zn$_7$P$_{22}$Br$_8$ than for Sn$_{24}$P$_{19.3}$Br$_8$, possibly due to the three-element alloying on the framework site for the former composition. The larger $B$ prefactor for Sn$_{24}$P$_{19.3}$Br$_8$ potentially indicates stronger phonon-phonon scattering than that for Sn$_{17}$Zn$_7$P$_{22}$Br$_8$, although it is not clear why this would be the case since we do not know the exact Debye temperature and Grüneisen constant for these compositions, two of the parameters that influence $B$. As shown in Table 4.1, the values of $C$ indicate very weak, if any, “rattling” in Sn$_{24}$P$_{19.3}$Br$_8$. This is presumably due to the shrinking of the tetrakaidecahedral cages within the framework due to the framework vacancies, whereas in Sn$_{17}$Zn$_7$P$_{22}$Br$_8$ this phonon-scattering mechanism is much more pronounced. In addition, the limited space for the dynamic disorder of Br yields a threefold difference in $\omega_0$ for Sn$_{24}$P$_{19.3}$Br$_8$ in comparison with Sn$_{17}$Zn$_7$P$_{22}$Br$_8$. In these fits we have assumed that the Br inside the dodecahedra do not produce the dynamic disorder observed for the guest atoms inside the tetrakaidecahedra, as has been demonstrated for other type I clathrates.\textsuperscript{46,130}
5. Type VIII Eu$_8$Ga$_{16}$Ge$_{30}$ clathrates for magnetic applications

Magnetic refrigeration based on the magnetocaloric effect (MCE) is a topic of great interest.\textsuperscript{135} While the concept itself is very old and magnetic cooling for producing ultralow temperatures dates back to the 1920s, the discovery of alloys exhibiting the so-called giant MCE has renewed interest for solid-state cooling applications in the intermediate to room temperature (77–300 K) range.\textsuperscript{135-137} Therefore, magnetic refrigeration technology is a promising alternative to conventional gas compression techniques.\textsuperscript{135} Long-range ferromagnetism and low-field giant MCE were observed in type VIII clathrate Eu$_8$Ga$_{16}$Ge$_{30}$. The results indicate that this material undergoes a second-order, ferromagnetic-paramagnetic transition at \~13 K, with long-range ferromagnetic ordering. The low-field giant MCE, together with the absence of thermal hysteresis and field hysteresis, makes it a very promising candidate material for active magnetic refrigeration in the low temperature regime below 20 K.

5.1 Magnetocaloric effect (MCE)

The magnetocaloric effect (MCE) is a magneto-thermodynamic phenomenon in which an externally applied changing magnetic field can strongly affect the spin degrees of freedom in a solid that results in a reversible change in temperature in a given specimen.\textsuperscript{135} Magnetic materials can be thought of as having two different heat reservoirs: the phonon excitations related to the lattice degrees of freedom, and magnetic excitations connected to the spin degrees of freedom.

In the magnetic refrigeration cycle\textsuperscript{136} depicted in Figure 5.1, a magnetocaloric substance undergoes an adiabatic magnetization, that is, initially randomly oriented magnetic moments are aligned by an external magnetic field, thus leading to a decrease in the entropy of the system. The insulated environment prevents the heat form “escaping” the material. Therefore, since the entropy change $\Delta S$ in a system at a given temperature $T$ absorbing an infinitesimal amount of heat $\delta Q$ is given as $\Delta S = \delta Q/T$, the net result is heating up of the specimen.
Figure 5.1 Schematic representation of a magnetic refrigeration cycle

The second stage of the MCE is isomagnetic enthalpic transfer, where heat is removed from the system by fluid or gas, say liquid helium for example, while the magnetic field is unchanged. The third stage, known as adiabatic demagnetization allows randomization of the magnetic moments by removing the magnetic field, which leads to cooling the material below the ambient temperature. At the final stage, the magnetocaloric material is placed in a thermal contact with the environment being cooled and heat migrates into the working material.

Magnetic refrigeration based on the MCE has recently received increased attention as an alternative to the compression-evaporation techniques. Magnetic refrigeration is also an environmentally friendly cooling technology, in this way similar to thermoelectric refrigeration, that does not use ozone depleting chemicals, hazardous chemicals, or green house gasses. Another important difference between the magnetic refrigeration and the conventional gas-compression techniques is the higher efficiency in
the former one. Magnetic refrigerators working with Gd show 60% of the Carnot efficiency compared with only about 40% in the best gas-compression refrigerators.\textsuperscript{138}

5.2 Crystal structure of type VIII Eu\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30} clathrate

The structural investigations\textsuperscript{139} of Eu\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30} show that it has two structural modifications, affiliated with the type I and VIII clathrates, respectively (Figure 5.2).

![Figure 5.2 Crystal structure of type VIII Eu\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30}](image)

Both structures are characterized by covalent $E_{46}$ networks ($E$=Ga, Ge) of fourfold bonded $E$ atoms with polyhedral cages occupied by Eu. The type I phase has two different polyhedral cages: $E_{20}$ pentagonal dodecahedra centered by Eu1 and $E_{24}$ tetrakaidecahedra centered by Eu2 (Eu1:Eu2=1:3). There are two Eu1 (2$a$ sites) and six Eu2 (6$d$ sites) atoms per unit cell. The type VIII phase has only one type of cage, a distorted pentagonal dodecahedron centered by Eu (8$c$ site) atom. The shortest Eu-Eu distance for type VIII Eu\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30} is 5.562 Å, whereas in the type I Eu\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30} it is 5.23 Å. The average distance between Eu and $E$ atoms that form the surrounding $E_{20}$ cage is 3.633 Å for the type VIII Eu\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30}. For the type I Eu\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30} the average Eu1-E
and Eu-E distances are 3.482 and 3.846 Å, respectively. There are 92 covalent bonds per unit cell, giving a total of 184 valence electrons that fill the valence band completely thus leading to semiconducting properties in these compounds. Measurements of the anisotropic displacement parameters\textsuperscript{47} show the stiffness of the framework relative to the larger anisotropic displacements of the encapsulated Eu atoms.

5.3 Synthesis of type VIII Eu\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30}

For both Eu\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30} structure types a stoichiometric mixtures of high purity starting elements were placed in BN crucibles, sealed under nitrogen in a quartz tube and induction melted at 1100 °C. The cooling process determines the product compound. Rapid water quenching leads to type I Eu\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30}. Type VIII Eu\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30} is obtained from the type I phase. The type I specimen was heated at a rate of 2\textdegree C/min to a final temperature of 675\textdegree C, and annealed at this temperature for two weeks. XRD data obtained on compositions of both phases are given in Figure 5.3.

Differential Scanning Calorimetry (DSC) investigations show an endothermal effect at $T_I=700\degree$C, that is attributed to the formation of the type I phase. The next thermal effect at $T_{VIII}=697\degree$C, originates from type I $\leftrightarrow$ VIII transformation in the clathrates phase. According to Leoni et al.\textsuperscript{142} this transformation is a reconstructive one. This would explain its endothermal character. It has been shown that the reaction is dependent on the starting state of the specimen, e.g., on the grain size of the type I phase used as a precursor to form the type VIII phase.
Figure 5.3 XRD patterns for type I (a) and type VIII (b) phases
5.4 Type VIII Eu₈Ga₁₆Ge₃₀ clathrate for magnetocaloric applications

Magnetic measurements were done in Dr. Hariharan’s Laboratory, using a commercial physical property measurement system from Quantum Design in the temperature range of 5–300 K at applied fields up to 7 T. The magnetic isotherms were measured with a field step of 0.05 mT in the range of 0–3 T and with a temperature interval of 3 K (1 K in the proximity of the Curie temperature, $T_C$) over a temperature range of 5–62 K. Figure 5.4 shows the temperature dependence of magnetization taken at a low applied field of 0.01 mT.

![Figure 5.4](image)

**Figure 5.4** Magnetization curves taken at 0.01 mT with increasing (heating) and decreasing (cooling) temperature. The corresponding $dM/dT$ curve for the heating branch is also overlaid to mark the transition temperature. The inset shows the magnetization curves taken at applied fields of 1, 2, and 3 T.

Figure 5.4 shows data at higher fields of 1, 2, and 3 T. The Curie temperature ($T_C$) of 12.6 K is defined by the minimum in $dM/dT$ (also shown overlaid on the $M-T$ curve in Figure 5.4). To check for the presence of any thermal hysteresis in the transition region, we measured the magnetization both while heating and cooling the specimen. As shown
in Figure 5.4, no thermal hysteresis is detected. This is beneficial for active magnetic refrigeration. An expected broadening of the transition takes place at larger applied fields but remains reasonably sharp even at a field of up to 3 T (inset in Figure 5.4). In a study reported by Hu et al. the compound MnAs$_{0.9}$Sb$_{0.1}$ displayed a smooth temperature variation of the magnetization under high fields, whereas the shape of the $M$-$T$ curve for MnAs was almost unchanged. As a result, MnAs exhibited a larger MCE compared to MnAs$_{0.9}$Sb$_{0.1}$. Our experimental observation reported here leads to a similar expectation that type VIII Eu$_8$Ga$_{16}$Ge$_{30}$ clathrate compound would show a large magnetic entropy change in the vicinity of its $T_C$. In Figure 5.5a we show a series of $M$-$H$ isotherms taken at temperature intervals of $\Delta T=3$ K from 5 to 53 K spanning the ferromagnetic transition region.

**Figure 5.5** a) Magnetization isotherms measured at different temperatures between 5 and 53 K with 3 K interval. b) The $H/M$ vs $M^2$ plots for representative temperatures around the $T_C$. 
A sharp change in magnetization is clearly observed in Figure 5.5a as the temperature nears and eventually crosses over $T_C$ from ferromagnetic to paramagnetic states. A noticeable feature in Figure 5.5a is that a large proportion of the change in magnetization occurs below 2 T. This is beneficial for practical application of MCE materials at modest fields.\textsuperscript{135-137} Since the magnitude of MCE and its dependence on temperature and magnetic field are strongly dependent on the nature of the corresponding magnetic phase transition,\textsuperscript{138} it is essential to analyze the magnetic transition further in this material. To do this, the measured data of the $M$-$H$ isotherms were converted into $H/M$ versus $M^2$ plots (the so called Arrott plots). These are shown in Figure 5.5b for representative temperatures near $T_C$. According to the Banerjee criterion,\textsuperscript{141} the magnetic transition is of second order if all the $H/M$ versus $M^2$ curves have a positive slope. On the other hand, if some of the $H/M$ versus $M^2$ curves show a negative slope at some point, the transition is of first order.\textsuperscript{141,143} For the case of Eu$_8$Ga$_{16}$Ge$_{30}$, the presence of the positive slope of the $H/M$ versus $M^2$ curves indicates that the magnetic transition is of second order. This result is consistent with the absence of thermal hysteresis (see Figure 5.1) and the specific heat data,\textsuperscript{139} all of which points toward a second-order magnetic transition. To elucidate the influences of the magnetic transition and long-range ferromagnetism on the MCE in Eu$_8$Ga$_{16}$Ge$_{30}$, the magnetic entropy change $\Delta S_M(T)$ is calculated from a family of isothermal $M$-$H$ curves (Fig. 5.4) using the Maxwell relation,\textsuperscript{1}

$$\Delta S_M = \mu_0 \left. \int_0^{H_{av}} \left( \frac{\partial M}{\partial T} \right)_H dH \right|_{H}$$

(5.1)

where $M$ is the magnetization, $H$ is the magnetic field, and $T$ is the temperature.

Figure 5.6 shows the magnetic entropy change $\Delta S_M(T)$ as a function of temperature for different magnetic field changes up to 3 T. From Figure 5.6 $\Delta S_M$ reaches a very high value of 11.4 J/kg K at ~13 K for $\Delta \mu_0 H$=3 T, indicating that this clathrate belongs to a class of giant MCE materials. This value is about twice as large as that reported for DySb\textsuperscript{144} (~6.5 J/kg K at 11 K = $\Delta \mu_0 H$=3 T) and is almost equal to that reported for ErRu$_2$Si$_2$\textsuperscript{145} (~12 J/kg K at 5.5 K for $\Delta \mu_0 H$=3 T) within a similar temperature range. It is also much larger than that of Gd\textsuperscript{137} (~10.2 J/kg K for $\Delta \mu_0 H$=5 T) and comparable with those of Gd$_5$Si$_2$Ge$_2$\textsuperscript{135} (~18 J/kg K for $\Delta \mu_0 H$=5 T) and
MnFeP$_{0.45}$As$_{0.55}$\textsuperscript{138} (~18 J/kg K for $\Delta \mu_0 H = 5$ T) near the transition region, although the transition temperatures vary in these latter materials. The relative cooling capacity, estimated using standard methods,\textsuperscript{137} is significantly larger for type VIII clathrate Eu$_8$Ga$_{16}$Ge$_{30}$ (~87 J/kg) than for DySb\textsuperscript{144} (~34 J/kg) and ErRu$_2$Si$_2$\textsuperscript{145} (~55 J/kg) for the same field change of 2 T. Compared to other magnetocaloric materials,\textsuperscript{135,140,146} Eu$_8$Ga$_{16}$Ge$_{30}$ has additional distinct technological advantages, such as no thermal hysteresis (Figure 5.1) and field hysteresis (inset of Figure 5.6), which are desirable for active magnetic refrigeration cycles.\textsuperscript{135-137} These results indicate that this composition is a promising candidate for magnetic refrigeration in the low temperature region useful for helium and hydrogen liquefaction. The origin of the giant magnetic entropy change in Eu$_8$Ga$_{16}$Ge$_{30}$ lies in the abrupt reduction in magnetization at the transition temperature. Moreover, the magnetic moment of 7.97 $\mu_B$ for this material, as determined from the magnetization curve at 5 K (see inset of Figure 5.6), is nearly equal to the free-ion moment of 7.94 $\mu_B$. This, together with the existence of the long-range ferromagnetic order, clearly indicates a parallel alignment of all the Eu$^{2+}$ magnetic moments and a strong coupling between these moments via the conduction-electron spins.\textsuperscript{139}
This coupling remains strong at the transition temperature ($T_C$), as evidenced by the fact that the $M$-$T$ curves remain sharp under high applied fields (see inset of Figure 5.4). Therefore the additional entropy change is attributed to the fact that the magnetic transition greatly enhances the effect of the applied magnetic field as the system enters a long-range three-dimensional ferromagnetic order completely from the paramagnetic phase within a narrow temperature range around the $T_C$. A recent study has shown that the existence of a short-range ferromagnetic order (i.e., the presence of magnetic clusters) is a major obstacle for obtaining a large MCE response in magnetic materials due to the high energy required to realign the individual spins by the applied magnetic field.\textsuperscript{147}
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