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# Electronic and atomic structure of $Ba_8Ga_{16}Ge_{30-x}Si_x$ type I clathrates: Ge and Ga XAFS study

# A N Mansour<sup>1,4</sup>, J Martin<sup>2</sup>, W Wong-Ng<sup>2</sup> and G S Nolas<sup>3</sup>

<sup>1</sup> Materials and Power Systems Branch, Naval Surface Warfare Center, Carderock Division, West Bethesda, MD 20817-5700, USA

<sup>2</sup> Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

<sup>3</sup> Department of Physics, University of South Florida, Tampa, FL 33620, USA

E-mail: azzam.mansour@navy.mil, joshua.martin@nist.gov, winnie.wong-ng@nist.gov and gnolas@usf.edu

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### Abstract

X-ray absorption fine structure spectroscopy at the Ga and Ge K-edges was used to study changes in the Ga and Ge electronic structure and local coordination geometry as a function of composition in Ba<sub>8</sub>Ga<sub>16</sub>Ge<sub>30-x</sub>Si<sub>x</sub> type I clathrates (x = 0, 7.5, 9.1, 10.7, 13.4 and 30). Based on XANES data, the partial density of unoccupied states with p character is modified for both Ga and Ge upon Si substitution. Among the specimens which contain both Ge and Si, we found that the specimen with the highest measured power factor (i.e., x = 7.5) has the lowest density of unoccupied states for both Ga and Ge. Our experimental results are qualitatively consistent with computational results based on density functional theory, indicating that a series of pertinent electronic states are modified by Si p states. This suggests that an increase in the electron density near the Fermi level for an optimal Si substitution leads to an increase in the Seebeck coefficient and consequently in the power factor, according to the Cutler-Mott relation. Based on quantitative analysis of EXAFS spectra, we found that Ga has more Si neighbors than Ge, indicating that Si resides preferentially next to Ga. Both the Ge–Ga/Ge and Ga–Ge/Ga coordination distances remain relatively unchanged ( $\sim$ 2.51 Å) regardless of the degree of Si substitution. Furthermore, the Ge-Si and Ga-Si coordination distances remain relatively unchanged at  $\sim 2.41$  and  $\sim 2.45$  Å, respectively, regardless of the degree of Si substitution. For the Ba<sub>8</sub>Ga<sub>16</sub>Si<sub>30</sub> specimen, on average, Ga is coordinated with 0.9 Ga and 3.1 Si at roughly the same distance of  $\sim$ 2.50 Å. The number of Ga–Ga bonds is consistent with the fact that Ga is distributed on the framework sites in a way which reduces the number of Ga-Ga bonds relative to that based on a random distribution. An understanding of the underlying physics of the structure-property relationship provides for potential additional routes for tuning the electronic properties of clathrates for thermoelectric applications.

(Some figures may appear in colour only in the online journal)

## 1. Introduction

Thermoelectric devices are solid-state devices that can effectively interconvert heat and electricity. The dimensionless

figure of merit,  $ZT = \alpha^2 T / \rho \kappa$ , is related to the conversion efficiency of a thermoelectric (TE) material, where  $\alpha$  is the Seebeck coefficient,  $\rho$  the electrical resistivity, *T* the absolute temperature, and  $\kappa$  the total thermal conductivity ( $\kappa = \kappa_{\rm L} + \kappa_{\rm e}$ ; the lattice and electronic contributions, respectively). However, these physical parameters are interdependent and

<sup>&</sup>lt;sup>4</sup> Author to whom any correspondence should be addressed.

optimization to achieve commercially practical efficiencies is challenging. Slack introduced a useful approach to identify these potential TE materials: the phonon-glass electronsingle-crystal (PGEC) concept [1]. An ideal PGEC material would possess thermal properties similar to an amorphous solid but with electrical properties similar to a 'good' single-crystal semiconductor. This approach has identified clathrates to be one class of candidate materials [2–4].

Clathrates are encapsulating crystal structures that comprise frameworks of atoms or molecules formed through the inclusion of atoms or molecules. In the type I clathrates, a framework of tetrahedrally bonded group IV elements (Si, Ge, or Sn) form polyhedral cages, each encapsulating a metal 'guest' atom. The dynamic disorder of these guest atoms effectively scatters lattice phonons to reduce  $\kappa$  [2, 3, 5]. However, the electrical properties of type I clathrates are dominated by the interaction of the guest atoms with the framework atoms [2, 6]. Tuning these properties by adjusting the carrier concentration is generally accomplished through framework substitution [2, 7] where the guest-framework interactions are further modified by the site occupancy and distribution of framework substituted atoms.

Martin et al [8, 9] introduced an additional mechanism to modify these atomic interactions by substituting smaller Si atoms within the Ga-Ge lattice framework of the Ba<sub>8</sub>Ga<sub>16</sub>Ge<sub>30</sub> clathrate. The resulting lattice contraction, also demonstrated by electrical measurements at high pressures [10], modified the orbital interaction between the guest atoms and the framework, and consequently, resulted in atypical trends in the composition dependent transport properties. The power factor  $(\alpha^2/\rho)$  was optimized upon Si substitution, differing from the expected rigid band semiconductor model. Recent theoretical calculations [11] have attempted to model the thermal and electrical properties by assuming the site occupancy for these elements. More accurate knowledge of this bonding could identify additional routes for tuning the electronic properties of this crystal system for TE properties. To further elucidate these structure-property relationships, we have employed synchrotron x-ray absorption fine structure (XAFS) spectroscopy on four silicon substituted Ba8Ga16Ge30 type I clathrates, namely, Ba<sub>8.07</sub>Ga<sub>15.66</sub>Si<sub>7.47</sub>Ge<sub>22.80</sub>, Ba<sub>8.06</sub>Ga<sub>15.74</sub>Si<sub>9.05</sub>Ge<sub>21.16</sub>, Ba<sub>8.08</sub> Ga<sub>15.76</sub>Si<sub>10.72</sub>Ge<sub>19.44</sub>, Ba<sub>8.10</sub>Ga<sub>15.84</sub>Si<sub>13.38</sub>Ge<sub>16.68</sub> (with power factors of 1.42, 1.23, 1.22, 0.98  $\mu$ W K<sup>-2</sup> cm<sup>-1</sup>, respectively), along with Ba8Ga16Ge30 and Ba8Ga16Si30 as reference standards [12], to establish the effect of silicon substitution on the density of states near the Fermi level as well as on the local atomic structure of Ge and Ga. Previous studies [13–17] have shown that XAFS spectroscopy is extremely useful in investigating structure in thermoelectric clathrate materials.

### 2. Experiment

The XAFS experiments were conducted on the bending magnet station X-11A of the National Synchrotron Light Source with the electron storage ring operating at electron energy of 2.8 GeV and a stored current in the range of

200-300 mA [18]. The XAFS spectra at the Ge K-edge (11103 eV) and Ga K-edge (10367 eV) were collected in transmission mode using a variable exit double-crystal monochromator with two flat Si(311) crystals detuned by 20% to minimize the harmonic-content of the beam. The incident and transmitted beam intensities were monitored using 30 cm long ionization chambers with a flowing mixture of Ar and He adjusted to yield 25% and 65% absorption for the incident and transmitted beam, respectively. A third 15 cm long ionization chamber with Ar/He mixture was used to monitor the transmitted intensity of Ba<sub>8</sub>Ga<sub>16</sub>Ge<sub>30</sub> as reference standard to insure accurate calibration of the energy scale for both the Ge and Ga K-edges. The XAFS spectra were collected at room temperature ( $\sim$ 300 K) and after cooling to  $\sim$ 115 K using liquid nitrogen in a specially designed sample cell suitable for mounting up to five samples at one time. The samples' chamber was evacuated prior to making the measurements and cooling the samples.

The powder material was ground and sifted through a 325 mesh. An appropriate quantity of the sifted powder for each specimen was thoroughly mixed with boron nitride. Approximately 100 mg of the mixture for each specimen was placed in a die and pressed into self-supporting pellet with dimensions of 5 mm  $\times$  12 mm. The absorption edge jump for Ga was near 0.7 while that for Ge was in the range of 0.5–1.1 depending on the degree of Si substitution. The x-ray absorption edge jump for each specimen was kept below 1.5 in order to minimize the effects of pinholes [19] and particle size [20] on XAFS amplitudes.

The XAFS spectra were calibrated with respect to the Ge and Ga K-edge energies of Ba8Ga16Ge30 at half-height, which have been assigned to 11 103 and 10 367 eV, respectively. The K-edge absorption was isolated by fitting the pre-edge region (-300 to -100 eV) to a first order polynomial, extrapolating over the entire range of the spectrum, and then subtracting the background from the entire spectrum. Energy independent step normalization was applied by fitting the post-edge region (100-1100 eV for Ge and 100-800 eV for Ga) to a cubic polynomial and extrapolating back to the edge energy. As implicitly demonstrated in earlier studies [14, 15], the leakage signal from Ga into the Ge region is negligible and can be completely ignored. The extended x-ray absorption fine structure (EXAFS),  $\chi(k)$ , was extracted using multi-node cubic spline procedures, which minimized the amplitude of non-physical peaks in the 0-0.9 Å region of the Fourier transform. The photoelectron wavenumber, k, for all samples was defined by assigning the edge energy to the inflection point energy. The data analysis up to this point was carried out using the WinXAS software package (version 3.1) [21, 22].

All fits were made using the curve fitting code FEFFIT of the UWXAFS software package [23] and the IFEFFIT suite of programs (Athena and Artemis) [24, 25]. The data were fitted using theoretical standards calculated based on the curved-wave scattering formalism of the FEFF Code (version 8.2) [26–28]. The FEFF calculations were performed using neutron diffraction data of Ba<sub>8</sub>Ga<sub>16</sub>Ge<sub>30</sub> for the Ge–Ga and Ga–Ge paths [29] and neutron diffraction data of Ba<sub>8</sub>Ga<sub>16</sub>Si<sub>30</sub>



Figure 1. Crystal structure of Ba<sub>8</sub>Ga<sub>16</sub>Ge<sub>30</sub>.

for the Ga-Si and Ge-Si paths (by replacing the Ga with Ge as the central absorbing atom) [30]. Type I clathrates form in a cubic lattice with space group Pm3n (see figure 1), with the framework atoms (Ge and Ga) occupying the three nonequivalent crystallographic sites 6c, 16i, and 24k. The guest atom (Ba) resides on the 2a site within the 20 atoms cage and the 6d site within the 24 atoms cage. Theoretical studies [30-32] as well as experimental results on other type I clathrates [33, 34] indicate Ga preferentially occupies the 6c and 24k sites and avoids the 16i site in order to minimize the number of Ga-Ga bonds. If we refer to the atoms occupying the 6c, 16i, and 24k sites by M1, M2, and M3, respectively, regardless of whether the site is occupied by Ge or Ga, the coordination distances (R) and coordination numbers (N)for the various atom pairs can be derived based on neutron diffraction data which were collected at 100 K [29]. For the M1–M3 pair R = 2.507 Å and N = 4, for the M2–M2 pair R = 2.422 Å and N = 1, for the M2–M3 pair R = 2.496 Å and N = 3, for the M3–M1 pair R = 2.507 Å and N = 1, for the M3–M2 pair R = 2.496 Å and N = 2, and for the M3–M3 pair R = 2.534 Å and N = 1. Taking into account the site occupancies, the weighted average of the Ge/Ga-Ga/Ge distance is estimated to be 2.495 Å.

For comparisons among the specimens, the Fourier transforms (FTs) were generated using  $k^2$ -weighted EXAFS spectra over the ranges of 2.0–16.0 Å<sup>-1</sup> for Ge and 2.0–12.8 Å<sup>-1</sup> for Ga with a Hanning window of 1.0 Å<sup>-1</sup>. However, the fits were performed in *r*-space over the range of 1.3–2.8 Å using Fourier transforms generated over the k-range of 3.0–12.0 Å<sup>-1</sup> for both Ge and Ga except for Ba<sub>8</sub>Ga<sub>16</sub>Si<sub>30</sub> where the fit range in *r*-space was 1.3–2.5 Å. For each specimen, the Fourier transforms of *k*,  $k^2$ , and  $k^3$  weighted EXAFS spectra for the 300 K and the ~115 K data were fitted simultaneously. The value of the many body amplitude reduction factor ( $S_0^2$ ) for Ge and Ga was determined

from the analysis of XAFS data for Ba8Ga16Ge30 and was estimated to be 1.0 for both Ge and Ga, in agreement with previous study [15], and was used for all specimens. For the Ba<sub>8</sub>Ga<sub>16</sub>Ge<sub>30</sub> specimen, the first coordination spheres of Ge and Ga were analyzed using Ge-Ga and Ga-Ge paths, respectively, and both sets of data were fitted simultaneously. This fit was performed under the following conditions: (1) N for Ge and Ga was constrained to the crystallographic value of 4, (2) the temperature dependence of thermal disorder was constrained to the Debye model and the Debye temperature for the Ge-Ga path was assumed to be similar to that of the Ga–Ge path, and (3) optimizing *R*, static disorder ( $\sigma_{\text{static}}^2$ ), the correlated Debye temperature ( $\theta_D$ ) and inner potential ( $E_o$ ). For the specimens with Si, the first coordination sphere of Ge was analyzed as the sum of contributions from Ge-Ga and Ge-Si paths while that of Ga was analyzed as the sum of contributions from the Ga-Ge and Ga-Si paths. In these fits, the following conditions were used: (1) the sum of the Ns for the Ge-Ga and Ge-Si paths as well as sum of the Ga-Ge and Ga-Si paths were constrained to the crystallographic value of 4, (2) the Debye temperature for the Ge-Ga and Ga-Ge paths was constrained to that determined for the Ba<sub>8</sub>Ga<sub>16</sub>Ge<sub>30</sub> specimen, (3) the Debye temperature for the Ge-Si and Ga-Si paths was constrained to the value determined for the Ga-Si path in the Ba<sub>8</sub>Ga<sub>16</sub>Si<sub>30</sub> specimen, (4) the inner potentials  $(E_{o})$  for the Ge–Ga and Ge–Si paths were constrained to equal the inner potential for the Ge–Ga path in the Ba<sub>8</sub>Ga<sub>16</sub>Ge<sub>30</sub> specimen, (5) the inner potential  $(E_0)$  for the Ga–Ge and Ga-Si paths was constrained to equal the inner potential for the Ga–Ge path in the Ba<sub>8</sub>Ga<sub>16</sub>Ge<sub>30</sub> specimen, except in the case of the Ba<sub>8</sub>Ga<sub>16</sub>Si<sub>30</sub> specimen where E<sub>0</sub> was optimized during the fit, (6) the static disorder for both the Ge-Si and Ga-Si paths was constrained to 0.0, and (7) optimizing the number of Ge/Ga-Ga/Ge bonds and their distances, the number of Ge/Ga-Si bonds and their distances, and the static disorder for the Ge-Ga and Ga-Ge bonds. An attempt to also optimize the static disorder for the Ge-Si and Ga-Si bonds resulted in a value close to 0.0, thus, its value was constrained to 0.0 for all specimens. It is also to be noted that the Debye temperature for the Ga-Ga path in Ba<sub>8</sub>Ga<sub>16</sub>Si<sub>30</sub> was constrained to that of the Ga-Ge path of Ba<sub>8</sub>Ga<sub>16</sub>Ge<sub>30</sub>. The number of fitting parameters was kept below the maximum number of independent data points allowed by the Brillouin theorem [35]. The goodness of each model is given by the value of the R-factor, which is the sum of the square of residuals between measured and model data normalized to the magnitude of the measured data.

### 3. Results and discussion

### 3.1. XANES

In figure 2, we display the combined spectrum for the Ge and Ga K-edges for  $Ba_8Ga_{16}Ge_{30}$ . The observed edge jumps for Ge and Ga are proportional to the x-ray absorption cross sections [36] and their composition in the material. An expanded view of the Ge and Ga x-ray absorption near edge structure (XANES) regions and their derivatives are



Figure 2. Combined room temperature XAFS spectra of Ga and Ge K-edges for Ba<sub>8</sub>Ga<sub>16</sub>Ge<sub>30</sub>.

shown as a function of Si stoichiometry in figures 3 and 4, respectively. The inset represents an expanded view of the peak region. According to the Fermi's golden rule, the experimental XAFS spectra are related to the product of the square of the transition matrix element and the density of unoccupied states above the Fermi level [37]. In the white line region, the edge resonances are dominated by contributions from unoccupied states above the Fermi level. Based on the dipole selection rules, the Ge and Ga edge resonances are dominated by contributions from unoccupied states with  $4p^2$  and  $4p^1$  character, respectively. For both Ge and Ga, the amplitude of the white line and, hence, the density of unoccupied states, is slightly modified with Si substitution. Qualitatively, these changes are consistent with results based on density functional theory which reported that several electronic states near the top of the valence band and the bottom of the conduction band were modified by the Si p states [11].

We quantified the extent of change in the density of unoccupied states by calculating the per cent of change in the XANES's areas for the Si-substituted specimens relative to that of undoped  $Ba_8Ga_{16}Ge_{30}$  (x = 0). Ideally, one would fit the XANES data to the sum of contributions from an arctangent function (to account for transitions to the continuum states) and a Gaussian or Lorentzian function to account for transitions to bound states. The arctangent function did match the rise in the edge data and accounted for the edge shift between the spectra. However, the Gaussian/Lorentzian component was not sufficient to accurately match the fine details in the white line region. Therefore, we used the following approach to more accurately capture the relative changes in the XANES's areas for the Si-substituted specimens. We re-aligned the spectra of figures 3 and 4 so that the inflection point energy for the Si-substituted specimens matches that of the unsubstituted specimen. The re-alignment of the spectra is also implicit if one calculates the areas based on fitting the XANES region with a combination of arctangent and a Gaussian or Lorentzian functions since



=0

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Figure 3. Normalized Ge K-edge XANES spectra (a) and their derivatives (b) for  $Ba_8Ga_{16}Ge_{30-x}Si_x$ . The inset is an expanded view of the peak region.

the centroid of each function moves in order to best match the experimental spectra. Then we subtracted the spectrum of the unsubstituted specimen from the spectra of the Si-substituted specimens for both the Ge and Ga edges. The difference spectra obtained in this way are shown in figures 5(a) and (b). In this way, the contribution from the continuum states to the total density of states is expected to cancel out. The areas for Ge and Ga were then calculated from the difference spectra over the energy ranges of 11093-11122 eV and 10357-10386 eV, respectively. The per cent changes in the Ge and Ga areas as a function of the level of Si substitution were then calculated relative to the total areas for Ge and Ga, respectively, of the unsubstituted specimen. The per cent changes in the areas for Ge are -2.40%, -0.53%, -0.87%, and -0.51% while those for Ga are -2.17%, -1.52%, -1.56% and -0.94%, for x = 7.5, 9.1, 10.7 and 13.4, respectively. A negative value for the relative change



**Figure 4.** Normalized Ga K-edge XANES spectra (a) and their derivatives (b) for  $Ba_8Ga_{16}Ge_{30-x}Si_x$ . The inset is an expanded view of the peak region.

is related to an increase in the density of occupied electronic states. As can be seen in figure 5, a significant reduction in the area for both Ge and Ga is observed when x = 7.5, where the power factor is highest [8]. At this level of Si substitution,  $\rho$ is the lowest (6.5 m $\Omega$  cm) among all Si-substituted specimens while the absolute value of the Seebeck coefficient,  $|\alpha|$ , is 96  $\mu$ V K<sup>-1</sup>. Furthermore, this specimen is unique in that the temperature dependence of  $\rho$  shows a transition from a semiconducting to a metallic behavior near 200 K. If one excludes this specimen with x = 7.5,  $\rho$  and  $|\alpha|$  decrease monotonically with increasing *x* for Ba<sub>8</sub>Ga<sub>16</sub>Ge<sub>30-x</sub>Si<sub>x</sub> [8, 9].

As can be seen from the derivative of XANES data, the Ge and Ga edges shift slightly to lower energy upon Si substitution, with the extent of the shift being greater in the case of Ga. A shift to lower energy typically indicates a lower oxidation state. That is, a shift to lower energy is consistent with increase in the density of occupied states or decrease in the density of unoccupied states near the Fermi level. The shift to lower energy and the decrease in the Ge and Ga K-edge areas in the case of the specimen with x = 7.5 may lead to a



2.0 0.9 1.0 1.1 1.2 1.3 1.4 1.5 Power Factor (μW/K<sup>2</sup>cm)

**Figure 5.** XANES difference spectra for Ge (a) and Ga (b) calculated for each specific Si substitution level by subtracting that of the unsubstituted specimen ( $Ba_8Ga_{16}Ge_{30}$ ). (c) Percentage change in Ge and Ga XANES areas for the Si-substituted specimens relative to that of  $Ba_8Ga_{16}Ge_{30}$  as a function of the power factor. The solid lines are used only as a guide to the eye.

significant enhancement in the density of occupied electronic states near the Fermi level, which may lead to an increase in  $\alpha$ , as proposed by Cutler and Mott [38]. While it is difficult to correlate changes in the density of states directly to either  $\rho$ or  $\alpha$ , the combined effects of the density of states on these parameters plays a critical role in achieving a high power factor for the specimen with x = 7.5. Optimization of the power factor rather than  $\rho$  or  $\alpha$  separately is more critical in





**Figure 6.** Ge K-edge  $k_{\chi}^2(k)$  EXAFS spectra (a) and Fourier transforms (b) as a function of the level of Si substitution (*x*). The FT range is 2.0–16.0 Å<sup>-1</sup> with a Hanning window of 1.0 Å<sup>-1</sup>.

achieving good thermoelectric performance since these two parameters are interrelated. In light of our findings, we believe density of states calculations on these types of materials is warranted.

### 3.2. EXAFS and Fourier transforms

The Ge K-edge EXAFS spectra,  $k^2(\chi)$ , and the corresponding phase uncorrected Fourier transforms as a function of the level of Si substitution are shown in figure 6 while those for the Ga K-edge are shown in figure 7 In both cases, the Fourier transforms display a major contribution centered near 2.3 Å and a much less pronounced contribution centered near 3.7 Å. For the Si-substituted specimens, these contributions correspond to backscattering from Ge, Ga, and Si neighbors. In the case of Ge, most of the change in the amplitude of the first and second shells in the Fourier transforms occurred at x = 7.5 with additional small reductions at higher levels of Si substitution. On the other hand, Si substitution has a much greater effect on the amplitude of the first and second

**Figure 7.** Ga K-edge  $k^2 \chi(k)$  EXAFS spectra (a) and Fourier transforms (b) as a function of the level of Si substitution (*x*). The FT range is 2.0–12.8 Å<sup>-1</sup> with a Hanning window of 1.0 Å<sup>-1</sup>.

shells in the Fourier transforms of Ga than that of Ge. In addition, further reductions in the amplitude of the first and second shells of the Fourier transforms of Ga occurred for the x = 10.7, 13.4 and 30 specimens.

In order to clarify the origin of variations in the amplitudes of the first shell, quantitative analysis was carried out using standard nonlinear square fitting procedures with the aid of the Artemis software package as discussed in the experimental section. A summary of local structure parameters for Ge and Ga is given in table 1. Comparisons of the magnitude and imaginary part of the Fourier transform of raw data and the fit data of the Ge–Ga and Ga–Ge paths for the specimen with x = 0 (Ba<sub>8</sub>Ga<sub>16</sub>Ge<sub>30</sub>) are shown in figure 8(a) (Ge K-edge data) and figure 8(b) (Ga K-edge data). Comparisons of the magnitudes and the imaginary parts of the Fourier transforms for the Ga–Ga and Ga–Si paths for the specimen with x = 30 (Ba<sub>8</sub>Ga<sub>16</sub>Si<sub>30</sub>) are shown in figure 9(a) (magnitudes) and figure 9(b) (imaginary parts).

**Table 1.** Summary of Ge and Ga local structure parameters for Ba<sub>8</sub>Ga<sub>16</sub>Si<sub>x</sub>Ge<sub>30-x</sub> (x = 0, 7.5, 9.1, 10.7, 13.4, and 30) type I clathrates. *N*,  $R, \sigma_{\text{static}}^2, \sigma_{\text{total}}^2$  (115 K),  $\sigma_{\text{total}}^2$  (300 K), and  $E_0$  are the coordination number, distance, static disorder, total disorder at 115 K, total disorder at 300 K, and inner potential, respectively. The thermal disorders were calculated from the optimized correlated Debye temperatures ( $\theta_D$ ) of 401(24) K for the Ge–Ga/Ge bonds, 401(24) K for the Ga–Ge/Ga bonds, and 520 (67) K for the Ga/Ge–Si bonds. The *R*-factor is a measure of the goodness of the fit and is listed for the 115 and 300 K data sets. Uncertainties in the last digit(s) are enclosed in parentheses.

					$\sigma_{\text{total}}^2(115 \text{ K})$	$\sigma_{\text{total}}^2(300 \text{ K})$		
$X_{Si}$	X–Y pair	Ν	R (Å)	$\sigma_{\rm static}^2 (10^{-3} \text{\AA}^2)$	$^{3}\text{ Å}^{2})(10^{-3}\text{ Å}^{2})$	$(10^{-3} \text{ Å}^2)$	$E_{\rm o}({\rm eV})$	R-factor
0 <sup>a</sup>	Ge–Ga	4	2.506(4)	2.0(4)	4.2	6.2	6.5(8)	0.0029, 0.0039
	Ga–Ge	4	2.495(3)	2.4(4)	4.6	6.6	5.0(7)	0.0046, 0.0070
7.5 <sup>a</sup>	Ge–Ga	3.58(12)	2.509(2)	2.9(4)	5.1	7.1	6.5(8)	0.0098, 0.0167
	Ge–Si	0.42(12)	2.434(36)	0.0	2.8	4.8	6.5(8)	
	Ga–Ge	3.27(7)	2.496(2)	3.2(3)	5.4	7.3	5.0(7)	0.0115, 0.0066
	Ga–Si	0.73(7)	2.462(13)	0.0	2.8	4.8	5.0(7)	
9.1 <sup>a</sup>	Ge–Ga	3.42(8)	2.507(2)	2.3(2)	4.6	6.5	6.5(8)	0.0060, 0.0054
	Ge-Si	0.58(8)	2.414(13)	0.0	2.8	4.8	6.5(8)	
	Ga–Ge	3.18(9)	2.494(2)	3.2(4)	5.4	7.3	5.0(7)	0.0097, 0.0125
	Ga–Si	0.82(9)	2.450(14)	0.0	2.8	4.8	5.0(7)	
10.7 <sup>a</sup>	Ge–Ga	3.30(9)	2.506(2)	2.5(2)	4.8	6.7	6.5(8)	0.0059, 0.0068
	Ge-Si	0.70(9)	2.409(13)	0.0	2.8	4.8	6.5(8)	
	Ga–Ge	2.95(12)	2.491(3)	3.4(5)	5.4	7.3	5.0(7)	0.0104, 0.0300
	Ga–Si	1.05(12)	2.457(14)	0.0	2.8	4.8	5.0(7)	
13.4 <sup>a</sup>	Ge–Ga	3.14(8)	2.507(2)	2.5(2)	4.7	6.6	6.5(8)	0.0044, 0.0095
	Ge–Si	0.86(8)	2.410(10)	0.0	2.8	4.8	6.5(8)	
	Ga–Ge	2.73(12)	2.489(4)	3.9(6)	6.1	8.0	5.0(7)	0.0184, 0.0288
	Ga–Si	1.27(12)	2.451(13)	0.0	2.8	4.8	5.0(7)	
30 <sup>b</sup>	Ga–Ga	0.86(11)	2.488(14)	0.0	2.4	4.4	10.1(9)	0.0146, 0.0112
	Ga–Si	3.14(11)	2.500(10)	0.0	3.0	5.0	10.1(9)	

<sup>a</sup> Fit range in *r*-space is 1.3–2.8 Å for both the Ge and Ga K-edges with FT range of 3–12 Å<sup>-1</sup>.

<sup>b</sup> Fit range in *r*-space is 1.3–2.5 Å for the Ga K-edge with FT range of 3–12 Å<sup>-1</sup>.

It is to be noted that the backscattering phases of Si and Ga or Ge are out of phase and their contributions significantly cancel out as clearly depicted by the data in figure 9. Comparisons of the magnitudes and the imaginary parts of the Fourier transforms for raw data, fit data, the contributions from the Ge-Ga and Ge-Si paths as well as the contributions from the Ga–Ge and Ga–Si paths for the specimen with x = 10.7are shown in figures 10(a)–(d). In all cases (x = 0, 10.7, 30) the raw and fit data are in satisfactory agreement despite the use of average distances for the Ge/Ga-Ga/Ge/Si paths. Examination of the fit results in table 1 reveals that the Ge-Ga/Ge and Ga-Ge/Ga distances for the Ba<sub>8</sub>Ga<sub>16</sub>Ge<sub>30</sub> are 2.506 and 2.495 Å, respectively. These values are in close agreement with the average frame work distance of 2.495 Å as determined based on neutron diffraction data (see section 2). It is to be noted that the Ga-Ge/Ga and the Ge-Ga/Ge distances are close to the sum of the covalent radii for Ga (1.26 Å) [39] and Ge (1.22 Å) [40]. Furthermore, the correlated Debye temperature for the Ge-Ga/Ge and Ga-Ge/Ga bonds of 401 (24) is consistent with previously reported value of 410 K [15] for n-type semiconducting material, which is also the case for our specimens. The correlated Debye temperature for the Ge-Ga/Ge and Ga-Ge/Ga bonds is about 55% greater than the Debye temperature associated with the Ga/Ge site atomic displacements based on temperature dependent single crystal Ba<sub>8</sub>Ga<sub>16</sub>Ge<sub>30</sub> neutron diffraction, which is 259 K for n-type material [29].

The results for the  $Ba_8Ga_{16}Si_{30}$  specimen show that on average, Ga has 0.9 Ga neighbors and 3.1 Si neighbors at distances of 2.488 and 2.500 Å, respectively. Within the

uncertainty in the data, the Ga-Ga and Ga-Si distances are similar. Nonetheless, these distances are intermediate to the Ga-Ga and Ga-Si distances of 2.52 and 2.43 Å, respectively, as derived based on the sum of the covalent radii for Ga (1.26 Å) and Si (1.17 Å) [40]. The Ga-Si distance for this specimen is also larger than the Ga-Si distance observed for the specimens with x = 7.5, 9.1, 10.7,and 13.4. The larger distance in the case of the specimen with x = 30 is consistent with the Ga edge shift to lower energy relative to all other specimens. The number of Ga neighbors is significantly less than what one would expect on the basis of a random distribution of Ga and Si on the 6c, 16i, and 24k crystallographic sites. This result indicates that only  $22\% \pm 3\%$  of the Ga neighbors is Ga compared to 35% based on a random distribution of Ga and Si on the three crystallographic sites. The lower percentage of Ga neighbors is consistent with the hypothesis that Ga atoms distribute on the framework crystallographic sites in a way to minimize the number of Ga-Ga bonds. The percentage of Ga neighbors in Ba<sub>8</sub>Ga<sub>16</sub>Si<sub>30</sub> ( $22\% \pm 3\%$ ), however, could be slightly larger than that previously reported for the Ba<sub>8</sub>Ga<sub>16</sub>Sn<sub>30</sub> composition  $(15\% \pm 5\%)$  [16]. As mentioned earlier, the correlated Debye temperature for the Ga-Ga bond in Ba8Ga16Si30 was constrained to the value of the correlated Debye temperature for the Ga-Ge bond in Ba<sub>8</sub>Ga<sub>16</sub>Ge<sub>30</sub> determined on the basis of our EXAFS spectra while that of the Ga-Si bond in Ba8Ga16Si30 bond was optimized during the fitting procedure. Accordingly, the correlated Debye temperature for the Ga-Si bond was estimated to be  $520\pm67$  K, about 55% greater than the Debye





**Figure 8.** Magnitude and imaginary part of the Fourier transforms of Ge K-edge  $k^2$ -weighted EXAFS of the raw data and the fit data of the Ge–Ga path (a) and magnitude and imaginary part of the Fourier transforms of Ga K-edge  $k^2$ -weighted EXAFS of the raw data and the fit data of the Ga–Ge path (b) for specimen with x = 0 (Ba<sub>8</sub>Ga<sub>16</sub>Ge<sub>30</sub>). The XAFS data were collected near the temperature of liquid nitrogen (~115 K). The FT range is 3.0–12.0 Å<sup>-1</sup> and the fit range in *r*-space is 1.3–2.8 Å for both the Ge and Ga data.

temperature associated with the Ga/Si atomic displacements determined based on temperature dependent single crystal  $Ba_8Ga_{16}Si_{30}$  neutron diffraction data, which is 336 K [30]. Clearly, the increase in the correlated Debye temperature relative to that associated with site disorder is similar for both the  $Ba_8Ga_{16}Si_{30}$  and  $Ba_8Ga_{16}Ge_{30}$  clathrates. Hence, we constrained the correlated Debye temperatures for the Ge–Si and Ga–Si paths in Si-substituted  $Ba_8Ga_{16}Ge_{30-x}Si_x$ specimens to the value of the correlated Debye temperature for the Ga–Si path in  $Ba_8Ga_{16}Si_{30}$ . It is to be noted that the inner potential parameter for the Ga–Ga and Ga–Si paths in this specimen is larger than that observed for the Ga–Ge and Ga–Si paths in other specimens. It is not uncommon to see variations in the reported values of Eo for the same X–Y pair of atoms in samples with different composition [41].

**Figure 9.** Magnitude (a) and imaginary part (b) of the Fourier transforms of Ga K-edge  $k^2$ -weighted EXAFS of the raw data, the fit data, along with the fit data for the Ga–Ga and the Ga–Si paths for specimen with x = 30 (Ba<sub>8</sub>Ga<sub>16</sub>Si<sub>30</sub>). The XAFS data were collected near the temperature of liquid nitrogen (~115 K). The FT range is 3.0–12.0 Å<sup>-1</sup> and the fit range in real space is 1.3–2.5 Å.

For the Si-substituted specimens, within the experimental uncertainty, the Ge-Ga/Ge and Ga-Ge/Ga distances remained unchanged from those of Ba8Ga16Ge30 regardless of the level of Si substitution in the range of 7.4 < x < 13.5. However, the Ge-Si distances of 2.41-2.43 Å for the Si-substituted specimens are significantly shorter than the Ge-Ga/Ge distance of Ba8Ga16Ge30 due, in part, to the smaller covalent radius of Si (1.17 Å). Furthermore, the Ga-Si distances (2.45–2.46 Å) for the Si-substituted specimens are also shorter than the Ga–Ge distance (2.50 Å) of Ba<sub>8</sub>Ga<sub>16</sub>Ge<sub>30</sub> as well as Ga–Si distance (2.50 Å) of Ba<sub>8</sub>Ga<sub>16</sub>Si<sub>30</sub> but are slightly greater than the sum of the covalent radii of Ga and Si, which is 2.43 Å. The smaller Ge-Si distance relative to the Ga-Si distance in the Si- substituted specimens is expected due to the smaller covalent radius of Ge relative to that of Ga. The changes in the type and number of neighbors to Ge and Ga are also important. The number of Ge-Si/Ga-Si bonds increased from 0.4/0.7, to 0.6/0.8, to 0.7/1.1 and 0.9/1.3 for Si substitution levels of 7.5, 9.1, 10.7 and 13.4, respectively.



**Figure 10.** Magnitude (a) and imaginary part (b) of the Fourier transforms of Ge K-edge  $k^2$ -weighted EXAFS of the raw data, the fit data, along with the individual fit data for the Ge–Ga and the Ge–Si paths for specimen with x = 10.7. Magnitude (c) and imaginary part (d) of the Fourier transforms of Ga K-edge  $k^2$ -weighted EXAFS of the raw data, the fit data, along with the individual fit data for the Ga–Ge and the Ga–Si paths for specimen with x = 10.7. Magnitude (c) and imaginary part (d) of the Fourier transforms of Ga K-edge  $k^2$ -weighted EXAFS of the raw data, the fit data, along with the individual fit data for the Ga–Ge and the Ga–Si paths for specimen with x = 10.7. The XAFS data were collected near the temperature of liquid nitrogen (~115 K). The FT range is 3.0–12.0 Å<sup>-1</sup> and the fit range in *r*-space is 1.3–2.8 Å.

Clearly, for each level of Si substitution, the number of Ga-Si bonds is greater than the number of Ge-Si bonds. This is to be expected since Ga in the Ba8Ga16Ge30 resides preferentially next to Ge rather than Ga and Si substitutes for Ge in the frame work structure. It is to be noted that the sum of the fractions of Ge-Si and Ga-Si bonds relative to the total number of Ge and Ga bonds, which is 8, are  $0.14 \pm 0.02$ ,  $0.18 \pm 0.02$ ,  $0.22 \pm 0.02$ , and  $0.27 \pm 0.02$  for Si substitution levels of 7.5, 9.1, 10.7 and 13.4, respectively. These fractions compare favorably with the fractions of the number of Si atoms relative to the total number of frame work atoms (Si + Ga + Ge), which are 0.16, 0.20, 0.23, and 0.29, respectively. The Ge-Ga/Ge and Ga-Ge/Ga distances remain unchanged upon Si substitution and those of Ge-Si and Ga-Si are smaller relative to those of Ge-Ga/Ge and Ga-Ge/Ga which indicate that the lattice contracts, as a result of Si substitution [7, 8], due to local bond contractions. These local bond contractions may lead to an abrupt change in the density of electronic states near the Fermi level and, thus, an increase in the Seebeck coefficient according to the Cutler–Mott relationship [38].

In table 1, we listed the static disorder as well as the total disorder (static + thermal) for the Ge–Ga, Ga–Ge, Ge–Si, and Ga–Si paths for each specimen. Since thermal disorder is temperature dependent, the total disorder was listed for

the two sets of data which were collected at 115 and 300 K. The static disorder for the Ge-Ga and Ga-Ge paths in Ba<sub>8</sub>Ga<sub>16</sub>Ge<sub>30</sub> were estimated to be 0.0020 and 0.0024  $\text{\AA}^2$ , respectively, and increased slightly in both cases upon Si substitution. The static disorder arises due to small differences in the bond lengths of atoms in the three framework crystallographic sites. However, as mentioned earlier in the experimental section, an attempt to optimize the static disorder for the Ge/Ga-Si paths yielded values very close to 0.0 but with a large error and, therefore, we constrained their values to 0.0 for all specimens with Si. The thermal disorder at each temperature is calculated by subtracting the static disorder which is temperature independent from the total disorder. The thermal disorder for each path at any temperature can also be calculated using the Debye model for lattice vibrations and the Debye temperatures determined from analysis of EXAFS spectra, namely, 401 and 520 K for the Ge/Ga-Ga/Ge and Ge/Ga-Si paths, respectively. For the Ba<sub>8</sub>Ga<sub>16</sub>Ge<sub>30</sub> specimen, the thermal disorder for the Ge/Ga-Ga/Ge path at 115 K and 300 K are estimated to be 0.0022 and 0.0042  $\text{\AA}^2$ , respectively. These thermal disorders remained unchanged upon Si substitution due to the fact that we constrained the Debye temperatures for these samples to those of the  $Ba_8Ga_{16}Ge_{30}$  specimen. The thermal disorders for the Ge/Ga–Si paths are also similar due to the fact that the Debye temperature was constrained to that of the  $Ba_8Ga_{16}Si_{30}$  specimen.

### 4. Summary

XAFS spectroscopy was used to investigate the effects of Si substitution in Ba<sub>8</sub>Ga<sub>16</sub>Ge<sub>30</sub> type I clathrates on the density of electronic states near the Fermi level and local atomic structures of Ga and Ge. Based on the XANES data, we show that the greatest decrease in the density of unoccupied states with p character occurred for the specimen with the highest power factor. Analysis of EXAFS spectra revealed that no change occurred in the coordination distances of the Ge-Ga/Ge and Ga-Ge/Ga bonds (~2.51 Å for both) with Si substitution for x = 7.5, 9.1, 10.7 and 13.4 in  $Ba_8Ga_{16}Ge_{30-x}Si_x$ . Furthermore, the coordination distance of the Ge-Si and Ga-Si bonds also remained unchanged with Si substitution at  $\sim$ 2.41 and  $\sim$ 2.45 Å, respectively. Furthermore, the number of Si neighbors for Ge and Ga increased with increase in the level of Si substation with the extent of increase is greater in the case of Ga than that of Ge at each level of Si substitution. These results indicate that Si substitution for Ge induces local distortions in the vicinity of Si which leads to contraction of the cubic lattice. In the case of the Ba<sub>8</sub>Ga<sub>16</sub>Si<sub>30</sub> specimen, we find that the number of Ga–Ga bonds is less than what one would expect on the basis of a random distribution of Ga and Si on the 6c, 16i, and 24k crystallographic sites. In addition, the Ga-Ga and Ga-Si distances are similar within the experimental uncertainties in the data. Based on these results, it is of interest to investigate framework doping leading to framework contractions on other clathrate types.

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