# Thermal conductivity of thermoelectric clathrates

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Transport properties of $Ba_8Ga_{16}Ge_{30}$ single-crystalline samples prepared with an excess of Ga are presented. The excess Ga does not only produces *p*-type transport properties but also a thermal conductivity ($\kappa$) that, unlike in any other $Ba_8Ga_{16}Ge_{30}$ samples reported in the literature, is similar to that of the iso-structural $Eu_8Ga_{16}Ge_{30}$ and $Sr_8Ga_{16}Ge_{30}$. These observations disagree with the commonly made assumption that $\kappa$ of $Eu_8Ga_{16}Ge_{30}$ and $Sr_8Ga_{16}Ge_{30}$ at very low temperatures is determined by phonons scattered from guest atom tunneling states, since such states are believed to be absent in $Ba_8Ga_{16}Ge_{30}$. Instead we propose that phonon charge carrier scattering must be considered in order to explain $\kappa$ at the low temperatures. The transport data also suggest that the resonant scattering, which dominates at intermediate temperatures, strongly depends on the charge carrier concentration.

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Clathrates have gained renewed attention due to their promising thermoelectric properties and potential for device application.[1–3] A large number of clathrate types and compositions exist and among them is the type-I clathrate with the formula $II_8III_{16}IV_{30}$. In these compounds the group-III and -IV elements (framework atoms) form a space-filling cage structure in which the group-II elements (guest atoms) are ionically bound.[4] The framework atoms form covalent bonds with a slightly distorted tetrahedral coordination environment. Electron density analysis has shown that each guest atom donates about two electrons to the framework and a valence-electron count gives 184 electrons per formula unit (f.u.) for 92 covalent bonds.[4] These clathrates are therefore expected to be intrinsic semiconductors, which is supported by band-structure calculations that predict band gaps from approximately 0.3 to 0.9 eV, depending on the composition and calculation method.[5,6] However, most reports in the literature show samples with metal-like and *n*-type properties although semiconducting properties were observed in two cases.[1,2] Zone refinement experiments followed by dopant concentration determinations indicate that the metal-like properties of $Ba_8Ga_{16}Ge_{30}$ stem from nonstoichiometry rather than chemical impurities.[7] Thus, the major contribution to the observed carrier concentration ($n$) comes from a III/IV content that deviates from the ideal 16/30 composition, where an excess of IV leads to *n*-type properties and an excess of III leads to *p*-type properties. Nevertheless, *p*-type properties have to date only been observed in slightly Sb-doped $Ba_8Ga_{16}Ge_{30}$ samples.[8] From the lattice thermal conductivity ($\kappa_L$) (Refs. 9 and 10) of $Sr_8Ga_{16}Ge_{30}$ and $Eu_8Ga_{16}Ge_{30}$ [$(Sr/Eu)_8Ga_{16}Ge_{30}$] and the ultrasonic attenuation[11] of $Sr_8Ga_{16}Ge_{30}$ it is believed that these two clathrates fulfill the phonon glass-electron crystal concept,[12] which is a guideline in the search for materials with enhanced thermoelectric properties. Neutron-diffraction experiments have shown that the degree of positional disorder on the guest atom sites is much smaller in $Ba_8Ga_{16}Ge_{30}$ than in $(Sr/Eu)_8Ga_{16}Ge_{30}$ (Ref. 13), indicating a lower density of tunneling states in the former one. This has been taken as evidence for the $\kappa_L \propto T^{\alpha}$ ($\alpha \approx 2$) dependence observed in $(Sr/Eu)_8Ga_{16}Ge_{30}$, but absent in *n*-type $Ba_8Ga_{16}Ge_{30}$, being due to scattering of the heat-carrying phonons by tunneling states.

In the first part of this paper we focus on the electrical transport properties of single-crystalline samples grown in an excess of Ga and confirm the hypothesis that Ga-rich samples have *p*-type properties. In the second part we show that the magnitude and temperature ($T$) dependence of $\kappa_L$ for *p*-type $Ba_8Ga_{16}Ge_{30}$ samples is much more similar to the ''glasslike'' $\kappa_L$ of $(Sr/Eu)_8Ga_{16}Ge_{30}$ than to $\kappa_L$ of *n*-type $Ba_8Ga_{16}Ge_{30}$. The large difference in the low-temperature $\kappa_L$ data for different $Ba_8Ga_{16}Ge_{30}$ samples can be attributed to different phonon charge carrier scattering rates. These results question whether the scattering of phonons from tunneling states is responsible for the observed low temperature $\kappa_L(T)$ of $(Sr/Eu)_8Ga_{16}Ge_{30}$.[9,10,13,14]

As starting material we have used the bottom section of a zone-refined $Ba_8Ga_{16}Ge_{30}$ ingot.[7] The large single-crystalline samples were obtained by recrystallizing nonstochiometric polycrystalline $Ba_8Ga_{16}Ge_{30}$ from molten Ga. The ingot was placed in Ga-flux (99.999%) in a corundum crucible sealed inside a stainless-steel bomb under argon and subsequently heated in a resistance furnace up to 1100 °C over 5 h. The reaction was held at 1100 °C for 1 h, cooled to 970 °C over 8 h, cooled to 950 °C over 12 h, cooled to 700 °C over 100 h, and finally cooled to room temperature over 24 h. The sample was isolated from the flux by soaking crystals in concentrated HCl for 12 h at 45 °C to remove the molten Ga. To check if any elemental Ga was left in the sample, the magnetic susceptibility was measured. No superconductivity was observed down to 1.8 K. The impurities in the purified crystal were identified (in ppm) by glow discharge mass spectrometry (Shiva Technologies): B, $<0.003$; Na, 0.025; Mg, 0.005; Al, 0.007; Si, 0.035; P, 0.002; S, 0.045; Cl, 0.16; K, 0.01; Ca, $<0.2$; Cr, 0.002; Fe, 0.04; Cu, 0.07; Zn, 0.2; As, $<0.02$; Se, $<0.01$; Sr, 1.3; In, $<0.02$. A reference sample was prepared with a similar synthesis procedure but from starting materials as purchased (Cerac). Stoichiometric

 

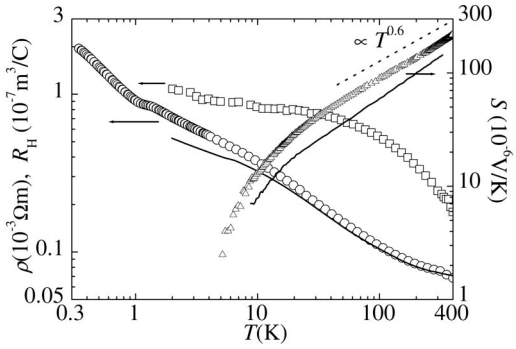


FIG. 1. Electrical transport properties for the pure $Ba_8Ga_{16}Ge_{30}$ sample and the reference sample. Electrical resistance ($\rho$) (circles) and Hall coefficient ($R_H$) (squares) relate to the left abscissa, thermopower ($S$) (triangles) to the right abscissa. Solid curves are for the reference sample.

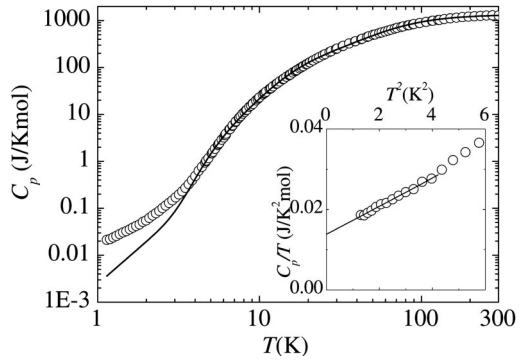


FIG. 2. Specific heat ($C_p$) for the pure $Ba_8Ga_{16}Ge_{30}$ sample as function of temperature ($T$). The solid line is a model fit to data above 5 K. The inset shows $C_p(T)/T$ as function of $T^2$, and the solid line represents a linear fit in the range 1.5 $K^2$ to 4 $K^2$.

amounts of Ba (99.7%), Ge (99.999%), and a large excess of Ga (99.999%) were mixed to give a final reaction mixture of 75 wt % of Ga.

Figure 1 shows the electrical properties of both the pure sample and the reference sample. In the whole temperature range the resistivity ($\rho$) and Hall coefficient ($R_H$) decrease monotonically with increasing temperature, but at approximately 1.5 K a kink in $\rho(T)$ is observed. $\rho$(2 K) for the pure sample is approximately 35% higher than for the reference sample, but as the temperature is increased the difference is diminished. The Hall resistivity as a function of the magnetic field was measured at 2 K and at 300 K for both samples (not shown), and is linear and positive in the measured range (up to 9 T). This indicates that the majority carriers are holes. The corresponding carrier concentrations ($n$) in a one-band model with a Hall scattering factor of unity are (reference sample in parentheses); $n(2\,\mathrm{K})=0.069$/f.u. (0.12/f.u.) and $n(300\,\mathrm{K})=0.29$/f.u. (0.48/f.u.). The purer sample has the lower $n$ and the difference in $n$(2 K) is of the same order of magnitude as the amount of impurities of the most impure element in the reference sample (Ba, $8\times0.3\%=0.024$ impurities/f.u.). From $\rho$(2 K) and $n$(2 K) we estimate an extremely low mean free path of the charge carriers ($l_e$) of approximately 1.2 Å. However, this value is a lower limit, since band-structure calculations predict a Hall scattering factor below unity.[6] Fits to either $\rho(T)$ or $R_H(T)$ with the formula for perfect intrinsic semiconductors, $\ln[\rho(T),R_H(T)] = \ln[\rho_0,R_{H0}(T)]+\varepsilon_G/(2k_BT)$, where $\varepsilon_G$ is the band gap, do not result in any well defined $\varepsilon_G$. This suggests that the charge carriers are excited from impurity-like bands that might originate from the disorder on the Ga/Ge sites. The thermopower ($S$) for both the pure and the reference sample is positive and increases with increasing temperature in the whole temperature range. Above 70 K both samples follow approximately a $T^{0.6}$ dependence and the deviation from the expected $S\propto T$ is explained by a smooth increase of $n$ with increasing temperature as can be seen from $R_H(T)$. Using the Mott relation, assuming that the transport properties are dominated by phonon scattering and that the carriers are degenerate, the band effective mass ($m_B^*$) of the charge carriers can be estimated from $S$ and $n$. At 300 K we find $m_B^* = 3.6m_0$, where $m_0$ is the free-electron mass. Using values of $S$ and $n$ down to 100 K only changes $m_B^*$ slightly, confirming the validity of the above assumptions.

The temperature dependence of the specific heat ($C_p$) of the pure sample is shown in Fig. 2 from 1.1 to 300 K. Above 5 K the electronic contribution to $C_p(T)$ is negligible and the lattice contribution can be described very well with a combined Debye and Einstein model.[9] The corresponding Debye ($\Theta_D$) and Einstein ($\Theta_E$) temperatures are $\Theta_D=324(4)$ K, $\Theta_{E1}=78(2)$ K, $\Theta_{E2}=38(1)$ K, and in good agreement with previous results.[14] The number of Debye and Einstein atoms are $N_D=42.8$ (6), $N_{E1}=9.7$ (5), and $N_{E2}=1.5$ (5), respectively. The inset of Fig. 2 shows that $C_p(T)/T$ varies almost linearly with $T^2$ between 1.3 $K^2$ and 6 $K^2$ which agrees well with $R_H(T)$ varying weakly in that temperature range. A linear fit to $C_p/T$ vs $T^2$ between 1.5 $K^2$ and 4 $K^2$ gives $\Theta_D = 311(10)$ K, in agreement with the modeling of $C_p(T)$ above 5 K. Combining the Sommerfeld coefficient $\gamma = 14\,\mathrm{mJ/(K^2\,mol)}$ with $n$(2 K) we find a density of states effective mass $m_{\mathrm{DOS}}^*=3.1m_0$. This is slightly smaller than $m_B^*$, but $m_{\mathrm{DOS}}^*$ and $m_B^*$ are only the same in the free-electron model and small deviations can be expected for real systems.

Figure 3 shows the temperature dependence of $\kappa_L$ of the two samples presented in this report (V and VI in the plot), obtained by subtracting the charge carrier contribution to $\kappa$ estimated using the Wiedemann-Franz law. $\kappa_L(T)$ of the pure sample was used in an earlier study.[15] In Fig. 3 we have also included $\kappa_L(T)$ of several clathrates from the literature $Ba_8Ga_{16}Ge_{30}$,[13,16,17] $Sr_8Ga_{16}Ge_{30}$,[9] $Eu_8Ga_{16}Ge_{30}$,[13] and an $n$-type $Ba_8Ga_{16}Ge_{30}$ sample taken from the zone-refined bar in the vicinity of where the starting material for the present study was taken from.[18] For the pure sample $\kappa_L(T)$ is proportional to $T^{1.5}$ from 0.23 to 1.5 K followed by a small kink and a broad dip in the range from approximately 10 to 50 K. In the measured range, $\kappa_L(T)$ of the reference sample tracks that of the pure sample closely, and the temperature dependence of $\kappa_L$ resembles that of $(Sr/Eu)_8Ga_{16}Ge_{30}$ much more than that of $n$-type $Ba_8Ga_{16}Ge_{30}$. $\kappa_L(T)$ of $(Sr/Eu)_8Ga_{16}Ge_{30}$ has earlier been compared to that of amorphous solids and modeled by a combination of scattering from tunneling states at low temperature and resonant scat-

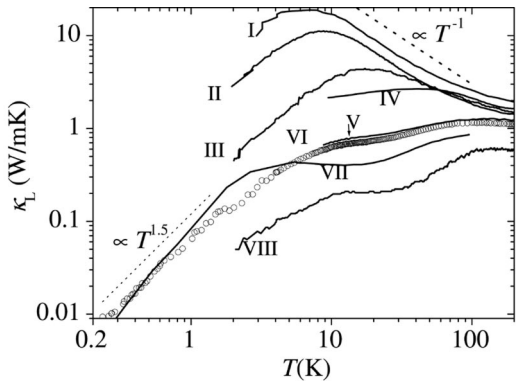


FIG. 3. Lattice thermal conductivity ($\kappa_L$) for the pure and reference $Ba_8Ga_{16}Ge_{30}$ sample. Data are also included for other $Ba_8Ga_{16}Ge_{30}$ samples published in literature. I: Polycrystal (after digitalization the data were corrected for the electronic contribution using the electrical resistivity) (Ref. 16). II: The sample comes from the vicinity in the zone-refined bar from which the pure sample was recrystallized. III: Single crystal (Ref. 13). IV: (Ref. 17). V: Reference sample (almost superimposed on the pure sample). VI: Pure sample. VII: $Sr_8Ga_{16}Ge_{30}$ polycrystal (Ref. 9). VIII: $Eu_8Ga_{16}Ge_{30}$ single crystal (Ref. 13).

tering, both related to the guest atoms, and Rayleigh scattering which accounts for different types of scattering mechanisms at higher temperatures.[9,10,14] In order to explain the large difference in $\kappa_L(T)$ between $Ba_8Ga_{16}Ge_{30}$ and $(Sr/Eu)_8Ga_{16}Ge_{30}$ it has been argued, on the basis of neutron-diffraction experiments, that tunneling states do not exist in $Ba_8Ga_{16}Ge_{30}$.[13] Although it cannot be excluded that the density of tunneling states is sample dependent, it appears more probable that the low temperature $\kappa_L(T)$ of $(Ba/Sr/Eu)_8Ga_{16}Ge_{30}$ is determined by phonons being scattered on charge carriers. We base this interpretation on two facts. First, the small kink in $\kappa_L(T)$ of the pure sample around 2 K is also observed in $\rho(T)$ at slightly lower temperature. This suggests that $n(T)$ does not increase smoothly around that temperature leading to a nonuniform increase in $\kappa_L(T)$. Second, we list in Table I various parameters related only to the charge carriers. When compared to Fig. 3 it is seen that the samples with the lowest $l_e$ and largest $m_B^*$ have the lowest $\kappa_L$.

It was shown by Ziman[19] that heat-carrying phonons can only be scattered from degenerate charge carriers if the phonon wave number ($q$) is below $2k_F$, where $k_F$ is the Fermi wave vector. This corresponds to a characteristic temperature ($T^*$) of approximately 15 K for the pure sample above which the phonon charge carrier scattering rate rapidly diminishes. If the carriers are degenerate then $\kappa_L \propto T^2/(\varepsilon_{\rm def}^2 m^{*2})$ below $T^*$, where $\varepsilon_{\rm def}$ is the deformation potential of the phonon-electron interaction.[19] The magnitude of $\varepsilon_{\rm def}$ has to be of the order 0.5 eV to obtain the $\kappa_L$ observed for the $Ba_8Ga_{16}Ge_{30}$ samples at the lowest temperatures. This value is comparable to what is obtained for other semiconductors with similar $n$, and it shows that phonon charge-carrier scattering cannot be neglected. In the theory by Ziman it is assumed that $ql_e \gg 1$. As can be seen from Table I this is not fulfilled for the $Ba_8Ga_{16}Ge_{30}$ samples presented in Fig. 3. A recent theoretical study on disordered/amorphous systems has shown that when a fraction of the charge carrier scatterers does not vibrate with the lattice, a substantial increase, when compared to the Ziman model, in the phonon charge-carrier scattering rate is expected when $0 < ql_e < 1$.[20] In the case of the type-I clathrates it is very likely that the low mobility of the charge carriers is a result of scattering on the guest atoms, which vibrate independently of the lattice. This leads to an increased phonon charge-carrier scattering rate as $l_e$ decreases. Numerical investigations of the expressions for the relaxation time given in Ref. 20 show that an approximate $\kappa_L \propto T^x$ dependence, with $1 < x < 2$, can be expected, but a general power law is difficult to predict because several parameters affect $x$. This, together with the temperature dependence of $n$ is consistent with the observed $T^{1.5}$ dependence. In terms of the phonon charge-carrier scattering model the variation of $\kappa_L$ between different $Ba_8Ga_{16}Ge_{30}$ samples at lowest temperatures can be explained by a combination of differences in both $l_e$, $m^*$, and to a lesser extent $n$, where a small $l_e$ and large $m^*$ lead to a low $\kappa_L$.

Above $T^*$ ($\sim$15 K) the phonon charge-carrier scattering rate is diminished and the difference in $\kappa_L$ between the $Ba_8Ga_{16}Ge_{30}$ samples must have another origin. The broad dip in $\kappa_L(T)$ of $p$-type $Ba_8Ga_{16}Ge_{30}$ is also observed for $(Sr/Eu)_8Ga_{16}Ge_{30}$ and is ascribed to resonant scattering of

TABLE I. Different charge-carrier parameters for the $Ba_8Ga_{16}Ge_{30}$ samples plotted in Fig. 3. The charge-carrier mean free path ($l_e$) and the band effective mass ($m_B^*$) are calculated from the electrical resistivity at 2 K ($\rho_{2\,\rm K}$), the thermopower ($S$), and from the charge-carrier concentration ($n$). $q_{\rm dom,2\,K}$ is the dominating phonon wave number at 2 K. For sample IV no electrical transport data are available. Sample V (reference sample) has similar properties to sample VI.

| Samples | $n$ ($10^{27}e^-/\rm m^3$) | $l_e$ (Å) | $m_B^*$ ($m_0$) | $q_{\rm dom,2\,K} l_e$ |
|---|---|---|---|---|
| I[a] | 1.1 | $\sim$300 | 1.8 | $\sim$10 |
| II | 0.84 | 30 | 2.2 | 1.0 |
| III[b] | $\sim$1–1.3 | $\sim$28–33 | $\sim$2.5–3.0 | $\sim$1.0 |
| VI | 0.069 | 1.2 | 3.6 | 0.04 |

[a]Reference 16.

[b]No exact $n$ is given in Ref. 13.

phonons from the guest atoms.[1,9,10,13,14,17] The magnitude of $\Theta_{E1}$ and $\Theta_{E2}$ supports that this is also the case for *p*-type $Ba_8Ga_{16}Ge_{30}$. The $\kappa_L \propto T^{-1}$ dependence from approximately 10 to 100 K in some of the clathrates is usually interpreted as a sign of anharmonic phonon-phonon umklapp scattering.[9] However, such a temperature dependence would only be expected above $\Theta_D$ and at temperatures below $\Theta_D$ a much more rapid and exponential decrease is expected. At the same time the phonon-phonon umklapp scattering relaxation rate is too large for playing any significant role in determining $\kappa_L$ in the clathrates unless the thermal motion of the atoms is extremely anharmonic. Instead we believe that the $\kappa_L \propto T^{-1}$ behavior of the *n*-type $Ba_8Ga_{16}Ge_{30}$ samples in the range from approximately 10 to 100 K can be interpreted by the presence of resonance scattering, but with a coupling between the phonons and the resonant scatterers which is lower than in $(Sr/Eu)_8Ga_{16}Ge_{30}$ or *p*-type $Ba_8Ga_{16}Ge_{30}$. We base this interpretation on the expression for the mean free path of resonant phonon scattering ($l_{res}$) (see, e.g., Ref. 9). In the limit where the phonon frequency ($\omega$) is lower than the resonance frequency $l_{res}^{-1} \propto \omega^2 T^2$, leading to $l_{res}^{-1} \propto T^4$ in the dominant phonon approximation. If it is also assumed that $C_p \propto T^3$, this leads to $\kappa_L \propto T^{-1}$. In $Ba_8Ga_{16}Ge_{30}$ $\Theta_E$ is of the order 80 K and below this temperature a $\kappa_L \propto T^{-1}$ dependence due to resonance scattering can be expected and is also confirmed by more detailed numerical calculations with the whole expression for $l_{res}$.

There are several possible explanations for the difference in the resonance coupling between different $Ba_8Ga_{16}Ge_{30}$ samples. One is that the charge carriers screen the ionically bound guest atoms and that the strength of the resonant coupling is partly determined by the sign and magnitude of *n*. Another explanation is that the guest-framework bond is affected by *n* and thereby influences the coupling. Indeed the band structure of $Ba_8Ga_{16}Ge_{30}$ shows that the conduction band consists of framework antibonding states hybridized with guest atom states, whereas the valence band is almost entirely framework bonding states.[6] The effect of varying *n* on the resonant coupling is difficult to predict from the band structure alone, but in any case the combination of thermal and charge carrier transport data suggest that the band structure plays an important role.

In conclusion, the synthesis of $Ba_8Ga_{16}Ge_{30}$ in Ga-flux leads to semiconducting samples with *p*-type properties. It has been shown that $m_B^*$ in *p*-type $Ba_8Ga_{16}Ge_{30}$ is larger than in *n*-type $Ba_8Ga_{16}Ge_{30}$ but similar to $m_B^*$ in *n*-type $(Sr/Eu)_8Ga_{16}Ge_{30}$ ($\sim 3-4 m_0$).[2,13,14,16] These results are in agreement with band-structure calculations[6] that indicate a stronger hybridization of the unoccupied guest atom *d* states with the framework states in $Ba_8Ga_{16}Ge_{30}$ than in $(Sr/Eu)_8Ga_{16}Ge_{30}$. This leads to similar valence bands for all three compounds, which in the case of $(Sr/Eu)_8Ga_{16}Ge_{30}$, furthermore, are similar to the conduction bands. For $Ba_8Ga_{16}Ge_{30}$ the conduction band is predicted to be different.

We have argued that phonon charge-carrier scattering cannot be neglected at the lowest temperatures for $Ba_8Ga_{16}Ge_{30}$. $\kappa_L(T)$ of *p*-type $Ba_8Ga_{16}Ge_{30}$ being similar to $\kappa_L(T)$ of $(Sr/Eu)_8Ga_{16}Ge_{30}$ disagrees with the commonly made assumption that $\kappa_L$ of $(Sr/Eu)_8Ga_{16}Ge_{30}$ is determined by scattering from guest atom tunneling states.[9,10,13,14] The differences in $\kappa_L$ between different *n*-type $Ba_8Ga_{16}Ge_{30}$ samples are qualitatively explained in terms of phonon charge-carrier scattering and the varying parameters $m^*$ and $l_e$. This model does not explain the difference in $\kappa_L$ between *p*- and *n*-type $Ba_8Ga_{16}Ge_{30}$ above 15 K. However, the transport data, in combination with band-structure calculations, suggest that the band structure plays a large indirect role on the coupling of the resonant scatters and the phonons.

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