Glasslike vs. crystalline thermal conductivity in carrier-tuned Ba$_x$Ga$_{16}$X$_{30}$ clathrates (X = Ge, Sn)

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(Dated: June 18, 2018)

The present controversy over the origin of glasslike thermal conductivity observed in certain crystalline materials is addressed by studies on single-crystal x-ray diffraction, thermal conductivity $\kappa(T)$ and specific heat $C_p(T)$ of carrier-tuned Ba$_x$Ga$_{16}$X$_{30}$ (X = Ge, Sn) clathrates. These crystals show radically different low-temperature $\kappa(T)$ behaviors depending on whether their charge carriers are electrons or holes, displaying the usual crystalline peak in the former case and an anomalous glasslike plateau in the latter. In contrast, $C_p(T)$ above 4 K and the general structural properties are essentially insensitive to carrier tuning. We analyze these combined results within the framework of a Tunneling/Resonant/Rayleigh scatterings model, and conclude that the evolution from crystalline to glassy $\kappa(T)$ is accompanied by an increase both in the effective density of tunnelling states and in the resonant scattering level, while neither one of these contributions can solely account for the observed changes in the full temperature range. This suggests that the most relevant factor which determines crystalline or glasslike behavior is the coupling strength between the guest vibrational modes and the frameworks with different charge carriers.

I. INTRODUCTION

The understanding of thermal conductivity behavior $\kappa(T)$ is of direct interest to any research involving the discovery, design and development of materials for thermoelectric conversion applications, where $\kappa(T)$ should be as small as possible, while at the same time thermopower $S(T)$ and electrical conductivity $\sigma(T)$ should be large. In the semiclassical theory for electron and phonon transport several mechanisms are known as contributors to heat conduction/phonon scattering in a material, consequently affecting its overall thermal conductivity.

In metals, heat conduction by charge carriers is the largest contribution, and is well described by the Wiedemann-Franz law $\kappa_c = L_0 T$, which directly relates the carrier thermal conductivity $\kappa_c$ with an appropriate Lorentz number $L \sim 2 - 3 \times 10^{-8}$ WΩ/K$^2$, the electrical conductivity $\sigma$ and the temperature $T$. Due to their typically large charge carrier densities $n_c$, metals have large $\sigma(n_c,T)$ and thus large $\kappa_c$ in the range of 50–500 W/m K at room temperature.

Conversely, semi-metallic, semi-conducting and insulating compounds have low $n_c$ and $\sigma(T)$, therefore small and often negligible $\kappa_c(T)$ and the overall heat conduction behavior $\kappa(T)$ near room temperature is in the range of 10 – 50 W/m K, governed mostly by contributions $\kappa_L(T)$ arising from the crystal lattice. At $T \to 0$, $\kappa(T) \to 0$ from basic thermodynamic principles, so within the first few Kelvins $\kappa(T)$ increases quickly as a power law $T^r$, with $1 \leq r \leq 3$ depending on which phonon scattering mechanisms dominate at low temperatures. At higher temperatures the phonon scattering is generally described as governed mostly by umklapp processes, for which the Debye approximation approach shows a decrease with a $T^{-1}$ dependence. Therefore, at some intermediate temperature usually around $10–50$ K, a characteristic “crystalline peak” is observed in $\kappa(T)$ for common compounds, due to the crossover from one regime to another.

The peak usually appears equally in polycrystalline materials since grain boundary scattering is in general a minor contribution unless the average grain size becomes very small or the temperature very low. However, glasses are an exception to the above because of two basic factors: the very low mean free path for both electrons and phonons, and the presence of low-energy tunnelling states (TS), i.e., different localized potential minima for atomic positions in their amorphous distribution of nuclei. This class of materials shows extremely low heat conduction and a universal behavior of $\kappa(T)$: the lowest temperature behavior (up to $\sim 1$ K) rises as $T^2$ due to scattering by the tunnelling states, then levels off as a characteristic intermediate temperature plateau (attributed to Rayleigh scattering). Above $\sim 20$ K it resumes a slow increase, until roughly levelling off again at higher temperatures.

In more recent years, the search for new and potentially useful thermoelectric materials has led to the discovery of compounds that not only have unusually low thermal conductivity, but whose general behavior resembles that of a glassy material despite the fact that they are true (albeit disordered) crystalline lattices. A prominent example is the intermetallic compound Sr$_8$Ga$_{15}$Ge$_{30}$, with a filled type-I clathrate structure (albeit disordered) crystalline lattice. A model was proposed

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FIG. 1: (Color online) The two cages of the type-I clathrate structure adopted by Ba$_{8}$Ga$_{16}$Ge$_{30}$. If we consider the cage “construction unit” as 4 atoms connected in zig-zag from top to bottom, then the larger $X_{24}$ cage (left) is made of 6 such units and the smaller $X_{20}$ cage (right) is made of 5 units.

to explain this material’s glasslike behavior, based on the idea that TS exist for the Sr(2) guest ion in the $X_{24}$ cage to which it is rather loosely bound because of an ion-to-cage size mismatch. A combination of phonon scattering by TS, resonant scattering on large, Einstein-like localized vibration modes (guest rattling) and Rayleigh scattering was used to adequately reproduce the experimental $\kappa(T)$ behavior (henceforth we will refer to this combination as the TRR model). Later investigations amply demonstrated a splitting of the Sr(2) site into four off-center positions, among which the ions could indeed tunnel.

As other clathrate compounds started being investigated, the TRR model was challenged by at least two other models. One proposes that the tunnelling states are not required, only an off-center vibration of the guest ions and another proposes that the guest ions don’t play a major role at all at low temperatures, but rather it is the phonon scattering on charge carriers that leads to the glasslike behavior.

In this work we address the issue by performing single crystal x-ray diffraction (SCXRD), thermal conductivity $\kappa(T)$ and heat capacity $C_p(T)$ experiments on Ba$_8$Ga$_{16}$Sn$_{30}$ (BGS) and Ba$_8$Ga$_{16}$Ge$_{30}$ (BGG) crystals, which have been tuned through the crystal growth process to display n-type or p-type majority charge carriers as a result of small imbalances in their Ga:Ge or Ga:Sn ratios. By analyzing the differences and similarities between the behaviors of these samples, we can test the applicability of the various models proposed to explain the origin of unusual glasslike behavior, in this case observed for p-type samples whereas the n-type samples show the normal crystalline peak.

FIG. 2: (Color online) Irregular cage of the type-VIII clathrate structure adopted by Ba$_8$Ga$_{16}$Sn$_{30}$. The four smaller cage spheres represent the $8c$ site, preferentially occupied by Ga atoms.

TABLE I: Average Ba:Ga:X content (X = Ge, Sn) in the four measured crystals as determined by electron-probe microanalysis.

| Sample | Starting Flux Composition | Crystal Composition |
|--------|--------------------------|--------------------|
| n-BGS  | 8 : 16 : 60              | 8.0 : 15.98 : 30.02|
| n-BGG  | 8 : 38 : 34              | 8.0 : 15.94 : 30.06|
| p-BGS  | 8 : 38 : 30              | 8.0 : 16.14 : 29.86|
| p-BGG  | 8 : 38 : 30              | 8.0 : 16.10 : 29.90|

II. EXPERIMENTAL DETAILS

Growth details of the batches used in this work are described in previous papers. Single crystalline polyhedrons of 3-10 mm in diameter were obtained by a self-flux method. The carrier type is tuned by choosing Ga or Sn flux in the case of BGS or by adjusting the relative Ge content in the initial mix with Ga flux in the case of BGG. The batch name, flux composition and crystal composition determined by a JEOL JXA-8200 electron-probe microanalyzer (EPMA) are summarized in table. The composition values are averages over 10 regions of each crystal, although there are random fluctuations of up to ±0.1 throughout the crystals. The values shown for the p-BGG sample should be considered a correction to those published in refs. since this was a more careful evaluation made on the same batch. As expected from charge balance principles, Ga-rich samples show p-type carriers while Ge-rich samples show n-type carriers.

Thermal conductivity experiments were performed using a steady-state method on home-made systems, in the range of 0.3-300 K (BGG) and 4-300 K (BGS), although reliable data is only obtainable up to about 150 K. At higher temperatures, thermal losses by radiation and wire conduction prevent the correct measurement of the intrinsic sample properties. The electronic contribution
III. EXPERIMENTAL RESULTS

A. Thermal Conductivity

The lattice thermal conductivity $\kappa_L(T)$ of all four samples is shown in Fig. 3 (symbols are as-measured experimental data points and solid lines represent fits to the data by the TRR model which will be detailed in the Discussion section). At 100 K and above (not shown), $\kappa_L(T)$ for BGS is roughly half that of BGG (about 1 and 2 W/m K respectively). This can be understood as a consequence of three main factors: (i) if the rattling of the guest ions is the main contributor to the unusually high phonon scattering level in these materials, the larger cage size in BGS leads to larger rattling of the guest ions; (ii) in the BGS unit cell all 8 guest ions vibrate with equal intensity (single crystallographic site for Ba in the Type-VIII clathrate structure), while in BGG only the 6 guest ions inside the $X_{24}$ cages show large rattling; and (iii) the heavier Sn atoms produce lower frequency phonons, which are more easily scattered.

Below 100 K, each sample behaves quite differently, depending more on the carrier type than on the compound. The two n-type samples increase towards a peak, while the p-type samples remain at a plateau, smaller by a factor of 3 – 4 in value than the n-type counterparts near the peak. Below 10 K, $\kappa_L(T)$ for all samples decreases fast and, in the case of BGG which was measured to lower temperatures, a gradual crossover to a $T^2$ regime is clearly observed. This implies a phonon mean free path inversely proportional to frequency which is the expected dependence when phonon scattering by tunnelling states is dominant. The $T^2$ behavior contrasts with a previously reported result showing a $T^{1.5}$ dependence for p-type BGG.\(^{15}\)

B. Heat Capacity

The data points in Figs. 3a and 3b show the as-measured specific heats $C_p(T)$ for the BGS and BGG
samples respectively, plotted as $C_p/T^3$ vs. $T$. This plotting style emphasizes the contributions of localized vibrations of guest atoms (Einstein oscillators), which appear as pronounced peaks over a “background” contribution of a Debye solid. For these samples, the charge carrier contribution is negligible above $\sim 4$ K, but responsible for the $T^{-2}$ upward curvature upon cooling below this temperature. A more traditional plot of $C_p/T$ vs. $T^2$ below $4$ K (not shown) is used to estimate with good accuracy the Sommerfeld coefficient $\gamma$ of the charge carriers and the Debye temperature $\Theta_D$ of the 46 framework atoms, and then subtract the host contribution $C_h$ (dotted lines) in order to isolate the Einstein-like contribution $C_g$ of the guest ions (dash-dotted peak).

Contrary to the heat transport data, in both BGS and BGG the heat capacity data show the same behavior above $\sim 4$ K for different carrier types. This result demonstrates there is no fundamental change in the entropic properties of these compounds within the range of deviations from stoichiometry studied. If the rattling behavior of the guest ion is not significantly changed for different carrier types in the framework, then it should be the coupling between the guest vibration and the frameworks with different carriers that changes. In other words, frameworks with holes have their phonon modes more effectively scattered by the Ba vibration than those with electrons.

### C. Single-Crystal X-Ray Diffraction

Tables II and III summarize the refinement results made for room temperature SCXRD data of n-BGS and p-BGS respectively. The anomalously large isotropic thermal parameter $B_{eq}$ of the Ba site compared to the Ga/Sn sites is a signature of the enhanced vibration (rattling) of the guest ion in the oversized cage, however, no relevant difference is observed between the crystals.

The resulting sets of data do not allow a detailed composition analysis for comparison with EPMA results, because the R factor was insensitive to occupation probability within deviations of $\pm 0.2$ from stoichiometry, but the framework sites show consistent preferential occupations for Sn(1) and Sn(2) in the respective 12d and 2a crystallographic sites, while Ga(4) has the preferential occupation of the 8c site (in accordance with the idea that the smaller Ga atom should more easily occupy the site with smaller bond distances between neighbors) and the 24g site remains more randomly occupied by Sn(3) and Ga(3). This is true for crystals with both types of carriers, the only consistent and relevant difference we could find in these refinements was a larger relative occupation of the 2a site by Ga(2) for the p-BGS samples (the top atom in Fig. 2). This could be where the “extra” Ga ions prefer to enter in Ga-rich samples, but whether or not this can have any influence on the overall guest/framework coupling would require more detailed investigation.

### IV. DISCUSSION

We now present and discuss the models used to analyze the data in Figs. 3 and 4. The specific heat is expressed as a sum of 3 main contributions:

$$C_p = C_c + C_D + C_E,$$  \hspace{1cm} (1)

where $C_c = \gamma T$ is the electronic specific heat of the charge carriers.

$$C_D = \frac{12\pi^4 N_D k_B}{5} \int_0^{\Theta_D/T} \frac{x^4 e^x dx}{(e^x - 1)^2}$$  \hspace{1cm} (2)

### TABLE II: Summary of crystallographic parameters from the structural refinement of a n-type Ba$_4$Ga$_8$Sn$_{30}$ single crystal. Space group $F\bar{4}3n$ (No. 217), $a = 11.586(1)$ Å, $Z = 1$, $R = 0.009$, $R_w = 0.009$, $B_{eq} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j a_j = 1.07(2)$.

| Atom     | site | $x$     | $y$     | $z$     | $B_{eq}$ (Å$^2$) | occupancy |
|-----------|------|---------|---------|---------|-----------------|-----------|
| Ba(1)     | 8c   | 0.68490(5) | 0.31510(5) | 0.31510(5) | 3.25(2) | 1 |
| Ga(1) / Sn(1) | 12d | 0.5000 | 0.0000 | 0.2500 | 1.69(2) | 0.152(16) / 0.848(16) |
| Ga(2) / Sn(2) | 2a | 0.5000 | 0.5000 | 0.5000 | 0.90(3) | 0.233(26) / 0.767(26) |
| Ga(3) / Sn(3) | 24g | 0.41565(4) | 0.14836(4) | 0.41565(4) | 1.308(14) | 0.315(10) / 0.682(10) |
| Ga(4) / Sn(4) | 8c | 0.36577(6) | 0.36577(6) | 0.36577(6) | 1.07(2) | 0.707(12) / 0.293(12) |

### TABLE III: Summary of crystallographic parameters from the structural refinement of a p-type Ba$_4$Ga$_8$Sn$_{30}$ single crystal. Space group $F\bar{4}3n$ (No. 217), $a = 11.587(1)$ Å, $Z = 1$, $R = 0.0218$, $R_w = 0.0157$, $B_{eq} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j a_j = 1.07(2)$.

| Atom     | site | $x$     | $y$     | $z$     | $B_{eq}$ (Å$^2$) | occupancy |
|-----------|------|---------|---------|---------|-----------------|-----------|
| Ba(1)     | 8c   | 0.68307(8) | 0.31493(8) | 0.31493(8) | 3.25(2) | 1 |
| Ga(1) / Sn(1) | 12d | 0.5000 | 0.0000 | 0.2500 | 1.69(2) | 0.152(16) / 0.848(16) |
| Ga(2) / Sn(2) | 2a | 0.5000 | 0.5000 | 0.5000 | 0.90(3) | 0.233(26) / 0.767(26) |
| Ga(3) / Sn(3) | 24g | 0.41565(4) | 0.14836(4) | 0.41565(4) | 1.308(14) | 0.315(10) / 0.682(10) |
| Ga(4) / Sn(4) | 8c | 0.36577(6) | 0.36577(6) | 0.36577(6) | 1.07(2) | 0.707(12) / 0.293(12) |
Ba(2) ions show a strongly anisotropic guest ions’ known physical properties. The starting point since larger rattling implies larger $\Theta_{E2}$, and the best fit naturally decreases this to $\Theta_{E1} = 87.2$ K, $\Theta_{E2} = 49.4$ K and $\Theta_{E3} = 87.1$ K. The similarity between $\Theta_{E2}$ of BGG and $\Theta_{E1}$ of BGS is reasonable, since the largest diameters of both cages are essentially the same ($\sim 8.2$ Å). The similarity between $\Theta_{E2}$ and $\Theta_{E1}$ in BGG is also reasonable since the $X_{20}$ cage size in the out-of-plane direction is very close to the $X_{20}$ cage size ($\sim 5.5$ Å). This means a further simplification can be made in the model by assuming only two parameters $\Theta_{E1}$ and $\Theta_{E2}$ with $p_{1}N_{E1} = p_{2}N_{E2} = 12$, where $\Theta_{E1}$ represents the 3D vibration of the Ba(1) ions and the 1D out-of-plane vibration of the Ba(2) ions; while $\Theta_{E2}$ represents the larger, 2D in-plane vibration of the Ba(2) ions. This results in the solid curve shown in Fig. 4b and, as with BGS, the TRR model it is written as

$$C_L(\omega, T) = \frac{1}{3} \int_0^{\omega_D} d\omega [C_L(\omega, T) v l]$$

(4)

where $C_L(\omega, T)$ is the phonon specific heat, $\omega_D$ is the Debye frequency, $v$ is the average sound velocity and $l$ is the phonon mean free path, which must be averaged over all major contributing scattering mechanisms. Thus, in the TRR model it is written as

$$l = (l_{TS}^{-1} + l_{Res}^{-1} + l_{Ray}^{-1} - 1 + l_{min}^{-1})$$

(5)

The low-energy excitations of the guest ions tunnelling between localized states scatter phonons as

$$l_{TS}^{-1} = A \left[ \frac{\hbar \omega}{k_B} \right] \tanh \left( \frac{\hbar \omega}{2k_BT} \right) + \frac{A}{2} \left( \frac{k_B}{\hbar \omega} + 1 + \frac{1}{BT^3} \right)$$

(6)

where $A$ and $B$ are microscopic parameters describing the tunnelling states characteristics. At higher energies,
TABLE IV: Parameters used to generate the solid line curves in Figs. 3 and 4 which best fit the respective experimental data set for lattice thermal conductivity and specific heat. See text for detailed descriptions.

| Symbol | Unit     | n-BGG | p-BGG | n-BGS | p-BGS |
|--------|----------|-------|-------|-------|-------|
| $A$    | $10^{1}/(\text{m K})$ | 1.4   | 2.5   | 2.5   | 17    |
| $B$    | $1/K^2$  | 0.1   | 0.1   | 0.1   | 0.1   |
| $A/B$  | $10^{5}/K/m$ | 1.4   | 2.5   | 2.5   | 17    |
| $C_i$  | $1/(m^2 K^2)$ | 0.2   | 2.0   | 0.7   | 5.0   |
| $\Theta_{E1}$ | K      | 87    | 87    | 50    | 50    |
| $\Gamma_1$ |       | 0.5   | 1.5   | 0.4   | 1.5   |
| $C_2$  | $1/(m^2 K^2)$ | 0.2   | 2.0   | -     | -     |
| $\Theta_{E2}$ | K      | 49$^a$| 49$^a$| -     | -     |
| $\Gamma_2$ |       | 0.5   | 1.5   | -     | -     |
| $D$    | $K^4/m$  | 0.85  | 0.5   | 2.8   | 1.7   |
| $\gamma$ | $\text{mJ/(mol K)}$ | 6     | 9     | 1.3   | 11    |
| $\Theta_D$ | K      | 288   | 288   | 200   | 200   |
| $v$    | $\text{m/s}$ | 2898  | 2898  | 2250  | 2250  |

$^a$Two-dimensional vibration (see text).

The phonons are scattered through a resonance effect against guest ion rattling as:

$$l_{\text{Res}}^{-1} = \sum_i \frac{C_i \omega_i^2 T^2}{(\omega_0^2 - \omega_i^2)^2 + \Gamma_i \omega_i^2 \omega_0^2},$$

(7)

where $C_i$ and $\Gamma_i$ are phenomenological parameters related to a simple mechanical oscillator.$^{20}$ We also need to include the empirical but always present, frequency-only dependent Rayleigh scattering

$$l_{\text{Ray}}^{-1} = D \left( \frac{\hbar \omega_0^4}{k_B} \right),$$

(8)

and finally the last term $l_{\text{min}} = 1 \text{ Å}$ is the cut-off limit.

Results from the best fits of the data shown in Figs. 3 and 4 are summarized in Table IV. The most relevant results in terms of comparing the p-type with n-type samples are the increase in the resonant scattering level ($C_i$), and in the TS scattering level. The latter can be expressed by the ratio $A/B = \bar{n} (\hbar \nu^2)/\pi k_B$, which in glasses is essentially a measure of the subset density of tunnelling states $\bar{n}$ that are able to strongly couple to the phonons and effectively scatter them.$^{25}$ Therefore, the increase in $A/B$ observed upon changing from n-type to p-type cages does not necessarily mean the total density of TS has increased, only that the existing states are more effectively coupled.

An interesting exercise can be made to help understand the influence of these different contributions in the TRR model. If we begin with the fitting results for $\kappa_L(T)$ of the n-type samples, it is impossible to fit the respective p-type $\kappa_L(T)$ by increasing the intensity of only one of these contributions (TS or resonant). The TS are mainly responsible for decreasing the low-temperature $\kappa_L(T)$ up to the first few Kelvins, and by itself the TS contribution is incapable of changing the peak into a plateau. Conversely, an increase in the resonant scattering level (based on fixed values of $\Theta_E = 50 K$ from heat capacity and increased phenomenological coupling strength parameters $C_i$), readily brings the peak down to a plateau/dip, but quickly loses its ability to follow the $\kappa_L(T)$ drop below about 10 K. Therefore, we may conclude that the TRR model adequately reproduces the entire range of $\kappa_L(T)$ for all samples up to 100 K, provided that the coupling of the framework phonons with the guest ion tunnelling and rattling is increased in p-type samples.

Let us now focus on some other proposals regarding candidate mechanisms for glasslike behavior in clathrates, which challenge the TRR model. First: is the presence of tunnelling states really necessary, or is off-center vibration a sufficient mechanism? The question was raised by Bridges and Downward$^{13,14}$ primarily based on the existing data at the time, where Sr and Eu guests clearly show off-center sites$^{10,11,12}$ and glasslike $\kappa(T)$, while Ba guests appear to show on-center vibration$^{10,11,12}$ (within experimental resolution) and a crystalline peak. Later studies demonstrated glasslike behavior for p-type BGC$^{15,20}$ and now for p-type BGS (this work), so this argument by itself is no longer valid, unless a closer look at the Ba vibration in these compounds through microscopic techniques shows that off-center vibration modes do exist for p-type samples (even if much smaller than for Sr and Eu guests) but not for n-type samples. Raman scattering and EXAFS studies are presently being conducted on our carrier-tuned BGG crystals, which may help clarify this issue. Still, good arguments were made by the authors in terms of describing how off-center vibration does indeed help enhance the coupling between guest vibration modes and the framework phonons.$^{13,14}$

A second challenge to the TRR model is: can the shift from crystalline to glasslike behavior be explained solely by phonon scattering mechanisms within the framework, i.e., by interactions between phonons and charge carriers? This question was raised in a series of papers by Bentien et al.$^{13,15,16,18}$ which we now discuss.

The first work$^{12}$ called attention to an observed $\kappa(T) \propto T^{1.5}$ dependence at low-temperature for p-BGG and a kink in their data at about 2 K (neither of which were reproduced with our crystals). They also pointed out that the phonon-charge carrier mechanism could not explain the lowering of $\kappa_L(T)$ above $\sim 15 K$, so the resonant scattering on the guest vibration was once again invoked, but to account for only the differences above 15 K. The second work$^{16}$ compared several polycrystalline samples of type-VIII and type-I Eu$_4$Ga$_{16}$Ge$_{30}$ (α-EGG and β-EGG respectively$^{22}$ all with n-type carriers), clearly demonstrating that β-EGG shows glasslike $\kappa_L(T)$ while α-EGG does not. The difference was interpreted in terms of changes in the band structure, with a much enhanced effective mass $m^*$ found in β-EGG. However, the cage sizes and shapes are also quite different between these two structures. The type-I $X_{24}$ cages are essentially the...
same size for all Ge clathrates (5.5 × 8.2 Å, see Fig. 1) but the type-VIII cage in α-EGG (6.7 × 7.5 Å ovoid similar to Fig. 2) is significantly smaller than that of BGS, so any change in \( \kappa_L(T) \) can also be argued or modelled in terms of changes in the Eu vibration modes and their coupling to the framework. Unfortunately α-EGG samples with p-type carriers are as yet unavailable, but it wouldn’t be surprising if they showed glasslike \( \kappa_L(T) \) as we found in p-BGS. The third and more recent work shows results for Ba\(_8\)Ni\(_{16}\)Ge\(_{46-x}\) similar to what we have obtained here for BGG and BGS, therefore the same analysis and discussion we have conducted here can also be applied to those results.

Still, it is obvious that the influence of charge-carriers cannot be neglected with respect to their density \( n_c \), effective mass \( m^* \), electronic mean free path \( l_e \), etc. It is quite clear from our measurements and all previously reported data on Ba-filled clathrates, that the p-type carriers are playing a relevant role in producing an increased phonon scattering in these compounds, which we view as yet another additional factor capable of contributing to lower \( \kappa_L(T) \), possibly through direct interaction with the phonons, but especially by mediating an enhanced coupling of these with the guest vibration modes. A few brief examples for such mediation possibilities are: 1) n-type frameworks could allow a greater degree of coherence in the vibrations of neighboring Ba guests than p-type frameworks, which would lead to larger mean free paths and less effective scattering; 2) Since the type and density of charge carriers result from stoichiometry imbalances, they may affect the framework rigidity at certain sites, and therefore how easily it can couple with the rattler ions.

V. CONCLUSION

We have succeeded in growing large single crystals of Ba\(_8\)Ga\(_{16}\)S\(_{3\text{0}}\) and Ba\(_8\)Ga\(_{16}\)Ge\(_{3\text{0}}\) with both n-type and p-type majority carriers, and found that these compounds show low temperature lattice thermal conductivity behavior strongly dependent on the carrier type. A shift from crystalline to glasslike behavior is observed for both compounds when changing the majority carriers from n-type to p-type through composition tuning. These differences can be mostly reproduced by an increase in resonant scattering, however, an increase in both resonant and tunnelling scattering levels are required to reproduce the full set of data below 100 K. Heat capacity and single-crystal x-ray diffraction data indicated that these increases are not the result of any major change in the guest ions’ vibrational behaviors, therefore a more effective coupling of the frameworks with p-type carriers to the TS and rattling vibrations of the guest ions is the most likely mechanism. The \( T^2 \) dependence in \( \kappa_L(T) \) obtained at lowest temperatures for both n-type and p-type Ba\(_8\)Ga\(_{16}\)Ge\(_{3\text{0}}\) indicates that tunnelling states should be present for the Ba(2) ions in this compound, therefore its mere presence is insufficient to guarantee glasslike \( \kappa_L(T) \).

In fact, our results indicate that the various proposed mechanisms which may lead to glasslike behavior are all partially correct and at the same time incomplete. The general scenario that we see emerging can indeed be expressed as: it’s all about the coupling. For reasons that still need to be explained microscopically, the n-type frameworks are more weakly coupled to the guest vibration modes than the p-type frameworks. Thus, the Ba ions’ smaller and (almost?) on-center vibration is not coupled strongly enough to the n-type framework phonons to produce the glasslike behavior, but the p-type framework crosses the necessary coupling strength threshold to achieve this scattering regime. In contrast, Sr and Eu ions in the type-I Ge clathrates have clearly off-center and larger rattling, capable of a strong enough coupling even with the n-type frameworks to produce glasslike behavior (no p-type frameworks have been reported yet for these compounds). In a series of carefully tuned Ba-based clathrates it should be possible to observe a continuous transition from glasslike to crystalline \( \kappa_L(T) \). Likewise, in a series of n-type (Sr,Eu)-based clathrates the same continuous transition should be observed not from carrier tuning, but from a physical or chemical reduction of cage size to dampen the off-center vibration level.

Acknowledgments

We thank M. Udagawa, F. Bridges and D. Huo for fruitful discussions, and Y. Shibata for the EPMA analysis. Specific heat and thermal conductivity measurements were carried out at Natural Science Center for Basic Research and Development (N-BARD) Hiroshima University. This work was financially supported by the Grants in Aid for Scientific Research(A) (No. 18204032), the COE Research (13CE2002) and the priority area “Skutterudite” (No. 15072205) from MEXT, Japan.

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