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Possible mechanism for glass-like thermal conductivities in crystals with off-center atoms

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In the filled Ga/Ge clathrate, Eu and Sr are off center in site 2 but Ba is on center. All three filler atoms (Ba, Eu, Sr) have low-temperature Einstein modes; yet only for the Eu and Sr systems is there a large dip in the thermal conductivity, attributed to the Einstein modes. No dip is observed for Ba. Here we argue that it is the *off-center displacement* that is crucial for understanding this unexplained difference in behavior. It enhances the coupling between the "rattler" motion and the lattice phonons for the Eu and Sr systems, and turns on/off another scattering mechanism (for 1 K$<T<$20 K) produced by the presence/absence of off-center sites. The random occupation of different off-center sites produces a high density of symmetry-breaking defects which scatter phonons. It may also be important for improving our understanding of other glassy systems.

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An important, universal, characteristic of glass-like systems is a low thermal conductivity κ; $\kappa(T)$ varies roughly as T^2 for $T<1$ K, forms a plateau/dip region somewhere in the range 5–40 K, and then increases slowly at higher temperatures. The low T behavior (<1 K) is well understood, and is attributed to a broad distribution of tunneling centers (or two-level systems), both in glasses and in some disordered crystals that exhibit glass-like behavior such as $(KBr)_{1-x}:(KCN)_x$,[1] while at high temperatures, Rayleigh scattering becomes important. However, the intermediate plateau/dip region is less well understood. Several explanations for the plateau have been proposed, but the model of Grannan *et al.*[1] for the mixed KBr:KCN system has an important general mechanism and appears to be applicable for both glassy and disordered crystalline materials. In their model, the plateau/dip is produced by a nearly localized mode (the libration modes of the CN ion about its center of mass, at THz frequencies) that resonantly scatters phonons very effectively. Similar models have been applied to glassy selenium[2] and disordered garnets.[3] The same approach has also been used to describe the glass-like thermal conductivity in the off-center Eu and Sr-filled clathrates,[4] in this case a "rattler" mode with a low Einstein temperature in the range 30–150 K (i.e., at THz frequencies) plays the role of the nearly localized mode. However, this model fails in explaining the difference in behavior between the Ba and Eu/Sr filled clathrates—no dip is observed for the on-center Ba system. It also cannot explain the $\kappa \propto T$ dependence observed from roughly 1–10 K.[5] Here we will argue that it is the off-center displacement of Eu and Sr that leads to the plateau/dip region in these systems.

In several compounds with large unit cells (skutterudites and type I clathrates), large cages or voids occur in the structure which can be "filled" with several types of atoms. This dramatically alters their physical properties.[6–9] When the "filler" ion is considerably smaller than the void, it is loosely bound and can "rattle" around—hence its name. The weak binding leads to a nearly local mode[10] described by a low Einstein temperature. A low thermal conductivity has been found in a number of such systems[4,5,11] and in a glass-like model for κ(T), used for the Eu and Sr clathrates.[4] Note that a very low value of κ is crucial for thermoelectric applications because the figure of merit $ZT=TS^2\sigma_e/\kappa$ (S is the Seebeck coefficient, σ_e the electrical conductivity) can be significantly increased. Hence, understanding the mechanisms that lead to a small κ, and particularly their ranges of validity, is very important.

Here we consider κ(T) for the (type I) Ga/Ge clathrates whose structure is formed of two cages with internal voids large enough to house another atom (sites 1 and 2); atoms placed in them, such as Eu, are referred to as Eu1 and Eu2. In the larger site 2 cage, Eu2, Sr2, and Ba2 all form rattlers with quite low Einstein temperatures;[5] however, Ba2 is on center while both Eu2 and Sr2 move off center.[12–17]

In Fig. 1(a), we replot the thermal conductivity data of Nolas *et al.*;[4] κ is small for Eu and Sr, and there is a well-defined dip associated with the Einstein temperatures of the rattlers.[4] Nolas *et al.* model the low thermal conductivity below 20 K for the Eu and Sr compounds using a broad distribution of off-center tunneling states. At slightly higher temperatures, they used two resonant scattering terms (two Einstein temperatures) to explain the dip (near 25 K), plus a Rayleigh scattering term which dominates at high T. Using this sum of terms, they were able to fit $\kappa(T)$ for both $Eu_8Ga_{16}Ge_{30}$ and $Sr_8Ga_{16}Ge_{30}$ over the range 5–100 K. However, a problem arises in using a tunneling model with tunneling splittings up to ~15 K; first, the inferred distribution of tunneling states from ultrasonic measurements is much narrower than in a glass,[18] and second (more importantly), very recent Mossbauer measurements indicate that the tunneling frequency is at most 0.44 GHz, i.e., ~0.02 K.[19] If one cuts off the tunneling density of states with a step function even at 1 K, then κ rises too rapidly below 15 K.

Similar experimental results for $\kappa(T)$ of these filled clathrates have also been observed by Sales *et al.*[5] [see Fig. 1(b)]; however, at low T, κ is considerably lower and the dip is less pronounced. More importantly, for the Eu and Sr data, $\kappa(T)$ decreases nearly linearly with T below 10 K, which cannot be fit with the above model.

The T-dependence for $Ba_8Ga_{16}Ge_{30}$ in which Ba2 is *on center*,[5] is more perplexing [see Fig. 1(b)]. For this system, κ

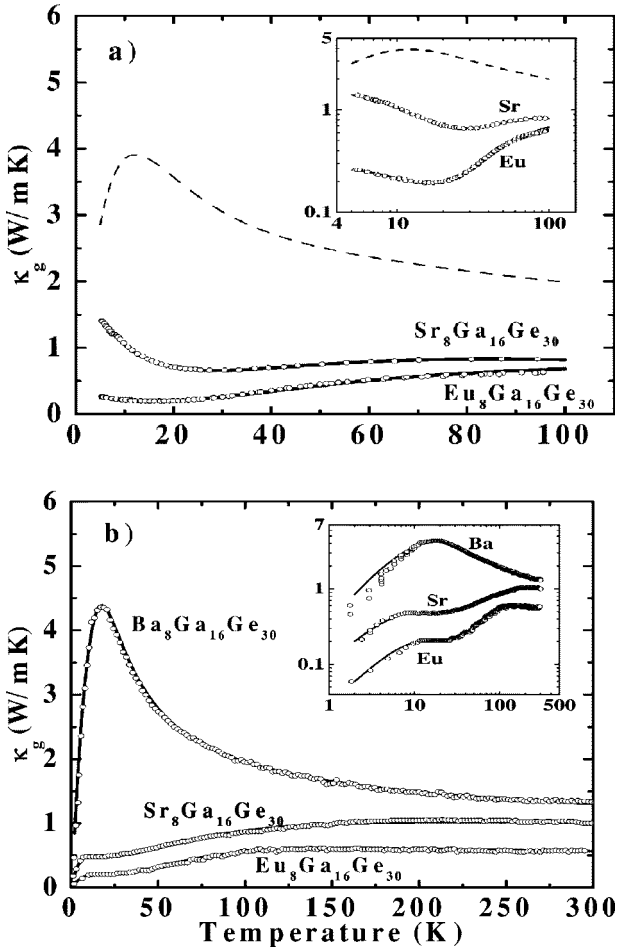

FIG. 1. (a) The lattice thermal conductivity for $Eu_8Ga_{16}Ge_{30}$ and $Sr_8Ga_{16}Ge_{30}$ from Ref. 4. Solid lines—the new fits discussed below; dashed line—the calculated result for $Sr_8Ga_{16}Ge_{30}$ if the resonant scattering contribution were reduced by a factor of 10. It shows a dependence similar to that of $Ba_8Ga_{16}Ge_{30}$ in (b). The inset shows a log-log plot. (b) Similar data for the Eu, Sr, and Ba clathrates from Ref. 5. Solid lines show the fits; for Eu and Sr the same model is used as for (a) but G and the C_i are larger; for Ba, the C_i are small and a finite sample size and an Umklapp term are needed at low T.

is much higher overall and there is no clear dip in κ(T), although the Einstein temperatures are only slightly larger than those of Eu and Sr,[5] thus the rattler-phonon coupling must be greatly reduced.[20] Also, the T dependence below 10–12 K is faster ($\kappa \sim T^{3/2}$) for the Ba clathrate. These results raise two important issues: (1) what determines the strength of the coupling between the rattlers and the phonons and (2) how can one understand the T dependence of κ from 1–15 K? We propose another mechanism to explain this temperature range; it may also contribute to κ in other glassy systems.

The off-center displacement appears to play two additional, crucial roles in increasing the phonon scattering (in addition to producing tunneling centers). First, from XAFS, the off-center atom is partially bonded to the nearest-neighbor Ga/Ge atoms on the side of the cage,[17] forming a random array of symmetry-breaking defects. We show below that a high density of such defects can lead to a $\kappa \sim T$ dependence at low and medium temperatures. A likely more important consequence of this bonding is that the motions of the off-center rattler atom are coupled more strongly to just a few of the closest atoms in the surrounding Ga/Ge framework and hence to the phonon modes, i.e., the motions of the Eu2 and nearest Ga/Ge atoms are positively correlated.

We first address the use of the tunneling model and the range of reasonable tunneling splittings. Sethna and co-workers[1] suggest that for the light CN molecule the tunneling splittings (for reorientations of the CN axis) might extend to about 1 K; measured tunneling splittings on similar, more dilute systems (CN^- and OH^-) are less than 3 K.[21,22] For heavy off-center ions such as Ag^+ and Cu^+ in the alkali halides, the observed tunneling energies are also low, much less than 1 K;[22] only for the light off-center $^7Li^+$ ion does the tunneling splitting reach 1.2 K at normal pressures.[23] The tunneling behavior can be finely tuned by applying hydrostatic pressure to reduce the potential barrier between equivalent off-center sites,[24,25] but even in such cases the tunneling splittings for heavy atoms such as Ag^+ are about 1 K when the off- to on-center transition begins to occur.[24]

Within the simple two-well tunneling model, having a tunneling splitting (~10–15 K) that is ~10% of the attempt frequency (the rattler frequency) is inconsistent with the assumptions for the model; for a heavy mass such as Eu, it leads to an unreasonably low potential barrier between the wells [<1 meV(12 K); i.e., less than the tunneling splitting]. On the experimental side, a broad distribution of tunneling states should also lead to a linear contribution to the heat capacity at low T when the tunneling states are excited; however, the heat capacity for the Ba, Sr, and Eu systems at low T is exponential and can be fit to an Einstein model;[5] thus there is no evidence for tunneling states extending up to 10–15 K in such data. With the recent observations that the tunneling frequencies are at most 0.02 K (Ref. 19) for the Eu system, another mechanism is needed to describe κ at low T.

Since atomic forces are generally a very strong function of the distance between the atoms/ions, the force between the central atom (e.g., Sr2 or Eu2) and each of the nearest equivalent Ga/Ge atoms in the cage, will increase substantially for an off-center displacement. The resulting vibrations of the off-center rattler/cage system then depend on the rigidity of the cage (the Ga/Ge cage is quite stiff[5,15]), the Eu2-Ga/Ge bond strength, and the number of Eu2-Ga/Ge bonds. In the limit of an idealized rigid cage, there would be no motion of the cage atoms (i.e., no phonon coupling) as the rattler atom vibrates; the reduced mass of the local mode would be that of the rattler atom as assumed previously.[15–17] For the opposite extreme of a very soft cage, the local mode reduced mass for motion along the bond direction would approach the reduced mass of the atom pair involved, e.g., Eu and Ge in $Eu_8Ga_{16}Ge_{30}$. In this case, there would be large motions of the nearest cage atoms (Ge) as a result of a local mode vibration, which would couple directly to the phonons of the clathrate framework. Because the clathrate cage is quite stiff, the reduced mass is expected to be close (but not equal) to the free rattler mass.

To further understand this coupling, consider a one-dimensional (1D) model of a cage (mass M) connected to a

rattler (mass m), and let the respective displacements be x and X. Then $Mx=mX$; we expect the matrix element for scattering to be proportional to $x/X=m/M$, and the coupling to $(x/X)^2$. The effective mass of the cage decreases when the rattler moves off center (because only a small fraction of the cage atoms are directly bonded to the rattler) and thus the coupling to phonons increases. Also note that for the off-center case, rattler vibrations could be either ~ radial (along the bond) or perpendicular to the bond. The latter are similar to libration modes and would have a lower Θ_E than for radial motion, which was not considered for the KCl:KCN system.

To investigate the various contributions to κ we first reproduced the calculation of Nolas *et al.*[4] κ is given by

$$\kappa = \frac{1}{3}\int_0^{\omega_D} c_s C(\omega,T) l(\omega,T) d\omega, \tag{1}$$

$$l(\omega,T) = (\Lambda_R^{-1} + \Lambda_{res}^{-1} + \Lambda_{TS}^{-1})^{-1} + l_{min}, \tag{2}$$

$$\Lambda_R^{-1} = D(\hbar\omega/k)^4,$$

$$\Lambda_{res}^{-1} = \sum_i C_i \omega^2 T^2 / [(\omega_{E_i}^2 - \omega^2)^2 - \gamma_{E_i}(\omega_{E_i}\omega)^2],$$

$$\Lambda_{TS}^{-1} = A(\hbar\omega/k_B)\tanh(\hbar\omega/2k_BT) + (A/2)(k_B/\hbar\omega + B^{-1}T^{-3})^{-1}, \tag{3}$$

where c_s is the speed of sound, $C(\omega,T)$ is the heat capacity of phonons with frequency ω, and $l(\omega,T)$ is the total mean-free path which has three components—Rayleigh scattering (Λ_R), resonant scattering from the Einstein modes (Λ_{res}), and a contribution from a broad distribution of tunneling states (Λ_{TS}); the lower limit is constrained to l_{min}. The Einstein frequencies ω_{E_i} were obtained from structural data and the constants $A, B, C_1, C_2, D, \gamma_{E_i}$ and l_{min} are given in Ref. 4. We obtained similar fits although the constants varied slightly. We then reduced the coupling to the resonant modes—the C_i constants—by a factor of 10 and left the other terms unchanged. This result is shown by the dashed line [Fig. 1(a)] and is very similar in shape to the data of Sales[5] for $Ba_8Ga_{16}Ge_{30}$ [Fig. 1(b)]. Thus, a major part of the difference in the T dependence of κ between $Ba_8Ga_{16}Ge_{30}$, and the Eu or Sr compounds can indeed be explained by a decreased coupling between on-center Ba2 and phonons in the Ga/Ge framework as described above.

An important parameter for probing the rattler-phonon coupling is the reduced mass μ, of the local mode oscillator: however, μ is not an easy parameter to obtain. One recent study of rattlers in the skutterudites,[26] found the reduced mass to be somewhat less than the atomic mass of the rattler (error ~20%), but more measurements are needed.

A second consequence of the rattler being partially bonded to a side of the cage is the formation of a high-density, random network of symmetry-breaking mass defects, i.e., one of the four off-center orientations is occupied, but the off-center site varies randomly throughout the crystal. The disorder introduced by the random occupation of one of the off-center minima provides insight as to why the crystal exhibits glass-like behavior. This model has similar features to the disorder introduced via irradiation of a quartz crystal,[27,28] but there is a key difference—the atoms are randomly displaced in the irradiated sample, which leads to a range of bond lengths and hence to the possibility of a broad distribution of tunneling states. For the Eu/Sr clathrates the off-center displacement is well defined; the disorder arises from a random occupation of the four off-center sites. Locally, such disorder changes the speed of sound as the phonon wave passes a rattler atom; the resulting phase changes must then be included. Note that in this case there is an interference in the scattering between different rattler sites, whereas Rayleigh scattering assumes a single scattering process.

Ziman has considered this type of scattering in some detail.[29] In his model, the effective mean-free path for this contribution is

$$\Lambda_{disorder}(q) = \frac{A}{L}\frac{c_s^2}{(\delta c_s q)^2}, \tag{4}$$

where q is the wave number, δc_s is the variation of the sound speed, L is the smallest distance between scatterers, and A is a numerical constant of order 1. For very short wavelengths $\lambda \ll L$, $\Lambda_{disorder}$ goes to a constant—but that is already included in the model of Nolas *et al.*[4] by the l_{min} term. Using the Debye model ($\omega=c_sq$) we replaced the tunneling contribution Λ_{TS}^{-1} in Eq. (3) by

$$\Lambda_{disorder}^{-1} = G\omega^2. \tag{5}$$

In Fig. 1(a) we show that with $G_{Eu}=3.7\times10^{-19}$ s^2/m ($G_{Sr}=6.4\times10^{-20}$ s^2/m), and a slight change of the C_i parameters, this model describes the T behavior of κ (of Ref. 4) just as well as by using the tunneling model. Taking $L\sim5\times10^{-10}$ m, these numbers imply $\delta c_s/c_s\sim7\%$ (Eu) and 3% (Sr). Note that this disorder mechanism is important at moderately long wavelengths, i.e., for temperatures up to 20–30 K, and alone would yield $\kappa(T)\sim T$.

Attempts to fit the data of Sales *et al.* for Eu and Sr[5] using the model of Nolas *et al.*[4] were not successful.[30] The data from 2–10 K vary nearly linearly with T and cannot be fit by the $\sim T^2$ dependence for the tunneling model at low T. However, we can fit the data quite well [Fig. 1(b)] using $\Lambda_{disorder}^{-1}$ but larger values for G and the C_i are needed to fit the lower thermal conductivity.

For Ba, much smaller values for C_i are needed, which confirms the earlier assertion that the coupling between phonons and the rattler vibrations is reduced. In addition, the $\Lambda_{disorder}^{-1}$ term cannot fit the low T data for Ba below 12 K; κ is higher and the faster T dependence suggests that a finite sample size contribution is needed at low T—details will be given in a separate paper.[30] The lack of a $\Lambda_{disorder}^{-1}$ term is consistent with Ba being on center, as in that case the $\Lambda_{disorder}^{-1}$ term should disappear.

In summary, we have pointed out that an off-center rattler enhances the scattering of phonons in two ways. First, the off-center displacement increases the coupling of the rattler motion to the phonons and hence increases a dip in the thermal conductivity near ~30 K. This provides an explanation

for the lack of a dip in $\kappa(T)$ for the on-center Ba system. Second, the off-center atom on the side of the cage, introduces a quasirandom set of "extra" atoms that will produce local changes in the sound velocity. This in turn leads to a mean-free path that varies as ω^{-2}, which provides an alternative explanation for the reduction of the thermal conductivity for $1\ \mathrm{K} < T < 20\ \mathrm{K}$. It results in a linear T dependence in this range which fits the data of Sales *et al.*[5] well.

Several questions remain to be answered: For the clathrates, what are the effective masses of the local Einstein modes and what are the actual tunneling splittings (there will be three levels) in these systems? Can the Sr system be moved on center via high hydrostatic pressure and thus allow an investigation of variations in the rattler-phonon coupling? Can these systems be optimized for thermoelectric applications over a particular T range, by varying the off-center rattler's mass and/or Einstein temperatures? More generally, does the off-center displacement play a role in producing the plateau/dip regions in other glassy systems?

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