The off-center "rattler" – A better candidate for achieving glass-like thermal conductivities in crystals?

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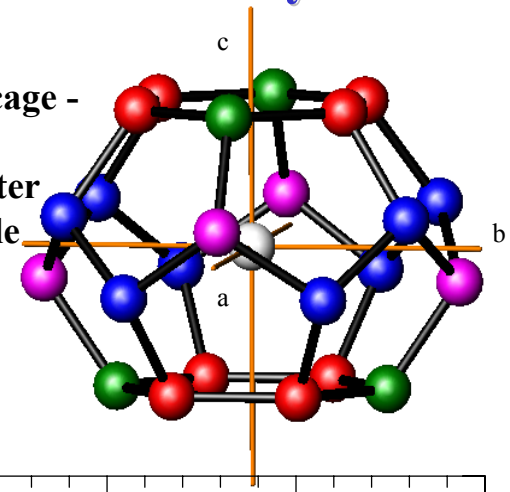
Introduction

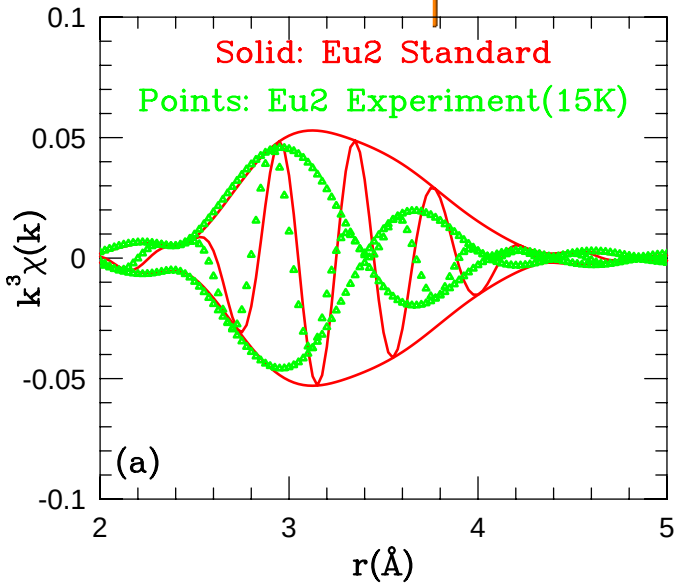
The Ga/Ge clathrates have 2 large cages in the structure (sites 1 and 2), which can be filled with several types of "filler" ions. Because the filler ion is smaller than the cage, it is loosely bound (it can "rattle" around) and can resonantly scatter phonons, which reduces the thermal conductivity (e.g. for Ba filler ions). In some cases, the ion can move off-center (e.g. Eu and Sr in site 2) which leads to even stronger phonon scattering and a glass-like thermal conductivity.

Ga/Ge Site 2 cage - Eu/Sr (white) moves off-center towards purple Ga/Ge atom.



EXAFS Data vs. Simulations (for Eu in site 2)

- Simulations using FEFF for site 2 are shown in red assuming a uniform broadening and an off-center displacement. The Fourier transformed EXAFS data for site 2 (Eu-Ga/Ge pairs) are shown in green. The data agree with the simulations at low r, but the amplitude is suppressed at higher r. Similar results were obtained for the Sr sample.
- The large amplitude for the shorter bonds indicates a small σ, while the smaller amplitude for the longer bonds corresponds to a much larger σ. A small σ for the closest neighbors implies bonding to the side of the cage, a stronger bonding than for the on-center case.



New Result

The off-center displacement plays two important additional roles in increasing the phonon scattering:

- The random filling of different off-center positions forms a random array of symmetry-breaking defects.
- The stronger bonding to the cage enhances the coupling between the "rattler" motion and the lattice phonons.

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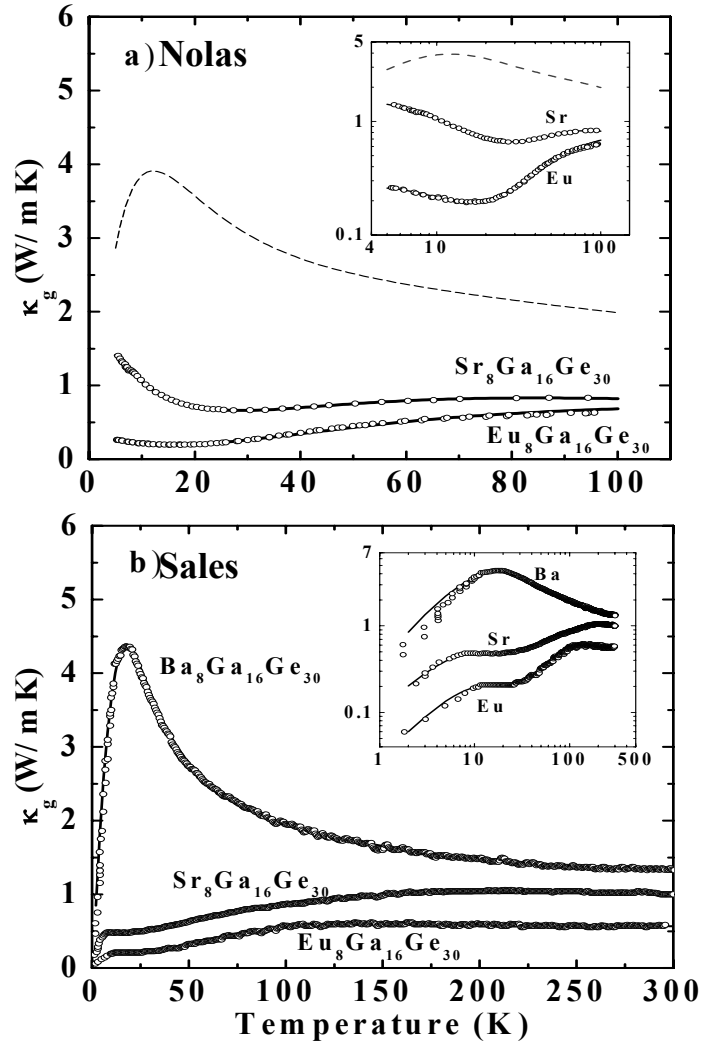
Calculations of thermal conductivity

- The model of Nolas *et al.*[1] (Eu/Sr samples), requires a very broad distribution of tunneling states; we argue this distribution is unlikely.
- An alternative model based on a high-density of strongly scattering defects – here the off-center atom, randomly bonded to one side of the cage – can also explain the low T dependence ; it provides insight as to why these crystalline materials exhibit a glass-like randomness.
- The off-center displacement also enhances the phonon-"rattler" coupling (the dip in κ near 20-30K for Sr and Eu - Fig. a) and b)).
- Fig. a) A fit of our model (lines) to Nolas' data (circles). The dashed line shows the effect of reducing the phonon-"rattler" coupling by a factor of 10. It qualitatively fits the (on-center) Ba data in Fig. b.
- Fig. b) We can also fit the data of Sales *et al.*[2] which has a slightly different temperature dependence at the lowest temperatures.

[1]Nolas, et. al. PRB 61, 3845 (2000)

[2]Sales et al. PRB 63, 245113 (2001)



Broader implications

- A new mechanism for a glass-like thermal conductivity in crystals.
- Suggests that systems with off-center "rattlers" may be optimized for possible thermoelectric applications.

Educational

- Ryan Baumbach (Undergraduate Student) worked on the EXAFS studies of the Eu/Sr clathrate systems for his senior thesis.
- Lisa Downward (Graduate student) worked on the calculations of thermal conductivity as part of her PhD thesis project.
- Both trained to use the XAFS technique and to run experiments at a Synchrotron source.