THERMOELECTRICS

Half-full glasses

The low thermal conductivity of some thermoelectric materials is commonly attributed to rattlers — atoms trapped in oversized cages. Two independent studies now show that rattlers indeed reduce thermal conductivity to glass-like values.

Cronin B. Vining
is at ZT Services, 2203 Johns Circle, Auburn, Alabama 36830-7113, USA.
e-mail: nature@zts.com

Thermoelectric devices transform thermal gradients into electric voltage and vice versa. They may be used one day in vehicles to improve the fuel efficiency by generating electricity from waste heat. In the Peltier cooling mode, they may also have a role in replacing the most common air-conditioning refrigerant (R-134a), a worse greenhouse gas than carbon dioxide. To obtain high efficiency, thermoelectric materials need a high electrical conductivity and low thermal conductivity. Particularly good thermoelectric properties are exhibited by the classes of filled skutterudites and clathrates. In these compounds, loosely bonded atoms filling the cages of the original structure are colourfully known as 'rattlers' (see Fig. 1), and they are believed to give rise to low, glass-like thermal conductivity. In this issue, inelastic neutron scattering studies by Koza *et al.*[1] on skutterudites (page XXX) and by Christensen *et al.*[2] on clathrates (page YYY) clarify the so-called 'phonon glass–electron crystal' (PGEC)[3] and rattler[4] concepts, popular strategies for improving thermoelectric energy-conversion efficiency. Interestingly, each study addresses whether the rattlers rattle and whether the phonons are glass-like, but they hold different views of what 'glass-like' means.

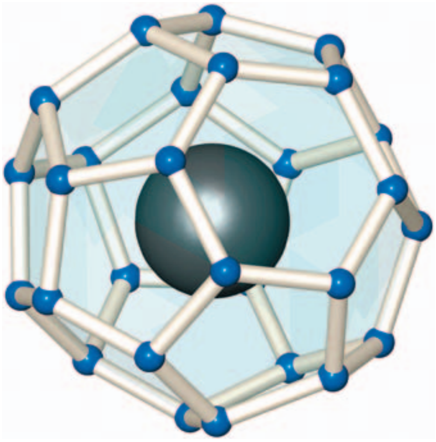

Figure 1 Phonon glass–electron crystal archetype. A hexakaidecahedra cage (blue atoms) enclosing a rattler guest atom (grey). This particular cage–guest geometry forms part of a clathrate crystal structure. The idea is that the cage atoms form a regular periodic crystal lattice along which electrons (or holes) can move fairly freely, ideally approaching the so-called electron crystal. The central rattler atom is commonly bigger, heavier and more loosely bound compared with the cage atoms. When the rattler moves about due to thermal agitation, it so disrupts the vibration modes of the cage that heat conduction along the cage is reduced nearly to values characteristic of glasses. Hence it has been described as a phonon glass, even though strictly speaking the atomic arrangement is entirely regular and crystal-like. Reprinted with permission from ref. 6. © 2008 RSC.

The PGEC concept, coined by Slack[3], is actually an elegant, proposal-friendly summary of ideas discussed by Ioffe in the 1950s[5]: for maximum thermoelectric energy-conversion efficiency, the lowest possible thermal conductivity, the highest possible electrical conductivity and the highest possible Seebeck coefficient (a measure of the thermally induced voltage) must be achieved in the same material at the same time. Glasses, amorphous materials with no regular periodic arrangement of atoms, have about the lowest thermal conductivity among known solids. As a phonon is a quantum particle representing a lattice vibration, we call a material with a low, glass-like thermal conductivity a phonon glass. Crystalline semiconductors, where the atoms form a regular periodic lattice, often have favourable electrical conductivity and Seebeck values. An electron crystal is a material that exhibits a crystal-like (high) electrical conductivity, even if the atomic structure is not a perfect crystal.

Inserting rattlers, a term also coined by Slack[4], into cages is one of the more promising methods of approaching the ideal phonon glass, while hopefully still maintaining an electron crystal — as the cages are, after all, crystalline. Hence the term PGEC expresses what we want, whereas rattlers are an attempt to get it.

To appreciate the motivation behind these studies we have to consider the classic equation for the thermal conductivity (κ) of solids due to phonons (the quantum particles representing lattice vibrations): $\kappa = 1/3Cvl$, where C is the heat capacity, v is the speed of the phonons, and l is the phonon mean free path. In particular, glasses are characterized by a very low mean free path. Inelastic neutron scattering studies, used in the present two papers, can reveal key details about the phonons, including their speed and sometimes their mean free path. Neutron studies are much more difficult than just measuring thermal conductivity, but the information provided is more detailed.

Both studies find that the phonon structure is well defined and can be understood in the usual framework of crystals. Not literally glass-like at all. Both studies find the vibration of the rattler is coupled to the vibration of the cage such that the cage vibration modes are qualitatively modified by the rattler, an effect referred to as 'avoided crossing' by Christensen and colleagues[2]. Figure 1 of ref. 2 provides a nice mini-tutorial on the cage–rattler interactions. Both studies agree that rattlers effectively lower the speed of the phonons and that this effect is important in the resulting low thermal conductivity values.

Curiously, Koza *et al.*[1] conclude that the phonon-glass concept**[Author: Changed 'rattler' to 'phonon-glass' as otherwise it seemed contradictory later when it says both studies supported the idea that rattlers reduce conductivity etc. OK?]** is 'not applicable' to skutterudites whereas Christensen *et al.*[2] conclude their rather similar results 'unambiguously' supports the concept in clathrates. This apparent disagreement arises because the phrase 'glass-like' is used differently in the two papers. Rattlers alter the phonon structure and thereby reduce the thermal conductivity. This was the spirit of Slack's conjecture

14 years ago[4], and both studies nicely confirm his insight. On the other hand, the phonon structure itself is not literally glass-like, only the thermal conductivity is. It seems rattlers work a bit differently to genuine glasses, achieving low thermal conductivity values by lowering the effective phonon speed rather than by lower mean free path values.

There may be some concern about overgeneralizing the present results. Each class of material, each rattler species, each doping and/or filling level and even each sample will be a little distinct. We cannot be certain if most, or many, or even any other rattlers will behave just like the samples studied here. That said, we now know that many features (cage–rattler coupling, avoided crossing, lower phonon speed) appear in both skutterudites and clathrates, at least for the particular samples studied. Not a huge dataset perhaps, but there is some basis to think these features will be fairly common.

Still, we should point out a notable difference between the two studies regarding the temperature dependence of the vibration frequency associated with the rattler. Koza *et al.*[1] find no temperature dependence in their study of rattler modes in skutterudites, whereas Christensen *et al.*[2] report a distinct temperature dependence for the analogous rattler modes in clathrates. The difference is likely to be real: the rattler bonding in clathrates seems to be more anharmonic — and therefore more rattler-like — than in skutterudites. This, too, may influence the different language used by each group to describe their work. Semantics aside, both studies paint a rather similar picture: rattler atoms strongly reduce phonon heat transport, which in any case is good for thermoelectric applications.

References

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