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When does a crystal conduct heat like a glass?

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ABSTRACT

Semiconducting crystalline materials that are poor conductors of heat are important as thermoelectric materials and for technological applications involving thermal management. A combination of neutron scattering, low-temperature ultrasonic attenuation and thermal conductivity measurements are reported on single crystals of the semiconductors $Sr_8Ga_{16}Ge_{30}$ and $Ba_8Ga_{16}Ge_{30}$. Taken together, these measurements suggest specific structural features that result in a crystal with the lowest possible thermal conductivity, namely that of a glass with the same chemical composition. Weakly bound atoms that 'rattle' within oversized atomic cages in a crystal result in a low thermal conductivity, but the present data show that both 'rattling' atoms *and* tunnelling states are necessary to produce a true glass-like thermal conductivity.

In the search for new thermoelectric materials, one of the holy grails has been to achieve a thermal conductivity that is truly 'glass-like' without ruining the electrical properties of the material (Slack 1995). In recent years, several steps along this path have been taken with the development of 'electron-crystal phonon-glass' (ECPG) materials such as filled skutterudites that combine the low thermal conductivities associated with glasses with the high electron mobilities associated with crystals (Morelli and Meisner 1995, Sales *et al.* 1996, Mahan *et al.* 1997, Nolas *et al.* 1998a). One of the keys to ECPG behaviour has been to find semiconducting materials in which one or more atoms per unit cell can 'rattle' (Keppens *et al.* 1998) in an oversized atomic 'cage'. These 'rattlers' resonantly scatter phonons and greatly reduce the thermal conductivity of the material, but generally not quite to glass-like levels. Recently, a truly glass-like thermal conductivity was observed in the Ge clathrate $Sr_8Ga_{16}Ge_{30}$ (Nolas *et al.* 1998b). In this material, one of the two Sr atoms

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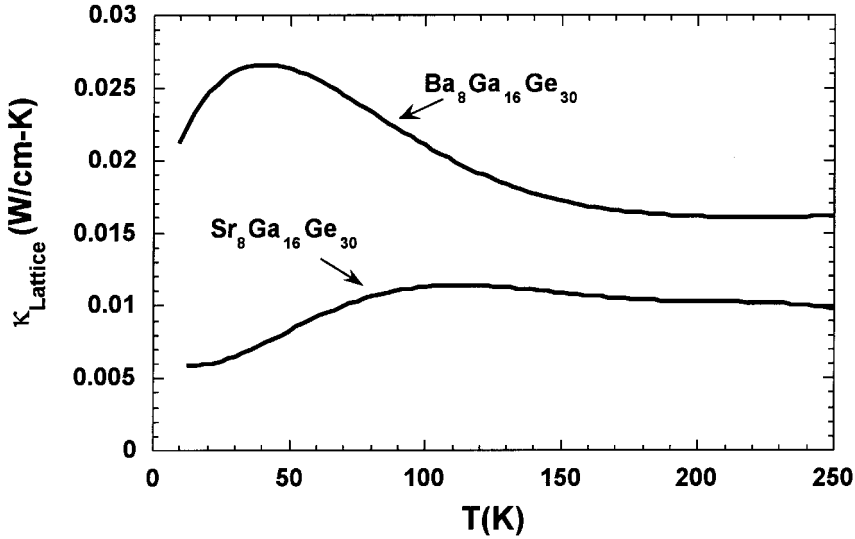

Figure 1. Lattice thermal conductivity versus temperature for $Sr_8Ga_{16}Ge_{30}$ and $Ba_8Ga_{16}Ge_{30}$ crystals. The lines are a least-squares fit of the data to a sixth-order polynomial. The thermal conductivity of the Ba clathrate, although small, has a crystalline temperature dependence whereas the temperature dependence of the Sr clathrate is glass like. Note, too, that the Ba clathrate has a room-temperature thermal conductivity more than 50% higher than that of the Sr clathrate. The Wiedemann–Franz law has been used to subtract the electronic contribution to thermal conductivity.

per unit cell has a large atomic displacement parameter† (rattles) (Chakoumakos *et al.* 2000) and resonantly scatters phonons (Cohn *et al.* 1999).

The thermal conductivity κ of glasses not only is very small‡ (Zeller and Pohl 1971, Phillips 1981) but also displays a universal temperature dependence; κ varies as T^2 below 1 K, has a plateau in the region from 1 to 10 K and is roughly independent of temperature above 100 K. This behaviour is qualitatively different from ordinary crystalline behavior, in which κ reaches a maximum between 20 and 50 K and shows no plateau. The difference between crystalline and glass-like behaviours is vividly illustrated in figure 1, which shows the thermal conductivity measured on $Sr_8Ga_{16}Ge_{30}$ and $Ba_8Ga_{16}Ge_{30}$ samples. These samples were prepared by slow cooling stoichiometric melts in evacuated C-coated silica tubes. The grain size of these samples was approximately 2 mm, and so the measured thermal conductivity is virtually uncontaminated by scattering from grain boundaries. The measurement technique has been described in detail elsewhere (Sales *et al.* 1997). The important

† Atomic displacement parameters (ADPs) (also Debye–Waller factors or thermal parameters) measure the mean-square displacement amplitude of an atom about its equilibrium position in a crystal. In the description of a new crystalline compound, crystallographers normally tabulate the room-temperature ADP values for each distinct atomic site in the structure. The various ADP values are thus some of the first information that is known about a new crystalline compound.

‡ It has been proposed by Slack (1979) and Cahill *et al.* (1992) that the minimum thermal conductivity of a crystalline solid corresponds to the value obtained if a glass were made with the same chemical composition. This corresponds to a mean free path of the heat carrying phonons of about 0.3 nm.

point is that the thermal conductivity of the Ba clathrate, although small, has a crystalline temperature dependence whereas the temperature dependence of the Sr clathrate is glass like. In addition, the Ba clathrate has a room-temperature thermal conductivity that is more than 50% higher than that of the Sr clathrate.

Structural refinements of $Sr_8Ga_{16}Ge_{30}$ and $Ba_8Ga_{16}Ge_{30}$ revealed that the temperature dependence of the ADPs $U(T)$ of the Sr and Ba have similar slopes, but the zero-temperature intercept is four times greater for Sr than for Ba, indicating a large component of positional disorder at the Sr site. It was observed that, if a fractionally occupied split-atom model is used for the Sr site, the $U(T)$ for Sr plots directly on top of the $U(T)$ for the Ba, effectively removing the disorder associated with the Sr atom position. To investigate this situation further, we used single-crystal neutron diffraction data to determine the nuclear density at the alkaline earth site at 15 K in both $Sr_8Ga_{16}Ge_{30}$ and $Ba_8Ga_{16}Ge_{30}$. The results appear in figure 2. The peak nuclear density is 2.68 fm Å^{-3} for the Sr case and 4.78 fm Å^{-3} for the Ba case; yet the coherent neutron scattering lengths are 7.02 and 5.07 fm for Sr and Ba respectively. This emphasizes that for the Sr case the nuclear density is much more smeared out in the cage than for the Ba case.

It is likely that the four lobes observed in the Sr nuclear density represent tunnelling sites and that the origin of the glass-like thermal conductivity in $Sr_8Ga_{16}Ge_{30}$ involves the tunnelling of Sr ions between the four sites displaced from the cage centre. The existence of tunnelling states in $Sr_8Ga_{16}Ge_{30}$ would not be surprising because tunnelling states are another universal property of glasses. It is only in a few cases, however, that the microscopic origin of the tunnelling has been identified (DeYoreo *et al.* 1986).

To confirm the presence of tunnelling states, the temperature dependence of the ultrasonic (US) attenuation $\alpha(T)$, was measured on a single crystal of $Sr_8Ga_{16}Ge_{30}$. The crystal was cut into a bar with dimensions 8 mm $\times$ 2 mm $\times$ 1 mm. Pulse-echo measurements at two frequencies (155 and 250 MHz) were performed at temperatures from 0.3 to 10 K and the results appear in figure 3. Clearly, the behaviour of $\alpha(T)$ at the lowest temperatures is very different from that expected for an ordinary crystalline material, for which $\alpha(T)$ is small and almost independent of temperature as $T \rightarrow 0$. Instead, the attenuation from 0.3 to 1 K shows a T^3 dependence and strongly resembles the $\alpha(T)$ of a structural glass such as GeO_2. So far, no evidence for glass-like excitations has been found in $Ba_8Ga_{16}Ge_{30}$, although we have not been able to grow a large single crystal suitable for US attenuation measurements.

The low-temperature thermal and acoustic properties of glasses were given a phenomenological explanation by the tunnelling model (TM) (Andersen *et al.* 1972). The TM postulates the existence of tunnelling states that couple to strain fields and that have a broad distribution in energy splittings. The TM successfully accounts for the thermal and acoustic behaviours of glasses below 1 K, and can explain both the T^2 behaviour of the thermal conductivity and the T^3 behaviour of the ultrasonic attenuation in terms of the interaction between phonons and tunnelling states. The observation of $\alpha(T) \propto T^3$ in a single crystal of $Sr_8Ga_{16}Ge_{30}$ is strong evidence that tunnelling states exist in this material. A detailed analysis of the acoustic attenuation data reveals that the density of tunnelling states is about 50 times smaller in $Sr_8Ga_{16}Ge_{30}$ than in structural glasses (e.g. GeO_2, and SiO_2) and that the energy distribution of tunnelling states is much narrower (Keppens and Laermans 1995). This is not surprising because, although the environment of the

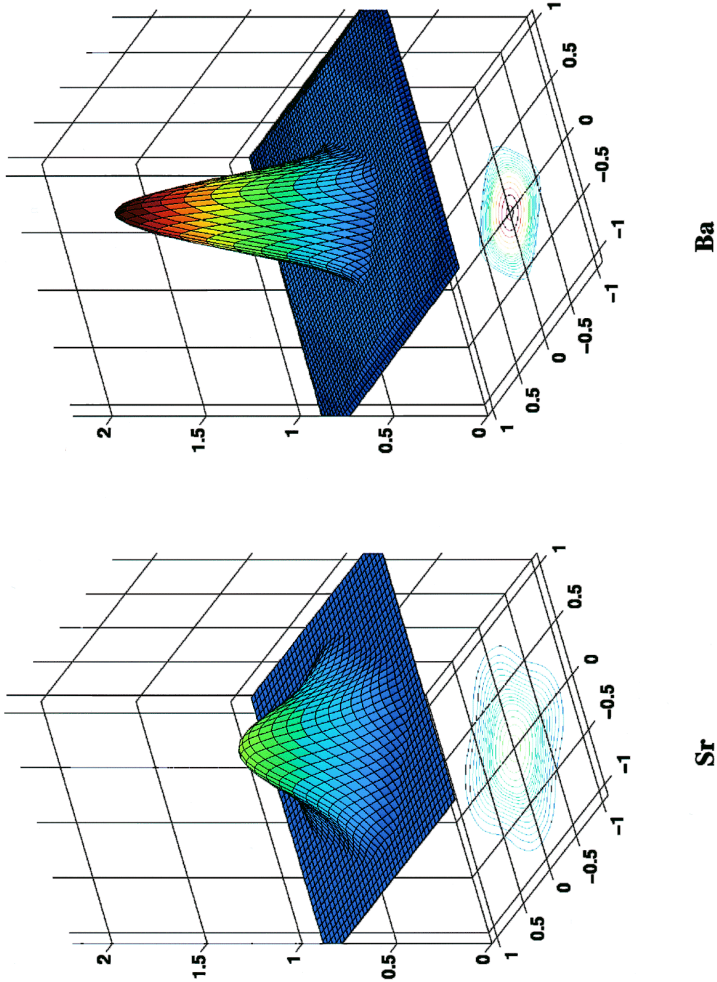

Figure 2. Nuclear density at the alkaline earth site located at $\frac{1}{4}, \frac{1}{2}, 0$ for both $Sr_8Ga_{16}Ge_{30}$ and $Ba_8Ga_{16}Ge_{30}$ at 15 K in difference Fourier maps determined from single-crystal neutron diffraction data. This site corresponds to the centre of a large cage composed of 24 atoms of Ge or Ga (randomly distributed) (Eisenmann *et al.* 1986, Chakoumakos *et al.* 2000). The amplitude along the vertical direction is proportional to the probability of finding the nucleus at a particular location near the $\frac{1}{4}, \frac{1}{2}, 0$ crystallographic site. The units in the x–y plane are in ångströms measured from the crystallographic site $\frac{1}{4}, \frac{1}{2}, 0$. Both maps are similarly scaled, and yet the coherent neutron scattering lengths are 7.02 and 5.07 fm for Sr and Ba respectively. This emphasizes that for the Sr case the nuclear density is much more smeared out in the cage than for the Ba case. These data strongly suggest that the Sr atoms tunnel between the four nearby lobes displaced from the cage centre.

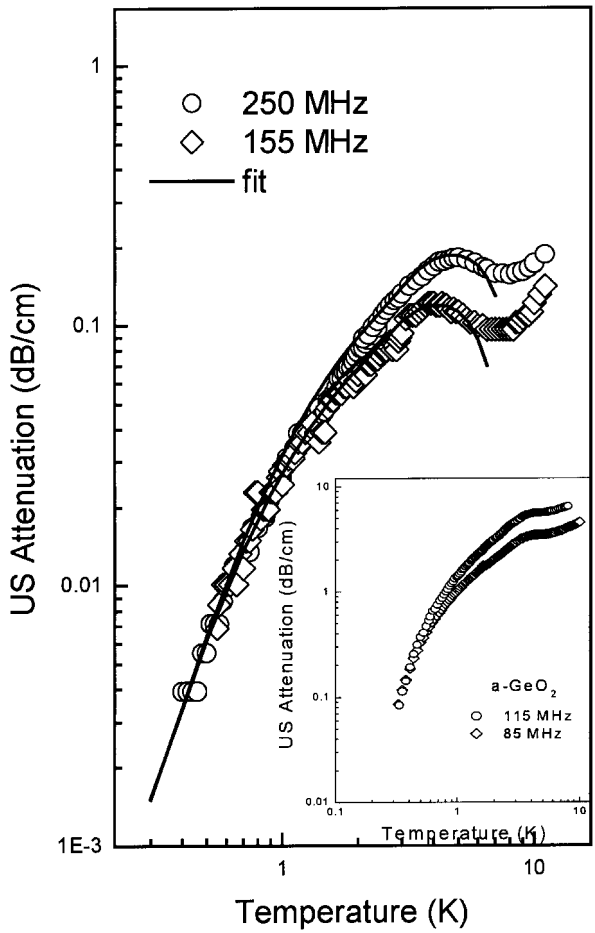

Figure 3. US attenuation data from a single crystal of $Sr_8Ga_{16}Ge_{30}$ measured at 250 and 155 MHz. For an ordinary crystalline material, the US attenuation is small and almost independent of temperature as $T \to 0$. By contrast, the attenuation in $Sr_8Ga_{16}Ge_{30}$ from 0.3 to 1 K shows a T^3 dependence and strongly resembles the attenuation of a structural glass such as GeO_2 (see inset). The $Sr_8Ga_{16}Ge_{30}$ data can be fitted using a tunnelling state model very similar to that used to model the US attenuation data from neutron-irradiated quartz (Keppens and Laermans 1995).

Sr ion can be different from site to site (the neighbouring ions can be either Ga or Ge), it is not as random as it would be in an amorphous solid.

In conclusion, we have shown that the glass-like thermal conductivity in $Sr_8Ga_{16}Ge_{30}$ has its origin in tunnelling states *and* 'rattling' associated with the Sr ion 'spreading' into its atomic cage. The unusual 'spreading out' of the nuclear density (or electron density in X-ray studies) is a distinct crystallographic signature that can be used in the search for new crystalline materials with ultralow thermal conductivity. Producing glass-like behaviour in a crystalline solid is important for thermoelectric applications and may be important in other areas where materials of low thermal conductivity are required. Also, because the tunnelling states in $Sr_8Ga_{16}Ge_{30}$ are so simple, this material may serve as a model system and as a

guide towards the microscopic understanding of the tunnelling states in amorphous solids.

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References

Andersen, P. W., Halperin, B. I., and Varma, C. M., 1972, *Phil. Mag.*, **25**, 1.
Cahill, D. G., Watson, S. K., and Pohl, R. O., 1992, *Phys. Rev.* B, **46**, 6131.
Chakoumakos, B. C., Sales, B. C., Mandrus, D., and Nolas, G. S., 2000, *J. Alloys Compounds*, **296**, 80.
Cohn, J. L., Nolas, G. L., Fessatisdis, V., Metcalf, T. H., and Slack, G. A., 1999, *Phys. Rev. Lett.*, **82**, 779.
DeYoreo, J. J., Knaak, W., Meissner, M., and Pohl, R. O., 1986, *Phys. Rev.* B, **34**, 8828, and references therein.
Eisenmann, B., Schafer, H., and Zagler, R., 1986, *J. less-common Metals*, **118**, 43.
Keppens, V., and Laermans, C., 1995, *Phys. Rev.* B, **51**, 8602.
Keppens, V., Mandrus, D., Sales, B. C., Chakoumakous, B. C., Dai, P., Coldea, R., Maple, M. B., Gajewski, D. A., Freeman, E. J., and Bennington, S., 1998, *Nature*, **395**, 876.
Mahan, G. D., Sales, B. C., and Sharp, J. W., 1997, *Phys. Today*, March, 42.
Morelli, D. M., and Meisner, G. P., 1995, *J. appl. Phys.*, **77**, 3777.
Nolas, G. S., Cohn, J. L., and Slack, G. A., 1998a, *Phys. Rev.* B **58**, 164.
Nolas, G. S., Cohn, J. L., Slack, G. A., and Schujman, S. B., 1998b, *Appl. Phys. Lett.*, **73**, 178.
Phillips, W. A., 1981, *Amorphous Solids: Low-temperature Properties* (Berlin: Springer).
Sales, B. C., Mandrus, D., and Williams, R. K., 1996, *Science*, **272**, 1325.
Sales, B. C., Mandrus, D., Chakoumakos, B. C., Keppens, V., and Thompson, J. R., 1997, *Phys. Rev.* B, **56**, 15081.
Slack, G.A., 1979, *Solid St. Phys.*, **34**, 1.
Slack, G. A., 1995, *CRC Handbook of Thermoelectrics* (Florida: Chemical Rubber Company Boca Raton), pp. 407–440.
Zeller, R. C., and Pohl, R. O., 1971, *Phys. Rev.* B, **4**, 2029.