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Darek Michalski and Mary Anne White

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Thermal conductivity of an organic clathrate: Possible generality of glasslike thermal conductivity in crystalline molecular solids

Darek Michalski and Mary Anne White[a)]
Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada

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Thermal conductivity is generally considered to be one of the macroscopic properties that differentiate glassy materials from crystalline solids, and understanding the physical processes that give rise to thermal resistance can provide useful insight into this and other structure-property relations. Despite the preponderance of molecular solids among known materials, there is rather little information concerning the temperature dependence of their thermal conductivities.

The usual view of heat conduction in insulators is that thermal energy is carried by acoustic phonons. By analogy between the heat-conducting phonons of an insulating solid and the heat-conducting molecules of a gas, to a first approximation the Debye model for gas phase heat conduction is useful to understand heat conduction in simple solids. This model relates thermal conductivity (κ) to the heat capacity per unit volume (C), the velocity (v) and the mean free path (λ) of the energy carriers, $\kappa = Cv\lambda/3$. For many insulating crystalline solids at temperatures near or above the Debye temperature (θ_D), C and v are nearly independent of temperature and λ decreases with increasing temperature due to increased probability of Umklapp processes, leading to a negative value of $d\kappa/dT$ for $T \gtrsim \theta_D$. At lower temperatures, with λ at the maximum value allowed by imperfections and boundaries, $d\kappa/dT$ is positive in line with the requirement that $C \rightarrow 0$ as $T \rightarrow 0$.

For amorphous materials, λ is short even at high temperatures, κ is much less than for comparable crystalline solids, and $d\kappa/dT \geqslant 0$ at all temperatures. The origins of the thermal resistance mechanism in glasses and their near-universal behavior are the subject of much current discussion. It is clear, from a phenomenological point of view, that very low values of κ of amorphous materials (compared to crystals) and the temperature dependence of κ are due to the character of the mean free path; SiO_2 provides a good example.[1] Measurement of the thermal conductivity of a clathrate hydrate first raised the issue of glasslike thermal behavior in a crystalline system.[2]

Here we report results of the determination of the thermal conductivity of the CBr_4 inclusion compound of hexakis(phenylthio)benzene, $HPTB \cdot 2CBr_4$. HPTB was synthesized by a published route,[3] and the CBr_4 clathrate was prepared from a solution of HPTB in chloroform with excess CBr_4. Single crystals were produced from microcrystals by repeated thermal cycling (heating to dissolve, cooling to preferentially precipitate on seed crystals). Thermal conductivity measurements were carried out using a steady-state method[4] from 39 to 146 K; at higher temperatures the CBr_4 guest could be pumped away. The structure of $HPTB \cdot 2CBr_4$ is trigonal,[5] and the temperature gradient for the measurements was along the c^* direction. While most of the measurements were made on a single crystal that was 6.4 mm long and 14 mm^2 in cross-sectional area, four measurements were taken on another single crystal of 26 mm^2 cross-sectional area. The two sets of measurements are indistinguishable, as illustrated in Fig. 1.

The rather low thermal conductivity of $HPTB \cdot 2CBr_4$ warrants consideration of the Einstein[6] minimum thermal conductivity model and its Cahill–Pohl[1] modification. Both models consider heat conduction as a random walk between localized oscillators (identical oscillators and oscillators of varying sizes and frequencies, respectively). Using the values of θ_D and θ_E from analysis of the heat capacity of $HPTB \cdot 2CBr_4$,[7] we find that both the Einstein and Cahill–Pohl models underestimate the thermal conductivity by a factor of 2–3, although the temperature dependence is similar. This shows that thermal resistance mechanisms are nearly, but not quite, at their maximum effectiveness. Nevertheless, the simple Debye model yields very low mean free paths, of the order of the minimum allowed free path (~6 Å).

Perhaps even more interesting than the magnitude of the thermal conductivity is its temperature dependence: $d\kappa/dT > 0$ throughout the measured temperature range. These results show the ''universal'' behavior characteristic of glassy materials when κ is appropriately scaled[8] to a ''universal'' form

$$\frac{\kappa}{C^*} = \left[\frac{T}{\theta_D}\right]^3 \int_0^{\omega_D} \frac{k_B \theta_D \tau_{\text{tot}}}{h} \frac{\hbar \omega^4}{k_B T^2} \times \frac{\exp\,(\hbar\omega/k_B T)}{(\exp\,(\hbar\omega/k_B T) - 1)^2}\, d\omega, \tag{1}$$

where $C^* = 4\pi k_B^3 \theta_D^2 / h^2 v$, the Debye cutoff frequency is ω_D, k_B is the Boltzmann constant, $\hbar$ is Planck's constant divided by 2π and v is the group velocity. This ''universal glassy'' behavior is shown in terms of reduced temperature, T/θ_D, in Fig. 2 in comparison with several amorphous materials and some other molecular solids; these materials show strikingly similar behavior.

[a)] Author to whom correspondence should be addressed; Electronic mail: MAWHITE@CHEM1.CHEM.DAL.CA

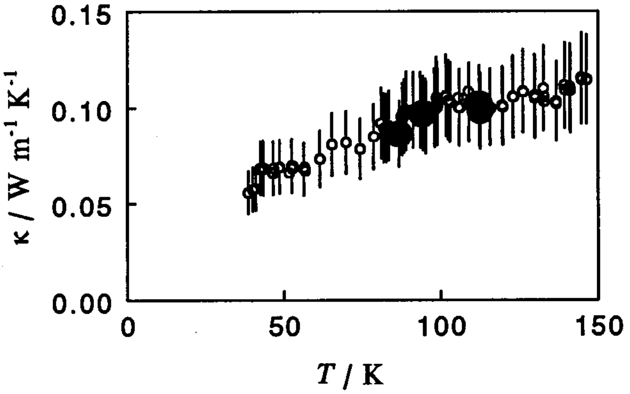

FIG. 1. Experimental values (Ref. 13) of the thermal conductivity (κ) of HPTB$\cdot$2CBr$_4$ as a function of temperature, T, including error bars. ○ and ● represent different samples, as described in the text.

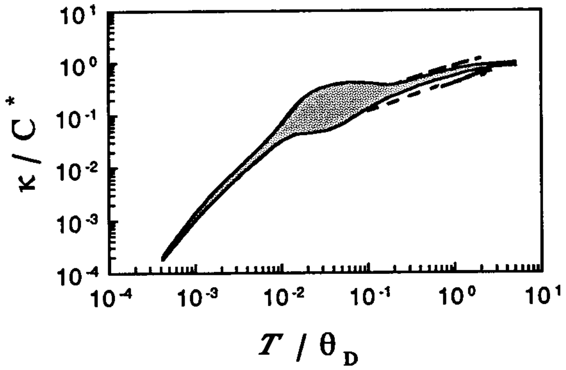

FIG. 2. Scaled (''universal'') thermal conductivities. The shaded area represents amorphous materials [SiO$_2$, B$_2$O$_3$, polybutadiene, poly(ethyleneterephthalate), polystyrene, poly(methylmethacrylate) (Ref. 8)]; – – – –, data for Dianin's compound (Ref. 11) and its CCl$_4$ clathrate (Ref. 12); - - - - -, data for the ethanol clathrate of Dianin's compound (Ref. 11); —, data for the present determination for HPTB$\cdot$2CBr$_4$.

In contrast with glasslike thermal conductivity in disordered systems (e.g., amorphous materials and CN$^-$ in KBr),[1] the present system is both crystalline and ordered (e.g., heat capacity analysis shows the CBr$_4$ guest to be rigid but librating[7]), yet the results fit the picture of glasslike thermal conductivity not very far from the minimum for localized oscillators. Resonant scattering of the acoustic phonons due to motions of the guest was used previously[4] to explain the thermal conductivity of THF clathrate hydrate, and this view is supported by recent molecular dynamics simulations.[9] Similar interactions between acoustic phonons and side chains have been proposed[10] to explain glasslike thermal conductivity in a crystalline organic polymer. Recent studies of Dianin's clathrand and its clathrates with mobile[11] and constrained[12] guests show that motion of molecular moieties leads to additional thermal resistance. The simplified physical picture of resonant scattering is that of energy hopping between the lattice and scatterers, thus effectively lowering the mean free path of acoustic phonons (i.e., damping the lifetimes of these phonons). A recent Raman spectroscopic investigation of HPTB$\cdot$2CBr$_4$ showed[7] the presence of several low-frequency optic modes in this material which would be in the correct frequency range for interaction with the heat-carrying acoustic phonons.

If low-lying localized optic modes are sufficient prerequisite to resonant scattering of acoustic phonons, the propensity of complex molecular crystals to have low-frequency optic modes could make glasslike thermal conductivity a wide-spread phenomenon in molecular solids. Further studies by direct methods would be required to elucidate the coupling mechanism. Nevertheless, given the prevalence of molecular materials, the common view of heat in solids being carried by long-wavelength acoustic phonons that are impervious to acoustic–optic coupling (this view leads to negative values of $d\kappa/dT$ for $T > \theta_D$), may indeed be a special case, only valid in those materials where optic and acoustic branches are well separated.

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[1] D. G. Cahill and R. O. Pohl, Annu. Rev. Phys. Chem. **39**, 93 (1988).
[2] R. G. Ross, P. Andersson, and G. Bäckstrom, Nature **290**, 322 (1981).
[3] A. D. Hardy, D. D. MacNicol, and D. R. Wilson, J. Chem. Soc. Perkin Trans. **2**, 1011 (1979).
[4] J. S. Tse and M. A. White, J. Phys. Chem. **92**, 5006 (1988).
[5] D. Michalski, M. A. White, P. K. Bakshi, T. S. Cameron, and I. Swainson, Can. J. Chem. **73**, 513 (1995).
[6] A. Einstein, Ann. Phys. **35**, 679 (1911).
[7] D. Michalski, R. T. Perry, and M. A. White, J. Phys.: Condens. Matter **8**, 1647 (1996).
[8] J. J. Freeman and A. C. Anderson, Phys. Rev. B **34**, 5684 (1986).
[9] R. Inoue, H. Tanaka, and K. Nakanishi, J. Chem. Phys. **104**, 9569 (1996).
[10] M. N. Wybourne, B. J. Kiff, and D. N. Batchelder, Phys. Rev. Lett. **53**, 580 (1984).
[11] M. Zakrzewski and M. A. White, Phys. Rev. B **45**, 2809 (1992).
[12] D. Michalski and M. A. White, J. Phys. Chem. **99**, 3774 (1995).
[13] Table of data available in D. Michalski, Ph.D. thesis, Dalhousie University, 1995.