Heat Transport by Fracton Hopping in Amorphous Materials

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The thermal conductivity κ of epoxy resin, MY750, cured with the stoichiometric quantity and twice that quantity of ethylene diamine, has been measured in the range 2–110 K. Both specimens show a plateau in κ in the liquid-helium region, and at higher temperatures κ has an additional term which is proportional to the temperature. This is in accord with the model of Alexander, Entin-Wohlman, and Orbach [Phys. Rev. B **34**, 2726 (1986)] for phonon-assisted fraction hopping above the plateau. The magnitude of this contribution, based on the theory of Jagannathan, Entin-Wohlman, and Orbach are in reasonable agreement with our experimental values.

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The study of the thermal properties of amorphous materials has been stimulated in recent years by the proposal of Alexander and Orbach that these materials should be treated as fractal systems. The spectra of their atomic excitations can then be interpreted as being a combination of propagating waves (phonons) at low energies and of localized excitations (fractons) beyond a certain energy whose wavelength corresponds to some characteristic structural length in the sample.

This model is able to account for the plateau in the thermal conductivity which is observed in almost all amorphous materials in the liquid-helium region. It is also able to explain the variations of both the specific heat and the thermal conductivity as the characteristic structural length is varied (Orbach and Rosenberg[1]).

The specimens used in these experiments are made from an epoxy resin hardened with ethylene diamine. The reason for using these rather complex polymers stems from the fact that by altering the proportion of hardener to resin it is possible to modify the cross-link density and hence to alter the characteristic molecular length of these materials. This is very important if one wishes to study these systems in the context of a fractal model because by changing the hardener concentration the transition from a quasicontinuum to a fractal system can be made to occur at different phonon wavelengths. Epoxy resins have the additional advantage that since they contain a large quantity of hydrogen they are well suited to study by incoherent inelastic neutron scattering; our initial investigations in this field (Dianoux, Page, and Rosenberg[2]) showed that the energy dependence of the density-of-states curves in these materials did vary with hardener concentration in a manner that was in accord with the predictions of the phonon-fracton model. The epoxy samples used in the present experiments are similar to those used in Refs. 1–3.

A further prediction of the theory (Alexander, Entin-Wohlman, and Orbach[4]) is concerned with the thermal conductivity at temperatures *above* the plateau. Earlier experiments suggested that the conductivity continued to rise with increasing temperature, but the lack of any supporting theory probably contributed to the lack of detailed measurements in this temperature region. Alexander, Entin-Wohlman, and Orbach[4] proposed that above the plateau the mechanism of thermal conduction might be that of phonon-assisted fracton hopping and they predicted that this would give rise to an additional term in the conductivity which would, at least at lower temperatures, be proportional to the temperature. The experiments described in this paper were made in order to investigate this prediction and as will be shown, it has been confirmed by experiment.

The thermal conductivities were measured with a Searle's bar technique in which one end of the sample is held at a fixed temperature while a constant heat input is applied to the other. The temperature gradient is assumed to be uniform and is calculated by measuring the temperature difference between the two points on the sample in a thermal analog of a four-terminal determination of the electrical resistivity.

For temperatures between 4.2 and 110 K, an Oxford Instruments CF1200 continuous-flow cryostat was used to measure the thermal conductivity. The coolant used was liquid helium throughout the temperature range. For the range 2–15 K, a conventional helium cryostat was used. In this apparatus a second heater at the cold end of the sample was used to increase the sample temperature above that of the helium reservoir up to a temperature of approximately 15 K. Using both of these experimental arrangements, we were able to measure the thermal conductivity in the range 2 to 110 K. In the temperature overlap region of the two cryostats there was good agreement between the two sets of readings.

The temperature gradient along the sample was measured with a gold +0.03% iron-Chromel thermocouple. A junction separation of ~ 7 mm was sufficient to give a reasonably accurate determination of the sample form factor (junction separation-sample cross-sectional area).

In order to reduce the thermal link between the two thermocouple junctions, a 60-cm length of the AuFe wire, wound loosely around a nylon screw, was used to connect them.

In both sets of apparatus the sample chamber was evacuated to a pressure of less than 5×10^{-6} Torr. Electrical connections from room temperature were wound around copper posts to provide thermal anchoring. A miniature diode thermometer supplied by the Institute of Cryogenics, Southampton University, and calibrated at the Clarendon Laboratory against a Tinsley 50-Ω rhodium-iron resistance thermometer was used to measure accurately the sample base temperature in the continuous flow cryostat. In the helium cryostat this temperature was measured by a separate thermocouple between the helium chamber and the specimen.

The thermocouple signals were carried via screened low-noise cables directly to a dc nanovolt amplifier (Keithley 148). The output from the amplifier was then passed to both a chart recorder and a digital voltmeter. In this way stable voltages of a few μV, with a resolution of 0.05 μV, could be measured.

Measurements were made on two samples of epoxy resin which were prepared by curing Araldite MY750 with the stoichiometric quantity and doubling the quantity of ethylene diamine (EDA). These are referred to as specimens EDA1X and EDA2X, respectively. In order to minimize the length of specimen needed to ensure heat flow parallel to the sample axis, the ends of the sample were machined perpendicular to the axis and a flat metal contact of copper braid was fixed across each end with Permabond epoxy resin. This defined isotherms which were orthogonal to the axis and provided a convenient means of attaching heaters. These heaters were made from 2-m lengths of 47 standard wire gauge Constantan wire, wound either around a protruding end of the lower (unanchored) copper braid or around the ends of both copper braids for measurements in the helium cryostat. The length of the samples was approximately 21 mm.

Besides small errors in measurement of heater power, sample form factor, and thermocouple resistivity, there are three further sources of error. The first is that the mean temperature of the specimen is not equal to the measured base temperature T_0; however, providing that $\Delta T/T_0 \leq 0.1$, this error is negligibly small. The second source of error, which may not be negligibly small, is due to radiative heat loss. A full treatment of this is given by Page[5] and is calculated to be less than 3% at 80 K. This is also in agreement with an estimate based on the expression given by Cahill and Pohl.[6] The third mechanism of heat loss is by thermal conduction down the various leads, but by using high thermal resistance wires this was reduced to less than 0.1%.

The thermal conductivities κ of EDA1X and EDA2X in the range 2–110 K are shown in Fig. 1. First, we note that there is good agreement between the two sets of

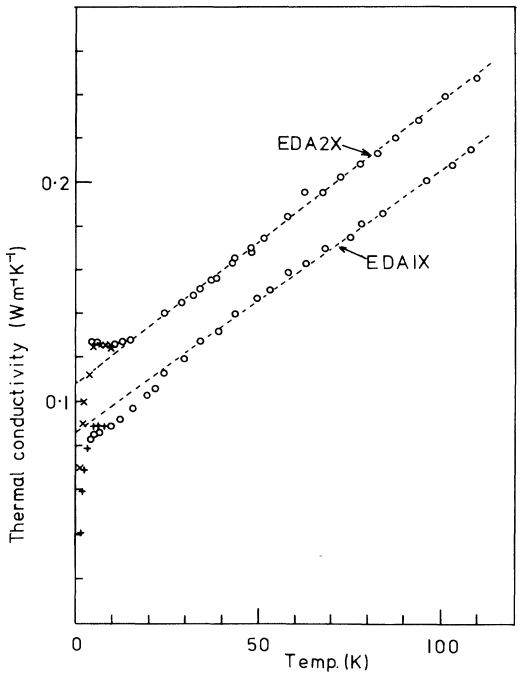

FIG. 1. The thermal conductivity of the two epoxy resin samples as a function of temperature. The linear region above ~30 K should be noted. Crosses denote readings taken in the helium cryostat and circles are those taken in the continuous-flow cryostat.

data obtained using different cryostats. Second, we see that above the plateau temperature there is a linear relationship between κ and T for both samples extending from ~30 to ~110 K, the upper limit of our measurement. The gradients of the straight lines fitted to the thermal conductivity above 30 K are 1.21×10^{-3} W m^{-1} K^{-2} for EDA1X and 1.30×10^{-3} W m^{-1} K^{-2} for EDA2X with an error of ±3%; i.e., there is an increase of 7.5% on going from EDA1X to EDA2X.

These measurements of κ vs T at high temperatures thus support the prediction of the fracton-hopping model.[4] On this basis the extrapolation of the straight line back to $T=0$ K gives information about the behavior of the phonon mean free path. Alexander, Entin-Wohlman, and Orbach[4] detail the consequences of the two extremes of behavior: $\kappa=\kappa_{\text{plateau}}+CT$, if the low-frequency (phonon) mean free path remains constant at higher temperatures, and $\kappa=CT$ if the low-frequency mean free path decreases strongly with increasing temperature. From our results we can see that neither extreme is the actual situation and that a low-frequency mean free path which decreases slowly with increasing temperature would explain the observations.

Jagannathan, Entin-Wohlman, and Orbach[7] have recently developed the theory in more detail and they have derived expressions for the phonon and fracton lifetimes in the processes (a) phonon+phonon → fracton and (b)

phonon + fracton → fracton. In order to calculate the magnitude of the fracton-hopping contribution [i.e., process (b)] it is necessary to know (or eliminate) the anharmonic coupling constant. Since this constant determines the phonon lifetime, the calculation can proceed by deriving this lifetime from measured values of the conductivity where the phonon conduction is dominant, i.e., just below the conductivity plateau. They show that the coefficient of the linear term in the hopping conductivity is then given by

$$\text{const} \times \frac{k_B \omega_c^2}{\zeta \tau_2 T_2 \omega_{\text{ph}}^2}, \tag{1}$$

where τ_2 is the phonon lifetime deduced from the value of the conductivity at a temperature T_2 which is just below the plateau, ω_{ph} is the dominant phonon frequency at that temperature, ω_c is the frequency of the phonon-fracton crossover, and ζ is the corresponding phonon wavelength. k_B is Boltzmann's constant. The constant is of order unity. An expression of this form can be obtained from Ref. 4 by substituting their equation for the phonon lifetime [Eq. (29)] into their expression for the hopping conductivity [Eq. (42)]. A more detailed derivation is given in Ref. 7, Eq. (27).

We have evaluated this expression for EDA1X and EDA2X. For ω_c we used the frequency at which the Raman scattering shows a very sharp change of slope (Table I of Boukenter, Duval, and Rosenberg[8]) and which they suggest indicates the onset of the fracton regime. This is much more clearly defined than is the change of slope in the density of states as deduced from inelastic neutron-scattering experiments (Rosenberg[3]). We took T_2 to be 2.4 K, which is just below the thermal conductivity plateau, and we determined τ_2 from the specific-heat and thermal-conductivity data of de Oliveira.[9] The values of these parameters are given in Table I.

With use of (1), the calculated values of the linear temperature term of the conductivity are 1.7×10^{-3} and 2.0×10^{-3} W m^{-1} K^{-2} for EDA1X and EDA2X, respectively. These should be compared with the experimental values of the data in Fig. 1 which are 1.21×10^{-3} and 1.30×10^{-3} ($\pm3\%$). If we take into account the fact that the precise value of the numerical constant in (1) is not known, the agreement between the theory (which is an absolute calculation) and experiment is very satisfactory.

TABLE I. Values of the parameters used in the evaluation of Eq. (1) for the two specimens EDA1X and EDA2X.

	$\hbar\omega_{\text{ph}}/k_B$ (K)	$\hbar\omega_c/k_B$ (K)	ζ (m)	τ_2 (s)	T_2 (K)
EDA1X	2.4	27.9	3.15×10^{-9}	1.42×10^{-10}	2.4
EDA2X	2.4	36.0	2.52×10^{-9}	2.45×10^{-10}	2.4

The constant prefactor in (1) is a function of the fraction dimensionality, the localization length, and the spectral dimension, which are not established with sufficient accuracy for our samples. If values of these quantities appropriate to a percolating network are used, the prefactor is approximately 0.6. This would bring the coefficients calculated in the previous paragraph down to 1.02×10^{-3} and 1.2×10^{-3}. Of course, not too much should be read into this, but it suggests that if the prefactor for our samples was known, better agreement between theory and experiment might be achieved.

While we have used the phonon-fracton model in order to interpret our experimental results, we are well aware that there is still some skepticism as to whether this model is a valid description of excitations in systems such as ours. In comparing experimental data with the model, it should be particularly noted that the linear region of thermal conductivity due to fracton hopping will *not* occur if anharmonic effects are strong and therefore one would not expect it to be observed at higher temperatures.

Thus Dixon and Nagel[10] show that the conductivity of *o*-terphenyl mixtures does not change on going from the solid to the liquid state and from this they suggest that a fracton model is inappropriate—but near the melting point the anharmonicity will be so strong that the fracton concept will probably collapse and a single-particle model (although with perhaps a spatial extent) might be more appropriate.

The measurements of Cahill and Pohl[6] have also been used to argue against the fracton-hopping model. They have observed that the thermal conductivities of six glasses do not follow a linear temperature dependence up to room temperature. But as discussed above, due to the onset of anharmonicity, one would not expect linearity over the entire temperature range and, indeed, their measurements clearly show that the thermal conductivity of amorphous SiO_2 does have a linear dependence on the temperature until $\sim$100 K. Hence we assert that their experiments can be interpreted in terms of the fracton-hopping model.

Löhneysen, Ratai, and Buchenau,[11] in experiments on the heat conductivity and specific heat of cross-linked irradiated polybutadiene, state that their results do not indicate any pronounced feature in going from the expected phonon-to-fracton regime. This work ignores the fact that a marked crossover region is not universal. There is no reason why it should not be smooth, and indeed it does appear to be so in the simulations of Yakubo and Nakayama.[12] One would then find a specific heat per T^3 vs T plot which would not change shape as the length scale is altered by irradiation.

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