Inelastic Neutron Scattering in Epoxy Resins: The Phonon-Fracton Density of States and the Specific Heat

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Inelastic neutron-scattering experiments have been used to determine the density of states, $G(E)$, of thermal excitations in epoxy resins. The results show that, over part of the range, $G(E)$ increases with an energy (E) dependence which is higher than E^2. This is in accord with the predictions of the phonon-fracton model of Derrida, Orbach, and Wu. Calculations of the low-temperature specific heat using the measured density of states are in reasonable agreement with experiment, but it is shown that these calculations are very sensitive to the values of $G(E)$ below $E = 1$ meV.

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In a recent paper[1] Derrida, Orbach, and Wu have calculated the density of states, $G(E)$, versus energy, E, relationship for a percolating network. They used the effective-medium approximation and showed that $G(E)$ is proportional to E^2 at low energies (phonons), but at higher E, where the excitation wavelength approaches some characteristic dimension of the system, $G(E)$ increases more rapidly than E^2 and it then increases much more slowly than in the phonon regime. This increase in the energy dependence of $G(E)$ beyond E^2 indicates the change from phonon (propagating) to fracton (localized) excitations. While these results have been derived for a percolating network, the general feature which they exhibit—i.e., the increase in the dependence of $G(E)$ above E^2 at the phonon-fracton boundary—is thought to be a more general feature of amorphous systems. Indeed, in order to fit their experimental specific-heat data on epoxy resins, Kelham and Rosenberg[2] and Nicholls and Rosenberg[3] had to assume that $G(E)$ varied more rapidly than E^2 over part of the energy range.

In the present work, the density of states of epoxy resin samples has been derived from inelastic neutron-scattering experiments. The specimens were made from Araldite MY 750 resin (DGEBA) hardened with simple organic compounds—ethylene diamine and other primary diamines. In these samples the structural dimensions were changed by varying the amount of hardener from the stoichiometric quantity for complete crosslinking to two and three times this amount. The effect of increasing the quantity of hardener is to prevent a completely cross-linked system from developing and this results in a material which has shorter structural units. The specimens were in the form of discs approximately 50 mm in diameter and they were only 0.2 mm thick so that the probability of multiple neutron scattering was less than 10%. The measurements were taken at the Institut Laue Langevin, Grenoble, on the time-of-flight spectrometer IN6. In order to reduce the effect of multiphonon processes and yet still obtain a good counting rate the specimens were cooled to 80 K. The neutron wavelength was 5.1 A (approximately 5 meV) and the resolution of the energy of the scattered neutrons was about 0.1 meV (1 meV = 11.6 K). Inelastic scattering data were taken for five different samples and a typical sample of a set of results is shown in Fig. 1.

The results were then analyzed to determine the density of states of the excitations. In each case it was found that there was an increase in the dependence of $G(E)$ above the E^2 dependence and this began at energies above about 1.15 to 1.5 meV (depending on the sample). In addition the onset of the rise above the E^2 relation depended on the size of the structural units, in accord with the discussion above.

An example is presented in Fig. 2 which gives log-log plots of $G(E)$ vs E. Figure 2(a) shows the results for DGEBA hardened with the stoichiometric quantity of ethylene diamine, while in Fig. 2(b) the sample had three times the stoichiometric quantity and hence had smaller structural units. The deviation from E^2 starts at about 1.15 meV in 2(a) while in 2(b) it does not deviate from E^2 until about 1.35 meV. The shift is in the direction which one would expect from the calculations of Ref. 1.

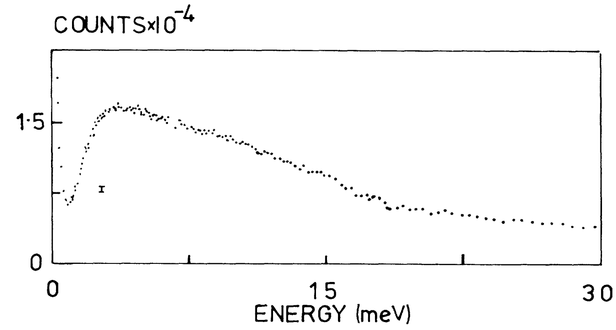

FIG. 1. A typical set of inelastic neutron-scattering data (stoichiometric hardener) as a function of neutron energy gained. The probable error limits are indicated by the bar.

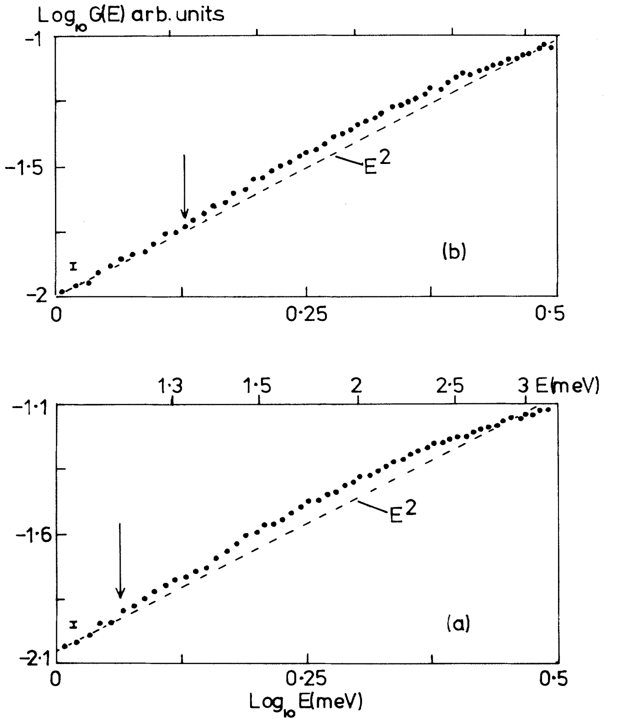

FIG. 2. The dependence of the density of states, $G(E)$, on the energy for two epoxy-resin samples, derived from the inelastic neutron-scattering experiments. The deviation at the arrows from the E^2 dependence (dashed line) should be noted. The bar indicates the probable error limits. (a) Specimen of MY 750 hardened with the stoichiometric quantity of ethylene diamine, (b) specimen of MY 750 hardened with three times the stoichiometric quantity of ethylene diamine. This should have shorter structural units than (a) and it should be noted that the breakaway from E^2 occurs at a higher energy than in (a).

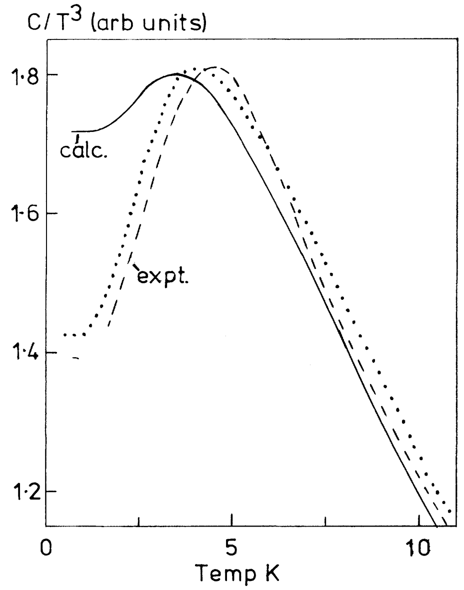

FIG. 3. The specific heat C, plotted as C/T^3 vs T, for MY 750 with stoichiometric hardener [Fig. 2(a)]. The experimental results are indicated by the dashed line and the values calculated from the data in Fig. 2(a) are indicated by the continuous line. The dotted line shows the results of calculations made with all values of $G(E)$ below $E = 1$ meV reduced by 21%.

To check whether these results give a true picture of the density of states, the specific heat in the range 2 to 15 K was calculated and compared with the experimental data of Farrell, de Oliveira, and Rosenberg.[4] The specific heat, C, of all these samples when plotted as C/T^3 vs T (to emphasize deviations from the Debye theory) shows that C/T^3 increases as the temperature is increased from 1.5 K and it then passes through a maximum at about 4–5 K before decreasing rapidly as the temperature is further increased to 15–20 K (see dashed line in Fig. 3).

In order to use the $G(E)$ results from the neutron-scattering experiments to calculate C/T^3 it is necessary to extrapolate the values for $G(E)$ below $E = 1$ meV because in this region the wings of the neutron elastic peak are beginning to intrude and also the number of counts is rather small. Thus in this region there is an uncertainty in $G(E)$ and it was assumed that it had an E^2 dependence which joined on to the rest of the $G(E)$ curve at 1 meV. The experimental (dashed) and calculated (continuous) curves are shown in Fig. 3 normalized to the peak of the experimental curve. It is seen that the general features of the experimental curve are reproduced but that the peak is at a slightly lower temperature and the initial rise from 1.5–4 K is not so marked.

Since, as already stated, there is some uncertainty in the values of $G(E)$ below 1 K, C/T^3 was also calculated with the values of $G(E)$ decreased by 21% for all values of E below 1 meV (dotted line in Fig. 3). This has the effect of increasing the temperature at which the maximum in C/T^3 occurs and it also increases the extent of the initial rise below the maximum. I place no significance on the reasonable fit which is now obtained between the neutron scattering and the specific-heat data, but this procedure shows the sensitivity of the results of specific-heat calculations to the precise values of $G(E)$ which are used, (especially at low energies); the possible errors in such calculations can be quite considerable.

It should also be pointed out that if the deviation above E^2 is ignored—i.e., if $G(E)$ is assumed to vary as E^2 until it decreases at higher energies—then no maximum in the C/T^3 curves will be obtained. This maximum, which is observed in all glassy materials, necessitates an increase in the power dependence of $G(E)$ beyond E^2 over part of the range.

The results of inelastic neutron scattering thus confirm the predictions of the phonon-fracton model that the density of states of the thermal excitations increases with a power dependence in energy which is higher than E^2. Calculations of the specific heat using this density of states give results which are similar to, although not in complete agreement with, experimental values.

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