FROM B
TOM

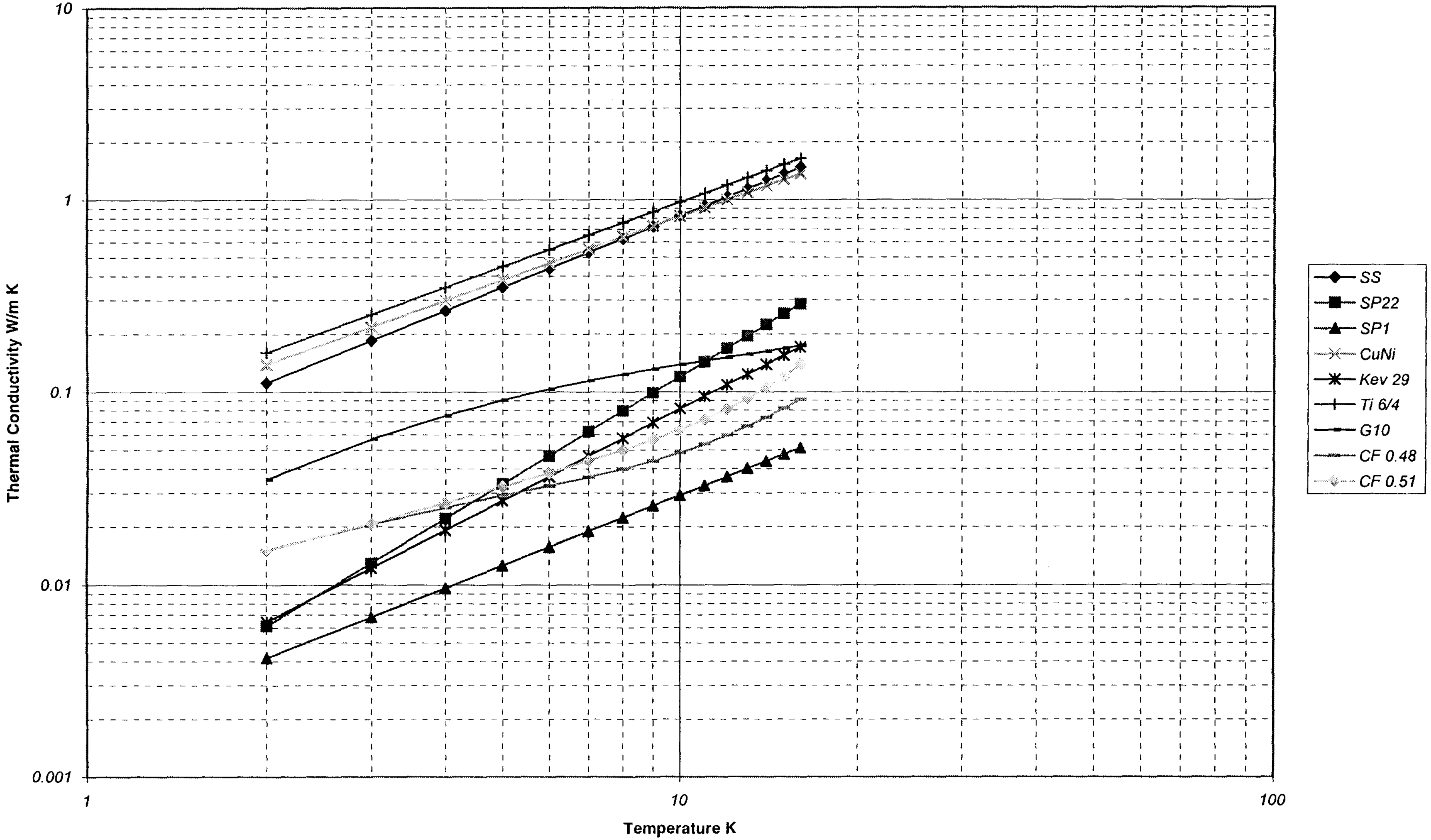
SPIRE-RAL-NOT-000163
MATERIALS PROPERTIES

Collected Materials

Source	*Cryo data book*	*Olson*	*Locatelli*	*Olson*	*Duband*		*Umezawa*	*Casen etal*	*Nich &Rosenberg*	
Validity					*5 - 40K*		*to 15K*	*20-300*	*2-20*	*2-20*
Material	*SS*	*SP22*	*SP1*	*CuNi*	*Kev 29*	*Kev 29*	*Ti 6/4*	*G10*	*CF 0.48*	*CF 0.51*
Designation	*type 340*				*Fibre*	*Cord*				
Const	*0.04745*	*0.0017*	*0.0018*	*0.065*	*0.00215*	*0.00215*	*0.07388*			
B	*1.2406*	*1.85*	*1.21*	*1.1*	*1.58*	*1.58*	*1.12*			

Temp	*SS*	*SP22*	*SP1*	*CuNi*	*Kev 29*	*Kev 29*	*Ti 6/4*	*G10*	*CF 0.48*	*CF 0.51*
2	*0.112123*	*0.006129*	*0.004164*	*0.139331*	*0.006428*	*0.006428*	*0.160576*	*0.03526*	*0.015123*	*0.015017*
3	*0.185418*	*0.012975*	*0.006801*	*0.217644*	*0.012198*	*0.012198*	*0.252873*	*0.056967*	*0.020605*	*0.020845*
4	*0.264943*	*0.022093*	*0.009633*	*0.298662*	*0.019217*	*0.019217*	*0.349007*	*0.075273*	*0.025146*	*0.026644*
5	*0.349445*	*0.033384*	*0.012619*	*0.381751*	*0.027341*	*0.027341*	*0.448098*	*0.090679*	*0.02907*	*0.032402*
6	*0.438138*	*0.046777*	*0.015734*	*0.46653*	*0.036468*	*0.036468*	*0.549612*	*0.103648*	*0.032668*	*0.038158*
7	*0.530475*	*0.062213*	*0.01896*	*0.55274*	*0.046526*	*0.046526*	*0.653186*	*0.114606*	*0.036196*	*0.044001*
8	*0.626051*	*0.079646*	*0.022285*	*0.640195*	*0.057454*	*0.057454*	*0.758556*	*0.123943*	*0.039882*	*0.050069*
9	*0.724552*	*0.099037*	*0.025698*	*0.728753*	*0.069206*	*0.069206*	*0.865523*	*0.132009*	*0.043916*	*0.056548*
10	*0.825726*	*0.120351*	*0.029193*	*0.818302*	*0.081741*	*0.081741*	*0.973928*	*0.139116*	*0.04846*	*0.063675*
11	*0.929369*	*0.143557*	*0.032761*	*0.908752*	*0.095025*	*0.095025*	*1.083644*	*0.14554*	*0.053641*	*0.071736*
12	*1.035305*	*0.16863*	*0.036398*	*1.000029*	*0.10903*	*0.10903*	*1.194565*	*0.151518*	*0.059553*	*0.081067*
13	*1.14339*	*0.195544*	*0.0401*	*1.092071*	*0.123728*	*0.123728*	*1.306602*	*0.157249*	*0.06626*	*0.092053*
14	*1.253495*	*0.224278*	*0.043862*	*1.184825*	*0.139098*	*0.139098*	*1.419679*	*0.162897*	*0.073789*	*0.105127*
15	*1.36551*	*0.254811*	*0.047681*	*1.278244*	*0.155118*	*0.155118*	*1.533731*	*0.168584*	*0.082139*	*0.120774*
16	*1.479338*	*0.287125*	*0.051553*	*1.372288*	*0.17177*	*0.17177*	*1.648699*	*0.174396*	*0.091274*	*0.139528*

Integrals										
Const	*0.021177*	*0.000596*	*0.000814*	*0.030952*	*0.000833*	*0.000833*	*0.034849*			
B	*2.2406*	*2.85*	*2.21*	*2.1*	*2.58*	*2.58*	*2.12*			
Integral 4	*0.472985*	*0.031008*	*0.017435*	*0.568879*	*0.029794*	*0.029794*	*0.658504*	*0.130518*	*0.057027*	*0.060166*
Integral 2	*0.100083*	*0.004301*	*0.003768*	*0.132696*	*0.004983*	*0.004983*	*0.151487*	*0.017716*	*0.01613*	*0.018486*
Difference	*0.372902*	*0.026707*	*0.013667*	*0.436183*	*0.024811*	*0.024811*	*0.507017*	*0.112801*	*0.040897*	*0.041681*
Integral 4	*0.472985*	*0.031008*	*0.017435*	*0.568879*	*0.029794*	*0.029794*	*0.658504*	*0.130518*	*0.057027*	*0.060166*
Integral 15	*9.141595*	*1.341109*	*0.323625*	*9.130314*	*0.90185*	*0.90185*	*10.85187*	*1.574569*	*0.593737*	*0.767777*
Difference	*8.66861*	*1.310101*	*0.306189*	*8.561435*	*0.872055*	*0.872055*	*10.19336*	*1.444052*	*0.536709*	*0.707611*
UTS typical Mpa	*580*	*50*	*50*	*450*	*3600*	*1500*	*1000*	*415*	*1500*	*1500*
	Data sheet	*guess*	*guess*	*data book*	*Duband*	*Duband*	*Data sheet*	*Cold 826* *Casen*	*DE estim*	*DE estim*
*FOM 2-4K *1e6*	**642.935**	**534.148**	**273.341**	**969.296**	**6.89208**	**16.541**	**507.017**	**271.81**	**27.2648**	**27.7871**
*FOM 15-4K * 1e6*	**14945.9**	**26202**	**6123.79**	**19025.4**	**242.238**	**581.37**	**10193.4**	**3479.64**	**357.806**	**471.741**
	8	10	6	9	1	2	7	5	3	4



From Tom B

SPIRE/Material Selection.xls

CFRP K < GFRP K FOR T < 20 K
(APPROX)

The thermal conductivity of one type of glass-fibre/epoxy and three types of carbon-fibre/epoxy composites has been measured from 2 to 80 K in directions parallel and perpendicular to the fibres for various volume concentrations of fibre. In the liquid helium region the conductivity of the carbon fibre composites is in general lower than that of epoxy alone. The conductivity of the fibres themselves has also been measured. The results on composites in the parallel direction are in good agreement with a volume average theory at all temperatures for glass, and above 10 K for carbon fibre, but below 10 K it would appear that account should be taken of the reduction in the phonon mean free path in the epoxy due to the presence of the fibres. In the perpendicular direction, allowance must be made for the acoustic mismatch between fibre and matrix and here the theory does not agree so well with the experimental results.

The thermal conductivity of glass-fibre and carbon-fibre/epoxy composites from 2 to 80 K

D.J. Radcliffe and H.M. Rosenberg

Keywords: cryogenic, thermal conductivity, composites

This paper describes the results of measurements of the thermal conductivity of composites made from carbon and glass fibres incorporated uniaxially into an epoxy-resin matrix. Measurements on bundles of fibres were also made. In the discussion we shall show that the results are in reasonable accord with current ideas. A preliminary account of this work has been given.[1]

Experimental techniques and specimens

The thermal conductivity was measured using the conventional Searle's bar technique. The composites were made in the form of small bars and gold-iron: chromel thermocouples were used to measure the temperature difference between two points along the specimen length when it was heated from one end. Liquid nitrogen, hydrogen and helium baths were used in a cryostat which covered the temperature range 2 to 80 K.

The glass fibre composites were prepared in the laboratory using an E-type glass fibre, Equerove XRE 23/29 (diameter 20 μm) from Pilkingtons Ltd. The resin was Epikote 828 with Epikure NMA hardener and BDMA accelerator in proportions 100:90:0.5 parts by weight respectively. Samples were prepared with various volume concentrations of fibre, V_f. Two types of specimen were cut so that measurements could be taken with the heat flow either parallel or perpendicular to the fibre axis.

The carbon fibre specimens were pultruded specimens prepared by Courtaulds Ltd. These were made from three types of PAN-based Grafil fibre which are identified as A (general purpose) HT (high tensile) and HM (high modulus). The fibres were approximately 7 μm in diameter and Epikote 828 was again used as the resin matrix. The values of V_f are given with the experimental results.

Carbon fibre is manufactured by first heating polyacrylonitrile (PAN) fibre under tension in an oxidizing atmosphere at about 200°C and then at above 1000°C in an inert atmosphere. The conditions of this final heat treatment determine the extent to which the fibres are graphitized. The higher the temperature the more complete is this graphitization and this yields the HM samples, which are those with the highest elasticity modulus. The HT and A type materials are produced at lower temperatures. Thus the HM fibres are composed of larger crystallites which are better aligned than are the A and HT-type fibres.

Glass fibres – results

The thermal conductivity of a bundle of 20 000 glass fibres and also of the bulk epoxy – resin are shown in Fig. 1. Both of these curves illustrate the behaviour which is typical of the conductivity of glassy materials. The conductivity increases as about $T^{1.8}$ at low temperatures, it then passes through a plateau region (from 8 to 20 K for glass and from 3 to 8 K for epoxy) above which the conductivity again rises slowly with temperature. It will be noted that the glass has a higher conductivity over the entire temperature range of the present experiments. Detailed discussions of the mechanisms which are responsible for the form of the curves are given in the literature.[2,3]

Glass fibre composites – conductivity parallel to the fibres, results and discussion

The thermal conductivity of the glass/epoxy composites parallel to the fibre direction is shown by the points in Fig. 2 for $V_f = 0.35$, 0.45 and 0.70. The conductivity is higher for the specimens with larger values of V_f, which is to be expected, and the form of the curves is very similar to that for the bundle of fibres (Fig. 1).

Since the heat flow is parallel to the fibres the total conductance of a specimen is equal to the sum of the conductances of the two components and the conductivity of the composite will be given by

$$K = V_f K_{\mathrm{fibre}} + (1 - V_f) K_{\mathrm{matrix}} \qquad (1)$$

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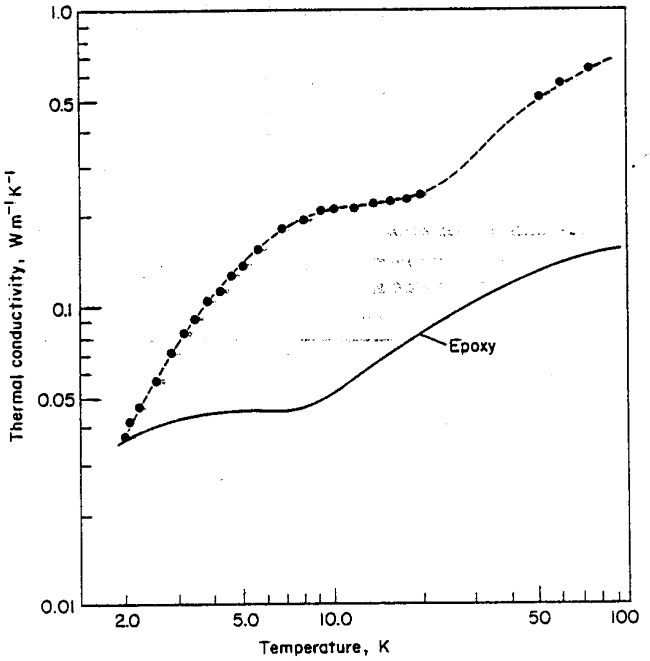

Fig. 1 The temperature dependence of the thermal conductivity of Equerove XRE fibreglass (●) (as deduced from measurements on a bundle of fibres) and of Epikote 828 epoxy resin (solid curve)

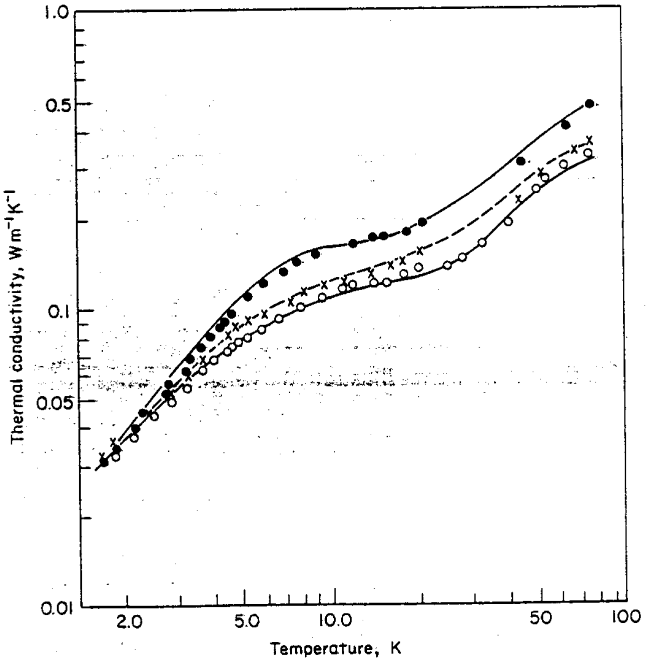

Fig. 2 The temperature dependence of the thermal conductivity of fibreglass/epoxy composites in a direction parallel to the fibres for specimens of various fibre volume concentrations, V_f. $V_f = 0.70$ (●), 0.45 (x), 0.35 (o). The solid lines are the results of calculations using (1)

Calculated values of K using the data of Fig. 1 in (1) are shown by the solid lines in Fig. 2 and it is seen that agreement with the measured values is very satisfactory. It is actually to within 5% over the whole temperature range.

Glass fibre composites – conductivity perpendicular to the fibre axis

The conductivity perpendicular to the fibre axis was measured in samples with $V_f = 0.33$, 0.46 and 0.77. The results are shown by the points in Fig. 3. In all cases the values are lower than for the corresponding samples when measured parallel to the fibres.

The results have been used to test the theory of Lord Rayleigh[4] who calculated the conductivity of a medium containing a square array of cylinders measured perpendicular to their axes. The expression he derived for the conductivity is:

$$K = K_m\left[1 - \frac{2V_f}{\nu + V_f - \dfrac{3V_f^4}{\nu^2\pi^4}S^2}\right] \qquad (2)$$

where

$$\nu = \frac{K_m + K_f}{K_m - K_f}$$

and

$$S = 0.032\,\pi^4$$

The solid lines in Fig. 3 show the values obtained by using this formula. Between 10 and 78 K there is agreement to within 5% or better with the experimental results, but as the temperature is reduced below 10 K the lack of agreement between theory and experiment becomes more serious, especially for the sample with the highest volume concentration of fibre. One reason for disagreement might be that (2) is for a square array of cylinders. This is hardly an accurate description of our samples and deviations might be expected to be greater at high values of V_f, where quite a large number of fibres will actually touch one another. However such a consideration if taken into account would only lead to an extra geometrical factor throughout the whole temperature range and since agreement is quite good above 10 K it is unlikely that it is the major source of the discrepancy.

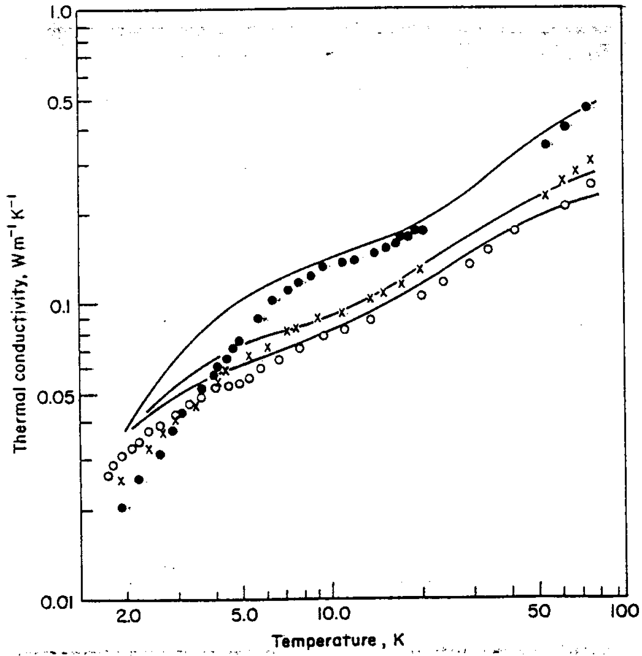

Fig. 3 The temperature dependence of the thermal conductivity of fibreglass/epoxy composites in a direction perpendicular to the fibres. $V_f = 0.77$ (●), 0.46 (x), 0.33 (o). The solid lines are the results of calculations using (2)

The most likely reason for the conductivity being lower than the calculated value is that there is an extra thermal resistance due to the acoustic mismatch which occurs at the boundaries between the fibres and the matrix. This will give rise to an additional scattering mechanism for phonons and it will reduce the thermal conductivity. Such a mismatch has been observed in measurements of particle-filled composites (see Garrett and Rosenber)[5] and is a well-established effect. In order to take the mismatch into account the parameter ν in (2) must be modified to ν'

where

$$\nu' = \frac{K_m + \rho K_f}{K_m - \rho K_f} \tag{3}$$

and

$$\rho = [1 + K_m k/a]^{-1} \tag{4}$$

a is the fibre radius and k is the thermal boundary-resistance coefficient which is given by the theory of Little[6] and it can be calculated from the measured sound velocities and density of epoxy and glass. However, it is found that on substituting ν' for ν, (2) still overestimates the conductivity. The discrepancy is most conveniently shown by plotting the values of k/a which would be necessary in order to obtain agreement between theory and experiment and those calculated from Little's theory. These are shown in Fig. 4. It will be noted that the observed magnitude of k/a is greater than that predicted by the theory and its temperature dependence is less steep. It would appear that theory and experiment should coincide at about 1 K. This type of discrepancy has been observed previously[7] and has not yet been satisfactorily explained. It is possible that there might be imperfect contact between the fibres and the resin through poor adhesion or because of the formation of bubbles, but the effect seems to be so general that this is not very likely. In addition, the fact that the agreement seems to improve at low temperatures gives support to the suggestion[3] that this extra boundary resistance is due to the fact that there is a cut-off frequency beyond which phonons have a very short mean free path in the resin. This effect will of course be more pronounced at higher temperatures. There is also the possibility that small scale boundary imperfections produce extra scattering. These would be less effective in scattering phonons of large wavelength compared with those of shorter wavelength. It should also be noted that the Little theory only applies to materials when the specific heat obeys the Debye T^3 law which is not the case for either epoxy or glass in our temperature region.

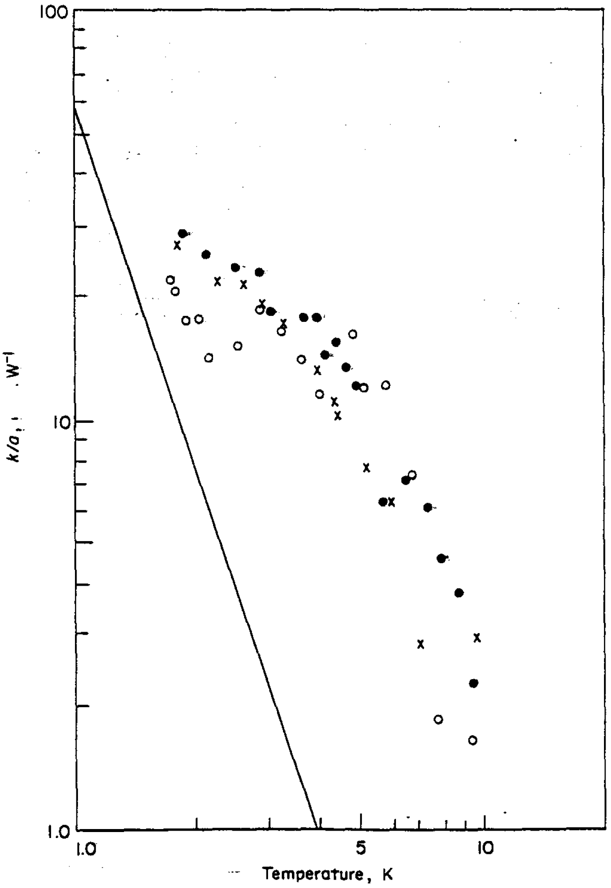

Fig. 4 Values of the ratio k/a in (4) which are necessary in order to give a boundary thermal resistance for fibreglass/epoxy which is in agreement with the experimental data. V_f = 0.77 (●), 0.46 (x), 0.33 (o). The solid line is the value of k/a as calculated from the theory of Little[6]

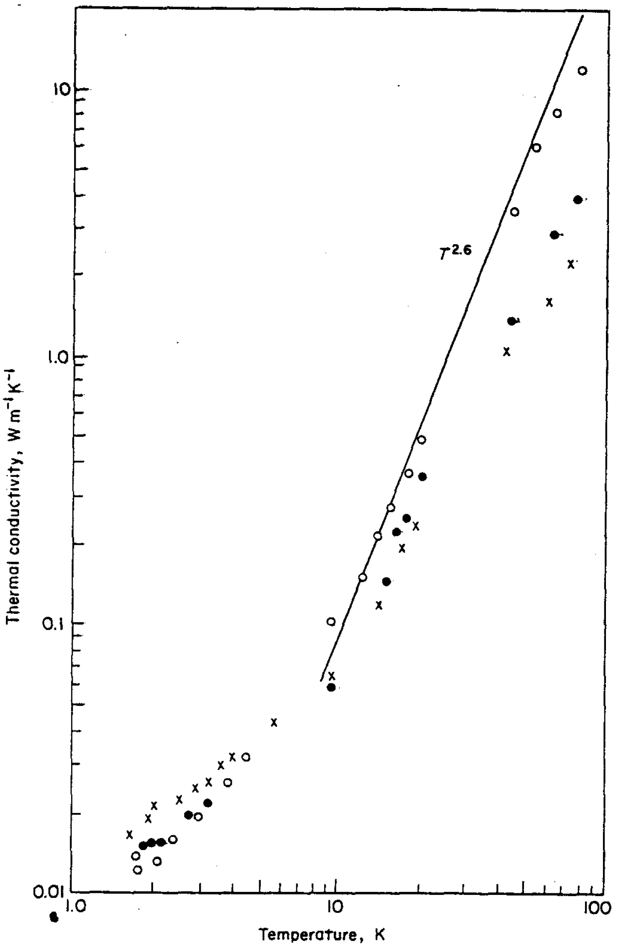

Fig. 5 The temperature dependence of the thermal conductivity of three types of Grafil carbon fibre as deduced from measurements on a bundle of fibres. HM type (o), HT type (●), A type (x)

Carbon fibres — results and discussion

The thermal conductivity of bundles of about 100 000 carbon fibres of each of the three types of fibre was measured and the results are shown in Fig. 5. Above about

10 K the HM fibre had the highest conductivity, followed by the HT and A types. Below 10 K the order was reversed with the A type having the highest conductivity. In the liquid helium region the conductivity was approximately proportional to T, but from 10 K to 50 K it varied as approximately $T^{2.6}$, $T^{2.1}$ and T^2 for the HM, HT and A types respectively.

A full discussion of these results is very complicated because of the very large anisotropy of graphite crystals and a detailed discussion is given by Radcliffe.[8] He concludes that the thermal conductivity of the fibres is due only to phonon heat transport and that the electrons play almost no part in the heat flow. In the liquid helium range the T^1 dependence can be explained by assuming that the dominant phonon wavelengths are larger than the crystallite sizes within the fibres, whereas at higher temperatures they are smaller than the crystallite sizes and so ordinary boundary scattering limits the phonon mean free path. This would suggest that the difference in the high temperature conductivity between the HM, HT and A type fibres is due to that fact the the HM has the largest size crystallites.

Carbon fibre composites — conductivity parallel to the fibres

The thermal conductivity of carbon fibre composites made from the three types of fibre are shown in Fig. 6. It should be noted that V_f for the A type is considerably less (0.31) than for the HM (0.51) and HT (0.48) types. Superficially, the curves for these composites show roughly the same type of behaviour as do the fibres alone.

The solid lines show the results of using the weighted aver formula (1). At higher temperatures the agreement with th measured values is quite good, but at 5 K this formula ove estimates the conductivity by about 20% and the discrepa becomes worse at lower temperatures. It will be recalled that for the glass fibre composites the agreement was very good over the entire temperature range.

We suggest that the discrepancy is due to the fact that the thermal conductivity of the resin is lower than the bulk value because the carbon fibres will limit the phonon mea free path in the resin. This effect will be more marked tha in the case of the glass fibre composites because the diameters of the carbon fibres are about three times smalle than the glass fibres and also the acoustic mismatch at the carbon/epoxy interface will be much greater than at the glass/epoxy interface. For a sample with $V_f = 0.5$ the mea free path between fibre surfaces is equal to the fibre diameter[9] and in our samples this is 7 μm. Using the mode of the phonon spectrum given by Kelham and Rosenberg[2] we can estimate the effect of this additional scattering mechanism on the thermal conductivity. This would reduc the conductivity of the epoxy by about 0.021 W m^{-1} K^{-3} between 2 and 4 K. This is just about the right decrease needed (it should be 0.020) to achieve good agreement between (1) and the measured values and it therefore suggests that the hypothesis for the decrease in the phono mean free path is a reasonable one.

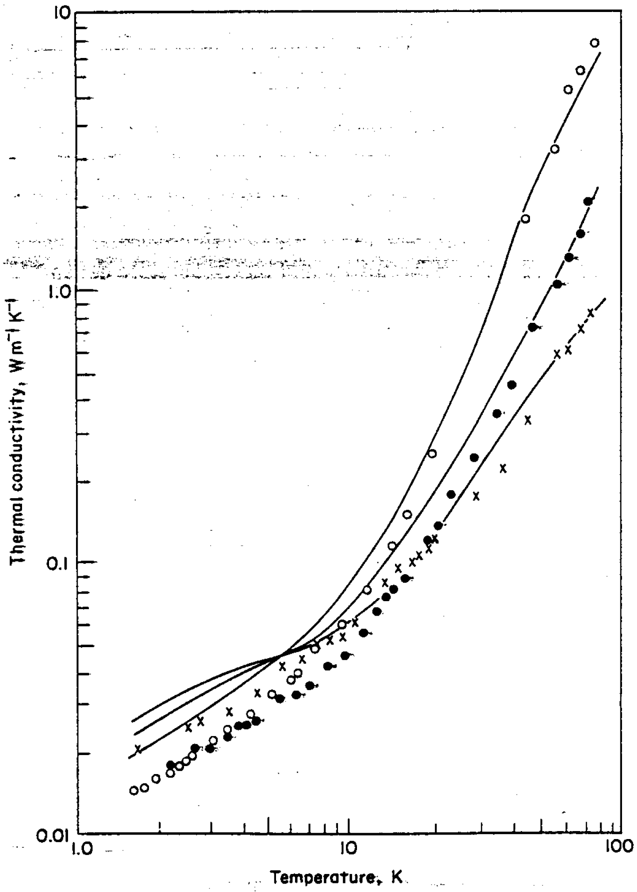

Fig. 6 The temperature dependence of the thermal conductivity of carbon fibre/epoxy composites in a direction parallel to the fibres. HM type, $V_f = 0.51$, (o), HT type, $V_f = 0.48$, (•), A type, $V_f = 0.31$, (x). The solid lines are the results of calculations using (1)

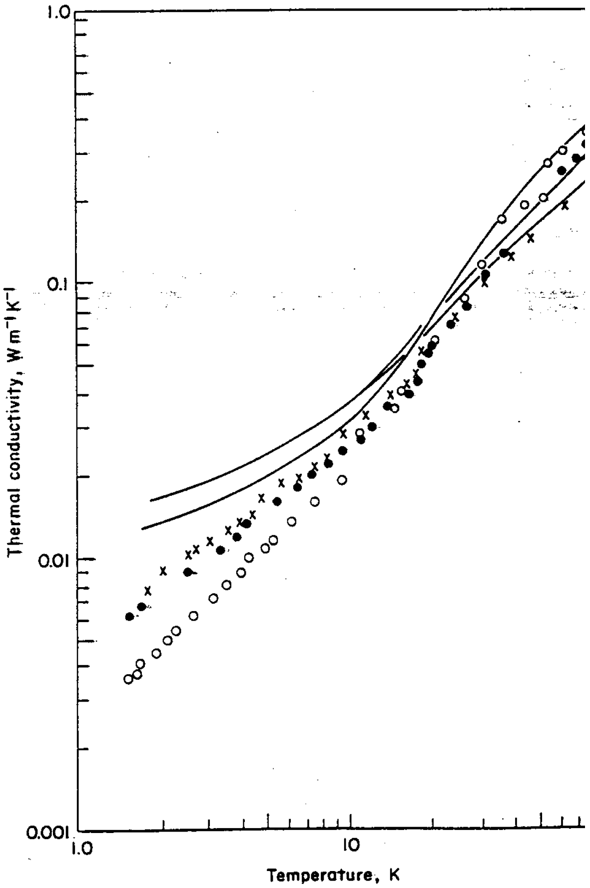

Fig. 7 The temperature dependence of the thermal conductivity carbon fibre/epoxy composites in a direction perpendicular to the fibres. HM type, $V_f = 0.50$, (o), HT type, $V_f = 0.50$, (•), A type, $V_f = 0.50$, (x). The solid lines are the results of calculations using (2) and an anisotropy value of 10

Composite conductivity perpendicular to the fibre

The conductivity perpendicular to the fibre axes for the three types of fibre composites is shown in Fig. 7. Note that here V_f is 0.50 for each of the specimens.

As in the case of the glass composites we can in principle use the Rayleigh formula, (2), to calculate the conductivity, but since graphite is so anisotropic we cannot assume that the conductivity along the fibre axis (which we measured, Fig. 4) is the same as that transverse to the axis. A study of the literature (see Radcliffe[8]) would suggest that an anisotropy ratio ($K_\parallel/K_\perp$) of about ten would be reasonable and the effect of using these values in (2) is shown by the full curves in Fig. 7. The discrepancy below about 10 K which still arises is, as in the case of glass fibre composites, due to acoustic mismatch between fibre and epoxy although in the case of carbon fibres this mismatch is so great that straightforward boundary scattering can be assumed as a first approximation. However, in view of our uncertainty regarding the anisotropy factor for graphite, it seems hardly profitable to make an estimate of the acoustic mismatch merely in order to get a better fit to the experimental data.

Conclusions

This work shows that it is possible to predict the thermal conductivity of fibre composites with reasonable confidence at temperatures above about 10 K in directions both parallel and perpendicular to the fibres. Below 10 K the predictions always overestimate the conductivity especially if the fibres are thin and anisotropic as is the case with carbon fibre. Carbon fibre/epoxy composites with their very low expansion coefficient and thermal conductivity and their high rigidity should be very suitable materials for cryogenic construction.

We should like to thank Dr G. Gould of Courtaulds Limited for providing us with the carbon fibre specimens. This work was done during the tenure of an SRC studentship by DJR

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