The thermal conductivity of several exfoliated graphites (Grafoil, Foam, and UCAR-ZYX graphite) has been measured in the range 2 to 300 K. The temperature dependence of the thermal conductivity is similar to that of near-single-crystal pyrolytic graphite, but the value is two orders of magnitude lower.

Thermal conductivity of several exfoliated graphites from 2 K to 300 K

C. Uher

Over the past decade considerable research interest has been shown in the adsorption and physical properties of both monolayer and multilayer films of helium and other inert gases. Various forms of exfoliated graphite with a large ratio of area to volume are traditionally used as substrates for such studies. As the measurements are made at low temperatures it is important to know the heat flow characteristics of the substrates. I have therefore measured the thermal conductivity from 2 to 300 K of the three most frequently used exfoliated graphite substrates: Grafoil, Foam, and UCAR-ZYX[2].

Grafoil is made by exfoliating ground-up natural crystals and rolling them into a thin sheet. The rolling press aligns the c-axis so that basal planes are inclined at $\leqslant 30°$ to the sheet, but the crystallite size is only about 100-200 Å. A less severe roll gives a much less dense material called graphite Foam. The UCAR-ZYX graphite is produced by a careful exfoliation from a stress-annealed near-single-crystalline pyrolytic graphite and is left unrolled. The crystallite size and orientation is estimated an order of magnitude better than that of Grafoil[3]; however, the density is smaller.

The thermal conductivity was determined by a steady-state method over the temperature range 2K - 300K. In the case of Grafoil and Foam, the thermal conductivity was measured both along a rolling direction, $K_{\parallel}$, and normal to the rolling plane, $K_{\perp}$. The thermal conductivity of ZYX graphite was investigated only along the exfoliated leaves; the measurement across the leaves might not make much sense due to layers being frequently separated from each other. The temperature gradient along the sample was set up by passing a known current through a high-stability, metal-film 10 KΩ resistor and the temperature difference was monitored by pairs of calibrated platinum and/or carbon-glass resistance thermometers (Lake Shore Cryotronics, Inc., NY). Since the thermal conductivity of all types of graphite is very small in the liquid helium temperature range, great care must be exercised in the choice of connecting wires to the heater and thermometers in order to keep the heat loss negligible. We used 0.045 mm diameter cupro-nickel-clad niobium-titanium wires to the heater and 0.07 mm diameter Evanohm wires to the thermometers. Even at the lowest temperature the thermal conductance of all connecting leads was never more than 1% of the conductance of the samples. (It is very helpful to apply a silver-solder coating to the ends of Evanohm wires before attempting the soft-solder joint).

The samples were cut by an air abrasive machine into: parallelipipeds when measuring along the rolling direction; and discs when measuring across the rolling planes. The dimensions and densities of the samples are given in Table 1. Since the thermal conductance along a single thin sheet of Grafoil (0.26 mm thick) is very small for measurement along the rolling planes, we joined eleven such layers in parallel using very thin films of GE-7031 varnish. In addition to increasing the thermal conductance by a factor of eleven, it also produced a much more rigid sample. Both ends of the parallelipipeds and two strips 1 mm wide, separated by 12 mm on each face of the sample, were copper plated.

(No strips were plated on ZYX graphite as it was difficult to prevent undesirable deposition of copper between the layers. Thermometers in this case were attached using silver-loaded GE-7031 varnish).

The plated surfaces were wet with low melting point Cerro-low solder. OFHC-copper cups filled with molten Cerrolow were placed over each end of the sample, one cup being attached to the cold finger of the cryostat and the other cup to a heater. Miniature Cerrolow-plated copper clamps containing the thermometers were then positioned over the plated strips on the sample, slowly heated until the solder melted, and gently tightened.

For the measurement across the rolling plane, the sample was sandwiched between an OFHC-copper disc containing

Table 1. Dimensions, density, and exponent in the temperature dependence of the thermal conductivity of the investigated samples.

Material	Dimensions, mm	Density, g cm^{-3}	Exponent in T^m 5K-50K
Grafoil $\parallel$	2.86 x 3.08 x 30	0.82	2.76
Grafoil $\perp$	ϕ8.54 x 0.26		2.47
Foam $\parallel$	4.50 x 3.75 x 30	0.172	2.82
Foam $\perp$	ϕ8.30 x 0.98		2.53
ZYX $\parallel$	4.43 x 1.9 x 30	~0.5	2.55

the heater and hot thermometers and a disc on the cold finger of the cryostat with a pair of cold thermometers. Highly conducting bonds were made through a thin layer of silver-loaded varnish.

A gold-plated radiation shield was placed over the sample and fastened to the base of the cryostat in order to minimise the radiation loss at higher temperatures. The hot end of the sample was never more than a degree above the base temperature and the radiation loss, even around room temperature, amounted to no more than 1-2% of the power supplied to the heater. At the start of each run, the experimental cell was evacuated and the sample degassed for 48 h at 40°C.

Experimental data are shown in Fig. 1. While the temperature dependence of the thermal conductivity of all exfoliated graphites investigated is similar to that of near-single-crystal pyrolytic graphites[4,5,6], the actual value of the
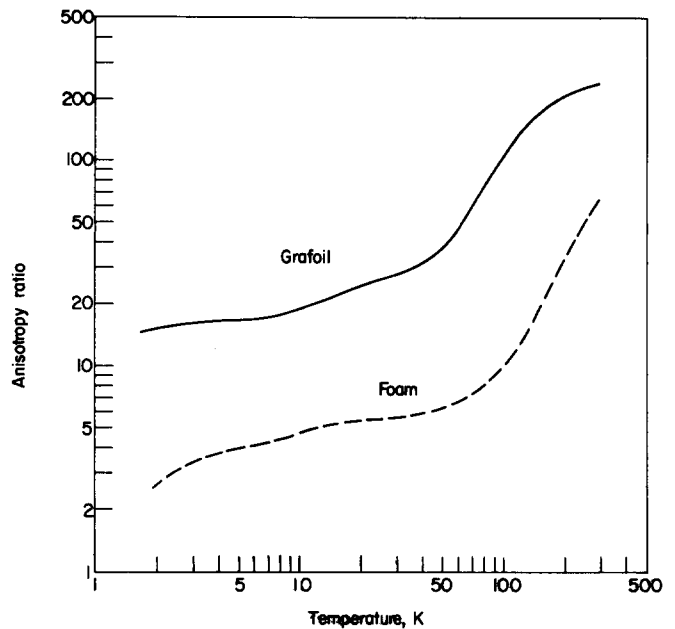
Fig. 2 Anisotropy ratio $(K_\parallel/K_\perp)$ for Grafoil and Foam plotted against T

thermal conductivity is lower by nearly two orders of magnitude. There are two main reasons for this: firstly, the density of the exfoliated graphites is much small than 2.2 $g\ cm^{-3}$, the density of near-single-crystal graphite (see Table 1) and, secondly, the size of the crystallites is smaller and they are only partially oriented. We can also see this trend clearly by comparing individual materials. Thus the thermal conductivity of Grafoil along the rolling direction is nearly an order of magnitude larger than the corresponding value for a much less dense and more misaligned Foam. In the transverse direction, however, the smaller density of Foam is compensated for by its greater degree of misorientation with the result that a larger fraction of the high conductivity, in-plane component contributes towards the transport. The overall effect is that in the transverse direction Grafoil and Foam look very similar. ZYX graphite, while having a smaller density than Grafoil, has larger and better aligned crystallites and therefore a higher thermal conductivity at low temperatures.

The thermal conductivity of Grafoil measured along the rolling direction in the present investigation is smaller by a factor of two to three and normal to the planes it is larger by a factor of two than the measurements of Hedge et al.[1] made on Grafoil in the range 1.7 to 4.2 K. More important, while the temperature dependences of the conductivity are similar across the rolling planes, they differ vastly along the rolling direction; a slower than linear temperature dependence observed by Hegde et al. is very uncharacteristic of the graphites. The discrepancy in the actual value of the thermal conductivity could be explained partly by the fact that their Grafoil sample was rolled to about half the thickness of the one measured here. Unfortunately Hegde et al. did not indicate the density of their Grafoil and it is possible that their sample had higher density and, hence, an apparent higher conduction along the planes. It is, however, very unlikely that a small density change would result in a dramatically different temperature dependence of the conductivity. Rather, one suspects that their data for the conduction along the planes are affected by a large heat loss along the leads.
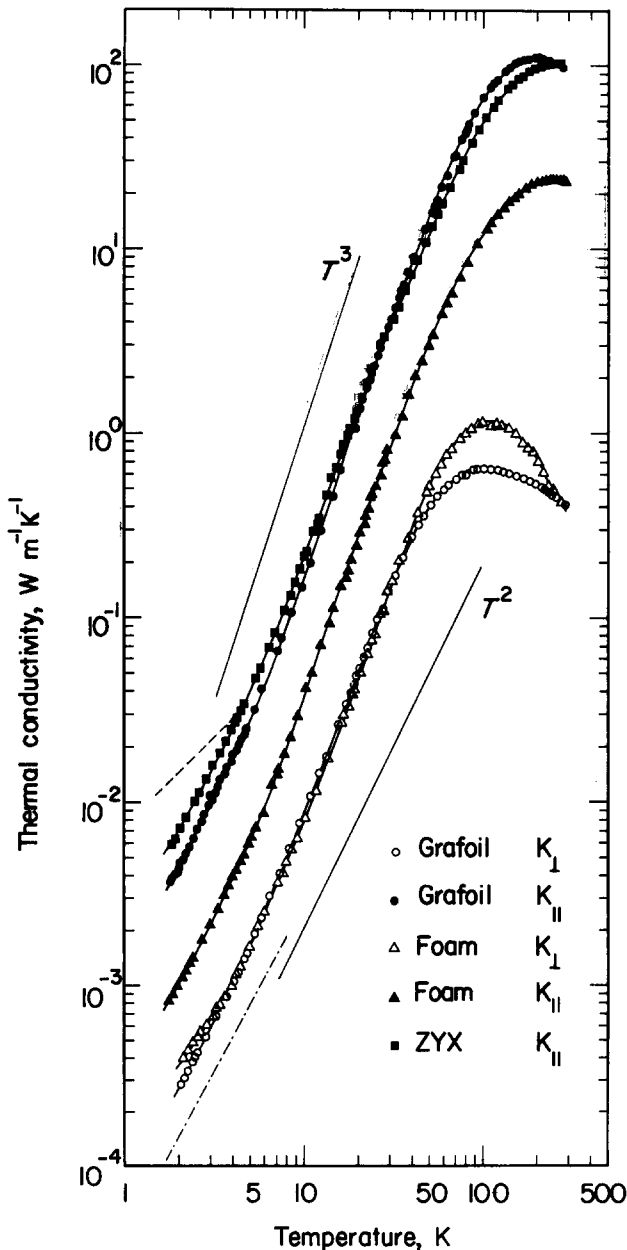

Fig. 1 Temperature dependence of the thermal conductivity of exfoliated graphites. A broken line and a chain line indicate the measurements of Hedge et al. made on Grafoil along the rolling direction and normal to the rolling plane respectively

The authors did not indicate the type of wires they used, but the danger is easily appreciated when realising that a single sheet of Grafoil which they measured has, at around 4 K, the same conductance as a single 46 swg copper wire more than 1 metre long. Apart from the possibility that we are comparing Grafoils of different density, it is difficult to explain the difference between the values of the thermal conductivity measured normal to the rolling planes. (While the conducticity here is typically a factor of 10^2 smaller, the geometrical ratio is about 10^4 times more favourable and the heat loss is a far less serious problem). In both cases the temperature difference across the Grafoil is not determined directly on its surface, but includes a contact resistance of either sintered gold or a thin layer of silver-loaded varnish. However, because of the very small sample conductivity this leads to an insignificant error.

Anisotropy of the thermal conductivity $(K_\parallel/K_\perp)$ is illustrated in Fig. 2. While the shape of the two curves is similar, the anisotropy of Grafoil is much larger than that of Foam. This is understandable because the severe rolling process used to produce Grafoil results in better alignment of the crystallites and approaches the layered graphitic structure far better than in the case of Foam. The anisotropy is a strong function of temperature. In the liquid helium range it is about 3 for Foam and 15 for Grafoil, increasing sharply above about 60 K and reaching 60 and 230, respectively, at room temperature. The behaviour is thus qualitatively similar to that observed for pyrolytic graphites [4,5].

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