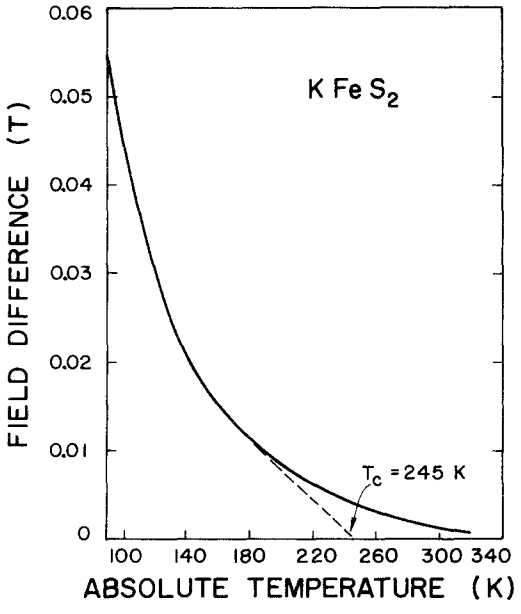

Figure 3 Temperature dependence of the field difference $H - H_0 = \lambda M$ in $KFeS_2$ at 9.25 GHz.

where λ is a constant and $H = h\nu/g\beta$ is the resonance field at high temperatures. The difference $H - H_0$ is plotted in Fig. 3 as a function of temperature. The results yield a transition temperature $T_c = 245$ K, which is consistent with the value obtained using the Mössbauer effect [2].

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Chemical characterization of Kevlar-49

The high-performance, high-modulus fibre Kevlar 49 is described by its manufacturer as an aromatic polyamide. An analysis by Penn and co-workers [1] showed that the polymer was largely poly (*p*-phenylene terephthalamide). However in their analysis only 70% of the terephthalic acid was recovered and none of the diamine. The nature of the amine was inferred from its degradation products. The possibility of other diamines, diacids or amino aromatic acids being incorporated in the polymer could not be discounted. In our method of analysis the yields of terephthalic acid and *p*-phenylene diamine indicate that the polymer is almost wholly poly(*p*-phenylene terephthalamide) (Fig. 1).

Aromatic amides are known to be readily and cleanly hydrolysed in concentrated sulphuric acid solution [2]. The amine can be recovered unchanged if sulphonation is avoided by using diluted acid. Simple aromatic amides are readily hydrolysed at 100° C, but Kevlar is unaffected at this temperature and requires temperatures in excess of 150° C.

The fibre (DuPont, Kevlar 49 roving, approximately 0.4 g), previously dried at 120° C for 2 h, dissolved in 90% sulphuric acid (10 g) on heating to 190–200° C, and within 15 min terephthalic acid separated from solution. The mixture was then cooled and poured into water (100 ml). The precipitate was collected, washed with water, dried and weighed. In a typical analysis 0.356 g of fibre gave 0.242 g of terephthalic acid which is 98% of that expected on the basis of the polymer being poly(*p*-phenylene terephthalamide). An infra-red spectrum confirmed the precipitate as terephthalic acid. The acid was esterified with methanol containing hydrogen chloride by refluxing until all the acid dissolved. The solution was then evaporated to dryness. The recovered ester was analysed by gas liquid chromatography (GLC) on SE30 and OV17 columns and found to be dimethyl terephthalate at better than 99% pure. The other

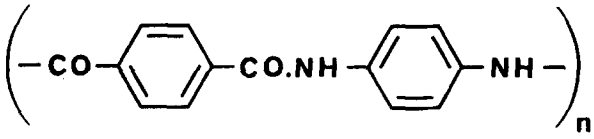

Figure 1 Poly (*p*-phenylene terephthalamide).

isomeric esters were not detected, nor any monofunctional acid ester from acids which might have been used to control the molecular weight of the polymer.

The hydrolysate, after removal of the precipitate, was neutralized with sodium hydroxide containing sodium metabisulphite (0.2 g). Sodium acetate (2.5 g) and acetic anhydride (1 ml) were then added, successively. The precipitated acetyl derivative was collected, washed with water and dried in a vacuum. An infra-red spectrum showed the material to be diacetyl *p*-phenylene diamine. GLC on a OV 210 column confirmed this identification and showed no impurities. From 0.490 g of Kelvar, 0.309 g of the diacetyl derivative was obtained corresponding to 78% of theoretical yield. However, this method does not give quantitative recovery of the diamine. When *p*-phenylene diamine was acetylated under the same conditions only 90% was recovered. Thus at least 85% of the diamine in Kevlar can be considered to be *p*-phenylene diamine.

An ultra-violet spectrum of the hydrolysate was not like that expected for *p*-phenylene diamine; however, if this amine is treated with 90% sulphuric acid at 190° C the spectrum obtained is very similar. This absorption is probably due to a highly absorbing oxidation product. The hydrolysate was investigated further by thin layer chromatography on silica gel using mixtures of chloroform, ethanol and aqueous ammonia (s.g. 0.88) as eluants. Other amines such as *m*-phenylene diamine, *p*-aminophenol and *p*-aminobenzoic acid were not detected.

Thus this analysis of Kevlar 49 fibre is consistent with its being solely a condensation polymer from terephthalic acid and *p*-phenylene diamine, confirming the conclusions derived from instrumental analysis of Gan and co-workers [3]. The suggestion by Brown and Ennis [4] that there are *p*-aminobenzoic acid derived groups in the polymer is not supported by the present work.

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Hardness anisotropy of α-Si_3N_4 single crystal

High hardness of silicon nitride (Si_3N_4) is exceedingly attractive in both cold and hot tribological applications [1, 2]. However, the hardness of Si_3N_4 varies widely depending upon the fabrication methods such as reaction sintering, hot pressing and chemical vapour depositing techniques [3–9]. This might be attributed not only to improper techniques and incipient cracking around an indenter in hardness measurements, but also to the composition, density (porosity), inclusions and microstructure of samples measured. To know the real hardness characteristic of Si_3N_4, the effect of crystallographic orientation on the hardness of α-Si_3N_4 single crystals has been examined.

Single crystals of α-Si_3N_4 for hardness measurements were needle-like crystals along the [0 0 0 1] or [2 $\bar{1}$ $\bar{1}$ 0] directions (up to 15 mm long, 1.5 mm^2 in cross-section) and pyramidal crystals with large (1 1 $\bar{2}$ 0) or (1 0 $\bar{1}$ 0) planes (up to 3.5 mm^2 area), which were prepared by pyrolysis of a NH_3 and H_2-carried $SiCl_4$ mixture on a heated graphite