Magnetic resonance in $KFeS_2$ single crystals

$KFeS_2$ is a monoclinic crystal (space group symmetry C^6_{2h}) with four formula units per unit cell [1]. The iron atoms are located at equivalent sites and are strongly bonded to sulphur atoms, forming $(FeS_2)^-$ ions. These ions are associated in chains of FeS_4 tetrahedra, which account for the fibrous character of the substance. The bonds between the tetrahedra are mainly covalent.

The magnetic properties of $KFeS_2$ have been investigated by Kerler *et al.* [2] and by Taft *et al.* [3, 4], using the Mössbauer effect. A magnetic phase transition was observed at 245 K [3].

In the present paper we report magnetic resonance measurements in the same compound, from which we were able to measure the magnetic parameters g and H_A and to obtain an independent determination of the transition temperature.

The specimens were prepared by fusing non-oxidized iron powder with potassium carbonate and sulphur and leaching the cold product in water [2]. The samples were characterized by X-ray diffraction. They were flat plates made of aligned single crystal fibres. The fibre long axis corresponds to the crystallographic c-axis. Typical dimensions were 1 cm x 0.2 cm x 0.01 cm, where the first dimension refers to fibre length.

Magnetic resonance measurements in the temperature range 90 to 320 K were made using a Varian E-12 X-band spectrometer equipped with phase sensitive detection and giving output in derivative form. The samples were mounted at the tip of a cold finger cryostat using liquid nitrogen. Stable temperature settings were assured with a copper–constantan thermocouple in conjunction with a proportional heat controller. The magnetic field was calibrated using a proton resonance gaussmeter. A digital frequency meter was used to measure the microwave frequency. All magnetic field data were converted to 9.25 GHz.

The room-temperature absorption spectrum of a typical sample is shown in Fig. 1. The resonance line is isotropic with $g = 2.0095 \pm 0.0005$. Fig. 2 shows the angular dependence of the resonance field at 100 K, with the magnetic field in the plane of the sample. The solid line is a least-squares fit to the equation

$$H_{\text{res}} = H_0 + H_A(3\cos^2\theta - 1) \qquad (1)$$

with $H_0 = 0.2873\,\text{T}, H_A = -0.0014\,\text{T}$.

The change in H_0 between 90 K and 320 K is of the order of 0.055 T. Since important changes in g are not expected, this suggests the presence of a demagnetization field [5]. In that case, the value of H_0 in Equation 1 is given by [5]:

$$H_0 = H - \lambda M \qquad (2)$$

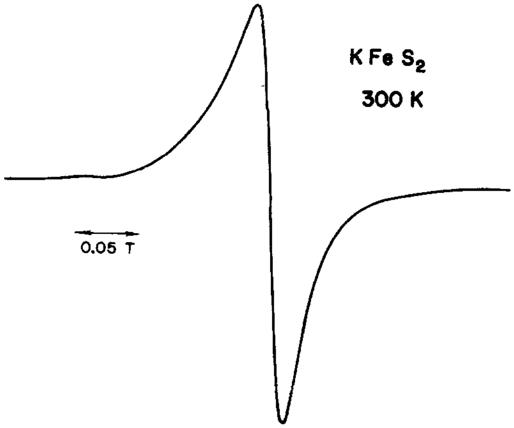

Figure 1 Room temperature absorption spectrum in $KFeS_2$ at 9.25 GHz.

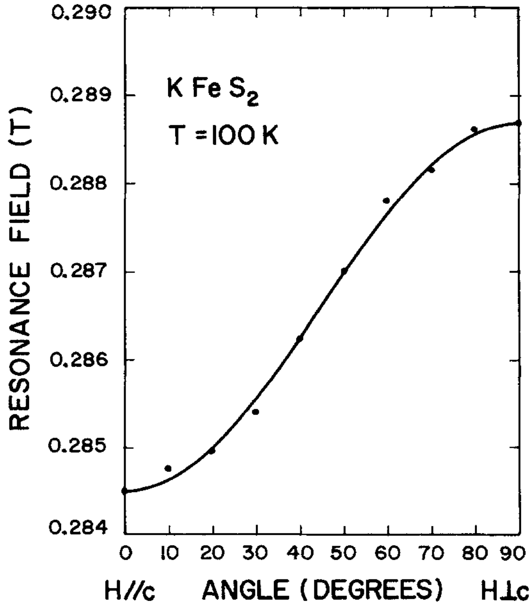

Figure 2 Angular dependence of the resonance field in $KFeS_2$ at 100 K and 9.25 GHz.

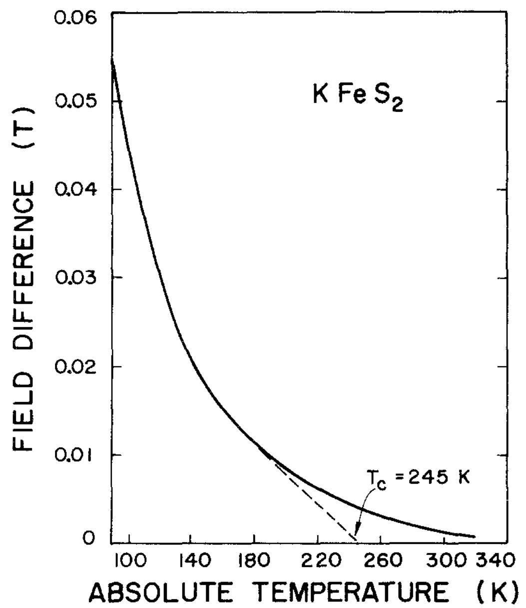

Figure 3 Temperature dependence of the field difference $H - H_0 = \lambda M$ in KFeS$_2$ at 9.25 GHz.

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