A broad-line nuclear magnetic resonance study of stress-induced crystallinity changes in poly(vinylidene fluoride)

J. Clements*, G. R. Davies and I. M. Ward
IRC in Polymer Science and Technology, University of Leeds, Leeds LS2 9JT, UK

(Received 29 May 1990; revised 18 July 1990; accepted 18 September 1990)

Many mechanisms have been proposed to explain the piezoelectric response of poly(vinylidene fluoride) (PVDF), but none of these are adequate to explain why d_{32} is so much less than d_{31}. Although it has been suggested that this difference could relate to the anisotropy of Poisson's ratios, direct measurement of the latter show that this explanation is not correct. The other viable explanation is that there are changes in crystallinity under stress. This possibility is tested in the present investigation using broad-line nuclear magnetic resonance measurements to estimate the change in crystallinity when drawn oriented samples are subjected to a tensile stress applied parallel or perpendicular to the draw direction. The results show that the crystallinity increases for a stress applied parallel to the draw direction and decreases for a stress applied perpendicular to the draw direction. The crystallinity changes give a positive contribution to d_{31} and a negative contributon to d_{32}, which can explain the relatively low figure for d_{32} compared with d_{31}.

(Keywords: crystallinity; poly(vinylidene fluoride); nuclear magnetic resonance; piezoelectricity; stress)

INTRODUCTION

There is continuing current interest in the structure and properties of poly(vinylidene fluoride) (PVDF) and its copolymers, especially with regard to understanding the mechanisms that are responsible for its piezoelectric and pyroelectric behaviour[1,2]. Although there have been many detailed analyses of the problem, the situation is still not resolved in a totally satisfactory manner. Work in this laboratory, where a comprehensive study of piezoelectric behaviour in PVDF has been combined with measurements of its anisotropic mechanical behaviour[3,4], has led to the conclusion that there was an element missing from the analysis, which could most probably be a reversible change in the crystallinity with stress and temperature.

Changes in the crystallinity of PVDF with temperature have previously been proposed[5] to explain its pyroelectric coefficient and qualitatively inferred from small-angle X-ray scattering (SAXS)[6] studies. Changes in crystallinity under stress have not been reported for PVDF, but such changes have been observed in other polymers[7–9]. The quantitative assessment of crystallinity change has been neglected by most experimentalists because of the difficulty of measuring small crystallinity changes in oriented stressed specimens.

We have recently shown that broad-line nuclear magnetic resonance (n.m.r.) techniques can successfully be used to detect the changes in the n.m.r. rigid fraction that occur when the sample temperature is changed. We identified the rigid fraction with the crystallinity and showed that this change could be an important contribution to the pyroelectric response of PVDF[10]. In this paper we report the results of a similar study of stress-induced crystallinity changes in PVDF.

EXPERIMENTAL

N.m.r. measurements were made on oriented samples of PVDF while the samples were subjected to a tensile stress parallel to or perpendicular to the draw direction. Experimental considerations dictated that these two sets of measurements were made on samples of different geometries. Measurements on samples stressed parallel to the draw direction were performed on oriented monofilament, while those perpendicular to the draw direction were made on strips cut from wide drawn sheet.

Preparation and characterization of oriented samples

Both the oriented monofilament and the drawn sheet were prepared from a commercial grade of PVDF (Solvey et Cie, Belgium, Solef Grade X10N, $M_n = 171\,000$, $M_w = 351\,000$).

Oriented monofilament was produced by melt spinning to give a product with a very low degree of molecular orientation, followed by drawing in glycerol at 80°C to give a final draw ratio of 4:1. This oriented monofilament showed a very high degree of crystalline orientation, a very high form I content (>95%) and a Young's modulus of 2.3 GPa.

Drawn sheets were prepared by compression moulding at 215°C to form nearly isotropic sheets, followed by drawing in air on an Instron tensile testing machine at 89°C at 0.4 mm min^{-1} to a final draw ratio of 4:1. This oriented sheet also showed a very high degree of crystalline orientation, a very high form I content (>90%) and a Young's modulus of 2.5 GPa.

N.m.r. measurements

The n.m.r. measurements were carried out using a Variant DP60 spectrometer operated at 60 MHz. A time averaging computer was used to add together the signals

---

* Present address: Department of Chemistry, University of Leeds, Leeds LS2 9JT, UK

0032-3861/91/152736-05

collected from several successive sweeps through the spectrum, in order to improve the signal-to-noise ratio.

An initial investigation into the broad-line n.m.r. behaviour of this material was undertaken by cutting short lengths of monofilament (≈ 6 mm long) and packing them, with their draw axes accurately parallel, into a circular slot machined into 6 mm diameter polytetrafluoroethylene (PTFE) rod. The orientation of the draw direction with respect to the static magnetic field (γ) could then be varied by rotating the PTFE rod in the n.m.r. spectrometer probe.

A simple loading rig was built to enable us to load the monofilament parallel to the draw direction. The sample took the form of 30 thicknesses of monofilament (which gave a bundle approximately 2 mm in diameter) wound around hooks incorporated into the loading rig. The sample was wound in such a way that the vertical axis of the spectrometer probe and the draw axes of the monofilament bundle were accurately parallel. The orientation of the sample with respect to the polarizing magnetic field could not be varied. Measurements were therefore restricted to just one orientation in which the sample draw direction and the magnetic field were perpendicular to each other ($\gamma = 90°$).

An equivalent experiment was performed on the wide sheet samples. Specimens were cut from the wide drawn sheets with their long dimension perpendicular to the draw direction. The ends were then cast in epoxy resin to prevent slippage in the loading grips. The sample was held in tension so that its long axis was parallel to the vertical axis of the spectrometer probe and the sample draw direction was parallel to the magnetic field ($\gamma = 0°$).

It was found that mechanical conditioning of the sample was essential. Conditioning consisted of successive loadings and unloadings up to the highest stress level of interest. Only after this conditioning process were consistent results obtained. We attribute this to the gradual lengthening of the more highly stressed strands resulting in a more uniformly stressed bundle.

THEORY

Calculation of n.m.r. rigid fraction

In order to obtain estimates of the rigid fraction from broad-line n.m.r. measurements, we have used a method originally proposed by Pranadi and Manuel[11] for isotropic polyethylene and subsequently developed by us for oriented poly(vinylidene fluoride) homopolymer[10] and oriented poly(vinylidene fluoride–trifluoroethylene) copolymer[12]. Here we will briefly outline the method used.

It was assumed that the composite broad-line n.m.r. spectrum consists of just two components, a broad component associated with the rigid regions and a somewhat narrower component associated with mobile material. The rigid regions give rise to an n.m.r. signal that can be considered to be a Pake doublet associated with the proton pair in the $-CH_2-CF_2-$ chain sequence. This doublet is broadened by intermolecular and intramolecular interactions to give a 'Gaussian doublet' lineshape.

The Gaussian doublet lineshape was defined as follows:

$$Y(\delta H) = a_1\left[\exp\left(-\frac{(\delta H - a_2)^2}{2a_3^2}\right) + \exp\left(-\frac{(\delta H + a_2)^2}{2a_3^2}\right)\right]$$

It consists of the superposition of two identical Gaussian lineshapes whose centres are separated by a field interval $2a_2$ and whose individual second moments about their centres are a_3^2. The area under this composite curve is $(8\pi)^{1/2}a_1a_3$ and the second moment is $\langle \delta H^2 \rangle = a_2^2 + a_3^2$. This lineshape was fitted to the outer part of the experimentally determined spectra with a_1, a_2 and a_3 as adjustable parameters using a least-squares procedure with parabolic extrapolation as described by Bevington[13].

RESULTS

Figure 1 shows the broad-line n.m.r. spectra for the monofilament at zero stress and at the maximum stress level of ≈ 83 MPa applied parallel to the draw direction. (This produced a strain of about 3.5%.)

Figure 2 shows the spectra for the drawn sheet at zero stress and at the maximum stress level of ≈ 85 MPa applied perpendicular to the draw direction. When comparing these data with those of *Figure 1* it should be remembered that the unstressed data are for different samples (monofilament and sheet) in different orientations ($\gamma = 90°$ and $\gamma = 0°$), hence their different appearance.

Two features of these spectra are immediately obvious: first, they are composite spectra, the simplest interpretation of this being that a narrow singlet is superimposed on a broad doublet; and secondly, the relative intensities of these two components changes as we load the sample.

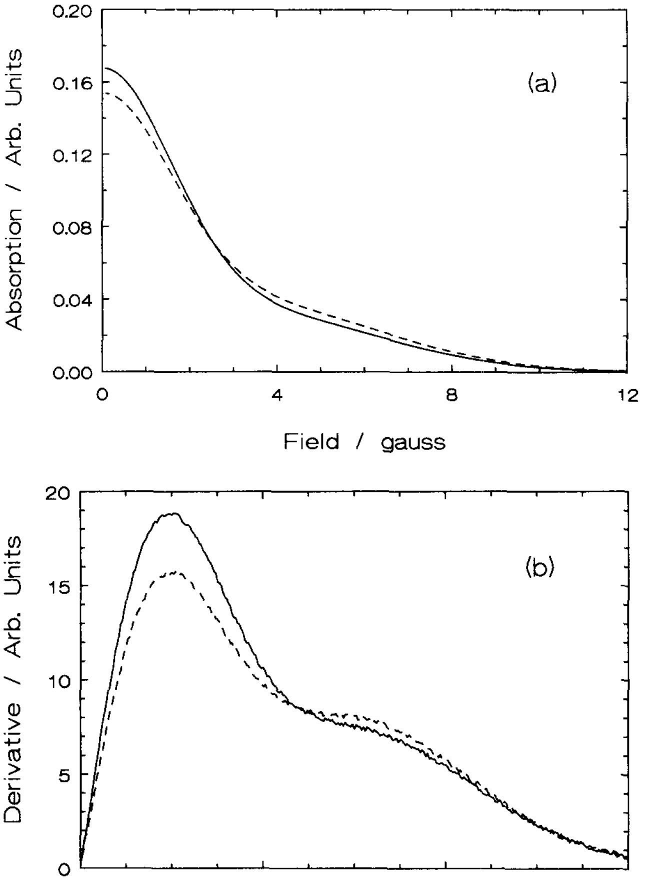

Figure 1 The n.m.r. spectra for the drawn monofilament at nominal zero stress (——) and with a tensile stress of 83 MPa applied parallel to the draw direction (----). $\gamma = 90°$ in both cases

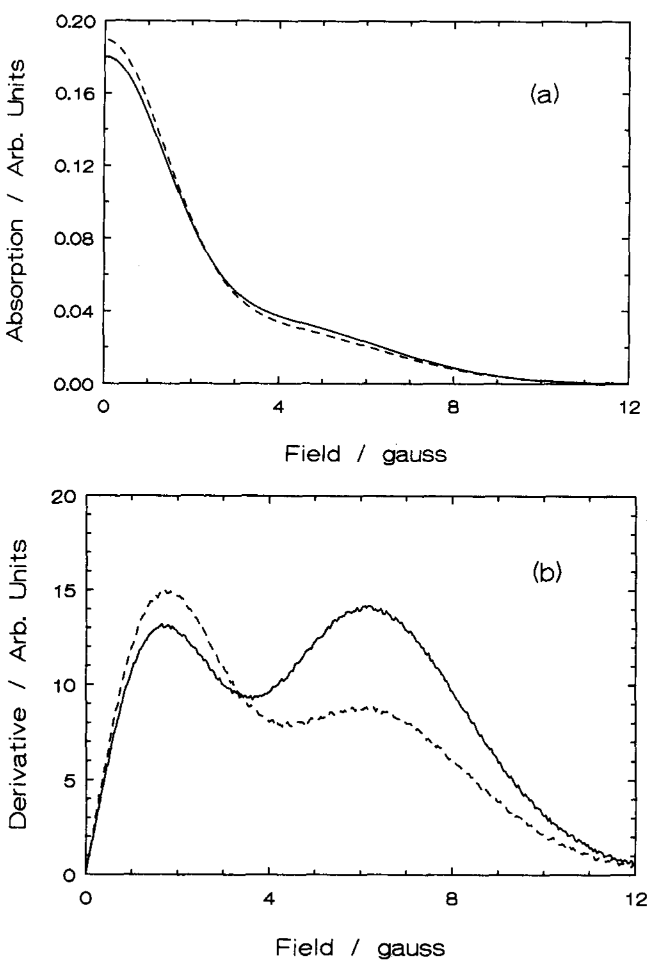

Figure 2 The n.m.r. spectra for the drawn sheet at nominal zero stress (——) and with a tensile stress of 85 MPa applied perpendicular to the draw direction (––––). $\gamma = 0°$ in both cases

The existence of these two distinct components suggests a structure that consists of a mobile (narrow) component and a rigid (broad) component. The rigid component may reasonably be identified as a doublet associated with the crystalline regions and the mobile component may be expected to be associated with the amorphous regions. In a related publication[12] we have established that this is indeed the case by a detailed study of the second moment anisotropy. We have also established that the narrower component is associated with a partially oriented mobile phase.

Figure 1 shows the broad component increasing in intensity while the narrower component decreases in intensity, whereas the opposite is the case in *Figure 2*. Consequently, we can infer that the fraction of rigid or crystalline material increases as the sample is loaded parallel to the draw direction, and decreases when the sample is loaded perpendicular to the draw direction.

The proportions of rigid and mobile material at each stress level were determined from the absorption spectra using the method outlined above. The rigid fraction f_R (using the nomenclature of our earlier papers) is given by the ratio of the integrated intensity of the rigid fraction component (the fitted Gaussian doublet) to the total integrated intensity. The spectra at each stress level were decomposed as accurately as possible using the additional information obtained at zero stress as a guide. At zero stress we were able to measure and decompose the spectra at a range of orientations: the results at $\gamma = 0°$ were particularly valuable since the doublet structure is more highly resolved in this case.

The results of the fitting procedure are tabulated in *Tables 1* and *2*. It is particularly interesting that the rigid fraction second moment $\langle \delta H^2 \rangle_R$ shows little or no variation with stress, indicating that the orientation of the rigid regions does not change appreciably as the stress level is changed. This is particularly important since it confirms that the changes observed in the spectra are principally due to the changes in the relative proportions of the rigid and mobile components.

The variation of the rigid mass fraction with stress is shown in *Figure 3*. It can be seen that, for tensile stresses

Table 1 Fitting parameters for Gaussian doublet, rigid fraction second moments and rigid fraction values f_R. Stress parallel to draw direction, field perpendicular to draw direction ($\gamma = 90°$)

Stress (MPa)	a_1	a_2 (G)	a_3 (G)	$\langle \delta H^2 \rangle$ (G^2)	f_R
0.0	0.031	3.41	2.96	20.38	0.462
10.1	0.033	3.51	2.85	20.46	0.472
22.1	0.033	3.46	2.92	20.47	0.478
31.7	0.032	3.48	2.96	20.86	0.482
42.8	0.034	3.42	2.90	20.12	0.488
64.8	0.035	3.46	2.89	20.32	0.511
83.2	0.036	3.40	3.02	20.68	0.540

Each value quoted above is the mean of five measurements. The standard error in the mean values of a_1, a_2 and a_3 is $\approx 3\%$ and that in the mean values of $\langle \delta H^2 \rangle$ and f_R is $\approx 2\%$

Table 2 Fitting parameters for Gaussian doublet, rigid fraction second moments and rigid fraction values f_R. Stress perpendicular to draw direction, field parallel to draw direction ($\gamma = 0°$)

Stress (MPa)	a_1	a_2 (G)	a_3 (G)	$\langle \delta H^2 \rangle$ (G^2)	f_R
0.0	0.034	3.60	2.67	20.12	0.458
8.56	0.033	3.51	2.69	19.56	0.456
17.12	0.032	3.46	2.81	19.89	0.454
25.68	0.032	3.52	2.73	19.86	0.440
34.24	0.032	3.53	2.73	19.94	0.441
42.80	0.032	3.50	2.66	19.32	0.441
51.36	0.033	3.51	2.71	19.68	0.438
59.62	0.033	3.52	2.60	19.19	0.434
68.48	0.031	3.56	2.70	19.98	0.424
77.04	0.034	3.69	2.49	19.84	0.430
85.60	0.030	3.51	2.75	19.87	0.424

Each value quoted above is the mean of five measurements. The standard error in the mean values of a_1, a_2 and a_3 is $\approx 3\%$ and that in the mean values of $\langle \delta H^2 \rangle$ and f_R is $\approx 2\%$

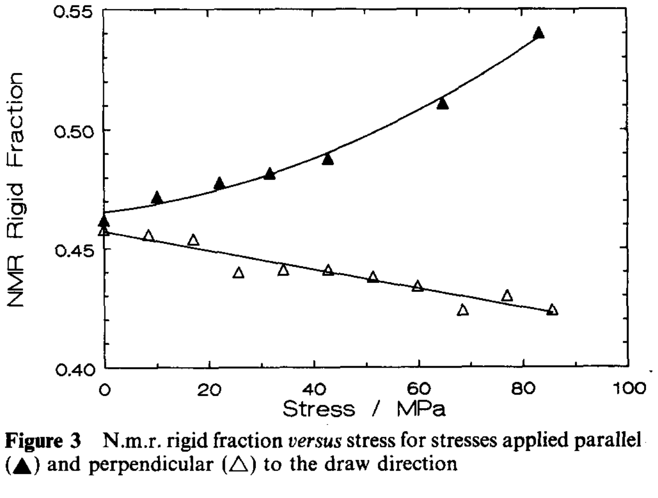

Figure 3 N.m.r. rigid fraction *versus* stress for stresses applied parallel (▲) and perpendicular (△) to the draw direction

applied parallel to the draw direction, the rigid mass fraction increases roughly parabolically with increasing stress, whereas, for stresses applied perpendicular to the draw direction, it decreases approximately linearly with increasing stress.

DISCUSSION

Qualitatively, it is clear that the stress causes changes in the n.m.r. rigid fraction and that these changes are in opposite directions for stresses applied parallel to or perpendicular to the draw direction. It remains to quantify the contribution that such changes would make to the piezoelectric coefficients assuming that these changes are due to changes in crystallinity. In order to illustrate the significance of these observations, however, we first describe the simplest contribution to d_{31} and d_{32} from changes in the thickness of a sample with deformable electrodes.

The charge Q on electrodes of area A on a short-circuited sample of polarization P is given by $Q=AP$. The polarization is the dipole moment (M) per unit volume (V), hence:

$$Q=AM/V \qquad \text{or} \qquad Q=M/t$$

where t is the sample thickness. Changes in thickness therefore produce a change in the charge on the electrodes even if the dipole moment of the sample is constant. It is readily shown[14] that this leads to $d_{31}=-Ps_{31}$ and $d_{32}=-Ps_{32}$, where s_{ij} is a mechanical compliance of the sample.

In general, even in uniaxially drawn sheets, s_{31} is of similar magnitude to s_{32} and this mechanism therefore predicts that d_{31} and d_{32} should be similar in magnitude. For the drawn sheet used in this study $s_{31}=-0.26\ \mathrm{GPa}^{-1}$ and $s_{32}=-0.25\ \mathrm{GPa}^{-1}$. Taking a typical polarization of $50\ \mathrm{mC\ m}^{-2}$ we would therefore predict $d_{31}=13.0\ \mathrm{pC\ N}^{-1}$ and $d_{32}=12.5\ \mathrm{pC\ N}^{-1}$ from this mechanism.

In fact, the observed values for the drawn sheet are: $d_{31}=20.9\ \mathrm{pC\ N}^{-1}$ and $d_{32}=2.0\ \mathrm{pC\ N}^{-1}$. In order to reconcile this discrepancy, a mechanism is obviously required that reduces d_{32} and increases d_{31}. The reversible stress-induced crystallinity changes seen here provide such a mechanism.

To quantify the effects of crystallinity change, we proceed as follows: We assert that M may be written as $M=V_cP_cS_F$, where V_c is the crystalline volume, P_c is the crystal polarization and S_F is a shape factor, which depends upon the shape of the crystallites and the relative permittivities of the crystalline and amorphous phases. Hence:

$$Q=AV_cP_cS_F/V \qquad \text{or} \qquad Q=A\chi P_cS_F$$

where χ is the volume fraction crystallinity.

The contribution from crystallinity change to the experimental piezoelectric coefficient d_{3i} is therefore given by:

$$d_{3i}=\frac{1}{A}\frac{\partial Q}{\partial \sigma_i}=P_cS_F\frac{\partial \chi}{\partial \sigma_i}=\frac{P}{\chi}\frac{\partial \chi}{\partial \sigma_i}$$

The change in crystallinity with stress is readily deduced for stresses applied perpendicular to the draw direction since these data show a linear stress dependence. Unfortunately, the data for stresses applied parallel to the draw direction do not show a linear stress dependence, and therefore the coefficient depends upon the fitting function used and the stress at which it is evaluated. We have chosen to fit a quadratic to the data and to evaluate its slope at zero stress, since most experimental piezoelectric data are obtained at low stresses.

The fractional change in crystallinity with stress deduced in this manner is $0.6\ \mathrm{GPa}^{-1}$ for a stress applied parallel to the draw direction (σ_1) and $-0.9\ \mathrm{GPa}^{-1}$ for a stress applied perpendicular to the draw direction (σ_2). If we again assume $P\sim 50\ \mathrm{mC\ m}^{-2}$ then these data imply large piezoelectric contributions of $+30\ \mathrm{pC\ N}^{-1}$ and $-45\ \mathrm{pC\ N}^{-1}$ respectively.

Clearly these coefficients are of significant size and in the correct direction. They are, however, much too large. A similar situation occurred when the change in crystallinity with temperature was studied[10] and the explanations given in that paper are equally applicable here. The n.m.r. experiment takes an appreciable time to gather the data, and hence it is an extremely 'low-frequency' measurement. Piezoelectric measurements are typically made at frequencies ~1 Hz or higher, and time may not allow the same crystallinity changes to occur. Also, it is assumed that the chains that crystallize do so in a similarly oriented fashion to the existing crystallites (in effect, that crystallization occurs on oriented nuclei) and that chains that 'melt' do so to a similar degree of disorientation to that pre-existing in the amorphous phase. It is quite possible that constraints upon the chains invalidate these assumptions.

Finally, it should be noted that the n.m.r. 'rigid fraction' is a measure of mass fraction crystallinity whereas the theory developed above requires the volume crystallinity. This relatively small correction has not been made in view of the large discrepancy between the observed and predicted effects. Also, the change in sample thickness caused by crystallinity change will contribute to the observed piezoelectric coefficients. This contribution is more than an order of magnitude smaller than that discussed above and would be accounted for by the measured s_{ij}, which include the effects of change in crystallinity on the sample thickness.

CONCLUSIONS

These data clearly show that significant n.m.r. changes occur when PVDF is subjected to tensile stresses. The rigid fraction increases when a stress is applied parallel to the draw direction and decreases when a stress is applied perpendicular to the draw direction.

If the rigid fraction is identified with crystallinity, then the magnitude of the changes is such that a significant part of the d_{31} piezoelectric response could arise from reversible crystallinity change.

In addition, the anomalous low value of d_{32} is caused by crystallinity changes nullifying other contributions to d_{32}.

ACKNOWLEDGEMENTS

We gratefully acknowledge the assistance of Mr D. L. M. Cansfield in the preparation of the drawn monofilament and Dr E. L. V. Nix of Thorn-E.M.I. for provision of the drawn sheets.

REFERENCES

1 Lovinger, A. J. 'Developments in Crystalline Polymers', Vol. 1, (Ed. D. C. Basset), Applied Science, London, 1982, Ch. 5
2 Lovinger, A. J. *Science* 1983, **220**, 4602
3 Nix, E. L., Holt, L., McGrath, J. C. and Ward, I. M. *Ferroelectrics* 1981, **32**, 103
4 Humphreys, J., Lewis, E. L. V., Ward, I. M., Nix, E. L. and McGrath, J. C. *J. Polym. Sci., Polym. Phys. Edn.* 1988, **26**, 141
5 Kepler, R. G. and Anderson, R. A. *J. Appl. Phys.* 1978, **49**, 4918
6 Schultz, J. M., Lin, J. S., Hendricks, R. W., Lagasse, R. R. and Kepler, R. G. *J. Appl. Phys.* 1980, **51**, 5508
7 Kaji, K. *Makromol. Chem.* 1974, **175**, 311
8 Morbitzer, L., Hentze, G. and Bonart, R. *Kolloid Z. Z. Polym.* 1967, **216–217**, 137
9 Fischer, E. W., Goddar, M. and Piesczek, W. *J. Polym. Sci. (C)* 1971, **32**, 149
10 Clements, J., Davies, G. R. and Ward, I. M. *Polymer* 1985, **26**, 208
11 Pranadi, H. and Manuel, A. J. *Polymer* 1980, **21**, 303
12 Clements, J., Davies, G. R. and Ward, I. M. *Polymer* in press
13 Bevington, P. R. 'Data Reduction and Error Analysis for the Physical Sciences', McGraw-Hill, New York, 1969
14 Davies, G. R. *Inst. Phys. Conf. Ser.* 1980, **58**, 50