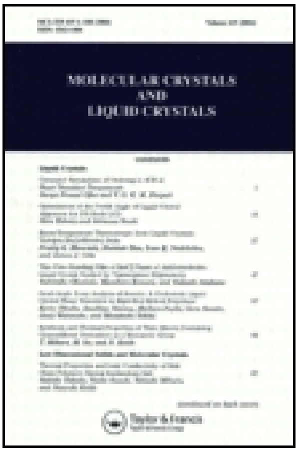


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Electro-Optic and Piezo-Optic Studies of an Antiferro-Ferri-Ferro-Electric System

W. K. Robinson [a], C. Carboni [a], H. F. Gleeson [a], M. Hird [b], P. Styring [b] & A. Seed [b]

[a] Department of Physics and Astronomy, Manchester University, Manchester, M13 9PL, UK

[b] School of Chemistry, The University of Hull, Hull, UK

Version of record first published: 23 Sep 2006.

To cite this article: W. K. Robinson, C. Carboni, H. F. Gleeson, M. Hird, P. Styring & A. Seed (1995): Electro-Optic and Piezo-Optic Studies of an Antiferro-Ferri-Ferro-Electric System, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 263:1, 69-79

To link to this article: http://dx.doi.org/10.1080/10587259508033571

Mol. Cryst. Liq. Cryst. 1995, Vol. 263, pp. 69–79
Reprints available directly from the publisher
Photocopying permitted by license only

ELECTRO-OPTIC AND PIEZO-OPTIC STUDIES OF AN ANTIFERRO-FERRI- FERRO-ELECTRIC SYSTEM.

W. K. ROBINSON, C. CARBONI, and H. F. GLEESON.
Department of Physics and Astronomy, Manchester University,
Manchester, M13 9PL, UK.
and
M. HIRD, P. STYRING and A. SEED.
School of Chemistry, The University of Hull, Hull, UK.

Abstract

A detailed study of a novel material exhibiting antiferro-, ferri-, and ferroelectric phases has been undertaken. The tilt angle, spontaneous polarisation and the dynamics of the helical unwinding have been examined as a function of temperature and voltage in all the phases of interest. The material exhibits large tilt angles (~31°) and values of spontaneous polarisation (~100nCcm^{-2}) in cases where the helix is totally unwound. The behaviour of tilt angle as a function of applied electric field is examined in the ferri- and antiferro-electric phases. A stepwise increase in tilt angle as a function of applied voltage in the ferri-electric phase is presented, as well as unusual behaviour in the antiferro-electric state. In addition, a preliminary investigation of the change in spontaneous polarisation as a function of pressure is presented. It is shown that the dependence of spontaneous polarisation in the ferroelectric phase is relatively weak.

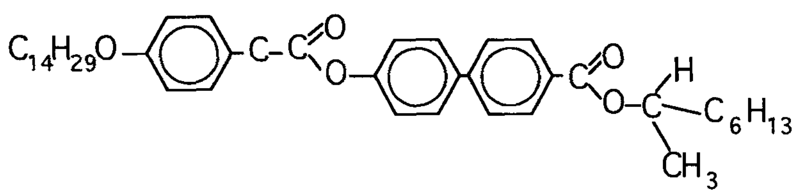
INTRODUCTION

Phenomena associated with chirality in liquid crystals have shown increasing importance with respect to both their fundamental scientific significance and their applicability to electrooptic and optoelectronic applications. The generation of novel physical properties, such as ferro-,ferri-, and antiferro-electricity in advanced materials has been of particular interest. Whilst such materials have found application in the device industry there is still much which is not known regarding the structures and phase transitions of these systems. In a family of chiral liquid crystals recently synthesised[1] a plethora of these new phases were found to occur, allowing an opportunity to study their behaviour and occurrence in some detail. The complex behaviour and switching mechanisms which may be observed in these systems is of great interest as they provide an insight into the structure of the antiferro- ferri- and ferro-electric liquid crystalline phases. Further, the application of pressure can bring about striking changes in the properties of liquid crystalline materials, revealing information regarding intermolecular interactions. There have, however, been relatively few studies of ferroelectric liquid crystals under pressure[2]. Pressure is expected to alter intermolecular interactions and therefore the spontaneous polarisation and other ferroelectric properties.

This paper describes a detailed study of a ferro-, ferri-, antiferro-electric system at atmospheric pressure and presents a preliminary study of the change in spontaneous polarisation with applied pressure. The electro-optic response time and hence viscosity is considered in both the ferro and ferri-electric phases. The tilt angle and spontaneous polarisation of the material is examined in all of the phases of interest. The behaviour of tilt angle as a function of applied voltage in the antiferro- and ferri-electric phases is described in some detail.

EXPERIMENTAL

Work has been carried out on a highly chiral material synthesised at Hull University. The structure and phase sequence at atmospheric pressure are shown below.



$$K \xrightarrow{80.3} S_C^* \xrightarrow{91.3} S_{C\alpha} \xrightarrow{91.4} TGBA \xrightarrow{95.0} I$$

$$(S_{CAnti}^* \xleftarrow{39.5} S_{CFerri}^* \xleftarrow{48.2} S_C^*)$$

The sample was maintained in a temperature controlled environment using a Linkam hot stage, and controller with an accuracy of ±0.1°C. The phase transition temperatures were determined using polarised microscopy. Approximate values for the pitch length were estimated by placing the sample in a homeotropically aligned cell and observing the change in colour of the selective reflection of the material.

All other measurements were taken with the sample held in 7.5μm thick planar aligned glass cells. The inner surface of the cells is coated with ITO film, which allows an electric field to be applied to the sample. Spontaneous polarisation (P_S) was measured using the current pulse technique[3]. In this method a triangular wave driving voltage is applied to the sample in the S_C^* phase and the molecules are forced to switch between their two tilted positions. As this switching occurs the polarisation dipole vector associated with each molecule reverses position resulting in a brief flow of current. The area under this current pulse is calculated using an on-line computer, and a value for the P_S is calculated from this. It is also possible to get information on the dynamics of helical unwinding by an electric field by performing single shot experiments[3] where one cycle of the driving signal only is allowed through to the sample. Where the single shot technique was employed, a delay of 10 seconds was allowed between each run to allow the helix to relax fully into its wound state. The spontaneous polarisation values obtained in this way have an accuracy of $\pm 2nCcm^{-2}$. In addition to the current pulse technique, spontaneous polarisation values were obtained using a Sawyer-Tower capacitance bridge circuit[4]. The hysteresis loops obtained gave information which complemented and confirmed the complex observations made using the current pulse technique.

The tilt angles were determined by optical microscopy. The sample was rotated between crossed polarisers and the angle between two positions of optical extinction was measured. This angle is twice the tilt angle. The measurements have an accuracy of $\pm 0.5°$.

Electrical response times were measured as the time between field reversal and the peak of the current pulse when a square wave driving signal was applied to the sample. These response times have an accuracy of $\pm 2\mu s$. Rotational viscosity was calculated[5] using information from the profile of the current pulse and a knowledge of the tilt angle and P_S.

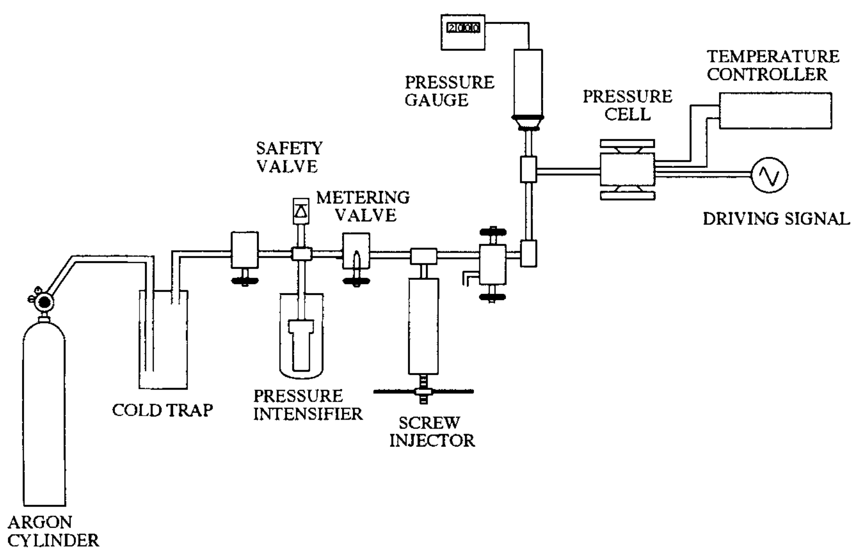


FIGURE 1. The apparatus used to investigate the pressure dependence of spontaneous polarisation[6].

Pressure measurements were taken using a high pressure system[6] shown in figure 1. The liquid crystal is held in the same type of glass cell as in the previous measurements. The cell is sealed with a flexible ultra violet curing adhesive and with a film of tightly stretched PTFE. The pressure can be measured with an accuracy of ±2 bar and the temperature with an accuracy of ±0.1 °C.

RESULTS AND DISCUSSION

The material has a pitch which selectively reflects light of wavelengths ranging from greater than 700nm to approximately 500nm in the ferroelectric phase and between approximately 400nm and 500nm in the antiferroelectric phase, which suggests that the helix winds up on cooling in the ferroelectric phase and unwinds in the antiferroelectric phase. There is a dramatic change in pitch on entering and leaving the ferrielectric phase. This phase has no iridescent colour in reflection, merely appearing to be grey.

Figure 2 shows the variation in spontaneous polarisation with temperature and applied field. At high applied fields the molecules will switch between two enforced unwound 'ferroelectric' states, irrespective of whether the phase is ferro, ferri or antiferroelectric in the absence of an applied field. At lower voltages it is expected that the effects of ferri and antiferroelectricity will be seen. There appears to be no convincing evidence for the expected drop in spontaneous polarisation in the ferri and antiferroelectric phases. Instead of this anticipated behaviour, figure 2 shows changes in the spontaneous polarisation due to the helix winding up and to the

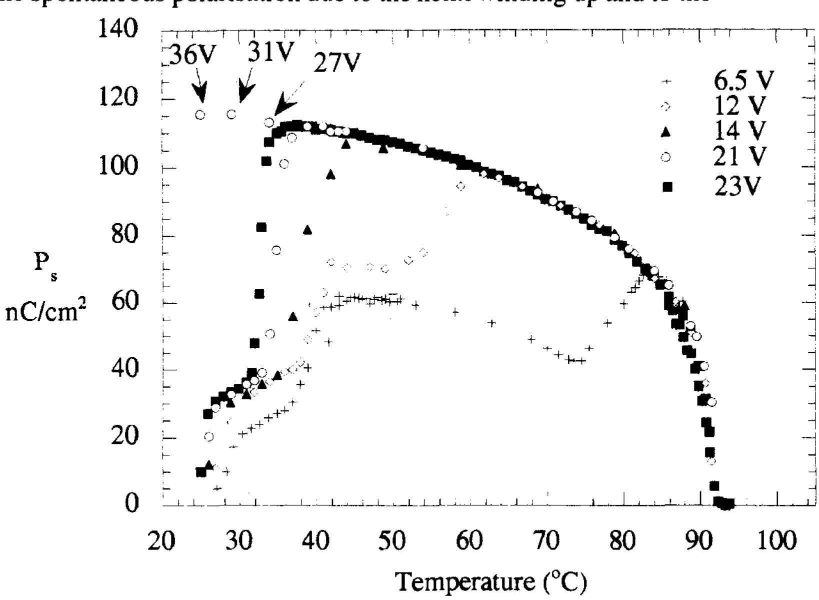


FIGURE 2. The temperature and voltage dependence of the P_s.

switching changing as the voltage falls below a certain critical threshold. Figure 3 shows how the current pulse response in the ferroelectric phase changes as the applied field is lowered. It can be seen that the height of the current pulse drops as the voltage is reduced, and the pulse splits into two peaks. This second pulse gives rise to a deformation in the P(E) hysteresis loop. The decrease of applied voltage in the ferroelectric phase changes the switching from a one step to a two step process[7] The two step process occurs in planar aligned cells as the helix is not free, but is pinned to disclinations near the surfaces of the cell. The first peak is thought to be due to the director rotating with the electric field, while the second peak is thought to be due to the movement of disclinations in the sample. This two step switching also occurs in the ferrielectric phase.

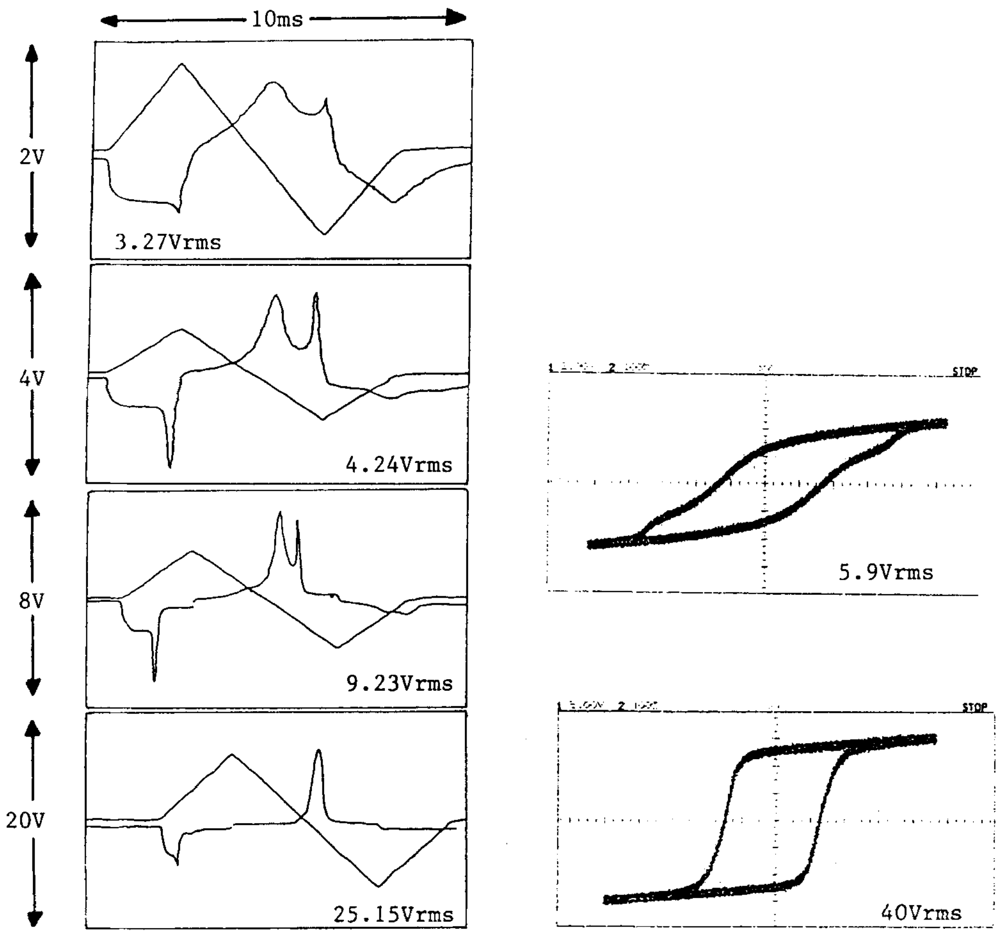


FIGURE 3. The effect of increasing voltage on the current pulse and hysteresis loops obtained in the ferroelectric phase. All measurements were taken at 59.5°C and at a frequency of 130Hz.

Figure 4 shows the effect of pressure on the P_S, which can be seen to increase with increasing pressure. This behaviour is as expected. The phase transition temperatures of the material are expected to increase as the pressure rises. Consequently an increase in the pressure at a fixed temperature will result in a movement away from the phase boundary, and a corresponding increase in the P_S. However the increase in this case can be seen to be very small, with a change in pressure of 200 bar producing a change in P_S equivalent to that obtained at atmospheric pressure by varying the temperature by about 2°C.

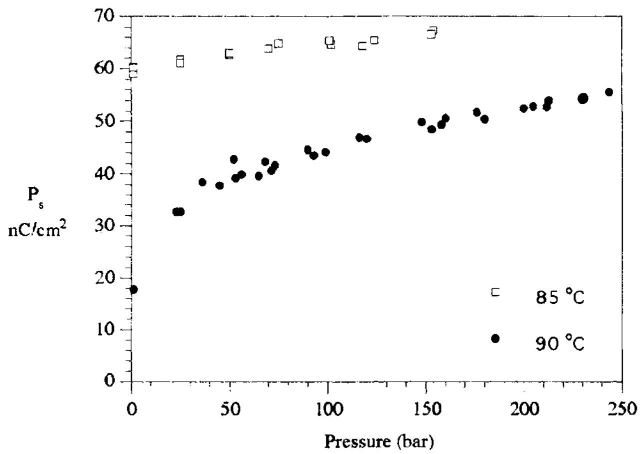


FIGURE 4. The effect of pressure on the spontaneous polarisation measured in the ferroelectric phase.

Figure 5 shows the dependence of tilt angle on temperature. The tilt angle is seen to saturate very rapidly to a value of~31°. The response of the tilt angle to applied voltage in the ferro, ferri and antiferroelectric phases can be seen in figure 6. The ferroelectric phase shows the expected linear variation in tilt angle with increasing field as the helix is unwound until saturation is reached. The ferrielectric phase also exhibits an intial linear increase in tilt angle with applied field. This is followed by a stepwise increase in tilt angle occurring as the applied field continues to increase, up to a saturation value equivalent to that observed in the ferroelectric phase. This stepwise behaviour is believed to be due to the ratio of opposing layers in the ferrielectric structure changing with voltage and has been observed in other systems[8]. The antiferroelectric phase also shows an unusual electric-field dependence. The tilt angle shows a dependence on the applied electric-field where the molecular ordering appears to change from a ferroelectric to an antiferroelectric state via a metastable state on decreasing field. Further, a hysteresis in tilt angle is observed depending on whether the field is

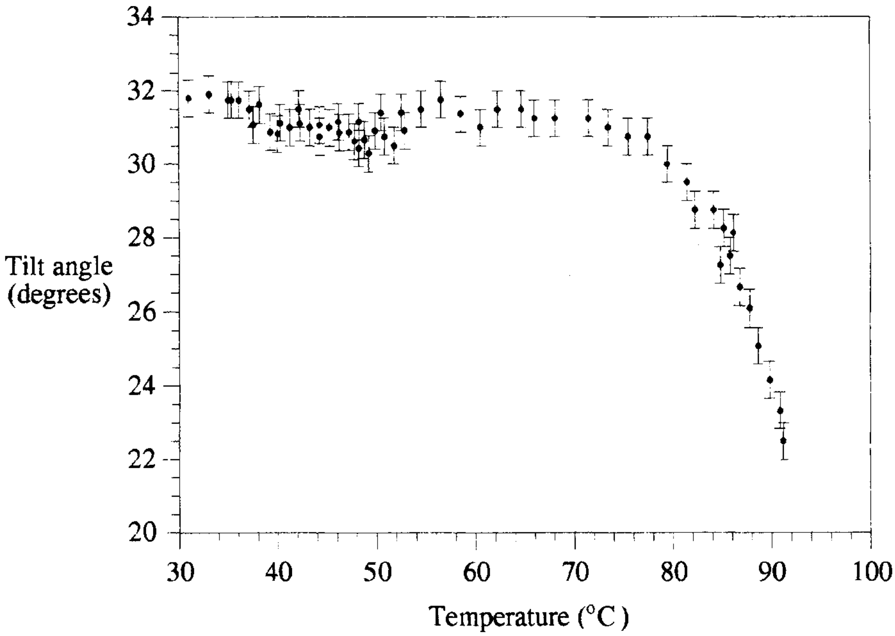


FIGURE 5. The temperature dependence of tilt angle. All measurements were taken using an applied voltage of 35.5V.

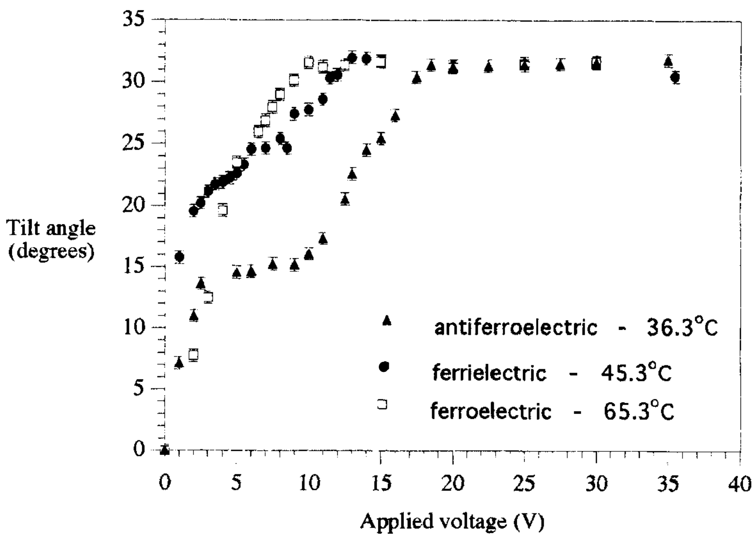


FIGURE 6. The dependence of tilt angle on applied voltage in the antiferro-, ferri- and ferroelectric phases.

increasing or decreasing, and the field at which the metastable state occurs is different in each case. Such behaviour in antiferroelectric systems has been reported elsewhere[9]. Supporting evidence for this metastable state can be seen in figure 2, where the P_S at this temperature is non-zero and has a similar voltage dependence to that of the tilt angle.

Figure 7 shows the electrical response time of the sample as a function of temperature. The switching gets very much slower as temperature is decreased. The change in rotational viscosity with temperature is shown in figure 8. The rotational viscosity is quite high and continuous across the ferroelectric to ferrielectric phase boundary.

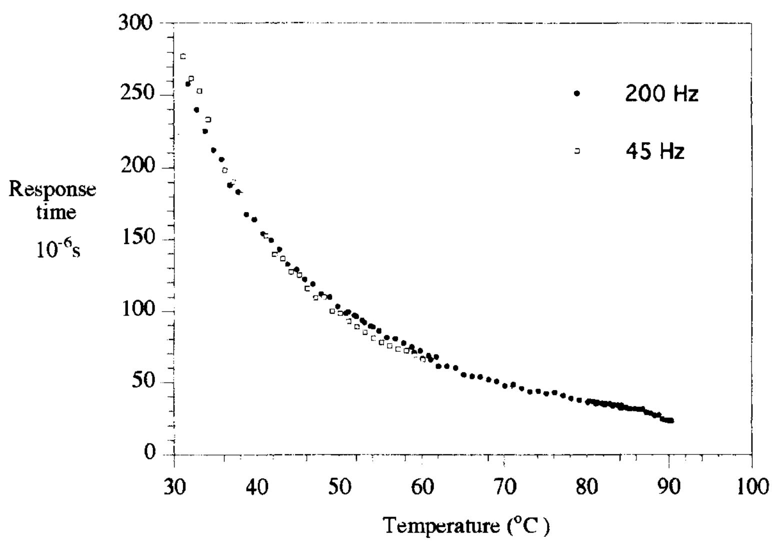


FIGURE 7. The dependence of response time on temperature at 35V.

The current pulse traces in figure 9 give information on the dynamics of helix unwinding. Initially the helix is unperturbed as the time interval between shots is sufficient for the helix to relax back to its wound state. The current due to the polarisation realignment starts to rise immediately with the applied field, showing that there is no threshold for deforming the helix. The response of the helix to the applied field appears to be very different in the ferro, ferri and antiferroelectric phases. There are two peaks superimposed on the main helix unwinding peak in the ferroelectric phase, and only one in the ferrielectric phase. It can be seen from figure 3 that this common peak in the ferro and ferrielectric phases appears to be associated with the second peak observed at low voltages in the current pulse profile. Therefore this spike in the unwinding profile is thought to be due to the movement of defects in the sample.

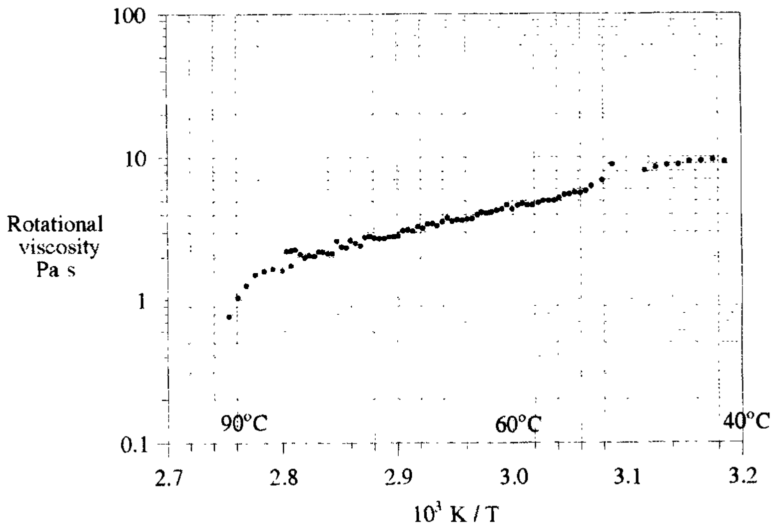


FIGURE 8. The dependence of rotational viscosity on temperature.

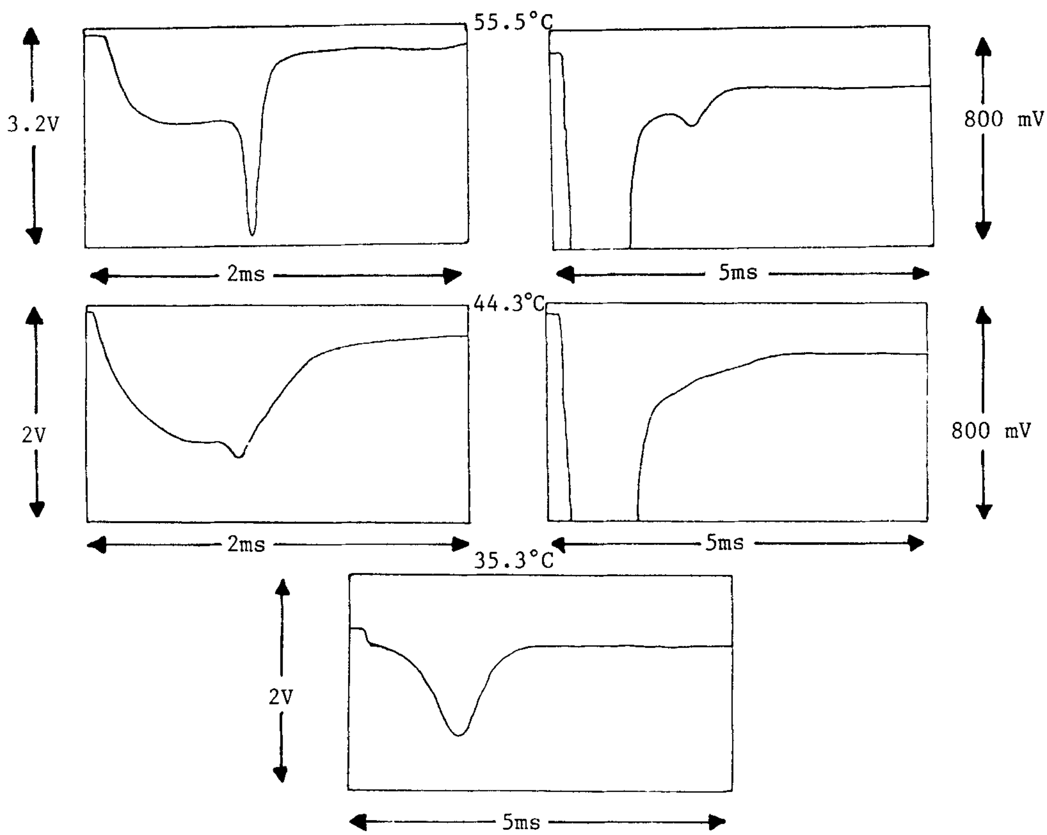


FIGURE 9. Current pulses in the ferro-, ferri- and antiferroelectric phases. The applied voltage was $40V_{rms}$ at 45Hz.

The basic shape of the main peak is the same in both ferro and ferrielectric cases but in the antiferroelectric phase this shape appears markedly different, indicating different switching mechanisms. Clearly a full understanding of the metastable state observed with applied field in the antiferroelectric phase is vital before the current pulse data can be accurately interpreted.

CONCLUSIONS

A detailed study of the ferro-, ferri- and antiferro-electric phases of a novel chiral material has been presented. In the ferroelectric phase, this tight pitch system underwent helical unwinding on application of an electric field. The saturated tilt angle and spontaneous polarisation values were relatively high at lower temperatures away from the $S_{C\alpha}$ phase. On approaching the $S_{C\alpha}$ phase transition both the tilt angle and spontaneous polarisation reduce continuously, but the phase transition is clearly not second order . The spontaneous polarisation within the ferroelectric phase showed a much weaker pressure dependence than was reported in reference 2, and the different behaviour may be attributed to the fact that the S_C^* to $S_{C\alpha}$ phase transition is not second order.

In the ferri-electric phase, the spontaneous polarisation and tilt angle measurements together show the expected behaviour. A stepwise increase in the observed tilt angle with increasing applied electric field was observed. However, both the spontaneous polarisation and tilt angle were zero at zero applied electric field, indicating that a macroscopic helicoidal structure exists in this phase, which must also be unwound before simple ferri-electric behaviour may be observed.

More complex electric field behaviour was observed in the antiferroelectric phase. The tilt angle and spontaneous polarisation increased from zero via an intermediate value before achieving the saturation value on application of an electric field. Further evidence of this complex behaviour was observed in the current pulse traces of this system.

Further investigations of this system and other related materials are underway both at atmospheric and elevated pressures with the aim of fully understanding the complex structures and electric field behaviour of these systems.

ACKNOWLEDGEMENTS.

This work has been carried out under a collaboration supported by the EPSRC and the MOD (grant numbers GR/H95860 and GR/H96249). The high pressure apparatus was established under an EPSRC project (grant number GR/G09238). WKR also thanks the EPSRC for a studentship and support to attend this conference. The authors are grateful to H Walton for assistance with current pulse measurements.

REFERENCES

1. J.W. Goodby, J. Mater. Chem. (1991), 1, 307; A. J. Slaney and J.W. Goodby, Liq. Cryst., 1991, 9, 849
2. S. Krishna Prasad, S. Khened and S. Chandrasekhar, Proceedings of the Ferroelectric liquid crystal conference, In press (1994).
3. K. Miyasato, S. Abe, H. Takezoe, A. Fukuda, E. Kuze, Jpn. J. Appl. Phys., 22 L661 (1983).
4. C. B. Sawyer and C. H. Tower, Phys. Rev., 35, 269 (1930)
5. C. Escher, T. Geelhaar and E. Bohm, Liquid Crystals, 3, 469 (1988)
6. C. Carboni, W. Robinson and H. Gleeson, Meas. Sci. Tech., 4, 1238 (1993)
7. M. Glogarova, J. Fousek, L. Lejcek and J. Pavel, Ferroelectrics, 58, 161 (1984)
8. T. Isozaki, K. Hiraoka, Y. Takanishi, H. Takezoe, A. Fukuda, T. Isozaki, Y. Suzuki and I. Kawamura, Liquid Crystals, 12, 59 (1992)
9. I. Nishiyama, E. Chin and J. Goodby, J. Mater. Chem., 3, 161 (1993), K. Hiraoka, Y. Takanishi, H. Takezoe, A. Fukuda, T. Isozaki, Y. Suzuki, and I. Kawamura, Jpn. J. Appl. Phys., 31, 3394 (1992)