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On the Variation of Pitch and Polarisation-Tilt Coupling in Chiral Smectic C

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We have carried out a detailed study of the thermal variation of spontaneous polarisation P_s, tilt angle θ and helical pitch p in the chiral smectic C phase of materials having varying degrees of P_s. The results, in particular the behavior of P_s/θ and p, are compared with the predictions of the extended meanfield model. The influence of different types of P_s-θ coupling terms is also discussed.

Keywords: chiral smectic, ferroelectric, helicoidal pitch, polarization-tilt coupling

INTRODUCTION

Although a considerable experimental and theoretical work has been done in characterising the bulk properties of the ferroelectric C* phase, the nature of the coupling between tilt and polarisation has not been well understood. A simple theoretical approach[1] expects (i) the spontaneous polarisation (P_s) and the tilt angle (θ) to be coupled in a linear way, i.e., the ratio P_s/θ is constant in the entire range of the C* phase, (ii) the helical pitch ($p = 2\pi/q$, q being the wavevector of the helix) to be invariant with respect to temperature. However, the experimental observations are not in accordance with these predictions. The ratio P_s/θ is weakly dependent on temperature deep in the C* phase, but shows a strong variation near the transition to the A phase. Likewise, far below the transition, the pitch increases slowly with temperature and shows a maximum below the transition temperature (T_c). Based on studies of these properties in DOBAMBC, extended mean-field models[2,3] with as many as eleven expansion coefficients were proposed. In these models, in addition to the terms considered in the simple model, a sixth order term in tilt and a biquadratic polarisation-tilt coupling terms are also taken into account. In order to reduce the number of coefficients involved, Carlsson *et al.*[2] worked out the theory using dimensionless forms of the equations. One of the quantities which plays a major role in the predictions of these authors, is the term β which is proportional to the ratio of bilinear to biquadratic coupling terms. The value of β is expected to determine the nature of the thermal variation of P_s/θ ratio and the helical pitch.

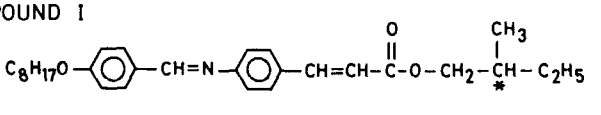
Most of the measurements[4–7] that exist in the literature present results wherein

not enough attention has been given to the region closer to T_c. The few high resolution studies have been done on materials exhibiting a low value of spontaneous polarisation.[3,5] In other words, systematic studies on substances exhibiting different degree of polarisation to tilt coupling have not been performed. With this point in view, we undertook a detailed study of the temperature variation of polarisation, tilt angle and pitch of materials having varying degree of P_s. The results are compared with the predictions of the extended mean field model.

EXPERIMENTAL

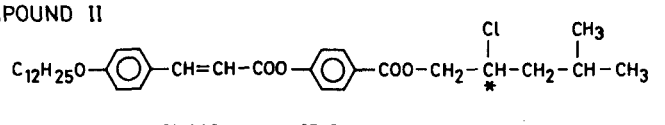
Measurements of P_s, θ and p have been carried out in three different compounds whose structural formulae and phase transition temperatures are given below:

COMPOUND I



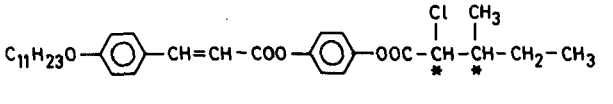
I $\xrightarrow{118.7°C}$ A $\xrightarrow{94.2}$ C* $\xrightarrow{67}$ I*

COMPOUND II



I $\xrightarrow{81.0°C}$ A $\xrightarrow{65.5}$ C*

COMPOUND III



I $\xrightarrow{99.5°C}$ A $\xrightarrow{83.5}$ C*

All these compounds were synthesised in the laboratory; compound I is well known in the literature as OOBAMBC and was kindly given to us by V. Surendranath, while compounds II and III were prepared by Sadashiva and Shivkumar.[8] As will be seen later, these substances have low, moderate and high polarisation values. Polarisation measurements were carried out using the set up described in an earlier paper,[9] and the tilt angle was determined by X-ray diffraction experiments. A standard optical diffraction method[10] was employed to measure pitch, but as we have used a novel method of acquiring and analysing the diffraction pattern it will be described briefly here. Figure 1 shows a schematic diagram of our diffraction set up. The diffraction pattern obtained using the sample (thickness ~100 μm) aligned in the "bookshelf" geometry, was made to fall on a screen. This image was captured by a high-resolution video camera (Philips VK4033) and was recorded on video tape for storage and analysis. The off-line analysis part consists of a high-resolution—262 Kpixels/Frame and 8 bit data resolution—Frame Grabber Card with 0.5 MB on-board memory in conjunction with a Frame Processor Board (Data Translation DT2851 and DT2858) both of which are plugged into PC AT I/O slots.

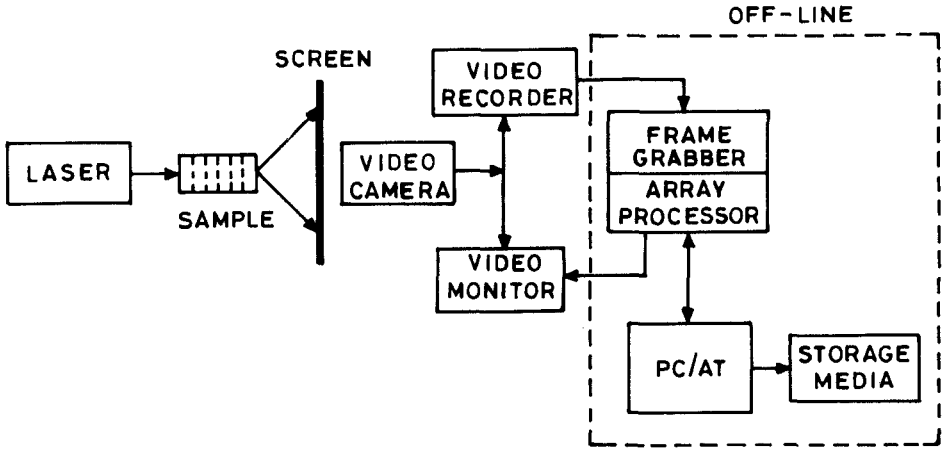


FIGURE 1 Schematic diagram of the optical diffraction set up used for pitch measurements.

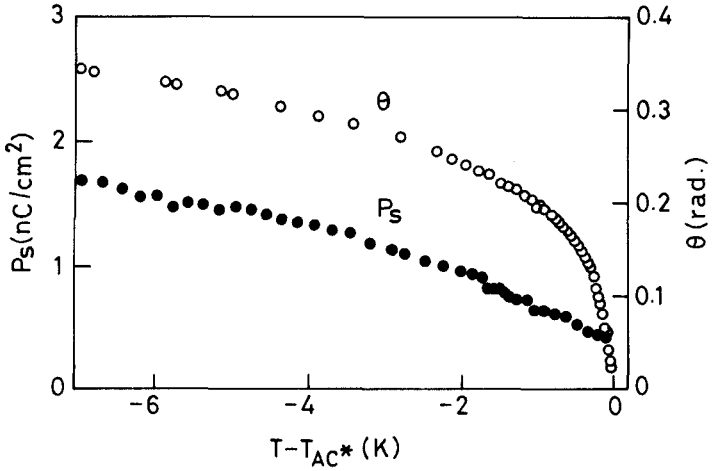


FIGURE 2 Temperature variation of the tilt angle θ (○) and polarization P_s (●) for compound I.

The cards accept the standard RS-170 PAL input and can be accessed and controlled through a high level language interface software. A user-written Fortran program converted the "image" files into ASCII format files which were later analysed using a peak finding macro program written in a commercial software environment (Quatro-Borland). The calibration of this set up was checked by measuring the pitch as a function of temperature for CE8 (BDH). Our data agreed to within 2% of the values reported[11] over the entire temperature range of measurement.

RESULTS AND DISCUSSION

The temperature variation of polarisation and tilt angle for the three compounds are given in Figures 2–4. Although a simple power law of the type

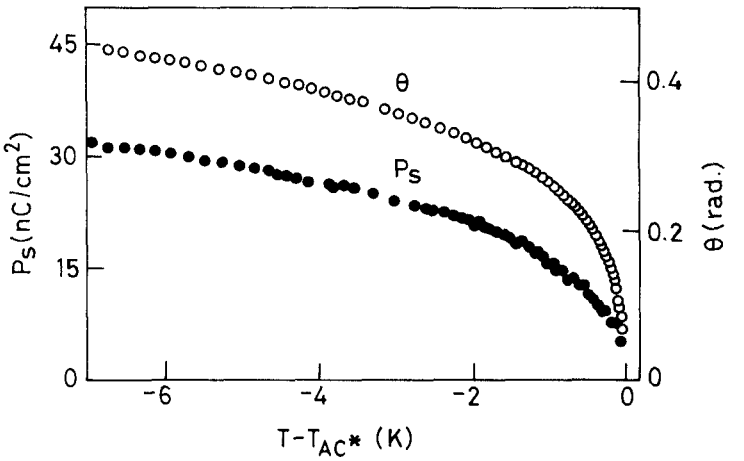


FIGURE 3 Thermal variation of θ (○) and P_s (●) for compound II.

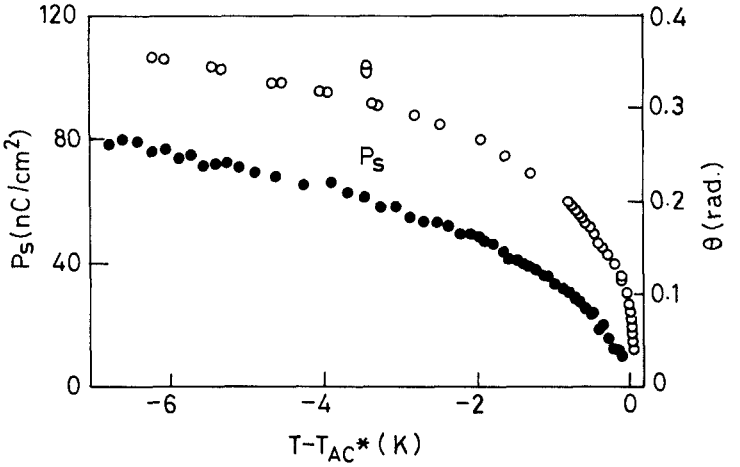


FIGURE 4 Temperature dependence of θ (○) and P_s (●) for compound III.

$$\theta = \theta_0[(T_c - T)/T_c]^{\beta 1} \tag{1}$$

$$P = P_0[(T_c - T)/T_c]^{\beta 2} \tag{2}$$

is able to describe the data well, it also showed that $\beta 1 \neq \beta 2$. Similar results have been obtained by other authors[4] also. (Note that β1 and β2 are just effective exponents and need not necessarily be critical exponents.) Figures 5–7 show the temperature variation of pitch for the three compounds. The results obtained for OOBAMBC are in agreement with the behavior seen earlier for this material[10] and its higher homolog.[12] Far below T_c, p increases slowly with temperature, reaches a maximum about 1 K below T_c and steeply drops in the range T_c-0.4 K. For compound II the behavior is different (Figure 6) in the vicinity of the transition, viz., the pitch remains at the maximum value it has attained right up to the transition

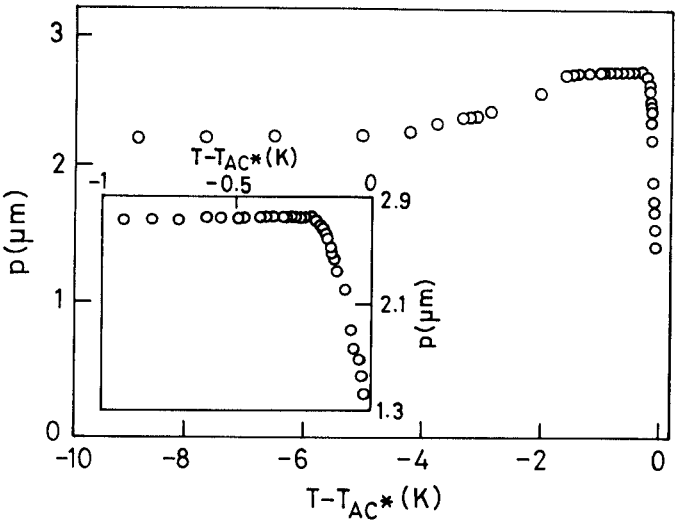


FIGURE 5 Pitch variation as a function of temperature for compound I. The inset shows the data in the vicinity of the transition on an enlarged scale.

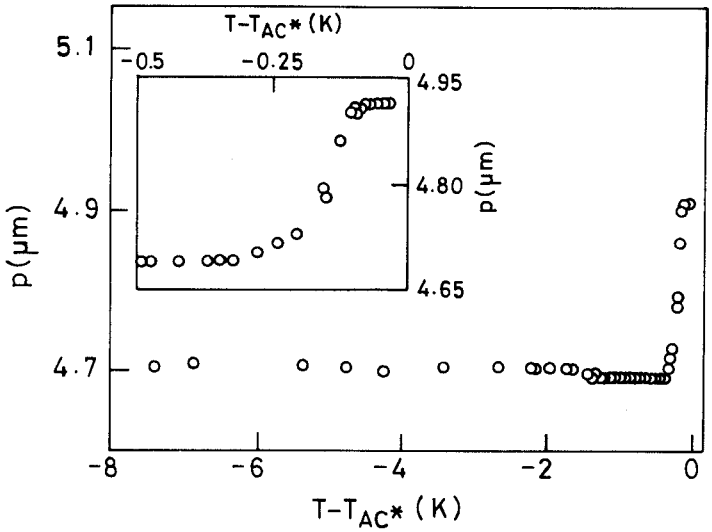


FIGURE 6 Temperature dependence of pitch for compound II. The data obtained within 0.5 K from the transition is shown in the inset.

and does not show the precipitous drop as in OOBAMBC. In compound III, pitch remains almost invariant with temperature except for a small drop in the immediate vicinity of the transition. A similar behavior was observed (though in a low-resolution experiment) earlier[7] in a material with a small range of C* phase (1 K). As such it may not be appropriate to compare our results with this report.

In order to compare our results with the predictions of the theoretical models,

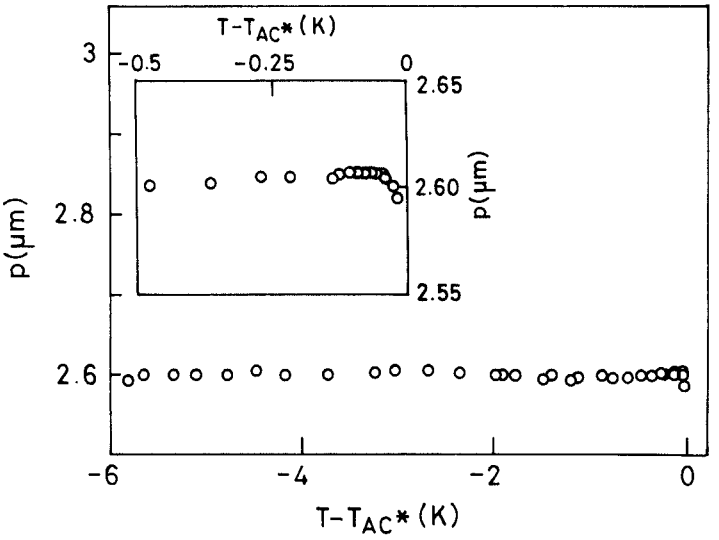


FIGURE 7 Plot of pitch versus temperature for compound III. The inset shows the data obtained within 0.5 K from the transition.

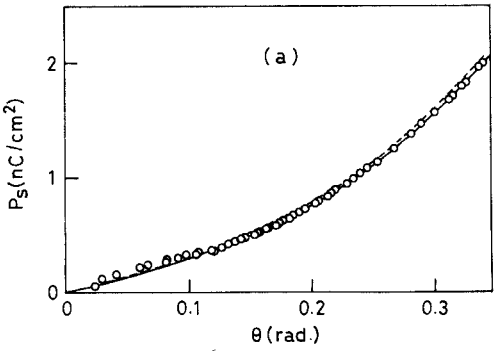


FIGURE 8a Plot of P_s versus θ for compound I. Circles denote experimental data, dashed and solid lines are obtained by fitting the data to Equations 6 and 7 respectively.

let us recall the following from the thermodynamic model of Carlsson *et al.*[2] The free-energy density of the system is expanded in two order parameters, θ and P

$$g = \frac{1}{2}a\theta^2 + \frac{1}{4}b\theta^4 + \frac{1}{6}c\theta^6 - \Lambda q\theta^2 + \frac{1}{2}K_3q^2\theta^2 + \frac{1}{2\varepsilon}P^2$$

$$- \mu qP\theta - CP\theta - \frac{1}{2}\Omega P^2\theta^2 + \frac{1}{4}\eta P^4 - dq\theta^4 \quad (3)$$

Here, only the coefficient $a = \alpha(T - T_c)$ is assumed to be temperature dependent. T_0 is the phase transition temperature of the corresponding racemic mixture, b, c, d and η are constants, K_3 an elastic modulus, Λ the Lifshitz coefficient, ε the high

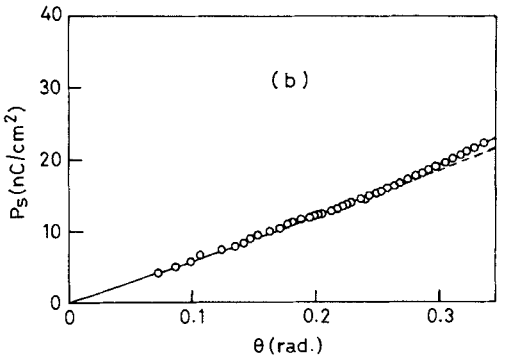


FIGURE 8b Plot of P_s versus θ for compound II. Measured points (○), fit to Equation 6 (– –) and Equation 7 (—).

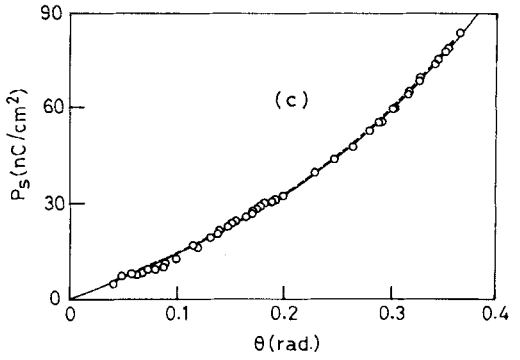


FIGURE 8c Plot of P_s versus θ for compound III. Measured points (○), fit to Equation 6 (– –) and Equation 7 (—).

temperature dielectric constant, μ and C the coefficients of the flexo- and piezo-electric bilinear coupling, and Ω the biquadratic coupling coefficient. In order to reduce the number of parameters from eleven, the authors rewrite Equation (3) in a dimensionless form

$$\tilde{g} = \frac{1}{2}(\beta^2 - \gamma\tau)\tilde{\theta}^2 + \frac{1}{4}\gamma\tilde{\theta}^4 + \frac{1}{6}\rho\tilde{\theta}^6 + \frac{1}{2}\tilde{P}^2 - \beta\tilde{P}\tilde{\theta} - \frac{1}{2}\tilde{P}^2\tilde{\theta}^2 + \frac{1}{4}\tilde{P}^4 - \nu\delta\tilde{P}\tilde{\theta}^3 \tag{4}$$

where $\tilde{P} = P/P^*$, $\tilde{\theta} = \theta/\theta^*$, $\tau = (T_c - T)/T^*$; the parameters with asterisk are the normalising quantities.
Minimising g w.r.t. $\tilde{P}$ we get

$$\tilde{P}^3 + (1 - \tilde{\theta}^2)\tilde{P} - (\beta + \nu\delta\tilde{\theta}^2)\tilde{\theta} = 0 \tag{5}$$

Also, in the limit $\nu\delta << \beta$ Equation (5) can be written as

$$\tilde{P}^3 + (1 - \tilde{\theta}^2)\tilde{P} - \beta\tilde{\theta} = 0 \tag{6}$$

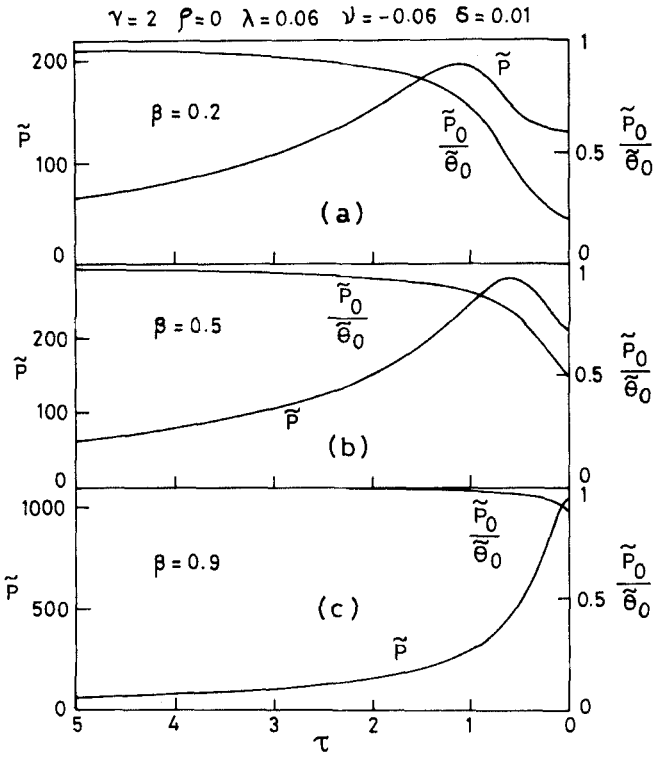


FIGURE 9 Theoretical behavior of $\tilde{P}/\tilde{\theta}$ and $\tilde{p}$ for different values of β (from Reference 2).

According to Carlsson *et al.*,[2] a good qualitative understanding of the behaviour of different parameters in the free energy expression (2) can be obtained by evaluating the coefficient β defined by

$$\beta = \frac{\tilde{\varepsilon}\,\tilde{C}\,\eta^{1/2}}{\Omega^{1/2}}$$

The value of β is expected to determine the thermal variation of P_s/θ and pitch.

Using the experimental data of P_s and θ and solving Equation (6) numerically we have obtained (Table I) the values of P^*, θ^* and β for the three compounds. Figures 8a–c show the experimental data and the fitting (dashed line). It is clear that the fit describes the data well. On the basis of experimental data on the dynamics of the pyroelectric response, Pozhidayev *et al.*[13] and Beresnev et al[14] proposed a simplified phenomenological model to interpret P_s/θ anomalies. According to them, P_s is composed of terms that are linear and cubic in θ, i.e.,

$$P_s = a_1\theta + a_2\theta^3 \tag{7}$$

Fitting done to this expression is also represented in Figure 8a–c (solid lines).

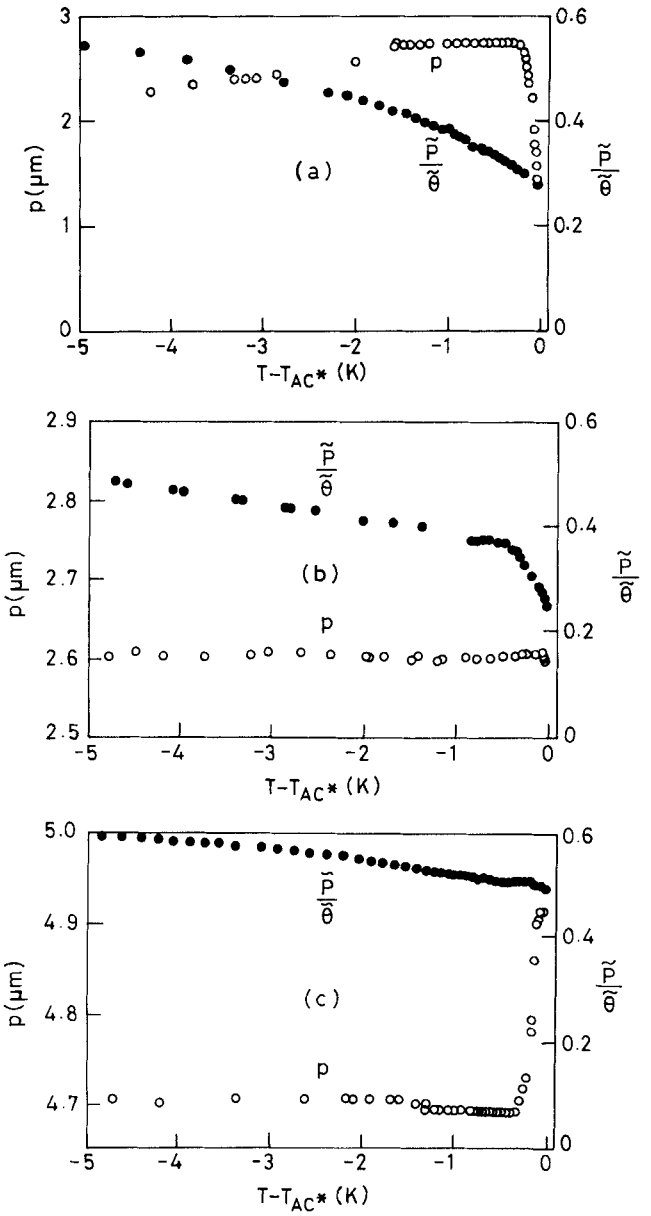


FIGURE 10 Experimental behavior of $\tilde{P}/\tilde{\theta}$ and $\tilde{p}$ for (a) compound I, (b) compound III, (c) compound II. The actual data of P_s/θ has been reduced to dimensionless form using the quantities listed in Table I.

Again the agreement is very good. In fact, Equation (7) is similar to the one given by the Landau model (with $\rho = \nu\delta = 0$) in the vicinity of the transition

$$\tilde{P} = \beta\tilde{\theta} + (\beta - \beta^3)\tilde{\theta}^3 \tag{8}$$

TABLE I

Fit parameters P*, θ* and β for the three compounds

Material	P^*	θ^*	β
Compound I	3.7	0.38	0.29
Compound II	140.7	1.2	0.49
Compound III	217.5	0.5	0.32

TABLE II

β values evaluated using the expressions given by thermodynamic model (Equation 6) and the polynomial equation (Equation 9)

Material	β†	$\beta = a_1\theta^*/P^*$	$\beta = a_1\theta_o/P_o$
Compound I	0.29	0.27	0.24
Compound II	0.49	0.48	0.57
Compound III	0.32	0.31	0.34

† From thermodynamic model.[2]

From Equations (7) and (8) we can write

$$\beta = a_1\theta^*/P^* \tag{9}$$

As already mentioned the temperature dependence of P_s and θ can be described by power law type of expressions (1) and (2). The amplitude term in these expressions, viz., P_0 and θ_0 give the values of P_s and θ far away from T_c. Table II lists values of β calculated by all the three methods. It is seen that there is a good agreement between numbers of column 1 and 2 while those in column 3 are slightly different. Thus the simple expression (7) not only describes the P_s versus θ behavior, but also can be used to estimate the coefficient β, a very important parameter in the generalised mean-field model.

It was pointed out earlier that in the framework of the generalised mean-field model, the parameter β determines the thermal variation of the ratio P_s/θ and helical pitch p. Theoretical curves for three different values of β are shown in Figures 9a–c. Experimental data of $\tilde{P}/\tilde{\theta}$ and pitch is shown in Figures 10a–c. The actual data of P_s/θ have been reduced to dimensionless form by using P^* and θ^* values listed in Table I. For the sake of comparison we have presented the results

TABLE III

Ratio of piezoelectric bilinear to biquadratic coupling term

Material	$Y = 2\beta/\tilde{P}\tilde{\theta}$	
	T_c - 1K	T_c - 5K
Compound I	5.35	1.55
Compound II	37.3	13.9
Compound III	10.7	2.7

of compound III in Figure 10b and of compound II in Figure 10c. Note that for compound I, $\tilde{P}/\tilde{\theta}$ does not show the "S" shaped behaviour expected for materials with low β values. It may be mentioned here that an earlier high-resolution study[3] on DOBAMBC also ruled out any such anomalous behaviour for P_s/θ ratio. In fact, the more recent microscopic model[15] does not predict the "S" shaped variation for any value of β. The variation of $\tilde{P}/\tilde{\theta}$ ratio and pitch p for compound II (Figure 10c) looks identical to the theoretical diagram 9c. $\tilde{P}/\tilde{\theta}$ is weakly dependent on temperature while p attains a maximum near the transition, but does not drop on approaching it. In the case of compound III, p remains almost invariant with temperature except for a small drop in the immediate vicinity of the transition. Although the β values in the theoretical and experimental cases are different the results clearly demonstrate the relationship between the values of β and the variation of P_s/θ ratio and pitch.

If only the bilinear coupling were to be the determining factor, the behaviour seen in a compound with a higher P_s value should have been closer to the classical case. But our results for compounds II and III (P_s for III is higher than II) show that other coupling terms are also important.

Using Equation (4) we have calculated the relative influence of the piezoelectric bilinear and biquadratic terms

$$Y = 2\beta/\tilde{P}\tilde{\theta}$$

Listed in Table III are the values of Y evaluated at $T_c - 1$ K and $T_c - 5$ K for the three compounds. It is seen that (i) the nature of coupling is dependent on the proximity to the transition, i.e., the influence of the biquadratic term is small near T_c and large far away from it, (ii) near the transition as well as away from it Y (compound II) > Y (compound III) > Y (compound I). The latter relation is quite significant and indeed justifies our analysis of Figures 10b and 10c.

In conclusion, we have studied the temperature variation of polarisation, tilt and pitch in the C* phase of three different compounds exhibiting low, moderate and high P_s values. The results clearly show the effect of the parameter β on the behavior

of P_s/θ and pitch p. The data also demonstrate the influence of the two P_s-θ coupling terms (piezoelectric bilinear and biquadratic) on the measured parameters. All these observations are generally in good agreement with the theoretical predictions of the generalised mean-field model.

Acknowledgment

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