KFKI-1987-70/E
PREPRINT

MEASUREMENT OF SPONTANEOUS POLARIZATION OF SMECTICS C DOPED WITH A CHIRAL ADDITIVE

L. BATA, N. ÉBER, L.A. BERESNEV* and L.M. BLINOV*

Central Research Institute for Physics
H-1525 Budapest 114, P.O.B. 49, Hungary

*Institute of Crystallography
USSR Academy of Sciences
117333 Moscow, Leninsky pr. 59

Presented at the

7th Liquid Crystal Conference of Socialist Countries, Pardubice, 31 August - 4 September 1987

and

1st International Symposium on Ferroelectric Liquid Crystals, Bordeaux-Archachon, 21-23 September 1987

HU ISSN 0368 5330

L. Bata, N. Éber, L.A. Beresnev, L.M. Blinov: Measurement of spontaneous polarization of smectics C doped with a chiral additive. KFKI-1987-70/E

ABSTRACT

The spontaneous polarization is measured in a homologous series of smectics C doped with a chiral additive. An unusual temperature dependence is found which can be well fitted using the generalized Landau model of ferroelectric smectics.

Л. Бата, Н. Эбер, Л.А. Береснев, Л.М. Блинов: Измерение спонтанной поляризации в смектике С, легированном киральной примесью. KFKI-1987-70/E

АННОТАЦИЯ

Измерялась спонтанная поляризация в гомологическом ряду смектиков С, легированном киральной примесью. Наблюдалась необычная температурная зависимость, которую хорошо можно описать, используя обобщенную модель Ландау для сегнетоэлектрических смектиков.

Bata L., Éber N., Beresnev L.A., Blinov L.M.: Spontán polarizáció mérése királis adalékkal doppolt szmektikus C-ben. KFKI-1987-70/E

KIVONAT

Megmértük a spontán polarizációt egy királis adalékkal doppolt szmektikus C homológ sorban. Szokatlan hőmérsékletfüggést tapasztaltunk, mely jól illeszthető a ferroelektromos szmektikusok általánositott Landau modelljének felhasználásával.

INTRODUCTION

Chiral smectic C (SmC^*) liquid crystals gained an increasing interest during the last years because of the delicate physical phenomena arising in these systems and the possibility of their practical application. Meyer et al.[1] have demonstrated that in SmC^* systems a spontaneous polarization occurs which can be easily oriented by an applied electric field, i.e. they are ferroelectrics. The bistable character and the short switching times of surface stabilized cells[2] promise favourable usability for optical shutters, modulators, matrix displays etc. In this respect the study of the spontaneous polarization, tilt angle and pitch of the system are of upmost importance. In the present paper we focus our attention onto the spontaneous polarization.

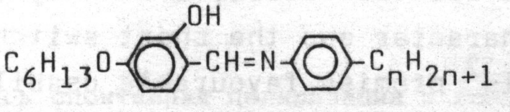
The number of measurements of the temperature dependence of the spontaneous polarization reported in the literature is continuously increasing[3]. These measurements have been performed on single compounds as well as mixtures and doped systems. In order to interpret the temperature dependence of the spontaneous polarization a theoretical model based on the Landau expansion of the free-energy density has been used[4]. According to this theory a square roote temperature dependence of the spontaneous polarization is expected near to the phase transition temperature. In the majority of papers[3] a rough agreement with the square roote type temperature dependence was detected or the experimental data were presented without further analysis.

A deviation from this behaviour has been found only recently in DOBAMBC[5]. Proposing a more general form of the Landau expansion, novel thermodynamic models have been constructed[6,7] which are capable to describe a set of experimental data measured on DOBAMBC at least in a qualitative way. Unfortunately DOBAMBC is not the ideal compound to check the theory due to its chemical instability and narrow SmC* range.

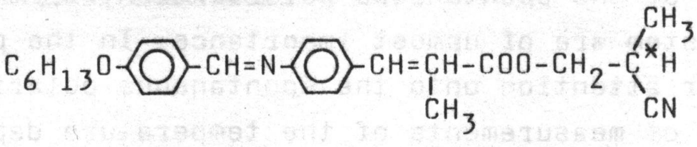
It is the purpose of this paper to study the SmA-SmC* phase transition on a homologous series of compounds having SmC* phase in a broad temperature range and analyze the experimental results on the basis of present theories.

COMPOUNDS

The smectic C phase formed by achiral molecules can be transformed into SmC* phase by dissolving suitable chiral molecules. Such mixed systems have been published e.g. by Kuczynski et al.[8] and Beresnev et al.[9]. In this paper we present results obtained on the homologous series of 6O.nSA, i.e.[10]



doped with 5 weight % of HOBACNPC, i.e.

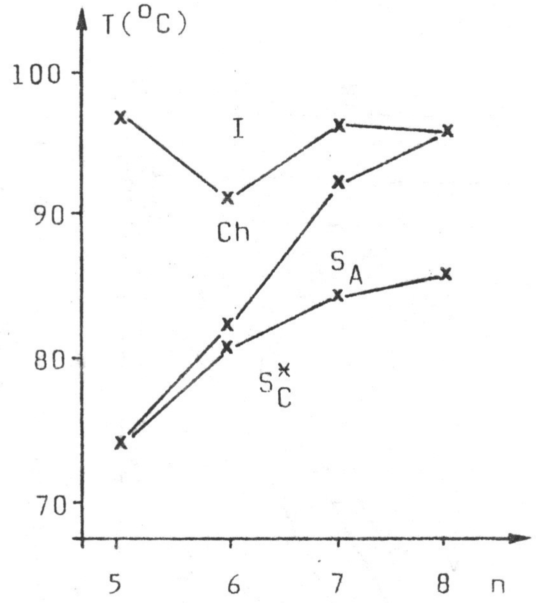


The transition temperatures of these mixtures are shown in Fig.1.

EXPERIMENTAL TECHNIQUE

The spontaneous polarization was studied by two independent methods, the pyroelectric[11] one and the Sawyer-Tower[12] technique. According to the pyroelectric method the spontaneous polarization is obtained upon graphical integration of the $\gamma_p(T)$ pyroelectric coefficient, i.e.

$$P_s(T) = \int_{T_c}^{T} \gamma_p(T)\,dt$$



n	S_C^*		S_A		Ch		I
8	.	86	.		–	96	.
7	.	84	.	92	.	96	.
6	.	81	.	82	.	91	.
5	.	74	–			97	.

FIGURE 1 Phase transition temperatures of the homologous series of 6O.nSA doped with 5 w% of HOBACNPC.

The pyroelectric coefficient is calculated from the voltage developing between the transparent electrodes of the liquid crystal cell when it is irradiated with laser pulses of different duration. The radiation (λ= 1.06 μm) of a YAG:Nd pulsed laser is absorbed within the liquid crystalline layer which contains a small amount ($<$0.5 %) of a soluable light absorbing dye. The temperature dependence of γ_p and the calculated P_s are shown in Fig.2. Since the laser beam causes only a local heating by the pyroelectric method we study only a small region of the sample which was irradiated. Therefore the temperature of this region can be determined relatively with high precision. The calculation of γ_p requires a calibration of the optical and thermal properties of the cell.

By the Sawyer-Tower method we measure the usual P-E hysteresis curve. Our loop tracer consisted of a Diamant bridge[12] which was connected to a microcomputer allowing measurements at low frequencies (1-10 Hz). The temperature dependence of the spontaneous polarization measured by this method is shown in Fig.3. For such measurements one has to prepare a planar oriented sample (smectic layers are perpendicular to the bounding surfaces). We

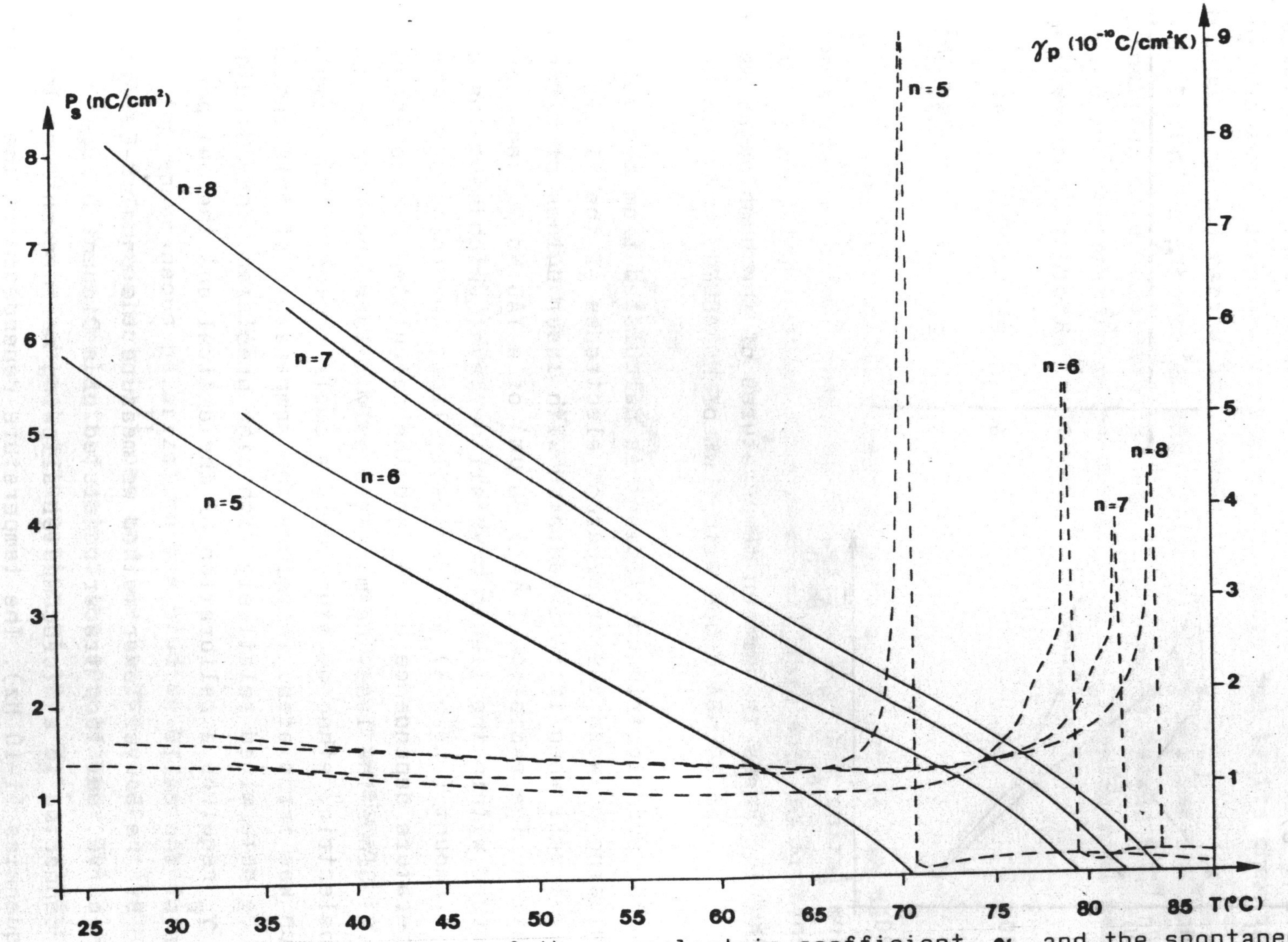


FIGURE 2 Temperature dependence of the pyroelectric coefficient γ_p and the spontaneous polarization P_s for the homologous series of mixtures 60.nSA/HOBACNPC.

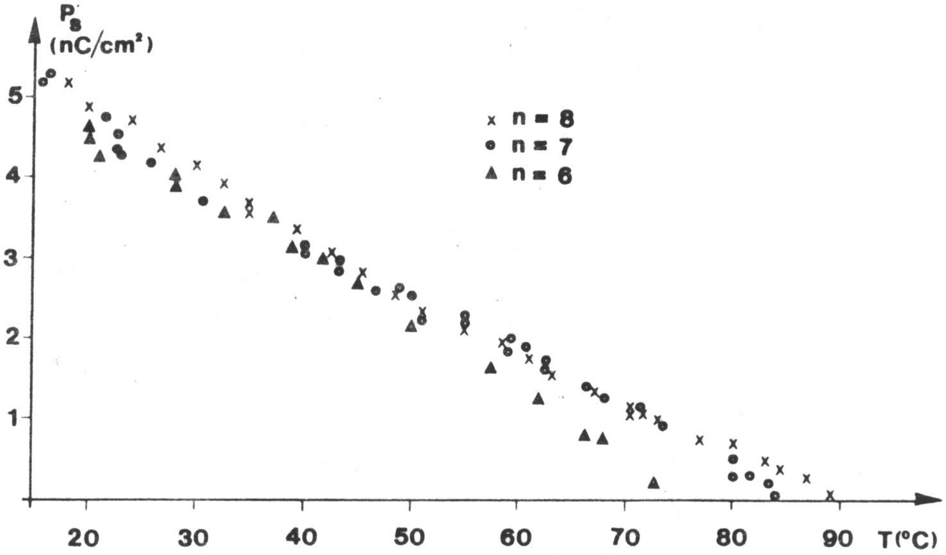


FIGURE 3 Spontaneous polarization measured by the bridge method for the homologous series of 6O.nSA/HOBACNPC.

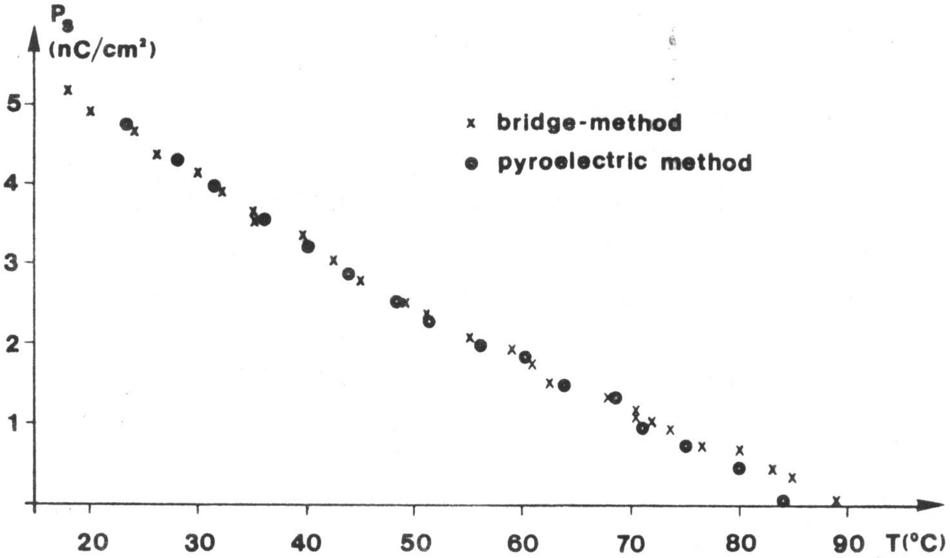


FIGURE 4 Comparison of the spontaneous polarization measured by two methods for 6O.8SA/HOBACNPC.

oriented the sample by a shear method[13]. The quality of orientation of the whole sample is important in this case, because any deterioration of the alignment leads to an effective decrease of the polarization. In Fig.4 we compare the temperature dependence of the spontaneous polarization measured by the two methods. The pyroelectric data were normalized at one point to the data obtained by Diamant bridge.

The difference in the absolute values may be connected with calibration problems of the pyroelectric cell and/or insufficient orientation of the cell used in the bridge method. Since the temperature inhomogeneities can cause an averaging in large area samples of the bridge method the pyroelectric technique yields a more precise temperature dependence especially near to the SmA-SmC^{*} phase transition.

The coincidence of the two temperature dependences is striking. Similar behaviour has been found not only for other members of this homologous series but for other doped systems as well[14].

The interpretation of this unusual temperature dependence (there is no sign of the square roote function) seems to be a good example to check the performance of different theoretical models.

COMPARISON WITH THE THEORY

Novel theoretical models of the ferroelectric SmC^{*} phase are based on the generalized Landau expansion. The free-energy density of the system is expanded in two order parameters, the tilt Θ and the polarization P.

According to the Ljubljana group[7] the free-energy density can be written in a dimensionless form as

$$\tilde{g}_o = \frac{1}{2}(\beta^2-\gamma\tau)\tilde{\Theta}^2 + \frac{1}{4}\gamma\tilde{\Theta}^4 + \frac{1}{6}\varrho\tilde{\Theta}^6 + \frac{1}{2}\tilde{P}^2 + \frac{1}{4}\tilde{P}^4 - \beta\tilde{P}\tilde{\Theta} - \frac{1}{2}\tilde{P}^2\tilde{\Theta}^2$$

where $\tilde{\Theta} = \Theta/\Theta^{*}$, $\tilde{P} = P/P^{*}$ and $\tau = (T_c-T)/T^{*}$ are the dimensionless tilt, polarization and temperature respectively. Here T_c is the

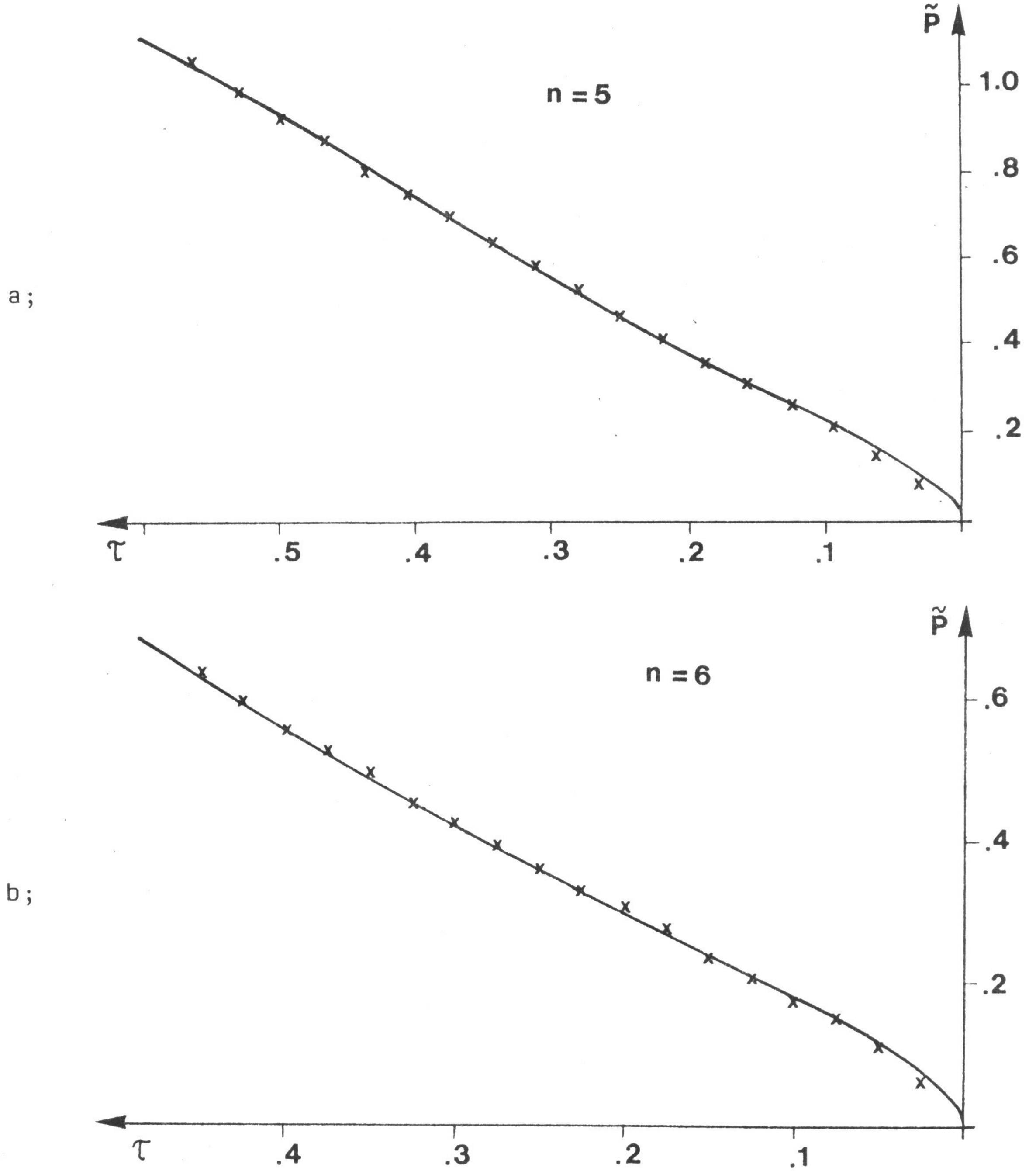


FIGURE 5 Dimensionless polarization versus dimensionless temperature. Continuous line is the fitted curve, crosses are measured points.

a; Mixture 60.5SA/HOBACNPC. Best fit parameters: $P^{*}=5.32$ nC/cm^2 , $T^{*}=80$ ^{o}C , $\beta=0.5$, $\gamma=1.35$, $\varrho=0$.

b; Mixture 60.6SA/HOBACNPC. Best fit parameters: $P^{*}=8.02$ nC/cm^2 , $T^{*}=100$ ^{o}C , $\beta=0.447$, $\gamma=1.6$, $\varrho=0$.

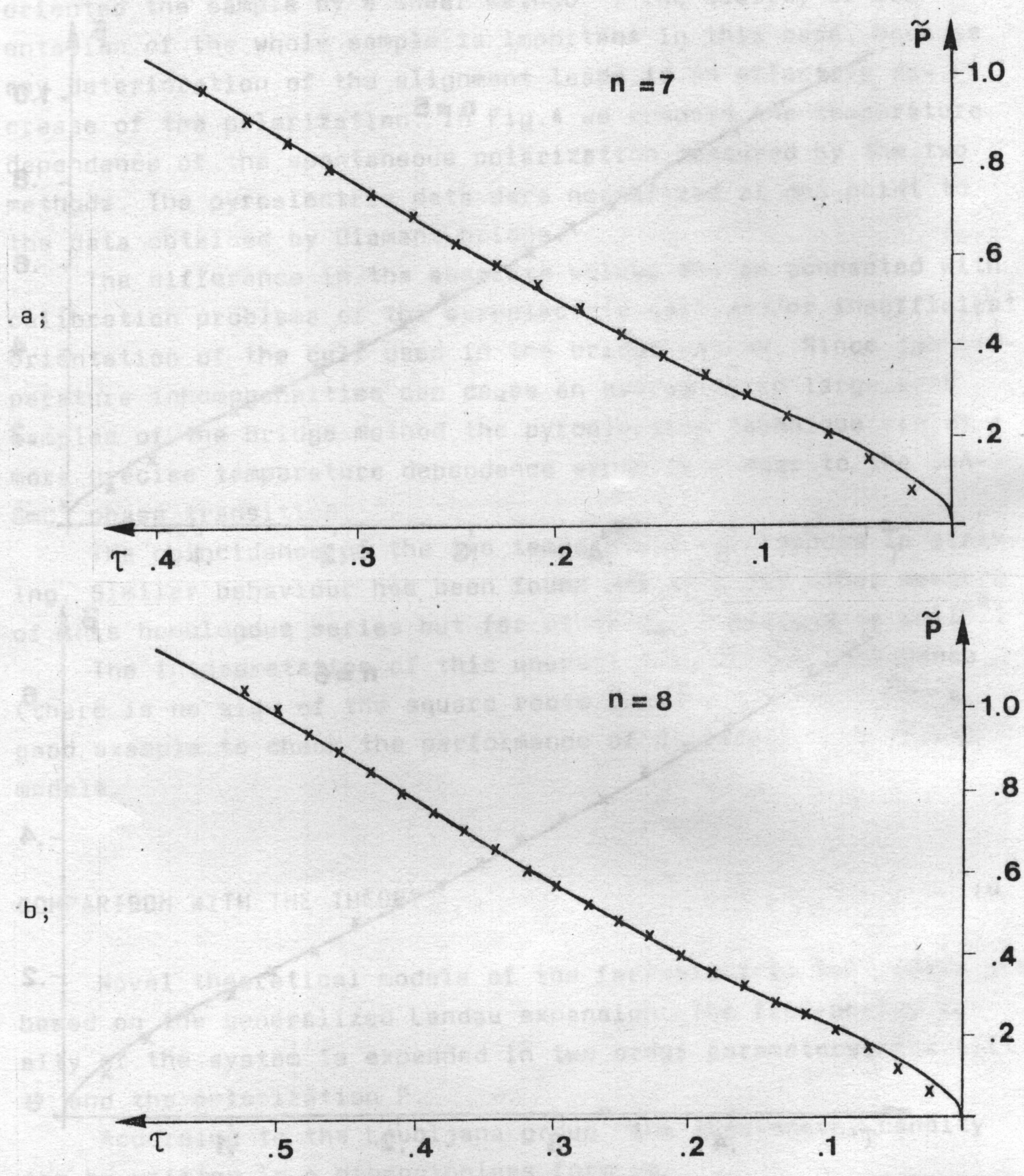


FIGURE 6 Dimensionless polarization versus dimensionless temperature. Continuous line is the fitted curve, crosses are measured points.

a; Mixture 60.7SA/HOBACNPC. Best fit parameters: $P^{*}=6.4\ \mathrm{nC/cm^2}$, $T^{*}=120\ ^{o}C$, $\beta=0.548$, $\gamma=1.2$, $\varrho=0$.

b; Mixture 60.8SA/HOBACNPC. Best fit parameters: $P^{*}=7.87\ \mathrm{nC/cm^2}$, $T^{*}=110\ ^{o}C$, $\beta=0.5$, $\gamma=1.3$, $\varrho=0$.

SmA-SmC* phase transition temperature. The scaling factors Θ^*, P^* and T^* as well as the parameters β, γ and ϱ are derived from the original parameters of the Landau expansion[7]. Minimizing g_0 with respect to the dimensionless tilt and polarization one can calculate the expected $\tilde{P}(\tau)$ and $\tilde{\Theta}(\tau)$ dependence.

In Figs.5ab and 6ab we plot the measured spontaneous polarization versus temperature for four members of the homologous series and compare them with the theoretical curves calculated with parameters yielding the best fitting. The extremely good agreeement is striking. We can conclude that the generalized Landau model[7] of smectic C* can explain the unusual temperature dependence of the polarization.

Since the temperature dependence of the tilt can also be obtained from the model, a further check would be to compare it with the measured tilt angle. However this, question is beyond of our present scope and will be discussed in a forthcoming paper.

REFERENCES

1. R.B. Meyer, L. Liébert, L. Strzelecki and P. Keller, J.Physique Lett., 36, L-69 (1975)
2. N.A. Clark and S.T. Lagerwall, Appl.Phys.Lett., 36, 899 (1980)
3. K. Skarp and G. Andersson, Ferroelectrics Letters, 6, 67 (1986)
   J.S. Patel and J.W. Goodby, Mol.Cryst.Liq.Cryst., 144, 117 (1987)
   Ch. Bahr and G. Heppke, Mol.Cryst.Liq.Cryst.Letters, 4, 31 (1987)
   Ch. Bahr and G. Heppke, Mol.Cryst.Liq.Cryst., 148, 29 (1987)
   K. Yoshino, M. Ozaki, S. Kishio, T. Sakurai, N.Mikami, R. Higuchi and M. Honma, Mol.Cryst.Liq.Cryst., 144, 87 (1987)
   T. Sakurai, M. Mikami, M. Ozaki and K. Yoshino, J.Chem.Phys., 85, 585 (1986)
   T. Inukai, S. Saitoh, H. Inoue, K. Miyazawa, K. Terashima and K. Furukawa, Mol.Cryst.Liq.Cryst., 141, 251 (1986)

4. S.A. Pikin, Structural Changes in Liquid Crystals (in Russian), Nauka 1981
S.A. Pikin and V.L. Indenbom, Uspekhi Fiz.Nauk, 125, 251 (1978)

5. C. Filipic, A. Levstik, I. Levstik, R. Blinc, B. Zeks, M. Glogarová and T. Carlsson, Ferroelecrics, 73, 295 (1987)

6. C.C. Huang, Mol.Cryst.Liq.Cryst., 144, 1 (1987)
S. Dumrongrattana, G. Nounesis and C.C. Huang, Phys.Rev.A, 33, 2181 (1986)

7. B. Zeks, T. Carlsson, C. Filipic and A. Levstik, Mol.Cryst.Liq.Cryst., in press
T. Carlsson, B. Zeks, A. Levstik, C. Filipic, I. Levstik and R. Blinc, Phys.Rev.A., 36, 1484 (1987)

8. W. Kuczynski and H. Stegemeyer, Chem.Phys.Lett., 70, 123 (1980)

9. L.A. Beresnev, E.P. Pozhidayev, L.M. Blinov, A.I. Pavluchenko and N.B.Etingen, Pis'ma Zh.Eksp.Teor.Fiz., 35, 430 (1982)
L.A. Beresnev, L.M. Blinov, V.A. Baikalov, E.P. Pozhidayev, G.V. Purvanetskas and A.I. Pavluchenko, Mol.Cryst.Liq.Cryst., 89, 327 (1982)

10. G.R. Allakhverdov, N.B. Terekhova, M.Yu. Zablotskaya and N.B. Etingen, 4th Liq.Cryst.Conf. of Soc. Countries, Tbilisi, 1981. Abstract D-2, vol.1., p.310

11. L.M. Blinov, L.A. Beresnev, N.M. Shtykov and Z.M. Elashvili, J.Physique Colloque C-3, 40, C3-269
L.M. Blinov, V.A. Baikalov, M.I. Barnik, L.A. Beresnev, E.P. Pozhidayev and S.V. Yablonsky, Liquid Crystals, 2, 121 (1987)

12. H. Diamant, K. Drenck and R. Pepinsky, Rev.Sci.Instr., 28, 30 (1957)

13. L. Bata, N. Éber and A. Jákli, Hungarian patent applied for

14. L.M. Blinov, Private communication