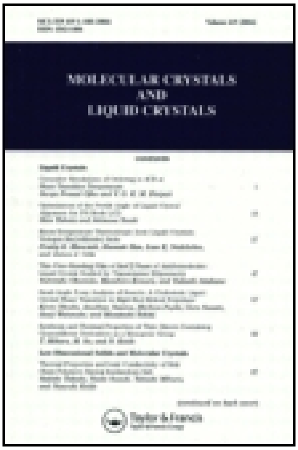

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Electric Field Induced Smectic A to Smectic C Transition in Ferroelectric Liquid Crystals

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The influence of an electric field on the SmC*–SmA transition of two new ferroelectric liquid crystals is investigated. At temperatures just above the SmC*–SmA transition double hysteresis loops are observed similar to that known for solid ferroelectrics indicating a field induced first order transition to the ferroelectric phase. The first order character of the SmC*–SmA transition of the two compounds under investigation is supported by DSC and tilt angle measurements. With field strength of about 50 kV/cm the transition temperature is enhanced by 1 K. The shift of the SmC*–SmA transition temperature, which is found to vary linearly with applied field strength, can be calculated by simple thermodynamic arguments.

Keywords: field induced phase transition, ferroelectric liquid crystals

I. INTRODUCTION

Phase transitions in liquid crystals are often associated with very small enthalpy effects. Therefore, it can be expected that the transition temperatures are sensitive to external fields. It was shown that the temperature of the nematic isotropic phase transition[1] as well as the transition temperatures in Blue Phase systems[2,3] can be shifted by the application of an electric field. In these cases the coupling parameter is the difference of the dielectric constants in both phases which results in an additional energy depending on the square of the electric field strength.

Ferroelectric smectic C* phases exhibit a spontaneous polarization which couples linearly to the electric field strength. In principle, corresponding to this coupling the SmC*–SmA transition temperature might be influenced by an external electric field.

There have been several theoretical and experimental studies concerning the SmC*–SmA transition. Almost all investigations concentrate on only one ferroelectric liquid crystal–the widely known DOBAMBC. The SmC*–SmA transition of this compound is reported to be of second order and corresponding Landau theories have been presented.[4,5,6] Concerning the influence of an electric field a monotonically decreasing line of critical temperatures separating a uniformly polarized SmC–phase from a SmC*–phase with distorted helicoidal structure at lower temperatures is predicted.[7,8] Because the electric field induces a small tilt in the SmA–phase,[9] at non zero field the SmA–phase is not distinguished by a sharp transition from the uniform SmC–phase[10] and only a SmC*(helicoidal)–SmC(unwound) transition should to be observed in the T/E diagram. Several experiments[11,12] have established this behaviour at higher field strengths, e.g. at temperatures some degrees below the SmC*–SmA transition, whereas near zero field the situation is complicated probably because of the unusual temperature dependence of the helical pitch near the SmC*–SmA transition of DOBAMBC.

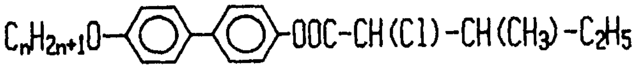
In solid ferroelectrics the effect of electric fields on the ferroelectric–paraelectric transition has been widely studied.[13] If an electric field is applied to a material showing a second order transition, the paraelectric phase is not distinguished by a sharp phase transition from the ferroelectric phase analogous to the behaviour of DOBAMBC. However, if the transition is of first order at zero field, then also in an external electric field a first order transition characterized by a jump of the polarization is to be observed. The temperature of this transition increases linearly with applied field strength and above a certain field strength the transition becomes continuous. A characteristic of a field induced first order transition to the ferroelectric phase in solid ferroelectrics is the appearance of double hysteresis loops at temperatures just above the zero field ferroelectric–paraelectric transition.[13,14]

When studying the recently reported ferroelectric liquid crystals exhibiting high values of the spontaneous polarization,[15,16] similar double hysteresis loops were observed in the neighbourhood of the SmC*–SmA transition. In this paper first experimental results concerning the influence of an electric field on the SmC*–SmA transition of the new compounds are reported.

II. EXPERIMENTAL RESULTS

The compounds under investigation belong to two homologous series of ferroelectric liquid crystals which show values of the spontaneous polarization up to 300 nC/cm^2, i.e. two orders of magnitude higher than that of DOBAMBC. The structural formulas are given below:

series "An"



series "Cn"

A. Behaviour without external electric field

The results reported in this paper concentrate on the compounds A7 and C7, i.e. the heptyloxy-homologs of the two series. Both compounds show isotropic, SmA, SmC*, and some more ordered smectic phases. The SmC*-SmA transition temperatures, as determined by a Mettler Fp 82 hot stage, are 73.4°C (A7) and 55.0°C (C7). The texture change observed in the microscope is very sharp compared to compounds showing a second order SmC-SmA transition (e.g. DOBAMBC) where the transition is characterized by a more continuous evolution of the texture of the SmC-phase to that of the SmA-phase.

To characterize the SmC*-SmA transition more in detail DSC measurements were performed. The DSC-traces of both compounds obtained on a Perkin-Elmer DSC-2 show a distinct peak at the SmC*-SmA transition. The peak area does not depend on the heating rate; for all rates from 5 K/min to 0.31 K/min an area corresponding to 1.2 J/g (A7), respectively, 1.8 J/g (C7) is determined. The peak height is enhanced by the factor of 1.4 when the heating rate is doubled as expected for a first order transition.[17] In Figure 1 the DSC-traces obtained with the slowest possible heating rate of the DSC-2 (0.31 K/min) are shown. For comparison the DSC-traces of DOBAMBC and 8.S.5, two compounds exhibiting a second order SmC-SmA transition, are recorded under identical conditions. The specific heat discontinuity, which is reported to be in the order of 0.1 J/gK for both DOBAMBC and 8.S.5,[18,19] produces only a small shift of the baseline, whereas the compounds under investigation show a very clear signal two to three orders of magnitude larger. The assumption of a first order transition is supported by preliminary x-ray measure-

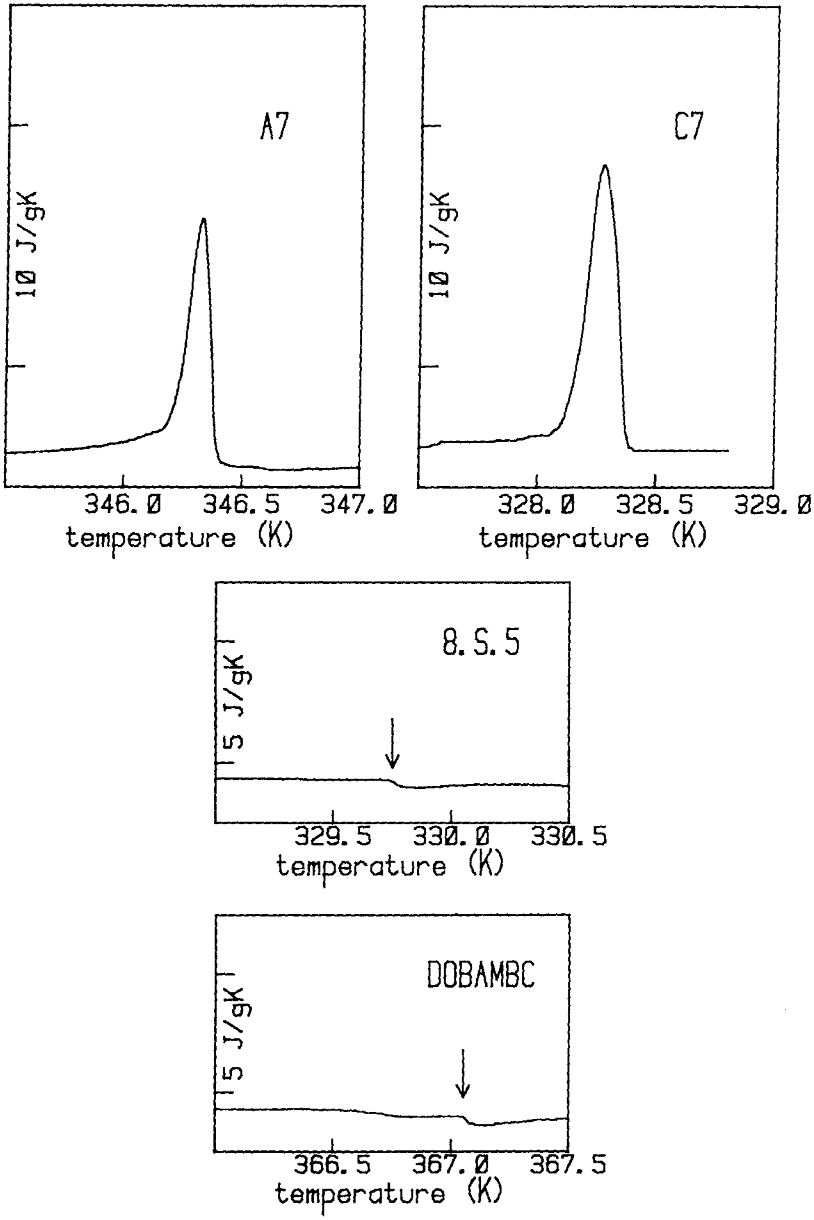


FIGURE 1 DSC-traces of the SmC*–SmA transition of the compounds under investigation obtained on a Perkin-Elmer DSC 2. (Heating rate 0.31 K/min, range 0.1 mcal/s, sample weight ≈5 mg.) For comparison DSC-traces of two compounds exhibiting a second order SmC–SmA transition (marked by arrow) are shown which are recorded under identical conditions.

ments on the compound C7 carried out with a temperature resolution better than 10 mK. At the SmC*–SmA transition a discontinuity in the smectic layer spacing of 0.15 nm was observed[20] corresponding to a jump of the tilt angle of about 20°.

B. Behaviour in external electric fields

In order to study the behaviour in an external electric field, the compounds are filled into a glass cell (thickness 9μm) in planar orientation allowing to apply an electric field parallel to the smectic layers. It should be noted that the helical structure of the SmC*–phase is completely unwound in a cell of 9 μm thickness with a voltage of 10 V and more applied. Therefore, in this paper the designation "SmC*" is used to label a smectic C phase with ferroelectric properties independently from the occurrence of a helical structure.

In Figure 2 the temperature dependence of the spontaneous polarization in the SmC*–phase is shown. The values are obtained by recording polarization hysteresis loops with a Diamant bridge[21] applying a sinusoidal ac voltage with a frequency of 50 Hz.

As shown in Figure 2, the spontaneous polarization of the compounds under investigation does not decrease continuously to zero when the transition to the smectic A phase is approached. Whereas in the SmC*–phase usual hysteresis loops of ferroelectric liquid crystals are obtained, above the zero field SmC*–SmA transition temperature the following behaviour is observed: Far above the zero field transition temperature Tc a straight line in the polarization versus field diagram is observed corresponding to the dielectric properties of the SmA–phase (Figure 3d). When Tc is approached two small hysteresis loops appear at high positive and negative field strength whereas for low field the linear P–E relation remains, i.e. the material, which is in the non-ferroelectric SmA-phase at low field, becomes ferroelectric under the influence of a high electric field (Figure 3c). The field strength at which the ferroelectric state is induced decreases with decreasing temperature. Close to Tc the two loops overlap (Figure 3b) and below Tc a regular hysteresis loop is observed (Figure 3a).

The double hysteresis loops shown in Figure 3 exhibit the same appearance as those obtained for solid ferroelectrics. For these materials the shift of the Curie point by a dc electric field and the observation of double hysteresis loops is a well known phenomenon.[13] It should be mentioned that a double hysteresis loop is observed only for materials showing a first order ferroelectric–paraelectric transi-

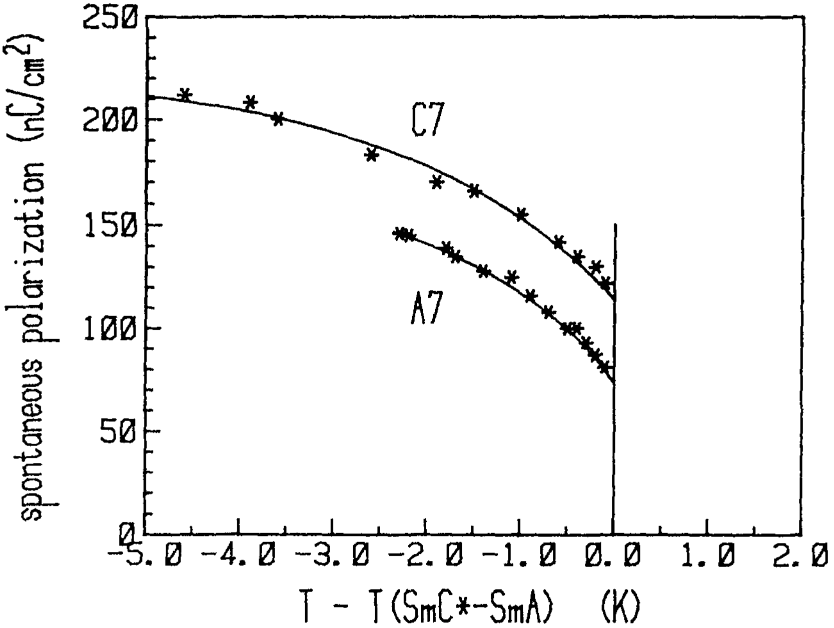


FIGURE 2 Spontaneous polarization of the compounds under investigation versus temperature difference to the zero field SmC*–SmA transition temperature detected optically in the same set-up. (Compound A7 shows a SmG–SmC* transition 2.5 K below the SmC*–SmA transition.) At the zero field SmC*–SmA transition temperature the hysteresis loops transform into double hysteresis loops as shown in Figure 3.

tion.[14,22-24] Accordingly, the appearance of double hysteresis loops in the ferroelectric liquid crystals under investigation may be interpreted as a consequence of a field induced first order transition from the non-ferroelectric SmA–phase to the ferroelectric SmC*–phase.

The shift of the SmC*–SmA transition temperature by an electric field is easy to observe in the microscope. When the sample is heated starting some degrees below the zero field SmC*–SmA transition temperature while a constant dc field is applied, a distinct texture change is observed very similar to that of the zero field SmC*–SmA transition. For both compounds the temperature at which this texture change occurs lies above the zero field transition temperature and is shifted linearly to higher values with increasing field strength (Figure 4). The texture change, which is very sharp for zero and low field strength, becomes more continuous in higher fields.

Additional information can be obtained from polarization measurements using the field reversal method.[25] If the direction of a con-

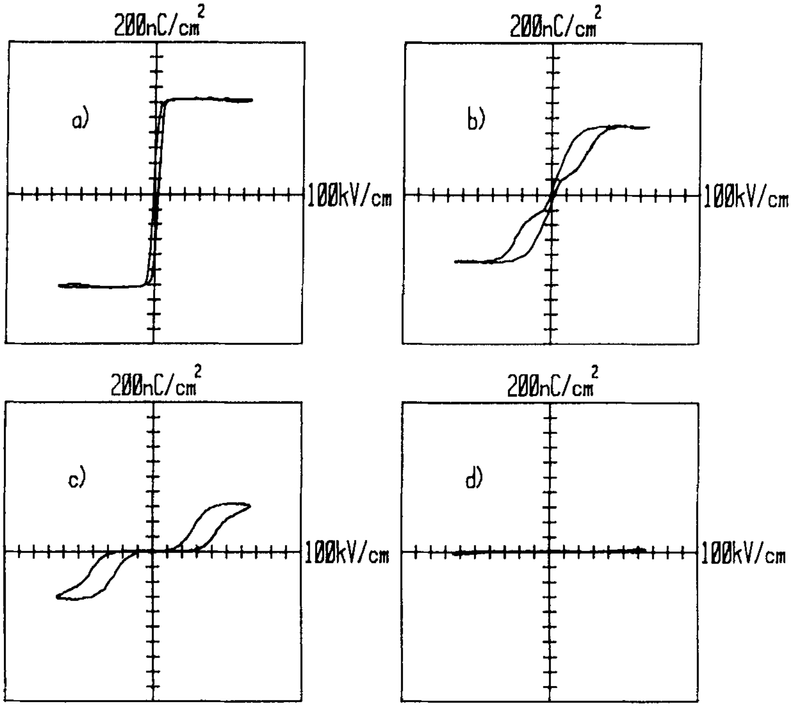


FIGURE 3 Polarization hysteresis loops of the compound C7 in the vicinity of the zero field SmC*–SmA transition temperature Tc. a) Tc − 0.1 K b) Tc + 0.3 K c) Tc + 0.7 K d) Tc + 1.7 K.

stant dc-field applied to the sample is reversed, the time integral of the transient current corresponds to the polarization of the sample. In the SmA–phase only the induced polarization contributes to the current, whereas in the SmC*–phase additionally a second current peak corresponding to the reversal of the spontaneous polarization occurs (Figure 5).

As shown in Figure 5 for the compound C7, the peak due to the reversal of the spontaneous polarization is still to observe at the zero field SmC*–SmA transition temperature of 55.0°C. With increasing temperature the peak vanishes within a temperature interval of less than 0.2 K when a voltage of 10 V at 9 μm is used for the measurements. It should be noted that even at 55.2°C and in the entire SmA–phase range a switching of the sample is observed optically which arises from the reversal of the field induced tilt in the SmA–phase known as electroclinic effect[9] which is rather large for this com-

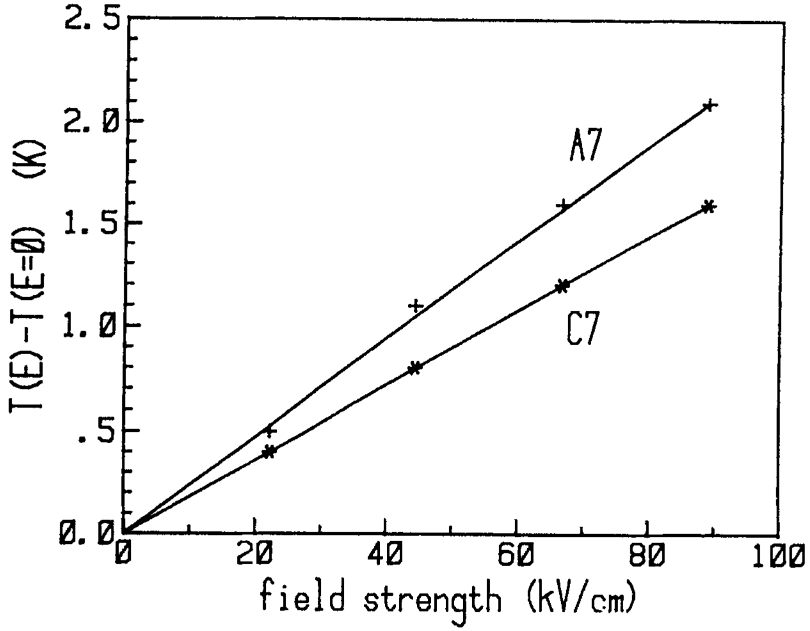


FIGURE 4 Temperature of the optically observed texture change versus applied dc field strength.

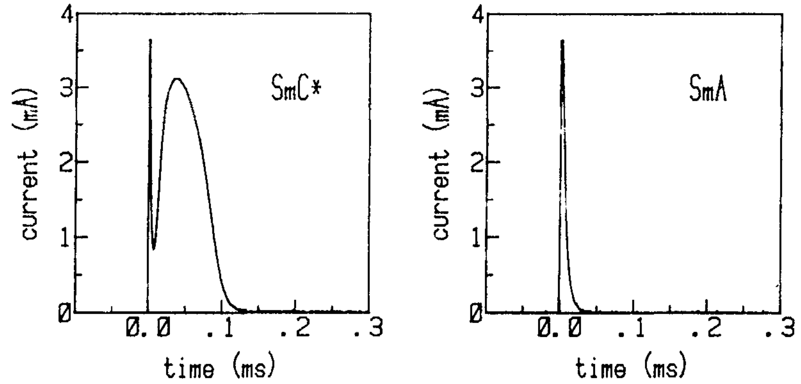


FIGURE 5 Current flow through the sample of the compound C7 induced by the reversal of a dc voltage of 10 V applied to the 9 μm thick cell. The integral of the curves divided by the electrode area corresponds to twice the polarization in an external field of 11.1 kV/cm. Right: In the SmA-phase (T = 55.2°C) only one peak due to the induced polarization is observed. Left: In the ferroelectric SmC*-phase (T = 55.0°C) additionally a second peak due to the spontaneous polarization occurs.

pound.[26] However, the reversal of the field induced tilt in the SmA-phase is obviously not connected with the reversal of a spontaneous polarization.

It is difficult to determine the exact temperature at which the current peak due to the reversal of the spontaneous polarization vanishes, because it would require a careful analysis of the total transient behaviour. Moreover, experimental imperfections e.g. the high resistance of the sample electrodes (about 1 kΩ) and the probably non-uniform sample thickness prevent a better resolution at the present stage of the experimental set-up.

Nevertheless, a discontinuous behaviour is revealed when plotting the total polarization of the sample (induced + spontaneous polarization) versus temperature (Figure 6). For voltages less than 30 V at 9 μm a steep decrease is observed corresponding to the disappearance of the current peak due to the spontaneous polarization.

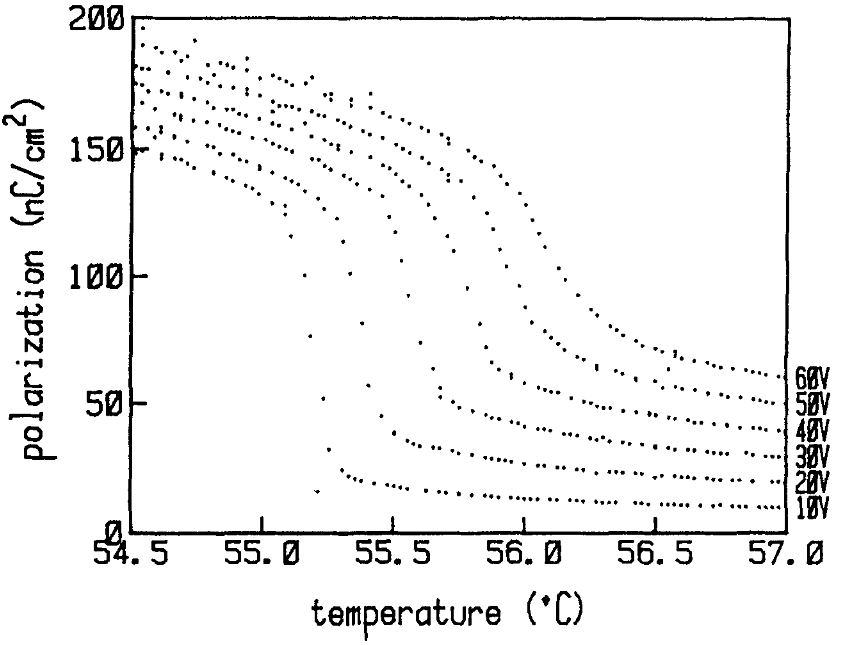


FIGURE 6 Temperature dependence of the total polarization (induced + spontaneous) of the compound C7 at different dc field strengths. The values are obtained by recording the current versus time curves continuously with a digital storage oscilloscope and calculating the integral with a Hewlett-Packard 85 computer while the sample is heated with a constant rate of 0.05 K/min and the applied dc voltage is reversed with a frequency of 10 Hz.

The temperature at which the drop of the polarization occurs is shifted linearly to higher values with increasing field strength while the shape of the curves becomes more continuous analogous to the behaviour of the optically observed texture change.

For the compound A7 a similar behaviour as for C7 is observed mainly differing in the field strength at which the transition appears to become continuous which is lower in the case of A7.

III. DISCUSSION

To interpret the experimental observations a first order SmC*–SmA transition is assumed (which has to be proved more distinctly by further investigations): At zero field the tilt angle jumps at the transition from zero in the SmA–phase to a finite value in the SmC*–phase. If a dc field is applied also the SmA–phase is tilted because of the electroclinic effect. Although both phases possess now the same symmetry they are still distinguished by a sharp transition characterized by a jump of the tilt angle. When an electric field is applied the transition from the SmC*–phase to the tilted SmA–phase can be detected either by the disappearance of the spontaneous polarization or by an optically observable texture change. Both experimental observations—texture change and disappearance of the spontaneous polarization—occur at the same temperature. With increasing field strength the transition temperature is shifted linearly to higher values with respect to the zero field SmC*–SmA transition temperature. At high field strength the discontinuity vanishes, i.e. there is a continuous evolution from the tilted SmA–phase to the ferroelectric SmC*–phase. This implies the existence of a critical point at which the first order transition line in the temperature versus field strength diagram ends. Even for high field strength the disappearance of the spontaneous polarization as well as the texture change occur in a narrow temperature range coinciding with the point of inflection in the polarization versus temperature curves and obviously continuing the low field transition line (Figure 3).

In solid ferroelectrics for the field induced shift of a first order ferroelectric–paraelectric transition a Clausius–Clapeyron type of equation is established[13]:

$$\frac{\Delta T}{E} = \frac{\Delta P}{\Delta S}$$

ΔP and ΔS are the polarization jump and the entropy change at the transition. Taking for the ferroelectric liquid crystals under investigation the values determined for the zero field SmC*–SmA transition (i.e. estimating ΔP as 80 nC/cm^2 (A7) and 110 nC/cm^2 (C7) (see Figure 2) and calculating ΔS from the DSC measurements) one gets values for the zero field slope $\Delta T/E$ of $2.4 \cdot 10^{-5}$ K/(Vcm^{-1}) (A7) and $2.0 \cdot 10^{-5}$ K/(Vcm^{-1}) (C7). These values are in good agreement with the experimentally observed slope of the transition lines which were determined from Figure 4 as $2.4 \cdot 10^{-5}$ K/(Vcm^{-1}) (A7) and $2.0 \cdot 10^{-5}$ K/(Vcm^{-1}) (C7).

In conclusion, to the knowledge of the authors, for the first time a linear shift of liquid crystal phase transitions induced by an electric field has been established. As compared to the classical experiment of Helfrich,[1] the effects are rather large at moderate field strength obviously due to the high spontaneous polarization exhibited by the new ferroelectric compounds. The field induced shift of the phase transition can be calculated by simple thermodynamic arguments assuming the transition to be of first order which is most probably the case for the two compounds under investigation.

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References

1. W. Helfrich, *Phys. Rev. Lett.*, **24**, 201 (1970).
2. G. Heppke, M. Krumrey and F. Oestreicher, *Mol. Cryst. Liq. Cryst.*, **99**, 99 (1983).
3. H. Stegemeyer and F. Porsch, *Phys. Rev. A*, **30**, 3369 (1984).
4. V. L. Indenbom, S. A. Pikin and E. B. Loginov, *Kristallografiya*, **21**, 1093 (1976).
5. A. Michelson, L. Benguigui and D. Cabib, *Phys. Rev. A*, **16**, 394 (1977).
6. R. Blinc, B. Zeks, I. Musevic and A. Levstik, *Mol. Cryst. Liq. Cryst.*, **114**, 189 (1984).
7. A. Michelson and D. Cabib, *J. Phys. Lett.*, **38**, 321 (1977).
8. G. Durand and Ph. Martinot-Lagarde, *Ferroelectrics*, **24**, 89 (1980).
9. S. Garoff and R. B. Meyer, *Phys. Rev. Lett.*, **38**, 848 (1977).
10. T. Carlsson and I. Dahl, *Mol. Cryst. Liq. Cryst.*, **95**, 373 (1983).
11. K. Kondo, H. Takezoe, A. Fukuda and E. Kuze, *Jpn. J. Appl. Phys.*, **22**, L43 (1983).
12. S. A. Rozanski and W. Kuczynski, *Chem. Phys. Lett.*, **105**, 104 (1984).
13. M. E. Lines and A. M. Glass, *Principles and Application of Ferroelectrics and Related Materials*, (Oxford University Press, 1979), pp. 169–173.
14. W. J. Merz, *Phys. Rev. A*, **91**, 513 (1953).
15. T. Sakurai, N. Mikami, R. Higuchi, M. Honma, M. Ozaki and K. Yoshino, *J. Chem. Soc., Chem. Commun.*, 978 (1986).

16. Ch. Bahr and G. Heppke, *Mol. Cryst. Liq. Cryst. Lett.*, **4**, 31 (1986).
17. P. Navard and J. M. Haudin, *J. Thermal Analysis*, **30**, 61 (1985).
18. S. Dumrongrattana, G. Nounesis and C. C. Huang, *Phys. Rev. A*, **33**, 2181 (1986).
19. C. A. Schantz and D. L. Johnson, *Phys. Rev. A*, **17**, 1504 (1978).
20. R. Shashidhar, private communication.
21. H. Diamant, K. Drenck and R. Pepinsky, *Rev. Sci. Instr.*, **28**, 30 (1957).
22. A. F. Devonshire, *Adv. Phys.*, **3**, 86 (1954).
23. B. A. Strukov, N. D. Gavrilyuk and V. A. Koptsik, *Kristallografiya*, **6**, 780 (1961).
24. K. Okada and H. Sugie, *Phys. Lett.*, **37A**, 337 (1971).
25. Ph. Martinot-Lagarde, *J. Phys. Lett.*, **38**, L-17 (1977).
26. Ch. Bahr and G. Heppke, *Mol. Cryst. Liq. Cryst.* (1987), in print.