

Electric-field-induced critical point in ferroelectric liquid crystals

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The observation of a new critical point in liquid-crystal phase transitions is reported. Detailed tilt angle, polarization, and susceptibility measurements of a ferroelectric liquid crystal in the presence of an applied dc electric field show that a first-order transition between the polarized smectic-*A* phase and the ferroelectric smectic-*C* phase terminates at a critical point in the temperature-field plane.

Smectic-*A* (Sm-*A*) and smectic-*C* (Sm-*C*) liquid crystals are orientationally ordered fluids with a one-dimensional density wave, the wave vector being either parallel (Sm-*A*) or tilted (Sm-*C*) with respect to the director (i.e., the average direction of the long molecular axis). Such a structure can also be considered as an arrangement of rodlike molecules in weakly defined layers with the molecules oriented on average parallel to the normal vector of the layers (Sm-*A*) or at a tilt angle θ to the layer normal (Sm-*C*). Many liquid-crystal compounds exhibit both the Sm-*A* and the Sm-*C* phase, the latter being the low-temperature phase.

If the constituent molecules are chiral (i.e., without mirror plane) and possess a permanent transverse dipole, a spontaneous polarization is present in each layer of the Sm-*C* phase,¹ the polarization vector pointing parallel to the layer plane and perpendicular to the tilted director. As a second consequence of the molecular chirality the director builds up a helical superstructure by precessing around the layer normal. The corresponding helical pitch usually amounts to several μm , the molecular short-range order being the same as in the nonchiral Sm-*C* phase. A dc electric field of sufficient strength unwinds the helical structure by aligning the polarization vectors of the smectic layers parallel to the field direction, thus producing a homogeneous orientation of the molecules.

The Sm-*C* phase of chiral molecules is an improper ferroelectric, i.e., the spontaneous polarization is not due to strong electrostatic interactions as in most solid ferroelectrics, the polarization is rather produced by the reduction of symmetry because of tilt and chirality. Accordingly, the phase transition from the Sm-*A* to the ferroelectric Sm-*C* phase of chiral molecules is mainly driven by the same tilt producing molecular interactions as are present in nonchiral compounds also. In both cases, chiral and nonchiral, the primary order parameter of the transition is described by the tilt angle θ between director and layer normal with the polarization—in the chiral case—coupled to it as a secondary parameter.²

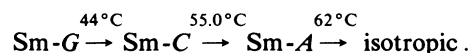
The coupling between tilt and polarization, which causes the spontaneous polarization in the Sm-*C* phase of chiral molecules, can also be observed in the Sm-*A* phase as the so-called electroclinic effect,³ a kind of inverse piezoelectric effect. The director in the Sm-*A* phase, usually being parallel to the layer normal, becomes tilted when a dc electric field is applied parallel to the layer plane. The direction of the induced tilt is perpendicular to

the field direction and the magnitude proportional to the applied field strength. Thus, in the presence of a dc electric field unwinding the helical structure of the Sm-*C* phase, both phases show a tilt angle with the same homogeneous tilt direction. Then, Sm-*A* and Sm-*C* phase have identical symmetry and are thermodynamically distinct only if a first-order transition exists at which the tilt angle shows a discontinuous behavior.

Experimentally, the Sm-*A*-Sm-*C* transition is in almost all compounds, chiral as well as nonchiral, found to be second order the tilt angle decreasing continuously to zero when approaching the transition from the low-temperature side. Recently, the first example for a first-order Sm-*A*-Sm-*C* transition was found⁴ in the chiral compound 4-(3-methyl-2-chloropentanoxyloxy)4'-heptyloxybiphenyl (abbreviated as C7) which shows a large spontaneous polarization in its Sm-*C* phase.⁵ The smectic layer spacing d in C7 [and thus the tilt angle θ , related to d by $\theta = \arccos(d_{\text{SmC}}/d_{\text{SmA}})$ ⁶] behaves discontinuously at the Sm-*C*-Sm-*A* transition. Furthermore, it was shown⁷ that the Sm-*C*-Sm-*A* transition temperature is increased by the application of a dc electric field, analogous to the behavior of solid ferroelectrics with a first-order transition.

In this paper, we present results establishing the first observation of a Sm-*C*-Sm-*A* critical point in ferroelectric liquid crystals. Measurements of tilt angle, polarization, and electric permittivity in the vicinity of the Sm-*A*-Sm-*C* transition of C7 in the presence of a dc electric field are reported. The first-order transition, characterized by a discontinuity of tilt angle and polarization, remains first order at moderate field strength and vanishes at higher field strength implying the existence of a critical point at the end of the first-order transition line in the temperature-field plane.

The C7 liquid crystal shows the phase sequence



The sample is filled into a conductively coated glass cell (thickness 10 μm , area 16 mm^2) with planar orienting surfaces. The cell within a temperature-controlled oven (temperature stability ≈ 10 mK) is placed under a polarizing microscope. By slow cooling from the isotropic phase to the Sm-*A* phase a homogeneous alignment is achieved (i.e., the director is parallel to the glass surfaces

and the smectic-layer planes are perpendicular to them). The tilt angle is determined optically by measuring the switching angle between the director positions at positive and negative applied dc field as described in Ref. 8. The method is applicable for both the Sm-*A* and Sm-*C* phase, if the switching field is of sufficient strength (≈ 5 kV/cm for our sample) to unwind the helix and produce a homogeneous alignment of the tilt direction in the Sm-*C* phase.

Figure 1 shows the tilt angle θ determined as a function of the applied dc field E at constant temperature. The zero-field Sm-*A*-Sm-*C* transition temperature T_{c0} of C7 is 55.0°C. At temperatures 2 K and more above T_{c0} we find a simple proportionality between θ and E . When the temperature is closer to T_{c0} , θ is proportional to E at low field, then increases more strongly, and tends to saturate at high field. Such a behavior is different to what is found in compounds exhibiting a second-order Sm-*A*-Sm-*C* transition where the θ - E curves are either linear or have negative curvature but do not show an *S*-like shape.⁹ When the temperature approaches T_{c0} , the nonlinear increase of θ becomes more pronounced and shifts to lower field. Below T_{c0} , θ is again almost linearly related to E and one can determine the intrinsic tilt in the Sm-*C* phase by extrapolating the θ values to zero-field strength.

The θ vs E curves shown in Fig. 1 have, in a way, the appearance of isothermes near a critical point at which a first-order transition vanishes. However, for a definite conclusion the number of data points is too small and one would have to collect much more θ values. Therefore, we decided to measure additionally the polarization which can be determined much faster than the tilt angle. Because of the coupling between both quantities, P should exhibit qualitatively the same behavior as θ . The polarization is determined by measuring the displacement current over a resistor in series with the cell when the applied dc field is reversed. The time integral of the current

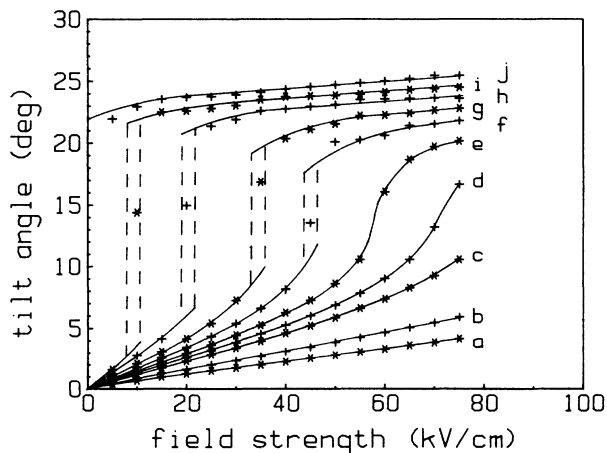


FIG. 1. Electric field dependence of the tilt angle, determined optically from the switching angle, at various temperatures near the zero-field transition temperature T_{c0} . The differences to T_{c0} are (in K): curve a, +3.1; curve b, +2.1; curve c, +1.6; curve d, +1.1; curve e, +0.9; curve f, +0.7; curve g, +0.5; curve h, +0.3; curve i, +0.1; curve j, -0.1. The lines are only guides to the eye (dashed lines indicate discontinuous transitions, broadened by experimental imperfections).

gives the electric displacement D corresponding to the polarization of our sample, enhanced by the amount of $\epsilon_0 E$ (ϵ_0 being the vacuum permittivity). The displacement current is monitored on a digital storage oscilloscope and D is calculated by a computer as described in Ref. 7. Thus, D can be determined quasicontinuously while the amplitude of the applied dc field is changed at a small constant rate.

Figure 2 shows the values of D measured as a function of field at constant temperature. The data were obtained with slow increasing or decreasing amplitude (rate ≈ 10 kV/cmh) of the applied square wave field (frequency 1 Hz). Whereas the curve recorded 1.0 K above T_{c0} reveals a continuous variation of D with E , the curves recorded at temperatures closer to T_{c0} exhibit a sharp increase of D in a narrow E interval. Because of a hysteresis between runs with increasing and decreasing E , we conclude that a first-order transition, characterized by a discontinuity of D (and thus of θ) is displayed by the D - E curves recorded 0.2, 0.4, and 0.6 K above T_{c0} . Experimental imperfections, such as sample impurities and small gradients in field strength and temperature, may result in the fact that the discontinuity of D , which should occur at a sharp E value in the ideal case, is spread in reality over a finite E interval. The first-order nature of the transition is demonstrated also by the occurrence of a two-phase region which is optically observed when the sample is watched in the microscope during the D measurements. Both, hysteresis and two-phase region, are definitely not present when the temperature is 1.0 K and more above T_{c0} . For $T = 0.8$ K + T_{c0} , a value which can be estimated to be near the critical temperature, the experimental resolution does not allow for a clear decision.

In addition to the measurements of the electric displacement D as a function of field at constant temperature, we have determined D as a function of temperature leaving the field constant. Figure 3 gives the results which are well in consistency with D measurements at constant temperature. The D values were determined with slowly

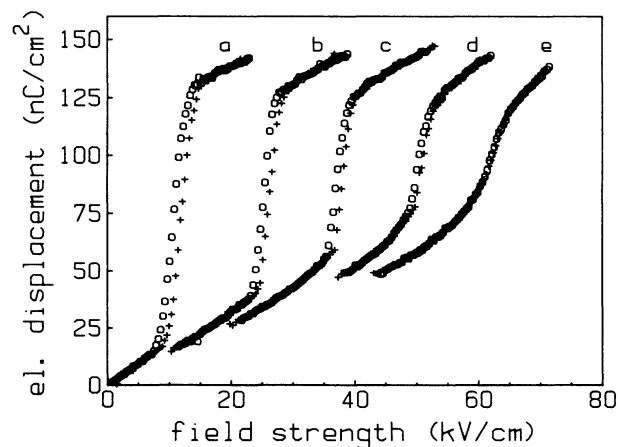


FIG. 2. Electric field dependence of the electric displacement at various temperatures near T_{c0} . The differences to T_{c0} are (in K): curve a, +0.2; curve b, +0.4; curve c, +0.6; curve d, +0.8; curve e, +1.0; "+": runs with increasing field, "0": runs with decreasing field.

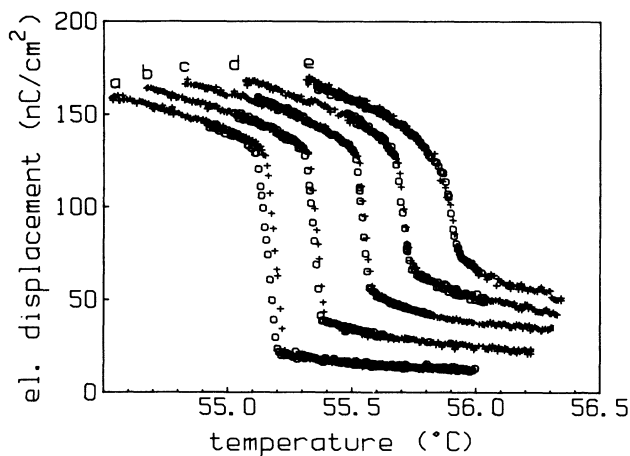


FIG. 3. Temperature dependence of the electric displacement at various field strengths. The values of E are (in kV/cm): curve a , 10; curve b , 20; curve c , 30; curve d , 40; curve e , 50; “+”: runs with increasing temperature, “O”: runs with decreasing temperature.

increasing or decreasing temperature (rate 10 mK/min). For a field strength of 10 kV/cm the D - T curve exhibits a discontinuous drop of D at $T \approx 0.2 \text{ K} + T_{c0}$ with a clear hysteresis between heating and cooling run, while for $E = 50 \text{ kV/cm}$ no discontinuity and no hysteresis could be observed.

The data presented in Figs. 1–3 show that the C7 liquid crystal in the presence of a low dc electric field exhibits a first-order transition characterized by a jump of polarization and tilt angle. With increasing field strength the transition temperature shifts to higher values while the discontinuity becomes smaller. At fields larger than about 50 kV/cm there is no first-order transition, but a continuous evolution from the polarized Sm- A to the ferroelectric Sm- C phase exists. Thus the overall experimental behavior of the ferroelectric liquid crystal is very similar to that of a liquid near the liquid-gas critical point, electric displacement and electric field strength corresponding to density and pressure, respectively. However, according to recent theoretical considerations,¹⁰ the dimensionality might differ from that of a liquid-gas critical point. A rough estimation of the critical-point coordinates of the C7 sample gives $T_c \approx 55.8^\circ\text{C}$ (i.e., 0.8 K above T_{c0}), $E_c \approx 50 \text{ kV/cm}$, and $D_c \approx 100 \text{ nC/cm}^2$.

A further indication for the critical point described above results from measurements of the susceptibility (either tilt susceptibility $d\theta/dE$ or permittivity $\epsilon = dD/dE$)

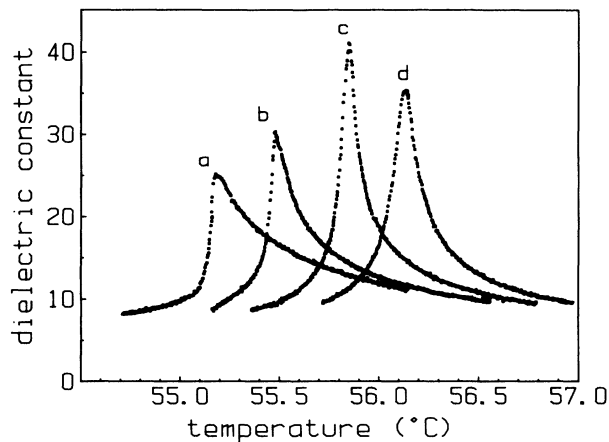


FIG. 4. Temperature dependence of the dielectric constant at various bias field strengths. The values of the bias field are (in kV/cm): curve a , 10; curve b , 30; curve c , 50; curve d , 70.

which should diverge at the critical point. Figure 4 shows the temperature dependence of the differential relative permittivity (dielectric constant), determined from capacitance measurements of the sample cell at various dc bias fields using a HP4274A LCR-meter (measuring voltage 0.1 V, frequency 100 Hz). Whereas at low fields (10 and 30 kV/cm) the permittivity ϵ shows a steplike discontinuity due to the first-order transition, a sharp, pronounced maximum, indicating the expected divergencelike behavior of ϵ , is observed when the field strength amounts 50 kV/cm (i.e., approximately the critical-field strength). On further increasing of the bias field the maximum of ϵ becomes lower and broadens. The continuous behavior of ϵ at 70 kV/cm reflects the continuous evolution from the Sm- A to the Sm- C phase at high external field.

In conclusion, we have shown that for a ferroelectric liquid crystal, which exhibits a first-order Sm- A -Sm- C phase transition, a line of first-order transitions exists in the temperature-field plane which terminates at a critical point. In addition to the shrinking of the discontinuity of polarization and tilt angle, this new type of critical point in liquid crystals is indicated by a divergence of the susceptibility.

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