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An EPR Study of the Orientational Transition in Smectic Liquid Crystals in a Magnetic Field

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Abstract—Spin probe EPR spectroscopy is used to detect an orientational transition in the smectic mesophase in 4-n-octyl-4'-cyanobiphenyl (8CB) liquid crystal under the action of an intense magnetic field (5.87 T).

Keywords: liquid crystals, EPR spectroscopy, smectic mesophase, orientational transitions, the magnetic field

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Monitoring the orientational transitions in the smectic A (SA) mesophase is an important problem of the physical chemistry of liquid crystals (LCs). In the present work, we propose a simple approach based on the EPR spin probe method. The Fredericks transition in nematic N mesophase can be easily observed in EPR spectrometer fields with a magnetic induction of <1 T. At the same time, to align the smectic mesophase, a magnetic field with an induction of $\gg 2$ T should be applied. This is because the phase state of the LC determines the critical magnetic field strength H_c of orientational transition. The ratio of the critical field strength H_c for the SA and N mesophases of LCs depends on the sample size d and thickness l of the molecular layer of the smectic: $H_c(\text{SA})/H_c(\text{N}) \sim (d/l)^{1/2}$ [1, 2]. For a diameter of the ampoule with the LC sample of 4 mm and a thickness of the smectic layer close to the length of a pair of LC molecules, $l = 3.5$ nm, the ratio of the H_c values is close to 1000. Therefore, the alignment of the LC director \mathbf{n} in the SA mesophase of LCs occurs only under the influence of an intense magnetic field of the NMR spectrometer [3–5]. If the original texture of a smectic is fixed by pre-cooling in the cavity of an EPR spectrometer, the rotation of the director \mathbf{n} during the orientational transition in the smectic under the action of a 5.87 T NMR cryomagnet field directed along the axis of the ampoule can be easily detected from a change in the EPR spectrum of a spin probe (stable nitroxyl radical R) dissolved in the liquid crystal. As a liquid crystal having both a smectic and a nematic mesophase, we selected 4-n-octyl-4'-cyanobiphenyl (8CB). Note that 8CB samples aligned in a magnetic field have a “memory”—the anisotropy of the orientational ordering of the LC persists after removal of the magnetic

field for an indefinitely long time in the SA and N mesophases.

EXPERIMENTAL

The liquid crystals were placed in standard quartz ampoules of diameter $d \sim 4$ mm. The LC material was 8CB ($T_{SN} = 306$ K, $T_{NI} = 315$ K). The spin probe was 4-phenyl-2,2,6,6-tetramethyl-3,4-hydroxypiperidine 1-oxide (a stable nitroxide radical, R-probe). A portion of spin probe was placed into standard quartz ampoules with a diameter of $d \sim 4$ mm and poured with 8CB heated to the isotropic state. The concentration of R dissolved in the liquid crystal medium was $\sim 3 \times 10^{-3}$ mol/L. The EPR spectra of radicals R in 8CB was recorded on Bruker EMX radiospectrometer at the minimum power of microwave radiation; the temperature of the cavity was maintained to within ± 0.1 K. Initially oriented 8 CB samples were prepared by cooling the nematic from 308 to 295 K in the magnetic field of the EPR spectrometer directed perpendicular to the axis of the ampoule. The alignment of the 8 MC molecules in the SA smectic was carried out in the magnetic field of a Bruker 250 NMR spectrometer directed along the axis of the ampoule at a magnetic induction of 5.87 T.

RESULTS AND DISCUSSION

After cooling the nematic mesophase of 8CB from 308 to 295 K in the cavity of the EPR spectrometer at a magnetic induction of ~ 0.3 T, the texture of the SA-1 mesophase, with the director perpendicular to the axis of the ampoule, is formed. The orientation ordering of the smectic manifests itself as a change in the pattern of the EPR spectrum of R-probe upon the rotation the

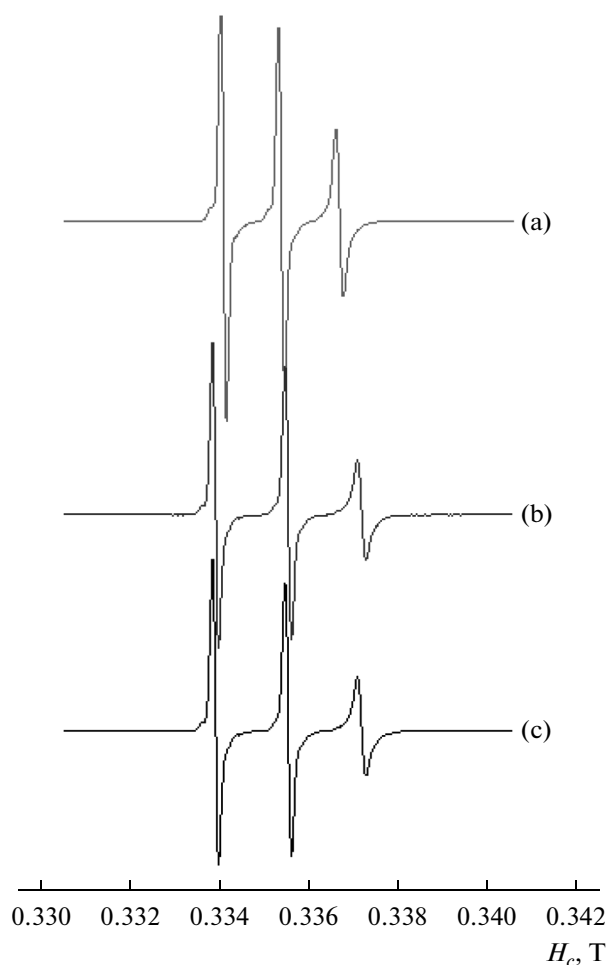


Fig. 1. (a) Spectrum of the R-probe in an ampule with the 8CB smectic prepared by cooling the nematic from 307 to 293 K, (b) after rotation of the ampule in the resonator by 90° , and (c) after treatment in a 5.87 T magnetic field.

ampule with the SA 8CB sample in the cavity. Upon rotation, the effective hyperfine coupling constant increases from $A_{N1} = 1.25$ mT to $A_{N2} = 1.65$ mT (Figs. 1a and 1c). This texture of the smectic persists indefinitely, with an EPR magnetic field below 1 T being insufficient to change it. The orientational transition to the smectic mesophase in an NMR magnetic field of $\gg 2$ T is easily observable, because in this case, the director \mathbf{n} of the LC turns to become parallel to the axis of the ampoule. To observe the orientational transition, the ampoule with the sample SA-1 8CB sample was kept into the cryomagnet of a NMR spectrometer (5.87 T) at 295–298 K ($\ll T_{SN}$) for 15 min. This treatment varies the anisotropic ordering of the smectic: the resulting sample, SA-2, is characterized by a homogeneous alignment of the director \mathbf{n} along the axis of the ampoule in the direction of the NMR field. The pattern of the EPR spectrum of the R probe in the SA-2 sample (Fig. 1c) with an effective HFC constant of $A = 1.65$ mT is independent of the rotation of the

ampoule in the resonator, since the orientation of the LC molecules in the SA-2 8CB sample remains perpendicular to the magnetic field of the EPR spectrometer. In fact, in an intense magnetic field, a single-crystal texture of the 8CB smectic arises. The same structure of the smectic can be obtained by cooling an 8CB nematic sample in a NMR magnetic field or by keeping a disordered smectic in an intense magnetic field. In the latter case, the sample becomes transparent, whereas the EPR spectra of the R-probe are identical in all cases. Structural “memory” retains the anisotropy of the orientational ordering induced by the magnetic field in the N and SA 8CB LC samples; only when heated to the isotropic phase temperature $T > T_{NI} = 315$ K and subjected to subsequent cooling, the N and SA texture of the sample becomes disordered.

Helfrich–Hurault orientational transition in the smectic mesophase of LCs under the action of an intense magnetic field is difficult to observe because it

involves the restructuring of the molecular layers of the smectic. A very large ratio of the critical fields, $H_c(\text{SA})/H_c(\text{N}) \sim (d/l)^{1/2}$ [1–3] leads to the fact that the critical field for smectic LCs of thickness $d = 1$ mm at $l = 2$ nm reaches 5 T. The novelty of the approach lies in the fact that the structural memory of LCs enables to study the nature of the smectic texture arising in the absence of the aligning NMR field by other spectroscopic methods. Such homogeneously orientationally ordered samples of 8CB smectic liquid crystals can be used to study the phase transition in LCs. In the region of SA–N phase transition, the unfreezing of the Fredericks orientational transition in the nematic mesophase should cause the rotation of the LC director in the direction of the magnetic field of the EPR

with a change of the pattern of the EPR spectrum of the spin probe.

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