

Alignment of Nematic Liquid Crystals on Single Crystal Surfaces

E. K. FROLOVA, O. G. SARBAY and A. S. SYBASHVILY

Institute of Physics Academy of Sciences of the Ukrainian SSR, Kiev, USSR

(Received January 7, 1983; in final form July 12, 1983)

It is shown that molecules of a nematic liquid crystal are oriented in the surface plane of single crystal of alkali halide. The symmetry of pattern obtained in parallel light between crossed polarizers reproduces the symmetry of the surface plane. The qualitative interpretation of this phenomenon is presented.

1. INTRODUCTION

It is known that nematic liquid crystals (NLC) are oriented on the planes of cleaved crystal surfaces¹ and well-polished (100) surfaces² of alkali halide crystals. Yet, the phenomenon has not been studied in detail.

This paper aims to study the orientation of NLC on different crystallographic surfaces of alkali halide crystals, to evaluate the NLC-solid surface binding energy and to discuss the model of the specific orientation effect on these substrates.

2. SAMPLES AND EXPERIMENTAL PROCEDURE

4-cyano-4'-pentylbiphenyl (NLC-1) and 4-cyano-4'-pentyloxybiphenyl (NLC-2) were investigated. Molecules of these substances are of the same steric shape and very close in size. These substances are nematic in the temperature ranges from 22 to 35°C and from 48 to 67.5°C, respectively for NLC-1 and NLC-2.^{3,4} Some investigations were per-

formed also with NLC-3, which is nematic between ca. -2 and 55°C . NLC-3 is a five-component mixture, consisting of 4-cyano-4'-pentylbiphenyl, 4-cyano-4'-propanoxybiphenyl, 4-cyano-4'-pentyloxybiphenyl, 4-cyano-4'-heptyloxybiphenyl and 4-cyano-4'-octyloxybiphenyl.

In order to prove that the observed phenomenon could not be attributed to contamination of the NLC, we investigated the orientation of the NLC in a LC-chromatographic cell.⁵ The orientation of both NLC-1 and -2 was planar and homogeneous along the whole length of the cell. As shown in ref. 5 this is a test of the purity of the NLC.

Different planes of alkali halide single crystals were used as substrates. The type of plane was determined with an accuracy better than $10'$ by an X-ray method. The crystals were mechanically polished up to the 14-th grade.

Some investigations were performed with naturally cleaved (100) surfaces of KBr, KCl, KI, NaCl and LiF single crystals.

A thin layer of NLC was obtained by dropping NLC on the substrate. Molecular alignment of the layer was determined by analysing the transmitted or reflected polarized light with the aid of a polarizing microscope or a projector.

NLC-1 and NLC-3 were studied at 25°C and NLC-2 at 55°C .

3. RESULTS

The pattern observed between crossed polarizers in parallel beams for light transmitted through a thin layer (thickness, a few microns; size of pattern about 1–2 cm in diameter) of NLC (NLC-1, NLC-2, NLC-3) on a well-polished (100) surface of the alkali halide crystals is shown in Figure 1. The pattern consists of four uniform sectors separated by narrow boundaries, forming the regular "cross" set at the center of the droplet. The "crosswise" boundaries are found to be along the [001] and [010] crystallographic axes of the substrate. If the crystal with such a pattern is turned around the optical axes between the crossed polarizers, all four sectors are darkened or brightened simultaneously. Complete darkening was observed when the sector boundaries were at a 45° -angle with the transmission direction of the polarizer or analyzer. This means that the molecules in the sectors are aligned in the substrate plane to form a 4-domain structure and the directors of the NLC in the neighbouring domains are normal to each other and set at an angle of 45° with the domain boundaries, i.e. they are oriented along the [011] and $[0\bar{1}1]$ axes of the substrate.

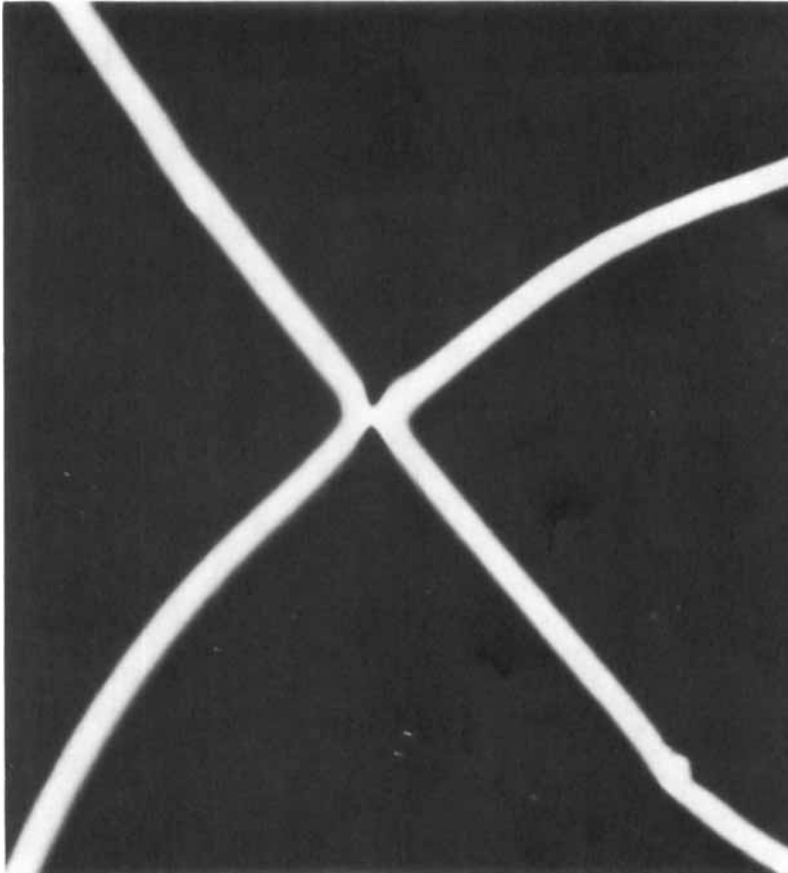


FIGURE 1 Photomicrograph of a thin layer of NLC-1 on the cleaved surface of KCl.

In this case, two different orientations of the directors relative to the domain walls are possible (Figure 2). The real arrangement of directors in the domains should be similar to that in Figure 2a, as follows from the analysis of the polarized light reflected at the Brewster angle from a KBr crystal with 4-domain NLC structure.

If the droplet is squeezed between two alkali halide plates with (100) surfaces, the second plate also shows its own four-sector pattern centered at the point of initial contact of the droplet with the second plate. When the crystallographic axes of both plates do not coincide, an eight-sector structure arises (Figure 3). In this case, as light passes through the NLC layer, rotation of light polarization takes place due to a different arrangement of the directors on the upper and lower

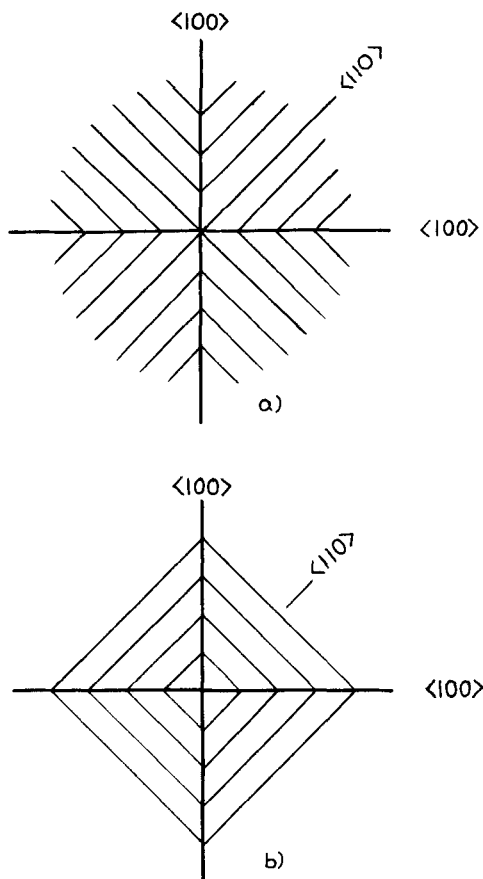


FIGURE 2(a, b) Two possible orientations of NLC molecules.

substrates, the rotation being in opposite directions in neighbouring sectors. This implies that orientation of the directors in subsurface layers is rigidly fixed by the substrates, whereas inside the volume of the layer, the directors turn smoothly from one subsurface orientation to another. If the crystallographic axes of both the plates in this sandwich structure coincide, say by turning one plate, the same pattern appears as that for the thin layer on a single substrate (Figure 1).

Almost planar orientation of the molecules of both NLC, yielding a three-sector pattern with the boundaries crossed in the droplet center approximately at an angle of 120° , was observed in a thin layer of NLC on the $\{111\}$ surface of alkali halide single crystals.

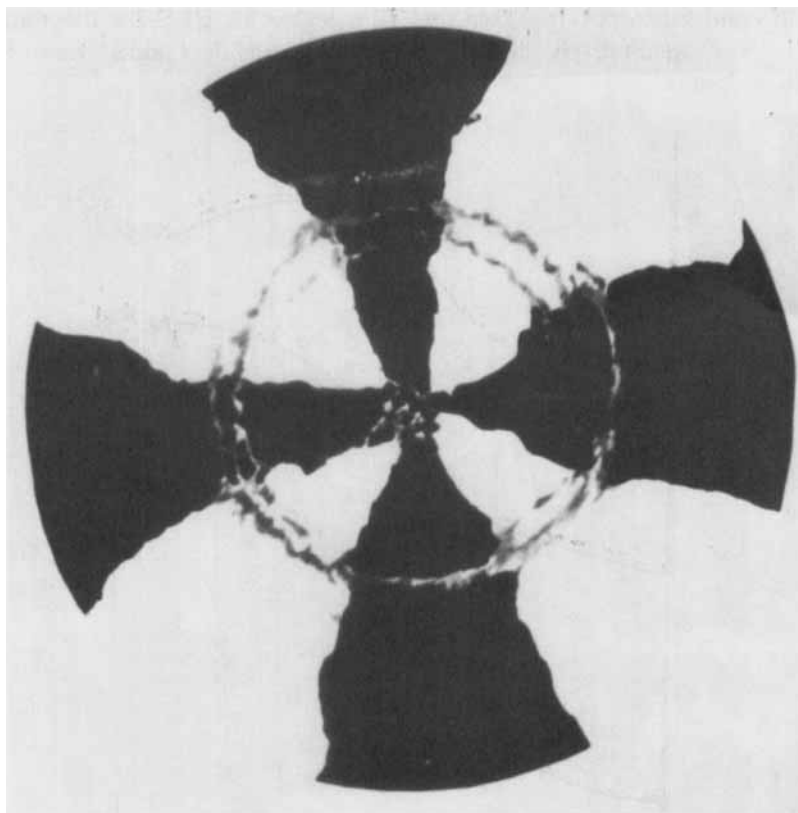


FIGURE 3 Photomicrograph of a thin layer of NLC-3 between two KBr substrates.

All the orientations described above were very stable over the whole range of the NLC phase. The observed regular patterns disappear if the NLC phase is transformed to the solid state or isotropic liquid. However, if the substance was cooled down from a temperature in the region of the isotropic liquid state (the starting temperature) to give the NLC phase, the same patterns appeared again provided the starting temperature of the cooled liquid was not higher than some critical value, which we call the memory temperature T_m . But these patterns were never restored in the case of the opposite transition from solid state to NLC state.

The restoration of the regular pattern in the NLC phase after heating up to the temperature T_m may be used to characterize the orientational interaction of a NLC with a substrate. Apparently, this temperature T_m may be directly related to the energy of NLC-substrate orientational interaction; in Figure 4, T_m is given for the

different substrates. It is seen that T_m is higher for NLC-2 and for all the NLC, qualitatively the behavior of T_m remains the same on varying the substrate.

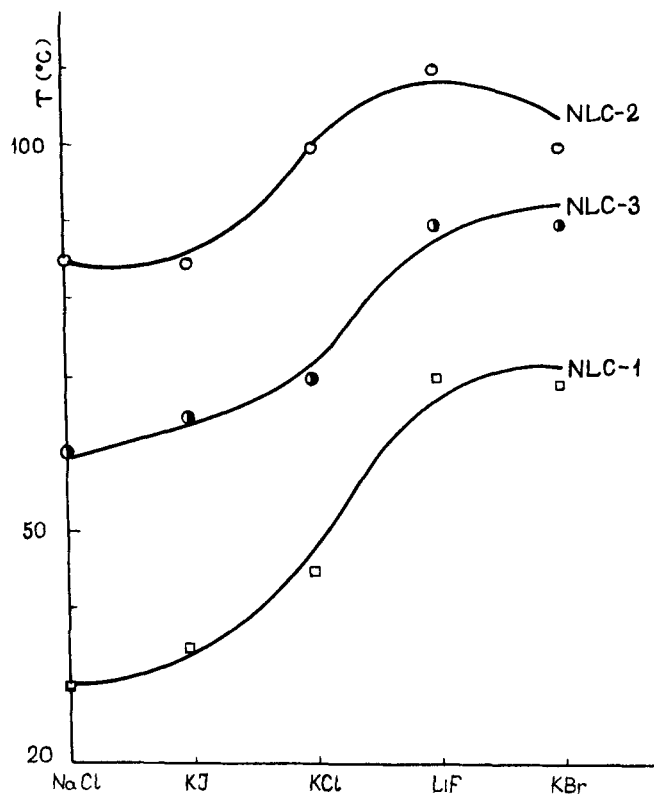


FIGURE 4 T_m for different substrates and liquid crystals.

4. DISCUSSION

Analysis of our data concentrates attention on two main problems: 1) which mechanism underlies formation of the planar orientation of NLC-1 and NLC-2 on alkali halide substrates; 2) what is the nature of the 3- and 4-sector structures of the NLC observed on alkali halide single crystal surfaces.

The orientation of a NLC in the thin layer is evidently defined by the orientation of the first adsorbed layer on the substrate. The interaction of the adsorbed layer with the substrate involves the three

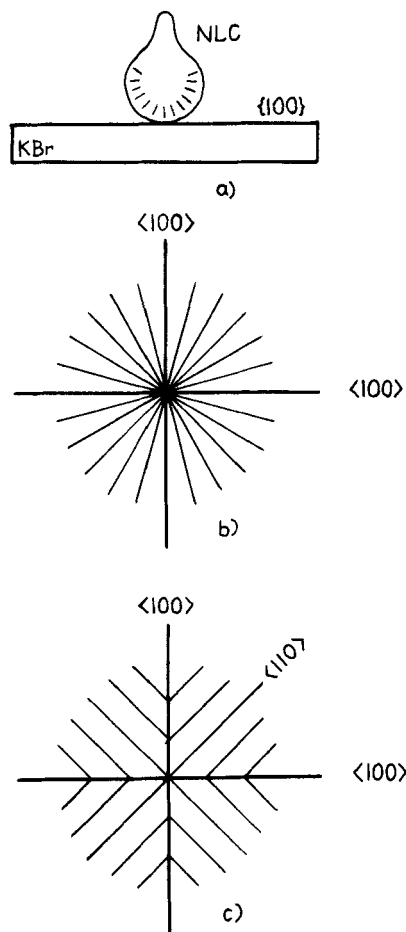


FIGURE 5 The model: (a) molecules are aligned normal to the free surface of the droplet; (b) director field near the surface at the moment of contact of the droplet with the substrate; (c) directors turn to the nearest light orientation axis.

types of force: 1) chemical binding forces providing a strong layer-substrate coupling; 2) van-der-Waals forces causing a relatively weak layer-substrate interaction; 3) electrical image forces.

The whole run of experiments provides evidence for weak binding of the NLC with the substrate, i.e. the layer-substrate interaction cannot be attributed to chemical binding.

But in alkali halide crystals, electrical image forces do not play an essential role. Here orientation must be due to some short-range multiple interaction. The van-der-Waals forces depend mainly on the

general structure of the molecule of the NLC, as well as on the substrate, which are nearly the same, as mentioned above for NLC-1 and NLC-2. Hence, the orientations of NLC-1 and NLC-2 on the surfaces are found to be identical, though in the latter case the orientation is more stable. From this point of view, it becomes clear that the NLC molecules on the (100) surface are oriented along the [011] axis, since in this direction there are alternate rows of identical atoms forming "atomic grooves" on this plane.

The formation of regular orientation patterns may be understood in terms of the following model. As follows from special experiments, the molecules of NLC-1 and NLC-2 are aligned on a free surface of a droplet normal to this surface. If a droplet has a spherical shape, and it touches the surface at some point, the molecules are expected to develop a "fan-shaped" orientation around the point of contact, in the case of their planar arrangement at the surface (Figure 5). When on this surface there are light orientation axes, the molecules will tend to align along the nearest axis. For the (100) surface of alkali halide single crystals, there are four directions of light orientation ([011], [0 $\bar{1}$ 1], [01 $\bar{1}$], [0 $\bar{1}$ $\bar{1}$]) from any point, and when a NLC droplet is set, this surface does show a four-sector pattern. For the (111) plane, there are three directions of light orientation of the $\langle 110 \rangle$ type, and a three-sector structure is observed.

5. CONCLUSION

The reported experimental data demonstrate that the orientation of liquid crystals on single crystal substrates exhibits some interesting features. Therefore it is desirable to extend systematic research to different types of liquid crystal and single crystal surfaces. These investigations may also be of practical interest due to the favourable effect of perfect surfaces on liquid crystal orientation.

Acknowledgment

The authors wish to thank Dr. S. M. Ryabchenko for helpful and encouraging discussions.

References

1. N. A. Tikhomirova and A. V. Guinsberg, in "*Advances in Liquid Crystal Research and Applications*", Pergamon Press, Oxford-Akademiai Kiado, Budapest-1980.

2. A. S. Sybashvily, E. K. Frolova, S. M. Ryabchenko, and O. G. Sarbey, *Proceedings of the Fourth International Liquid Crystal Conference of Socialist Countries*, Tbilisi, USSR (October 1981).
3. B. R. Ratna and R. Shashidhar, *Mol. Cryst. Liq. Cryst.*, **42**, 113 (1977).
4. G. W. Gray, K. J. Harrison, and J. A. Nash, in "*Liquid Crystals and Ordered Fluids*", Vol. 2, Ed. J. F. Johnson and R. S. Porter, Plenum Press, New York (1974), p. 617.
5. M. Ohgawara and T. Uchida, *Jap. J. Appl. Phys.*, **20**, 1, L75 (1981).