Electric-field-induced molecular reorientation of a magnetically biased ferronematic liquid-crystal film

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Electric-field-induced molecular reorientation is studied in the magnetically biased ferronematic liquid-crystal (FNLC) film. A theory derived from the free energy of the system is given. To investigate the field-induced distortion, we have measured the optical birefringence which depends on the integration of the director orientation. In our experiment, the electric-field-induced molecular reorientation of FNLC biased at different magnetic fields has been obtained. The electric-field-induced molecular reorientation of FNLC films biased at fixing magnetic field with different thicknesses has also been measured. Furthermore, hysteresis phenomena have been observed. At higher magnetic field intensities, it seems that the magnetic particles flocculate into large clumps.

I. INTRODUCTION

Investigation of electro-optical and magneto-optical effects in nematic liquid crystals (NLC's) have been reported by many authors. It was observed by Fréedericksz that if a liquid-crystal cell is aligned so that the smallest dielectric constant is parallel to the applied field, there exists a threshold field below which the crystal orientation is unaffected.[1] Above the threshold, the orientation of the director gradually distorts toward the minimum-energy configuration. The threshold and subsequent distortion have been calculated for various possible geometries. If the field is oriented neither parallel nor perpendicular to the director, there no longer exists a threshold field as was shown by Malraison *et al.*[2]

Generally, a few volts is enough for observing the electro-optical effect on NLC; but high magnetic field intensities ($\geq 10^3$ G), required in order to overcome its anistropic diamagnetic susceptibility ($\chi_a \simeq 10^{-7}$ cgs units), are needed to investigate the magneto-optical effect of NLC. Brochard and de Gennes[3] have proposed that χ_a can be increased by uniformly mixing ferromagnetic grains in one liquid crystal. It was observed by Chen and Amer[4] that a ferronematic liquid crystal (FNLC) i.e., a highly disperse magnetic suspension with a NLC as its carrier, is easily oriented by a relatively weak ($H \leq 10$ G) external magnetic field. It is also found that the magnetic grain is coupled to the nematic matrix such that the local magnetization **M** of the sample is perpendicular to the local nematic director **n**. It is obvious that even at a very low concentration of the solid phase the initial magnetic susceptibility of a liquid-crystal suspension is between four and six orders of magnitude higher than the susceptibility of a pure NLC and a FNLC is easily oriented by a relatively weak ($H \leq 10$ G) external magnetic field. Therefore electro-optical and magneto-optical effects of FNLC's, which represent a new variety of liquid-crystal material, are of great interest from the general physics viewpoint, and also in respect of applications.

In this paper, we will deal with the electro-optical behavior of a FNLC which is biased by a low magnetic field. Our previous work[5] showed that there will be no threshold voltage for the Fréedericksz transition, once the FNLC is tuned by an external magnetic field to obtain a pretilt angle. We also showed that the birefringence measurements and theoretical results are in good agreement at the low-field regime. In this paper, a more detailed study of the influence of an electric field on the FNLC with pretilt angle obtained by applying an external magnetic field is presented. To investigate the field-induced molecular reorientation, we measured the optical birefringence, which depends on the integration of the director orientation. A theoretical derivation of the optical birefringence of this system is given in Sec. II. The relation between the optical birefringence and the system parameters, such as the electric field, magnetic field, film thickness, and elastic constants of the FNLC, is obtained. The electric-field-induced molecular reorientation of a FNLC biased at different magnetic fields is demonstrated in our experiment. We also measured the electric-field-induced molecular reorientation of FNLC films biased at a fixed magnetic field but with different thicknesses. Furthermore, hysteresis phenomena will be shown. From experimental results we also find that the magnetic particles flocculate into large clumps at high magnetic field intensities.

II. THEORY

This section describes the theory of the optical birefringence induced by the electric-field-induced molecular reorientation of a FNLC biased by a low magnetic field. In the simplest case of the FNLC's are aligned homeotropically (perpendicular to the electrodes) and the distortion takes places in a single plane. Consider a homeotropically aligned FNLC with thickness D. The geometry is depicted in Fig. 1. The magnetic grain is coupled to the nematic matrix such that the local magne-

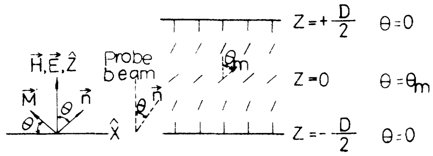

FIG. 1. Molecular geometry.

tization $\mathbf{M}$ of the sample is perpendicular to the local nematic director $\mathbf{n}$. The total free-energy density composed of the elastic, magnetic, electric, and entropy terms is

$$F_d = F_{el} + F_m + F_{dc} + F_S = \tfrac{1}{2}K_{11}(\nabla\cdot\mathbf{n})^2 + \tfrac{1}{2}K_{22}[\mathbf{n}\cdot(\nabla\times\mathbf{n})]^2 + \tfrac{1}{2}K_{33}[\mathbf{n}\times(\nabla\times\mathbf{n})]^2 - \mathbf{M}\cdot\mathbf{H} - \frac{\Delta\epsilon}{8\pi}(\mathbf{E}\cdot\mathbf{n})^2 + \frac{f k_b T}{V}\ln f \ , \tag{1}$$

where the constitutive parameters K_{11}, K_{22}, and K_{33} are known as the splay, twist, and bend elastic constants, respectively; k_b is the Boltzmann constant; f is the filling factor that is the volume fraction of the magnetic grain; V is the volume of the sample; and $\mathbf{H}$ and $\mathbf{E}$ are the magnetic and electric fields, respectively. To find the field-induced molecular reorientation of the FNLC film, we must know the average local orientation of the molecules $\mathbf{n}$. This can be obtained by minimizing the total free energy F_t of this system, $F_t = \int F_d dV$. For $\mathbf{H}=H\mathbf{z}$ and $\mathbf{E}=E\mathbf{z}$, we assume $\mathbf{M}$ and $\mathbf{n}$ lying in the $\mathbf{x}$-$\mathbf{z}$ plane and being a function of z only. If $\theta(z)$ is the angle between $\mathbf{n}$ and $\mathbf{z}$ at z, then $\mathbf{n}=\sin\theta(z)\mathbf{x}+\cos\theta(z)\mathbf{z}$ and $\mathbf{M}=-M\cos\theta(z)\mathbf{x}+M\sin\theta(z)\mathbf{z}$. The free energy per unit area of this system can be written in the following form:

$$F = \int_{-D/2}^{D/2} dz \left[\tfrac{1}{2}K_{33}(1+K\sin^2\theta)\left[\frac{d\theta}{dz}\right]^2 - MH\sin\theta(z) - \frac{\Delta\epsilon}{8\pi}(E\cos\theta)^2 \right] , \tag{2}$$

where $K=(K_{11}-K_{33})/K_{33}$; $M=M_s f$, where M_s is the saturation magnetization of the magnetic grain; and $\Delta\epsilon=\epsilon_{\parallel}-\epsilon_{\perp}$ is the dielectric anisotropy due to the quasistatic electric field.

By minimizing the free energy using the Euler-Lagrange equation, one can readily show that

$$(1+K\sin^2\theta)\left[\frac{d\theta}{dz}\right]^2 + 2A\sin\theta + 2B\sin^2\theta = C \ , \tag{3}$$

where $A=MH/K_{33}$ and $B=-\Delta\epsilon E^2/8\pi K_{33}$. When $z=0$, then $d\theta/dz=0$ and $\theta=\theta_m$, we obtain $C=2(A\sin\theta_m + B\sin^2\theta_m)$, so that

$$\frac{d\theta}{dz} = \pm[1+K\sin^2\theta(z)]^{-1/2} \times\{C-2[A\sin\theta(z)+B\sin^2\theta(z)]\}^{1/2} \ . \tag{4}$$

When we take the boundary condition $\theta(Z=\pm D/2)=0$, then

$$\frac{D}{2}C^{1/2} = \int_0^{\theta_m}(1+K\sin\theta)^{1/2} \times\left[1-\frac{2(A\sin\theta+B\sin^2\theta)}{C}\right]^{-1/2} d\theta \ . \tag{5}$$

To gain a quantitative insight into the physics responsible for the observed orientational distortion, we will derive the dependence of the optical birefringence on the molecular reorientation. The FNLC can be treated as a uniaxial optical material and the average local orientation of the FNLC molecules is the optical axis. For a uniaxial material, the effective index of refraction n_{eff} of the extraordinary ray depends on the angle θ between the optical axis and the direction of light propagation is given by

$$\frac{1}{n_{eff}^2(\theta)} = \frac{\cos^2\theta}{n_0^2} + \frac{\sin^2\theta}{n_e^2} \ ,$$

i.e.,

$$n_{eff}(\theta) = \frac{n_0 n_e}{(n_e^2\cos^2\theta + n_0^2\sin^2\theta)^{1/2}} \ , \tag{6}$$

where n_0 and n_e are, respectively, the ordinary and maximum extraordinary refractive indices of the sample.

The field-induced molecular reorientation of the FNLC can be found by measuring the corresponding induced change in birefringence. It can be shown that the change in phase difference δ is given by

$$\delta = \frac{2\pi}{\lambda}2\int_0^{D/2}(n_{eff}-n_0)dz = \frac{4\pi}{\lambda}\int_0^{D/2}\left[\frac{n_0 n_e}{(n_e^2\cos^2\theta+n_0^2\sin^2\theta)^{1/2}} - n_0\right]dz \ , \tag{7}$$

where λ is the wavelength of the normally incident laser beam used to measure the birefringence change.

In order to obtain an analytic solution, we now limit our attention to the small molecular orientation distortion ($\theta_m \ll 1$). One can readily show that

$$\theta(z) = \theta_0(z)\left[1-\frac{\Delta\epsilon E^2 D^2}{32\pi K_{33}}\right] \ , \quad \theta_m = \frac{MHD^2}{8K_{33}}\left[1-\frac{\Delta\epsilon E^2 D^2}{32\pi K_{33}}\right] \ , \tag{8}$$

where $\theta_0(z)=(MH/8K_{33})(D^2-4z^2)$ is the pretilt angle, and that the phase difference is given by

$$\delta = \frac{\pi}{60\lambda K_{33}^2}(n_e-n_0)D^5M^2H^2\left[1-\frac{\Delta\epsilon E^2 D^2}{32\pi K_{33}}\right]^2 \ . \tag{9}$$

The last equation shows that the phase difference heavily depends on the external electric field, magnetic field, sample thickness of the FNLC, and properties of the FNLC, which include the magnetization of magnetic grains, anisotropic dielectric constant, elastic constant, and refractive indices. It is easily shown that there is no threshold voltage of the Fréedericksz transition, when the FNLC is biased by external magnetic field. It is also shown that the phase difference will be mutually enhanced by external electric and magnetic fields.

III. EXPERIMENTAL METHOD

The NLC used for this work was *N*-(*p*-methoxy)benzylidene-(*p*-butyl)aniline (MBBA). The magnetic particles were γ-Fe_2O_3 needles 0.5 μm long and had an aspect ratio of $\sim$7:1. Their magnetic dipole moment pointed along the long axis of the particle and was 70 emu/g. To prevent clumping, these needles were coated with dimethyl octadecyl aminopropyl trimethorysilyl chloride (DMOAP).[4] The samples were achieved by mixing MBBA and γ-$F_{e2}O_3$ as the suspension. The volume filling factor f was 1.89×10^{-6}. The slide glass substrates were coated first with indium tin oxide (ITO) as transparent electrodes and then with DMOAP to achieve the homeotropic alignment.[6] The sample was sandwiched between two slide glasses with a mylar spacer. The thickness of the sample film was determined by conoscopy.[7] The sample film was inspected very carefully by a crossed-polarized microscope and conoscopy before the optical measurements.

The birefringence measurement setup is shown in Fig. 2. Polarized light at wavelength $\lambda=632.8$ nm from a He-Ne laser was divided into two beams with a beam splitter. The main beam passed successively through the sample, a quarter-wave plate, and a rotating polaroid before reaching the photodetector *A*. The reference beam passed through the chopper which had a frequency of 13.25 Hz, then was detected by photodetector *B*. The homeotropic film was placed horizontally with the unperturbed liquid-crystal director vertically (in the z direction). An external magnetic field was applied vertically by a pair of Hemholtz coils on the FNLC film, then a quasistatic electric field at 1 kHz was applied normal to the glass window of the sample film. The polarization of the probe beam made a 45° angle with the horizontal component of the earth's field which aligned the magnetization **M** of the sample in its direction. The axis of the quarter-wave plate was adjusted to be along the laser polarization direction. It was shown by Lim and Ho[8] that the phase difference δ of the extraordinary ray and the ordinary ray of the probe beam after passing through the sample was equal to the relative phase difference of the sinusoidal time-dependent wave from the probe beam and square wave from the reference beam which were detected by the detectors *A* and *B*, respectively. The relative phase between these two beams was measured with a sensitive phasemeter and was digitally displayed or logged. A microcomputer auto-control system was used to change the electric field and to record the phase difference.

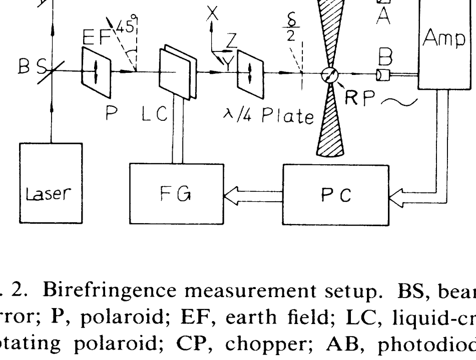

FIG. 2. Birefringence measurement setup. BS, beam splitter; M, mirror; P, polaroid; EF, earth field; LC, liquid-crystal cell; RP, rotating polaroid; CP, chopper; AB, photodiodes; Amp, lock in amplifier; PC, Apple II; FG, function generator.

IV. RESULTS AND DISCUSSION

To obtain a quantitative insight into the physics responsible for the observed orientational distortion, we studied the dependence of the optical birefringence on the strength of the applied electric voltages, pretilt angles induced by external magnetic field, and the thickness of the FNLC films. To compare with the prediction of Eq. (9), we plot the square root of the phase difference versus the square of the voltage as shown in Fig. 3. After least-squares fitting, all six samples with different pretilt angles show linear the relation $\delta^{1/2}=\delta_0^{1/2}[1-(\Delta\epsilon V^2/32\pi K_{33})]$, where δ_0 is the phase difference with zero voltage. One can get the effective elastic constant K_{33} for each sample from the slope of these straight lines. It is obvious that the larger the pretilt angle the smaller the effective elastic constant.

The results of birefringence measurements for various magnetic-field-induced pretilt angles are shown in Figs. 4

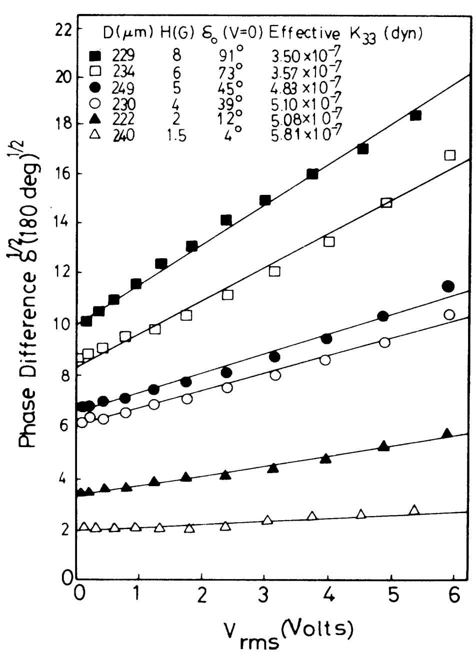

FIG. 3. Phase-difference dependence on voltage, $\delta^{1/2}\propto V^2$, as predicted by Eq. (9).

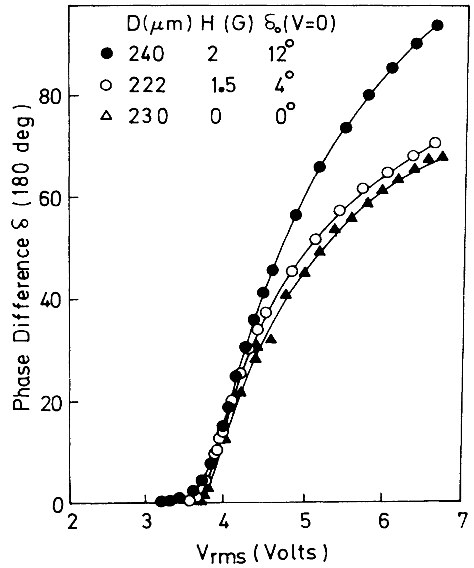

FIG. 4. Phase difference vs voltage for the sample with low various magnetic-field-induced pretilt angles.

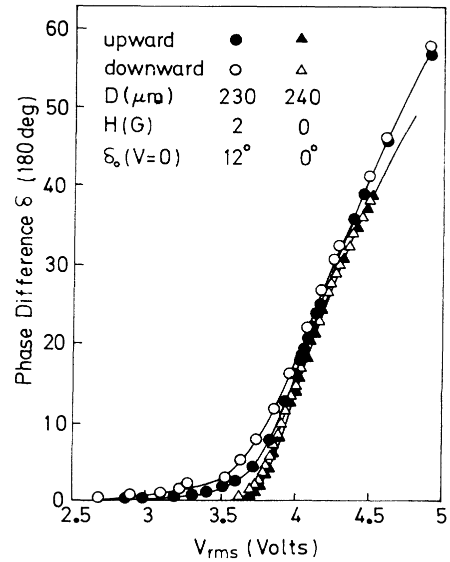

FIG. 6. Hysteresis of FNLC.

and 5. Figure 4 shows the phase difference as a function of E for the sample with small pretilt angles. It is observed that there is a threshold voltage of the Fréedericksz transition for the FNLC cell without pretilt angle; but there is no threshold voltage once the FNLC is tuned by an external magnetic field to obtain a pretilt angle. Obviously, the larger the pretilt angle, the larger the phase-difference increase is when the voltage increases. In other words, the enhancement of the electric-field-induced molecular reorientation of the FNLC by the magnetic field is significant. These results are familiar, as predicted by Eq. (9), such that the measured phase difference δ is proportional to the strong coupling of electric and magnetic fields. For samples having larger pretilt angles, the curves of phase difference versus external voltage shown in Fig. 5 show crossing behavior. The phase difference increases with pretilt angle below 4 v, but it decreases with pretilt angle when the voltage is greater than 4.5 v. This phenomenon occurs because the magnetic particles clump into aggregates. A possible explanation is that the larger the magnetic field (to induce a larger pretilt angle), the easier the clumping into aggregates. Thus the effective magnetization M will decrease, so that the phase difference decreases. This could be

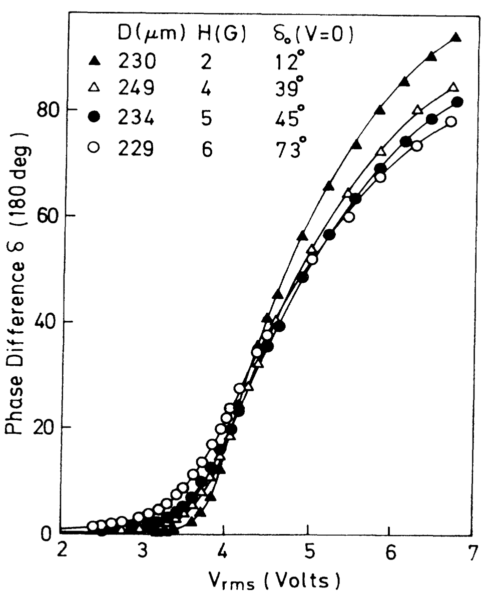

FIG. 5. Phase difference vs voltage for the sample with various high magnetic-field-induced pretilt angles.

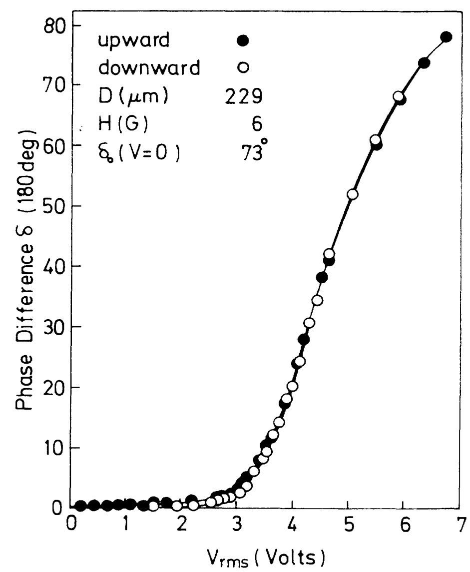

FIG. 7. Hysteresis of FNLC at larger pretilt angles.

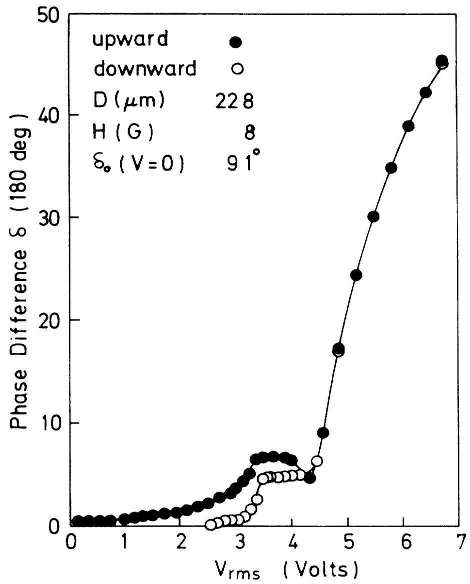

FIG. 8. A flat region appears in the hysteresis curves of the FNLC.

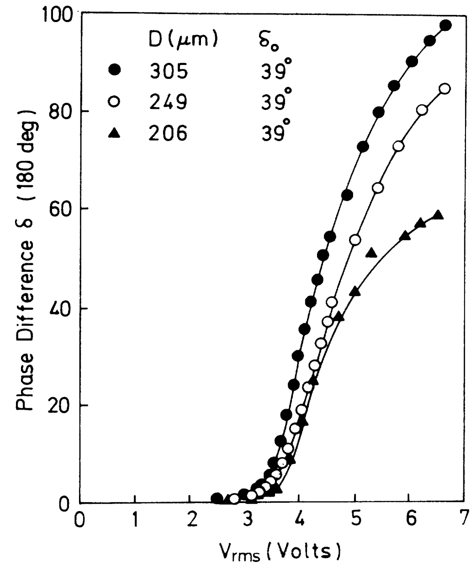

FIG. 10. Dependence of the field-induced birefringence on the thickness of the FNLC films.

confirmed by hysteresis experiments.

Figure 6 shows a comparison of the FNLC without pretilt angle and with pretilt angle induced by the magnetic field, when the external electric field is gradually increased from 0 to 7 v and then reversed. It is easily seen that for the sample without pretilt angle, hysteresis is not distinguished; but for the sample with pretilt angle, hysteresis occurs. However, when the pretilt angle is gradually increased, the curves mutually cross as shown in Fig. 7. The crossing phenomenon could be explained if the magnetic grains partially clump into aggregates, which will decrease the effective magnetization M, a similar result as discussed previously. Figure 8 shows that as the magnetic field applied to a FNLC increases further, there is a flat region, i.e., the phase difference does not change with external voltage. The reason for this flat region is not understood clearly and needs further study. For the sample with very large pretilt angle, the phase difference will saturate at high field fixed as shown in Fig. 9. In other words, the optical birefringence will be maintained at a fixed level independent of the applied electric field.

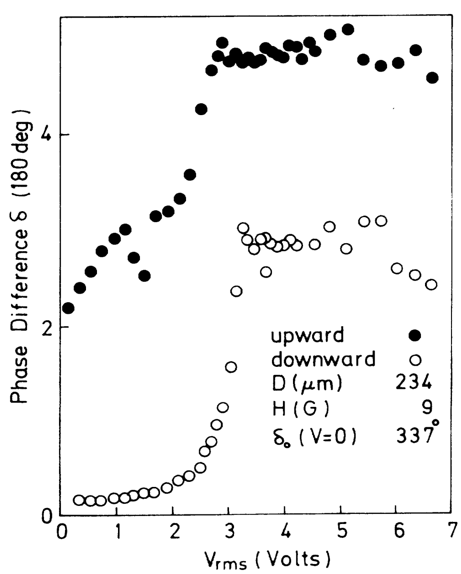

FIG. 9. Hysteresis of FNLC at the saturation region.

The influence of the thickness of FNLC film is shown in Fig. 10. The thicker the FNLC film, the larger the change of phase difference. This is in agreement with our theoretical prediction. It is generaly true that the cell thickness has great influence on the field-induced molecular reorientation of a FNLC.

V. CONCLUSION

Electro-optical effects on liquid crystals have played an important role for the application of liquid crystal display (LCD). The technology of the pretilt angle of a NLC film is very important in LCD's. Changing the pretilt angle can improve the response time of a NLC. In general, a short response time can be reached by surface treatment which will induce a large pretilt angle and by fixing the pretilt angle of the NLC. In this paper, the FNLC is investigated; a small and changeable pretilt angle can appear by applying a low magnetic field to the FNLC. It is actually seen that there is no threshold voltage of the Fréedericksz transition for a FNLC biased by an external magnetic field. We also deal with the electro-optical effect of a FNLC biased by an external low magnetic field. The coupling effect of magnetic field and electric field has been also studied. The magnetic field can enhance the electro-optical effect of a FNLC.

Theoretically, we have derived the electric-field-induced molecular reorientation of a FNLC biased by magnetic field and the optical birefringence which depends on the electric-field-induced molecular reorientation of a FNLC. We have also obtained the relationship between the optical birefringence and the electric-field-induced molecular reorientation of a NLC under the small-angle approximation. From theory, one can easily see the mutual enhancement of the optical birefringence between the external electric field and magnetic field.

Experimentally, we have shown that the variable pretilt angle of a FNLC film can be achieved by a weak magnetic field. No threshold voltage exists for such a pretilt sample. Our quantitative measurement shows that in the low-field regime the square root of the phase retardation varies linearly with the square of the applied voltage. We have also observed the electric-field-induced molecular reorientation of a FNLC biased at difference magnetic field at same thickness and biased at fixing magnetic field at different thickness. These results agree with our theoretical prediction. Furthermore, hysteresis phenomena have been observed too.

From experimental results we know that the magnetic grains clump into aggregates. Clumping grains are very complex and are not easily controlled, so that it needs a more detailed analysis. If the magnetic particles do not clump into aggregates, the pretilt angle can be tuned higher by the external magnetic field.

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