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Chiral order in uniform nematics: A third-rank pseudotensor associated with the linear electroclinic effect

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Abstract

Using the traditional uniaxial orientational order a third-rank pseudotensor of three independent elements has been found which distinguishes between chiral and nematic order. The linear electroclinic [EC] effect observed recently in a chiral nematic liquid crystal is explained to be the natural linear one, Pockel's effect, associated with the chiral order tensor. The theoretical results are generalized tentatively to discuss the EC effect in smectics. Based on the feature of nonlinear susceptibility the ratio of tilt angle to field intensity is estimated and the result agrees with experiment.

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Since the prediction of the EC effect by Garoff and Meyer,[1] considerable experimental and theoretical studies have been carried out in probing the origin of the spontaneous polarization, the critical behavior near the smectic-A [S_A] to smectic-C* transition[2], the polar interaction with solid substrate[3], and the relation with molecular conformation distributions[4]. Electro-optic devices based on the effect have been proposed.[5] In all previous cases, smectic symmetry has been required; however, a recent experimental result[6] indicates that the same EC effect can occur in nematics. This presents a challenge to theory, to understand the phenomenon.

The basic theory[6] for the EC effect notes that an electric field (which is a polar vector) applied perpendicularly to a special axis (unique to a chiral sample), will couple linearly to any pseudovector (which can be present in chiral symmetry) with the same direction, giving rise to molecular rotation about the field. In smectics both the layer normal and the optic axis can naturally provide the pseudovector. On the other hand, since nematics are described by one direction only,[7] *i.e.*, the director n, it is difficult to follow the same argument as in smectics. To overcome this difficulty a new order parameter which describes the orientation of another molecular axis different from the usual one must be introduced.[6] However, the treatment has obviously been outside the scope of the uniaxial-nematic theory, and the constituent molecules of nematic liquid crystal [NLC] are not generally characterized by biaxial symmetry. Major fundamental questions are whether the EC effect might still be described by a uniaxial theory, and how to introduce an order

parameter to describe the chiral characteristics of chiral NLC. In this Letter we show that it is not necessary to break the uniaxial symmetry to explain the EC effect, provided that special attention is paid to the chiral properties.

A NLC is traditionally characterized by a second rank tensorial order parameter $Q_{ij} = S(n_i n_j - \frac{1}{3}\delta_{ij})$, where S is the average of $P_2(\cos\theta)$, P_2 is the second-order Legendre polynomial and θ the angle between $\mathbf{n}$ and the molecular orientation direction. In thermal equilibrium and in uniform textures of NLC with uniform S and $\mathbf{n}$, the order parameter does not distinguished centrosymmetric ($D_{\infty h}$) from noncentrosymmetric (D_∞) ordering. In spite of the pioneering works for cholesterics such as the elastic theory established by Oseen and Zocher[8] and a pseudo-order introduced by de Gennes,[9] there is still no method to recognize chiral ordering in uniform NLC. The reason for this is that de Gennes's pseudo-order and the continuum theory of cholesterics are closely related to a helical deformation of the textures. In other words the order vanishes in uniform case of NLC.

In this paper, we give the first complete analysis of the chiral order associated with a third-rank pseudotensor of three independent elements in a uniform NLC. As an application we show how the EC effect in NLC is connected with the order tensor: it is a new case of a common linear electro-optic effect well known as Pockel's effect in crystals. Based on this unified picture of nonlinear susceptibility we generalize the theory to discuss the EC effect in smectics and are able to estimate the ratio of tilt angle to field intensity, in good agreement with experiment. This may be seen as important progress,

since the symmetry arguments[1] for the existence of EC effect give no prediction for the magnitude of the resultant tilt angle with an electric field.

We start by examining the relationship between macroscopic and microscopic order parameters. The microscopic order parameters can be revealed by the susceptibility of a single molecule in response to an external field, which is generally described by a tensor γ and closely related to the molecular symmetry. To find the corresponding macroscopic susceptibility we first rotate γ by an arbitrary rotation $R(\phi,\ \theta,\ \psi)$, where ϕ, θ, and ψ are the Euler angles of the rotation, then perform a statistical average. In a uniaxial NLC, the angles ϕ and ψ are assumed to be isotropically distributed (this is specially addressed in our present theory and differs from other models of EC effect), so averages over them can be carried out explicitly, and averages over θ give the orientational order parameters. From the general formalism for the rotation of tensor[10] it is found that the lowest-rank tensor which can recognize the chiral order of NLC is the following third-rank pseudotensor (with summation convention),

$$CH_{ijk} = A_1\varepsilon_{ijl}n_l n_k + A_2\varepsilon_{ilk}n_l n_j + A_3\varepsilon_{ljk}n_i n_l \ , \qquad (1)$$

where ε_{ijk} is the Levi-Cevita antisymmetric tensor of the third rank and the A's are three independent parameters which combine the order parameter S and the microscopic susceptibilities γ_{ijk}

$$A_1 = (\frac{1-S}{6})N[\gamma_{312} - \gamma_{321} + \gamma_{231} - \gamma_{132}] + (\frac{1+2S}{6})N[\gamma_{123} - \gamma_{213}] \ ,$$

$$A_2 = (\frac{1-S}{6})N[\gamma_{312} - \gamma_{321} + \gamma_{123} - \gamma_{213}] + (\frac{1+2S}{6})N[\gamma_{231} - \gamma_{132}] \ , \quad (2)$$
$$A_3 = (\frac{1-S}{6})N[\gamma_{231} - \gamma_{132} + \gamma_{123} - \gamma_{213}] + (\frac{1+2S}{6})N[\gamma_{312} - \gamma_{321}] \ ,$$

where axis 3 refers to the molecular long axis and N is the number density of the molecules. The nonvanishing γ_{ijk} $(i \neq j \neq k, \quad i \neq k)$ are entirely defined in terms of the molecular symmetry, so measurements on CH_{ijk} give us certain information on the molecules. For instance, from Eq.(2) one can find that the tensor CH vanishes if the constituent molecules have a mirror symmetry perpendicular to the long molecular axis, and does not disappear in the isotropic phase, *i.e.*, $S = 0$. The latter case is manifested in the optical activities of cholesteric liquid crystals in their isotropic phases.[11] The tensor CH with $S = 0$ can serve to describe the so-called optically active liquids.[12] Another example which should be mentioned is that for a molecular symmetry of $\bar{4}$ tetragonal class the tensor CH again disappears because the relations, $\gamma_{123} = \gamma_{213}$, $\gamma_{132} = \gamma_{231}$, and $\gamma_{312} = \gamma_{321}$, hold for the symmetry. It is also clear that the tensor CH will vanish unless the molecule is chiral, which eliminates any substances (such as MBBA) having mirror plane. Moreover, one can prove that the symmetry of CH is D_∞, so we are left with the tensor as our only choice to distinguish chiral order from normal nematic order which has $D_{\infty h}$ symmetry. In other words to recognize whether a uniform NLC has chiral order or not one must examine the effects connected with susceptibilities which are described by a third-rank tensor. In the following we shall show that the EC effect is such a case.

When a dc electric field $\mathbf{E}$ is applied to a crystal, the dielectric tensor $\mathbf{e}^{(0)}$ is

modified, and it may be assumed in the first approximation that the change of the tensor is linearly related to $\mathbf{E}$, *i.e.*, in tensor notation the dielectric tensor becomes

$$e_{ij} = e_{ij}^{(0)} + e_{ijk}^{(1)} E_k \equiv e_{ij}^{(0)} + \Delta e_{ij} \ . \quad (3)$$

This also changes the optical anisotropic properties, giving the linear electro-optic effect first noted by Pockel. The third-rank tensor $\mathbf{e}^{(1)}$ is the susceptibility for the effect. Because of the existence of the third-rank tensor shown in Eq.(1) the same effect must be present in chiral NLC. Considering that the dielectric tensor must be symmetric (here we neglect for the moment the discussion on the optical activity),[13] we take the unique form of $\mathbf{e}^{(1)}$ in terms of the chiral order tensor as

$$e_{ijk}^{(1)} = CH_{ijk} + CH_{jik} = (A_2 - A_3)(\varepsilon_{ilk} n_l n_j - \varepsilon_{jlk} n_l n_i) \ . \quad (4)$$

Then we can rewrite Eq.(4) from Eqs.(1) and (2) as

$$e_{ijk}^{(1)} = \frac{1}{2} SN(\gamma_{231} + \gamma_{321} - \gamma_{312} - \gamma_{132})(\varepsilon_{ilk} n_l n_j - \varepsilon_{jlk} n_l n_i) \ . \quad (5)$$

Physically this means that the linear electro-optic effect vanishes in the isotropic phase, and is quite different from the optical activity. From Eqs. (3) and (4) one finds a simple form for the change of the dielectric tensor

$$\Delta e_{ij} = (A_2 - A_3)[(\mathbf{n} \times \mathbf{E})_i n_j + n_i (\mathbf{n} \times \mathbf{E})_j] \ . \quad (6)$$

We can now give a discussion of the EC effect in NLC. The geometry of the sample is assumed to be same as in Ref. 6 and shown in Fig. 1. The applied dc field **E** is perpendicular to the sample along the x direction and the director **n** is along the z axis. Since the dielectric anisotropy $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$ has been assumed to be negative, no Freedericksz transition occurs, and the electric field induced effect is the modification of the dielectric tensor given by Eq. (6) as

$$\Delta e_{yz} = \Delta e_{zy} = (A_2 - A_3)E \ , \tag{7}$$

and other components are zero. In matrix notation the dielectric tensor now changes into

$$\mathbf{e} = \begin{pmatrix} \varepsilon_{\perp}\,, & 0\,, & 0 \\ 0\,, & \varepsilon_{\perp}\,, & (A_2 - A_3)E \\ 0\,, & (A_2 - A_3)E\,, & \varepsilon_{\parallel} \end{pmatrix} \tag{8}$$

This means that the **E** field induces a biaxial property of the optical dielectric permittivity although the molecular orientational order is uniaxial. The symmetric matrix can be rediagonalized into diagonal form. Here we omit giving the detailed derivation[10] and put forward the result that the new diagonal axis of matrix (Eq. (8)) is still in y-z plane but rotated by an angle θ about the x axis, where θ satisfies the exact equation:

$$\frac{1}{2}\tan 2\theta = (A_2 - A_3)E/\Delta\varepsilon \ . \tag{9}$$

Physically the main direction of **e** is also that of the optical axis. So the same tilt θ of the optic axis in the y-z plane proportional to the applied field should be observed. In other words, the EC effect is a natural result of the chiral order coupling with the electric field. Experimentally[6] the range of the observed θ is in the order of 10^{-4}; therefore Eq. (9) may be simplified to $\theta = (A_2 - A_3)E/\Delta\varepsilon$, a linear relation between θ and E. From the physical view point, however, the linear relation of $\theta \propto E$ is conceptually incorrect. As shown in Eq. (9) the maximum magnitude of the tilt θ is $\pi/4$ only, and the sign (at fixed direction of E) depends on that of $(A_2 - A_3)$, *i.e.*, the handedness of the chirality of the material (see Eq. (5)). Therefore, rigorously stated, the relationship between θ and E is nonlinear and should saturate for sufficiently large field. This picture comes from our basic assumption that the EC effect is not due to the molecular rotation but the nonlinear susceptibilities of the molecules. To support this feature we need furthermore experimental study.

Up to now all the experiments have been performed with an ac applied field to overcome the electrohydrodynamic effects by dc field and there is no direct comparison between the present theory and experiment, nevertheless, in the remainder of the paper we give a simple discussion of the behavior of the dc EC effect near the S_A-to-nematic transition. As shown in Eq. (9) $d\theta/dE$ is characteristic by $(A_2 - A_3)/\Delta\varepsilon$. Since $(A_2 - A_3) \propto S$ (see Eq. (5)) and $\Delta\varepsilon$ in the nematic phase is closely related to S, the variation of $d\theta/dE$ with temperature should be small. This seems to be born out by the experiment (see Fig. 2 of Ref. 6). In principle, since the S_A phase has the same uniaxial ordering as

nematics, this theory may be generalized to analyze the critical behavior at the S_A-N transition. The transition from the low ordered nematic state into the layered structure of the S_A phase is characterized by a decrease in the fluctuation of the molecules. Therefore strong changes of the order parameter S cannot be expected. On the other hand, the layer structure will increase the stronger dipole-dipole interactions of short range at N $\rightarrow$ S_A transition, and result in a more crystalline behavior in S_A phase. Therefore $d\theta/dE$, *i.e.*, $(A_2 - A_3)/\Delta\varepsilon$ is suitable for the discussion with crystal model. As the starting point of the present theory of EC effect shown in Eq. (3), the $(A_2 - A_3)$ is referred to the second susceptibility $\chi^{(2)}$, and $(\varepsilon_\parallel - 1)/4\pi$ and $(\varepsilon_\perp - 1)/4\pi$ are referred to the first ones $\chi^{(1)}$. With commonly accepted estimate of $\chi^{(2)} \sim 10^{-6}$ *esu* in nonlinear optics and $\Delta\varepsilon \sim 1$ one can obtain the order of $d\theta/dE$ to be $10^{-9} \sim 10^{-10}$ m/V which is in agreement with experiment.[2,6] Moreover, the nonlinear optics of crystals, known as Miller's rule,[14] states that the ratio of $(\chi^{(2)}_{123}/\chi^{(1)}_{11}\chi^{(1)}_{22}\chi^{(1)}_{33})$ is almost a constant, giving the empirical relation $(A_2 - A_3)/\Delta\varepsilon \sim k(\varepsilon_\perp - 1)(\varepsilon_\parallel - 1)$ where k is a constant. This suggests that the behavior of $d\theta/dE$ is the same as that of $\varepsilon_\perp$ or $\varepsilon_\parallel$. Fortunately, the prediction is surprisingly confirmed by a recent experimental observation by Bahr and Heppke,[2] who found a very similar behavior of the temperature dependences of $d\theta/dE$ and $\varepsilon_\perp$ in smectic phases. Both quantitative and qualitative agreement with the nonlinear susceptibility of crystals supports the evidence for the present assumption that the EC effect is due to the nonlinear susceptibility of the molecules, rather than to their rotation. From the above discussion one

has found that the EC effect can reveal the chiral order, *i.e.*, the difference of A_2 and A_3. The EC effect is inadequate to determine all three independent chiral anisotropy parameters, A_1, A_2, and A_3. Here we only predict tentatively that the measurement of the anisotropic optical activities in any three different directions of the sample may be suitable for the purpose. Of course it is necessary to consider other contributions of EC effect, such as a pretransitional effect corresponding to the local existence of layers even in nematics and a possible statistical bias between "right" and "left" tilt with an electric field in a chiral uniaxial medium. At present these are still a difficult task both for theory and experiment. Here we should also point out that how to define the third susceptibilities for the chiral property is still not apparent. There needs a fundamental theory that can sufficiently show the relationship between the phenomenological constants (A_1, A_2, A_3) and the origin of the pitch of the unconstrained chiral nematic. It is also possible that the phenomenological parameters A_1, A_2, and A_3 may relate to a second order parameter which describes the tendency for the molecules to align a secondary axis along the director whenever (owing to a thermal fluctuation) the primary axis is not so aligned. In this meaning the present theory is an approximate one (up to "zero-order") for the generalized theory to include the second order parameter.

In conclusion, we have found a third-rank pseudotensor of three independent elements which distinguishes chiral order from the usual nematic order. The order tensor is required to describe the general properties of nematic and smectic phases containing chiral molecules. In particular, we have shown that

the electroclinic effect occurring in both nematic and smectic liquid crystals may be a natural result of the linear electro-optical effect, known as Pockel's effect, associated with the new order tensor. Thus the tilt of the optical axis caused by the field is not due to molecular rotation, but rather due to the molecular nonlinear susceptibility of the chiral symmetry of NLC. The behavior of this effect near the S_A-N transition can be well explained by this hypothesis. We believe there will be many opportunities to generalize the chiral order tensor to restudy problems formerly dealt with by de Gennes's model, which predicted only two forms of molecular orientation, parallel and perpendicular to the long axis. In our future publication[10] we will give some other interesting examples. Here we only point out that one should supplement the EC susceptibilities $A_2 - A_3$ (see Eq.(4)) besides providing normal dielectric anisotropy $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$ to give a complete information on a NLC of chiral ordering. This is significant for LC manufacture.

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References

[1] S. Garoff and R. B. Meyer, Phys. Rev. Lett. **38**, 848(1977); Phys. Rev. A**19**, 338(1979).

[2] R. Qiu, J. T. Ho, and S. K. Hark, Phys. Rev. A**38**, 1653(1988); C. Bahr and G. Heppke, Phys. Rev. A**37**, 3179(1988); J. Xue and N. A. Clark, Phys. Rev. Lett. **64**, 307(1990).

[3] J. Xue and N. A. Clark, Phys. Rev. Lett. **64**, 307(1990).

[4] S. Lee and J. S. Patel, Phys. Rev. Lett. **66**, 1449(1991).

[5] G. Andersson, et al., Appl. Phys. Lett. **51**, 640(1987); K. Nakagawa, et al., Ferroelectronics **85**, 39(1988).

[6] Z. Li, R. G. Petschek, and C. Rosenblatt, Phys. Rev. Lett. **62**, 796(1989).

[7] P. G. de Gennes, *The Physics of Liquid Crystals* (Oxford University, London, 1974).

[8] C. W. Oseen, Trans. Faraday Soc. **29**, 883(1933); H. Zocher, *ibit*

[9] P. G. de Gennes, Mol. Cryst. Liq. Cryst. **12**, 193(1971).

[10] A. Sugimura and Ou-Yang Zhong-can, The detailed derivation on the theoretical results will be submitted elsewhere. In this study we also discuss some other interesting effects associated with the present chiral order.

[11] H. de Vries, Acta. Cryst. **4**, 219(1951).

[12] J. A. Giordmaine, Phys. Rev. **138A**, 1599(1965).

[13] For example, see M. Born and E. Wolf, *Princeples of Optics* (Pergamon, Oxford, 1975).

[14] R. C. Miller, Appl. Phys. Lett. **5**, 17(1964)..

Figure Caption

Figure 1. Schematic representation of sample cell. The director n is assumed to be parallel to z axis. The directions along z and z' axis in $y - z$ plane represent the principal axis of the dielectric tensor without and with applied field **E** (along x axis), respectively.

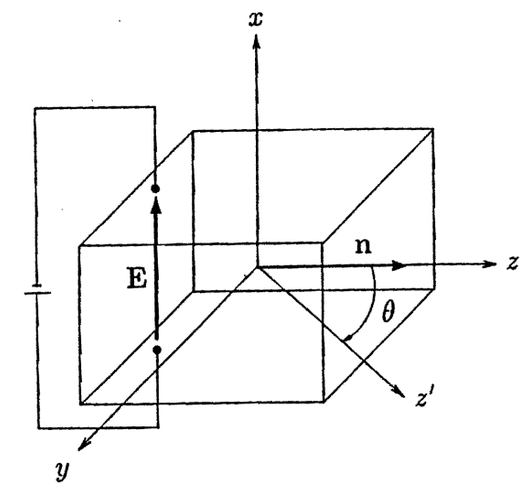

Figure 1