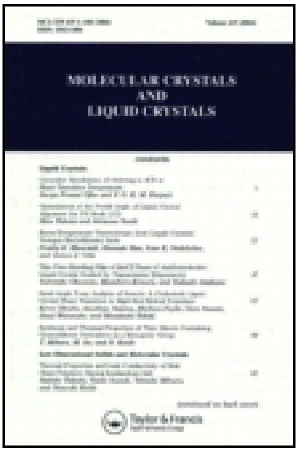

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Mesophase Structures Related to Modulated Distributions of Defects and Impurities

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MESOPHASE STRUCTURES RELATED TO MODULATED DISTRIBUTIONS OF DEFECTS AND IMPURITIES

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Abstract The effects of distributions of dislocations, disclinations and charge admixtures on the structural transformations in thin LC films are discussed in the framework of the phenomenological approach. The quasiequilibrium spatial modulation of polarization in the ferroelectric LC after or under the external field actions is described as the result of modulated distributions of free charges and disclinations. The electrostatically induced growth of spiral domains in Langmuir monolayers at the air-water interface is described as the result of modulated distributions of the tilt angle and free charges in the chiral polarized thin film. The chiral smectic A* phase is described as the periodic distribution of dislocation walls and disclination loops in the layered system.

Keywords: mesophase, ferroelectric, modulated distributions, disclimations, spiral domains, dislocations

INTRODUCTION

The experimental data and theoretical considerations point to essential role of surface treatments, boundary conditions, defects, impurities and admixtures for structural transformations and physical properties of thin molecular films. At the determinate conditions defects and impurities are not distributed chaotically in such films, but instead

they must be parts of macrostructures. Thus modulated distributions of defects and impurities (admixtures) can arise inevitably under the actions of external fields, temperature changes etc. The present paper shows examples of such macroscopical structures which can be thermodynamically equilibrium or quasiequilibrium. The paper suggests models for observable quasiequilibrium large-scale modulations of the strong spontaneous polarization in ferroelectric liquid crystals,[1] for observable two-dimensional spiral textures in Langmuir monolayers containing polar molecules, chiral admixtures and charge impurities,[2] for observable one-dimensional spiral structures in chiral smectics A*.[3]

Large-scale modulations in ferroelectric LC are characterized by unusual temperature and field dependencies of the spatial period which strongly differ from the equilibrium pitch behavior and can not be explained in the framework of traditional approach. The experiments[1] show the important role of free charges and, probably, disclinations in these modulations. The present paper exploits the idea that bonding of free charges on disclinations is a reason for stabilization of such modulations. The spiral textures in Langmuir monolayers[2] are characterized by some threshold conditions and, probably, phase separations. The present consideration makes the attempt to take into account the mentioned material properties to describe the threshold behavior and phase states of such textures. The chiral smectic A* is the phase of great interest and it was predicted[4] that some distributions of dislocations can be responsible for this phase state. The present paper considers the model with the classical dislocation term for the interface energy in the approximation of continuous distribution of dislocations. This model describes the first and second order phase transitions between ordinary smectic A, chiral smectic A* and cholesteric phases, the corresponding temperature dependence of pitch being calculated.

LARGE-SCALE MODULATION OF POLARIZATION IN FLC

The paper[1] reported about observations of the periodic domain structure in ferroelectric liquid crystals with the period which is much larger than the period of thermodynamically equilibrium helicoidal structure in such materials. The authors[1] noted the essential role of free electric charges screening the large spontaneous polarization. Such a structure is nonequilibrium in general: it appears after or during the action of external electric field and transforms to ordinary equilibrium helix with small pitch after switching off the field. Therefore the explanations of observed phenomena in the framework of the model of proper ferroelectricity[1] meet difficulties.

Another model can be suggested for discussion of these phenomena if one takes into account the presence of free electric charges in such liquid-crystalline ferroelectrics with sufficiently strong spontaneous polarization. The strong external field E untwists the polarization helix with the initial pitch h_o and causes the emergence of excess of ions with different signs at the opposite boundaries of a sample. The basic idea of the model goes as follows . After switching off the external field free charges start to bleed under the action of the field E' due to the surface charge density and the process of recovery of the initial helix starts also. Due to the surface conditions and topological reasons the disclinational loops appear inevitably at the same time with orientational walls of helix during the transient process. Initially on the relaxation start the quantity of such loops is small since their formation demands energy expenditure, correspondingly the transient pitch of helix h can be larger than h_o. In this case flowing of free charges can play the essential role for the stabilization of such a helix which is nonequilibrium. This stabilization is conditioned by the following reason: there is an inhomogeneity of the macroscopic polarization $\vec{P}$ around the disclination core, the corresponding polarizational charge is neutralized by flowing charges, therefore such compensated loop must be stable and lose an ability to move as in ordinary ferroelectrics.[5] The another part of free charges forms double-electric layers near the film surfaces with the field E_s inside the layers with thickness r. Figure 1 shows the basic features of this model.

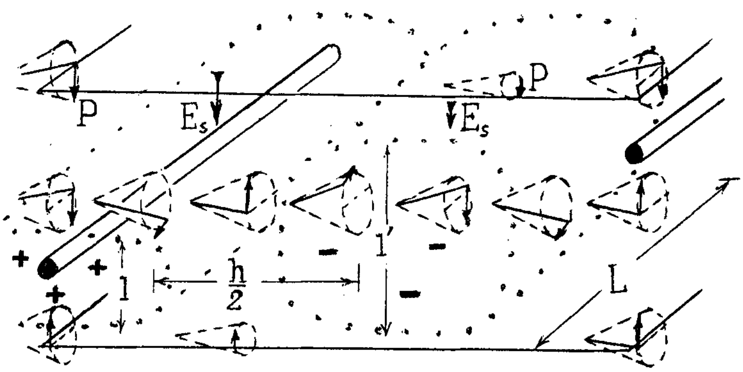

FIGURE 1 Model for the large-scale modulation of the polarization in FLC stabilized by disclinations with charged coats.

The qualitative estimation of the free energy density F under conditions described above is given by the equation

$$F = -\frac{h_\circ}{h} PE_s\tau + \frac{U^2}{2h^2} - \frac{\lambda}{h} P^2 \exp(-\frac{h}{\xi}) - \theta E(\frac{U}{h}) \qquad (1)$$

The first term in (1), where

$$\tau = -(\frac{r}{d})^2 \sqrt{\frac{E_c}{E_s}} (1 - \sqrt{\frac{E_c}{E_s}}) ,$$

d is the film thickness, describes the ordinary effect of untwisting by the E_s field at the critical value $E_s = E_c$

$$E_c \sim \frac{K\theta}{\mu h_\circ^2} (\frac{d}{r})^2 ,$$

where θ is the tilt angle, K is the elastic constant, μ is the piezoelectric coefficient.[6] The magnitude h^{-1} characterises here the number of walls in the spiral structure.

The second term in (1) characterises the role of the charge density gradient along the z-axis (the axis of helix), the magnitude U has the dimensional representation of an electric potential related to the charge density. One can think that the magnitude U characterises some electric conditions in vicinity of disclinations with compensated charges.

It is known that arise of disclinations is energetically favourable in twisted structures.[7] The existence of these orientational defects in the chiral smectic C* was observed experimentally.[8]

The third term in (1) characterises the energy of disclinational loops in the polarizational helix with the pitch h, the number of these loops n per unit length along the axis of helix being proportional to $\exp(-h/\xi)$. where $\xi = (T/P^2)$, T is proportional to the absolute temperature. The number of disclinations is determined by the probability for them to overcome a potential barrier by thermal fluctuations.[6] It is assumed that in materials with strong spontaneous polarization the energy of disclination is quadratic in the polarization $P \sim \mu\theta$ and exceeds the corresponding term related to elastic orientational deformations which is proportional to $K\theta^2$. The constant λ has the dimensional representation of a length characterising disclinations.

The forth term in (1) characterises the original flexoelectric effect related to modulated distributions of charge density (or potential U) and director $\vec{n}$. Its invariant form can be written as the term

$$- E_i U n_j \frac{\partial n_i}{\partial x_j} \qquad (2)$$

with a dimensionless coefficient which below will be included in the function $\theta(T)$.

It is assumed in (1) that the magnitudes U, λ, E_s and r are the phenomenological parameters of the chiral smectic C* with charge impurities neutralizing the polarization divergence at disclinations. The magnitudes $h_o(T)$ and $\theta(T)$ are the equilibrium parameters of such a smectic. The transient magnitude h is found from the condition $\partial F/\partial h = 0$. The quasiequilibrium character of this structure is related to possible relaxation of the structure under the action of internal and external fields.

In the case of a completely compensated disclination, i.e., one which has enough charge on it at all times to neutralize the polarization divergence completely, no driving force is available to provide for the kinetic energy of motion of the disclination with a charged coat. Practically speaking the time of relaxation of such a structure is infinite. If the compensation is incomplete, then the problem is considerably more complicated and similar to the domain wall formation in solid ferroelectrics.[9] The compensation can be incomplete either because the compensating charge is inadequate to eliminate the depolarization field or else because the compensating charge lags behind the disclination in its motion. The conductivity of LC (contrary to ordinary ferroelectrics) seems enough to provide for an appreciable neutralization. There may be relatively stationary charge distributions which give the disclination an equilibrium position.

One can see from Eq.(1) and Eq. $\partial F/\partial h = 0$ that the pitch h is the complex function of the spontaneous polarization P at fixed other parameters. If the potential U is sufficiently large, i.e., $U^2 \gg \lambda T$, one can find that

$$h \approx \frac{U^2}{U \theta E + h_o P E_s \tau} \qquad (3)$$

In this case the number of disclinations is proportional to

$$n \sim \exp\left[-\frac{U^2P^2}{T(\theta EU + h_\circ PE_s\tau)}\right] \qquad (4)$$

i.e., it sharply changes when the field E (at $E_s=0$) increases from zero value up to $E \sim (P^2U/T\theta)$ and it is saturated above this value of the field. If the potential U is sufficiently small, i.e., $U^2 \ll \lambda T$, one can find that

$$h \approx \frac{U^2}{\lambda P^2 + \theta EU} \qquad (5)$$

and the number of disclination is saturated since

$$\exp(-\frac{h}{\xi}) \sim \exp(-\frac{U^2}{T\lambda}) \sim 1 \; .$$

One can conclude from (3) and (5) that the period h substantially depends on the potential U (or the charge density). The temperature dependence of pitch is determined by the temperature dependences of polarization and equilibrium pitch, i.e., by $P \sim \mu\theta \sim \mu(T_c-T)^{1/2}$ and $h_\circ(T)$. In absence of the bias field E and the subsurface field E_s at $U^2 \gg \lambda T$ one has the equation

$$h \sim \frac{U^2}{K} h_\circ(T)(T_c-T)^{-1} \quad , \qquad (6)$$

but at $U^2 \ll \lambda T$ one can find that

$$h \sim \frac{U^2}{\mu^2\lambda}(T_c-T)^{-1} \qquad (7)$$

The Eq.(6) shows that the effect of chiral doping in ferroelectric mixtures can be appreciable since such doping change the equilibrium pitch $h_\circ(T)$. The Eqs.(6) and (7) describe the observed temperature dependences of the quasiequilibrium pitch h in various mixtures.[1]

If the field E_s is finite, its effect near the transition temperature T_c can be efficient since the critical field $E_c \sim \theta d^2$ is small here. The larger the layer thickness d the smaller the temperature interval near the T_c point $\sim \theta^2 \sim d^{-4}$ where the domains disappear (the pitch is infinite). At lower temperatures the quasiequilibrium pitch h does not depend on the thickness d. These effects of thickness are observed in experiments.[1]

In the alternating electric field $\tilde{E} = A \exp(i\omega t)$, the free charges compensating the polarizational charge can execute forced oscillations which induce the macroscopic oscillations of polarization Δ near disclinations:

$$\Delta = NQy ,$$

where N is the number of charges (± Q) in the unit volume, the charges ±Q being separated by the distance y. If Q is the charge related to a disclination with the length L and the effective size of charged atmosphere l along the y-axis, one can estimate $N \sim (n/lL)$. The oscillations of polarization Δ' in walls with the width h are also possible,

$$\Delta' \sim N'Qy', \quad N' \sim (hl'L)^{-1}, \quad y' \sim (m/m')y,$$

where l' is the corresponding size along the y-axis, $m = \rho^* lhL$ and $m' = \rho^* l'hL$ are the corresponding oscillating masses, ρ^* is the mass density. The local field E_{loc} which excites such oscillations includes the terms:

$$E_{loc} = \tilde{E} + \beta\Delta + \beta'\Delta' = \tilde{E} + \left(\beta n + \frac{\beta' l^2}{l'^2 h}\right)\frac{Qy}{lL} , \qquad (8)$$

where β and β' are the Lorentzian factors which describe the effects of charges related to neighbouring disclinations and walls in the quasi-equilibrium helix. These charges have the same order of value $Q \sim U$. If, for example, the density of polarizational charge ρ_{pol} is determined by the flexoelectric effect:

$$\rho_{pol} \sim l^{-1} P_{flexo} \sim (\theta U/hl) \quad \text{or} \quad \rho'_{pol} \sim (\theta U/hl'),$$

$$Q \sim \rho_{pol} hlL \sim Q' \sim \rho_{pol} hl'L \sim \theta UL. \qquad (9)$$

The equation of motion for the oscillator related to the disclination reads[4]:

$$m\ddot{y} + 2m\gamma\dot{y} + ky = QE_{loc}$$

or

$$\ddot{\Delta} + 2\gamma\dot{\Delta} + \omega_o^2\Delta = \frac{nQ^2}{\rho^* hl^2 L^2}\tilde{E} , \qquad (10)$$

where γ is the viscosity coefficient, k is the elastic constant,

$$\omega_o^2 = \frac{k}{m} - (\beta n + \frac{\beta' l^2}{l'^2 h}) \frac{Q^2}{\rho^* h l^2 L^2} .$$

It is possible to estimate the ratio (k/m) if one takes into account that small relative displacements of charges of opposite signs under the action of field result in appearance of noncompensated charges with the density $\sigma \sim \rho_{pol} y$ on the opposite surfaces of the volume lhL. These charges change the enegry of electric field inside the volume on the magnitude of the order of

$$\varepsilon^{-1} \sigma^2 lhL \sim \varepsilon^{-1} \rho^2_{pol} (lhL) y^2 \sim \frac{k}{2} y^2 ,$$

the elastic force being equal to -ky, i.e., the ratio k/m can be approximated by

$$\frac{k}{m} \sim \frac{\rho^2_{pol}}{\varepsilon \rho^*} \tag{11}$$

where ε is the average dielectric permeability. By Eq.(9) one can find from (11) that

$$\omega_o^2 \sim \frac{(\theta U)^2}{\rho^* l^2} \left(\frac{1}{\varepsilon h^2} - \frac{\beta n}{h} - \frac{\beta' l^2}{l'^2 h^2} \right) \tag{12}$$

It is necessary to underline the qualitative character of the expressions written above: the coefficients β and β' are unknown, the sizes l and l' can depend on surface properties and specific features of a disclination, generally speaking l and l' are functions of r, h and d. The most important features of Eq.(12) are the dependences on the potential U, the tilt angle θ and the pitch h. The dependence on h has two parts: the term with the nonanalytical dependence on wave number $q \sim h^{-1}$ related to disclinations and the terms with analytical dependences on q, the wave vector being raised to even powers (the local field must be independent of the sign of q).

At some conditions the magnitude ω_o^2 can be positive: if $\varepsilon^{-1} > \beta'(l/l')^2$ and h is sufficiently large, for example, at zero bias field. In this case the solution of Eq.(10) has the resonance character at the frequency of alternating field $\omega = (\omega_o^2 - 2\gamma^2)^{1/2}$ and the polarization inhomogeneity must differ from a simple harmonic distribution: one can observe several orders of light diffraction.[1] At the resonance conditions the temperature dependence of q can remarkably differ from expressions (3) and (5) which were observed experimentally.[1] Generally speaking the existence of quasistationary spatially modulated structures under the action of alternating field is possible only at specific relationship between the field amplitude A and the wave number q.[10] The general feature of such a phenomenon is its threshold character: the structure does not arise at zero field A, the threshold values A_c and q_c have the evident proportionality $A_c^2 \sim Kq_c^2$, the critical voltages being equal to several volts. If one takes into account the effect (2) then one can conclude that the modulation of the tilt angle $\theta(z)$ is possible in connection with the spatial distribution of the free charge density. The dimensioness consideration shows that in the last case one has the proportionality $A^2 \sim Kq^2$ above the threshold. The experiment[1] shows this proportionality at low resonance frequencies which are specific to flexoelectric phenomena.

SPIRAL DOMAINS IN LANGMUIR MONOLAYERS DOPED BY FREE CHARGES AND CHIRAL MOLECULES

Möhwald[2] had observed the electrostatically induced growth of spiral lipid domains in the presence of cholesterol. This interesting phenomenon takes place in the monomolecular layer on the water surface. Möhwald[2] underlined the importance of free electric charges and chiral molecules and proposed a qualitative model for the formation of spiral domains. The present paper considers a model which admits a quantitative solution and analytic results which can explain characteristic features of the phenomenon.

The present model has the following peculiarities. Molecules in the flat monolayer can have tilt deviations θ from the normal z to the layer plane, the magnitude θ is a function of the cylindrical coordinates r and α, $\theta(r,\alpha) \to 0$ at $r \to 0$. The corresponding distribution of the free charge density $\rho(r,\alpha)$ has the relatively small finite value ρ_o in the point r = 0. There is the polar action $\vec{P}$ (electric polarization of molecules or the external field from a subsurface) on molecules in the monolayer along the normal to it. In accordance with the model, the director $\vec{n}$ has the projections n_z and $\vec{m}$ (in the plane xy), $|\vec{m}| = \theta$. The chiral symmetry of the system admits the following invariants in the free energy expansion.

Nonchiral invariants in orthogonal coordinates:

$$\frac{1}{4}\theta^4 + \frac{1}{2}\varepsilon\theta^2 + \frac{1}{2}\mu\rho^2 + \frac{1}{2}g\left[\left(\frac{\partial\rho}{\partial x}\right)^2 + \left(\frac{\partial\rho}{\partial y}\right)^2\right] + \frac{1}{2}K_1\left(\frac{\partial m_x}{\partial x} + \frac{\partial m_y}{\partial y}\right)^2 + \frac{1}{2}K_2\left(\frac{\partial m_x}{\partial y} - \frac{\partial m_y}{\partial x}\right)^2 + a\rho P_z n_z\left(\frac{\partial m_x}{\partial x} + \frac{\partial m_y}{\partial y}\right) . \quad (13)$$

The last term in (13) is similar to the flexoelectric effect (2).

Chiral invariants:

$$bn_z\left(m_x\frac{\partial\rho}{\partial x} + m_y\frac{\partial\rho}{\partial y}\right) + c\rho n_z\left(\frac{\partial m_x}{\partial y} - \frac{\partial m_y}{\partial x}\right) . \quad (14)$$

The material parameters ε, μ, g, K_1 and K_2 are positive. It will be proposed below, for simplicity, that $K_1 = K_2 = K$. It is seen from (13) that the finite tilt angle θ cannot arise spontaneously but it can be induced by the vector field $\vec{P}$. It is convenient to find the magnitudes $\vec{n}$ and ρ as functions of the cylindrical coordinates r and α. The model distribution $\vec{m}(r,\alpha)$ with the components $m_\alpha = 0$ and $m_r = \theta(r,\alpha)$ will be discussed (see Fig.2).

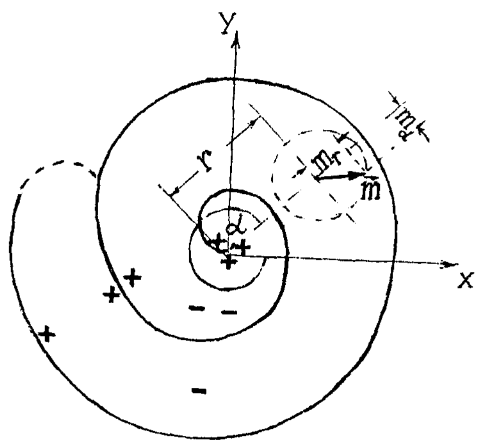

FIGURE 2 Model for spiral domains in Langmuir monolayers doped by free charges and chiral molecules.

The corresponding equations for the functions $\rho(r,\alpha)$ and $\theta(r,\alpha)$ in the frame work of the present model read:

$$\theta^3 + \varepsilon\theta - E\frac{\partial\rho}{\partial r} - \frac{c}{r}\frac{\partial\rho}{\partial\alpha} - K[\frac{\partial}{\partial r}(\frac{1}{r}\frac{\partial(\theta r)}{\partial r}) + \frac{1}{r^3}\frac{\partial^2(\theta r)}{\partial\alpha^2}] = 0, \quad (15)$$

$$\mu\rho + E\frac{1}{r}\frac{\partial(\theta r)}{\partial r} + \frac{c}{r}\frac{\partial\theta}{\partial\alpha} - g[\frac{1}{r}\frac{\partial}{\partial r}(r\frac{\partial\rho}{\partial r}) + \frac{1}{r^2}\frac{\partial^2\rho}{\partial\alpha^2}] = 0 \quad (16)$$

where $E = aP - b$. For sufficiently large values of the parameter E and for large distances r, one can find that the nonlinear term in Eq.(15) is small, and these equations have some "classical" linear solutions at some threshold conditions, the magnitudes E and q being connected by a certain relationship. The corresponding term in the free energy these large distances must equal zero. At sufficiently small distances $r < R$ the nonlinear term in Eq.(15) is substantial and the solutions differ from the "classical" ones. The characteristic magnitude R should be found from the corresponding solutions.

For $r > R$, one can find the solutions $\theta(r,\alpha)$ and $\rho(r,\alpha)$ as the following expansions in terms of $(1/r)$:

$$\rho = \rho^* \quad [\frac{1}{r} - \frac{cqE(2\varepsilon + Kq^2)}{\varepsilon(\varepsilon + Kq^2)r^2}] \cos(qr-\alpha-\alpha^*) + \frac{(q\varepsilon - K\mu)}{gq(\varepsilon + Kq^2)r^2}$$

$$\sin(qr - \alpha - \alpha^*) + O(cE^2/r^3) \quad , \quad (17)$$

$$\theta = \rho^* \quad [-\frac{Eq}{r(\varepsilon + Kq^2)} + \frac{c}{\varepsilon r^2}] \sin(qr - \alpha - \alpha^*) +$$

$$+ \frac{1}{r^2}\frac{E(E^2 - \mu K)}{g(\varepsilon + Kq^2)^2} \cos(qr - \alpha - \alpha^*) + O(cE^2/r^3) \quad ,$$

where ρ^* and α^* are some constants, the wave number q must be found. The substitution of (17) into (13) and (14) and equation of the free energy to zero give the threshold values q_c and E_c:

$$q_c^2 = \sqrt{\frac{\varepsilon\mu}{gK}}, \quad E_c^2 = (\sqrt{\mu K} + \sqrt{\varepsilon g})^2. \quad (18)$$

One can see from (17) that in fact the parameter of expansion is the magnitude const(E/r), i.e., the characteristic distance R is proportional to the "field" E.

For $r \ll R$, one can find the expansions

$$\theta = \theta_1 r + \theta_3 r^3 + O(r^5),$$
$$\rho = \rho_o + \rho_2 r^2 + O(r^4), \tag{19}$$

where the coefficients are given by the relations

$$\theta_1 \sim \frac{\mu}{E}\rho_o, \quad \rho_2 \sim \frac{\varepsilon\mu}{E^2}\rho_o, \quad \theta_3 \sim \frac{\mu^2\varepsilon}{E^3}\rho_o, \quad \rho_4 \sim \varepsilon\theta_3, \dots \tag{20}$$

Thus one can see from (19) and (20) again that the parameter of expansion is the magnitude const(r/E), i.e., really $R \sim E$.

The analytical solutions (17)-(20) show that the distributions $\theta(r,\alpha)$ and $\rho(r,\alpha)$ are classical spirals with the equation $r = (\alpha + \alpha^*)q^{-1} > R$ for lines of equal phases. At $r \gg R$ the distributions are negligible. It means that the turns of spiral can be observable in a circle with the radius $R \sim E$, the larger field E the larger quantity of turns $Rq \sim E^2$. The centers of such spiral arise occasionally in the monolayer. These peculiarities of the phenomenon are in accordance with experimental data.[2] It is necessary to underline that here, as in the previous problem, flexoelectric and chiral properties in presence of free charges play the decisive role.

The present model gives a qualitative explanation of spiral configuration of domains in such a monolayer. The experimental data[2] show the finite number of turns with sharp borders in spiral domains. This fact can be explained by existence of disclination lines. Really, the director deviations can be more complicated: one should consider the nonlinear model with the nonzero components n_r and n_α. This problem is similar to the considered one in Ref.[11] where it was shown that spiral domains are inevitably conjugated with disclination lines because of topological reasons. In such a case, for the fixed field value, the number of turns in spirals must be finite since the length of a disclination spiral is limited because of its power unfavourableness.

CHIRAL SMECTIC PHASE A*

Renn and Lubensky[4] had predicted the helical smectic A* phase between the cholesteric and ordinary smectic A phases, the A* phase being constructed from rotated blocks of smectic A layers. These mutual rotations of blocks are provided by the network of screw dislocations. Lavrentovich et al.[3] reported about experimental observation of this type of smectics. The twist-grain-boundary phase predicted in Ref.[4] is the analog of the Abrikosov phase in superconductors with molecular chirality as the analog of the external magnetic field. Vigman and Filev[12] had shown that the first order cholesteric (the normal metal)-smectic A (the Meissner phase) phase transition must occur at $a=a_c<0$, where a is a coefficient in the term $a|\psi|^2$ in the free energy expansion for a smectic A, $|\psi|$ is the smectic order parameter. The finite value a_c is determined by smectic fluctuations in the cholesteric phase in which the pretransitional growth in the pitch of the cholesteric helix must occur and it is not described by a universal power law.

It is shown in the present paper that the formation of a helical smectic A* can be described directly by taking into account the dislocations in the framework of the classical knowledge about epitaxial dislocations and the energy of grain subboundaries.[13] This energy per unit area of the dislocational wall qualitatively is proportional to $-\varphi\ln\varphi$, where φ is the angle of disorientation of neighbouring crystalline layers. One can think that there is the linear relation between the wave number q and the angle φ in the helical smectic A*. This model assumption means that either dislocations are distributed more or less continuously or else the size of A-phase blocks along the z-axis is much smaller than the pitch of helix $2\pi q^{-1}$ (see Fig.3). The corresponding term in free energy density can be written in the form

$$-g|\psi|^2 q^2 \ln q , \qquad (21)$$

where g is the constant, the magnitude $g|\psi|^2$ plays the role of an effective elastic modulus of the smectic, q being proportional to the number of walls per unit length along the axis of helix. The term (21) is substantial if the constant g is sufficiently large, i.e., if one can neglect the pretransitional change of the cholesteric pitch,

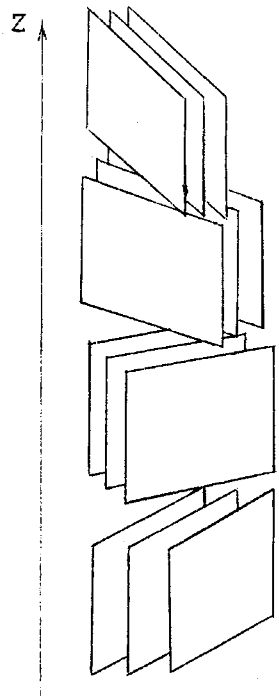

FIGURE 3 Model for the chiral smectic phase A*. The rotation of blocks of smectic planes is shown.

mentioned above, in the vicinity of the point a=0. If g is small, then the smectic fluctuations play the predominant role.

Thus the present model gives the following expression for the free energy density F:

$$F = a|\psi|^2 + \frac{b}{2}|\psi|^4 + \frac{1}{2}K(q - q_o)^2 - g|\psi|^2 q^2 \ln q , \qquad (22)$$

where parameter a changes its sign at $T = T_o$, $b > 0$, $g > 0$, q_o is the cholesteric wave number, K is the Frank constant. Minimization of F by $|\psi|$ and q results in corresponding equations for ψ and q which have the following solutions. At the point $a = a^* = gq_o^2 \ln q_o < 0$ the second order phase transition from the cholesteric phase to the helical smectic A* phase (the Abrikosov phase) occurs. One has in the A* phase:

$$|\psi|^2 \sim (1 + \frac{4g^2}{bK} q_o^2 \ln^2 q_o)t , \quad t > 0,$$

$$t = \frac{-a + gq_o^2 \ln q_o}{b} \ll 1, \qquad t^* = t(a^*) = 0 ,$$

$$q \approx q_o + \frac{2g}{K} q_o \ln q_o t < q_o .$$

At the point t = t'

$$t' \approx \frac{K}{2g} \ll 1 ,$$

the first order phase transition from the A* phase to the A phase occurs, the jump of the wave number value at t = t' being equal to

$$q' \approx \frac{q_o}{\ln q_o} \ll q_o .$$

If one admits the existence of disclinations discussed in previous sections, then the expression (22) should be complicated by the term

$$- c\, q \exp(-1/q\xi)$$

which adds a qualitative feature to the discussed results. One can show that for relation between phenomenological parameters

$$\frac{K\xi^2}{c} q_o^3 \approx \exp(-\frac{1}{q_o\xi}) , \qquad (23)$$

the point t = 0 is a critical one:

$$|\psi|^2 \approx \frac{4g\xi^2}{b} q_o^4(-\ln q_o)^{3/2} \exp(-\frac{1}{2q_o\xi})\, t^{1/2} ,$$

$$q \approx q_o - 2\xi^2 q_o^3 (-\ln q_o)^{1/2} \exp(-\frac{1}{2q_o\xi})\, t^{1/2} .$$

For the relation (23), one determines the first order phase transition at the point t = t':

$$t' \approx \frac{1}{2}(\xi q_o)^{-3} |\ln q_o|^{-1} \exp(-\frac{1}{q_o\xi})$$

$$q' \approx q_o[1 - (2q_o\xi)^{1/2} \exp(-\frac{1}{q_o\xi})] .$$

Strictly speaking it is necessary to take into account the fluctuations of the orientational order, as in the case of the transition between smectic A and nematic phases, that can change the order of the transition between cholesteric and smectic A* phases: from the second order to the weak first order. Experiments[3] show that this transition is of the weak first order, the phase A* exhibits a significant rigidity in shear deformations, these facts verify the model (21). The experiment shows also that there are some concentration waves for the components in the investigated mixture. This interesting feature of the phenomenon is very similar to results of previous sections.

The considered model is useful not only for liquid crystals but for the more general problem of crystal growth, for example, for the epitaxial growth of thin molecular films on an anisotropic crystalline substrate. Taking into account the ordinary orientational terms (quadratic in the angles of disorientation of growing grains and a substrate) and the energy of the wall of epitaxial dislocations one can describe a off-beat orientational phase transition of growing grains: experiments show specific reorientation of crystalline grains to a given direction at a critical dimension of the grain.

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