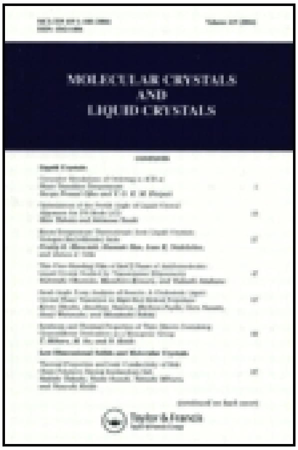

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The Effects of Spontaneous Strains at the D_{hd}-D_{rd} Phase Transition in HAT Series

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Spontaneous strain effects at the D_{hd}-D_{rd} phase transition in HAT columnar liquid crystal systems are taken into account. The transition is then treated as a paraelastic-ferroelastic transition, which is known in some crystal systems, but has never been discussed in liquid crystal systems. The anomaly of the elastic compliance near the transition is discussed. The critical exponents remain the same as our previous work, namely those of the three dimensional Heisenberg model with cubic anisotropy.

By means of Landau theory and group theoretic techniques, the present authors[1] have given a discussion of the disordered hexagonal-disordered rectangular (D_{hd}-D_{rd}) phase transition in the columnar liquid-crystal systems of HAT (hexa-n-alconoylaxy-triphenylene) series, which has been observed experimentally.[2,3] That work focused on the analysis of the change in symmetry and a possible mechanism for the phase transition. The Ginzburg-Landau-Wilson Hamiltonian obtained was in the same universality class as that for the three dimensional Heisenberg model with cubic symmetry. However, a rigid lattice structure was assumed, i.e. the small distortion which accompanies the D_{hd}-D_{rd} transition was ignored. In this work, we will take this effect into account. The appearance of distortions means that certain spontaneous strains are present below the transition. The relevant elastic energy and the coupling between the order parameters and the spontaneous strain degrees of freedom should be included in the Landau free energy. With this energy included, the phase transition can be considered as paraelastic-ferroelastic (or prototypic-ferroelastic) transition which was discussed in crystal systems by Aizu.[4] In the sense of Aizu, a system is called ferroelastic when it satisfies:

(1) There is more than one "orientation state."[4] These states are identical or enantiomorphous in crystal structure and different in strain. (2) Different orientation states can be transformed from one to another by an external stress. (3) A stress-strain hysteresis loop exists.

The D_{hd}-D_{rd} transition in HAT columnar liquid crystal systems corresponds to a symmetry change, in the plane perpendicular to the columns, from a two dimensional space group p6mm(G_o) in the higher symmetry (HS) phase to p2gg(G) in the lower symmetry (LS) phase.[1] There are three appropriate parameters $\{\eta_i\} = \{\eta_1, \eta_2, \eta_3\}$, and the Landau free energy, $F(\{\eta_i\})$, expanded up to fourth-order in $\{\eta_i\}$, takes the form:[1]

$$F(\{\eta_i\}) = \frac{1}{2} r \sum_{i=1}^{3} \eta_i^2 + u \sum_{i=1}^{3} \sum_{j=1}^{3} \eta_i^2 \eta_j^2 + v \sum_{i=1}^{3} \eta_i^4. \tag{1}$$

The symmetry of a LS phase is determined by the orientation of the order parameter vector of the LS phase in an abstract space ϵ which is spanned by the basis functions of the irreducible representation (IR) of p6mm relevant to the D_{hd}-D_{rd} transition. The orientation is obtained by minimizing the Landau free energy with respect to the order parameters subject to the constraint $\gamma_1^2+\gamma_2^2+\gamma_3^2 = 1$ ($\eta_i = \eta\gamma_i$). There are three possible orientation states in the LS phase and their orientations in ϵ space are [1,0,1], [0,1,0] and [0,0,1] respectively. The patterns of the HS phase and the LS phase with orientation [1,0,0] are shown in Figure 2(a) and (b) of Ref. 1.

To find the suitable spontaneous strain components which appear in the D_{rd} phase after the D_{hd}-D_{rd} transition, we start from the expression of the elastic free energy density, F_e. It can be read off from Ref. 5 as

$$F_e = \frac{B^0}{2}(\partial_x U_x + \partial_y U_y)^2 + \frac{D^0}{2}[(\partial_x U_x - \partial_y U_y)^2 + (\partial_x U_y + \partial_y U_x)^2]$$

$$+ \frac{K_{33}^0}{2}[(\partial_{zz}^2 U_x)^2 + (\partial_{zz}^2 U_y)^2] + \frac{A^0}{2}\theta^2 + C^0\theta[\partial_x U_x + \partial_y U_y], \tag{2}$$

where $\vec{U}$ is the displacement vector, the z axis is chosen to be parallel to the column axes, and θ represents the bulk expansion (or dilation) and can be expressed as $\theta = \partial_x U_x + \partial_y U_y + \partial_z U_z$. Also, A^0, B^0, C^0, D^0 and K_{33}^0 are elastic constants. The meaning of each term has been explained in Ref. (5). In the present paper, only the effects of homogeneous distortion will be taken into account, i.e. we consider that $\vec{U}$ linearly depends on spartial position $\vec{r}$. Other elastic effects beyond this will be ignored. We further define $\partial_x U_x = e_1$, $\partial_y U_y = e_2$, $\partial_z U_z = e_3$, $\partial_x U_y + \partial_y U_x = e_6$ where e_1, e_2, e_3, and e_6 are now homogeneous in space. Eq. (2) can then be written as

$$F_e = \frac{B^0}{2}(e_1 + e_2)^2 + \frac{D^0}{2}[(e_1 - e_2)^2 + e_6^2] + \frac{A^0}{2}(e_1 + e_2 + e_3)^2 + C^0(e_1 + e_2 + e_3)(e_1 + e_2). \tag{3}$$

In discussing paraelastic-ferroelastic phase transitions, we do not need to use the full strain elastic energy as given by Eq. (3). As pointed out by several authors,[6,7,8] only those terms which are associated with the spontaneous strains are important. In crystal systems, spontaneous strain components in a given phase transition are these components which are forbidden in the HS phase, but will be allowed in the LS phase.[6,7] The number and the suitable form of the spontaneous components in all the possible paraelastic-ferroelastic transitions are totally determined by the relevant point groups of the HS and LS phases which belong to two different crystal systems and have been systematically worked out.[6] The standard procedures can be found in Refs. (4b and 7).

The independent spontaneous strain variables for the D_{hd}-D_{rd} transition can be directly identified from Eq. (3). The arguments are the following. The point groups of D_{hd} and D_{rd} phases are D_{6h} and D_{2h} (Schoenflies symbol) respectively and can be further written as $D_{6h} = C_{6v} \otimes C_s$ and $D_{2h} = C_{2v} \otimes C_s$. All the four independent strain variables, i.e. $e_1 + e_2$, $e_1 + e_2 + e_3$, $e_1 - e_2$, and e_6 appearing in Eq. (3), are invariant under the subgroup C_s so that the C_s symmetry is preserved in the LS phase after the transition. Therefore, instead of the D_{6h} and D_{2h} point groups, we can only consider the symmetry changes between the C_{6v}(HS phase) and C_{2v}(LS phase) point groups without loss of generality. The former refers to the two dimensional hexagonal system and the latter to the rectangular system. The strains which can be used as spontaneous strain variables should not be invariant under the HS point group C_{6v}.[7] It is easy to check that $e_1 + e_2$ and $e_1 + e_2 + e_3$ are invariant under C_{6v} (the transform of e_1, e_2, and e_3 under the symmetry operations is the same as x^2, y^2 and z^2 respectively) and therefore should be excluded as spontaneous strain variables. The other two variables, $e_2 - e_1$ and e_6 are not invariant under C_{6v}, and consist of the basis of the IR of the point group C_{6v} which can be identified as the IR τ_6 of C_{6v} in Zak's table.[9] They will be seen to give the spontaneous strains in D_{rd} phase. For compactness, we denote $e_2 - e_1$ and e_6 as χ_1 and χ_2 respectively. One can then imagine an abstract two dimensional space Ω with $[\chi_1, \chi_2]$ as a vector in the space Ω. Spontaneous strain components in a given orientation state are the components of a vector $[\chi_1^0, \chi_2^0]$ which is invariant under the point group of the orientation state under consideration. The elastic free energy which is associated with these strain degrees of freedom can be expressed as

$$F_e(\chi_1, \chi_2) = \frac{1}{2}D^0(\chi_1^2 + \chi_2^2) \tag{4}$$

Although χ_1 and χ_2 are the bases of the IR τ_6 of C_{6v}, it is also the basis of one of the two dimensional IR of the space group p6mm with $\vec{k} = 0$, which is homomorphic to τ_6 of the point group C_{6v}. So $F_e(\chi_1, \chi_2)$ is also invariant under p6mm (the HS space group).

The coupling terms $F_c(\eta_i, \chi_i)$ were suggested to have the form[6]

$$F_c(\eta_i, \chi_i) = \delta[\chi_1\Psi_1^{(n)}(\eta_i) + \chi_2\Psi_2^{(n)}(\eta_i)] \tag{5}$$

where $\Psi_1^{(n)}(\eta_i)$ and $\Psi_2^{(n)}(\eta_i)$ are the n^{th} power homogeneous functions of η_i which transforms in the same way as χ_1 and χ_2 so as to keep $F_c(\eta_i, \chi_i)$ invariant under p6mm. Hence, n cannot be unity because $\{\chi_i\}$ and $\{\eta_i\}$ belong to different IRs of p6mm. $\Psi_1^{(n)}(\eta_i)$ and $\Psi_2^{(n)}(\eta_i)$ can be obtained by projecting $[\Gamma^n]$ upon τ_6,[6] where Γ is the IR of p6mm which corresponds to the D_{hd}-D_{rd} transition. Only the smallest n, n_F, which gives non-zero $\Psi_1^{(n)}(\eta_i)$ and $\Psi_2^{(n)}(\eta_i)$ need be considered in Eq. (5). n_F is called the "faintness" index.[6,10] In our system, $n_F = 2$ and $\Psi_1^{(2)}(\eta_i)$ and $\Psi_2^{(2)}(\eta_i)$ can be taken as

$$\Psi_2^{(2)}(\eta_i) = 2\eta_1^2 - \eta_2^2 - \eta_3^2 \tag{6a}$$

$$\Psi_2^{(2)}(\eta_i) = \sqrt{3}(\eta_2^2 - \eta_3^2) \tag{6b}$$

This form is the same as that given in Ref. (6) for the crystal system corresponding to a symmetry change from p6mm to pba2 (or p2gg). Now, the full Landau free energy can be written as

$$F_L = \frac{1}{2}r\sum_{i=1}^{3}\eta_i^2 + u\sum_{i=1}^{3}\sum_{j=1}^{3}\eta_i^2\eta_j^2 + v\sum_{i=1}^{3}\eta_i^4 + \frac{1}{2}D^0(\chi_1^2 + \chi_2^2) + \delta[\chi_1(2\eta_1^2 - \eta_2^2 - \eta_3^2) + \sqrt{3}\chi_2(\eta_2^2 - \eta_3^2)] \tag{7}$$

We denote the symmetry operations of the C_{6v} point group as h_i (i = 1, 2, 3, 4, 5, 6, 19, 20, 21, 22, 23, 24) which have the meanings given by Kovolev.[11] The h_i are defined with respect to a chosen oblique coordinate frame with $\vec{a}_1$ and $\vec{a}_2$ as its basis. We also choose a two dimensional Cartesian coordinate system to define the elastic strain variables as shown in Figure 1.

The existence of coupling terms between the order parameters and the spontaneous strain variables in Eq. (7) is essential in order to explain how the spontaneous strains appear below the transition temperature.[10] The allowable spontaneous strain components in the LS phase should not break the symmetry of D_{rd} phase. When the tem-

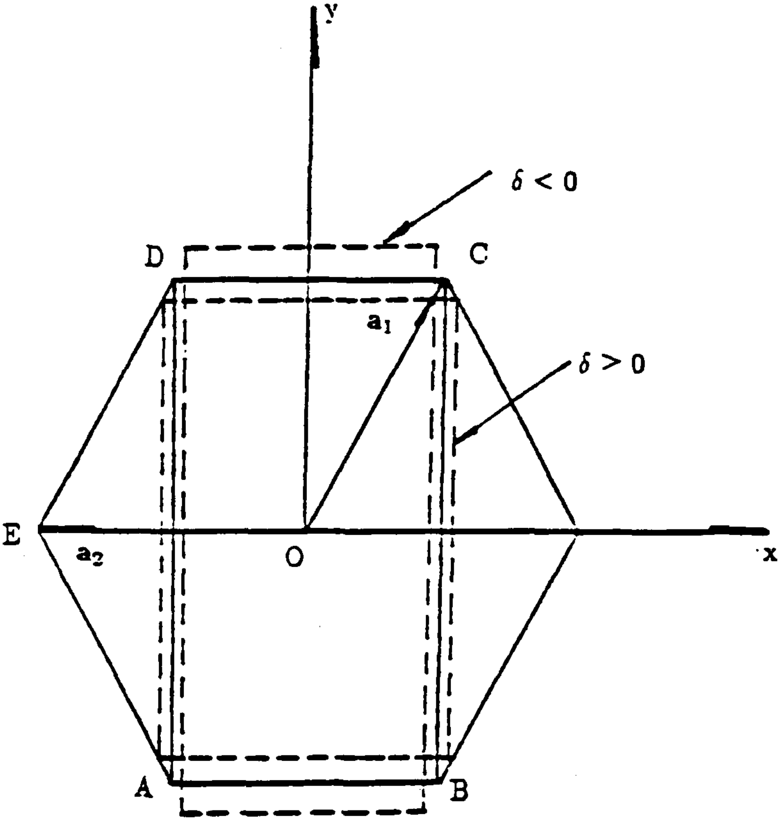

FIGURE 1 $\vec{a}_1$ and $\vec{a}_2$ are the basis vectors of the two dimensional hexagonal lattice structure, upon which the symmetry operations h_1 through h_6 and h_{19} through h_{24} are defined; OCDE and ABCD are unit cells in the HS phase and the LS phase corresponding to the [1,0,0] orientation state respectively; the spontaneous variables are defined upon the Cartesian coordinate system x-y; and the dotted lines represent the distorted rectangular system because of the spontaneous strains $[\chi_1^0, 0]$.

perature is not too close to the transition point, one can employ mean field theory. The stress components conjugate to χ_1 and χ_2 are:

$$S_1 = \frac{\partial F_L}{\partial \chi_1} = D^0 \chi_1 + \delta(2\eta_1^2 - \eta_2^2 - \eta_3^3) \tag{8a}$$

$$S_2 = \frac{\partial F_L}{\partial \chi_2} = D^0 \chi_2 + \sqrt{3}\, \delta\, (\eta_2^2 - \eta_3^2) \tag{8b}$$

Spontaneous strain components χ_1^0, χ_2^0 can be obtained by putting $S_1 = 0$ and $S_2 = 0$ in Eqs. (8a) and (8b). So, we have

$$\chi_1^0 = -\frac{\delta}{D^0}(2\,\eta_1^2 - \eta_2^2 - \eta_3^2) \tag{9a}$$

$$\chi_2^0 = -\frac{\delta}{D^0}\sqrt{3}\,(\eta_2^2 - \eta_3^2). \tag{9b}$$

In the HS phase, Eqs. (9a) and (9b) just give $\chi_1^0 = 0$ and $\chi_2^0 = 0$. In the LS phase, corresponding to different orientation states, we have

$$[1,0,0] \rightarrow \chi_1^0 = -\frac{2\delta\eta^{02}}{D^0},\ \chi_2^0 = 0 \tag{10a}$$

$$[0,1,0] \rightarrow \chi_1^0 = \frac{\delta\eta^{02}}{D^0},\ \chi_2^0 = -\frac{\sqrt{3}\eta^{02}}{D^0} \tag{10b}$$

$$[0,0,1] \rightarrow \chi_1^0 = \frac{\delta\eta^{02}}{D^0},\ \chi_2^0 = \frac{\sqrt{3}\eta^{02}}{D^0} \tag{10c}$$

where η^0 is the minimum value of the magnitude of $[\eta_1,\eta_2,\eta_3]$.

The distorted rectangular phase, with its spontaneous strain components given by Eq. (10a) in the [1,0,0] state, is indicated by the dotted lines in Figure 1. Different orientation states can be transformed each other by suitable symmetry operations which belong to the HS point group.[4] For example, using the explicit matrix representation of h_2 and h_3 in the space Ω, their actions on $[\chi_1^0, \chi_2^0]$ will transform Eq. (10a) to (10b) and (10c) respectively. So, the distorted rectangular phases corresponding to the spontaneous strain components given by Eqs. (10b) and (10c) can be obtained by rotating the pattern in Figure 1 by 60° or 120° about the z axis. In each case, the symmetry of the D_{rd} phase is preserved.

The behaviour of the elastic compliance near the transition in the paraelastic-ferroelastic transition has been previously discussed by Aizu.[10] However, Aizu's results were obtained by means of mean field theory and can be expected to be valid only when the system is not too close to the transition line. Near the transition a different behaviour of the elastic anomaly can be expected, and the renormalization group theory should be employed. To allow for fluctuations, instead of Landau free energy F_L, we need the Ginzburg-Landau Wilson free energy, F, which can be directly obtained from a generalization of Eq. (7). This is

$$F = \int d^3x \left\{ \frac{1}{2} r \sum_{i=1}^{3} \eta_i^2 + \frac{c}{2} \sum_{i=1}^{3} \sum_{\alpha=1}^{3} \nabla_\alpha \eta_i \nabla_\alpha \eta_i + u \sum_{i=1}^{3} \sum_{j=1}^{3} \eta_i^2 \eta_j^2 \right.$$

$$+ v \sum_{i=1}^{3} \eta_i^4 + \frac{1}{2} D^0 (\chi_1^2 + \chi_1^2) + \delta[\chi_1(2\eta_1^2 - \eta_2^2 - \eta_3^2)]$$

$$\left. + \sqrt{3}\chi_2(\eta_2^2 - \eta_3^2)] - \chi_1 S_1 - \chi_2 S_2 \right\}. \qquad (11)$$

In Eq. (11), S_1 and S_2 are external stresses which act on the system. The purpose of adding the external stresses is to predict the critical behavior of the elastic compliance which is the response of the elastic strain to the external stress. Such external stresses will lead to a different symmetry from that of the original stress-free system.[12] All the results obtained from Eq. (11) can apply to the stress-free system only when the external stresses go to zero. The rigid lattice model corresponding to Eq. (11) is given in Eq. (13) of Ref. [1]. In order to discuss the influence of the elastic strains on the critical behavior, a simple approach is to remove the strain from the partition function by integrating over χ_1 and χ_2 to obtain an effective free energy. By doing so, we will get new fourth order terms in the order parameters which correspond to a long range interaction and which stem from the free surface effect.[13] For the case in which the elastic energy has same form as in an isotropic system and the spatial dimensionality is three, the free surface effect has been discussed by Wegner.[13] The results depend upon the sign of the specific heat exponent, α, for the rigid lattice. If $\alpha > 0$, the phase transition turns to be first order; if $\alpha < 0$, there exist two possible cases: (1) for strong coupling, the phase transition will be first order (2) for weak coupling, the transition remains second order with the same exponents as in the rigid model. In case (2), the free surface effect can be ignored. Aharony[12] generalized the results of case (2) to the three dimensional Heisenberg system with the elastic energy having cubic symmetry and with a more general coupling.

Because our system corresponds to $n=d=3$, and the D_{hd}-D_{rd} transition is experimentally found to be second order,[3] for the same reasons as Aharony's,[12] we will discard the long-range terms which appear in the effective free energy after removing the strain variables in Eq. (11). Following procedures similar to those in Ref. [12], we can write the effective free energy as

$$F_{eff} = \int d^3x \left\{ \frac{1}{2} \sum_{i=1}^{3} r_i \eta_i^2 + \frac{1}{2} c \sum_{i=1}^{3} \sum_{\alpha=1}^{3} \nabla_\alpha \eta_i \nabla_\alpha \eta_i + u \sum_{i=1}^{3} \sum_{j=1}^{3} \eta_i^2 \eta_j^2 + v \sum_{i=1}^{3} \eta_i^4 \right\} \tag{12}$$

where

$$r_1 = r + \frac{4\,\delta S_1}{D^0}, \tag{13a}$$

$$r_2 = r - \frac{2\delta}{D^0}(S_1 - \sqrt{3} S_2), \tag{13b}$$

and

$$r_3 = r - \frac{2\delta}{D^0}(S_1 + \sqrt{3} S_2). \tag{13c}$$

Except for purposes of computing the anomaly of the elastic compliance, the critical behaviour of the stress-free system can be obtained by setting $S_1 = 0$, and $S_2 = 0$ in Eqs. (12) through (13). Then Eq. (12) takes the same form as Eq. (13) of Ref. [1]. If $v < 0$ and $u + v > 0$ a stable D_{rd} phase after a continuous D_{hd}-D_{rd} transition exists.[1] So, for zero applied stress, the critical exponents are expected to be the same as those of the three dimensional Heisenberg model.[1]

Let us now determine the elastic compliance component $\left(\frac{\partial \chi_1}{\partial S_1}\right)_0$. (The subscript "0" means the external stress is put equal to zero after differentiation). The easiest way to compute this is to put $S_2 = 0$ and S_1 nonzero. This corresponds to a compression (or dilation) in x direction, which is counterbalanced by a dilation (or compression) in y direction.[5] The effective free energy Eq. (12) then takes a form similar to Eq. (3) of Ref. [12]; i.e.,

$$F_{eff} = \int d^3x \left\{ \frac{1}{2}\left(r + \frac{4\delta S_1}{D^0}\right)\eta_1^2 + \frac{1}{2}\left(r - \frac{2\delta S_1}{D^0}\right)(\eta_2^2 + \eta_3^2) + \frac{1}{2}c\sum_{i=1}^{3}\sum_{\alpha=1}^{3}\nabla_\alpha\eta_i\nabla_\alpha\eta_i + u\sum_{i=1}^{3}\sum_{j=1}^{3}\eta_i^2 + v\sum_{i=1}^{3}\eta_i^4 \right\} \tag{14}$$

The behaviour of the elastic compliance components $\left(\frac{\partial\chi_1}{\partial S_1}\right)_0$ near the transition can be found by following Refs. [12] and [15]. From Figure 1, one can see that the distortion in the LS phase due to the spontaneous strain depends on the sign of δ which can be determined by the experimental result. If δS_1 is negative, $r + \frac{4\,\delta S_1}{D^0}$ approaches zero before $r - \frac{2\,\delta S_1}{D^0}$, so η_1 now is the order parameter and dominate the transition. Such a stress is in favor of the appearance of [1,0,0] state in the LS phase. The critical behaviour will be the same as in the three dimensional Ising model.[12,14] If δS_1 is positive, $r - \frac{2\,\delta S_1}{D^0}$ approaches zero first, the order parameters are then η_2 and η_3 which are in favor of [0,1,0] or [0,0,1] states in the LS phase. The critical behavior is the same as in the three dimensional x-y model. In the S_1-T plane, these two cases correspond to two second order phase transition lines which join at a bicritical point ($S_1 = 0$, $T = T_c$ ($S_1 = 0$)) (See Figure 1 of Ref. [12])

The critical behaviour of the elastic compliance can be derived from the scaling relation of the bicritical point which reads[12]

$$F(T,S_1) \approx |t|^{2-\alpha} f(\hat{S}_1/|t|^{\phi}) \tag{15}$$

where $t = \frac{T - T_c\,(S_1 = 0)}{K_B T}$, $\hat{S}_1 = \frac{S_1}{k_B T}$, α is the specific-heat exponent, and ϕ the crossover exponent. From Eq. (15), we can conclude that the elastic compliance $\left(\frac{\partial\chi_1}{\partial S_1}\right)_0$ in the vicinity of the bicritical point diverges as $|t|^{-\bar{\gamma}}$ with $\bar{\gamma} = 2\phi + \alpha - 2 \simeq 0.4$ (for $n = 3$, $d = 3$, $\alpha \simeq -0.10$ and $\phi \simeq 1.25$).[12,14,17] We can also show that $\left(\frac{\partial\chi_2}{\partial S_2}\right)_0 = \left(\frac{\partial\chi_1}{\partial S_1}\right)_0$, as symmetry demands.

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