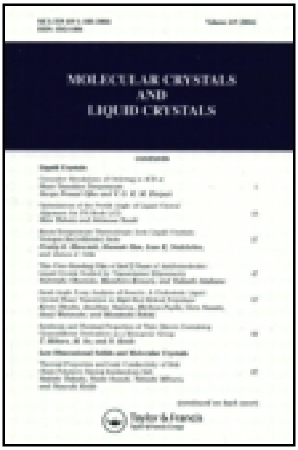

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The Competition Between Long-Range Antiferroelectric Order and Short-Range Antiferroelectric Forces as a Possible Cause of Reentrant Behavior in Polar Liquid Crystals

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The Competition Between Long-Range Antiferroelectric Order and Short-Range Antiferroelectric Forces as a Possible Cause of Reentrant Behavior in Polar Liquid Crystals

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In the present paper one of of possible ways of explanation of reentrant behavior in polar liquid crystals (LC) is proposed. The smectic A-phase (S_{Ad}) existing between high temperature nematic phase (N) and reentrant nematic phase (N_{re}) is considered as a partially bilayer smectic A-structure ($1 < d < 21$) with long-range antiferroelectric order. Each layer of such structure consists of two interpenetrating macroscopic sublayers with mutually opposite alignments of molecular dipoles. In addition, it is assumed that each molecule feels not only some molecular mean field (made by all LC molecules) defining macroscopic layer structure with long-range antiferroelectric order, but also interacts with nearest neighbours by means of short-range antiferroelectric forces of Ising's type. By analogy with McMillan's theory in the approximation of ideal orientational order the single-particle distribution functions for the molecules with different dipole orientations are introduced and self consistent equations determining the smectic order parameter are written. The temperatures of the $N \rightarrow S_{Ad}$ second order transitions together with the temperature dependence of smectic order parameter are determined by the solution of these equations. It is shown that when the increase of short-range antiferroelectric forces with decreasing temperature is sufficiently rapid then the reentrant $S_{Ad} \rightarrow N_{re}$ transition is possible. Thus the appearance of reentrant nematic phase in polar LC can be considered as a consequence of the competition between long-range antiferroelectric order in the S_{Ad}-phase and short-range antiferroelectric forces. In the framework of proposed model the reentrant phase diagram very similar to experimental that for some polar LC is obtained. For the same LC the pressure dependences of the heat capacity discontinuities at the $N \rightarrow S_{Ad}$ and $S_{Ad} \rightarrow N_{re}$ second order phase transitions are determined.

1. INTRODUCTION

The extraordinary phase sequence, namely nematic (N) → smectic A (S_{A_d}) → reentrant nematic (N_{re}) occurs with decreasing temperature in strongly polar liquid crystals (LC) consisting of molecules having end groups (CN or NO_2) with large permanent dipole moment (~4D). This sequence may be observed in binary mixtures[1,2] in pure compounds at high pressure,[3] and, finally even in pure compounds at atmospheric pressure.[4] Furthermore, the more complicated phase sequences, namely $N \rightarrow S_{A_d} \rightarrow N_{re} \rightarrow$ reentrant smectic A (S_{A_1}) and even $N \rightarrow S_{A_d} \rightarrow N_{re} \rightarrow S_{A_d} \rightarrow N_{re} \rightarrow S_{A_1}$[5-8] occur in some polar LC.

X-ray studies[9,10] show that the smectic layer thickness d in the S_{A_d}-phase existing between high temperature nematic phase and reentrant nematic phase is not commensurate with molecular length l and varies for different compounds from 1.1 l up to 1.6 l (hence the S_{A_d}-phase is called "partially bilayer" smectic A-phase) whereas the smectic layer thickness in S_{A_1}-phase is almost equal to the molecular length ($d \approx 0.99l$).[11] It should be added that dielectric studies[12] of the S_{A_d}- and S_{A_1}-phases revealed their antiferroelectric ordering.

A phenomenological description of reentrant behavior in LC has been given by Pershan and Prost.[13] This theory is based on the assumption of existence of a certain density most favourable for smectic ordering. Using this assumption in the framework of Landau's theory the authors not only describe the $N \rightarrow S_{A_d} \rightarrow N_{re}$ phase sequence but also obtained for some LC (at the chosen values of fitting parameters) phase diagrams (in the pressure-temperature variables) very similar to experimental ones. However, Pershan and Prost's theory firstly is not microscopic and secondly it does not explain why the reentrant behavior takes place only in polar LC with partially bilayer S_{A_d}-phase and is not observed in LC with classic monolayer smectic A-phase ($d = 1$).

A first microscopic description of reentrant behavior in polar LC was proposed by de Jeu and Longa.[14] Their theory is based on the assumption of the pairing of molecules (monomers) with antiparallel dipole moments. Each pair (dimer) is a completely symmetrical unit (it's total dipole moment is equal to zero) with the bulk core formed of overlapped hard aromatic parts of molecules and two flexible alkyl chains at the ends. The length of dimer may vary from molecular length l up to $2l$ and corresponds to the smectic layer thickness of the S_{A_d}-phase. Dimer concentration increases with decreasing temperature and above a certain concentration the S_{A_d}-phase can be formed (according to the model unpaired monomers also take part in the formation of this S_{A_d}-phase). Further, an increase of the dimer concentration with decreasing temperature gives rise to enhancement of the repulsive forces between their hard cores that may result in destruction of the smectic layers and appearance of the N_{re}-phase. However it should be noted that the considerable increase of dimer concentration supposed in de Jeu and Longa's theory must give rise to a strong decrease of the dielectric anisotropy of polar LC and a significant increase of smectic layer thickness that is in contradiction with experiment.[15]

More sophisticated theory of reentrant behavior in polar LC was proposed by Indekeu and Berker.[16-19] In this theory the lattice model of polar LC with ideal orientational order is used. The polar LC molecules can be situated at certain discrete positions (with a small step $l' << l$) in the direction perpendicular to smectic layer plane. The intermolecular interaction is defined by model pair potential for modified dipole-dipole interaction. In theory the various configurations of stable groups consisting of three molecules are considered and each molecular triplet is assumed not interact with another molecules. The effective averaged couplings between molecules in each triplet are classified as "strong," "moderate" and "weak". When the strength of moderate coupling is closer to the strength of strong coupling than to that of the weak one, then, according to Indekeu and Berker's theory, the molecular triplets form a two-dimensional polymer with long-range antiferroelectric order in the plane perpendicular to direction $\vec{n}$. The appearance of such a polymer gives rise to the density modulation along the director $\vec{n}$ (i.e. the appearance of a smectic A-phase). In the opposite case, when the moderate coupling is closer to the weak coupling than to the strong, then the nematic phase takes place. By choosing suitable values of interaction constants for the model pair potential, one can describe in the framework of Indekeu and Berker's theory not only the appearance of a N_{re}-phase but also the multiple reentrant phase transitions. However, one can make the following general comment on this theory. It is not clear how the non-interacting (consequently independent of each other) molecular triplets can form an ordered system such as the smectic-A phase is.

In the present paper a simple microscopic description of reentrant behavior in polar LC is proposed. It is assumed that in the S_{A_d}-phase the polar molecules form a partially bilayer smectic A-structure with long-range antiferroelectric order. Each layer of such a structure consists of two interpenetrating macroscopic sublayers with mutually opposite alignments of molecular dipoles. In addition it is supposed that each molecule feels not only some molecular mean field (made by all LC molecules) defining a macroscopic layer structure with long-range antiferroelectric order, but also interacts with nearest neighbours by means of short-range antiferroelectric forces of Ising's type. By analogy with McMillan's theory[20] in the ideal orientational order approximation the single-particle distribution functions for the molecules with different dipole orientations are introduced and self consistent equations determining the smectic order parameter are written. The temperatures of the $N \rightarrow S_{A_d}$ transitions together with the temperature dependence of the smectic order parameter can be determined by the solution of these equations. It is shown that when the increase of the strength of Ising's short-range antiferroelectric forces, caused by decrease of average intermolecular distance with decreasing temperature is sufficiently rapid, then the reentrant $S_{A_d} \rightarrow N_{re}$ transition is possible. Thus the appearance of a reentrant nematic phase in polar LC with the partially bilayer smectic A-phase can be considered as a consequence of the competition between long-range antiferroelectric order and short-range antiferroelectric forces. Also, it is shown that the reentrant $S_{A_d} \rightarrow N_{re}$ transition can be induced by increase of applied pressure. In the framework of the proposed model, one can obtain for some polar LC the reentrant phase diagrams (in variables pressure-temperature) very similar to experimental ones.[21] For the same LC the pressure dependencies of the heat capacity discontinuities at the $N \rightarrow S_{A_d}$ and $S_{A_d} \rightarrow N_{re}$ second order phase transitions as well as the temperature dependencies of smectic order parameter are determined.

2. MICROSCOPIC DESCRIPTION OF S_{A_d}-PHASE WITH DUE REGARD FOR SHORT-RANGE ANTIFERROELECTRIC FORCES OF ISING'S TYPE

Let us consider polar LC consisting of molecules possessing the permanent dipole moment localized at one of the molecular ends ("head") and aligned parallel to the long molecular axis. For simplicity, let us assume that orientational order in the LC is ideal (the long axes of all molecules are oriented parallel to director $\vec{n}$ aligned along the z-axis). This assumption is reasonable enough because the temperatures of experimentally observed $N \rightarrow S_{A_d}$ and $S_{A_d} \rightarrow N_{re}$ transitions are considerably lower than those of isotropic (I)-N transitions in polar LC.[3-6,21]

As it was said in the Introduction the S_{A_d}-phase existing between high temperature nematic phase and reentrant nematic one is the partially bilayer smectic A-phase ($l < d < 2l$) and according to dielectric studies[12] the antiferroelectric ordering takes place in the S_{A_d}-phase. Hence, one can imagine the possible antiparallel packing of polar molecules in the S_{A_d}-phase shown in Figure 1a. This packing corresponds to a partially bilayer smectic A-structure with long-range antiferroelectric order. Each layer of such a structure consists of two interpenetrating macroscopic sublayers with mutually opposite alignments of molecular dipoles. In References 22 and 23, it was shown that by analogy with McMillan's theory in a mean field approximation the bilayer (or partially bilayer) smectic A-structure with long-range antiferroelectric order in polar LC with ideal orientational order can be described by the following single-particle distribution function:

$$f_0(z, S) = A^{-1} \exp[(V_0/k_BT)S\sigma \cos(2\pi z/d)] \qquad (1)$$

where V_0 is the interaction constant determining the strength of the single-particle molecular field pseudopotential, σ is the smectic order parameter, s is the variable equal to $+1$ for the polar molecules with dipole moment aligned parallel to director $\vec{n}$ ("up") and -1 for polar molecules aligned in opposite direction ("down"), z is the coordinate of the molecular centre, T is the absolute temperature of the LC, k_B is the Boltzmann constant, and A is the normalization constant. In addition, by

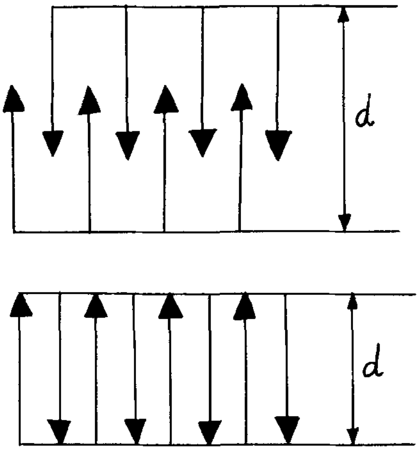

FIGURE 1 a) Partially bilayer smectic A- phase (S_{Ad}) with long-range antiferroelectric order in polar LC ($l < d < 21$); b) Monolayer smectic A-phase (S_{A1}) with short-range antiferroelectric order in polar LC ($d = l'$).

analogy with McMillan's theory[20] the smectic order parameter σ is defined by the self consistent equation

$$\sigma = \langle S \cos(2\pi z/d) \rangle_s = \int_0^d S \cos(2\pi z/d) f_0(z, s)\, dz \Big/ \int_0^d f_0(z, s)\, dz \qquad (2)$$

It should be noted that the single-particle distribution function (1) describes the system of molecules interacting with each other by means of sufficiently long-range forces (dispersion forces, induction forces and dipole-dipole forces). The resulting effect of these forces on the probe molecule is completely defined by a mean molecular field. Really each LC molecule feels not only such a mean molecular field but also interacts to several nearest neighbours by means of short-range (mainly steric) forces. It was proposed by Cladis[1] that such short-range forces can compensate the interactions stabilizing smectic ordering and consequently are responsible for the appearance of the reentrant nematic phase. Therefore we have to take into account the short-range interaction between LC molecules. In order to introduce into our further consideration the short-range forces destabilizing the smectic order in polar LC we can use the idea proposed by Prost[24] of the competition between both partially bilayer and monolayer types of smectic ordering in these LC. This assumption is based on the results of X-ray studies of some polar LC, such as T8[10] which revealed in the N_{re}-phase the coexistence of cybotactic groups of both the already destroyed S_{A_d}-phase and a monolayer S_{A_1}-phase appearing after N_{re}-phase. It was shown in Reference 22 that the S_{A_1}-phase in polar LC can be represented as monolayer ($d = 1$) smectic A-structure with short-range antiferroelectric order shown in Figure 1b. Each layer of such a structure consists of coexisting microscopic domains with mutually opposite alignments of molecular dipoles. Therefore one can conclude that, in polar LC with reentrant behavior, the intermolecular forces causing the destruction of smectic A-structure with long-range antiferroelectric order (S_{A_d}-phase) and stabilizing the structures with short-range antiferroelectric order have to exist. These forces can be described in the simplest way by a short-range antiferroelectric interaction of Ising's type

$$W(S_1, S_2) = V_1 S_1 S_2 \qquad (3)$$

where S_1 and S_2 are the variables introduced above defining the orientations of two neighbouring molecules and V_1 is the interaction parameter depending on average intermolecular distance r. It is easily seen that the interaction (3) corresponds to repulsive forces between neighbouring molecules oriented parallel to each other ($S_1 S_2 = +1$) and attractive those between molecules oriented antiparallel to each other ($S_1 S_2 = -1$). In other words, this interaction promotes development of short-range antiferroelectric order in polar LC. In order to take into account the short-range intermolecular forces in the framework of single-particle description we have to add to the single-particle pseudopotential in Equation (1) the energy of Ising's interaction between a given molecule and all it's nearest neighbours. Then the total energy of molecule with coordinate of molecular centre z and orientation s is given by

$$V(z, S') = -V_0 S\sigma \cos(2\pi z/d) + SV_1 \sum_i S_i, \tag{4}$$

where the sum in the second term is taken over all nearest neighbours of the considered molecule. It is obvious that $\Sigma_i S_i = n(z, s = +1) - n(z, s = -1)$, where $n(z, s = \pm 1)$ are the numbers of nearest neighbours oriented "up" and "down" respectively. If any molecule with centre situated within certain small volume v_0 around a given molecule can be considered as it's nearest neighbour then

$$n(z, s = +1) - n(z, s = -1) = \frac{1}{2} n_0 v_0 (f(z, s = +1) - f(z, s = -1))$$

where n_0 is the average density of molecular number in LC and $f(z, s)$ is the single-particle distribution function with due regard for short-rnage forces of Ising's type. This function can be represented as

$$f(z, S) = A^{-1} \exp \left\{ S(\sigma/t)\cos(2\pi z/d) - \frac{1}{2} S(\alpha/t)[f(z, s = +1) - f(z, s = -1)] \right\} \tag{5}$$

where $t = (k_B T/V_0)$ is the reduced temperature of LC and $\alpha = n_0 v_0 V_1/V_0$. The smectic order parameter σ now is defined by Equation (2) in which the function $f_0(z, s)$ is replaced by $f(z, s)$ and normalization constant A is given by

$$A = \int_0^d f(z, s)\, dz \tag{6}$$

Then the free energy F of our LC is determined by

$$(F/Nk_B T) = (1/2t) \left[\sigma^2 - (\alpha/4d) \cdot \int_0^d [f(z, s = +1) - f(z, s = -1)]^2\, dz \right] - \ln(A/d) \tag{7}$$

where N is the total number of LC molecules.

Equations (2), (5) and (6) completely determine the single-particle distribution function and smectic order parameter for polar LC. In the general case these equations can be solved only numerically and the solution minimizing the free energy at given temperature must be selected from two possible solutions corresponding to nematic phase ($\sigma = 0$) and S_{A_d}-phase ($\sigma \neq 0$). However, if the possible transitions $N \to S_{A_d}$ and $S_{A_d} \to N_{re}$ are assumed to be second order phase transitions (this assumption is valid for the most polar LC with reentrant behavior) then the equations (2), (5) and (6) can be analytically solved in the neighbourhood of the points of these transitions. Let us introduce the new variable $y = 1/2[f(z, s = +1) - f(z, s = -1)]$ which according to (5) must satisfy the equation

$$y = \frac{1}{2}A^{-1} \sum_{s=\pm 1} S \exp\{S(\sigma/t)\cos(2\pi z/d) - S(\alpha/t)y\} \tag{8}$$

Now if the smectic order parameter σ and the variable y are assumed to be small values in the neighbourhood of the possible $N \to S_{A_d}$ transition point (that is valid for the second order phase transition), then with accuracy to small values of first order one can find

$$y = (\sigma/(t + \alpha))\cos(2\pi z/d) \tag{9}$$

Hence, in the neighbourhood of the $N \to S_{A_d}$ transition point the single-particle distribution function can be approximately expressed as

$$f(z, S) = 1 + (S\sigma/(t + \alpha))\cos(2\pi z/d) \tag{10}$$

Substituting expression (10) into Equation (2) one can obtain the equation for small smectic order parameter

$$\sigma = \sigma/2(t + \alpha) \tag{11}$$

which in addition to the zero solution ($\sigma = 0$, N-phase) has a non-zero solution ($\sigma \neq 0$, S_{A_d}-phase) under the condition

$$t = 1/2 - \alpha \tag{12}$$

determining the point of the $N \to S_{A_d}$ second order transition.

The detailed temperature dependence of parameter α will be considered in the next section of present paper. However, even now we can make the reasonable enough assumption that the parameter α (i.e. strength of short-range forces of Ising's type) increases with decreasing temperature because of decrease of average intermolecular distance r. Therefore one can imagine three possible cases shown in Figure 2.

In the first case, parameter α sufficiently slowly increases with decreasing temperature t and crosses the straight line $1/2 - t$ only once; that corresponds to the existence of a single $N \to S_{A_d}$ transition, i.e. the ordinary phase sequence in LC. In the second case, parameter α increases more rapidly with decreasing temperature

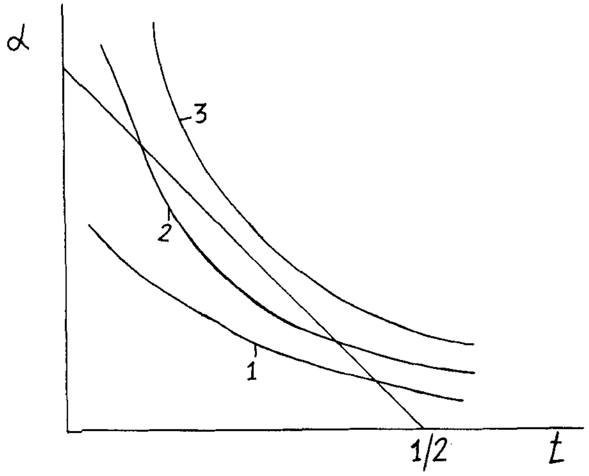

FIGURE 2 The possible temperature dependences of parameter α. 1) slow increase of α with decreasing temperature; 2) more rapid increase of α with decreasing temperature; 3) very rapid increase of α with decreasing temperature.

and crosses the straight line 1/2 − t twice. The first crossing corresponds to the $N \rightarrow S_{A_d}$ transition and the second that corresponds to the transition of the S_{A_d}-phase to the reentrant nematic phase. Finally, in the third case parameter α increases so rapidly with decreasing temperature that the crossing of α and 1/2 − t straight line is impossible, i.e. the S_{A_d}-phase is not observed in polar LC. Thus the existence (absence) of partially bilayer S_{A_d}-phase and the appearance of reentrant nematic phase in polar LC are completely determined by the speed of increase of parameter α (i.e. strength of short-range forces of Ising's type) with decreasing temperature. It should be added that the average intermolecular distance in LC also decreases under pressure. Therefore increasing the applied pressure can stimulate the extra growth of short-range antiferroelectric intermolecular forces (i.e. parameter α) and consequently induce the appearance of N_{re}-phase in polar LC having no reentrant nematic phase at atmospheric pressure.

One of the most important characteristics of the second order phase transitions is the heat capacity discontinuity in the transition point. In order to calculate the heat capacity discontinuity at the second order transition between N- and S_{A_d}-phases let us use the expression (7) for the free energy F which in the neighbourhood of transition point can be represented as

$$F/Nk_BT = a\sigma^2 + b\sigma^4 + \cdots \tag{13}$$

where

$$\begin{aligned} a &= \frac{1}{2t}\left(1 - \frac{1}{2(t + \alpha(t))}\right), \\ b &= 1/64\ (t + \alpha(t))^4 \end{aligned} \tag{14}$$

According to Landau's theory of second order phase transitions[25] the heat capacity discontinuity under constant pressure in the transition point is given by

$$\Delta C_p = T\frac{\left(\frac{\partial a}{\partial T}\right)^2}{2b} \tag{15}$$

Using the expressions (14) and taking into account that $\partial/\partial T = k_B/V_0\, \partial/\partial t$ one can easily obtain

$$(\Delta C_p)_{N\to S_{Ad}} = 2Nk_B\left(1 + \left(\frac{\partial\alpha}{\partial t}\right)_P\right)^2 \tag{16}$$

This expression will be used in the calculations in next section of present paper. Now it should be noted that since $\alpha(t)$ increases with decreasing temperature then $(\partial\alpha/\partial t)_p < 0$ and $(\Delta C_p)_{N\to S_{Ad}} < 2Nk_B$. Thus the heat capacity discontinuity at the $N \to S_{A_d}$ second order transition calculated with due regard for short-range antiferroelectric forces of Ising's type is always smaller than 2 Nk_B this value is given by McMillan's theory for the nematic-smectic A second order transition in LC with ideal orientational order).

At last it should be noted that the average energy for short-range antiferroelectric interaction of Ising's type between given molecule and all it's nearest neighbours is different from zero only in smectic A-phases with long-range antiferroelectric order for which $f(z, s = +1) \neq f(z, s = -1)$. In monolayer smectic A-phases with short-range antiferroelectric order (S_{A_1}) shown in Figure 1b $f(z, s = +1) = f(z, s = -1)$, and consequently the energy of short-range antiferroelectric interaction between a given molecule and all it's nearest neighbours is equal to zero. Possibly this fact can explain the absence of reentrant behavior in LC with a monolayer smectic A-phase.

3. PHASE DIAGRAM FOR THE $N \to S_{A_d}$ TRANSITIONS AND IT'S COMPARISON WITH EXPERIMENT. THE DEPENDENCE OF THE HEAT CAPACITY DISCONTINUITIES ON THE PRESSURE AND TEMPERATURE DEPENDENCE OF THE SMECTIC ORDER PARAMETER

As it was said in previous section of the present paper, the phase polymorphism in polar LC is determined by the dependence of parameters on temperature and pressure. Indeed, the Equation (12) determining the temperature of the $N \to S_{A_d}$ second order transition can be rewritten as

$$T = T^* - \alpha^*[r(P, T)] \tag{17}$$

where $T^* = 1/2(V_0/k_B)$ is the absolute temperature of the $N \to S_{A_d}$ transition in the absence of short-range antiferroelectric forces of Ising's type and $\alpha^*[r(P, T)]$

$= (V_0/k_B)\alpha$. Differentiating Equation (17) with respect to the pressure one can obtain

$$\frac{dT}{dP} = -\frac{d\alpha^*}{dr}\left[\frac{\partial r}{\partial P} + \left(\frac{dr}{dT}\right)\frac{dT}{dP}\right] \tag{18}$$

As was said above, the assumption of increasing parameter α^* with decreasing average intermolecular distance r is sufficiently reasonable. The corresponding dependence of α^* on r can be proposed in the simplest way as $\alpha^* \propto r^{-\beta}$, where β is the unknown for the present parameter. Taking into account that $1/r(\partial r/\partial T) = \gamma/3$ and $-1/r(\partial r/\partial P) = \sigma^*/3$ where γ and σ^* are respectively the LC thermal expansion coefficient and the LC compressibility one can derive from (18) the following equation

$$dT\left\{1 - \left[\left(\frac{\beta\gamma}{3}\right)(T^* - T)\right]^{-1}\right\} = (\sigma^*/\gamma)\, dP \tag{19}$$

Simple integration of this equation gives

$$\left(\frac{\beta\gamma}{3}\right)^{-1} \ln\frac{T^* - T}{T^* - T_1} + T - T_1 = (\sigma^*/\gamma)(P - P_1) \tag{20}$$

where T_1 is the temperature of the $N \rightarrow S_{A_d}$ second order transition at certain fixed (for example, atmospheric) pressure P_1. The Equation (20) determines the dependence of the $N \rightarrow S_{A_d}$ transition temperature T on the pressure P, i.e. allows us to obtain the P-T phase diagram for polar LC. The direct consequence from Equation (20) is the existence of a maximum pressure P_m (this pressure corresponds to a temperature $T_m = T^* - (\beta\gamma/3)^{-1}$ on the $N \rightarrow S_{A_d}$ phase transition line) above which the S_{A_d}-phase is not observed. In the neighbourhood of the (P_m, T_m) point the $N \rightarrow S_{A_d}$ phase transition line is described by simple parabolic equation

$$(P_m - P) = \frac{1}{2}\left(\frac{\beta\gamma^2}{\sigma^*}\right)(T - T_m)^2 \tag{21}$$

Thus Equation (20) describes the P-T phase diagram having parabolic shape in the neighbourhood of it's top (P_m, T_m) that is typical for polar LC with the reentrant nematic phase.

It is clearly seen from Equation (20) that to draw the P-T phase diagram for a given polar LC, we have to know the temperature T_1 of the $N \rightarrow S_{A_d}$ phase transition at certain pressure P_1 and the values of the parameters T^*, $(\beta\gamma/3)$ and (σ^*/γ). For most polar LC, the typical values of the thermal expansion coefficient and compressibility are the following[13]:

$$\gamma \sim 10^{-3}\text{K}^{-1}; \quad \sigma^{*-1} \sim 50 \text{ kbar}; \quad (\sigma^*/\gamma) \sim 20\text{K/kbar}.$$

However, we have no information about the values of T^* and β. In addition, these values can be very different for different materials. Therefore, for to draw the P-T phase diagram for given polar LC we have to know at least two experimental points (P_1, T_1) and (P_2, T_2) for the $N \rightarrow S_{A_d}$ phase transitions.

In order to check the possibility of drawing of the reentrant P-T phase diagram from Equation (20) we used the experimental P-T phase diagram for the polar LC 90CPBB with a reentrant nematic phase.[21] The $N \rightarrow S_{A_d}$ transition point at atmospheric pressure ($T_1 = 468$ K) and the top of the P-T phase diagram ($T_m = 433$ K, $\Delta P_m = P_m - P_1 = 0.54$ kbar) were taken as the first and second experimental points, respectively. Then Equation (20) can be written as

$$(T^* - T_m)\ln\frac{T^* - T_m}{T^* - T_1} + T_m - T_1 = (\sigma^*/\gamma)\Delta P_m \tag{22}$$

This equation was solved at the various values of the ratio (σ^*/γ) (close to the mentioned above value of 20 K/kbar). For each value of (σ^*/γ) the solutions for T^* and $(\beta\gamma/3)$ were determined from the Equation (22) and then the whole P-T phase diagram was drawn from the Equation (20). The best coincidence of the drawn phase diagram with experiment that was obtained at $(\sigma^*/\gamma) = 16$, K/kbar $T^* = 523.5$ K and $(\beta\gamma/3) = 0.0112\ \mathrm{K}^{-1}$ (see Figure 3). It is clearly seen from this figure that almost all experimental points are lying on the calculated curve. It seems to us that this result is hopeful enough.

Now let us determine the heat capacity discontinuities at the $N \rightarrow S_{A_d}$ and S_{A_d}

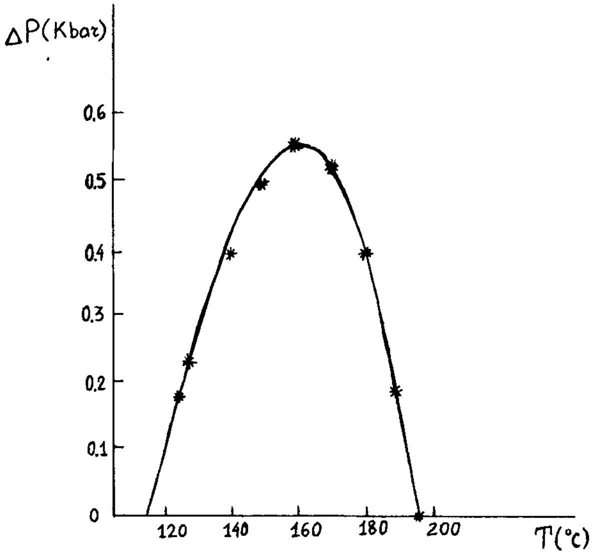

FIGURE 3 The P-T reentrant phase diagram for polar LC 90CPBB. ——— = calculated curve ($T^* = 523.5$ K, $(\sigma^*/\gamma) = 16$ K/kbar, $(\beta\gamma/3) = 0.0122\ \mathrm{K}^{-1}$); * = experimental points.[21]

$\rightarrow N_{re}$ phase transitions. Using the made above assumption that $\alpha^* \propto r^{-\beta}$ one can obtain that

$$\left(\frac{\partial \alpha^*}{\partial T}\right)_P = -\left(\frac{\beta\gamma}{3}\right)\alpha^* = -\left(\frac{\beta\gamma}{3}\right)(T^* - T) \qquad (23)$$

Substituting this relation into Equation (16) we can find the following expression for the heat capacity discontinuity at the $N \rightarrow S_{A_d}$ transition

$$(\Delta C_p)_{N\rightarrow S_{Ad}} = 2Nk_B\left[1 - \left(\frac{\beta\gamma}{3}\right)(T^* - T)\right]^2 \qquad (24)$$

where T is the transition temperature. The pressure dependences of the heat capacity discontinuities at the $N \rightarrow S_{A_d}$ and $S_{A_d} \rightarrow N_{re}$ transitions are shown in Figure 4 (at the values of T^* and $(\beta\gamma/3)$ used in the drawing of the P-T phase diagram shown in Figure 3. It is seen that the heat capacity discontinuities at the both $N \rightarrow S_{A_d}$ and $S_{A_d} \rightarrow N_{re}$ transitions have maxima at atmospheric pressure and almost linearly decrease with increasing pressure achieving the zero value at the top of phase diagram (P_m, T_m). Thus the increase of pressure gives rise to elimination of difference (from thermodynamical point of view) between nematic-, S_{A_d}- and reentrant nematic phase.

Also we determined the temperature dependences of the smectic order parameter by the numerical solution of the Equations (2), (5) and (6). Besides, we used the following dependence of the parameter α on both the pressure and temperature:

$$\alpha(P, T) = \alpha(P_0, T_0)\exp\left[\left(\frac{\beta\sigma^*}{3}\right)(P - P_0) - \left(\frac{\beta\gamma}{3}\right)(T - T_0)\right] \qquad (25)$$

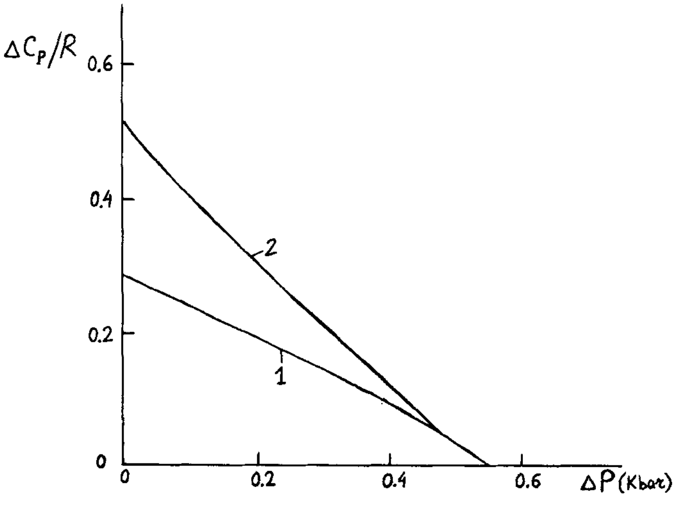

FIGURE 4 The pressure dependences of the heat capacity discontinuities at the $N \rightarrow S_{Ad}$ and $S_{Ad} \rightarrow N_{re}$ second order transitions in 90CPBB. 1) the $N \rightarrow S_{Ad}$ transition; 2) the $S_{Ad} \rightarrow N_{re}$ transition.

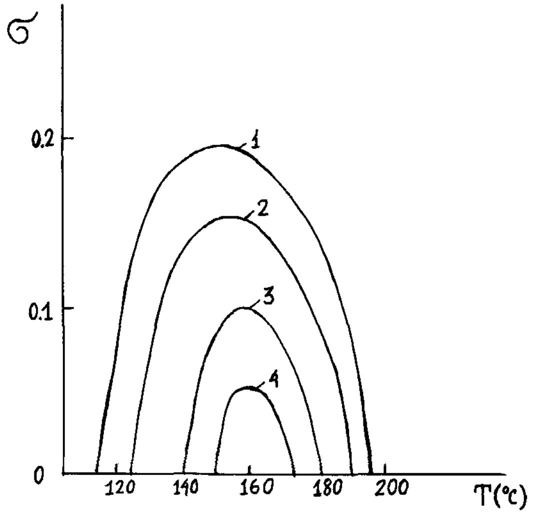

FIGURE 5 The temperature dependences of the smectic order parameter for 90CPBB at the various values of extra pressure. 1) $\Delta P = 0$; 2) $\Delta P = 0.2$ kbar; 3) $\Delta P = 0.4$ kbar; 4) $\Delta P = 0.5$ kbar.

which is a direct consequence of the mentioned above assumption that $\alpha \propto r^{-\beta}$. The obtained temperature dependences of the smectic order parameter at atmospheric pressure as well as at three values of applied pressure ΔP (0.2 kbar, 0.4 kbar and 0.5 kbar) are shown in Figure 5. It is seen that in all cases the smectic order parameter at first increases with decreasing temperature from the zero value at the $N \rightarrow S_{A_d}$ second order transition point. Then it achieves the maximum value and decreases to zero (at the $S_{A_d} \rightarrow N_{re}$ transition point) with further decreasing temperature. Also, it is clearly seen that the maximum value of the smectic order parameter decreases with increasing extra pressure.

Thus all obtained results allow us to conclude that the competition between long-range antiferroelectric order in the S_{A_d}-phase and short-range antiferroelectric forces really can be a possible cause of reentrant behavior in polar LC.

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