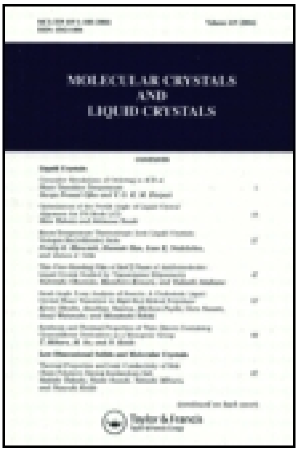


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Unusual Isostructural Phase Transitions Sequence Under External Field Influence

Vladimir A. Konoplev [a] , Vladimir K. Pershin [a] , Roman A. Raewsky [a] & Dmitry E. Isaichenko [a]

[a] Ural State Technical University, Ekaterinburg, 620002, Russia

Version of record first published: 04 Oct 2006

*Mol. Cryst. Liq. Cryst.*, 1997, Vol. 301, pp. 411–417
Reprints available directly from the publisher
Photocopying permitted by license only



# UNUSUAL ISOSTRUCTURAL PHASE TRANSITIONS SEQUENCE UNDER EXTERNAL FIELD INFLUENCE

VLADIMIR A. KONOPLEV, VLADIMIR K. PERSHIN,
ROMAN A. RAEVSKY AND DMITRY E. ISAICHENKO
Ural State Technical University, Ekaterinburg, 620002, Russia



Abstract The influence of an external orienting field on isostructural transformations taking place in the stability area of smectic state is studied on the basis of a broaden version of the de Gennes model of smectic A (Sm) liquid crystal. It is predicted that the external field can suppress the isostructural $Sm_1$–$Sm_2$ phase transition in some systems and, conversely, it can induce the isostructural smectic state in other ones. The most unexpected case includes the situation when both phenomena can be realized in one and the same system, so that two $Sm_1$–$Sm_2$–paranematic points take place in the "field–temperature" phase diagram simultaneously.

## INTRODUCTION

More than a decade ago Shashidkhar et al.[1] reported miscibility, high pressure and X–ray studies of some liquid crystal binary mixtures. These studies showed clearly that for certain concentrations these mixtures exhibit smectic A–smectic A phase transitions (PT). In Reference[2] it was also announced about the first observation of the smectic A–smectic A critical point. Detailed studies showed that the first order PT between smectic phases which have the same symmetry terminates in a critical end point. This feature of the smectic A–smectic A PT is qualitatively reproduced by a broaden version of the de Gennes model[3,4]. The aim of the present paper is investigation within this model of the influence of an external magnetic (or electric) field on isostructural phase transitions taking place in smectic state.

## FORMALISM

The free energy potential of smectic A mesophase in the external field H is taken in the form[3]

$$F = \tau_1 Q^2/2 - \beta Q^3/3 + \gamma Q^4/4 + \tau_2 S^2/2 + bS^4/4 - \chi QS^2 - \mu Q, \quad (1)$$

where positive values $\beta$, $\gamma$, b and $\chi$ are material constants; the value $\mu=\chi_a H^2/3$ ($\chi_a>0$) describes the dimensionless contribution bound up with the action of the external magnetic (or electric) field. Parameters $\tau_k=a_k(T-T_c^k)$, ($a_k>0$, k=1,2) characterize deviation of the system temperature T from temperatures $T_c^1, T_c^2$ of corresponding mean–field phase transitions bound up with the orientational (Q) and translational (S) order parameters in the case when the latters are non–interacting. From a mathematical point of view, the expression (1) corresponds to the specific case of the $X_{1,0}$ type catastrophe[5]. Equations of state corresponding to the relation $\nabla F(Q,S)=0$ describe three namely the smectic A ($S\neq0, Q\neq0$), nematic (N) and paranematic (pN) ($S=0, Q\neq0$ at $\mu\neq0$) or isotropic liquid (IL) ($S=0, Q=0$ at $\mu=0$) states and can be written in the form

$$\gamma Q^3-\beta Q^2+\tau_1 Q-\mu-\chi S^2=0, \tag{2}$$

$$S(\tau_2-2\chi Q+bS^2)=0. \tag{3}$$

Determinant of stability matrix is equal to zero at the condition

$$\tau_1-2\beta Q+3\gamma Q^2-2\chi^2/b=0. \tag{4}$$

According to applied catastrophe theory[5], Eqs. (2)–(4) describe the model separatrix dividing the control parameters space $\{\tau_1, \tau_2, \beta, b, \gamma, \chi, \mu\}$ into open areas with topologically different structure of the thermodynamic potential (1).

Analysis of stability conditions of mesomorphic states shows that there is a region where two real positive decisions of Eqs. (2), (3), corresponding to two different smectic A ($Sm_1$,$Sm_2$) states with the same symmetry, take place. The line of isostructural $Sm_1$–$Sm_2$ PT is described by the system of five equations

$$F_{Sm_1}(Q_1,S_1)=F_{Sm_2}(Q_2,S_2),\quad \nabla F_{Sm_1}(Q_1,S_1)=0,\quad \nabla F_{Sm_2}(Q_2,S_2)=0$$

relative to eleven variables ($Q_1,Q_2,S_1,S_2,\tau_1,\tau_2,\mu,\beta,b,\gamma,\chi$) where $Q_k$, $S_k$ (k=1,2) are the equilibrium values of the order parameters of the $Sm_1$ and $Sm_2$ phases, respectively. Its decision can be found analytically in the following form

$$\tau_1=2\chi^2/b+2\beta^2/(9\gamma)-3\gamma(\tau_2\chi/b-\mu)/\beta. \tag{5}$$

The line of isostructural PT begins in the triple $Sm_1$–$Sm_2$–pN point (TP) with coordinates

$$\tau_2^{TP} = 2\chi\beta/(3\gamma) + 6\chi^3/(b\beta) - 2\chi\sqrt{D}/(b\beta), \tag{6}$$

$$\tau_1^{TP} = -\gamma(\tau_2^{TP})^2/(4\chi^2) + \tau_2^{TP}\beta/(2\chi) + 2\chi\mu/\tau_2^{TP}, \tag{7}$$

where

$$D = 3b^2\beta\{\beta^3/(27\gamma^2) + 2\beta\chi^2/(3b\gamma) - \mu\} + 9\chi^4,$$

and terminates in the end critical point (CP) with coordinates

$$\tau_1^{CP} = 2\chi^2/b + \beta^2/(3\gamma),\ \tau_2^{CP} = b\{\mu - \beta^3/(27\gamma^2)\}/\chi, \tag{8}$$

It can be found from Eqs.(2)–(4) that the coordinates of the Sm–N or Sm–pN tricritical point (TCP) confirm to the following requirement

$$\tau_1^* = -3\gamma(\tau_2^*)^2/(4\chi^2) + \tau_2^*\beta/\chi + 2\chi^2/b, \tag{9}$$

where the value $\tau_2^*$ is dependent on the parameters and, in particular, on the field as

$$b\gamma\chi\tau_2^3 + b\beta\tau_2^2 + 4\chi^3\tau_2 - 4b\chi^2\mu = 0. \tag{10}$$

It can be shown that there can occur none or one TCP at $\mu=0$ and none or two TCP at $\mu\neq0$ on the phase Sm–pN boundary. Moreover, these two points can coincide at some value of the field giving rise to the so called double TCP[3].

## RESULTS AND DISCUSSION

The Sm $(\tau_2,\tau_1)$ phase diagram (PD) at $\mu=0$ and at the following values of the parameters $\beta=1$, $\gamma=2$, b=9, $\chi=1$ is presented in Figure 1a. The curves of first and second order PT are drawn by solid and dashed lines, respectively. Field dependencies of the coordinates of the $Sm_1$–$Sm_2$ end critical point (CP) (the straight chain–dotted line parallel to the $\tau_2$–axis), the $Sm_1$–$Sm_2$–pN triple point (TP) (the dashed parabolic line) and the TCP (the right handside of the dotted parabolic line), calculated according to formulae (6)–(10), are also marked off.

The results of the $(\mu,\tau)$–PD calculations are shown in Figures 2,3. According to the Landau theory, thermodynamic way describing temperature evolution of the specific mesogeneous system corresponds to the straight line directed from the third quadrant to the first one of the Cartesian $(\tau_2,\tau_1)$–plane. The suitable versions of the thermodynamic

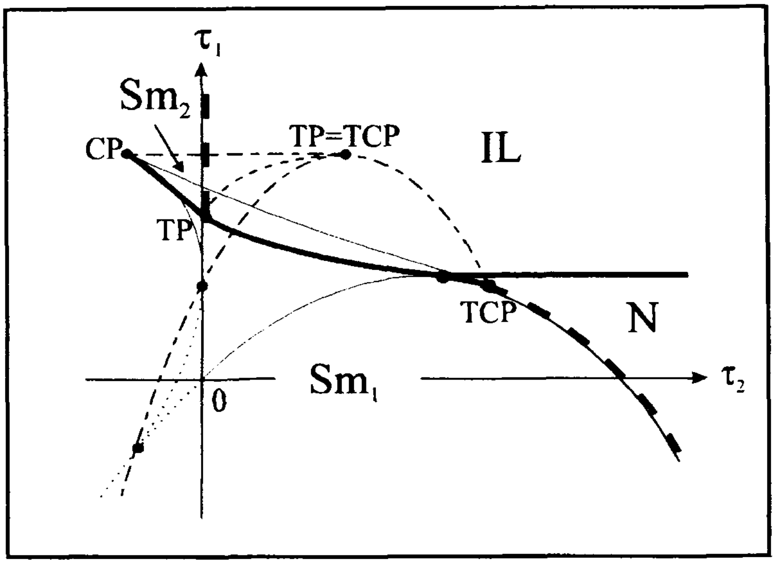


FIGURE 1 The ($\tau_2$, $\tau_1$) phase diagram of smectic A liquid crystal.

ways conformed with appropriate ($\mu$,$\tau$)–PD are shown at the insertions into the same Figures. Figures 2a and 2b give the description of two different mechanisms of smectic phase suppression. The first one complies with the situation when the high–temperature smectic becomes identical to its low–temperature counterpart due to realization of the end $Sm_1$–$Sm_2$ CP (Figure 2a). This mechanism resembles the one observed in Reference[2] experimentally, other than under the influence of the field but at the mixture concentration change. The second mechanism is in accordance with that known as the bounded mesomorphism[6]:the $Sm_2$ phase is suppressed by the field due to formation of the $Sm_2$–$Sm_1$–pN TP at $\mu=\mu_0^{(1)}$ (Figure 2b). Note that at $\mu>\mu_0^{(1)}$ the TCP can be realized on the $Sm_2$–pN phase boundary (Figure 2b) and it is not realized if the thermodynamic way passes through the vertex of parabolic TCP and TP curves in Figure 1. The latter case corresponds to the situation when the $Sm_1$–$Sm_2$–pN TP and the $Sm_1$–pN TCP coincide. Figure 2c describes the ($\mu$, $\tau$)–PD where a new isostructural smectic phase becomes available under the field action (at $\mu=\mu_0^{(2)}$). This effect is also known in physics of partially ordered systems as induced mesomorphism[7]. As it can be seen from this Figure, the further increasing of the field (at $\mu>\mu_0^{(2)}$) leads, as in Figure 2a, to the origin of the end

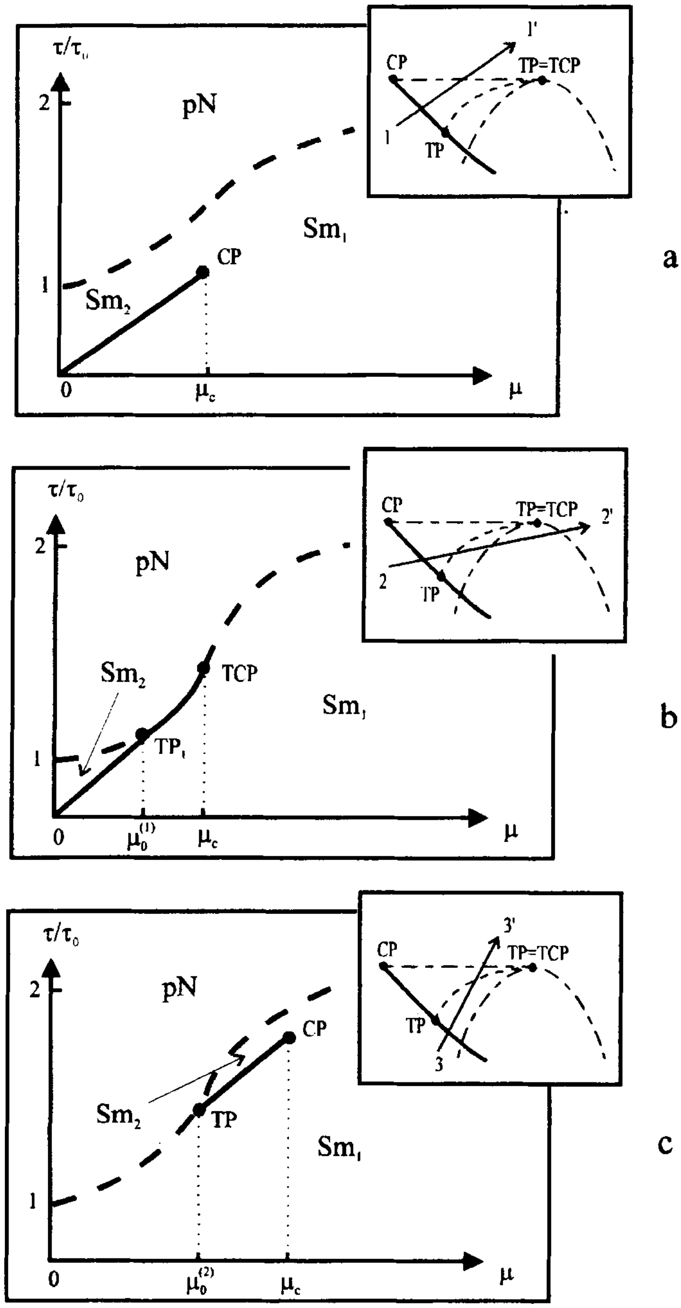


FIGURE 2 The ($\mu$, $\tau$) phase diagrams of smectic A for thermodynamic ways depicted as the arrows 1–1'(a),2–2'(b),3–3'(c) in the insertions.

$Sm_1$–$Sm_2$ CP.

The most intriguing $(\mu,\tau)$–PD is presented in Figure 3. As it can be seen from the insertion into this Figure, the thermodynamic way consistent with this PD has the same features as the ones in Figures 2b and 2c simultaneously. This thermodynamic way crosses twice the TP parabolic curve. The result is that the $(\mu,\tau)$–PD in Figure 3 possesses at the same time the features of the ones in Figures 2b and 2c, i. e. the effects of suppression and subsequent induction of isostructural smectic state can be observed in one and the same system. It can be seen from Figure 3 that at $\mu=0$ the $Sm_1$–$Sm_2$–IL and at $0<\mu<\mu_0^{(1)}$ the $Sm_1$–$Sm_2$–pN PT sequences take place. At $\mu=\mu_0^{(1)}$ the high temperature $Sm_2$ state disappears in the $Sm_1$–$Sm_2$–pN triple point ($TP_1$). At $\mu_0^{(1)}<\mu<\mu_0^{(2)}$ the first order $Sm_2$–pN PT is realized. At $\mu=\mu_0^{(2)}$ the second $Sm_1$–$Sm_2$–pN triple point ($TP_2$) and the $Sm_2$ phase are induced by the field again. At $\mu=\mu_c$ the end $Sm_1$–$Sm_2$ CP appears in which the difference between various smectic states disappears, at $\mu>\mu_c$ the only second order $Sm_1$–pN PT remains.

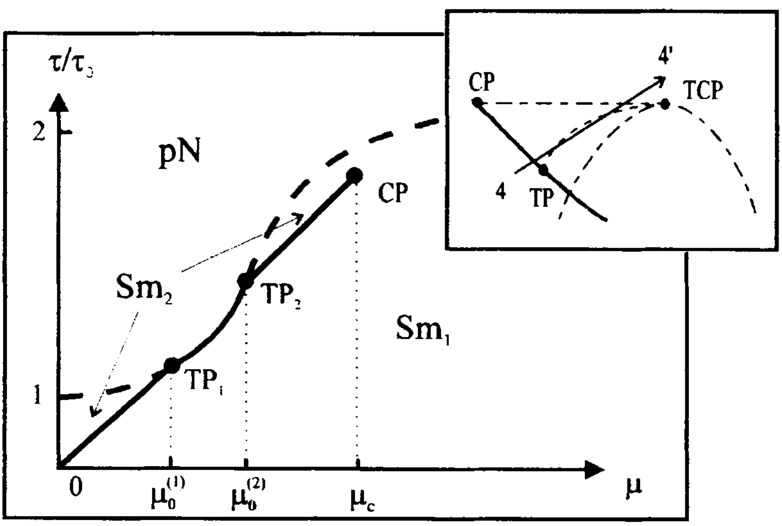


FIGURE 3 The $(\mu, \tau)$ phase diagram of smectic A for thermodynamic way depicted as the arrow 4–4' in the insertion.

## CONCLUSION

The main result of the paper consists in the prediction of the "field–temperature" PD with unusual sequence of isostructural smectic PT: at first, the smectic phase is suppressed by the field and, than, its increase gives rise to induction of the isostructural phase again. Explanation of the topologic structure of this PD lies in the possibility of realization of two effects namely bounded and induced mesomorphism. Both phenomena are observed experimentally under the action of the factor other than the external field (concentration, pressure, chemical molecular modification). Nothing prevents to think that these effects can be realized under the field action. Note that the values of the field $\mu_0^{(1)}$, $\mu_0^{(2)}$ in Figures 2, 3 are not restricted by the parameters of the model under consideration and can, in principal, be essentially smaller than the corresponding value of the Wojtowicz–Sheng effect. This makes it possible to observe the discussed phenomena experimentally.

Support by the RFFI Grant No 95–02–04783 is acknowledged.

## REFERENCES

1. R. Shashidkhar, B. R. Ratna and S. K. Prasad, Mol. Cryst. Liq. Cryst. Lett., 102, 105 (1984).
2. S. Somasekhara and G. Heppke, Phys. Rev Lett., 59, 1209 (1987).
3. V. A. Konoplev, Vl. K. Pershin and R. A. Raevsky, Mol. Cryst. Liq. Cryst., 260, 531 (1995).
4. Vl. K. Pershin, Zhurn.Fiz.Khim., 69, 67 (1995).
5. V. I. Arnold, A. N. Varchenko and S. M. Gussein–Zade, Pecularities of Differentiable Maps (Nauka, Moscow, 1982).
6. R. Shashidkhar, S. Chandrasekhar, Mol. Cryst. Liq. Cryst., 49, 297 (1983).
7. S. Chandrasekhar, N. V. Madhusudana, in Progr. Liq. Cryst., pp. 539–584 (1978).