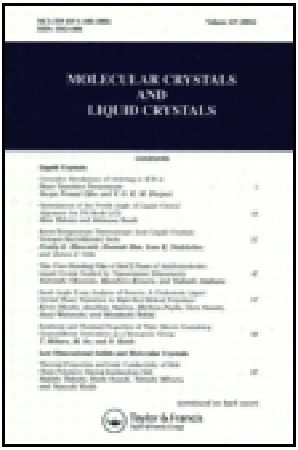

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

On the Landau Description of the Reentrant Behavior in Liquid Crystals

N. A. P. Vaz [a] [b] & J. W. Doane [a]

[a] Department of Physics and Liquid Crystal Institute, Kent State University, Kent, Ohio, 44242

[b] Centro de Fisica da Materia Condensada, INIC, Lisbon, Portugal

To cite this article: N. A. P. Vaz & J. W. Doane (1983): On the Landau Description of the Reentrant Behavior in Liquid Crystals, Molecular Crystals and Liquid Crystals, 101:1-2, 35-45

To link to this article: http://dx.doi.org/10.1080/00268948308072481

Mol. Cryst. Liq. Cryst., 1983, Vol. 101, pp. 35–45
0026-8941/83/1012-0035/$18.50/0

Printed in the United States of America

On the Landau Description of the Reentrant Behavior in Liquid Crystals†

N. A. P. VAZ‡ and J. W. DOANE

Department of Physics and Liquid Crystal Institute, Kent State University, Kent, Ohio 44242

(*Received March 10, 1983*)

A Landau description of the reentrant nematic phase transition has been proposed by Cladis assuming a temperature dependent coupling between the nematic and smectic order parameters. In this paper it is shown that the reentrant phase transition can be driven by a temperature independent coupling between the nematic and smectic order parameters by removing some of the simplifications made by Cladis on the form of the expansion of the free energy excess in terms of the order parameters. A comparison of the results with experimental phase diagrams obtained for mixtures of some cyanobiphenyls, suggests that the coupling should, however, exhibit a weak temperature dependence. The possibility of double reentrancy is also discussed in this theoretical framework.

INTRODUCTION

Since 1975 when reentrant phase transitions were first observed to occur in liquid crystalline materials[1] several theories for the nematic-smectic A-nematic sequence of phase transitions, viz the reentrant nematic polymorphism, have now been proposed. Among them there are phenomenological[2-7] and microscopic[8-11] theories. Although some of them[8,9] have been successful in describing also the double reen-

---

†Work supported in part by the National Science Foundation, Solid State Chemistry grant DMR82-04342.

‡On leave from Centro de Fisica da Materia Condensada, INIC, Lisbon, Portugal.

trancy phenomena,[12] i.e. the nematic-smectic A-nematic-smectic A mesomorphic polymorphism, the understanding of the reentrancy behavior in liquid crystals may still be far from being definitive. One reason is that the class of materials for which reentrant phase transitions may occur is not yet firmly established. In fact, while in the earlier work reentrancy was observed only in materials made up of molecules possessing a strong terminal polar group, Demus and collaborators have recently discovered a reentrant nematic phase in binary systems of terminal nonpolar compounds.[13]

It is therefore natural to expect that, at present, phenomenological theories may still provide valuable insight into the understanding of the reentrant phenomena despite the fact that they give little clues as to the nature of the intrinsic molecular forces responsible for the reentrant behavior.

In this paper we wish to elucidate some aspects of the Landau theory which has been applied by Cladis to describe the reentrant nematic phase transition.[3] In her work, Cladis was successful in predicting the onset of this reentrant phase transition as a result of a coupling between the nematic and smectic order parameters.[3] However, some simplifications on the form of the excess free energy expansion in terms of the order parameters were made which, as a result, lead to the requirement that the coupling constant between the nematic and smectic order parameters should be temperature dependent in order to be able to minimize the free energy excess of the reentrant phase.

By using a more suitable expansion of the free energy excess in terms of the order parameters, we will show that the reentrant phase transition can be driven by a temperature independent coupling between the nematic and smectic order parameters. A weak temperature dependence of the coupling constant may still be assumed but now as a means of producing a better overall agreement between theory and experiments, particularly when these are performed using materials with molecules possessing strong terminal polar groups.

In particular, comparison of the theoretical predictions with experimental results (phase diagrams) obtained for a binary mixture of 8OCB (octyloxycyanobiphenyl) and 6OCB (hexyloxycyanobiphenyl) to which a chiral material, CE2, has been added in different amounts (0–12 wt%) indicate that the coupling constant should exhibit a weak temperature dependence.

The possibility of describing double reentrancy in this framework of the Landau theory is also discussed.

THEORY

Within the usual framework of the Landau theory of phase transitions in liquid crystals, the difference between the free energy per unit mass of the nematic and smectic phases and the isotropic phase, $\Delta F = F_N + F_S - F_I$ is expanded in a power series of the (scalar) nematic order parameter, Q, and the (scalar) smectic order parameter, ψ. In this context the cholesteric phase is suitably described by the same order parameter Q that is associated with the nematic orientational order. Therefore, in what follows, the use of the terms nematic and cholesteric should be considered interchangeable.

Considering a first-order isotropic to nematic phase transition and assuming a second-order nematic to smectic A phase transition as some experimental work has supported,[14] the leading terms in the expansion of the free energy excess are:

$$\Delta F = \tfrac{1}{2}\alpha Q^2 + \tfrac{1}{3}\beta Q^3 + \tfrac{1}{4}\gamma Q^4 + \tfrac{1}{2}a\psi^2 + \tfrac{1}{4}b\psi^4 \qquad (1)$$

where $\alpha = \alpha_0(T - T_{\mathrm{NI}})$ and $a = a_0(T - T_{\mathrm{NA}})$ with T_{NI} and T_{NA} denoting the isotropic to nematic and nematic to smectic A transition temperatures.

The coefficients α_0, γ, a_0 and b are positive while β is a negative constant as is required to ensure a first-order isotropic to nematic phase transition.

Eq. (1) differs from that postulated by Cladis[3] in that we have included a term in Q^3 as full symmetry considerations require. Although the inclusion of this term leads to a somewhat more complicated analytical calculation of the transition temperatures, it will be shown that it is responsible for some qualitative differences in the interpretation of the onset of the reentrant phase.

Assuming now a coupling between the nematic and smectic order parameters,[3] we add, in first approximation, a new term to the free energy excess expressed by Eq. (1):

$$\Delta F = \tfrac{1}{2}\alpha Q^2 + \tfrac{1}{3}\beta Q^3 + \tfrac{1}{4}\gamma Q^4 + \tfrac{1}{2}a\psi^2 + \tfrac{1}{4}b\psi^4 + \tfrac{1}{2}\eta Q^2\psi^2 \qquad (2)$$

where η is the coupling constant. Since we are interested in describing reentrant phase transitions exhibited by mixtures of liquid crystals at constant pressure, we define η as a function of the relative concentration of one of the components, say y, by the following equation:

$$\eta = \eta_0(y - y_0) \tag{3}$$

where y_0 is a fitting parameter.

Once the free energy excess has been postulated, Eqs. (2) and (3), the remaining task is to find the equilibrium solutions for Q and ψ and calculate the phase boundaries. The values of the order parameters below the isotropic phase transition are obtained by minimizing ΔF with respect to Q and ψ. Excluding the trivial solution we get a pair of coupled equations:

$$\begin{aligned} \alpha + \beta Q + \gamma Q^2 + \eta\psi^2 &= 0 \\ a + b\psi + \eta Q^2 &= 0 \end{aligned} \tag{4}$$

which have a solution:

$$\begin{aligned} Q &= \frac{1}{2\gamma'}\left[-\beta + \sqrt{\beta^2 - 4\alpha'\gamma'}\right] \\ \psi^2 &= -(a + \eta Q^2)/b \end{aligned} \tag{5}$$

where $\alpha' = \alpha - a\eta/b$ and $\gamma' = \gamma - \eta^2/b$. In order to ensure that this solution is stable it is required that $\Delta F_{QQ}\Delta F_{\psi\psi} - (\Delta F_{Q\psi})^2 > 0$ where F_{ij} denotes the second partial derivative of ΔF with respect to $i, j \equiv Q, \psi$. The stability criterion is then $\gamma' > 0$ or, equivalent, $\eta^2 < b\gamma$; in other words, the solution is stable in the weak coupling limit.

Since we are assuming a second-order nematic to smectic A phase transition, the phase boundary that delineates the temperature range of the smectic A phase is simply given by $a + \eta Q^2 = 0$ where $a = a_0(T^*_{\mathrm{NA}} - T_{\mathrm{NA}})$ and Q is determined from Eq. (5a) for $T = T^*_{\mathrm{NA}}$. T^*_{NA} is the renormalized T_{NA} transition temperature due to the coupling between the order parameters; clearly, if $T^*_{\mathrm{NA}} \leq T_{\mathrm{NA}}$ then $\eta \leq 0$ and if $T^*_{\mathrm{NA}} > T_{\mathrm{NA}}$ then $\eta < 0$. Since we have introduced the coupling as a means of describing the occurrence of the reentrant nematic phase, its effect should correspond to favoring the stability of the nematic phase over that of the smectic phase.[3] This case corresponds to choosing a positive value for η and $T^*_{\mathrm{NA}} \leq T_{\mathrm{NA}}$.

Incidentally, de Gennes[15] had already discussed the possibility of a coupling between the nematic and the smectic order parameter, though in a different context (actually before the reentrant phase transitions were discovered in liquid crystals). However, with the form of the excess free energy expansion then postulated by de Gennes in which the coupling was negative, T_{NA} would not be renormalized if the nematic to smectic A phase transition were to be of second-order.

We will therefore, in what follows, consider only a positive coupling between the nematic and smectic order parameters: $\eta > 0$, $T^*_{NA} \le T_{NA}$. Starting from $a + \eta Q^2 = 0$, using Eq. (5a) and after some manipulation the renormalized nematic to smectic A transition temperature, T^*_{NA}, can be shown to be a solution of the following equation:

$$\left[\gamma a_0\left(T^*_{NA} - T_{NA}\right) - \eta\alpha_0\left(T^*_{NA} - T_{NI}\right)\right]^2 + \eta\beta^2 a_0\left(T^*_{NA} - T_{NA}\right) = 0 \tag{6}$$

In the absence of coupling, $\eta = 0$, we get $T^*_{NA} = T_{NA}$ as it would be expected. However, if $\eta \neq 0$, Eq. (6) is a quadratic equation in $T^*_{NA}(\eta)$. It is interesting to note that although Eq. (6) does not contain explicitly the coefficient b, its derivation depends on the inclusion of the term $bQ^3/3$ in the free energy excess.

It is now easy to show that Eq. (6) describes a phase boundary containing a reentrant nematic to smectic A phase transition, at least within some choice of the material parameters. If we denote $\delta = (\eta\alpha_0/\gamma a_0) \propto \eta$, $\varepsilon = (\beta^2/\alpha_0\gamma)$, $\Delta = T_C - T_{NA} > 0$ and $t = T_{NA} - T^*_{NA} > 0$ the solution, $t = t(\delta)$, of Eq. (6) is given by:

$$t = \frac{\delta}{2(1-\delta)^2}\left\{\varepsilon + 2\Delta(1-\delta) \pm \sqrt{\varepsilon[\varepsilon + 4\Delta(1-\delta)]}\right\}. \tag{7}$$

Since[16] $\varepsilon = \beta^2/\alpha_0\gamma = 9(T^*_C - T_C)/2 > 1$, where T^*_C is the transition temperature of the first-order isotropic to nematic phase transition and $\delta > 0$, Eq. (7) will describe a reentrant phase transition boundary provided that $1 \le \delta \le 1 + \varepsilon/4\Delta$. Within reasonable limits of the material parameters, say $\varepsilon = 4$ and $\Delta = 10$, Figure 1 shows the predicted phase diagram. Clearly, scaling factors can be introduced to properly adjust the limits of both t and δ. We will not attempt doing so, however, for reasons that will be explained later.

The important feature of Eq. (6), or Eq. (7), is that it predicts a reentrant phase transition even when the coupling constant between the nematic and the smectic order parameters, η or δ, is temperature independent. This feature, as mentioned before, is a direct result of the inclusion in the free energy excess of a term proportional to Q^3.

Before comparing these results with the experimental data, we will make some remarks on the possibility of describing the double reentrant phenomena, i.e., a nematic-smectic A-nematic-smectic A polymorphism. Two ways can be envisaged for that purpose: we may either [see Eq. (3)] let η_0 be a suitable function of the temperature or a more complicated function of the relative concentration of one of the components, or we may include in the expansion of the free energy excess higher order terms for the coupling energy between the order parameters. The first hypothesis bears little interest since one has no simple way of establishing the temperature dependence of η_0. However, it is instructive to analyze the consequences of including in Eq. (2) a coupling term proportional to $Q^3\psi^2$. For the sake of simplicity, we may neglect higher order terms in powers of the two coupling constants, now η and ρ. After performing similar calculations to those used in deriving Eq. (6), we get:

$$(\gamma a - \eta\alpha)^2 + \eta a(\beta - a\rho/2b)^2 = 0 \tag{8}$$

where, as before, $a = a_0(T^*_{NA} - T_{NA})$ and $\alpha = \alpha_0(T^*_{NA} - T_{NI})$. Since Eq. (8), which describes the phase boundary of the smectic A temperature range, now contains cubic terms in T^*_{NA}, it will describe a double reentrancy at least for suitable values of the material parameters.

COMPARISON WITH EXPERIMENTAL RESULTS

The binary mixture 6OCB and 8OCB is known[3,17] to exhibit a reentrant nematic phase transition for concentrations of 6OCB less than ~ 28 wt%. In order to easily produce a family of phase diagrams exhibiting the reentrant phase we have added to this binary mixture 4″-(2-methylbutylphenyl)-4′-(2-methylbutyl)-4-biphenylcarboxylate (CE2) in several different concentrations (0–12 wt%). The changes in the phase diagram that are produced by the addition of CE2 are discussed elsewhere.[18] Of interest here is the fact that since CE2 is a chiral material, by adding it to a binary mixture of 6OCB and 8OCB the nematic phase becomes twisted; twisted nematic or cholesteric phase. The reentrant polymorphism is then that of a reentrant twisted nematic (or cholesteric) phase. This is not an inconvenience, however, since in the framework of the Landau theory we may consider the nematic and the twisted nematic phases indistinguishable; at least for the purposes of this paper.

In Figure 2 (solid dots) we have plotted the experimental data concerning the nematic to smectic A phase boundary in the range of concentration of 6OCB of interest; that for which the reentrant phase is observed. The horizontal axis, y, is the relative concentration of 6OCB; $y = x/(1 - x)$ where x is the weight percent of 6OCB in the binary mixture with 80CB. A simple inspection of Figure 2 shows that the data points are approximately described by parabola curves while the theoretical curve (Figure 1) shows noticeable different magnitudes of the slope of t *vs* δ for the normal and the reentrant phase transitions. We attempted to fit the data to the region of the curve $t = t(\delta)$ close to its apex but the fits were still not acceptable.

In order to improve the fits we could, as mentioned earlier, consider more terms on the expansion of the free energy or let $\eta_0 = \eta_0(t)$ [see Eq. (3)]. The latter appears to be a reasonable assumption since, as discussed by Cladis,[3] the coupling constant may be expected to vary with temperature. The argument resides on the fact that for mixtures of compounds with strong terminal polar groups, pairing of the molecules may be an important factor in discussing the stability of the

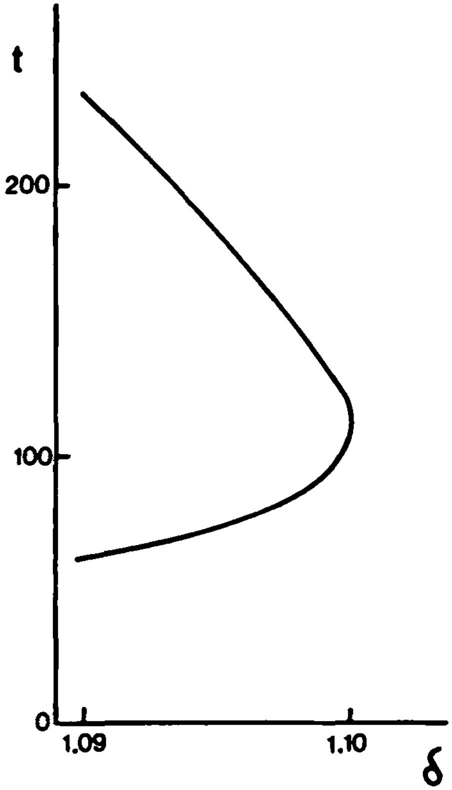

FIGURE 1 Plot of $t = T_{NA} - T_{NA}^*$ versus the parameter δ [see Eq. (7)]. δ is proportional to the relative concentration of one of the components in a mixture and T_{NA} and T_{NA}^* are the non-renormalized and renormalized nematic to smectic A transition temperatures, respectively. The renormalization is due to a temperature independent coupling between the nematic and smectic A order parameters.

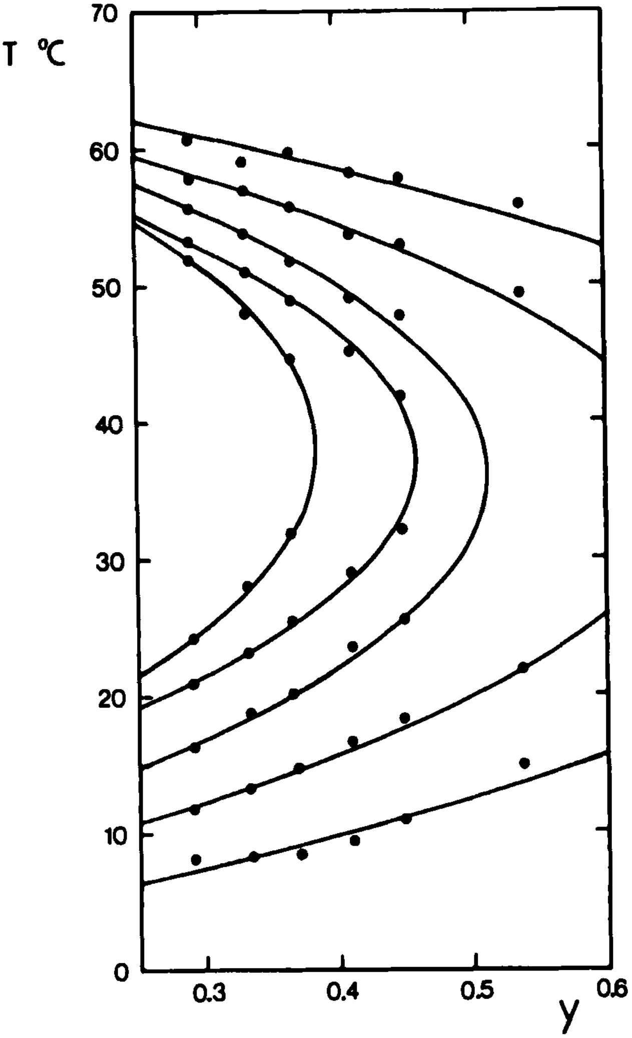

FIGURE 2 Plot of the values of the temperature versus the relative concentration of 6OCB in 8OCB corresponding to the apexes of the fitted curves shown in Figure 3.

smectic phase in favor of the nematic phase. Since this pairing is found to (weakly) change with temperature,[3,19] one may also expect a (weak) temperature dependence of η_0.

Assuming that $\eta_0 \propto (T_0 - T)/T_0$, where T_0 is some adjustable parameter, we were able to produce good agreement between the experimental data and theory (Figure 2, solid lines). The relevant parameters that are obtained from the fitting (which contains four

TABLE I

Values of the relevant fitting parameters associated with each nematic to smectic A phase boundary of a 60CB and 80CB binary mixture to which chiral CE2 has been added in different amounts

	CE2 (wt%)				
	0	3	6	9	12
Y_{apex}	0.385	0.459	0.512	0.659	0.882
T_{apex}(°C)	38.09	37.18	36.14	35.20	34.24
$T_{y=0}$(°C)	66.09	63.72	65.91	66.10	67.14
y_0	−0.327	−0.441	−0.242	−0.196	−0.0738

adjustable parameters) are given in Table I. In particular, the values for the nematic to smectic A transition temperature which are obtained extrapolating to zero (pure 60CB with CE2) are in good agreement with the experimental values determined under the polarizing microscope.

In Table I we also show the values of y_0 [see Eq. (3)] in order to be able to argue in favor of the choice of $\eta \sim y - y_0$ where y is the relative concentration of 60CB, instead of $\eta \sim x - x_0$ where x is the weight percent of 60CB. Fits made with the later assignment of η give values for x_0 which change sign with increasing concentration of CE2. Since this change in sign does not appear reasonable, we have defined $\eta \sim y - y_0$ or, which is equivalent, $\eta \sim N - N_0$ where N is the molecular ratio 60CB : 80CB. Although this choice is in agreement with that of an independent work,[20] the matter of a proper choice of the parameter describing the relative concentration of the components remains an open question.

Finally, it appears instructive to inspect the relation between the values of T_{apex} and Y_{apex} obtained for the family of curves shown in Figure 2. We have plotted in Figure 3 the values of T_{apex} *vs* Y_{apex} given in Table I. This figure shows a monotonic decrease of T_{apex} with increasing values of Y_{apex}.

Since we have generated the family of curves by adding different but small amounts of CE2 to the binary mixture of 60CB and 80CB, we may expect the material parameters to be essentially the same for all samples.

A relation between the values of T_{apex} and $Y_{\text{apex}} \sim \delta_{\text{apex}} \equiv \delta_{\text{A}}$ can then be obtained from Eq. (7):

$$T_{\text{apex}} = T_{\text{NA}} - \frac{\delta_{\text{A}}[\varepsilon + 2\Delta(1 - \delta_{\text{A}})]}{2(1 - \delta_{\text{A}})^2},$$

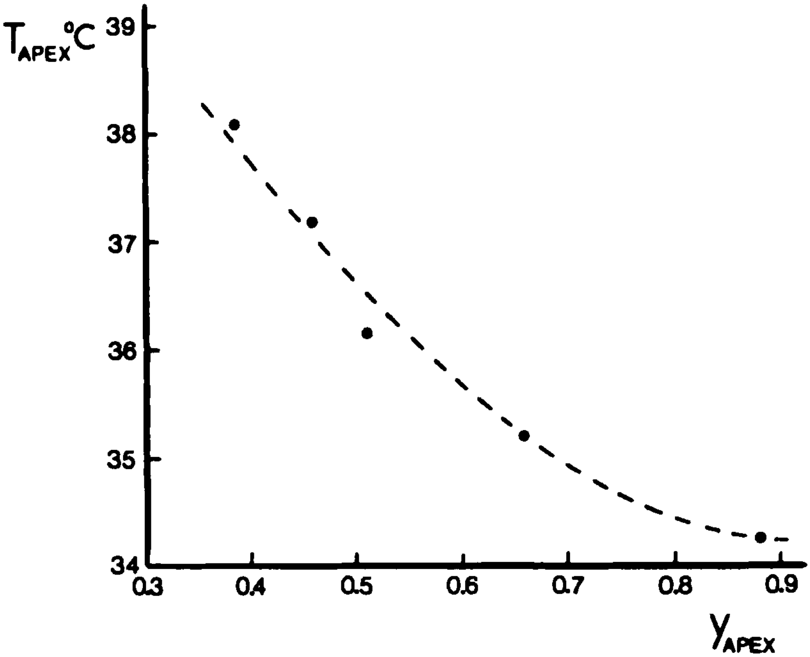

FIGURE 3 Illustrative comparison between the experimentally determined values of the nematic to smectic A transition temperatures (solid dots) obtained for a binary mixture of 6OCB and 8OCB to which CE2 has been added in different amounts and (solid lines) the fitted curves calculated assuming a temperature dependent coupling between the order parameters. y is the relative concentration of 6OCB in 8OCB (wt% 6OCB/wt% 8OCB).

from which it is easy to show that $(dT_{\text{apex}}/d\delta_A) > 0$ when $1 < \delta \leq 1 + \varepsilon/4\Delta$; but this is in contrast with the experimental results (Figure 3). By assuming a weak temperature dependence of the coupling constant the sign of the relative change of T_{apex} with δ_{apex} is reversed and appears then in qualitative agreement with the experimental observations.

CONCLUSIONS

We have shown that the nematic reentrant phase transition can be described within the framework of the Landau Theory of phase transitions as the result of a temperature independent coupling between the nematic and smectic order parameters. However, the agreement between theory and some experimental results is poor. The reason is believed as residing on the fact that the compounds used in the experiments (cyanobiphenyls) have strong terminal polar groups which favor a tendency for molecular pairing and, furthermore, that this pairing is found to be (weakly) temperature dependent. In this case one would expect the coupling between the order parameters to be weakly temperature dependent. Assuming a (weak) temperature dependence of the coupling, good agreement between theory and data was obtained. Further evidence for this assumption is given by the fact that the relation between the values of the temperature and concentration at the apexes of the nematic to smectic A phase boundary of several phase diagrams is only then properly accounted for.

References

1. P. E. Cladis, *Phys. Rev. Lett.*, **35**, 48 (1975).
2. P. S. Pershan and J. Prost, *J. Phys. (Paris)*, **40**, L-27 (1979).
3. P. E. Cladis, *Mol. Cryst. Liq. Cryst.*, **67**, 177 (1981).
4. C. Coulon and J. Prost, *J. Phys. (Paris)*, **42**, L-244 (1981).
5. N. A. Clark, *J. Phys. (Paris)*, **40**, C3-345 (1979).
6. G. Heppke and F. Schneider, *Proc. Int. Liquid Crystal Conf., Bangalore*, Heyden, London (1980), p. 147.
7. J. Billard, *Proc. Int. Liquid Crystals Conf., Bangalore*, Heyden, London (1980), p. 155.
8. G. R. Luckhurst and B. A. Timimi, *Mol. Cryst. Liq. Cryst. Lett.*, **64**, 253 (1981).
9. N. A. Berker and J. S. Walker, *Phys. Rev. Lett.*, **20**, 1469 (1981).
10. K. Hida, *J. Phys. Soc. Jap.*, **50**, 3869 (1981).
11. L. Longa and W. H. de Jeu, *Phys. Rev.*, **A26**, 1632 (1982).
12. F. Hardouin, G. Sigaud, M. F. Achard and H. Gasparoux, *Sol. St. Commun.*, **30**, 295 (1979).
13. G. Pelzl, S. Diele, I. Latif, W. Weissflog and D. Demus, *Cryst. Rev. and Technol.*, **17**, 78 (1982).
14. G. B. Kasting, K. J. Lushington and C. W. Garland, *Phys. Rev.*, **B22**, 321 (1980).
15. P. G. de Gennes, *Mol. Cryst. Liq. Cryst.*, **12**, 193 (1974).
16. P. G. de Gennes, "The Physics of Liquid Crystals" (Clarendon, Oxford, 1974).
17. P. E. Cladis, D. Guillon, F. R. Bouchet and P. L. Finn, *Phys. Rev.*, **A23**, 2594 (1981).
18. N. A. P. Vaz, Z. Yaniv and J. W. Doane, *Mol. Cryst. Liq. Cryst. Lett.*, **92**, 75 (1983).
19. N. A. P. Vaz, Z. Yaniv and J. W. Doane (submitted for publication).
20. A. R. Kortan, H. V. Kanel, R. J. Birgeneau and J. D. Litster, *Phys. Rev. Lett.*, **47**, 1206 (1981).