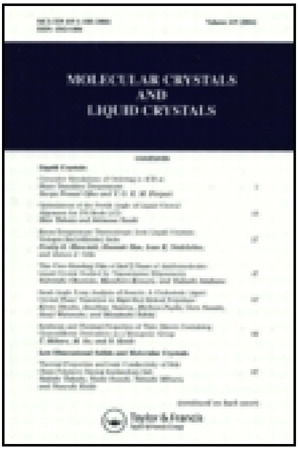

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

On the Transition between Cholesteric and Nematic Phases in Magnetic Field

Mamoru Yamashita [a] , Hatsuo Kimura [a] & Huzio Nakano [a]
[a] Department of Applied Physics, Nagoya University, Nagoya, 464, Japan
Version of record first published: 14 Oct 2011.

To cite this article: Mamoru Yamashita , Hatsuo Kimura & Huzio Nakano (1981): On the Transition between Cholesteric and Nematic Phases in Magnetic Field, Molecular Crystals and Liquid Crystals, 68:1, 79-87

To link to this article: http://dx.doi.org/10.1080/00268948108073555

Mol. Cryst. Liq. Cryst., 1981, Vol. 68, pp. 79–87
0026-8941/81/6801-0079 $06.50/0

On the Transition between Cholesteric and Nematic Phases in Magnetic Field†

MAMORU YAMASHITA, HATSUO KIMURA and HUZIO NAKANO
Department of Applied Physics, Nagoya University, Nagoya 464, Japan.

(*Received July 21, 1980*)

Singularities at the critical lines bounding the cholesteric and nematic phases on the magnetic field versus temperature plane are investigated. Critical exponents, α and γ, of the specific heat and magnetic susceptibility are found both unities. By regarding the inverse of pitch of the cholesteric structure as an order parameter, it is found that the exponents β and δ are zero and infinity, respectively, and these exponents satisfy the scaling relations, $\alpha + 2\beta + \gamma = 2$ and $\alpha + \beta(\delta + 1) = 2$. In relation to the discommensurate charge density wave in layer structure materials, it is noted that the transition from the nematic to cholesteric phase occurring with the change of magnetic field and/or temperature is interpreted as a condensation process of solitons.

1 INTRODUCTION

A magnetic (electric) field as applied to liquid crystal molecules exerts torques to the component molecules. In case of positive anisotropy of diamagnetic susceptibility of the molecule, it has been shown that the cholesteric phase is wound off by the applied magnetic field H perpendicular to the pitch, and changes to a nematic phase as the field reaches a critical field.[1] This fact has been ascertained experimentally.[2,3] We discuss this phase transition in this paper.

The critical value, H_c of the field at which the phase transforms is inversely proportional to the pitch p_0 at no magnetic field.[1] The pitch p_0 varies monotonically with temperature and changes sign at a certain temperature in some cases.[4] In the phase diagram on the field versus temperature plane the cholesteric and nematic phases are bounded by critical lines, at which phase transitions occur. In Section 2 we discuss the singularities near these critical lines,

† This work was reported at the 8th International Liquid Crystal Conference June 30–July 4, 1980 titled as "Effect of the Magnetic Field on the Cholesteric Phase."

where the specific heat and the magnetic susceptibility are found to diverge with the exponents, unity, in the cholesteric side but no singularity in the nematic side. At the intersection point of the two critical lines, any physical quantities do not diverge.

The elastic free energy[5] on which our discussions are based is essentially similar to the free energy of the charge density wave (CDW) in some layer structure materials introduced by McMillan.[6] In Section 3 the cholesteric to nematic phase transition is investigated on the basis of the theory of CDW. The excitation energy of soliton in the nematic phase vanishes at H_c and the transition to the cholesteric phase can be regarded as a spontaneous production of solitins or a condensation of solitons. The density of solitons is determined from the balancing of the excitation energy or chemical potential of soliton with the interaction energy between solitons. Finally discussion and some concluding remarks are given in Section 4.

2 PHASE DIAGRAM AND CRITICAL SINGULARITIES

The free energy of the cholesteric phase is expressed in terms of the director field $\mathbf{n}(\mathbf{r})$ as[5]

$$F = \tfrac{1}{2}\int d^3r[K_1(\nabla\cdot\mathbf{n})^2 + K_2\{\mathbf{n}\cdot(\nabla\times\mathbf{n}) + q_0\}^2 + K_3(\mathbf{n}\cdot\nabla\mathbf{n})^2 - \chi_a(\mathbf{H}\cdot\mathbf{n})^2], \tag{1}$$

where K_1, K_2 and K_3 denote the elastic constants for splay, twist and bend distortions, respectivley, χ_a the anisotropy of diamagnetic susceptibility and q_0 the inverse of pitch p_0 multiplied by 2π. We assume the twist axis of the cholesteric phase is in the direction of z-axis, the magnetic field $\mathbf{H}$ in that of y-direction and a positive anisotropy, $\chi_a > 0$.

For the preliminary of following discussions, we review the cholesteric to nematic phase transition.[1] The director field $\mathbf{n}$ is expressed in terms of an angle $\phi(z)$ of $\mathbf{n}$ with the x-axis around the pitch axis as

$$(n_x(z), n_y(z), n_z(z)) = (\cos\phi(z), \sin\phi(z), 0). \tag{2}$$

By substituting (2) into (1), the free energy is rewritten down as

$$F = \frac{K_2S}{2}\int dz\left[\left(\frac{d\phi}{dz} - q_0\right)^2 - \xi^{-2}\sin^2\phi\right], \tag{3}$$

where S is the cross-section of the system and ξ the magnetic coherence length given by

$$\xi = (K_2/\chi_a)^{1/2}H^{-1}. \tag{4}$$

The stationary condition with $\phi(z)$, $\delta F/\delta\phi = 0$, leads to

$$\frac{d^2(2\phi)}{dz^2} + \xi^{-2}\sin(2\phi) = 0, \quad (5)$$

which is no other than a static sine-Gordon equation. The periodic solution of Eq. (5) is obtained as

$$\sin\phi(z) = \mathrm{sn}\left(\frac{z}{\kappa\xi}\right), \quad (6)$$

where sn u is Jacobi's sn-function and κ is a constant satisfying $0 < \kappa \leq 1$. The pitch p is determined from (6) as

$$p = 4\xi\kappa K(\kappa), \quad (7)$$

where $K(\kappa)$ denotes the complete elliptic integral of first kind. The free energy per unit volume is calculated from (3) and (6) as

$$g = \left(\frac{K_2 q_0^2}{2}\right)\left\{1 - \frac{\pi}{K(\kappa)}(q_0\xi\kappa)^{-1} + \left(\frac{2E(\kappa)}{K(\kappa)} - 1\right)(q_0\xi\kappa)^{-2}\right\}, \quad (8)$$

where $E(\kappa)$ is the complete elliptic integral of second kind. The minimum condition for g leads to the value of κ given by

$$E(\kappa)/\kappa = \frac{\pi q_0 \xi}{2}. \quad (9)$$

By inserting from (9) into (8), the free energy density for the cholesteric phase is obtained as

$$g_{ch} = \frac{K_2 q_0^2}{2}(1 - (q_0\xi\kappa)^{-2}). \quad (10)$$

The pitch p determined from Eqs. (7) and (9) increases proportionally with the magnetic field and diverges at a critical field H_c given by

$$H_c = \frac{\pi}{2}\left(\frac{K_2}{\chi_a}\right)^{1/2} q_0. \quad (11)$$

The inverse of pitch in the cholesteric phase is found to change monotonically with temperature T and changes sign at a certain temperature T^* in some cases[4] of pure compounds as well as binary mixtures, in such a way as shown in Figure 1. By taking into consideration of this fact with Eq. (11), we obtain the phase diagram on H-T plane as shown in Figure 2, where N represents the nematic phase, Ch_+ and Ch_- the cholesteric phases wound inversely with each other and I and Cr the isotropic and crystalline phases, respectively. Phase boundaries between the cholesteric and nematic phases are critical lines. Some experiments[3] evidence such a phase diagram.

We can discuss the singularities on the basis of Eqs. (9) and (10). The susceptibility is obtained as

$$\begin{aligned} \chi &= \partial^2 g_{ch}/\partial H^2 \\ &\sim \chi_a E^2(\kappa)\kappa^{-1}K^{-3}(\kappa)\mathrm{d}K/\mathrm{d}\kappa \\ &\sim |H_c - H|^{-1}\ln^{-2}|H_c - H|. \end{aligned} \tag{12}$$

The temperature dependence of the free energy (10) is exclusively due to that of q_0. On the basis of relations (9) and (10), it is seen that the specific heat C depends on the field, similarly to χ, in the form

$$\begin{aligned} C &= \frac{\partial^2 g_{ch}}{\partial T^2} \\ &\sim |H_c - H|^{-1}\ln^{-2}|H_c - H|. \end{aligned} \tag{13}$$

By making use of (11), the temperature dependences of the susceptibility and the specific heat at a constant field are found as

$$\chi \sim |T - T_c|^{-1}\ln^{-2}|T - T_c|, \tag{14}$$

$$C \sim |T - T_c|^{-1}\ln^{-2}|T - T_c|, \tag{15}$$

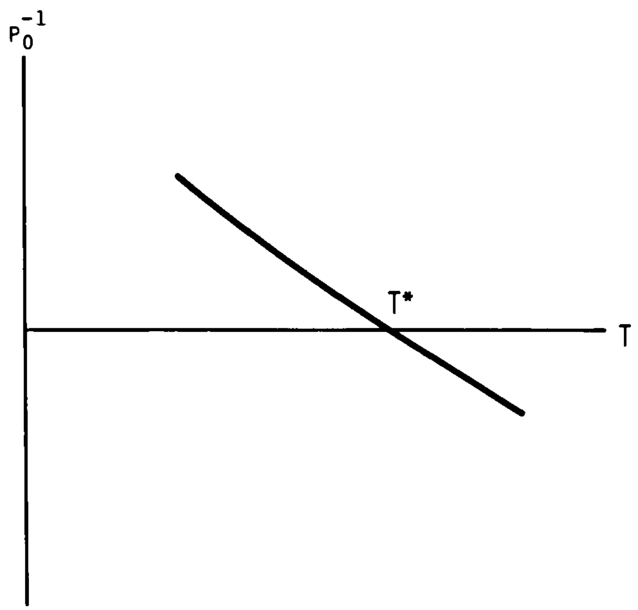

FIGURE 1 Relation of the inverse of pitch to the temperature in the case that the sign of the pitch changes at T^*.

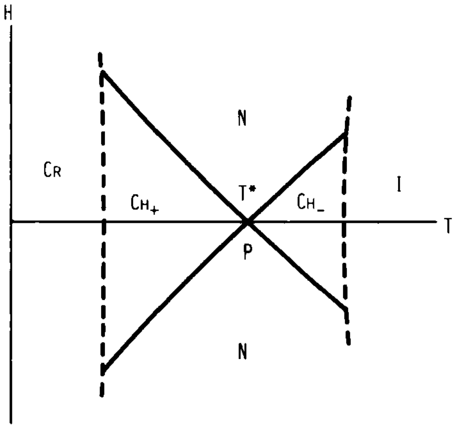

FIGURE 2 Phase diagram on the magnetic field versus temperature plane, corresponding to the same case as in Figure 1.

where T_c is given by

$$H = \pi/2(K_2/\chi_a)^{1/2} q_0(T_c). \tag{16}$$

The critical exponents α and γ are both regarded to be unities according to (14) and (15). By regarding the inverse of pitch, q, as an order parameter, the exponent β and δ are found to be zero and infinity, respectively, because we have[1] $q \sim \ln^{-1} |T - T_c|$ and $q \sim \ln^{-1} |H - H_c|$. These exponents satisfy the scaling relations[7]

$$\alpha + 2\beta + \gamma = 2,$$
$$\alpha + \beta(\delta + 1) = 2. \tag{17}$$

Although the inverse of pitch is not directly equal to a quantity conjugate to the magnetic field, it is related to $\partial g_c/\partial H$ by the equation

$$\frac{q}{\pi} = 2^{-1}(\chi_a K_2)^{-1/2}\left(\frac{H}{H_c}\right)\left(\frac{\partial g_c}{\partial H} + \chi_a H \kappa^{-2}\right). \tag{18}$$

The singularities mentioned above appear only in the cholesteric phase near the critical line and no singularity does in the side of nematic phase. It can be shown from the free energy (1) that the nematic phase is stable even if the magnetic field is smaller than the critical field and insufficient to lower the free energy of nematic phase below that of cholesteric phase, because the correlation functions of fluctuations of the director field **n** are found to have Ornstein–Zernike's type for non-vanishing magnetic field and even in the presence of q_0 in (1).

Next, we notice a peculiar feature at the intersection point P of the critical lines in Figure 2. The free energy (11) is singular on both of the critical lines except for P, because q_0 in (11) vanishes at the point P. Along the line passing P, the free energy (11) is non-singular, so long as the line never crosses either of the two critical lines.

3 SOLITON CONDENSATION

In the previous section, the divergence of the cholesteric pitch is identified with the cholesteric to nematic phase transition. In this section, we investigate the transition from the side of the nematic phase.

As mentioned above, the nematic phase is stable even if the magnetic field is smaller than the critical field. Now we investigate the excitation of solitons in the nematic phase. One soliton solution of the stationary condition (5) for $\phi(z)$ is obtained as

$$\phi = 2\tan^{-1}\exp\left(\frac{\pm z}{\xi}\right) - \frac{\pi}{2}, \tag{19}$$

where the boundary condition is given as $\phi = \pi/2$ and $-\pi/2$ at $z = \infty$ and $-\infty$, respectively. The plus and minus signs on the exponent correspond to the soliton and anti-soliton, respectively. By substituting (19) into (3), the excitation energy ΔF is obtained as

$$\Delta F = 2\sqrt{K_2\chi_a}\; S\,(H \mp H_c). \tag{20}$$

Thus, the excitation energies of soliton and anti-soliton are unequal and the soliton one vanishes at the critical field. The cholesteric solution (6) under the condition (9) coincides with one soliton solution (19) with κ equal to unity. If the interaction between solitons could be neglected, many solitons will be produced as H reaches H_c. However, the repulsive interaction[9] brings about a free energy of a many soliton state larger than the sum of individual soliton energies. If we regard ΔF as the chemical potential of soliton, the transition from the nematic to cholesteric phases can be considered as a condensation of solitons, where the soliton density equal to q/π (or $2/p$) is determined by the balancing between the chemical potential and the interactions of solitons. By the use of (7), the free energy density (8) can be rewritten down as

$$g = \frac{K_2 q_0^2}{2}\left\{1 - \left(\frac{\pi}{2\kappa}\right)^2\left(\frac{H}{H_c}\right) + \left(\frac{HE(\kappa)\kappa}{H_c} - 1\right)\frac{q}{q_0}\right\}, \tag{21}$$

where

$$\frac{q}{q_0} = \left(\frac{\pi}{2}\right)^2\left(\frac{H}{H_c}\right)/(\kappa K(\kappa)). \tag{22}$$

For small q ($\kappa \sim 1$), g is reduced to

$$(g - g_{nc}) \simeq \left(\frac{\Delta F}{S}\right)\frac{q}{\pi}, \tag{23}$$

where g_{nc} equal to $(1 - \pi^2/4)$ is the free energy density of the nematic phase at the critical field H_c. The relation between g and q is shown in Figure 3 for several values of the magnetic field. For the case $H > H_c$, the free energy is minimum at $q = 0$ and the nematic phase is realized. For $H < H_c$ a non-vanishing value of q is realized, corresponding to the cholesteric phase characterized by the pitch (7) with (9). The expression (23) for the excess free energy density linear with q is regarded as the contribution of free solitons. The range in which the linear free energy (23) is valid increases with the magnetic field. This is due to the fact that the spread of a soliton equal to ξ is inversely proportional to the magnetic field and consequently the interaction decreases with the magnetic field. In any way, the repulsive interaction between solitons raises the free energy from the linear value (23).

Heretofore, q is regarded as an order parameter. The field conjugate to q is the chemical potential ΔF, which depends linearly on H, as shown in (20). In this respect, the exponents β and δ obtained in the previous section is regarded to be reasonable, by taking also into consideration (18).

The free energy (3) is similar to that introduced by McMillan[6] to investigate the commensurate-incommensurate transition of CDW in the layer structure

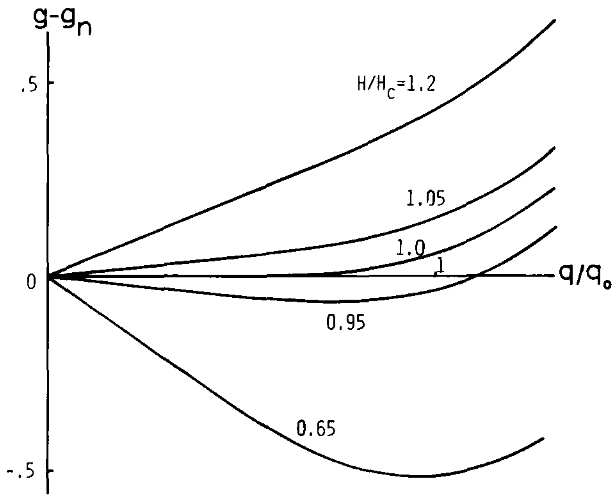

FIGURE 3 Excess free energy density as a function of pitch for various values of magnetic field, where g_n denotes the free energy density of the nematic phase obtained from (21) with $\kappa = 1$ and $q = 0$. As the unit of free energy, $K_2 q_0^2/2$ is utilized.

materials. The physics in those materials is quite different from the present one but both the problems are mathematically equivalent. In CDW, the incommensurate phase is regarded as condensed phase of discommensurations which correspond to the solitons in the present case.

4 DISCUSSION AND CONCLUDING REMARKS

We have presented the phase diagram on the magnetic field versus temperature plane for cholesterics, where the critical phenomena near the boundaries between the cholesteric and nematic phases were investigated. The phase transition was also investigated as a condensation of solitons by comparing with the theory of CDW in the layer structure materials.

Lubensky[10] has shown that the cholesteric phase is unstable with respect to the fluctuation of director field and can only be stabilized through the boundary condition. On the other hand, the present authors[11] have shown that the stability is recovered even by a small magnetic field. Thus, the phase transition from the cholesteric to nematic phases can be recognized as a phase transition in the sense of thermodynamics of an infinite system.

On the basis of the expression for the free energy of distortion, no singularity has been found near the phase boundary in the side of nematic phase. However, the excitation energy of soliton at the nematic phase vanishes at the critical point, where a central peak is expected to appear in the optical scattering intensity. In this respect, it is expected that the critical region is narrow because the excitation energy of soliton is proportional to the cross-section of the system.

The authors would like to thank Dr. Prost, for his valuable discussion, who kindly informed his interesting investigation[12] on dynamics of cholesteric liquid drop placed on rubbed glass surface.

References

1. P. G. de Gennes, *Solid State Commun.*, **6**, 163 (1968). R. B. Meyer, *Appl. Phys. Letts.*, **12**, 281 (1968).
2. E. Sackmann, S. Meiboon and L. C. Snyder, *J. Am. Chem. Soc.*, **89**, 5981 (1967). G. Durand, L. Leger, F. Rondelez and M. Veyssie, *Phys. Rev. Letts.*, **22**, 227 (1979). R. B. Meyer, *Appl. Phys. Letts.*, **14**, 208 (1969). G. H. Heilmeier and J. E. Goldmacher, *J. Chem. Phys.*, **51**, 1258 (1969). F. J. Kahn, *Phys. Rev. Letts.*, **24**, 209 (1970).
3. J. J. Wysocki, J. Adams and W. Haäs, *Phys. Rev. Letts.*, **20**, 1024 (1968). H. Baessler and M. M. Labes, *Phys. Rev. Letts.*, **21**, 1791 (1968).
4. H. Baessler and M. M. Labes, *J. Chem. Phys.*, **52**, 631 (1970). Y. Uematsu and I. Uematsu, *ACS Symposium Series 74*, ed. A. Blumstein (American Chemical Soc., Washington, D.C., 1978), 136. H. Kimura, M. Hosino and H. Nakano, *J. de Phys. (Paris)*, **40**, C3-174 (1979), and works cited therein.
5. F. C. Frank, *Discuss, Farady Soc.*, **25**, 19 (1958).
6. W. L. McMillan, *Phys. Rev.*, **B14**, 1496 (1976).

7. H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Clarendon Press, Oxford, 1971), p. 185.
8. P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon Press, Oxford, 1974), p. 248.
9. J. Rubinstein, *J. Math. Phys.*, **11**, 258 (1970).
10. T. C. Lubensky, *Phys. Rev. Letts.*, **29**, 206 (1972).
11. M. Yamashita, H. Kimura and H. Nakano, *Prog. Theor. Phys.*, **64**, 1079 (1980).
12. J. Prost and H. Gasparoux, *Mol. Cryst. and Liq. Cryst.*, **22**, 25 (1973).