RAPID COMMUNICATIONS

PHYSICAL REVIEW E VOLUME 51, NUMBER 3 MARCH 1995

Mean-field phase diagram of a coupled XY-Ising model for discotic liquid crystals

M. Hébert and A. Caillé
Centre de Recherche en Physique du Solide and Département de Physique, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1
(Received 9 September 1994)

A simple model Hamiltonian is derived to describe the hexagonal disordered D_{hd} and hexagonal ordered D_{ho} columnar phases of discotic liquid crystals with a restricted set of parameters. Characterizing a rigid helical column by an XY-like angular variable and by an Ising-like helicity variable reduces the three-dimensional problem to a coupled XY-Ising Hamiltonian on a triangular lattice. A Landau-type mean-field free energy expansion for two kinds of order parameter is described. The period-3 phase diagram exhibits many types of phases including those with total Ising (helicity) disorder with XY order. This feature is proposed as the structure of the hexa(hexylthio)triphenylene (HHTT) compounds in the D_{hd} phase. The phase diagram also shows phases with two columns of opposite helicity to the third one and phases where 1/3 of the columns have helicity disorder. These helicity states are relevant to the D_{ho} phase of (HHTT) compounds.

PACS number(s): 61.30.Cz, 64.70.Md, 75.10.Dg

Recent experiments performed on discotic liquid crystalline compounds [such as hexa(hexylthio)triphenylene (HHTT)] have revealed interesting phases [1,2]. At first and relevant to our study, these experiments report the characteristics of the phases exhibited by the HHTT compound [1]. Apart from the high temperature isotropic liquid I phase ($T>93\,^{\circ}$C) and the low temperature monoclinic crystal K phase ($T<62\,^{\circ}$C), *two* intermediate columnar liquid crystalline phases are encountered. At $T\simeq 93\,^{\circ}$C, the disklike HHTT molecules form columns themselves arranged on a triangular lattice. This liquid crystalline hexagonal disordered discotic (D_{hd}) phase is characterized by the long-range triangular order of the positions of the columns and liquidlike [3] positional and orientational order of the molecules within a column. As the temperature is further reduced ($T\simeq 70\,^{\circ}$C), the system enters a new phase (the discotic hexagonal ordered D_{ho} or H liquid crystalline phase) which was viewed as a simultaneous ordering of the intracolumnar position and orientation of the molecules (an order-disorder transition within columns, in a system that retains a two-dimensional array of columns). We advocate that the true nature of this phase is still an open question and remains to be further specified. The order of phase transitions has been reported as continuous for the isotropic (I)$\leftrightarrow D_{hd}$ phase transition and first order for the other two [2]. The second interesting aspect is the particular molecular configuration in the D_{ho} phase [1,2]. In this phase, the D_3 symmetry molecules are equally spaced in the stack and rotated by an angle α of approximately 45° from one to the other [see Fig. 1(a)]. The columns may be viewed as helices that can have either left-handed or right-handed helicity. The columns are arranged on a triangular array composed of three sublattices [see Fig. 1(b)] resulting from two orderings. First, one in every three columns is displaced by half an intracolumnar intermolecular distance in the $\hat{z}$ direction (along the stacking axis), the other two being at the same height [see Fig. 1(b)]. This displacement is thought to be a mechanism to relieve part of the frustration due to interdigitation of molecules in a triangular environment. Second, even if the interpretation of experimental results is very sensitive to the helicity pattern of the columns [2], there emerge two most probable patterns. The first scheme has the helicity of the displaced column opposite to the other two columns, and the second has a random helicity for the displaced column while the undisplaced columns have the same helicity.

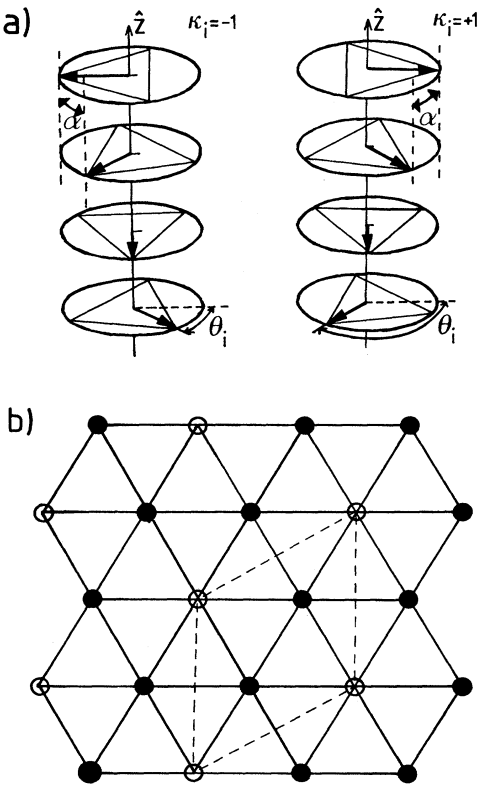

FIG. 1. (a) Schematic side view of a half period of HHTT in the D_{ho} phase. The full period is composed of 8 molecules of D_3 symmetry symbolized by triangles. (b) The period-3 triangular lattice of columns. Displaced columns are represented by open dots and undisplaced columns by full dots. The dotted lines represent the unit cell in the D_{ho} phase.

A theoretical effort has been deployed to try to understand these and other features of the phases of the HHTT compound. An early model was developed to account for the random helicity sometimes proposed for the D_{ho} phase [4]. The anisotropy in the intermolecular potential parameters was shown to be a possible mechanism responsible for the randomness in one of the columns within this simple model. In addition, the ground state phase diagram with respect to helical pitch and the strength of the anisotropy field was investigated [5]. A helical pitch of 8 molecules (threefold internal symmetry) was found to be unstable to the sixfold anisotropy field, the stable structure having a higher order of commensurability or being incommensurate. In contrast, the threefold anisotropy field stabilizes the 8-molecule helical pitch of the columns for small and moderate values of the anisotropy field. This leads us to conclude that even in the low temperature region of the D_{ho} phase, the displaced columns are strongly perturbed by the sixfold anisotropy field created by their environment. The commensurability effects at $T\neq 0$ are presently being investigated, and will be reported elsewhere [6].

The first step in developing a phenomenological Hamiltonian for the interaction between two helical columns is the description of their state by structural parameters. The helicity of the columns is represented by an Ising-like variable $\{K_i\}$ and the in-plane orientation of the columns by the angle $\{\theta_i\}$ (of XY character) made by one of the branches of a molecule with the $\hat{x}$ axis in a reference plane [see Fig. 1(a)]. This represents by itself a simplifying approximation that neglects all fluctuations in the rotation and vertical position of individual molecules. The change in helicity of a column, which could occur via the untwisting of the helix, is depicted in a first-order approximation as a simple flip of the variable $\{K_i\}$. The vertical position degrees of freedom of each molecule are intentionally omitted on the basis that they are presumed to be rigidly frozen by steric hindrance interactions much stronger than those controlling the molecular angular degrees of freedom.

Labeling a column by its site index i, the phenomenological Hamiltonian is derived using the mass density function for a column described by the $\{K_i\}$ and $\{\theta_i\}$ (in cylindrical coordinates) [4].

$$M^{K_i}(\rho,\theta-\theta_i,z)=\sum_{n=0}^{\infty}\{A_n^{K_i}(\rho,z)\cos[n(\theta-\theta_i)] +B_n^{K_i}(\rho,z)\sin[n(\theta-\theta_i)]\}. \quad (1)$$

The goal is to construct a Hamiltonian from the moments $\psi_{lm}^{K_i}(\theta_i)$ of the mass density (1) defined by

$$\psi_{lm}^{K_i}(\theta_i)\equiv\frac{4}{(\pi\rho)^3}\int_0^{2\pi}d\theta x^l y^m M^{K_i}(\rho,\theta-\theta_i,z), \quad (2)$$

with $x=\rho\cos\theta$ and $y=\rho\sin\theta$, that is invariant with respect to the symmetry group of the triangular lattice. Note that $\psi_{lm}^{K_i}(\theta_i)$ is still a function of ρ and z. The first nonzero independent moments are such that $l+m=3$. Constructing a Hamiltonian to second order in the ψ's that is invariant with respect to the two-dimensional triangular lattice symmetry group gives, for nearest neighbor interactions only,

$$\mathcal{H}=-(J/2)\sum_{\langle ij\rangle}[\psi_{30}^{K_i}(\theta_i)\psi_{30}^{K_j}(\theta_j)+\psi_{03}^{K_i}(\theta_i)\psi_{03}^{K_j}(\theta_j)] -(G/2)\sum_{\langle ij\rangle}\psi_{03}^{K_i}(\theta_i)\psi_{03}^{K_j}(\theta_j). \quad (3)$$

In order to restrict the parameter space, an averaging process over ρ and z is performed. Keeping only the important features of the helices (D_3 symmetry and 8 molecule pitch), the columns can be idealized as three intertwined spirals. The mass density of this idealized column is given by

$$M^{K_i}(\rho,\theta-\theta_i,z)\propto\delta(\rho-R)\sum_{n=0}^{2}\delta((2\pi z/l_z)K_i-(\theta-\theta_i) -(2\pi n/3)). \quad (4)$$

The spatial extent of a full 8-molecule period is l_z and the diameter of the column is $2R$. The Hamiltonian (3) can then be rewritten as

$$\mathcal{H}'=-(J'/2)\sum_{\langle ij\rangle}(1+K_iK_j)\cos(\phi_i-\phi_j) -(G'/2)\sum_{\langle ij\rangle}(1-K_iK_j)\cos(\phi_i+\phi_j), \quad (5)$$

with $\phi_i=3\theta_i$. This Hamiltonian describes the interaction between neighboring columns on a triangular lattice with $K_i=\pm 1$ and $0\leq\phi_i\leq 2\pi$ and is similar to that of Ref. [4] but with the addition of helical degrees of freedom. Note that the sign of G' is not determinant since changing $G'\rightarrow -G'$ and $\phi_i\rightarrow\phi_i+(\pi/2)$ leaves Hamiltonian (5) unchanged.

In this idealization of the helix by the mass density (4), it is easy to see that the displacement by half an intracolumnar intermolecular distance of a column can be viewed as a rigid rotation of $\alpha/2$ [see Fig. 1(a)]. The $\hat{z}$-direction positional frustration, transposed as a part of the angular frustration, is relieved by solving the whole angular frustration problem. This also saves us from the introduction of anisotropy in the exchange parameters. In fact, if we assume that the interaction between molecules is dependent only on their distances, we are led to conclude that exchange parameters between neighboring columns (displaced and undisplaced) must be close to each other (the distances being different [2] by less than 1%).

A similar model (with $G'=0$) that couples Ising (K_i) and XY variables on a square lattice has been studied extensively in relation to the fully frustrated XY models and Josephson junction arrays in a transverse magnetic field [7]. The Hamiltonian (5) has two added features. First, the G' term which results from the octupolar nature of the columns, and second, both Ising variables (K_i) and XY variables are inscribed on a triangular lattice. For $J'<0$, this last feature brings an added double-valued symmetry for the chirality ordering of the rotational degrees of freedom around a triangular plaquette. As a result of this, our system has two sets of competing Ising variables: the helicities K_i of the columns and the chirality of a plaquette.

For the purpose of revealing the origins of the helicity and XY frustrations in these systems, the two terms of the Hamil-

tonian (5) are discussed separately. For $G'=0$, irrespective of the sign of J', the ordering of the angular degrees of freedom brings about a ferromagnetic order of the helicities K_i. At a helicity domain wall in a ferromagnetic ordered state, the prefactor $(1+K_iK_j)$ vanishes, leaving uncoupled orientational degrees of freedom. As a result, we understand that both the helicity and angular transitions occur at the same temperature [7]. The Ising helicity variables should show true long-range ferromagnetic order, while the XY variables should exhibit pure Kosterlitz-Thouless order for $J'>0$, and a new single transition combining Kosterlitz-Thouless ordering of the XY variables with long-range order of the staggered chirality for the triangular plaquettes in the case of $J'<0$.

For $J'=0$, irrespective of the sign of G', the second term of Hamiltonian (5) breaks the rotation invariance of the XY variables, permitting true two-dimensional XY order. Furthermore, $\cos(\phi_i+\phi_j)$ can be made either positive or negative to accommodate the sign of G' (without further frustration), leaving an effective antiferromagnetic exchange parameter for K_iK_j on a triangular lattice. These Ising variables are frustrated and forced in a disordered state at all temperatures [8]. Now, if both J' and G' are different from zero, the competition between the two terms frustrates the system even further. Note that not all these features of Hamiltonian (5) will be revealed here, due to the limitations of the mean-field approximation, and will be addressed elsewhere [9].

The mean-field method of Bak and von Boehm [10] is being adapted here for two kinds of order parameters (corresponding to $\{K_i\}$ and $\{\theta_i\}$). We start the derivation of the Landau-type expansion of the free energy of (5) by defining pseudospin variables and their average values

$$C_i=\cos\phi_i,\ S_i=\sin\phi_i,\ c_i=\langle C_i\rangle,\ s_i=\langle S_i\rangle,\ k_i=\langle K_i\rangle. \quad (6)$$

Hamiltonian (5) is reduced to the mean-field Hamiltonian

$$\mathscr{H}_{MF}=-\sum_i [h_i^C C_i+h_i^S S_i+h_i^K K_i] \quad (7)$$

with

$$h_i^C=\sum_j [(J'+G')+(J'-G')k_ik_j]c_i,$$

$$h_i^S=\sum_j [(J'-G')+(J'+G')k_ik_j)s_i,$$

$$h_i^K=\sum_j [(J'-G')c_ic_j+(J'+G')s_is_j]k_i. \quad (8)$$

To sixth order in the expansion, the free energy is

$$\mathscr{F}=\beta^{-1}\sum_i \left[\frac{k_i^2}{2}+\frac{k_i^4}{12}+\frac{k_i^6}{30}+(c_i^2+s_i^2)+\frac{(c_i^2+s_i^2)^2}{4}\right.$$

$$\left.+\frac{5(c_i^2+s_i^2)^3}{36}\right]-\frac{1}{2}\sum_{\langle ij\rangle}\{[(J'-G')c_ic_j$$

$$+(J'+G')s_is_j]k_ik_j+(J'-G')s_is_j+(J'+G')c_ic_j\}. \quad (9)$$

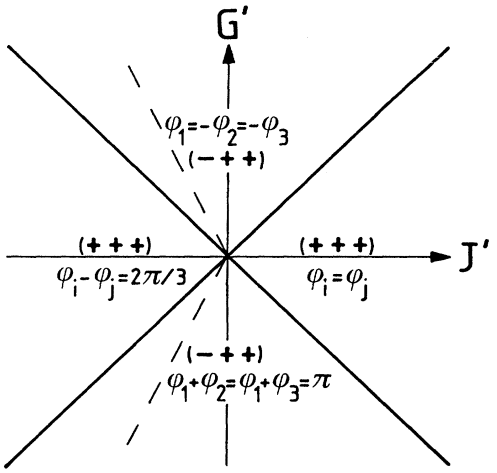

FIG. 2. Ground state phase diagram for Hamiltonian (5). The + and − refer to the helicity configuration ($\{K_i\}$). Solid thick lines delimit different helicity configuration domains. Broken lines delimit phases with different relation between angles [the region between solid thick and broken lines has $\phi_1+\phi_2=-(\phi_1+\phi_3)$].

We assume that at $T=0$ and throughout the entire thermal phase diagram, the period-3 basal plane structure is maintained (other studies, such as Monte Carlo, could verify this assumption). The ground state phase diagram is shown in Fig. 2. It has been obtained by minimizing the interaction energy (5) for three sites. The phase diagram is obtained by numerically minimizing the free energy (9) for the three sites of an elementary plaquette (Fig. 3 and Table I). The knowledge of the $T=0$ phase diagram has been used in the very low temperature region where the mean-field approximation fails to give good results.

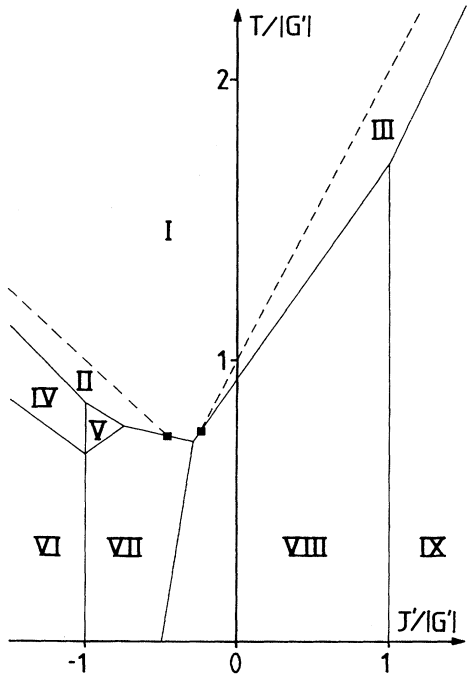

FIG. 3. Mean-field phase diagram of model (5) for $G'=-1.0$. Solid and dashed lines represent first- and second-order transitions. Critical end points are represented by squares.

The high temperature isotropic phase I has both Ising and XY disorder. As the temperature is lowered, the first phases to stabilize (except for a small region around $J'=-0.4|G'|$) have total helicity disorder with an XY order (phases II and III). Note that we are reporting these phases with Ising disorder and XY order in coupled XY-Ising models. This is in agreement with early Monte Carlo and renormalization group results [9]. Reducing the temperature further stabilizes phases with partial helicity order for $J'<-0.75|G'|$ (phases IV and V). The low temperature phases have both helicity and XY orders (phases VI–IX). In the region around $J'=-0.4|G'|$, the system goes directly from the high temperature I phase to the low temperature helicity and XY ordered phases (phases VII or VIII) through a first-order transition. The two second-order transition lines meet first-order transition lines at critical end points located at $(J',T) \simeq (-0.47,0.73)$ and $(-0.25,0.75)$ in units of $|G'|$ as indicated by squares on Fig. 3. At the present time, this region lacks a proper theoretical treatment, and a thorough study of the critical end points is under way.

We have also determined the $G'=0$ phase diagram to compare with earlier work [7]. For both $J'>0$ and $J'<0$, only two phases are obtained: the low temperature phase with full helicity and XY orders and the high temperature disordered I phase. These phases are separated by a first-order phase transition. For $J'>0$ ($J'<0$), the helicity configuration is $(+++)$ and ferromagnetic $\phi_i=\phi_j$ (120° state $\phi_i-\phi_j=\pi/3$) for the XY part, with a critical temperature of $T_c\simeq 1.1J'$ ($T_c\simeq 0.55|J'|$). There is no intermediate helicity disordered with XY ordered phase. It is now clear that the G' term is responsible for the stabilization of phases with partial or full helicity disorder with XY order and that it is at the origin of the helicity frustration as suggested earlier.

The mean-field phase diagram (Fig. 3) of Hamiltonian (5), constructed to model the HHTT compound in its D_{ho} phase, is in qualitative agreement with experimental observations. It is to be remembered that these results are relevant only in regions of the phase diagram where fluctuations can be ignored. Without anisotropy in the exchange parameters, it is possible to stabilize the helicity configurations most probable for HHTT in the D_{ho} phase, namely $(0++)$ and $(-++)$, over a large portion of the phase diagram. A surprising feature of model (5), for $G'\neq 0$, is the presence of phases with total helicity disorder with XY order (phase II and III). It is tempting to naively associate these phases with the liquid crystalline D_{hd} phase of HHTT, since in this phase the columns conserve their two-dimensional structure [2]; the full helicity disorder would account for the disappearance of the peaks related to the helicity of the columns [1,2]. This bold assumption would have to be checked both experimentally and theoretically with calculations going beyond the mean-field approximation. Note that even the order of transitions would be correct (first order for the $D_{ho}\leftrightarrow D_{hd}$ transition and second order for the $D_{hd}\leftrightarrow I$ transition). Instead of being an order-disorder transition within the columns, we infer that the $D_{ho}\leftrightarrow D_{hd}$ transition is the result of the two-dimensional disorder of the helicity from one column to the other, thus explaining the fact that the two-dimensional array of columns is preserved during this transition [1,2].

TABLE I. Explicit configurations associated with the mean-field phase diagram of Fig. 3.

Phase	Helicity	Order parameters
I	(000)	$k_i=0,\ c_i=0,\ s_i=0$
II	(000)	$k_i=0,\ c_1=0,\ c_2=-c_3,\ s_i=0$
III	(000)	$k_i=0,\ c_i=0,\ s_i=s_j$
IV	$(0++)$	$k_1=0,\ k_2=k_3,\ c_i=0,\ s_1=0,\ s_2=-s_3$
V	$(0+-)$	$k_1=0,\ k_2=-k_3,\ c_i=0,\ s_1=0,\ s_2=s_3$
VI	$(+++)$	$k_1\geqslant k_2=k_3,\ c_i=0,\ s_1\geqslant\|s_2\|=\|s_3\|$
VII	$(-++)$	$\|k_1\|\geqslant k_2=k_3,\ c_i=0,\ s_1\geqslant s_2=s_3$
VIII	$(-++)$	$k_1=-k_2=-k_3,\ c_1\geqslant\|c_2\|=\|c_3\|,\ s_i=0$
IX	$(+++)$	$k_i=k_j,\ c_i=c_j,\ s_i=0$

In conclusion, we have derived a simple Hamiltonian to model the HHTT compound in the D_{ho} phase and, to some extent, the D_{hd} phase. The derivation is based on the symmetry of helical columns, and the resulting Hamiltonian (5) couples Ising and XY variables. The mean-field phase diagram reveals the existence of $(-++)$ and $(0++)$ phases, considered to be the most probable helicity configurations of HHTT in the D_{ho} phase. The G' term, resulting from the fact that the octupolar entities are disposed on a triangular lattice, is responsible for new partial or total helicity disordered with XY order phases. It is suggested (and would have to be verified experimentally) that the D_{hd} phase of HHTT is characterized by full helicity disorder, rather than intracolumnar positional and orientational disorder [3].

We thank M.L. Plumer for useful discussions. This work was supported by the National Sciences and Engineering Research Council of Canada, the Fonds pour la Formation des Chercheurs et de l'Aide à la Recherche du Québec, and the Centre de Recherche en Physique du Solide.

[1] P.A. Heiney, E. Fontes, W.H. de Jeu, A. Reira, P. Carroll, and A.B. Smith III, J. Phys. (Paris) **50**, 461 (1989); M. Pesquer, M. Cotrait, P. Marsau, and V. Volpilhac, *ibid.* **41**, 1039 (1980).

[2] E. Fontes, Doctoral dissertation, University of Pennsylvania, 1989.

[3] J. Prost, in *Symmetries and Broken Symmetries*, edited by N. Boccara (IDSET, Paris, 1989), p. 161.

[4] M.L. Plumer, A. Caillé, and O. Heinonen, Phys. Rev. B **47**, 8479 (1993).

[5] A. Caillé, M. Hébert, and M.L. Plumer, Phys. Rev. B **49**, 3104 (1994).

[6] A. Caillé and M. Hébert (unpublished).

[7] Jooyoung Lee, E. Granato, and J.M. Kosterlitz, Phys. Rev. B **44**, 4819 (1991) and references therein.

[8] G.H. Wannier, Phys. Rev. **79**, 357 (1950).

[9] M. Hébert and A. Caillé (unpublished).

[10] P. Bak and J. von Boehm, Phys. Rev. B **21**, 5297 (1980).