Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Unusual Thickness-Dependent Thermal Behavior in Chiral Smectic Free-Standing Liquid-Crystal Films

C. Y. Chao [a], C. R. Lo [a], Y. H. Liu [a], D. R. Link [b], J. E. Maclennan [b], N. A. Clark [b], M. Veum [c], C. C. Huang [d] & J. T. Ho [e]

[a] Department of Physics and Astronomy, National Central University, Chung-Li, Taiwan, ROC

[b] Condensed Matter Laboratory, Department of Physics, University of Colorado, Boulder, Colorado, USA

[c] Department of Physics and Astronomy, University of Wisconsin, Stevens Point, Stevens Point, Wisconsin, USA

[d] School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota, USA

[e] Department of Physics, University at Buffalo, The State University of New York, Buffalo, New York, USA

Version of record first published: 18 Oct 2010

Mol. Cryst. Liq. Cryst., Vol. 412, pp. 393/[2003]–400/[2010], 2004

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490440309

UNUSUAL THICKNESS-DEPENDENT THERMAL BEHAVIOR IN CHIRAL SMECTIC FREE-STANDING LIQUID-CRYSTAL FILMS

C. Y. Chao, C. R. Lo, and Y. H. Liu*
Department of Physics and Astronomy, National Central University, Chung-Li 32054, Taiwan, ROC

D. R. Link†, J. E. Maclennan, and N. A. Clark
Condensed Matter Laboratory, Department of Physics, University of Colorado, Boulder, Colorado 80309, USA

M. Veum
Department of Physics and Astronomy, University of Wisconsin at Stevens Point, Stevens Point, Wisconsin 54481, USA

C. C. Huang
School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455, USA

J. T. Ho
Department of Physics, University at Buffalo, The State University of New York, Buffalo, New York 14260, USA

We observe, in free-standing films of a chiral smectic liquid crystal, a series of discrete transitions in the relative orientation of the tilt of the interior and surface layers. These transitions include a remarkable reentrant synclinic-anticlinic-synclinic ordering sequence of the film surfaces in the presence of

One of us (C. Y. C.) would like to thank Prof. Jan Thoen for helpful discussions. We are grateful to Dr. M. D. Wand for the MDW1397 sample. This work was supported by the National Science Council, Taiwan, ROC, under Grant Nos. NSC 89-2112-M-008-004, NSC 90-2112-M-008-003, and NSC 91-2112-M-008-048, the National Science Foundation, USA, under Grants No. DMR98-09555 and No. DMR96-14061, and NASA under Grant No. NAG3-1846.

*Corresponding author. E-mail: cychao@phy.ncu.edu.tw

†Current Address: Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Meguro-ku, O-okayama 2-12-1, Tokyo 152-8552, Japan.

an electric field upon cooling. The profiles of the associated heat-capacity anomalies are found to be strongly thickness-dependent and exhibit a novel crossover behavior in reduced dimensions.

Keywords: heat capacity; liquid-crystal films; phase transition; synclinic and anticlinic ordering

The bulk smectic-*A* (Sm-*A*) liquid crystal (LC) phase involves stacked two-dimensional (2D) fluid layers in which the mean molecular long axis $\boldsymbol{n}$ is along the layer normal $\boldsymbol{z}$. At lower temperatures, or at the LC-air interface, a collective reorientation of $\boldsymbol{n}$ away from $\boldsymbol{z}$ can appear, producing "tilted" smectic layers characterized by the tilt angle θ and azimuthal angle φ. A tilted smectic layer is degenerate in energy with respect to changes in φ, and is thus a physical manifestation of the 2D *XY* model. In a stacking of layers, the overall structure depends on interlayer interactions and on thermal fluctuations. These combine to produce a variety of bulk phases, the basic ones being the monolayer smectic-*C* (Sm-*C*), where the azimuthal orientation φ in adjacent layers is the same ($\Delta\varphi = 0$, synclinic), and the bilayer smectic-C_A (Sm-C_A), where the tilt is opposite ($\Delta\varphi = \pi$, anticlinic). Additionally, a variety of more complex phases have also been observed, having larger unit cells and/or $\Delta\varphi \neq 0,\pi$ [1–4]. When the molecules are optically active, the corresponding chiral ferroelectric phases (Sm-C^*, Sm-$C_A{}^*$, etc.) are formed, in which each tilted layer possesses a polarization normal to $\boldsymbol{z}$ and $\boldsymbol{n}$ [5], enabling possible transitions between these states induced by an applied in-plane electric field. The thermal transition between the bulk tilted phases (which can be thought of as stacking of coupled 2D *XY* layers) and the Sm-*A* is of great interest, exhibiting both first- and second-order behavior which can be affected by an electric field [6–9].

A powerful tool for the study of tilted smectic has been the free-standing film, where a discrete number N of smectic layers are bounded by free surfaces. Such a structure is strongly influenced by interfacial effects, and becomes increasingly affected by fluctuation phenomena as N decreases. Thus, it has been found that a Sm-*A* – Sm-*C* transition that is first order in the bulk can be second order in films with small N (<15) [10]. In two- and three-layer films, the transition from Sm-C^* to Sm-$C_A{}^*$ is found to be characterized by the inversion of the tilt and polarization direction in a single smectic layer [11]. Additionally, because the interaction between layers extends beyond nearest neighbors and depends on the proximity of the LC-air interface, tilted smectic films can have quite different tilt structure from the bulk [12,13].

In this paper, we report the results of heat-capacity and optical measurements in free-standing films of a chiral smectic liquid-crystal material

which exhibits novel fluctuation effects, as well as a remarkable set of N-dependent transitions among different states of tilt organization. These transitions include a reentrant synclinic-anticlinic-synclinic ordering sequence of the film surfaces in the presence of an electric field upon cooling. The profiles of the associated heat-capacity anomalies are found to be strongly thickness dependent and exhibit a novel crossover behavior in reduced dimensions.

Our experimental technique for making heat-capacity measurements has been described elsewhere [14]. The depolarized reflected light microscopy technique was used to visualize the orientations of the azimuthal angle φ [15]. The material used was [4″-carboxy-(1-(R)-trifluoromethylheptyl)-phenyl]-2′,3′-difluoro-4″-(7,7,8,8,9,9,10,10,10-nonafluorodecyloxy) -biphenyl carboxylate (MDW 1397). Bulk MDW1397 exhibits the isotropic, Sm-A, Sm-C^* and Sm-C_A^* phases upon cooling [16]. Free-standing Sm-A films of MDW1397 from 3 to 21 molecular layers were drawn over a hole of radius 8 mm for heat-capacity measurements and 3 mm for optical observations. The exact number N of smectic layers was determined by optical reflectivity [17]. Electrodes on either side of the 3-mm hole were used to apply an in-plane ac electric field E of up to 25 V/mm at a frequency of 0.1–1 Hz to suppress flow instabilities.

Above 74°C in the Sm-A phase, we determine from the brightness of the uniform texture under depolarized microscopy in the presence of arbitrarily small fields that the optic axis of the film aligns parallel to the field $\boldsymbol{E}$. This anticlinic ground state was reported previously in other materials [11,15]. We find that, for values of E above a critical field E_c, the optic axis reorients by 90° to align perpendicular to $\boldsymbol{E}$, transforming to the synclinic state, as illustrated in Figure 1. The temperature dependence of E_c for an 8-layer MDW1397 film is also shown in Figure 1.

Upon cooling below 74°C, in the absence of an external electric field, we observe a series of phase transitions indicated by a moving boundary separating different textures caused by a slight temperature gradient across the film. Based on the optical observations, we can propose a model for the phase transitions as depicted in Figure 2. The first transition at T_1 corresponds to a spontaneous surface anticlinic-synclinic transition. The transition temperature T_1 increases as the film becomes thinner. At T_2, the film transforms to a state characterized by a large transverse polarization (perpendicular to the tilt plane), indicative of a uniform synclinic state (Sm-C^*). Below T_3, in addition to the transverse polarization present in all films, we find that thicker films exhibit small **c**-director fluctuations, but thinner films show surprisingly large c-director fluctuations (indicating a small net polarization). This state, which does not exist in the 3-layer film, is thought to have a synclinic interior, but with surface layers which are anticlinic with respect to their adjacent layers, as sketched in Figure 2.

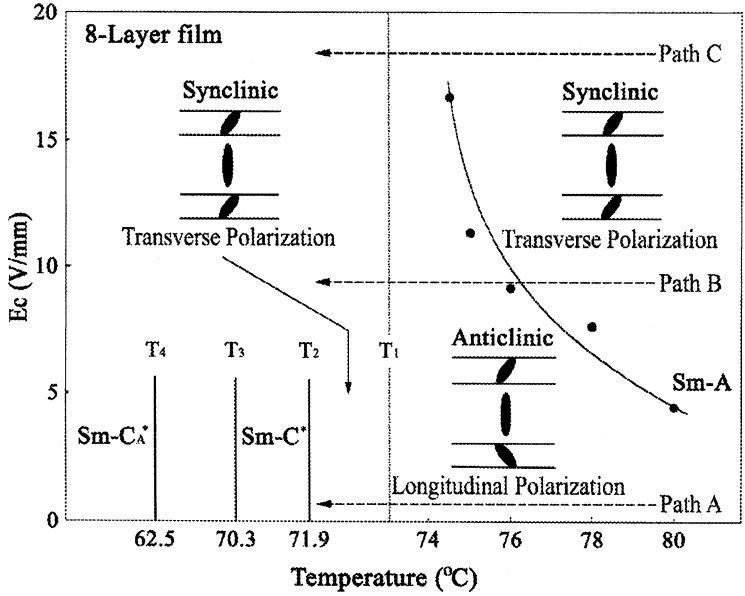

FIGURE 1 Temperature dependence of the anticlinic-synclinic critical electric field E_c in an 8-layer Sm-*A* film. Subsequent phase transitions are seen at T_1, T_2, T_3 and T_4. Paths A, B and C denote cooling runs in the presence of different electric field.

Finally, below T_4, the films exhibit the typical odd-even layering effect of the antiferroelectric Sm-C_A^* phase, in which films with an odd number of layers have a net transverse polarization and films with an even number of layers have a net longitudinal polarization (in the tilt plane) [15]. The schematics of the entire transition sequences in 3-, 4-, and 8-layer films are summarized in Figure 2.

The thermally-driven surface anticlinic-synclinic transition at T_1 and the field-induced anticlinic-synclinic transition in Sm-*A* films result in a variety of phase sequences occurring when cooled in the presence of different values of the electric field, as illustrated in Figure 1 for an 8-layer film. When a Sm-*A* film is cooled along path A in the presence of a relatively weak electric field, the surface layers remain anticlinic until T_1 is reached at 74°C, and then switch to be synclinic. Along path B in the presence of a medium field of around 10 V/mm, the surface layers are initially synclinic at high temperature, becoming anticlinic below around 75.5°C, before returning to a synclinic state at 74°C. Finally, along path C at an even higher field, it is possible for the surface layers to remain continually synclinic, with the crossing of 74°C marked only by a slight increase in optical contrast caused by a change in the tilt angle. While similar behavior along paths A and C

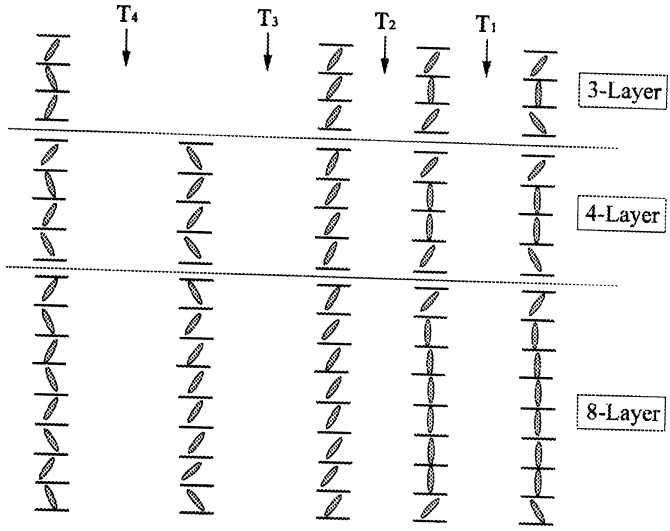

FIGURE 2 Schematics of the entire transition sequences in 3-, 4-, and 8-layer films in the absence of external electrical field.

have been observed previously in different compounds [13], the reentrant behavior along path B caused by the competition between thermal and electric-field effects is quite unique.

Utilizing our high-resolution free-standing film calorimeter, we have measured the heat capacity of MDW1397 films between 3 and 21 layers. No thermal anomaly can be detected for films thinner than 6 layers. Films between 6 and 21 layers thick are found to exhibit only *one* heat-capacity anomaly at around T_2, which increases as the films become thinner. Based on our optical observations, we believe the heat-capacity anomaly at T_2 corresponds to the Sm-A – Sm-C^* phase transition. Figure 3 displays the temperature dependence of the heat capacity for MDW1397 films of different layer thickness upon cooling. Unlike the only previous thermal study of the Sm-A–Sm-C transition in free-standing films [18], in which a noticeable rounding of the heat-capacity anomaly was reported in films below 25 layers, the anomaly in MDW1397 is found to remain sharp in films down to 8 layers. Surprisingly, the profile of the heat-capacity anomaly depends strongly on the film thickness. The heat-capacity anomaly is steeper on the high-temperature side for $N<10$, but is steeper on the low-temperature side for $N>10$. For $N\geqq 15$, the low-temperature side of the anomaly is characterized by an initial steep drop that is followed by an abrupt change in slope. To examine the extent to which the profile of the heat-capacity anomaly may be affected by the first-order nature of the transition, we have

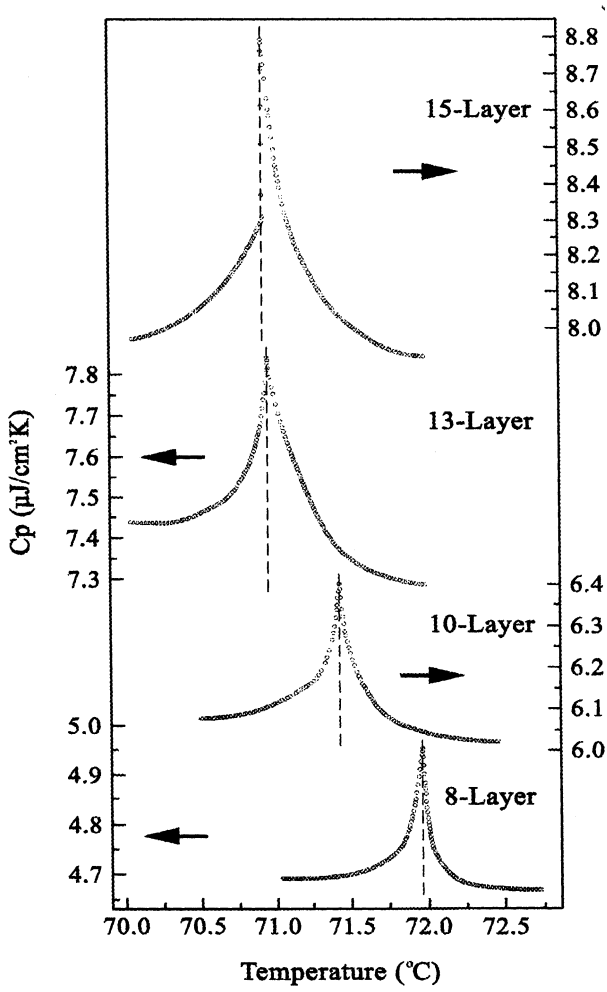

FIGURE 3 Heat capacity in MDW1397 films of different thickness near the interior Sm-*A*–Sm-C^* transition at T_2.

conducted detailed thermal hysteresis studies using a temperature ramping rate of about 10 mK/min in both directions. We obtained the same heat-capacity profiles on cooling and heating runs and found thermal hysteresis of about 40 mK, 70 mK, and 300 mK (with resolution of 50 mK) for the Sm-*A*–Sm-C^* transition in films of 7–12 layers, 13–14 layers, and 15–21 layers, respectively. Thus the transition is essentially continuous to within our resolution in films of 7–12 layers. For films below 15 layers, our data also reveal that the magnitude of the heat-capacity peak varies by less than

5% between heating and cooling runs, suggesting that this transition is at most weakly first order. Moreover, the width of the two-phase coexistence region is estimated to be no larger than 50 mK. Thus the observed change in the asymmetry of the heat-capacity anomaly with thickness appears to be an intrinsic phenomenon unrelated to the slightly first-order nature of the transition. It should be noted that the heat-capacity anomaly is significantly rounded in films of 7 and 6 layers, and is not detectable in films thinner than 6 layers.

The complex phase-transitional behavior observed can be described as follows. At higher temperature, the molecules on the surface of the Sm-*A* phase are tilted at an angle θ with respect to the layer normal. This tilt is due to a surface ordering effect arising from the broken symmetry at the air-smectic interface. The two surfaces of the film are anticlinically coupled [13], but in a sufficiently large electric field they can be forced into a synclinic state. The observed increase in the threshold field as the temperature decreases toward T_1 is somewhat surprising in view of the spontaneous synclinic configuration below T_1. We speculate that it could be due either to an increase in the coupling between the surfaces or to a decrease in the difference between transverse and longitudinal polarizations as T_1 is approached. Although several models [4,19–23] involving an interlayer coupling extending beyond nearest neighbors have been proposed to explain the wide variance in orientational ordering among the different types of Sm-C^* phases, the fundamental nature of this coupling is not well understood. If we consider the broken symmetry at the air-smectic interface to be effectively a surface electric field, then it is not surprising that the surface tilt has a discontinuous increase below T_1. When θ increases above a critical value θ_c, the anticlinic coupling of the surfaces can no longer be maintained and the surfaces switch to a synclinic orientation. For MDW1397, θ_c is exceeded below T_1, so that only the interior Sm-*A* layers make the transition to the Sm-C^* at T_2.

In our thermal results, the large hysteresis and the sharp kink on the low-temperature side of the heat-capacity anomaly in films of 15 or more layers indicate that the interior Sm-*A*–Sm-C^* transition is first order, which is probably due to the influence of a large spontaneous polarization ($\sim$120 nC/cm^2) in these films [7,8]. In films thinner than 15 layers, surface interactions (of penetration depth about 7 layers) strongly influence the interior first-order transition, which becomes more continuous with decreasing film thickness, similar to what was observed in another material [10]. The surface ordering field suppresses the strong thermal fluctuations, resulting in the heat-capacity anomaly becoming narrower in films less than 13 layers. The asymmetry in the anomaly observed in films of 12–14 layers can be explained by the formation of an interior uniform synclinic state (Sm-C^*) with a large transverse polarization on the low-temperature side,

reducing the fluctuations. The increasing importance of surface interactions with decreasing film thickness is responsible for the highly unusual thickness-dependent crossover behavior observed here. In thinner films of 10–7 layers, the influence of the surface field, which is generally expected to stabilize the high-temperature phase [10], dominates over the effect of reduced dimensionality, suppressing the fluctuations on the high-temperature side of the heat-capacity anomaly.

In summary, we have found an interesting sequence of surface and interior phase transitions in free-standing films of a chiral smectic material. The heat-capacity anomaly at the Sm-*A*–Sm-*C** transition exhibits an unusual dependence on film thickness. The rich variety of phenomena observed illustrates the competition among surface interactions, low-dimensional fluctuations and electric-field effects in these chiral smectic films.

REFERENCES

[1] Fukui, M., Orihara, H., Yamada, Y., Yamamoto, N., & Ishibashi, Y. (1989). *Jpn. J. Appl. Phys.*, *28*, L849.
[2] Chandani, A. D. L., Gorecka, E., Ouchi, Y., Takezoe, H., & Fukuda, A. (1989). *Jpn. J. Appl. Phys.*, *28*, L1265.
[3] Mach, P., Pindak, R., Levelut, A.-M., Barois, P., Nguyen, H. T., Huang, C. C., & Furenlid, L. (1998). *Phys. Rev. Lett.*, *81*, 1015.
[4] Levelut, A.-M. & Pansu, B. (1999). *Phys. Rev. E*, *60*, 6803.
[5] Meyer, R. B., Liebert, L., Strzelecki, L., & Keller, P. (1975). *J. Phys. (Paris) Lett.*, *36*, 69.
[6] Dumrongrattana, S., Nounesis, G., & Huang, C. C. (1986). *Phys. Rev. A*, *33*, R2182.
[7] Shashidhar, R., Ratna, B. R., Nair, G. G., Prasad, S. K., Bahr, Ch., & Heppke, G. (1988). *Phys. Rev. Lett.*, *61*, 547.
[8] Liu, H. Y., Huang, C. C., Min, T., Wand, M. D., Walba, D. M., Clark, N. A., Bahr, Ch., & Heppke, G. (1989). *Phys. Rev. A*, *40*, 6759.
[9] Bahr, Ch. & Heppke, H. (1990). *Phys. Rev. A*, *41*, 4335.
[10] Bahr, Ch. & Fliegner, D. (1992). *Phys. Rev. A*, *46*, 7657.
[11] Bahr, Ch. & Fliegner, D. (1993). *Phys. Rev. Lett.*, *70*, 1842.
[12] Link, D. R., Natale, G., Clark, N. A., Maclennan, J. E. Walsh, M., Keast, S. S., & Neubert, M. E. (1999). *Phys. Rev. Lett.*, *82*, 2508.
[13] Johnson, P. M., Olson, D. A., Pankratz, S., Bahr, Ch., Goodby, J. W., & Huang, C. C. (2000). *Phys. Rev. E*, *62*, 8106.
[14] Geer, R., Stoebe, T., Pitchford, T., & Huang, C. C. (1991). *Rev. Sci. Instrum.*, *62*, 415.
[15] Link, D. R., Maclennan, J. E., & Clark, N. A. (1996). *Phys. Rev. Lett.*, *77*, 2237.
[16] Wand, M. D. (private communication).
[17] Young, C. Y., Pindak, R., Clark, N. A., & Meyer, R .B. (1978). *Phys. Rev. Lett.*, *40*, 773.
[18] Stoebe, T., Reed, L., Veum, M., & Huang, C. C. (1996). *Phys. Rev. E*, *54*, 1584.
[19] Cepic, M. & Zeks, B. (1995). *Mol. Cryst. Liq. Cryst.*, *263*, 61.
[20] Lorman, V. L. (1995). *Mol. Cryst. Liq. Cryst.*, *262*, 437.
[21] Pikin, S. A., Hiller, S., & Haase, W. (1995). *Mol. Cryst. Liq. Cryst.*, *262*, 425.
[22] Roy, A. & Madhusudana, N. (1996). *Europhys. Lett.*, *36*, 221.
[23] Akizuki, T., Miyachi, K., Taksnishi, Y., Ishikawa, K., Takazoe, H., & Fukuda, A. (1999). *Jpn. J. Appl. Phys.*, *38*, 4832.