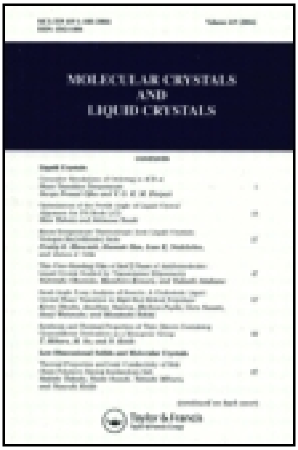

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Thickness-Dependent Smectic-*A* – Smectic-*C** Transition in Chiral Smectic Free-Standing Liquid-Crystal Films

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We have conducted heat-capacity measurements near the smectic-A – smectic-C phase transition in free-standing films of a chiral liquid-crystal compound. The heat-capacity behavior confirms the evolution of the transition in the interior layers from first to second order as a function of film thickness suggested earlier in tilt angle measurements. The asymmetry in the heat-capacity anomaly exhibits an interesting crossover in thinner films. We also observed the phase transitions leading to the crystallization to the tilted crystal-G in these films at lower temperatures. The surface ordering strength in these films is found to be much larger than that in other smectic films, which we speculate is due to the molecular tilt.*

Keywords: chiral free-standing liquid-crystal thin films; high-resolution ac calorimetry; smectic-*A*–smectic-*C** transition; smectic-*C** – crystal-*G* transition

Among smectic liquid crystals, the wave vector describing the one-dimensional mass-density wave is parallel to the molecular director in the smectic-*A* (Sm-*A*) phase, and tilted with respect to the director in the smectic-*C* (Sm-*C*) phase. When the molecules are optically active, a chiral Sm-*C* (or Sm-*C**) phase is formed which exhibits ferroelectric properties [1]. Experimental evidence indicates that the Sm-*A* – Sm-*C* transition is second order in a majority of compounds

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[2]. Earlier experimental studies [3,4] on bulk 4-(3-methyl-2-chloropentanoyloxy)-4′-heptyloxybiphenyl (C7), a material exhibiting large spontaneous polarization, have established that the Sm-A – Sm-C^* transition is first order except under a unique applied electric field strength [5].

Studies of the tilt order on surfaces and in thin films have been a subject of intense current interest because they provide useful information about the interlayer coupling and fluctuations associated with the molecular tilt. A powerful tool for the study of tilted smectic has been the free-standing film, where a discrete number N of smectic layers is bound by free surfaces. Such a structure is strongly influenced by interfacial effects, and becomes increasingly affected by fluctuation phenomena as N decreases. It was found that, in C7 films, the jumps in the tilt angle near the Sm-A – Sm-C^* phase transition observed in thicker films disappear for films thinner than 16 layers [6]. Furthermore, because the molecules in the outermost layers are always tilted, the optical measurements also suggested that there may be no Sm-A – Sm-C^* transition in films thinner than 6 layers. However, since ellipsometry determines the *average* molecular tilt in the films, this work did not provide definitive evidence about the nature of the transition for $N < 16$ and for $N < 6$. Thus it is highly desirable to have additional thermal measurements on these films to provide complementary information about the transitions. However, it is also worthy to conduct the advanced high-resolution ellipsometry experiments [7] which can yield more physical parameters than the average tilt in studying this transition. To date, there have been relatively few such studies in the past. An earlier calorimetric study of the Sm-A – Sm-C in thin films suggests that Gaussian fluctuations may be important in reduced dimensions [8]. More recently, it has been found in free-standing films of {4″-carboxy-[1-(R)-trifluoromethylheptyl]-phenyl}-2′,3′-difluoro-4″-(7,7,8,8,9,9,10,10,10-nonafluorodecyloxy)-biphenyl carboxylate (MDW1397) that the Sm-A – Sm-C^* transition, which is first order in thick films, can be second order in films of less than 15 layers [9]. In this paper, we report the results of high-resolution heat-capacity measurements in thin free-standing films of C7, which provide important supporting evidence about the nature of the Sm-A – Sm-C^* transition in thin films of less than 16 layers. The profiles of the heat-capacity anomalies are found to be strongly thickness-dependent and exhibit the interesting crossover behavior reported previously only in MDW1397. We also studied the transformation of these films to the crystal-G (Cry-G) phase at lower temperatures. The penetration depth of the surface ordering by the surface tilted Cry-G phase can be up to seven molecular layers, which is consistent with the evolution of the Sm-A – Sm-C^* transition with film thickness.

Our experimental technique for making heat-capacity measurements in free-standing liquid-crystal thin films has been described elsewhere [10]. The upper temperature limit of our calorimeter for studying ultrathin free-standing liquid-crystal films is about 90°C because of the rapidly increasing noise from both thermocouples at the higher temperatures. Bulk C7 material has the following phase sequence on cooling: isotropic (62°C) Sm-*A* (55°C) Sm-C^* (44°C) Cry-*G* [5]. Free-standing C7 films were drawn over a hole of radius 8 mm at about 59°C in the Sm-*A* phase. The exact number of smectic layers N in our films was determined by optical reflectivity [11]. We measured the heat capacity of C7 films from 4 to 23 molecular layers on successive cooling and heating runs. Figure 1 displays the temperature dependence of the heat capacity for C7 films of different layer thickness upon cooling. It was known from the earlier optical experiment [6] that the observed heat-capacity anomaly in Figure 1 corresponds to the Sm-*A* – Sm-C^* phase transition. The transition temperature increases as the films become thinner. Unlike the previous thermal study of the Sm-*A* – Sm-*C* transition in thin free-standing films [8], in which a noticeable rounding of the heat-capacity anomaly was reported in films below 25 layers, the anomaly in C7 is found to remain sharp in films down to eight layers. It should be noted that the heat-capacity anomaly is significantly rounded in films of five to seven layers, and is not detectable in films thinner than five layers. Interestingly, the profile of the heat-capacity anomaly depends strongly on the film thickness. In Figure 1, we find that 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 $N \geq 15$, we find that there is a discontinuous drop in the low-temperature side of the heat-capacity anomaly. This result indicates the Sm-*A* – Sm-C^* transition in films of 15 or more layers is first order, which is probably due to the influence of a large spontaneous polarization ($\sim 200\,\mathrm{nC/cm^2}$) in these C7 films [3–4,9].

To examine whether the heat-capacity anomaly in thinner films ($N<15$) may be affected by the first-order nature of the transition, we have conducted detailed thermal hysteresis studies. From repeated runs using different samples, we obtained the same heat-capacity profiles on cooling and heating runs of about 10 mK/min and found thermal hysteresis of about 30 and 70 mK (with a resolution of 50 mK) for the Sm-*A* – Sm-C^* transition in films of 8–10 layers and 11–14 layers, respectively. Thus the transition is essentially continuous to within our resolution in films of 8–10 layers. For films below 10 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 second order or at most weakly first

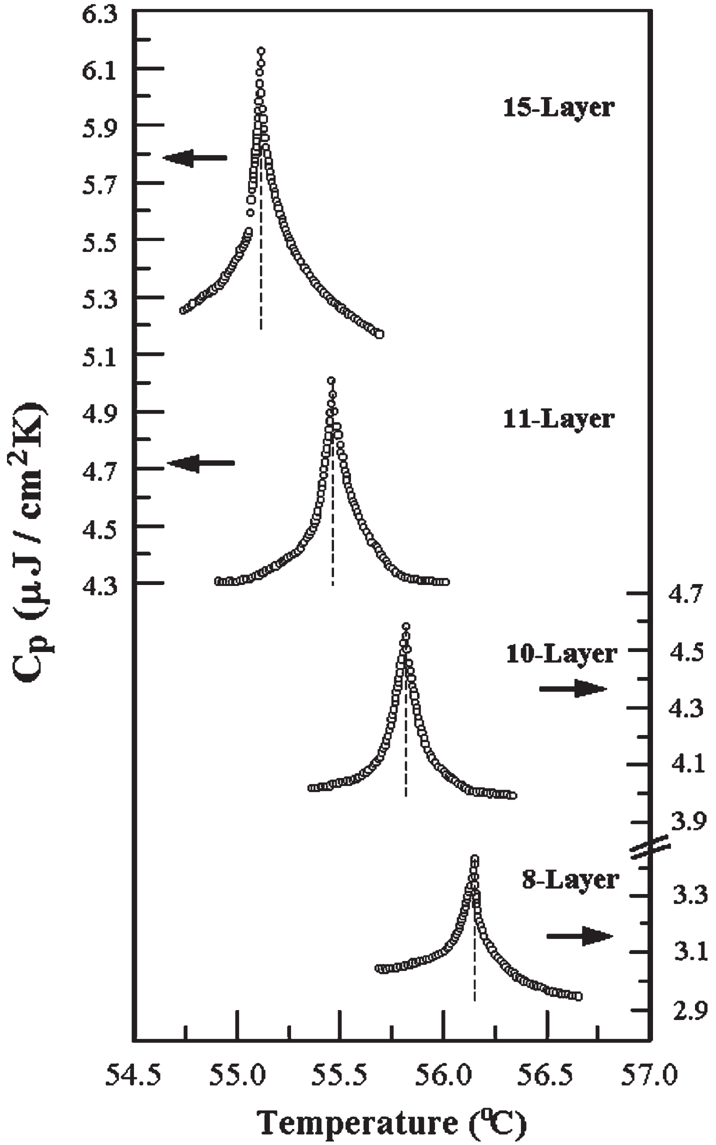

FIGURE 1 Heat capacity in C7 films of different thickness near the Sm-*A* – Sm-C^* transition.

order. Moreover, the width of the two-phase coexistence region is estimated to be no larger than 50 mK by taking closer examinations on the vicinity of the heat-capacity peaks. 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.

We can compare our heat-capacity results on C7 with other measurements near the Sm-*A* – Sm-C^* transition in thin films. First, our data provide important thermodynamic confirmation of the behavior in C7 that was suggested by average tilt angle measurements [6]. Our results clearly show that the vanishing discontinuity in the average tilt angle at the Sm-*A* – Sm-C^* transition for films of less than 16 layers is indeed due to the interior layers undergoing a continuous transition under the strong influence of the outer layers. The fact that the thermal anomaly vanishes in films of less than five layers also confirms the earlier suggestion by ellipsometry that the two outermost layers are always tilted. Second, the crossover in the asymmetry of the heat-capacity anomaly observed here in C7 are similar to those seen in MDW1397 films [9], suggesting that this phenomenon could be quite common. We believe that, in C7 films thinner than 15 layers, the surface interactions strongly influence the first-order Sm-*A* – Sm-C^* transition which develops with decreasing film thickness into a continuous evolution, similar to the earlier observation [9]. Thus, the penetration depth of surface interactions in C7 films should be around seven molecular layers. It is also quite clear that the increasing importance of surface interactions with decreasing film thickness is responsible for the interesting thickness-dependent crossover behavior observed here. The asymmetry in the anomaly observed in films of 11–14 layers can be explained by the formation of a uniform Sm-C^* state with a large transverse polarization on the low-temperature side, reducing the fluctuations. In thinner films of 8–10 layers, the influence of the strong surface field, which is generally expected to stabilize the high-temperature phase [6], dominates over the effect of reduced dimensionality, suppressing the fluctuations on the high-temperature side of the heat-capacity anomaly. Our data strongly suggests the reduced dimensionality and surface interactions may strongly influence the nature of the Sm-*A* – Sm-C^* transition. Further experiments on other liquid-crystal compounds exhibiting the Sm-*A* – Sm-C^* transition in thin films to examine the generality of these results would be highly desirable.

On further cooling, the multiple-step Sm-C^* – Cry-*G* phase transitions leading to the crystallization of these films were observed. The heat-capacity data from 13-, 15-, 18-, and 23-layer films are shown in Figure 2. Two well-defined peaks and onestep are clearly seen for films thicker than 13 layers. Figure 2 indicates that the magnitude of the surface heat-capacity anomaly is independent of film thickness.

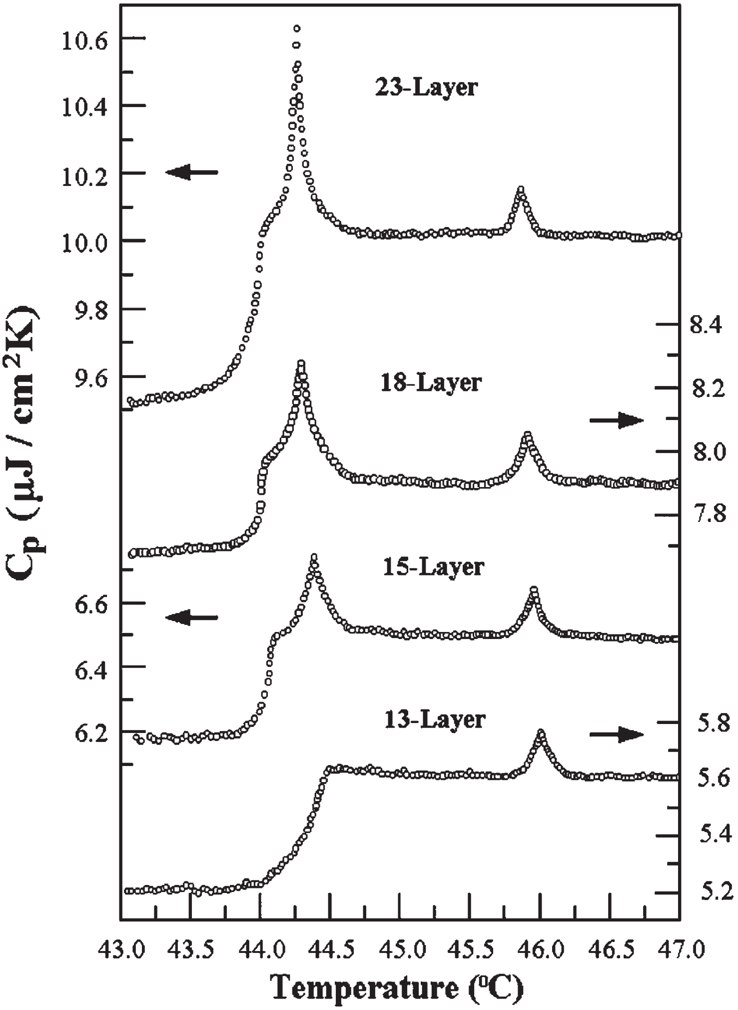

FIGURE 2 Heat-capacity data from 13-, 15-, 18-, and 23-layer films of C7 films near the Sm-C^* – Cry-G transition.

The surface transition temperature (approximately 46°C) is found to be higher than the bulk transition temperature. Successive heating and cooling runs have demonstrated thermal hysteresis of less than 30 mK, suggesting that this surface transition in these films appears to be continuous to within our resolution. However, attempts to fit the data to a simple power-law form failed. The second heat-capacity peak is found to grow significantly with increasing film thickness.

The size of the second heat-capacity anomaly in 15-, 18-, and 23-layer films is larger than that of the surface anomaly, indicating that this transition corresponds to two or more adjacent-to-surface Sm-C^* layers transforming into the Cry-G^* phase while the two outermost surfaces are in the Cry-*G* phase. Finally, the interior Sm-C^* layers freeze into the Cry-*G* phase near the bulk transition temperature at about 44°C. This transition related to the interior layer ordering of these C7 films appears only as a change in slope of the heat capacity. In films thinner than 14 layers, the second heat-capacity peak is absent but replaced by a broad step change in the heat capacity, exemplified by the 13-layer data in Figure 2. We believe the reason for the disappearance of the second heat-capacity anomaly in these thinner films (for $N<14$) is very likely due to the influence of the strong ordering field (of penetration depth also about 7 layers) from two Cry-*G* surfaces which severely suppresses the interior Sm-C^* – Cry-*G* phase-transitional thermal fluctuations. Thus, under the influence of the surface ordering field, the interior layers can possess a very different thermal signal than the outermost surface layers. There is a possibility that transformation of the interior from the Sm-C^* to the Cry-*G* phase is not a direct one, but might involve a tilted hexatic phase as an intermediate step. We have conducted preliminary structural measurements on these films and found that not any intermediate phase is resolvable in the interior transition by electron diffraction, suggesting that this interior Sm-C^* – Cry-*G* phase transition is indeed a direct one. But, we observed visually that the diffraction at the surface and adjacent-to-surface transitions often consisted in part of rapidly rotating hexaticlike arcs. However, since the motion of the arcs was fast compared to the typical exposure time of several seconds, we were unable to record equilibrium diffraction patterns showing the evidence for the intermediate tilted hexatic phase. The result in these films observed here is somewhat similar to the thermal behavior of Sm-*A* – crystal-*B* (Cry-*B*) layer-by-layer transitions of orthogonal free-standing liquid-crystal films of N-(4-n-butyloxybenzylidene)-4-n-octylaniline (40.8) compound [12,13]. The effective penetration length of the surface ordering found in the study of Ref. [12] is slightly less than one molecular layer. Interestingly, in C7 films the thermal behavior of both the Sm-*A* – Sm-C^* and Sm-C^* – Cry-*G* transitions suggests that the penetration length of the surface ordering is about 7 molecular layers, implying that the surface ordering field is considerably stronger in C7 than in 40.8. We speculate that its physical mechanism is possibly similar to the long-range tilt-induced ordering effect observed in an earlier study [14], in which the tilt of the surface smectic-*I* (Sm-*I*) phase is found to induce hexatic order into the interior

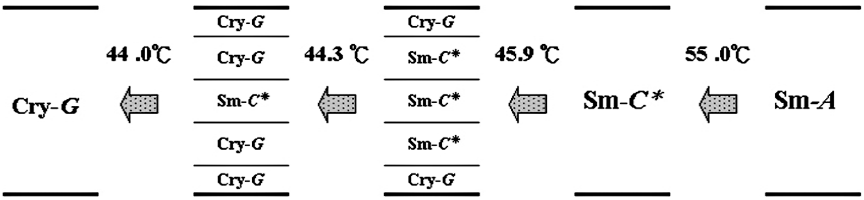

FIGURE 3 The complete phase sequence in a 15-layer C7 film below 59°C upon cooling.

Sm-*C* phase in a very thick film. Nevertheless, our data also represent the first experimental observation of multiple-step Sm-C^* – Cry-*G* freezing transitions near the bulk crystallization temperature in thin liquid-crystal films. The entire phase transition sequence in C7 films is summarized in Figure 3.

In summary, our result provides the first thermal evidence that the first-order Sm-*A* – Sm-C^* transition in *thin* free-standing films of the chiral liquid-crystal material C7 with large spontaneous polarization can be second-order in films less than 15 layers. The heat-capacity anomaly at the Sm-*A* – Sm-C^* transition exhibits an interesting crossover behavior as a function of film thickness in reduced dimensions. This result is qualitatively similar to the thermal study of MDW1397 films [9], and also supports some of the observations in the earlier experiment of C7 films [6]. Our result in C7, together with the other results reported in Refs. [9,15,16], shows that the thickness-dependent phase transitions in liquid crystals is a very prevalent and interesting phenomenon that is not fully understood and should be studied further. We also report the tilted surface Cry-*G* phase occurring at the lower temperatures. Its thermal behavior suggests stronger surface ordering field than the orthogonal surface Cry-*B* phase in 40.8 films, probably due to the molecular tilt.

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