

Comparative x-ray measurements of a de Vries smectic-A material in bulk and confined geometries

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X-ray investigations have been carried out on a material exhibiting the de Vries smectic-A (Sm-A) phase in bulk and confined geometries. In the confined geometry realized by confining the material in an Anopore membrane, while the minimal layer shrinkage feature characteristic of the de Vries materials is retained, the overall change of the layer spacing from the Sm-A to the Sm-C phase is much less compared to the bulk geometry and also the transition gets smeared out. A “crossover” behavior, which has been recently ascribed to different molecular packing arrangements within the Sm-A phase, is seen in both geometries. With the support from data on another non-de Vries type of material we suggest that the associated feature may not be due to a phase transition, but competition between the thermally driven stretching and molecular tilt.

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Smectic-A (Sm-A) and smectic-C (Sm-C) liquid crystals are layered phases possessing quasi-long-range positional order in one dimension represented by a mass-density wave [1]. The wave vector of this density wave is along the director in the case of the Sm-A phase, while it is tilted in the case of the Sm-C phase. Owing to this feature the layer spacing is significantly lower in the tilted Sm-C phase than in the orthogonal Sm-A phase. About 30 years ago Diele *et al.* [2] reported a material in which the layer spacing was similar in the Sm-A and Sm-C phases. To explain this feature de Vries [3] suggested a new type of Sm-A phase in which the molecules are tilted with respect to the layer normal just as in the Sm-C phase but the tilt directions of different layers are uncorrelated. A more general version of this wherein the azimuthal correlation even within the layers is short-ranged has also been predicted. The de Vries Sm-A phase exhibited by materials particularly composed of chiral molecules has attracted much attention recently [4] owing to the nonobservation of zigzag defects as a direct consequence of this minimal layer shrinkage across the Sm-A–Sm-C (rather chiral Sm-C) phase transition. The technological importance lies in the fact that the zigzag defect structure causes a reduction in the effective optical tilt angle degrading the quality of the electro-optic device.

The influence of geometrical restrictions on the liquid crystalline transitions has been of significant interest in recent times [5]. Different types of porous materials have been very effectively used for such purposes. These include polymer matrices, well-known examples of which are polymer dispersed liquid crystals, porous glasses with randomly oriented and interconnected pores, silica gels and aerosil with broad pore size distributions, and the commercially available filter membranes such as Millipore, Nuclepore, and Anopore membranes. Of these, the Anopore membranes are attractive as they have highly parallel cylindrical pores with narrow size distributions and smoother cavity surface. The effect of confinement has been mostly studied on the isotropic-nematic transition (Iso-N) [6–10], but transitions involving smectic-A (Sm-A) [11,12], chiral smectic-C (Sm-C*) [13–16], hexatic-B [17], and crystal-B [18,19] phases have

also been investigated. Here we report experimental investigations of the influence of confined geometry on the de Vries Sm-A phase.

Measurements were carried out on *trans*-1,4-cyclohexanedi-n-octyloxybenzoate (TCOB), which is one of the classic de Vries materials [20]. This compound exhibits the following phase sequence in the cooling mode:

Isotropic 178.3 °C smectic-A 118.8 °C smectic-C
 110.4 °C crystal-B.

These transition temperature values are in close agreement with those reported by de Vries [20]. For measurements in confined geometry, the sample was filled in Anopore membranes (Whatman, USA). These membranes are made from aluminum oxide and have parallel cylindrical pores penetrating the 60 μm thickness normally, with a nominal pore size of 200 nm. The procedure adapted to fill the sample into the pores of the Anopore membrane is described elsewhere [19]. The x-ray diffraction experiments were done using Cu $K\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$) from a fine focus sealed-tube generator in conjunction with double mirror focusing optics. The mirror optics provides a nearly parallel beam over a long working distance. The detector was an image plate detector (MAC Science, Japan, model DIP 1030) with an effective resolution of $100 \times 100 \mu\text{m}^2$.

Figures 1(a) and 1(b) show the raw intensity versus the scattering angle (2θ) profiles obtained in the Sm-A phase of the bulk and Anopore samples, respectively. The profiles are sharp, clearly defined and are quite similar in both the geometries, a feature that is true in the Sm-C and Cr-B phases as well. For the bulk sample, the onset of the Sm-A–Sm-C transition was signified by a clear change in the peak 2θ value; the change appeared to be very gradual for the Anopore sample. In contrast, even on a qualitative level, a significant jump in the peak 2θ position was seen across the Sm-C–Cr-B transition in both the geometries. The detailed temperature dependence of the layer spacing (d) across the Sm-A–Sm-C transition in the two geometries is shown in Fig. 2. First, notice that for the bulk sample the overall change in the d value is quite small in agreement with the observation in Ref. [20]. The minimal layer shrinkage seen

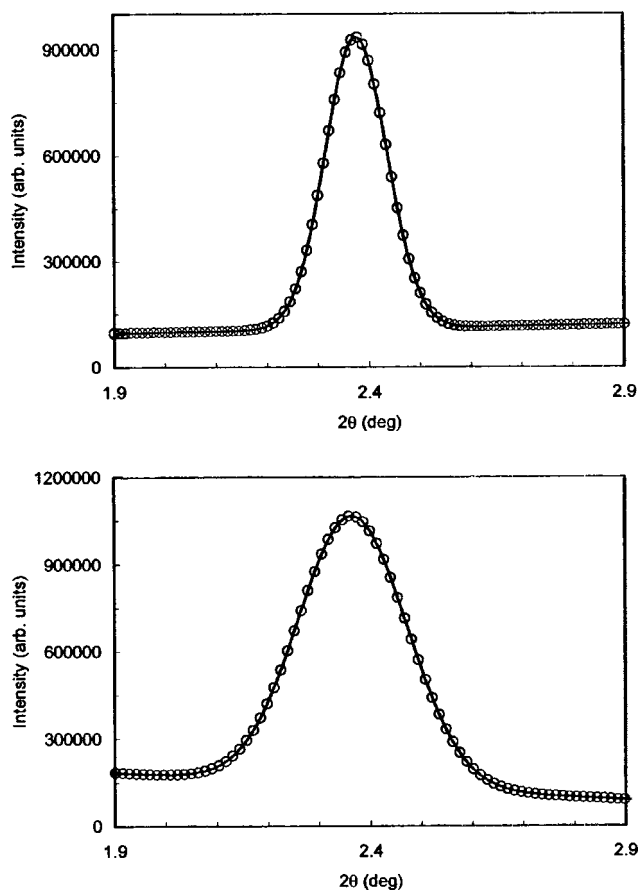


FIG. 1. X-ray intensity vs diffraction angle 2θ profiles in the Sm-A phase of TCOB sample in the (a) bulk and (b) confined geometries.

puts the Sm-A phase of this material in the class of de Vries Sm-A. Upon confinement in the Anopore membrane the qualitative behavior is the same as that for the bulk sample. However, the total change is smaller and more importantly the Sm-A–Sm-C transition gets smeared out. In fact, similar features were observed [16] by us for another, but chiral, material, termed A7, exhibiting a first order Sm-A–chiral Sm-C (Sm-C*) transition. Although then not analyzed in those terms, we now realize that having only ~ 1 Å change across the transition to the Sm-C* phase, the Sm-A phase of A7 may also be of the de Vries type [21].

In order to test whether the smearing out of the Sm-A–Sm-C transition is a general feature realized upon confinement in Anopore membranes, we conducted the experiments on another material, (8OSI*) exhibiting such a transition and having a large (3.5 Å) layer spacing change between the Sm-A to the Sm-C* phases. It may be mentioned that the change is continuous through the transition with no observable jump; such a large change in the d value implies that it cannot be a de Vries material. The thermal variation of the layer spacing in the bulk and restricted (Anopore 200 nm) geometries is shown in Fig. 3. The Anopore sample shows a 3 °C shift in the transition temperature and a slight increase in the absolute value of d in the Sm-A phase. The shift in the transition temperature is a general feature when the material is confined and although the magnitudes of the

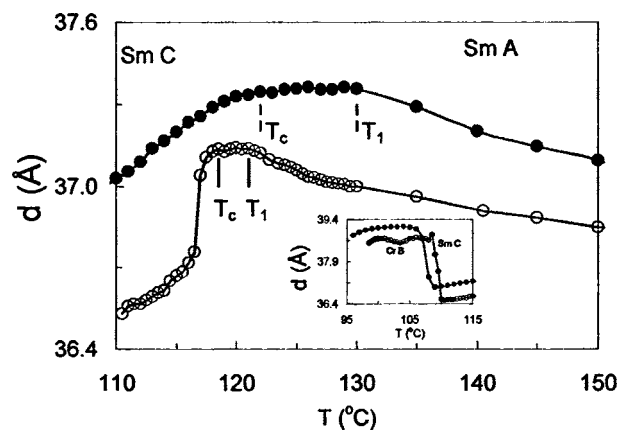


FIG. 2. Thermal variation of the layer spacing d across the Sm-A–Sm-C transition of the de Vries compound TCOB sample in the bulk (○) and Anopore (●) geometries. Notice that the transition is smeared out for the Anopore sample. See text for explanations of the notations T_c and T_1 . The inset shows the temperature dependence of d across the Sm-C–Cr-B transition for the bulk (○) and confined (●) geometries. The solid line through the data points is only a guide to the eye.

shift could be different, it is seen irrespective of the phases involved [5,9,16,17]. The small increase in the d value was also observed for the A7 compound and it has been explained due to the hydrophobic interaction between the membrane surface and the alkyl tail of the liquid crystalline molecule [16]. But for these differences, which are not significant from the viewpoint of the current studies, the 8OSI* sample behaves essentially similar in the bulk and confined geometries. To facilitate a better comparison in the thermal variation of the layer spacing, the data is plotted by accounting for the shift in the transition temperature and normalizing the d value in the Sm-A phase of the bulk and Anopore

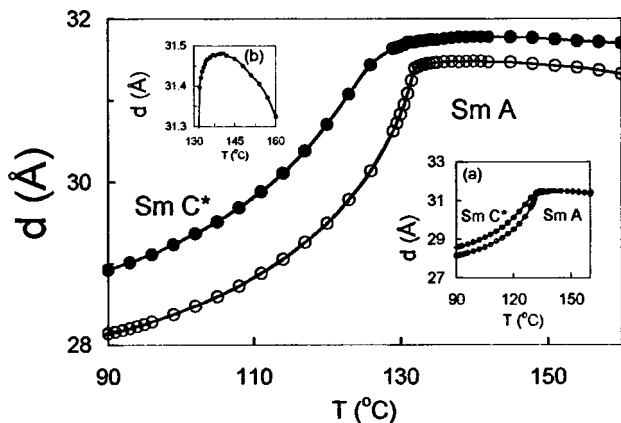


FIG. 3. Temperature dependence of the layer spacing d across the Sm-A–Sm-C* transition of the non-de Vries compound 8OSI* sample in the bulk (○) and Anopore (●) geometries, showing a substantial change in the d value from the Sm-A to the Sm-C* transition. Inset (a) shows the same data normalized for the transition temperature and d values in the Sm-A phase of the two geometries. Inset (b) shows the data obtained in the bulk geometry on an enlarged scale to illustrate the presence of a plateau-like region for this sample also.

samples. The data shown in the inset (a) of Fig. 3 emphasizes the similarity in the behavior.

A feature to be noted in the data for TCOB is that in the Sm-A phase away from the transition to the Sm-C phase the layer spacing increases with decreasing temperature and in the vicinity of the transition (at a temperature marked T_1 in Fig. 2) shows a plateau before exhibiting a smooth drop at T_c , the Sm-A–Sm-C transition temperature. In fact such a result was seen by us about 10 years ago [22] in a material exhibiting a partially bilayer Sm-A to a partially bilayer Sm-C phase. Recently, Huang *et al.* [23] have observed a similar behavior in a chiral material with minimal layer shrinkage across the Sm-A–Sm-C* transition and argue that T_1 marks a transition between the high temperature conventional Sm-A to the low temperature de Vries Sm-A phase. It is thus possible that TCOB, a classic de Vries material also exhibits such a crossover transition. Further the TCOB sample in the Anopore geometry also exhibits such a feature, although the plateau region exists over a larger temperature range. A different viewpoint that we would like to argue is based on our results for 8OSI*, which as seen above, has a large variation of d between the Sm-A–Sm-C* phases and thus cannot be termed as a de Vries material. The inset (b) of Fig. 3 shows on an enlarged scale the temperature variation of d in the Sm-A phase for 8OSI*. Note that there appears to be the crossover behavior similar to the ones seen for the de Vries materials mentioned above. Therefore we suggest that the change of slope in the thermal variation of d in the Sm-A phase may not be associated with an additional transi-

tion. A possible alternative explanation could be the following. The large increase in d with decreasing temperature in the Sm-A phase is due to the thermally driven stretching of the alkyl chains [24]. Below T_c , the tendency of the molecules to tilt with respect to the layer normal results in a decrease in the layer spacing [25]. Thus in the temperature range between T_c and T_1 , the competition between the two opposing trends could lead to the observation of a plateau region [26]. This would mean that the effect at T_1 is only an artifact and not due to any thermodynamic phase transition. This is perhaps the reason Huang *et al.* [23] did not observe any calorimetric signature at T_1 .

In summary, we have carried out x-ray investigations on a classic material exhibiting the de Vries Sm-A phase in bulk and confined geometries. In the confined geometry, while the minimal layer shrinkage feature characteristic of the de Vries materials is retained the overall change of the layer spacing from the Sm-A to the Sm-C phase is much less compared to the bulk geometry. Further the transition gets smeared out in the confined case. We have also observed the “crossover” type of behavior in the Sm-A phase recently reported by Huang *et al.* [23], ascribing it to a possible transition from the conventional to the de Vries Sm-A phase. Comparing the results obtained on another non-de Vries type of material we suggest that the associated feature may not be due to a phase transition, but competition between the thermally driven stretching and molecular tilt.

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- [1] See, e.g., S. Chandrasekhar, *Liquid Crystals*, 2nd ed. (Cambridge University Press, Cambridge, England, 1992).
- [2] S. Diele, P. Brand, and H. Sackman, *Mol. Cryst. Liq. Cryst.* **16**, 105 (1972).
- [3] A. De Vries, in *Abstracts of the Fifth International Liquid Crystal Conference, Stockholm*, edited by G. H. Brown (ILC Society, Kent, OH, 1974), p. 150; A. De Vries, *Mol. Cryst. Liq. Cryst.* **41**, 27 (1977); A. De Vries, A. Ekachai, and N. Spielberg, *Mol. Cryst. Liq. Cryst. Lett.* **49**, 143 (1979).
- [4] M. D. Radcliffe, M. L. Brostrom, K. A. Epstein, A. G. Rappaport, B. N. Thomas, R. Shao, and N. A. Clark, *Liq. Cryst.* **26**, 789 (1999); F. Giesselmann, P. Zugenmaier, I. Dierking, S. T. Lagerwall, B. Stebler, M. Kaspar, V. Hamplova, and M. Glogarova, *Phys. Rev. E* **60**, 598 (1999); Yu. P. Panarin, V. Panov, O. E. Kalinovskaya, and J. K. Vij, *J. Mater. Chem.* **9**, 2967 (1999); M. S. Spector, P. A. Heiney, J. Naciri, B. T. Weslowski, D. B. Holt, and R. Shashidhar, *Phys. Rev. E* **61**, 1579 (2000); N. A. Clark, T. Bellini, R.-F. Shao, D. Coleman, S. Bardon, D. R. Link, J. E. MacLennan, X.-H. Chen, M. D. Wand, D. M. Walba, P. Rudquist, and S. T. Lagerwall, *Appl. Phys. Lett.* **80**, 4097 (2002).
- [5] For an excellent collection of review articles in this field, see *Liquid Crystals in Complex Geometries*, edited by G. P. Crawford and S. Zumer (Taylor & Francis, London, 1996).
- [6] M. Kuzma and M. M. Labes, *Mol. Cryst. Liq. Cryst.* **100**, 103 (1983).
- [7] G. P. Crawford, R. Stannarius, and J. W. Doane, *Phys. Rev. A* **44**, 2558 (1991).
- [8] G. S. Iannacchione and D. Finotello, *Phys. Rev. Lett.* **69**, 2094 (1992).
- [9] M. D. Dadmun and M. Muthukumar, *J. Chem. Phys.* **98**, 4850 (1993).
- [10] G. P. Sinha and F. M. Aliev, *Phys. Rev. E* **58**, 2001 (1998).
- [11] G. S. Iannacchione, J. T. Mang, S. Kumar, and D. Finotello, *Phys. Rev. Lett.* **73**, 2708 (1994).
- [12] T. Bellini, N. A. Clark, and D. W. Schaefer, *Phys. Rev. Lett.* **74**, 2740 (1995).
- [13] F. M. Aliev, in *Liquid Crystals in Complex Geometries*, edited by G. P. Crawford and S. Zumer (Taylor & Francis, London, 1996), p. 345.
- [14] M. Skarabot, S. Kralj, R. Blinc, and I. Musevic, *Liq. Cryst.* **26**, 723 (1999).
- [15] S. A. Rozanski, R. Strannarius, F. Krenes, and S. Diele, *Liq. Cryst.* **28**, 1071 (2001).
- [16] K. L. Sandhya, S. K. Prasad, D. S. Shankar Rao, and Ch. Bahr, *Phys. Rev. E* **66**, 031710 (2002).
- [17] C. V. Lobo, S. K. Prasad, and D. S. Shankar Rao, *Phys. Rev. E* **69**, 051706 (2004).
- [18] J. Werner, K. Otto, D. Enke, G. Pelzl, F. Janowski, and H. Kresse, *Liq. Cryst.* **27**, 1295 (2000).
- [19] K. L. Sandhya, Geetha G. Nair, S. K. Prasad, and Anjuli Khandelwal, *Liq. Cryst.* **28**, 1847 (2001).
- [20] A. de Vries, *J. Chem. Phys.* **71**, 25 (1979).
- [21] It must be remarked that C7, a structurally similar material has

- been pointed out to be having the de Vries Sm-A phase. O. E. Panarina, Y. P. Panarin, J. K. Vij, M. S. Spector, and R. Shashidhar, *Phys. Rev. E* **67**, 051709 (2003).
- [22] D. S. Shankar Rao, Ph.D. thesis, Univ. of Bangalore, 1993 (unpublished).
- [23] C. C. Huang, S. T. Wang, X. F. Han, A. Cady, R. Pindak, W. Caliebe, K. Ema, K. Takekoshi, and H. Yao, *Phys. Rev. E* **69**, 041702 (2004).
- [24] A. De Vries, *Mol. Cryst. Liq. Cryst.* **11**, 361 (1970); W. L. McMillan, *Phys. Rev. A* **6**, 936 (1972).
- [25] M. Delaye and P. Keller, *Phys. Rev. Lett.* **37**, 1065 (1976); K. C. Lim and J. T. Ho, *ibid.* **40**, 1576 (1978); M. Skarbot, K. Kocevcar, R. Blinc, G. Heppke, and I. Musevic, *Phys. Rev. E* **59**, R1323 (1999).
- [26] It may be pointed out that the temperature dependence of d is not linear, particularly for the bulk TCOB sample, at temperatures above T_1 . In fact, there are indications of such supralinear (increasing negative slope with decreasing temperature) behavior of the values of the intercolumnar distance within the columnar phase [E. Fontes, P. A. Heiney, and W. H. De Jeu, *Phys. Rev. Lett.* **61**, 1202 (1988)]. Thus, at least in some materials, the stretching of the alkyl chains may not cause a simple linear increase in d with decreasing temperature. Anyway, since the overall change itself is much smaller in the Anopore TCOB sample, this effect will also be smaller.