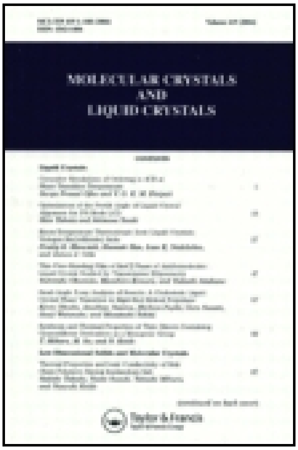


Molecular Crystals and Liquid Crystals

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

Investigation of the Smectic-A-Smectic-C* Transition in Liquid Crystals by Adiabatic Scanning Calorimetry

K. Denolf [a] , B. Van Roie [a] , G. Pitsi [a] & J. Thoen [a]

[a] Laboratorium voor Akoestiek en Thermische Fysica Departement Natuurkunde en Sterrenkunde, Katholieke Universiteit Leuven, Celestijnenlaan, Leuven, Belgium

To cite this article: K. Denolf, B. Van Roie, G. Pitsi & J. Thoen (2006): Investigation of the Smectic-A-Smectic-C* Transition in Liquid Crystals by Adiabatic Scanning Calorimetry, Molecular Crystals and Liquid Crystals, 449:1, 47-55

To link to this article: http://dx.doi.org/10.1080/15421400600580204

Mol. Cryst. Liq. Cryst., Vol. 449, pp. 47–55, 2006

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400600580204

Investigation of the Smectic-A–Smectic-C* Transition in Liquid Crystals by Adiabatic Scanning Calorimetry

K. Denolf
B. Van Roie
G. Pitsi
J. Thoen
Laboratorium voor Akoestiek en Thermische Fysica Departement
Natuurkunde en Sterrenkunde, Katholieke Universiteit Leuven,
Celestijnenlaan, Leuven, Belgium

We performed Adiabatic Scanning Calorimetry (ASC) measurements on two ferroelectric liquid crystals: S-(-)-4-(2′-methylbutyloxy)phenyl 4-n-octyloxybenzoate and S-(-)-2-methylbutyl 4-n-nonanoyloxybiphenyl-4′-carboxylate. Our experiments showed that no latent heat was present for the smectic-A – smectic-C (AC*) transition to within the experimental resolution. Therefore the AC* transition in both samples can be classified as a continuous one. By fitting the specific heat data we showed that this phase transition can be described by an extended mean-field model.*

Keywords: Adiabatic Scanning Calorimetry; ferroelectric liquid crystals; smectic-A; smectic-C*

1. INTRODUCTION

During the last few years the smectic-A-smectic-C* (AC*) phase transition in liquid crystals has been studied extensively. In the smectic-A phase, the liquid crystal molecules show an orientational order, just like in the nematic phase, and additionally they show a translational order in one dimension. The molecules are packed in layers and they are oriented according to a director perpendicular to the layers. The smectic-C* phase is similar to the smectic-A phase, the molecules

Address correspondence to K. Denolf, Laboratorium voor Akoestiek en Thermische Fysica Departement Natuurkunde en Sterrenkunde, Katholieke Universiteit Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium. E-mail: katleen.denolf@fys.kuleuven.ac.be

are also packed in layers, but the director is tilted with respect to the layer normal and rotates around the direction perpendicular to the smectic layer. The director tilt angle, θ, is the order parameter of this AC* transition which has two degrees of freedom.

According to the theoretical predictions of de Gennes [1], the AC* phase transition should belong to the three-dimensional *XY* universality class (n = 2, d = 3). This hypothesis was not in accordance with experimental studies done in the past: early experiments suggested a classical Landau mean-field behavior for the AC* transition [2–5], later results, however, indicated a tricritical character [6].

In this paper we present the results of Adiabatic Scanning Calorimetry (ASC) measurements of two compounds exhibiting an AC* phase transition. The ASC technique allows us to directly measure the temperature dependence of the enthalpy $H(T)$ (including latent heat if present) and derive also the temperature dependence of the specific heat capacity $c_p(T)$.

2. EXPERIMENT

2.1 Samples

The two ferroelectric liquid crystals studied in this experiment S-(-)-4-(2′-methylbutyloxy)phenyl 4-n-octyloxybenzoate (D1 for short) and S-(-)-2-methylbutyl 4-n-nonanoyloxybiphenyl-4′-carboxylate (D2 for short) were synthesized at the Military University of Technology in Poland by prof. R. Dabrowski. The phase sequence of the liquid crystals on cooling down is the following:

$$\text{For D1}: \quad \text{I} \xrightarrow[60^\circ\text{C}]{} \text{Sm-A} \xrightarrow[43.5^\circ\text{C}]{} \text{Sm-C}^* \xrightarrow[42.5^\circ\text{C}]{} \text{Cr}$$

$$\text{For D2}: \quad \text{I} \xrightarrow[59.5^\circ\text{C}]{} \text{Sm-A} \xrightarrow[41.5^\circ\text{C}]{} \text{Sm-C}^* \xrightarrow[39^\circ\text{C}]{} \text{Cr}$$

For the experiments we used 0.96 g of D1 and 1.19 g of D2 in our calorimetric measuring cell.

2.2. Adiabatic Scanning Calorimetry

We used Adiabatic Scanning Calorimetry to study the AC* transition in the two ferroelectric liquid crystals. This calorimetric technique is the only one that is capable to measure the temperature dependence of the enthalpy and the specific heat capacity simultaneously with a very high resolution.

The sample is placed into a holder and a known heating power is applied via an electric heater. The resulting temperature change as a function of time is measured by means of a thermistor and the total heat capacity (this is the heat capacity of the sample and the sample holder) is obtained from:

$$C = C_h + C_s = \frac{P}{\dot{T}} = \frac{P^{el} + P^{leak}}{\dot{T}} \tag{1}$$

$\dot{T} = dT/dt$ can be calculated by numerically differentiating the measured $T(t)$ data and P^{el} is the known electrical power applied to the sample. The only problem left is that in general P^{leak}, the power that flows away because of possible heat leaks in the system, is unknown. In order to avoid heat leakage during a heating run different shields are placed around the sample holder to create an adiabatic environment, connections between the successive stages are minimized and the space between the stages is evacuated. To cool down a sample, a negative power is needed. That is why for a cooling run, no electrical power is applied and the shields surrounding the sample are at a slightly lower temperature and kept at a constant temperature difference with the sample cell. For both cases, heating runs and cooling runs, the power applied to the sample can thus be known and the total heat capacity can be calculated. After subtracting the heat capacity of the holder, which can be measured easily doing a calibration experiment, from the total heat capacity and dividing this result by the sample mass, one obtains the specific heat capacity of the sample.

During our experiments two different adiabatic scanning calorimeters were used. One, used to measure D1, where the sample holder is surrounded by two shields made of good conductive material. Each shield contains a thermistor or a platinum resistance to measure the temperature and a heating coil to control the temperature of the shield. The third shield has no heating coil but is surrounded by an air oven. In the other calorimeter, used to measure D2, the sample holder is surrounded by two shields. The temperature of the inner shield is controlled by a heating coil and a thermistor and the outer shield is surrounded by a temperature controlled water bath. In order to maintain the thermodynamical equilibrium, very slow scanning rates (2 mK/min) were applied to the samples.

An important advantage of using the ASC technique is that the enthalpy change of sample can be measured directly, by inverting the $T(t)$ data:

$$H(T) - H(T_s) = P(t(T) - t(T_s)) \tag{2}$$

with T_s the starting temperature of the run. Thus the latent heat of a first order transition can be determined, if present, and we are able to distinguish a first order transition from a continuous one. More information about this technique can be found in literature [7,8].

3. RESULTS AND DISCUSSION

3.1. Latent Heat

Phase transitions can be classified into first order and continuous ones. A perfect first order transition is characterized by an infinitely steep jump in the enthalpy, also called the latent heat. As previously mentioned this latent heat, if present, can be directly measured, using Adiabatic Scanning Calorimetry. For the two investigated liquid crystals, no latent heat was observed to within the experimental resolution

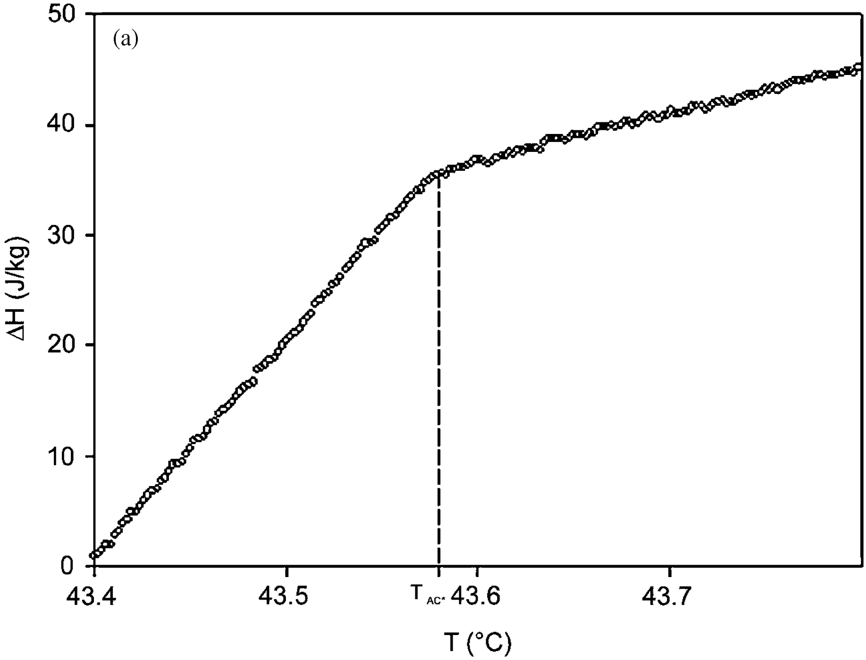


FIGURE 1 Temperature dependence of the enthalpy for D1 (a) and D2 (b) near the AC* transition. Note that for clarity a linear background was subtracted from the enthalpy data for both samples. To within the experimental resolution ($\Delta H_L < 1\,\text{J/kg}$), no latent was observed for these two liquid crystal compounds.

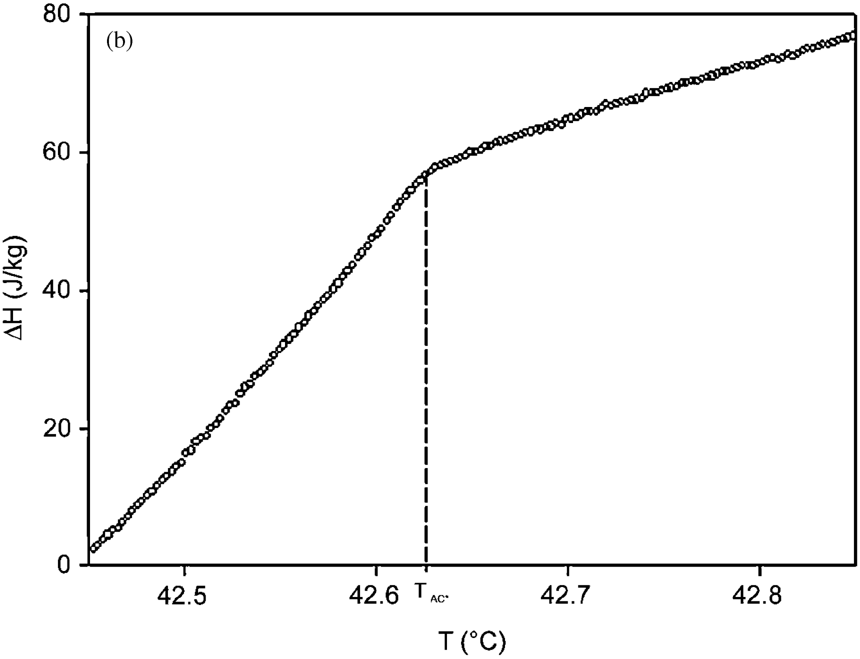


FIGURE 1 Continued.

($\Delta H_L < 1$ J/kg). This is shown in Figure 1. These observations give a quantitative proof for the continuous character of the AC* transition.

3.2. Specific Heat Capacity

As mentioned in the introduction, the AC* transition should, according to theoretical predictions, belong to the three-dimensional XY universality class. Early experiments suggested a classical Landau mean-field behavior for this transition [2–5], later results, however, indicated a tricritical character [6].

Figure 2 shows the specific heat capacity as a function of temperature for the two investigated ferroelectric liquid crystals. For both samples, the specific heat curve shows pretransitional effects on the low temperature side and a rather abrupt jump on the high temperature side. These observations suggest a mean-field behavior.

According to the Landau theory, the free energy can be written as a power series in the order parameter θ:

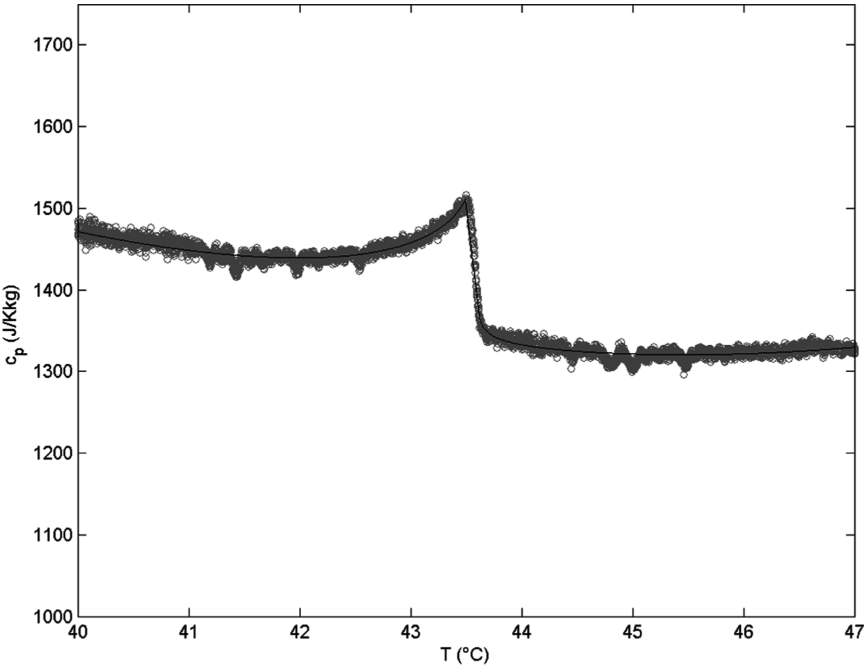
$$f = f_0 + at\theta^2 + b\theta^4 + c\theta^6 \tag{3}$$

In this expression a, b and c are the expansion coefficients, $t = (T - T_c)/T_c$ is the reduced temperature difference and f_0 is the non singular part of the free energy. Using this free energy expansion, an expression for the specific heat capacity can be obtained [9]:

$$c = c_0 \qquad (T > T_c) \tag{4}$$

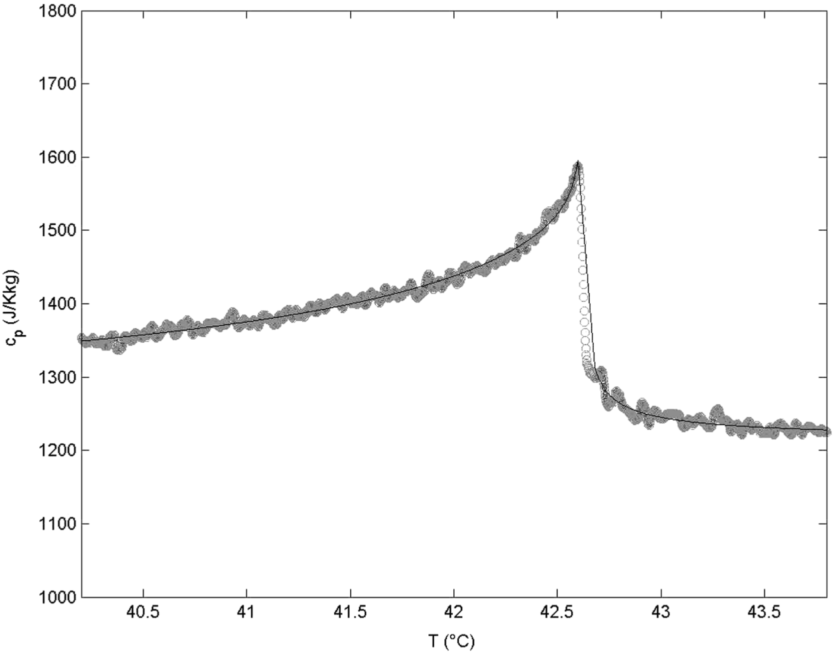
$$c = c_0 + AT|T_m - T|^{-1/2} \qquad (T < T_c) \tag{5}$$

In this expression $c_0 = B + Et$, $A = \sqrt{\frac{a^3}{12c(T_c)^3}}$ and $T_m = T_c\left(1 + \frac{t_0}{3}\right)$ with $t_0 = b^2/ac$. The first term, c_0, represents the f_0 contribution to the specific heat where B and E are two constants that characterize the linear background. Because of the presence of pretransitional fluctuations on both sides of the c_p-curve (Fig. 2), Gaussian fluctuation terms should



(a)

FIGURE 2 Comparison between experimental $c_p(T)$ data (obtained from a cooling run) near the AC* transition in D1 (a) and D2 (b) and the theoretical fits with the predictions by a mean field model (expressions (6) and (7)). To fit the $c_p(T)$ data obtained for D1, an additional term was added to expression for c_0 (expression (8)).



(b)

FIGURE 2 Continued.

be included in the fitting expressions (4) and (5). [9,10,11]

$$c = c_0 + c_g\left(\frac{T}{T_c}\right)^2 |t|^{-1/2} \quad (T > T_c) \tag{6}$$

$$c = c_0 + AT|T_m - T|^{-1/2} + \frac{\sqrt{2}}{2} c_g\left(\frac{T}{T_c}\right)^2 |t|^{-1/2} \quad (T < T_c) \tag{7}$$

After fitting the c_p-data of D2 to the expression above (Fig. 2(b)), our presumption of a mean-field like behavior is confirmed for this liquid crystal. For D1, however, a complication arose fitting the c_p-data with expressions (6) and (7) because of the crystalline phase which is only 1°C below T_{AC^*}. As can be seen in Figure 2(a), the AC* transition seems to be superimposed on a nonlinear precursory increase associated with the smectic-C*-crystalline transition. To take this effect into account, we introduced a higher order term in the expression for c_0 [12]:

$$c_0 = B + Et + Ft^2 \tag{8}$$

TABLE 1 Parameter Values for Fitting $c_p(T)$ Data of D1 and D2 near the AC* Transition with Expressions (6) and (7). To Fit the $c_p(T)$ Data Obtained for D1, an Additional Term was Added to for c_0 (expression (8))

	B (J/kgK)	E (J/kgK)	F (J/kgK)	A (J/kgK$^{-3/2}$)	T$_m$ (°C)	T$_c$ (°C)	c$_g$ (J/kgK)	χ^2
D1	1323 ± 2	-361.10 ± 3.10	$350.10^3 \pm 2.10^3$	0.383 ± 0.002	44.04 ± 0.02	43.576 ± 0.004	0.51 ± 0.01	1.050
D2	1202 ± 2	$5.10^2 \pm 1.10^2$		0.790 ± 0.002	43.36 ± 0.02	42.627 ± 0.002	1.47 ± 0.02	1.305

The parameter values for fits to our D1 and D2 data with expressions (6) and (7) are summarized in Table 1.

It should also be noticed that the nature of the AC* transition can be affected by the thermal history of the sample. If a heating run is performed after the sample entered into the smectic-C*-crystalline region, a peculiar behavior across the smectic-A-smectic-C* and smectic-A-isotropic transition was observed. This strange effect was not observed when the sample was cooled or heated across the AC* transition and is apparently caused by undercooling effects.

4. CONCLUSIONS

The smectic-A-smectic-C* phase transition in S-(-)-4-(2′-methylbutyloxy)phenyl 4-n-octyloxybenzoate and S-(-)-2-methylbutyl 4-n-nonanoyloxybiphenyl-4′-carboxylate was investigated by Adiabatic Scanning Calorimetry. Thanks to the ability of measuring the enthalpy change of a sample directly and the great precision of this calorimetric technique we were able to show that the AC* transition is a continuous one, since no latent heat was observed within the experimental resolution ($\Delta H_L < 1\, J/kg$). After fitting the specific heat data it was shown that the AC* transition in these compounds can be described by a mean field model.

REFERENCES

[1] de Gennes, P. G. (1973). *Mol. Cryst. Liq. Cryst.*, *21*, 49.

[2] Huang, C. C. & Viner, J. M. (1982). *Phys. Rev.*, *A25*, 3385.

[3] Huang, C. C. & Dumrongrattana, S. (1986). *Phys. Rev.*, *A34*, 5020.

[4] Chan, T., Bahr, Ch., Heppke, G., & Garland, C. W. (1993). *Liq. Cryst.*, *13*, 667.

[5] Yang, F., Bradberry, G. W., & Sambles, J. R. (1994). *Phys. Rev.*, *E50*, 2834.

[6] Ema, K., Tagaki, A., & Yao, H. (1997). *Phys. Rev.*, *E55*, 508.

[7] Thoen, J., Bloemen, E., Marynissen, H., & Van Dael, W. (1982). *Proceedings of the 8th symposium on Thermophysical Properties, National Bureau of Standards, Maryland 1981*, Sengers, J. V. (Ed.), American Society of Mechanical Engineers: New York, 422–428.

[8] Thoen, J. (1997). In: *Physical Properties of Liquid Crystals*, Demus, D., Goodby, J., Gray, G., Spiess, H.-W., & Vill, V. (Eds.), Wiley-VCH: Weinheim, 208–232.

[9] Mercuri, F., Marinelli, M., Zammit, U., Huang, C. C., & Finotello, D. (2003). *Phys. Rev.*, *E68*.

[10] Reed, L., Stoebe, T., & Huang, C. C. (1995). *Phys. Rev.*, *E 52*, R2157.

[11] Ma, S.K. (1976). *Modern Theory of Critical Phenomena*, Benjamin-Cummings: Reading, MA.

[12] Thoen, J. & Seynhaeve, G. (1985). *Mol. Cryst. Liq. Cryst.*, *127*, 229–256.