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## Liquid Crystals

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### **A specialized apparatus for the study of liquid crystals at high pressures**

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## A specialized apparatus for the study of liquid crystals at high pressures

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A pressure system specially designed for the study of liquid crystal materials at high pressures up to 4 kbar is presented. The pressure system is based on a hydrostatic screw injector and uses either oil or gas as the pressure transmitting medium. The type of measurements which can be performed with the instrument include polarized microscopy, optical spectroscopy, electrooptic and electrical measurements. The different measurements performed place specific constraints on the design of the apparatus and the pressure cells, and details are given. A preliminary study of the smectic A modification of the twist grain boundary phase ( $TGB_A$ ) at high pressures is presented. The pressure versus temperature phase diagram shows (i) a negative gradient of the  $TGB_A$ /isotropic phase boundary line and (ii) that the  $TGB_A$  phase does not exist at pressures above about 250 bar. Following Lubensky's analogy between the  $TGB_A$  phase and type II superconductors, the disappearance of the  $TGB_A$  phase at high pressure may imply that the Landau–Ginsburg parameter  $\kappa$  decreases with pressure.

### 1. Introduction

The properties of liquid crystal materials at atmospheric pressure are generally well-understood, though there are still relatively few studies of these materials at high pressures (Shashidhar *et al.* [1], Pollmann *et al.* [2] or more recently the work of Urban and co-workers [3]). The study of the properties of liquid crystals as a function of pressure as well as temperature allows a much more detailed analysis of the ordering in the materials and of the intermolecular interactions. Triple points or new mesophases may be observed at high pressures. The possibility of studying the behaviour of critical phenomena as a function of pressure provides a means to test the Landau–de Gennes theory. The order of some phase transitions may change with pressure (see for example [2 (e)]).

We present in this paper an instrument which is specially designed for the study of liquid crystals at high pressures. We describe the pressure system and some of the specialized specimen cells. We also present some typical measurements obtained with the instrument, including a preliminary study of the smectic A modification of the twist grain boundary phase ( $TGB_A$ ) at high pressure.

### 2. Specification and constraints

The design of a pressure system and specimen cells for the study of liquid crystals has to take into account a number of constraints which are related to both the nature of

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the materials investigated and the type of measurements usually made on liquid crystals. These measurements include:

- (i) polarized microscopy for phase characterization;
- (ii) optical spectroscopy to study the selective reflection of light from chiral phases;
- (iii) electrooptic measurements to determine the response times and threshold voltages of electric field induced distortions;
- (iv) electrical measurements to determine the spontaneous polarization of ferroelectric systems.

Such measurements are performed with films which are only a few microns thick. The films are usually produced between glass plates with appropriate surface treatments and transparent electrodes. It is desirable and, for some experiments, essential that the thickness of the specimen is maintained constant when the pressure is applied. In materials with several smectic phases, the subtle changes observed by polarizing microscopy at the phase transitions are sometimes more obvious on free standing films, where there are no constraints on the surfaces, than in traditional glass cells (see for example [4]). Therefore, ideally, the cell design will allow the pressurization of both traditional liquid crystal cells and free standing films.

Because the physical properties of liquid crystals are extremely temperature dependent, and some liquid crystal phases are stable only over a small temperature range, it is essential to measure and regulate accurately the temperature of the specimen. Apart from some special cases, a precision of  $0.1^{\circ}\text{C}$  in the measurement of the temperature is acceptable. The overall dimensions of the specimen cell must be such that the cell can be readily incorporated in existing instruments such as a polarizing microscope or a spectrometer. This constraint can be in conflict with high pressure requirements; the cell must be both small and robust. In the operation of the apparatus, we must also bear in mind that the behaviour of thin films of some smectic phases can be far from that of a perfect hydrostatic fluid. Finally, in all cases, the overriding constraint is to avoid contamination of the specimen by the pressurizing medium.

### 3. The pressure system

The pressure system, to be described, is a hydrostatic system based on a screw injector pressure generator. We have opted for a hydrostatic system rather than a diamond anvil in order to keep the specimen cell well-separated from the pressure system. A separated specimen cell gives greater flexibility for the incorporation of the cell in existing instruments. The pressure system is outlined in figure 1. The pressure transmitting fluid used can be either oil or argon gas. The use of oil makes it possible to vary the pressure from 0 to 4 kbar with one single span of the screw injector, but places severe constraints on the design of the specimen cell to avoid contamination of the specimen. Purified argon may be brought in direct contact with the liquid crystalline material and therefore gives greater flexibility in the design of the cell and makes it possible to pressurize free standing films. However we must bear in mind that some materials, for example pentylcyanobiphenyl (5CB, Merck Ltd., U.K.) can, at high pressures, dissolve argon which acts as an isotropic solute and may affect the behaviour of the material. High pressures cannot be achieved with argon using the screw injector alone. A reservoir of purified argon at high pressure is needed. The pressurised argon is obtained by first purifying the gas from a commercial cylinder through a cold trap and then condensing it in a reservoir at liquid nitrogen temperature. The required amount

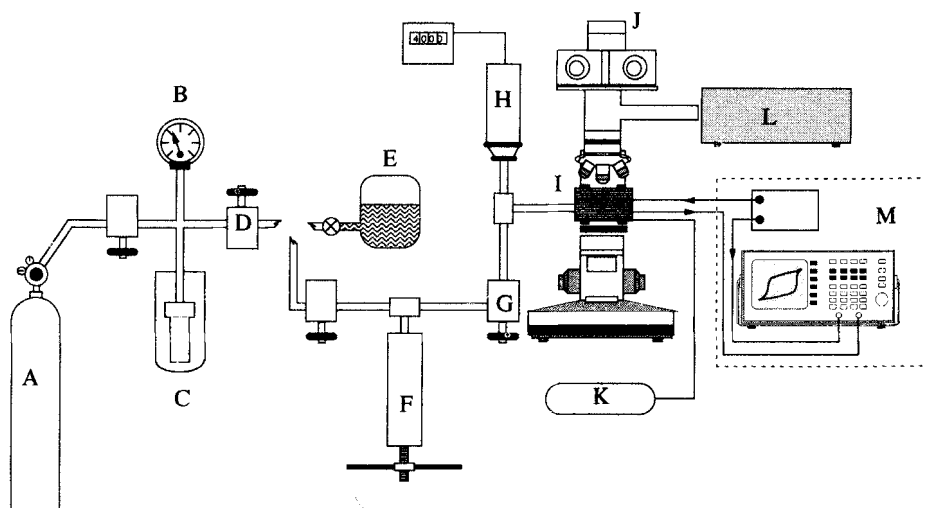


Figure 1. The pressure system up to 4 kbar (60 000 psi). A, argon cylinder; B, manometer; C, liquid nitrogen; D, metering valve; E, oil; F, screw injector; G, metering valve; H, pressure gauge; I, specimen cell; J, polarizing microscope; K, temperature control; L, optical spectrometer; M, Sawyer-Tower bridge.

of argon is allowed to expand into the pressure system through a metering valve and the pressure in the system is roughly set by regulating the temperature of the reservoir. The pressure in the cell is finely adjusted to the desired value using the screw injector.

The pressure of the fluid in the system is measured with a strain gauge bridge pressure sensor and transducer model HR28 from Intersonde Ltd.. The signal conditioner for the transducer is a K9010 microprocessor-based process indicator from Intersonde Ltd. This precision instrument has an in-built routine for auto-zero setting and auto-calibration to be carried out when the transducer has reached its final process temperature. Using this system, the pressure of the fluid in the system is measured with an accuracy of  $\pm 2$  bar.

#### 4. The specimen cells

One of the main constraints on the design of the cell is, as already mentioned, the conflicting requirements of small size and robustness. We describe in this section two of the cells we have developed—a multi-purpose cell and a specialized cell in which the thickness of the observed specimen is maintained constant.

##### 4.1. Multi-purpose cell

Details of the multi-purpose cell for polarized microscopy are shown in figure 2. In order to minimize the strain on the bolts holding the lid of the cell, the diameter of the pressurized chamber is made as small as possible. In the present design the diameter of the chamber is 12 mm. The body of the cell is made of stainless steel. The lid is held by eight 4 mm, high-tensile steel bolts and sealed by a direct metal to metal contact seal. The hot stage inside the pressurized chamber is a copper block whose temperature can be regulated within  $0.1^\circ\text{C}$  in the range ambient to  $200^\circ\text{C}$ . The optic path is through a 2 mm diameter hole and two sapphire windows. Because of the slight birefringence of sapphire, high quality windows with the optic axis of the sapphire parallel to the optic axis are used. The windows are sealed with a special resin for high pressures and high

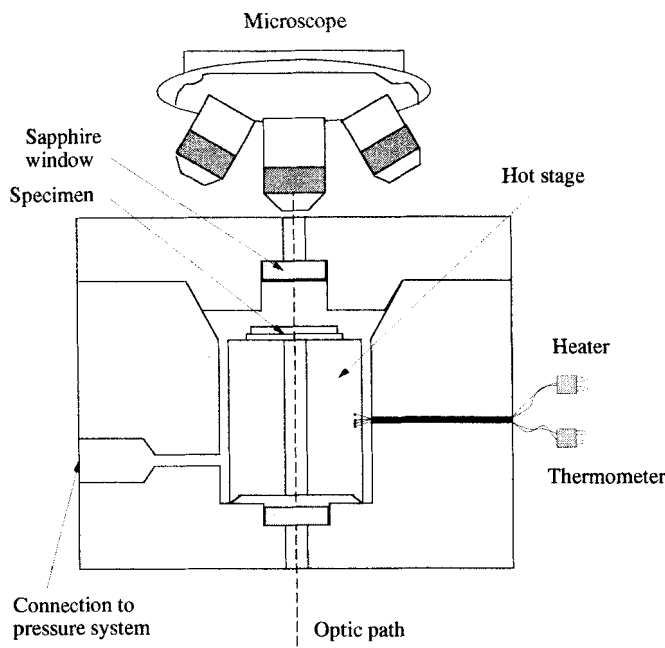


Figure 2. Pressure cell for polarized microscopy. The cell may be used for observation with transmitted light or reflected light.

temperatures (Stycast 2762 from Grace Electronic Material). The pressurizing fluid is argon, therefore, prior to any experiment, it is essential to assess the solubility of argon in the material studied. For materials which are affected by argon, the specimen is contained between two sheets of glass sealed with PTFE. In this configuration, the thickness of the sample does not remain constant when the pressure is applied. For materials that are not affected by argon, the sample is either placed in an open cell or observed as a free-standing film. In the open cell, the two panes of glass are kept apart with  $10\ \mu\text{m}$  thick stainless steel spacers.

For the observation of free-standing films, the material, in its smectic phase, is spread on an electron microscope sample-holder grid. If, as is the case for the chiral ester (14P1M7) described in § 5.2, the material is crystalline at room temperature, the grid can be slowly cooled to room temperature and, because of the small mesh size, most of the free-standing films produced crystallize without breaking. It is then possible to assemble the pressure cell at room temperature. The grid is placed in the multipurpose cell (see figure 2), in line with the optic path, in good thermal contact with the hot stage, and in place of the two panes of glass marked as the specimen in the figure, such that both sides of the film come into contact with the pressure transmitting fluid. The material was spread on the mesh at the temperature of  $80^\circ\text{C}$  ( $S_2^*$  phase). The thickness of the free-standing films produced on the electron microscope grids were between  $10\ \mu\text{m}$  and  $100\ \mu\text{m}$ , ensuring that any phase transitions observed were those of the bulk material, not ones associated with surfaces, as may occur in very thin films.

Figures 3 and 4 show free-standing films of 14P1M7 produced on an electron microscope mesh. Figure 3, taken at room temperature, shows within the same grid both crystallized films and films super-cooled in the antiferroelectric  $S_4$  phase (which appears blue). The films in the antiferroelectric phase can remain supercooled for several hours. Figure 4 shows the films in the  $TGB_A$  phase.

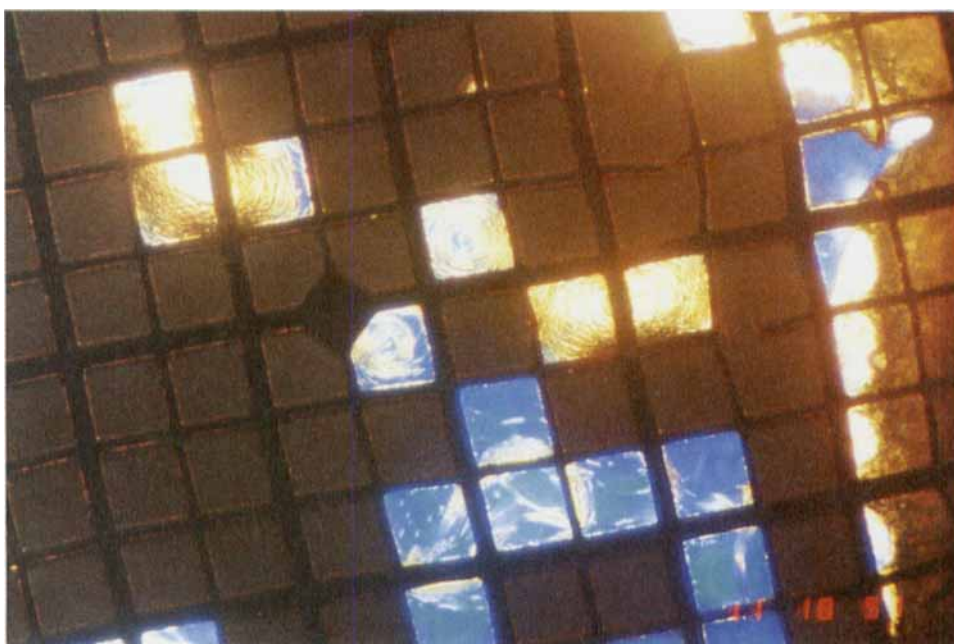


Figure 3. Films of 14P1M7 on a 50 gauge electron microscope sample holder grid at room temperature. The films are in either the crystalline or the antiferroelectric phase.

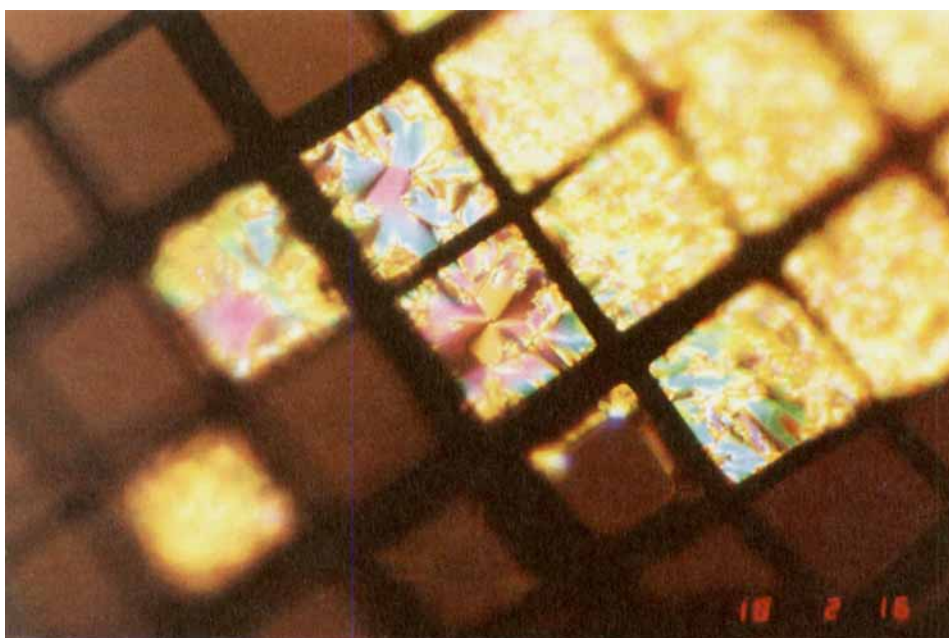


Figure 4. Free-standing films of 14P1M7 in the  $TGB_A$  phase.

The advantage of using free-standing films is that the surface is not constrained and there is thus less supercooling observed. Also, for some systems, particularly the TGB phases described in §5.2, there is very good contrast in the optical textures of free-standing films, making phase assignment far easier. However, in the observation of free-standing films using the high pressure system, the materials necessarily come into direct contact with the pressure transmitting fluid, in this case argon. As already stated, materials may well dissolve argon at high pressures, and this technique is clearly only useful for materials which do not dissolve argon on the time scale of the experiment. When argon is dissolved in the specimen, the transition temperatures depend on the amount of solute present and the transition temperatures at constant pressure are not reproducible. Additionally, when the sample is returned to atmospheric pressure, some argon will remain in the sample and the transition temperatures as measured at atmospheric pressure will change. Thus it is clear when the sample has been contaminated with argon. However, the best way to ascertain that the specimen is not affected is to repeat the experiment in a sealed cell. This was done for all our measurements carried out on free-standing films.

#### 4.2. *Constant sample-thickness cell*

A cell with constant sample thickness is shown in figure 5. The optical observation can only be made in reflected light. The pressure transmitting medium used with this cell is oil. The specimen is placed in the small reservoir in the sample holder and allowed to overflow in a thin (approximately 10  $\mu\text{m}$ ) recess on the side of the reservoir. The bottom of the reservoir is a deformable copper membrane through which the pressure is applied to the specimen. The observation is made over the recess where the thickness of the specimen is not affected by the deformation of the copper membrane. The sapphire window is treated with a common aligning agent prior to the assembly of the cell. The seal between the window and the steel sample holder is a Poulter type seal. In this configuration, contamination of the specimen by the pressure transmitting fluid is not a concern. If there is contamination (i.e. if the seal fails), the sample is visually destroyed when the oil leaks into the specimen chamber.

### 5. Test measurements

In this section we compare our test measurements performed on 5CB with previous measurements by Shashidhar [2(e)]. We also show some of our preliminary measurements on a compound exhibiting a TGB<sub>A</sub> phase.

#### 5.1. *Isotropic-nematic phase transition of 5CB.*

In order to assess the overall behaviour of our instrument, we have repeated the previous measurements of Shashidhar [2(e)] on the nematic to isotropic phase transition of 5CB. Measurements were carried out on both free-standing films and sealed cells. The nematic to isotropic phase transition was determined optically, and pressure and temperature were measured with an accuracy of  $\pm 2$  bar and  $\pm 0.2^\circ\text{C}$ , respectively. Our measurements are compared in figure 6 to the results of Shashidhar. The solid curve is calculated with the relation

$$T_p = T_0 + AP - BP^2,$$

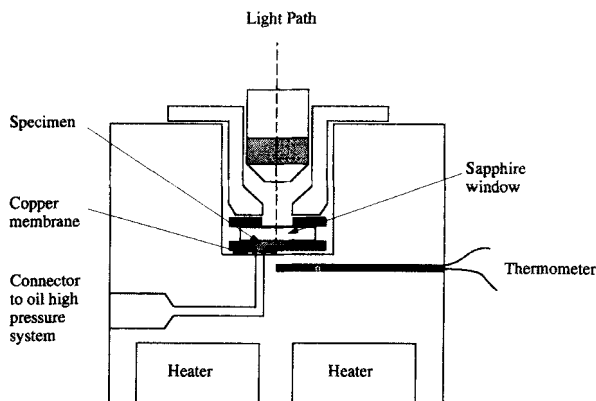


Figure 5. Pressure cell for observation of selective reflection. The observation is made on the area of the cell where the thickness of the specimen remains constant.

where  $P$  is the pressure,  $T_P$  the transition temperature at pressure  $P$ , and  $T_0$  the transition temperature at atmospheric pressure. The coefficients  $A$  and  $B$  are those obtained by Shashidhar

$$A = 40.3^\circ\text{C kbar}^{-1} \quad \text{and} \quad B = 2.64^\circ\text{C kbar}^{-2}.$$

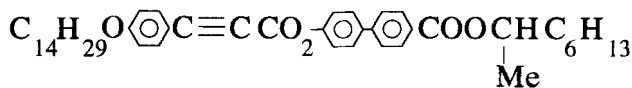
The agreement between Shashidhar's measurements and ours is well within experimental error.

In the course of taking the measurements on a free-standing film of 5CB, we noticed that the compound dissolved argon if the gas was allowed to come into direct contact with the sample. At pressures above 300 bar, repeated measurements at constant pressure on a free-standing film of the material showed a progressive lowering of the phase transition temperature (up to  $5^\circ\text{C}$ ) as increasing amounts of argon were dissolved in the sample. The measurements shown in figure 6 were taken using a sealed glass cell in which there was no possibility of sample contamination.

### 5.2. The twisted grain boundary phase

The twisted grain boundary phases (TGB) have recently attracted much attention from both theoreticians and experimentalists. The existence of the  $\text{TGB}_A$  phase was first predicted theoretically by Renn and Lubensky in 1981 [5]. Renn and Lubensky based their work on the analogy drawn by de Gennes between the smectic A phase and the type II superconductors [4]. The  $\text{TGB}_A$  phase was then observed by Goodby *et al.* [6, 7] in materials with a high degree of chirality. Materials displaying a twisted grain boundary smectic C phase ( $\text{TGB}_C$ ) or a twisted grain boundary chiral smectic C phase ( $\text{TGB}_C^*$ ) have now been synthesized. The structure of the TGB phases is a lattice of screw dislocations superimposed on the usual layered structure of the smectic phase.

For our initial studies, we have chosen a material with a relatively large temperature range over which the  $\text{TGB}_A$  phase is stable at atmospheric pressure. The material is 14P1M7, one of the chiral esters recently synthesized by Slaney and Goodby:





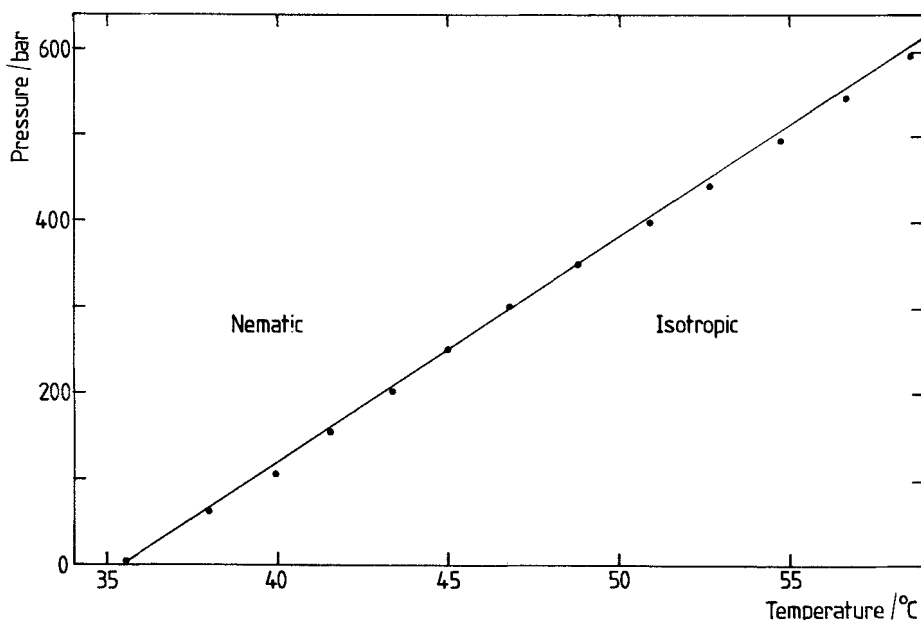
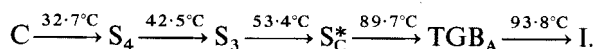


Figure 6. The pressure versus temperature phase diagram of 5CB. The solid line is calculated using the parameters determined by Shashidhar *et al.* [2] (●, experiment).

The temperature range over which the  $TGB_A$  phase is stable is  $4^\circ\text{C}$ . The phase sequence of the material at atmospheric pressure is



The lower smectic phases  $S_4$  and  $S_3$  are respectively antiferro and ferrielectric phases.

We have studied the high temperature side of the pressure–temperature phase diagram both for a sealed homeotropically aligned specimen and a free-standing film, in order to examine the stability of the  $TGB_A$  phase. The relevant portion of the phase diagram is shown in figure 7. The phase transitions were determined optically, and the pressure and temperature accuracy were  $\pm 2$  bar and  $\pm 0.2^\circ\text{C}$ , respectively. There was no significant dissolution of argon in the free-standing film of 14P1M7. Nevertheless the data shown in figure 7 were obtained with the specimen contained in a sealed cell and confirmed on the free-standing film. Because of the possibility of supercooling at the phase transition of interest, the measurements were repeated several times on both heating and cooling. Work is still in progress on this compound and will be the object of a separate publication. We can however at this stage make the following observations.

- (i) The gradient of the phase boundary lines in the pressure versus temperature phase diagram is negative. We are confident that this behaviour is not the result of dissolution of argon in the sample as (a) the measurements were carried out using a sealed cell, as well as on free-standing films, and (b) all of the tests to determine contamination described at the end of § 4 revealed no such problem. Thus the purity of the sample is the same before and after the experiments were carried out.

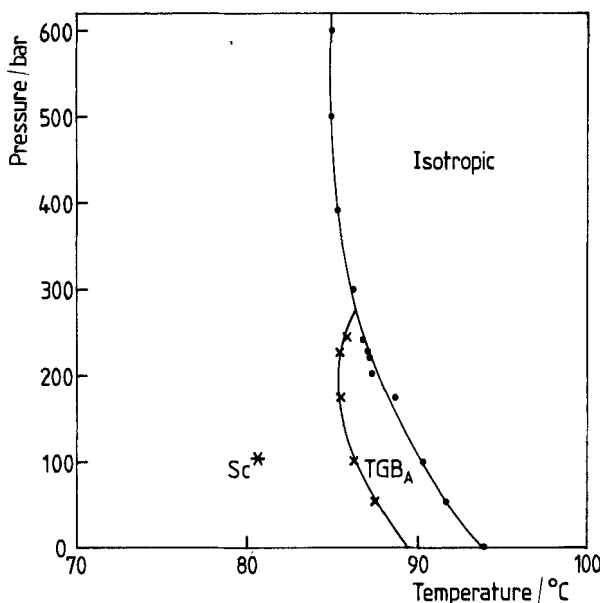


Figure 7. High temperature portion of the pressure-temperature phase diagram of the chiral ester 14P1M7.

A negative gradient of the  $TGB_A$  isotropic phase boundary is certainly unexpected. Such behaviour has been observed before for transitions between liquid crystal phases; for example Liebert and Daniels [8] have observed a negative gradient of the smectic A to nematic phase boundary line in CBOOA. However, in the case of CBOOA the phase boundary is part of an elliptical boundary resulting from reentrant nematic behaviour, and this cannot be the explanation here.

According to the Clausius-Clapeyron equation  $dP/dT = \Delta S/\Delta V$ , and the negative gradient implies that there is an increase in volume at the transition to a more ordered phase. Whilst unusual, such behaviour is not unheard of—perhaps the most common example of a phenomenon of this sort is provided by water, where there is certainly an increase in volume at the (first order) water to ice phase transition. In the present compound, we have an increase in volume at the transition from isotropic to  $TGB_A$  and another increase in volume at the transition from the  $TGB_A$  to  $S_C^*$  phase. Note that the negative gradients of the phase boundary lines do not imply a continuous increase in volume with pressure; the increase in volume occurs only at the phase transition. This particular result is interesting in its own right and experiments on other TGB systems are currently underway to determine whether this is typical of the phase boundary.

- (ii) The stability of the  $TGB_A$  phase is reduced at high pressure and the phase does not exist above about 250 bar. For the  $TGB_A$  phase to form, the Landau-Ginsburg parameter  $\kappa = \lambda/\xi$ , where  $\lambda$  is the penetration depth and  $\xi$  is the coherence length, must satisfy  $\kappa > (2)^{-1/2}$  [6]. The disappearance of the  $TGB_A$  phase at high pressure implies that  $\kappa$  decreases with increasing pressure. Work to determine independently the pressure dependence of  $\lambda$  and  $\xi$  is underway.

## 6. Conclusions

The examples given in § 5 show that the apparatus readily lends itself to accurate studies of phase transitions on both conventional aligned thin films and free-standing films, provided that care is taken regarding possible sample contamination. The instrument has also already been successfully tested in conjunction with an optical spectrograph for the study of the pressure dependence of the pitch in chiral nematics and for the observation of pressure-induced blue phases. In addition, some preliminary electrical measurements determining the variation of spontaneous polarization of a ferroelectric material through a pressure-induced phase transition have been made. Although still in the early stages of its development, the instrument is now fully operational. Work is currently underway on a systematic study of the whole series of chiral esters synthesized by Slaney and Goodby. The study includes the investigation of the TGB<sub>A</sub> phase, the antiferroelectric and ferroelectric phases and the blue phases. We are also investigating the evolution of the critical phenomena with pressure.

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