

CHAPTER I

INTRODUCTION

Liquid crystals¹(also known **as** mesophases) are states of matter in which the degree of molecular ordering is intermediate between those of a crystalline **solid** and an isotropic liquid. **They** possess many of the mechanical properties of a liquid like high fluidity, inability to support shear, etc. At the **same** time, they are **similar** to crystals in that they exhibit **anisotropy** in their optical, magnetic **and** electrical properties. Liquid crystallinity may be induced by purely thermal effects and is known **as** thermotropic mesomorphism. Liquid crystalline phases are also **formed** in solutions of **amphiphilic** molecules in water or in other polar solvents over a range of concentrations. These are called **lyotropic** liquid crystals.

The molecules of **mesogenic** compounds are, in general, geometrically anisotropic. Until recently, it was believed that for **mesomorphism** to occur, **the** molecules must be long and rod like. But very recently, **Chandrasekhar et al²** have established, for the first time, **that simple disc** shaped molecules **may also form stable mesophases**.

On the basis of X-ray and optical studies, they have proposed a structure for these disc like mesogens in which molecules are arranged in columns. The different columns form a two dimensional lattice like array as shown in figure 1.1. These columnar structure, has subsequently been confirmed by precise X-ray studies of Levelut.³ In this thesis, we are concerned only with thermotropic liquid crystals composed of elongated or rod like molecules.

Following Friedel⁴ thermotropic liquid crystals composed of rod like molecules are classified broadly into three types: (a) nematic, (b) cholesteric, and (c) smectic.⁵

Nematic: A simplified picture of the arrangement of the rod like molecules in the nematic phase is shown in figure 1.2a. This phase is characterised by a high degree of orientational order of the molecules without any long range translational or positional ordering. In other words, the molecules tend to align themselves with their long axis parallel to some preferred direction usually denoted by a unit vector $\hat{n}$, called the director. This preferred direction varies from point to point in the medium, but a homogeneously aligned specimen is

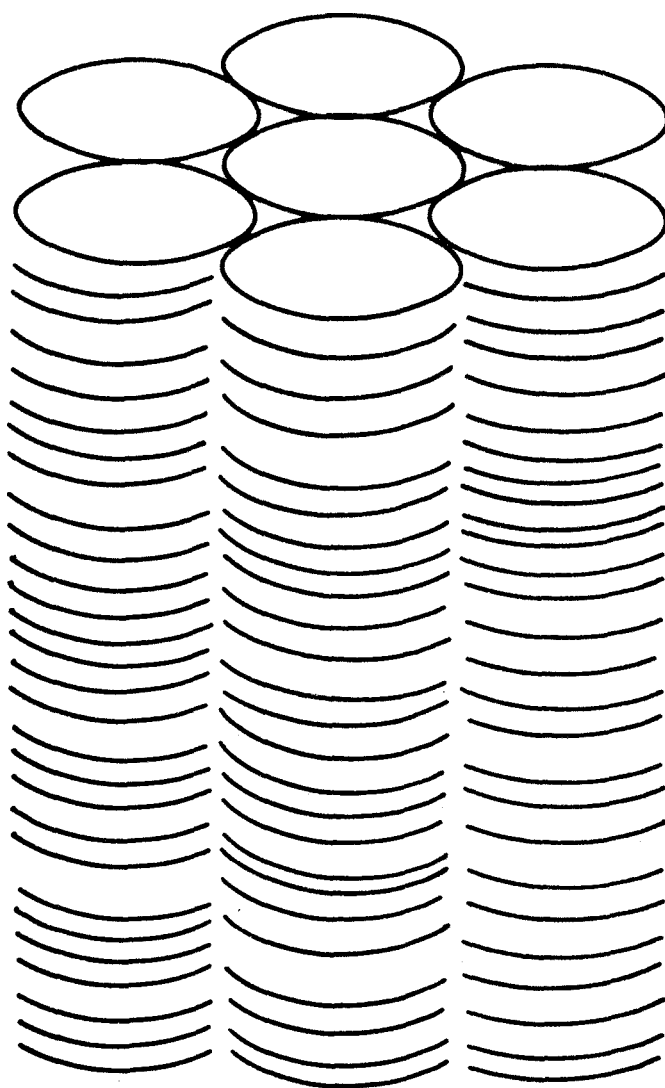


Figure 1.1

**Schematic representation of columnar
phase of disc-like molecules**

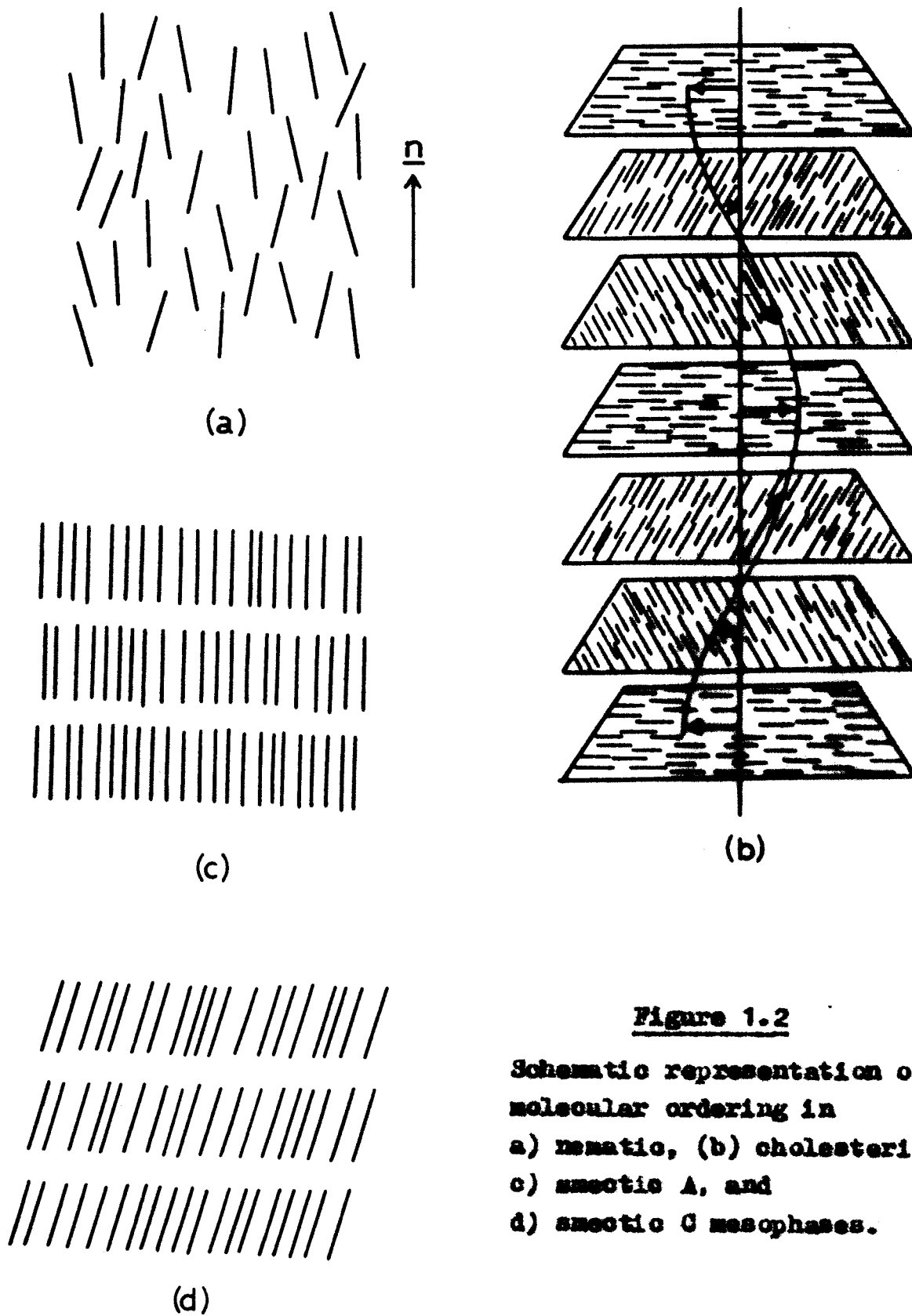


Figure 1.2

Schematic representation of molecular ordering in a) nematic, (b) cholesteric, c) smectic A, and d) smectic C mesophases.

optically uniaxial, positive **and** strongly birefringent.

Cholesteric: Cholesteric mesophase is basically also of the nematic type except that its structure has a screw axis **superimposed normal** to the preferred molecular direction (figure 1.2b). This helical **structure** imparts certain unique properties to the cholesteric like the exceptionally **high** optical rotatory power, **selective** reflection of a circularly polarised light, **etc.** **Thermodynamically**, this phase is often considered to be practically identical to the nematic phase. In fact, a nematic **liquid** crystal is **just** a cholesteric of infinite pitch and there is no phase transition between nematic **and** cholesteric phases in a given material when heated.

Smectic : In smectics, the molecules are arranged in well defined layers. Smectics are classified into several types depending on the order within a layer and on the interlayer correlations. For example, in **smectic A** (figure 1.2c), the molecules are normal to the layer with their centres **irregularly** spaced in a '**liquid like**' fashion. Smectic C, on the other hand, is a tilted form of smectic A wherein the **molecules** are tilted with respect to the layer normal (figure 1.2d). Two distinct types

of smectic B phase have been identified: in the first, molecules **are** not **only** normal to the layer but also **hexagonally** close packed within the layer like a 3-dimensional crystal, while the other is a stack of interacting '**hexatic**' **layers** with in-plane short range positional correlation and a long range three dimensional six fold '**bond-orientational**' order. Smectic **F** consists of **weakly** correlated layers in which the tilted molecules are packed so that the molecular long axis form a **hexagonal** net in a plane perpendicular to them giving a structure of monoclinic symmetry. A number of higher order **smectics** like G, H, ... etc. are known but considerable **confusion** exists in regard to the structural **classification** of the more ordered smectic modifications.

Sequence of phase transitions

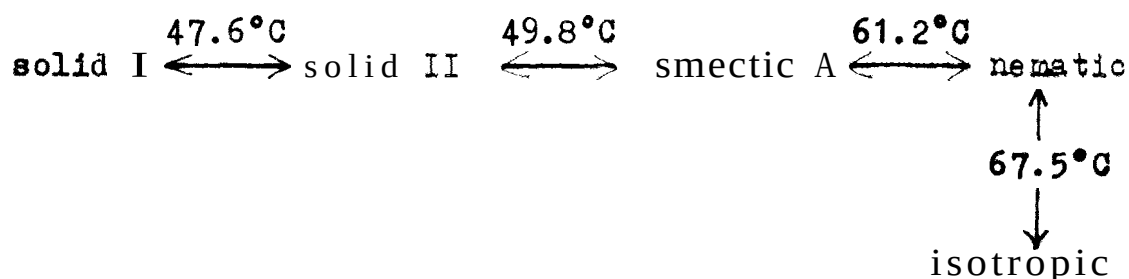
Some typical examples of mesophase transitions in the thermotropic liquid **crystals** are given below. The sequence of the transitions, on heating, is from the smectic **phases** to the nematic **and** finally to the **isotropic** phase of maximum disorder. In other words, as the temperature increases, ordering of the molecule decreases. This is **what is** expected, generally from the principle of thermodynamics. All the transitions **listed** below,

except one, are enantiotropic, i.e., they take place reversibly on **heating** and **cooling**. But it is to be noted that the temperature at which the **mesophase crystallises** is **always** lower than the melting point, i.e., **mesophase normally** eupercools. In the case of **terephthal-bis-n-butyl aniline**, the **smectic H** phase occurs only **during** cooling and hence is **monotropic** in character.

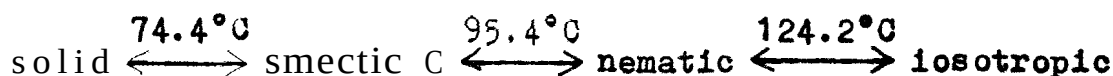
1. 4,4'-di-Methoxyazoxybenzene (p-azoxyanisole) (PAA)



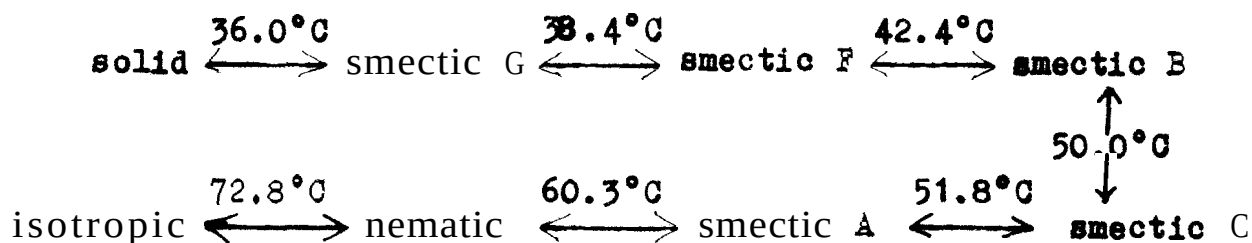
2. 4-Nitrophenyl-4'-n-octyloxybenzoate (NPOOB)



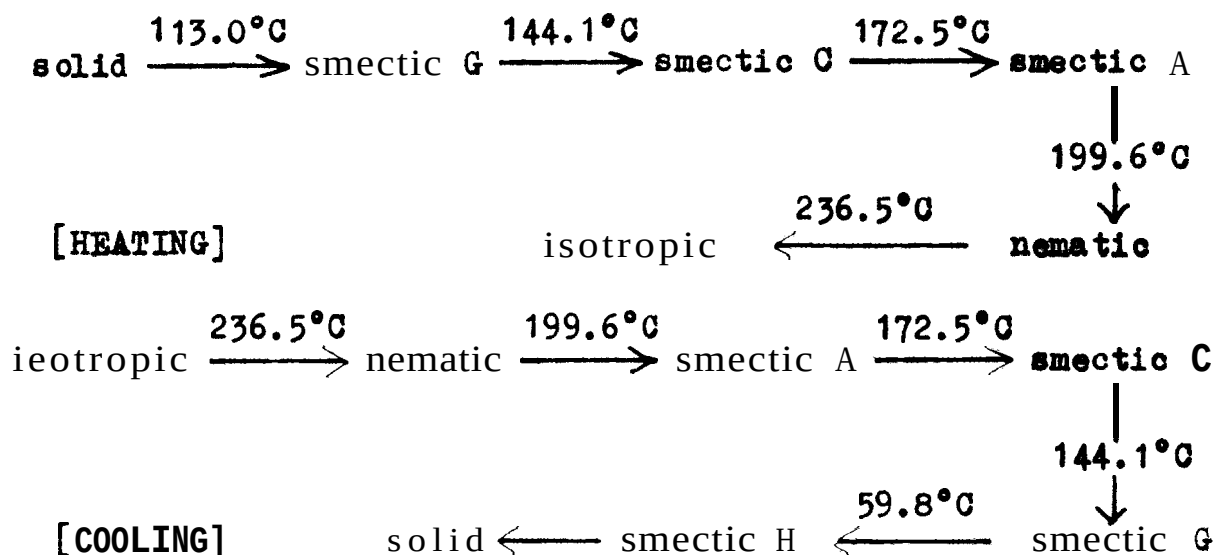
3. 4,4'-di-Heptyloxyazoxybenzene (HOAB)



4. N-[4-n-pentyloxybenzylidene)-4'-n-hexylaniline (50.6)



5. Terephthal-bis-n-butylaniline (TBBA)



4

This thesis describes the results of a variety of experiments conducted on the phase transitions in liquid orystals at high pressures.

Although the first high pressure studies on liquid crystals were carried out as early as 1899 by Hulett,⁶ within a decade of the discovery of the liquid orystals, there were only two more pressure studies in the next seventy years; one by Puschin and Grebenschtschikow⁷ in 1926, and the other by Robberecht⁸ in 1938, both on PAA. But, since 1970, there has been a considerable growth of activity in this field and a number of new and interesting

phenomena have been discovered,⁹ viz., pressure induced mesomorphism,¹⁰ suppression of mesophases,¹¹ change in the character of the transition either from first order to a second order (tricritical behaviour)^{11,12} or from monotropic to enantiotropic,¹³ reentrant behaviour,¹⁴ odd-even behaviour of dP/dT for successive members of homologous series of compounds,¹⁵ etc. These results are of fundamental importance and involve significant thermodynamical and structural implications. This thesis presents the results of our experimental investigations which throw further light on some of these aspects.

The study of liquid crystals under pressure presents certain problems which are not normally encountered in the study of the solid state. For instance, liquid crystals have rather high chemical reactivity and hence react not only with materials that are normally used as containers but also with all pressure transmitting media, liquid, solid or gas. Hence special care should be taken to prevent the contamination of the liquid crystalline sample either by container material or by pressure transmitting medium. Further, liquid crystalline transitions are generally characterised by low heats and therefore somewhat difficult to detect. A high pressure cell for the study of liquid crystals has therefore to be

designed after taking into account all the above considerations.

The studies described in the present thesis have been carried out using three different pressure equipment, namely, (1) 200-ton hydraulic press **incorporating** the piston cylinder device for DTA experiments, (2) Optical cell with sapphire windows for the detection of **the phase** transition by light transmission technique, and (3) **diamond** anvil cell for optical studies for pressures beyond four **kilobar**.

The 200 ton hydraulic **press**¹⁶ and the diamond anvil cell^{17,18} being facilities already **existing** in the laboratory, are described only briefly, while the high pressure optical cell (sapphire cell) which **has** been designed, fabricated and assembled by the author is described in detail in chapter II. The **cell** is made of hardened steel which can be closed on both sides by two steel plugs with a central hole for optical observations. These plugs keep the **sample** assembly in position. **The** central hole of the upper cap is sealed by an optically polished **sapphire** rod which also forms a part of **the** sample assembly. A thin section of the **sample** is sandwiched between **this** sapphire rod and a second one which

is essentially free as it is not used to seal the cap. These two sapphire cylinders sandwiching the sample fit snugly inside a **fluran** tube and an effective seal is realised by tightly wrapping a thin steel wire round the tubing at the two ends. The inner spacer (low **pressure** sealer), a washer and a spring center the bottom sapphire of the sample assembly and keep it under a light **tension**. The third sapphire rod which is completely isolated **from the** sample assembly seals the bottom end of the pressure cell. A glass rod **is** kept in the space between **this** third sapphire rod and the bottom sapphire rod **of** the sample assembly **to** prevent the oil from filling **the** space and cutting down the intensity of the transmitted light, The special features of the optical cell **are:**

- (1) Pressure is directly applied to the sample without the need of any pressure intensifier, (2) The sample **is** prevented from **direct** contact with the pressure transmitting **oil** by a **fluran** tube, (3) **Fluran** being an elastomer material, **transmits** pressure very well but does not permit the oil to seep **through** it, (4) only very small quantity of the samples are required for a set of experiments, (5) control and maintenance of sample thickness using washers, and (6) temperatures can be read to an accuracy of $\pm 0.025^{\circ}\text{C}$. Using **this** optical cell, we **have** carried

out detailed investigations on different kinds of phase transitions occurring in liquid crystals, and the results of these investigations **are** described in **chapters III - VII.**

Reentrant Behaviour

As indicated earlier, when a **thermotropic** liquid crystal is heated, transitions take place from a well ordered solid phase to a less ordered phase like smectic or nematic and finally to the isotropic phase of **maximum** disorder. But, recently, Gladis,¹⁹ while working with the mixtures of N-p-cyanobenzylidene-p-n-octyloxyaniline (CBOOA) and p-[(p-hexyloxybenzylidene)amino]benzonitrile (HBAB) made the interesting discovery that it **is** possible to obtain a nematic phase on either heating or cooling a smectic A phase. She noticed that smectic A - nematic transition temperature of the mixtures **becomes** multi-valued with increasing **concentration** of HBAB. The sequence of phase transition on cooling is

isotropic $\rightarrow$ nematic $\rightarrow$ smectic A $\rightarrow$ **nematic.**

Thus the nematic phase occurs **again** at a lower temperature than the smectic A **phase.** This lower temperature nematic phase has **been** designated as the '**reentrant nematic**' phase in analogy with other **similar** effects observed **in**

condensed matter physics.^{20,21} From the measurement of bend elastic constant K_{33} of HBAB/CB00A mixtures, Cladis has shown that there is no macroscopic difference between the two nematic phases.

Subsequently, Cladis et al¹⁴ observed for the first time the reentrant phenomenon in a pure compound, viz., 4'-n-octyloxy-4-cyanobiphenyl (8 OCB) at high pressures. A similar behaviour has also been observed in CB00A, mixtures of 8 OCB and 6 OCB and also CBNA and CBHA, all at high pressures.^{22,32}

More recently, the reentrant behaviour has also been observed in pure compounds at atmospheric pressure, for the first time, by Madhusudana et al²³ in our laboratory and also by Hardouin et al²⁴ in France at about the same time.

The reentrant phenomenon in liquid crystals both at elevated pressures and at room pressure is one of the rare examples where a phase transition takes place from an apparently more ordered (smectic) state at a higher temperature to an apparently less ordered (lower temperature nematic) state. This interesting observation has therefore opened up an entirely new field of investigation, resulting in a tremendous surge of activity in

the field of synthesis of more such compounds. **Tinh** and **Gasparoux**,²⁵ **Heppke et al**,²⁶ **Urs and Sadashiva**³¹ and others have synthesised several reentrant compounds in quite a short time.²⁷⁻³⁰

In spite of the relatively large number of compounds that are now known to exhibit the reentrant nematic phase at atmospheric pressure, there has been only a single pressure study on a room pressure reentrant nematogen³² so far. We have carried out detailed and precise pressure studies on eight room pressure reentrant nematogens synthesised by **Sadashiva**³³ and more recently by **Urs and Sadashiva**.³¹ The results of these investigations form the subject matter of chapter III.

The compounds studied are the 11th and 12th members of 4 different homologous series, viz., (1) 4-cyanophenyl-3'-methyl-4'(4''-alkylbenzoyloxy)benzoates (CPMBB), (2) 4-cyanophenyl-3'-methyl-4'(4''-alkyloxycinnamoyloxy)benzoate (CPMCB), (3) 4-cyanophenyl-3'-methyl-4'(4''-alkyloxy- α -methylcinnamoyloxy)benzoate (CPM α MCB) and (4) 4-cyanophenyl-3'-methoxy-4'(4''-alkyloxy- α -methylcinnamoyloxy)benzoate (CPMeO α MCB). Two of these (11 CPMCB and 11 CPM α MCB) exhibit enantiotropic reentrant nematic phase while the others show monotropic reentrant nematic phase.

The important results obtained are -

- (i) For all the compounds, smectic A - nematic (A-N) phase boundary is elliptic in shape.
- (ii) There exists a maximum pressure P_m up to which smectic A phase exists.
- (iii) For two compounds, viz., 12 CPMCB and 12 CPM α MCB, the smectic A - reentrant nematic transition which is monotropic at 1 bar becomes enantiotropic at high pressures. This is the first observation of such a change in character of a transition involving the reentrant nematic phase.
- (iv) P_m is sensitive to change in molecular length - the addition of an alkyl end group increases the value of P_m drastically. The addition of a lateral group on the other hand, does not affect P_m so much.
- (v) P_m is related to the range of the nematic phase at 1 bar (=R) and hence the nematic ordering at atmospheric pressure. A plot of $\log P_m$ vs. R is a straight line and the data is expressible as $P_m = P_0 \exp(-mR)$. The constants ' P_0 ' and ' m ' have been evaluated by a least square fit of the data points to a straight line. A similar plot

has also been made for a number of reentrant compounds for which the P_m values are known and these data also fall on a straight line, but with a different slope (i.e., with different P_0 and m values). It is very interesting to see that data for all three phenyl ring compounds fall on one line while those for the compounds with 2 phenyl rings fall on the second line. It has therefore been concluded that for a reentrant nematogen the maximum pressure of smectic stability is uniquely related to the nematic range R and hence the stability of the nematic ordering, the constant of proportionality being dependent on the molecular structure. It is also noted that P_0 for the two phenyl ring compounds is much higher than that for 3 phenyl ring substances, showing thereby that the stability of smectic A phase in the former is higher. This in turn implies that the formation of reentrant nematic phase is more favoured in compounds with three phenyl rings, a fact which is well supported by the experimental observations.

There have been some attempts to give theoretical explanations for the experimental results obtained on the reentrant phenomenon, especially the shape of the smectic A - nematic phase boundary in the pressure-temperature plane, and to understand the thermodynamics

of the smectic A - reentrant nematic transition, **Pershan** and **Prost**³⁴ have shown that the smectic A - reentrant nematic phase transition follows from the Landau theory if one **assumes** the existence of an optimum density for smectic ordering. Recent high resolution **Xray** scattering experiments of **Kortan et al**³⁵ strongly support this concept of 'optimum density'. Similarly, extending the **McMillan's** treatment of the smectic A phase, **Luckhurst** and **Timimi**³⁶ have developed the molecular theory **for** the reentrant nematic - smectic A mesophases. A **thermo-**dynamic model of the reentrant nematic and smectic A transition has been developed by **Clark**³⁷ and **independently** by **Klug and Whalley**,³⁸ the brief outline of which **is** given in chapter IV. They have shown that **we** can get the general equation of the A-N phase boundary by **first expressing** the difference in the **Gibbs** free energy between the nematic **and** smectic A phase in terms of temperature **and** pressure and then equating it to zero. **The** general equation thus obtained, **turns** out to be the equation to a conic. Using the **original** data of **Cladis** on 8 OCB as well **as** on the mixtures of CBNA and **CBHA**, **Clark** has shown that the best fit of the experimental data is obtained with an ellipse and **has** calculated the various thermodynamic parameters. In chapter IV, we

have made an attempt to fit our experimental data points to an ellipse by the method of least square fit. It is found that the fit is very good for all the compounds studied. It is therefore **confirmed** that for all reentrant compounds, irrespective of the fact whether **they** show reentrant nematic phase at room pressure or at elevated pressures, the smectic A - nematic phase boundary is elliptical in shape. **Further**, we **have** also evaluated the ratios of various thermodynamic parameters like $\Delta\alpha/\Delta\beta$, $\Delta\beta/\Delta C_p$, **etc.** which determine the phase boundary. **These** are tabulated in detail in chapter IV.

Recently **Chen** and Lubensky³⁹ **have** proposed an interesting application of the concept of **Lifshitz** point to the **NBC** point: a triple point where nematic-smectic A (N-A), smectic A - smectic C (**A-C**), and nematic - smectic C (N-C) phase boundaries **intersect** in a phase diagram. The first observation of the **NAC** point was by Johnson et al⁴⁰ who on the basis of differential scanning calorimetry measurements and optical microscopy observations reported that the temperature-concentration diagram of binary mixtures of heptyl and octyl-oxy-p'-pentyl phenyl thiobenaoate

($\overline{7S5}$ and $\overline{8S5}$) shows a polycritical NAC point. They have also presented a phenomenological Landau type theory which qualitatively describes the observed phase diagram. Sigaud et al⁴¹ have also discovered a binary system which exhibits an NAC point with a slightly different topology. As mentioned earlier, Chen and Lubensky termed the NAC point as a Lifshitz point. However, de Hoff et al⁴² on the basis of precise a.c. calorimetry experiments and Safinya et al,⁴³ on the basis of high resolution Xray studies, have concluded that the NAC point is definitely not a Lifshitz point, but is instead a multicritical point. An NAC point has never been observed so far in a single component system and we have carried out pressure studies on a number of compounds with a view to observing such a point in the P-T diagram of a single component liquid crystalline system. In chapter V, we present the results of our pressure studies on two compounds, viz., N-(4-n-pentyloxybenzylidene)-4'-n-hexylaniline (50.6) and 4-(4-n-decyloxybenzoyloxy)benzylidene-4'-cyanoaniline (10 BBCA). Experiments were conducted on 50.6 with a diamond anvil cell and the data were brought to an absolute scale by conducting a calibration experiment using a DTA cell. It is seen that the temperature range

of **smectic A** which is about 8.9°C at one bar diminishes with **increasing** pressures and becomes as **small** as 0.7°C at 4 kbar. At higher pressures, the range of the **A** phase decreases even further but the rate of decrease **is very** slow. At 8 kbar, the maximum pressure up to which **we** have studied the compound this range is about 0.4°C . Had the resolution of our experimental set up been less than what it is at present, we might have concluded that C-A and A-N phase boundaries intersect at about 4 kbar. However, the precision of our data shows that this **is not** in fact the case. **We** can therefore only infer that the NAC point for **this compound** will probably occur at a **pressure** higher than 8 kbar. **Further, it may be** mentioned that special care was taken in DTA experiment to see if A-N transition shows a tricritical **behaviour** since a tricritical point should precede the **NAC** point if it is a **Lifshitz point**. It was observed **that** the first order character of the A-N transition diminishes with increasing pressure up to about 4 kbar, but beyond this pressure, the **change** is hardly detectable. The **A-N** transition remains first order, though weakly so, **right** up to 8 kbar.

In the case of **10EBCA** experiments were conducted using the high pressure optical cell with light trans-

mission as the probe to detect the phase transition.

It is quite interesting to see that the range of smectic **C** which is initially **13°C** at **1** bar, decreases quite rapidly with the increase of pressure and finally the **C** phase is completely bounded at 0.52 kbar, thus resulting in a **RN - C - A** point at 0.52 kbar and 86.0°C. Experiments were also conducted using DTH cell to determine the **nature** of the transition and **it is** found that **RN - C** and **C - A** transitions are essentially continuous in nature while **RN - A** transition is definitely of first order. In other words, it appears that the two second order phase boundaries, **viz.**, **RN - C** and **C - A** culminate **and** continue as a first order **RN - A** phase boundary. **We** have **thus** observed a new kind of multicritical point, namely, **RN - C - A** point in this compound.

As regards to the topology of the **P-T diagram** is concerned, it has been observed that **RN - C** and **RN - A** lines are not continuous through the **RN - C - A** point. The **C - A** line which **is** straight till very **close** to the **RN - C - A** point and approaches it slightly obliquely. **The** **RN - A** phase boundary appears to have a curvature right from the **RN - C - A** point. On the **basis** of topology alone, it is hard to **make** any definitive conclusion regarding the nature of this point. **Further experiments**

like measurements of elastic constants, high resolution X-ray studies, etc. are required to be conducted at high pressures in order to provide more information concerning the nature of this point.

As mentioned earlier in the chapter, smectic C phase is a tilted form of smectic A, the molecules within the layer being tilted with respect to the layer normal. It has long been recognized that the temperature variation of the tilt angle in the smectic C phase depends very much on the type of the phase that exists immediately after it at a higher temperature. If the higher temperature phase is smectic A, then the tilt angle is rather small and shows a strong temperature dependence. On the other hand, when a smectic C phase precedes a nematic phase, then the tilt angle is independent of temperature. Very recently, de Vries⁴⁴ has made an interesting observation that in the case of *n*-pentyl-4(4'-*n*-decyloxybenzylidene-amino)cinnamate (PDBC), the tilt angle in the smectic C phase which is about 15° , does not depend on the temperature although the smectic C phase precedes the smectic A phase. He has observed that this tilt angle remains practically the same not only at the smectic C - smectic A transition, but even after it, i.e., even in the smectic A phase. Hence it is quite interesting to study the pressure

behaviour of the compounds exhibiting these three kinds of smectic C phases, with a view to examine the way the pressure affects these phases. In all, we have studied 4 compounds. They are (1) 4-n-pentyloxyphenyl-4'-n-decyloxybenzoate (50 PDOB) and 4-n-heptyloxyphenyl-4'-n-decyloxybenzoate (70 PDOB) in which the tilt angle is strongly temperature dependent and goes to zero at the smectic C - smectic A transition, (2) Nonyloxybenzoic acid (NOBA) in which the tilt angle is temperature independent, and (3) PDBO discussed earlier. The results of these studies carried out using either a diamond anvil cell (in conjunction with a DTA cell for pressure determination) or the high pressure optical cell, are discussed in chapter VI. The results show clearly that in all the cases, the smectic C phase is suppressed at high pressures showing thereby that a tilted structure is somehow not favoured at high pressures. Further, it is worth noting that the suppression of smectic C phase occurs regardless of the nature of the smectic C phase at one bar. High pressure X-ray studies are required to understand the role of pressure dependence of layer spacing on the stability of smectic C phases.

In chapter VII, we have discussed the pressure studies on 7S5, 8S5 and their mixtures with a view to

studying the effect of adding a heavy atom, namely, sulphur in the ester linkage group on the stability of various mesophases under pressure, and also if possible to observe the 'NAC' point either in pure compounds or in their mixtures under pressure. As mentioned earlier, the temperature-concentration diagram of the binary mixtures of $\bar{7}S5$ and $\bar{8}S5$ shows the 'NAC' point. $\bar{7}S5$ has a monotropic smectic C phase and a nematic phase, while $\bar{8}S5$ exhibits the smectic A and nematic phases in addition to the smectic C and a higher order smectic phase both of which are monotropic in character. When these two compounds are mixed together, the range of smectic A phase progressively decreases and finally for a mixture of 42% mole fraction of $\bar{7}S5$, it is completely suppressed, thereby forming the 'NAC' point. It is well known that most of the effects like tricritical behaviour, reentrant phenomenon, etc. observed in binary mixtures by varying the concentration,^{45,19} can also be observed in a single component liquid crystalline system by changing pressure.^{12,46,47,14} We have therefore carried out pressure studies on $\bar{7}S5$, $\bar{8}S5$ as well as their binary mixtures with concentration close to 42% (vie., 35%, 40% and 45% mole fraction of $\bar{7}S5$) to see if we can get NAC point at high pressures. It is observed that in all the

cases, the range of the smectic A phase, instead of decreasing, increases with pressure. This increase in the stability of smectic A phase is accompanied by the decrease in the range of smectic C phase which is finally bounded at high pressures. The suppression of the smectic C phase in $\bar{7}S5$ takes place at a pressure of 1.61 kbar and in the case of $\bar{8}S5$ it is at a much higher pressure, viz., 4.1 kbar presumably because of its higher stability at 1 bar. Thus, it has not been possible to observe the WAC point in $\bar{8}S5$ under pressure. It must also be pointed out that Cladis et al⁴⁸ have also carried out pressure studies up to 2 kbar on $\bar{8}S5$ which has a monolayer smectic A phase with a view to seeing if it exhibits the reentrant behaviour. They have observed that the A-N phase boundary is linear throughout and hence no reentrant behaviour is observed. Our studies carried up to a pressure of 4 kbar also show that the A-N phase boundary is unusually straight and does not show any sign of curvature towards the pressure axis. Therefore, we can conclude that the bilayer smectic A is essential for the reentrant nematic phase to appear. In the case of binary mixtures of $\bar{7}S5$ and $\bar{8}S5$ also, the range of smectic A phase increases monotonically with pressure, the rate of increase depending on the concentration (composition). In the case of mixture with 0.45 mole fraction of $\bar{7}S5$, wherein there is no

smectic A phase, the smectic C - nematic transition which is enantiotropic to start with, changes its character and becomes monotropic beyond a pressure of 0.22 kbar. To our knowledge, this is the first instance of smectic C - nematic transition showing a change in character from enantiotropic to monotropic. Our failure to observe the NAC point either in $\bar{7}S5$ and $\bar{8}S5$ or in their binary mixtures under pressure indicates that the monolayer smectic A phase cannot be bounded by applying pressure. On the other hand, pressure appears to have the effect of increasing the stability of such a monolayer smectic A phase.

It may be recalled that in chapter IV we have evaluated the ratios of the various thermodynamic parameters, viz., $\Delta\alpha/\Delta\beta$, $\Delta\alpha/\Delta C_p$, etc. associated with the A-N phase boundary which is elliptical in shape, for several reentrant nematogens. But the determination of the individual parameters requires an accurate knowledge of any one of these parameters, viz., thermal expansion (α), isothermal compressibility (β) and the specific heat (C_p). The plesothermal or heat of compression method^{49,50} provides the basis for a precise determination of thermal expansion directly as a function of pressure. It is to be noted that to obtain ' α ' to a comparable accuracy by a

conventional technique like piezometry, one would have to determine the volume change to an accuracy of 1 in 10^{-4} which is extremely difficult to achieve in a high pressure experiment. In appendix I, we have discussed the results of our piezothermal studies on 8 OCB as a function of pressure along 4 different isotherms in the vicinity of smectic A - nematic transition. These experiments were conducted at the Laboratoire de Physique, Université Marie Curie and Pierre Curie, Paris. The basic principle of the method is to measure the quantity of heat liberated by a known volume of the sample under a pressure variation.^{51,52} This heat is measured as an e.m.f. using a set of 500 thermocouples which are electrically in series but thermally in parallel. From our studies, it is found that ' α ' exhibits an anomaly at the A-N transition. The height of the peak which is a measure of this anomaly decreases with increasing temperatures and at the highest temperature studied, viz., 77.6°C, there is hardly any anomaly. Generally it is far more difficult to achieve a fine variation of pressure than of temperature, and hence to that extent, the experimental value of a , particularly close to A-N phase boundary do not have the required precision to make a good estimate of the exponent ' γ ' associated with

the pressure variation of ' α '. Nevertheless, we have made an **attempt** to fit all the data points to the equation of the type

$$a = a_0 + P_r a_1 + A|P_r|^\gamma \quad \text{for } P < P_0$$

and

$$a = a_0' + P_r a_1' + A|P_r|^\gamma \quad \text{for } P > P_0$$

where a_0 , a_1 , a_0' and a_1' are all adjustable parameters, P_0 is the pressure corresponding to A-N transition and $P_r = |P - P_0| / P$ is the reduced pressure. The base lines with respect to which the expansion coefficients have **been** evaluated for this fitting consist of two linear parts, one in the nematic **and** the other in the smectic A phases. The data points at pressures farthest from P_0 have been used to obtain **these** two linear **base line parts** which intersect at the A-N transition pressure P_0 . This appears to yield a reasonably good fit over the entire range of pressure investigated, giving a value of the exponent $\gamma = 0.22$. It may also be mentioned that an integration of ' α ' versus pressure curve essentially leads to a term which should be a function of entropy. **Thus it** is not surprising that the trends of our a versus pressure curve with increasing temperatures resemble generally C_p versus temperature curves **with** increasing pressure obtained

for the **same** compound by Garland et al.^{53,54} .

Some of the results discussed in this thesis **have been** published in the following papers:

- 1 **The search for a Lifshitz point in a single component liquid crystalline system: A high pressure study of 50.6** (in collaboration with R. **Shashidhar** and S. Chandrasekhar) - **Mol. Cryst. Liq. Cryst.** 64(Lett.) (1980) 101.
- 2 **Piezothermal studies in the vicinity of the smectic A - nematic transition in 4'-n-octyloxy-4-cyanobiphenyl (8 OCB)** (in collaboration with R. **Shashidhar**, L. Ter Minassian and B. R. Ratna) - **J. de Phys.** 43 (Lettres) (1982) L-239.
- 3 **High pressure studies on polymorphic liquid crystals** (in collaboration with R. **Shashidhar**, G. Venkatesh, D. Demus and W. Weissflog) - **Mol. Cryst. Liq. Cryst.** 84 (1982) 275.
- 4 **High pressure studies on reentrant nematogens** (in collaboration with R. Shashidhar and M. S. Urs) - **J. de Physique** (in press)
- 5 **A new multicritical point in a single component liquid crystal: High pressure study of DOBBCA** (in collaboration with R. Shashidhar and S. Chandrasekhar) - **Mol. Cryst. Liq. Cryst.** Letters (submitted).

6. Effect of pressure on the stability of **smectic C** phase (in collaboration with R. **Shashidhar**, G. Venkatesh, Mary Neubert and J.P. **Ferrato**) - to be presented at the **Ninth International Liquid Crystal Conference**, Bangalore, December 1982.
7. Pressure studies *on* $\bar{7}S5$, $\bar{8}S5$ and their **mixtures** (in collaboration with R. **Shashidhar**) - to be presented at the Ninth International Liquid Crystal Conference, Bangalore, December 1982.
8. The **thermodynamics** of the elliptical phase boundaries of the reentrant nematogens (in collaboration with R. Shashidhar) - to be presented at the Ninth **International Liquid Crystal Conference, Bangalore**, December 1982.

References

- 1 O. Lehmann, *Flussige Kristalle* (1904), Engelmann, Leipzig.
- 2 S. Chandrasekhar, B.K.Sadashiva and K.A.Suresh, *Pramana*, 9 (1977) 471.
- 3 A.M.Levelut, *J. de Phys. Lettres*, 40 (1979) L-81.
- 4 G. Friedel, *Ann. Phys.* 18 (1922) 273.
- 5 See for example, S. Chandrasekhar, 'Liquid Crystals' Cambridge University Press, Cambridge (1977).
- 6 G.A.Hulett, *Z. Phys. Chem.* 28 (1899) 629.
- 7 N.A.Puschin and I.W. Grebenschtschikow, *Z.Phys.Chem.* 57 (1926) 270.
- 8 J.Robberecht, *Bull. Soc. Chim. Belg.*, 47 (1938) 579.
- 9 S. Chandrasekhar and R. Shashidhar, 'High Pressure Studies of Liquid Crystals', *Advances in Liquid Crystals*, 4 (1979) 83.
- 10 S. Chandrasekhar, S. Ramaseshan, A.S.Reshamwala, B.K.Sadashiva, R.Shashidhar and V.Surendranath, *PROC. International Liquid Crystals Conference, Bangalore, December 1973*, *Pramana Suppl.* 1, p.117.
- 11 R.Shashidhar and S.Chandrasekhar, *J. de Phys.* 36 (1975) C1-49.
- 12 P.H.Keyes, H.T.Weston and W.B.Daniels, *Phys.Rev.Lett.* 31 (1973) 628.

- 13 R. Shashidhar, Mol. Cryst. Liquid Cryst. 43 (1977) 71.
- 14 P.E.Cladis, R.K.Bogardus, W.B.Daniels and G.N.Taylor, Phys. Rev. Lett. 39 (1977) 720.
- 15 G.Venkatesh, R. Shashidhar and D. S. Parmar, Proc. International Liquid Crystal Conference, Bangalore, December 1979, Ed. S.Chandrasekhar, Heyden, London (1980) p. 373.
- 16 G. Venkatesh, Ph. D. Thesis, Bangalore University (1981).
- 17 S. Chandrasekhar, R. Shashidhar and K.V. Rao, 'Advances in Liquid Crystal Research and Applications' Ed. L. Bata, Pergamon Press, p. 123 (1981).
- 18 R. Shashidhar and K.V.Rao, Proceedings of the International Liquid Crystals Conference, Bangalore, December 1979, Ed. S.Chandrasekhar, Heyden, London, (1980) p. 131.
- 19 P. E. Cladis, Phys. Rev. Lett. 35 (1975) 48.
- 20 P. Schlottman, J. Low. Temp. Phys. 20 (1975) 123.
- 21 A.C.Anderson, W.Reese and J.C.Wheatley, Phys. Rev. 130 (1963) 1644.
- 22 P.E.Cladis, R.K.Bogardus and D. Aadsen, Phys. Rev. A18 (1978) 2292.
- 23 N. V.Madhusudana, B.K.Sadashiva and K.P.L.Moodithaya, Current Science, 48 (1979) 613.
- 24 F.Hardouin, G.Sigaud, M.F.Achard and H.Gasparoux, Phys. Lett. 71A (1979) 347.

- 25 N.H.Tinh and H. Gasparoux, Mol. Cryst. Liq. Cryst. Letters 49 (1979) 287.
- 26 G. Heppke, R. Hopf, B. Kohne and K. Praefcke, 'Advances in Liquid Crystal Research and Applications', Ed. L. Bata, Pergamon Press (1981) p. 141
- 27 B.K.Sadashiva, Proceedings of the International Liquid Crystals Conference, Bangalore, December 1979, Ed. S. Chandrasekhar, Heyden, London (1980) p. 165.
- 28 N.H.Tinh, Jousset-Dubien and C. Destrade, Mol. Cryst. Liquid Cryst. Lett. 56 (1980) 257.
- 29 D. Demus, G. Pelzl, A. Wiegeleben and W. Weissflog, Mol. Cryst. Liquid Cryst. Lett. 56 (1980) 289.
- 30 W. Weissflog, G. Pelzl, A. Wiegeleben and D. Demus, Mol. Cryst. Liquid Cryst. Letters 56 (1980) 295.
- 31 M. Subramanya Raj Urs and B.K.Sadashiva, Mol. Cryst. Liquid Cryst. Letters, 72 (1982) 227.
- 32 P.E. Cladis, Proceedings of the International Liquid Crystal Conference, Bangalore, December 1979, Ed. S. Chandrasekhar, Heyden, London (1980) p. 105.
- 33 B.K.Sadashiva, Mol. Cryst. Liquid Cryst. 53 (1979) 253.
- 34 P. S. Pershan and J. Prost, J. de Physique Lettres 40 (1979) L-27.
- 35 Kortan, A.R., Von Kanel, H, Birgeneau, R.J. and Litster, J.L., Phys. Rev. Lett. 47 (1981) 1206.

- 36 G.R.Luckhurst and B.A.Timimi, Mol. Cryst. Liquid Cryst. Lett. 64 (1981) 253.
- 37 N.A.Clark, J. de Physique Lettres, 40 (1979) C3-345.
- 38 D.D.Klug and E.Whalley, J.Chem.Phys. 71 (1979) 1874.
- 39 J. Chen and T.Lubensky, Phys. Rev. A14 (1976) 1202.
- 40 D.L.Johnson, D.Allender, R. De Hoff, C. Maze, E. Oppenheim, and R.Reynolds, Phys. Rev. B16 (1977) 470
- 41 G. Sigaud, F. Hardouin and M. Achard, Solid State Commun. 23 (1977) 35.
- 42 R. De Hoff, R. Biggers, D. Brisbin, R.Mahamood, G. Gooden, and D.L.Johnson, Phys. Rev. Lett. 47 (1981) 664.
- 43 C. Safinya, R.Birgeneau, J.D.Litster and M.E.Neubert, Phys. Rev. Lett. 47 (1981) 668.
- 44 A. de Vries, Mol. Cryst. Liquid Cryst. Lett. 41 (1977) 27.
- 45 D.L.Johnson, C. Maze, E.Oppenheim and R. Reynolds, Phys. Rev. Lett. 34 (1975) 1143.
- 46 R. Shashidhar and S. Chandrasekhar, J.de Phys. 36 (1975) C1-49.
- 47 R. Shashidhar and G.Venkatesh, J. de Physique, 40 (1979) C3-396.
- 48 P.E.Cladis, D.Guillon, J. Stamatoff, D.Aadsen, W.B.Daniels, M.E.Neubert and R.Griffiths, Mol. Cryst. Liquid Cryst. Lett. 49 (1979) 279.

- 49 L. Ter Minassian and Ph. Pruzan, J.Chem. Thermo-
dynamics, 9 (1977) 375.
- 50 L. Terminassian, Ph. Pruzan and A. Soland, J.Chem.
Phys. 75 (1981) 3064.
- 51 L. lterminassian, J.C.Petit, Nguyen Van Keit and
Brunard, J. Chem. Phys. 67, (1970) 265.
- 52 A.H.Fuchs, Ph. Pruzan and L. Terminassian,
J. Phys. Chem Solids 40 (1979) 369.
- 53 G.W. Garland, G.B.Kasting and K.J.Lushington,
Phys. Rev. Lett. 43 (1979) 1420.
- 54 G.B.Kasting, K.J.Lushington and G.W.Garland,
Phys. Rev. B22, (1980) 321.