CHAPTER IV

DIELECTRIC STUDIES OF REENTRANT NEMATOCENIC SYSTEMS

Part I. Studies on Strongly Polar Reentrant Mesogens

4.1 INTRODUCTION

For a long time it was presumed that the general sequence of phase transitions occurring in a polymesomorphic material (on cooling) should be

Isotropic → Nematic → Smectic → Solid

But in 1975, Cladis[1] reported an exciting departure from this sequence. She found that in certain mixtures of n-p-cyanobenzylidene-p'-octyloxyaniline **(CBOOA)** and p-[(p'-hexyloxybenzylidene)-amino]benzonitrile (HBAB) the nematic-smectic **A** transition temperature becomes multivalued, the nematic phase occurring at higher as well as at lower temperatures relative to the smectic A phase. The phase diagram for this binary system obtained by Cladis[1] is given in Fig.4.1. It is seen that for the mixtures in a certain concentration range, the sequence of phase transition (on cooling) from the isotropic phase is

Nematic → Smectic **A** → Nematic → Solid

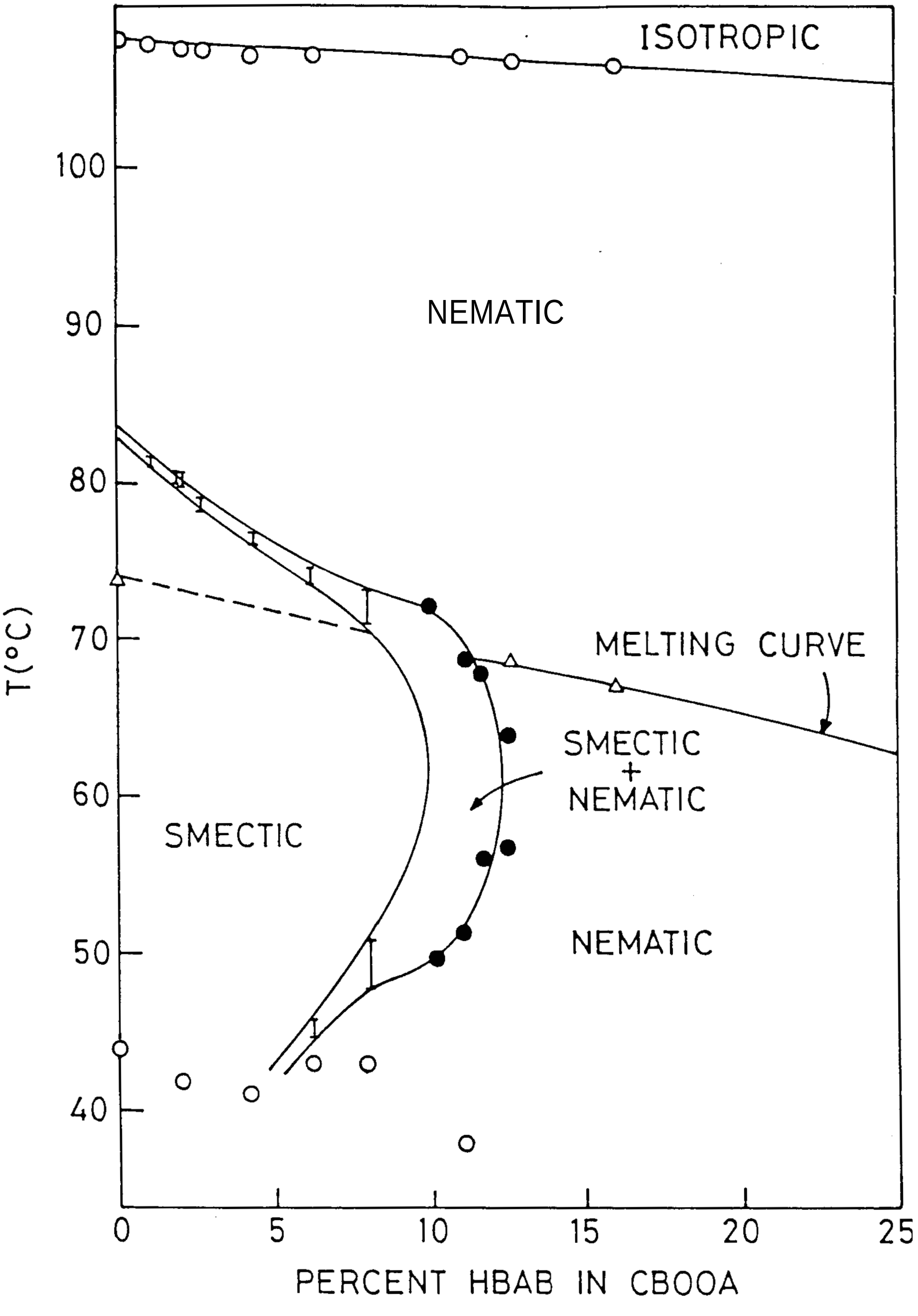


Figure 4.1

Isobaric phase diagram (T-X) for mixtures of CBOOA and HBAB (Ref. 1)

The lower temperature phase was later designated as the **reentrant nematic phase.** The appearance of a higher symmetry phase at a lower temperature compared to a less symmetric one is not special to liquid crystals. There are quite a few examples in other fields of condensed matter physics. The pressure dependence of the ^{3}He melting temperature[2] is an early example of reentrant behaviour. Some other systems exhibiting the reentrant phenomena are, superconductors doped with magnetic impurities[3] and rare earth superconducting materials which order magnetically at a temperature below the superconducting transition.

Cladis[1] also measured the bend elastic constant (K_{33}) for the CBOOA/HBAB mixtures. It showed a similar pretransitional increase on either side of the smectic A phase. It was therefore concluded that no macroscopic difference exists between the normal, i.e., high temperature nematic and the reentrant nematic phases.

Subsequently, Cladis et al.[4] found the reentrant nematic (N_{re}) phase in a pure compound at elevated pressures. The pressure-temperature diagram of 4-n-octyloxy-4'-cyanobiphenyl (8OCB) is shown in Fig.4.2. It shows the following features:

i) the nematic-smectic A phase boundary curves towards the pressure axis resembling the arc of an ellipse.

ii) the reentrant nematic phase exists in the pressure range

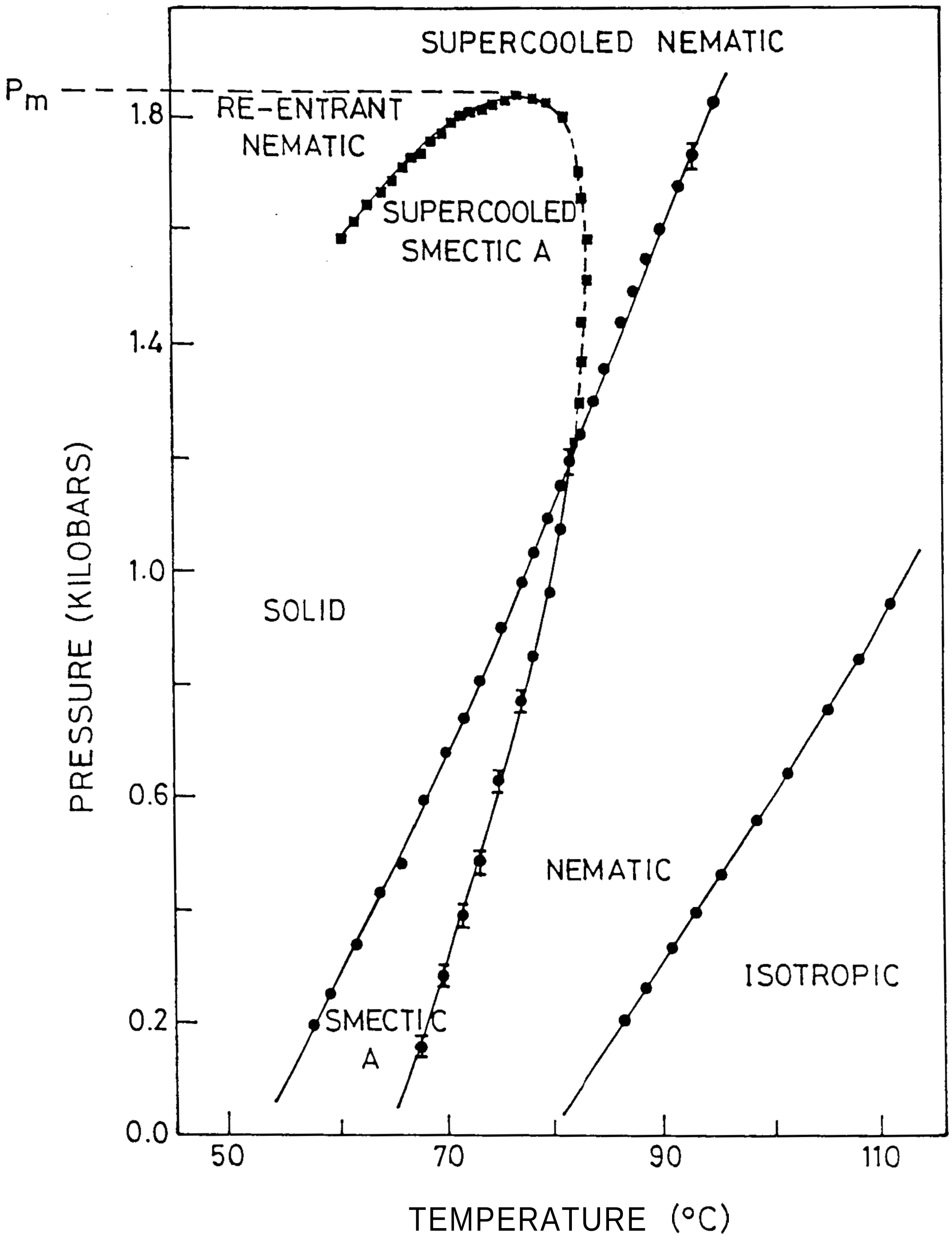


Figure 4.2

P–T diagram of 80CB
(Ref. 4)

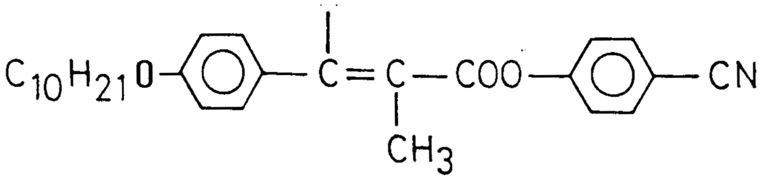
1.6 - 1.8 kbar.

iii) beyond a pressure P_m (about 1.8 kbar) the smectic A phase ceases to exist and there 'is only a nematic phase.

Further high pressure studies[5,6] on CBOOA, mixtures of 4-n-octyloxy-4'-cyanobiphenyl/4-n-hexyloxy-4'-cyanobiphenyl (8OCB/6OCB) and mixtures of N-p-cyanobenzylidene-p-nonylaniline/N-p-cyanobenzylidene-p-heptylaniline (CBNA/CBHA) also revealed the existence of the N_{re} phase in these systems.

Until the beginning of 1979, the N_{re} phase was seen either in mixtures at atmospheric pressure or in single component systems at high pressures. In early 1979, investigations by the Bordeaux group[7,8] and by Madhusudana et al.[9] resulted in the observation of the reentrant nematic phase in single component systems at atmospheric pressure. The molecular structures of the compounds in which Madhusudana et al.[9] made this observation are given in Figure 4.3. The materials in which Hardouin et al.[7] and Tinh and Gasparoux[8] made this observation are 4-n-octyloxy-benzoyloxy-4'-cyanostilbene (T_8) and 4-nonyloxybenzoyloxy-4'-cyanotolane respectively. The molecular formulae and the transition temperatures of these materials are shown in Fig.4.4. It is interesting to note that the two systems studied by the Bordeaux group showed not only the reentrant nematic phase but also a reentrant smectic A

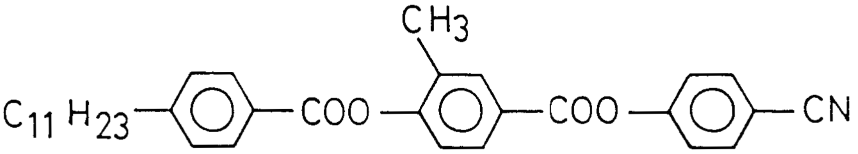
1)



trans-p-n-decyloxy-α-methyl-p'-cyanophenyl cinnamate

(10 OMCPC)

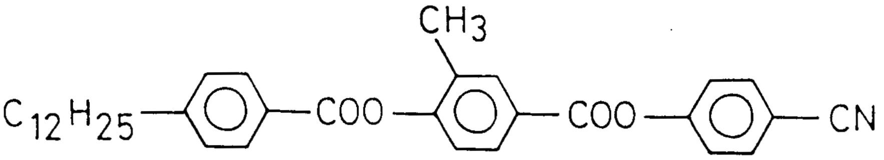
2)



4-cyanophenyl-3-methyl-4(4-n-undecylbenzoyloxy) benzoate

(11 CPMBB)

3)



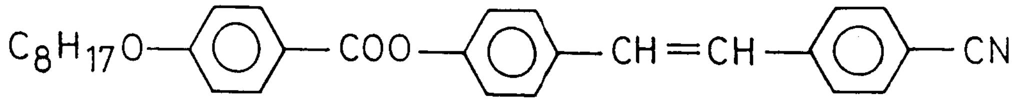
4-cyanophenyl-3-methyl-4(4-n-dodecylbenzoyloxy) benzoate

(12 CPMBB)

Figure 4.3

Chemical structures of (1) 10 OMCPC, (1) 11 CPMBB and (3) 12CPMBB (Ref. 9).

1)

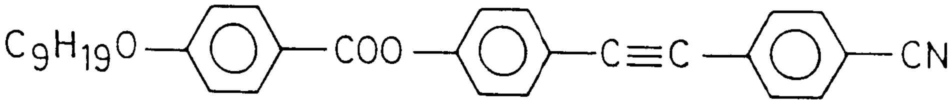


4-n-octyloxy-benzoyloxy-4'-cyanostilbene

(T_8)

$$K \xrightarrow{94.5} S_A \underset{}{\overset{96}{\rightleftarrows}} N \overset{138}{\rightleftarrows} S_A \overset{247}{\rightleftarrows} N \overset{283}{\rightleftarrows} I$$

2)



4-nonyloxybenzoyloxy-4'-cyanotolane

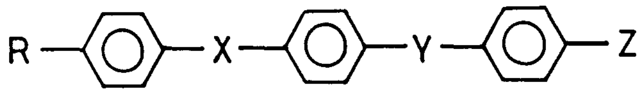
$$K \overset{90}{\text{———}} S_A \overset{(75.7)}{\text{———}} N \overset{141}{\text{———}} S_A \overset{183}{\text{———}} N \overset{239}{\text{———}} I$$

Figure 4.4

The list of structural formulae and transition temperatures in °C of (1) 4-n-octyloxy-benzoyloxy-4'-cyanostilbene (Ref. 7) and (2) 4-nonyloxy benzoyloxy-4'-cyanotolane (Ref. 8).

phase.

The observation of the N_{re} phase in pure compounds at atmospheric pressure initiated a tremendous activity in the synthesis of reentrant nematogens.[10,11] Presently a large number of three phenyl ring single component systems are known which exhibit the reentrant behaviour at atmospheric pressure. A typical molecular structure of a three phenyl ring compound which is likely to show reentrance would be

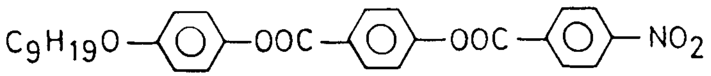


where R is the end chain, X and Y are the bridging groups and Z is the strongly polar end group. When Z=CN, in order to obtain N_{re} phase, the longitudinal component of the dipole moment of "X" linkage must be in the same sense as that of the CN end group. The direction of the longitudinal component of the dipole of "Y" linkage does not appear to have any effect on the occurrence of reentrant nematic phase. (For the latest review, see Ref. 12.)

For $Z=NO_2$, the N_{re} phase is observed less often and only when the dipole moment of "X" opposes that of the terminal NO_2 group. This kind of molecular structure has given rise to the discovery of triply reentrant phenomenon observed by the Bordeaux group[13] in 4-nonyloxyphenyl-4'-nitrobenzoyloxy benzoate ($DB9ONO_2$) whose molecular structure is shown in Table 4.1. When the material

Table 4.1

The molecular structure of $DB9ONO_2$ along with the sequence and temperatures of transition. (The transition temperatures are given in degree Celsius)



4-nonyloxyphenyl-4^{1}-nitrobenzoyloxy benzoate

$$\begin{tikzcd}
K \arrow[r, "109"] & S_{\tilde{C}} \arrow[r, shift left, "118"] \arrow[d, shift left, "96"] & S_{A_1} \arrow[l, shift left] \arrow[r, shift left, "124"] & N_{re} \arrow[l, shift left] \arrow[r, shift left, "127"] & S_{A_{d_{re}}} \arrow[l, shift left] \arrow[r, shift left, "138"] & N_{re} \arrow[l, shift left] \arrow[r, shift left, "156"] & S_{A_d} \arrow[l, shift left] \arrow[r, shift left, "195"] & N \arrow[l, shift left] \arrow[r, shift left, "224"] & I \arrow[l, shift left] \\
& {[S_{C_2}]} \arrow[u, shift left] \arrow[d] & & & & & & & \\
& S_{C_2} \arrow[r] & S_{A_2} \arrow[r] & S_{\tilde{C}} & & & & &
\end{tikzcd}$$

Ref. 13

(Additional sequence observed by Shashidhar et al.[14])

was initially discovered, the sequence of transition reported to be shown by it are also given in Table 4.1. However the more recent experiments by Shashidhar et al.[14] showed the existence of another smectic A phase, viz., A_2 phase intervening between smectic $\tilde{C}$ and smectic C_2 phases.

As pointed out in the preceding paragraph, the reentrant behaviour is generally exhibited by single component systems with a strongly polar terminal group. (Some exceptions to this, viz., the occurrence of reentrant nematic phase in terminally non-polar materials have been reported by Halle group.[15,16] This will be discussed in Part II of this chapter.) It was pointed out by Madhusudana and Chandrasekhar[17] that in such strongly polar systems the neighbouring molecules favour an antiparallel configuration. These correlations in turn lead to a bilayer structure. Since it is well known[18] that these antiparallel correlations manifest themselves in the dielectric properties of the medium, we have undertaken detailed dielectric investigations on materials exhibiting different types of reentrant behaviour.

4.2 MATERIALS

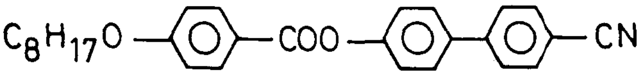
The structural formulae and the transition temperatures of the materials studied are given in Table 4.2. They are 4-cyanobiphenyl-4"-n-octyloxybenzoate (8OBCBP), a mixture of 4-(4'-nonyloxy

TABLE 4.2

Structural formulae, the sequences and temperatures of transitions in °C of the compounds studied

---

1 4-Cyanobiphenyl-4"-n-octyloxybenzoate (8 OBCBP)

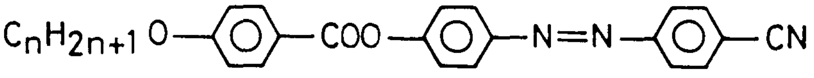


$$\mathrm{I} \overset{234.4}{\text{———}} \mathrm{N} \overset{197}{\text{———}} \mathrm{A_d} \overset{118.2}{\text{———}} \mathrm{N_{re}}$$

2 30 mol % 4-(4'-nonyloxy benzoyloxy)-4'-cyano azo benzene (9OBCAB)

\+

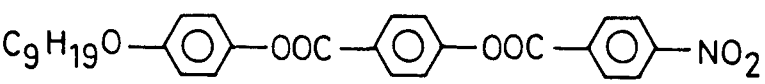
4-(4'-octyloxy benzoyloxy)-4'-cyano azo benzene (8OBCAB)



n = 8 & 9

$$\mathrm{I} \overset{256}{\text{———}} \mathrm{N} \overset{182}{\text{———}} \mathrm{A_d} \overset{159.3}{\text{———}} \mathrm{N_{re}} \overset{91}{\text{———}} \mathrm{A_1}$$

3 4-Nonyloxy phenyl-4'-nitro benzoyloxy benzoate (DB9ONO$_2$)



$$\mathrm{N} \overset{195}{\text{——}} \mathrm{A_d} \overset{156}{\text{——}} \mathrm{N_{re}} \overset{138.5}{\text{——}} \mathrm{A_{d(re)}} \overset{124}{\text{——}} \mathrm{N_{re}} \overset{121.5}{\text{——}} \mathrm{A_1} \overset{119}{\text{——}} \tilde{\mathrm{C}} \overset{100}{\text{——}} \mathrm{A_2} \overset{96}{\text{——}} \mathrm{C_2}$$

---

benzoyloxy)-4'-cyano azo benzene (9OBCAB) and 4-(4'-octyloxybenzoyloxy)-4'-cyanoazobenzene (8OBCAB) and finally DB9ONO_2. 8OBCBP exhibits the nematic, smectic A_d and reentrant nematic phases. Pure 9OBCAB shows a reentrant nematic phase and in addition the second smectic A phase, viz., A_1 phase. The smectic A_1 phase in this material is metastable and it was not possible to measure the dielectric constants in this phase owing to crystallization setting in. We therefore had to make a mixture of 30 mole % of 9OBCAB in 8OBCAB which gave the same sequence of transition as 9OBCAB, but gave a stable smectic A_1 phase. Finally the material DB9ONO_2, as remarked earlier, shows perhaps the richest variety of phases in any single component system seen so far. Because of the fact that the nematic phase reenters twice (see the sequence of the transition given in Table 4.1) and the smectic A_d phase reenters once, this material is popularly known as a triply reentrant mesogen.

4.3 RESULTS **AND DISCUSSIONS**

We shall now describe the results of our dielectric studies on the materials described in the previous section.

4.3.1. **8OBCBP**

a) Static

Fig.4.5 gives the temperature variation of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ along

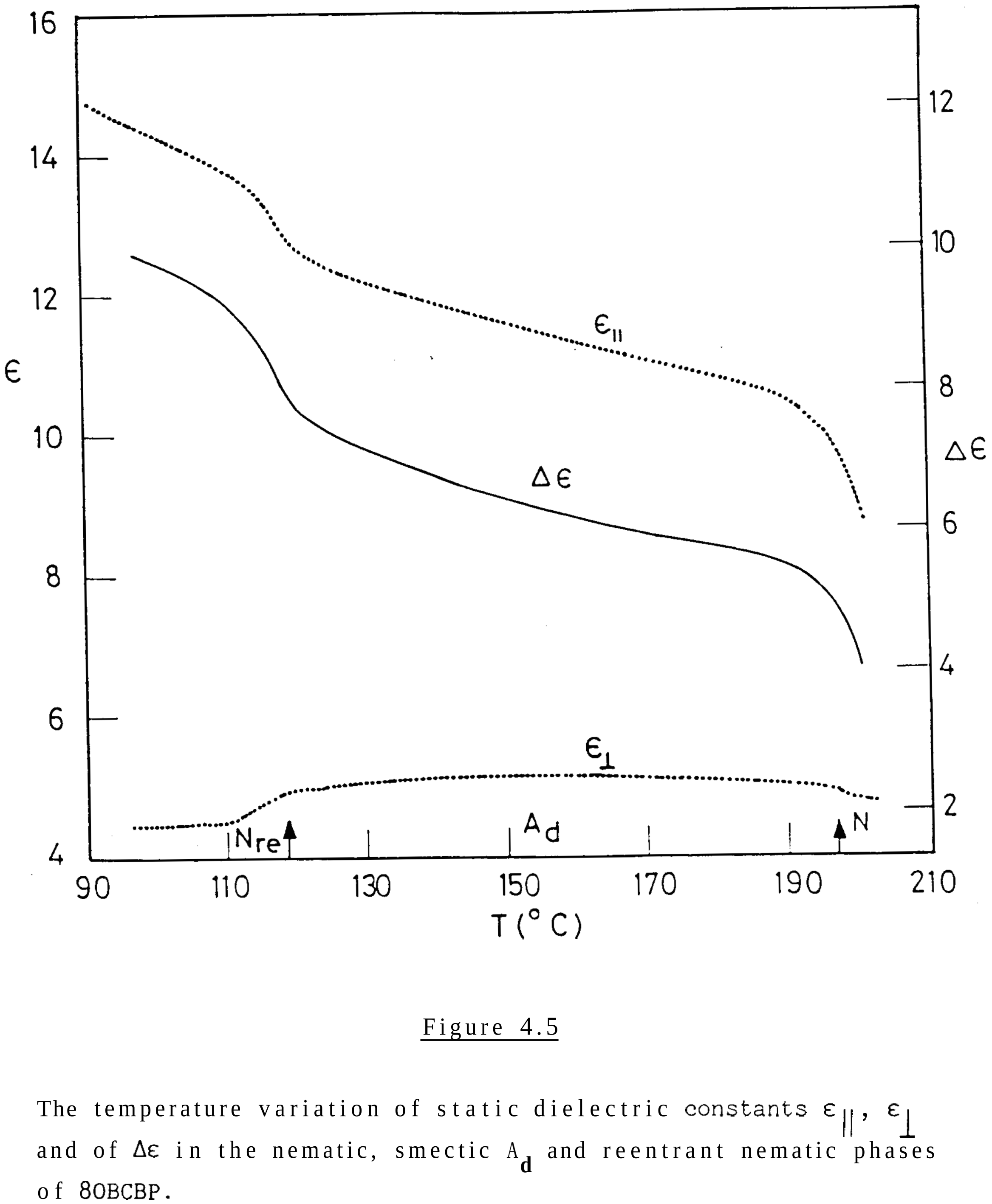


Figure 4.5

The temperature variation of static dielectric constants $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$ and of $\Delta\varepsilon$ in the nematic, smectic A_d and reentrant nematic phases of 8OBCBP.

with the dielectric anisotropy $\Delta\varepsilon$ in the nematic, smectic A_d and reentrant nematic phases. It is seen that on cooling from the high temperature nematic phase, $\varepsilon_{\parallel}$ increases continuously while $\varepsilon_{\perp}$ more or less remains constant. The increasing trend of $\varepsilon_{\parallel}$ continues through the nematic-smectic A_d (N-A_d) transition there being no discontinuity. At the smectic A_d-reentrant nematic (A_d-N_{re}) transition, $\varepsilon_{\parallel}$ shows an increase while $\varepsilon_{\perp}$ shows a small decrease and consequently $\Delta\varepsilon$ shows a pronounced increase at the A_d-N_{re} transition. These results would indicate that the dipolar changes accompanying the A_d-N_{re} transition are more pronounced than those accompanying the N-A_d transition. The increase in $\varepsilon_{\parallel}$ at the A_d-N_{re} transition indicates a decrease in antiparallel correlations on going from the A_d to N_{re} phase. A similar result has been observed for other reentrant systems as well.[19,20]

b) <u>Dispersion</u>

Fig.4.6 gives typical loss curves ($\varepsilon''_{\parallel}$ vs. f) in the nematic, smectic A_d and reentrant nematic phases. It is clear that on the whole the maxima of loss curves show an increase with decrease in temperature which reflects the general trend of the variation of $\varepsilon_{\parallel}$ with temperature. Typical Cole-Cole plots obtained in N, A_d and N_{re} phases are shown in Figs.4.7 and 4.8. In all the three phases, well defined semicircles are seen with their centres lying on the horizontal axis signifying the single relaxation process in

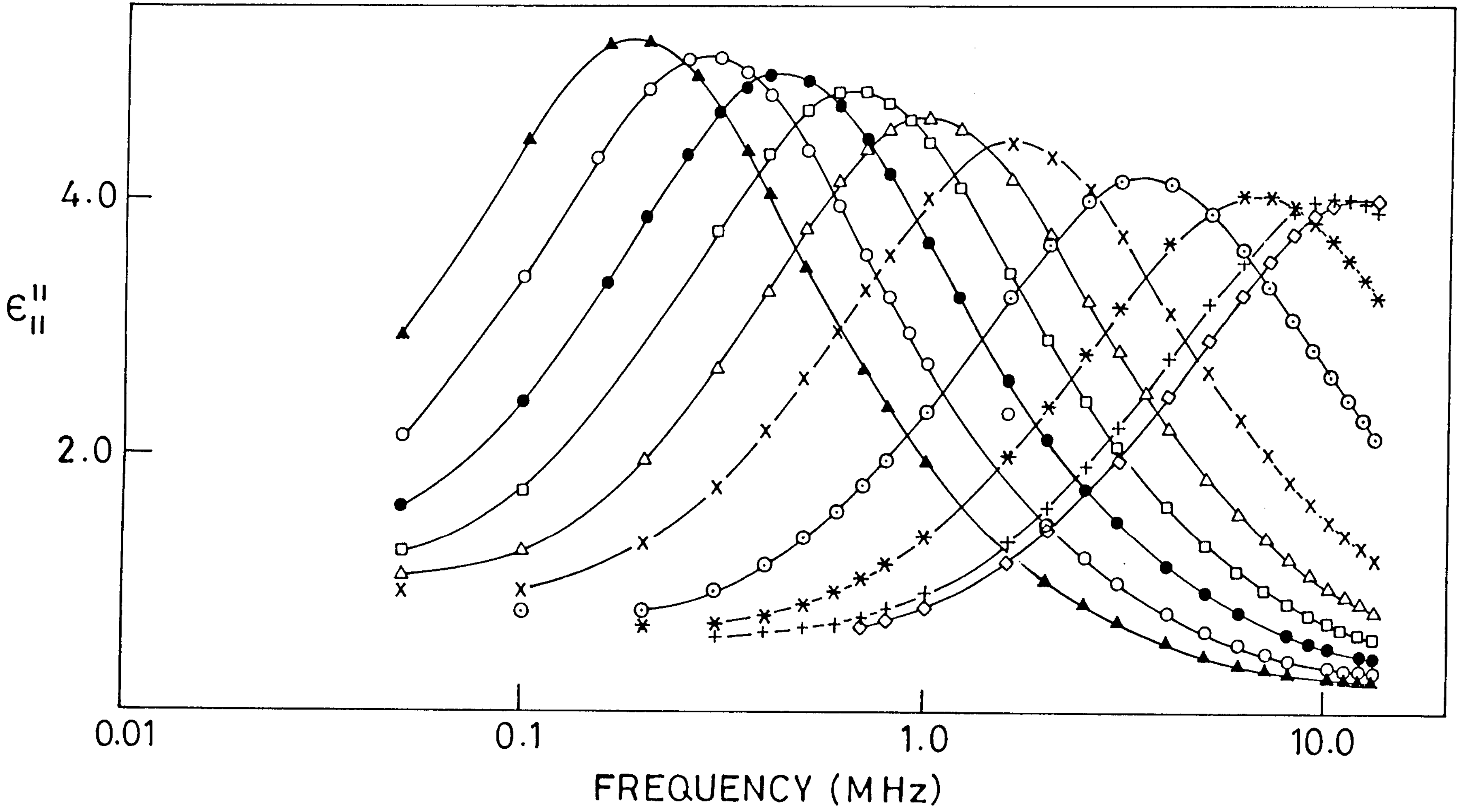


Figure 4.6. The representative loss curves in the nematic (◇ 206.2°C, + 200.2°C), smectic A_d (✱ 179.5°C, ⊙ 157.2°C, × 137.3°C, △ 126.9°C, □ 120.15°C) and reentrant nematic phase (● 113.95°C, ○ 106.35°C, ▲ 100°C) of 8OBCBP.

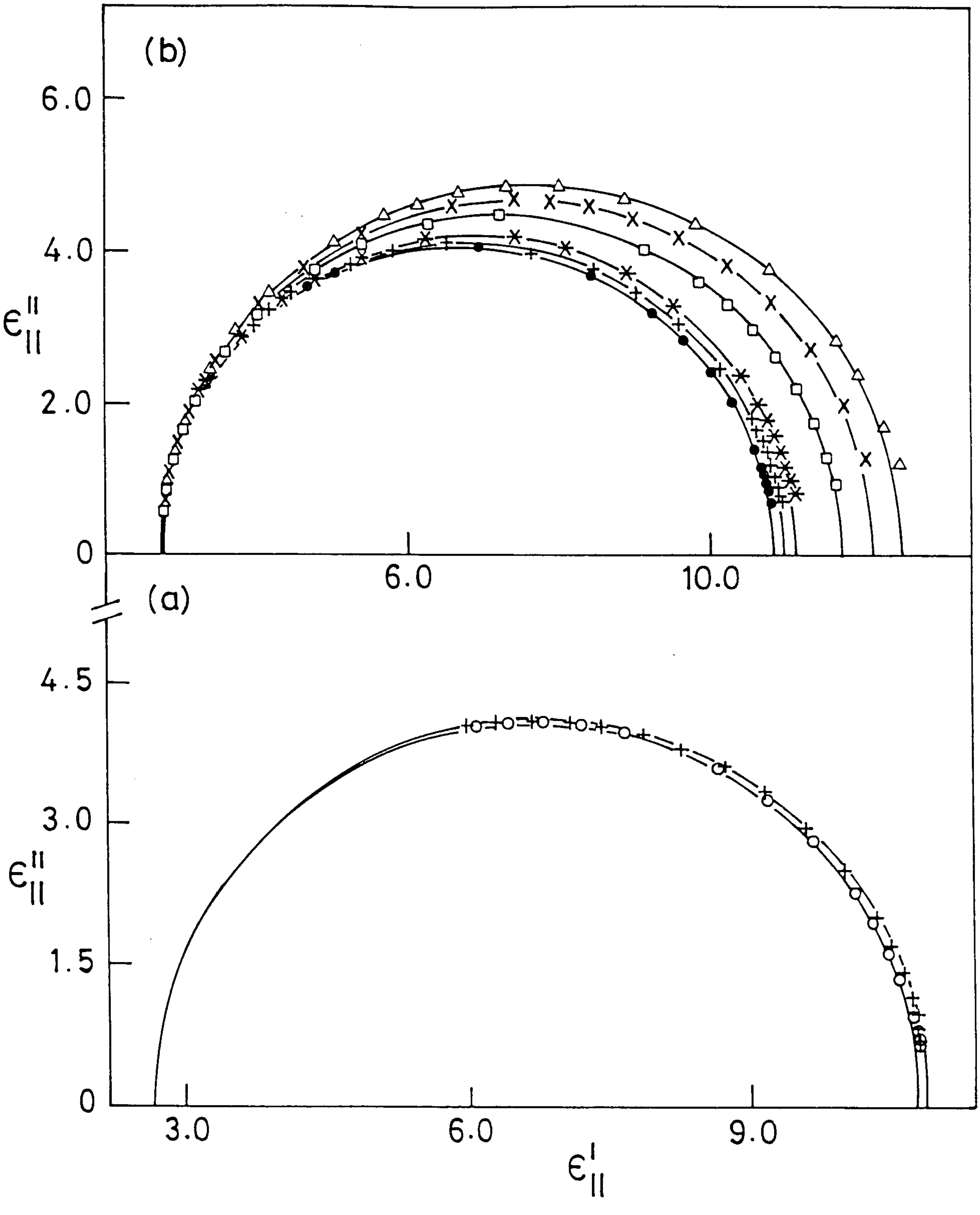


Figure 4.7

Representative Cole-Cole plots for the (a) nematic (+ 206.2°C, o 200.15°C) and (b) smectic A_d phase (● 179.5°C, + 167.7°C, ✶ 157.25°C, ☐ 137.3°C, x 126.9°C and A 120.15°C) of 8OBCBP.

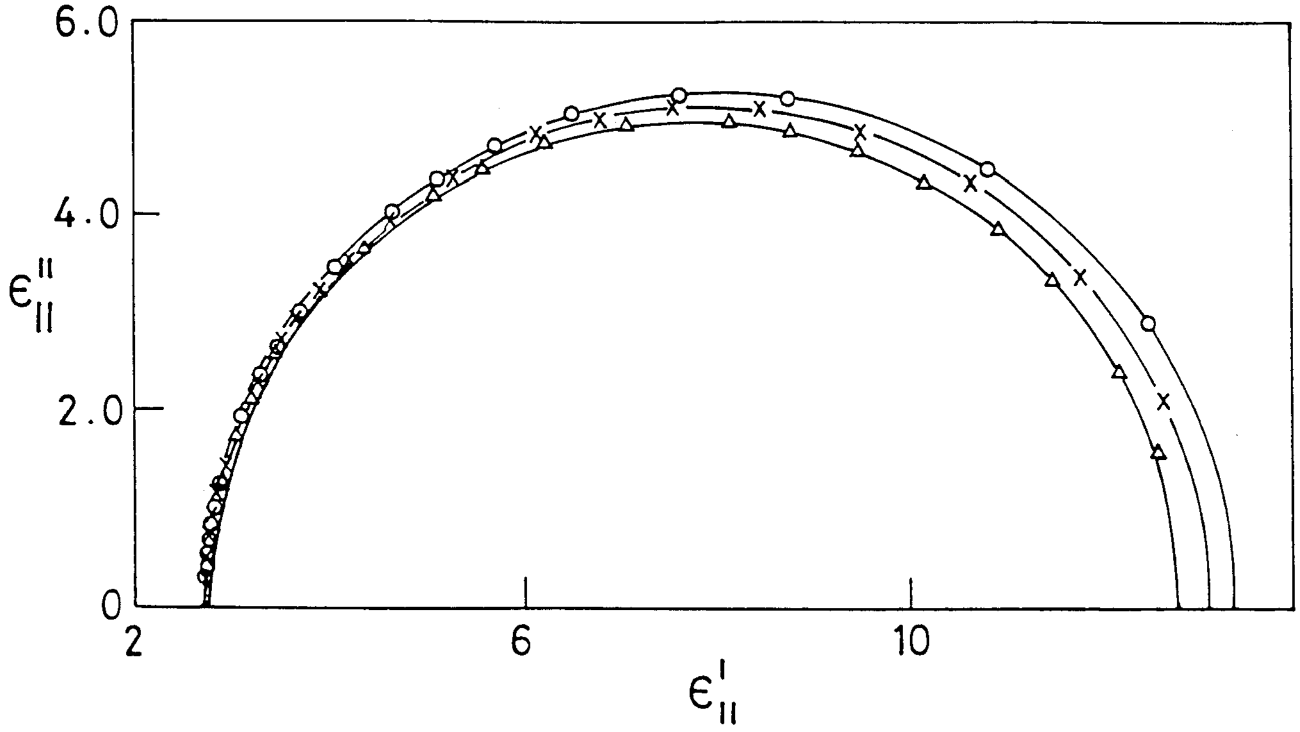


Figure 4.8

The representative Cole-Cole plots in the reentrant nematic phase (Δ 113.95°C, x 106.35°C, o 100°C) of 8OBCBP.

all the three phases. The values of relaxation frequencies (f_R) obtained from loss curves and Cole-Cole plots at various temperatures are listed in Table 4.3. f_R values could not be obtained from the loss curves at the higher temperatures in the normal nematic phase due to the high values of the frequencies involved. In such cases f_R values are obtained from Cole-Cole plots only. A plot of f_R versus $1/T$ is shown in Fig. 4.9. The following features are seen from this figure.

1) The activation energy W in the reentrant nematic phase is higher than in the normal nematic phase. It may be recalled that the first observation of such a difference in W between the two nematic phases was by Ratna et al.[21] Since then a similar behaviour has been seen in most of the reentrant systems studied so far.[20] The difference in W in the two nematic phases can be ascribed to a difference in the molecular associations in these phases. It is interesting that although Xray studies do not show any difference between the two nematics on a structural level, the dielectric dispersion studies do indicate pronouncedly different molecular associations in the two nematic phases.

2) The Arrhenius plot in the srnectic A_d phase is not linear at all. In fact it has a pronounced curvature which changes continuously as the N_{re} phase is approached. As a consequence, it is not possible to ascribe any meaningful value of W in the A_d phase.

TABLE 4.3

Frequency of relaxation (f_R) as a function of temperature in the nematic, smectic A_d and reentrant nematic phases of 8OBCBP

S.No.	Temperature (°C)	Frequency of relaxation (in MHz)		Mean f_R
		From loss curve	From Cole-Cole	
		N Phase		
1	219.37	-	16.75	16.75
2	214.85	-	14.8	14.8
3	210	-	13.16	13.16
4	206.2	-	11.818	11.818
5	202.45	-	11.18	11.18
6	200.15	10	10.268	10.134
7	197.35	9.6	9.618	9.609
		A_d Phase		
8	196.25	9.4	9.439	9.420
9	194.1	8.95	8.98	8.965
10	191.8	8.6	8.606	8.603
11	188.3	7.9	7.87	7.885
12	182.0	7.1	6.98	7.04
13	179.5	6.4	6.32	6.36
14	171.85	5.4	5.3	5.35
15	167.7	4.75	4.69	4.72
16	162.7	4.05	4.06	4.055
17	157.25	3.42	3.39	3.405
18	152.7	2.95	2.94	2.945
19	148.3	2.525	2.51	2.518
20	143.25	2.075	2.064	2.07
21	137.3	1.6	1.62	1.61
22	132.4	1.26	1.29	1.275
23	126.9	0.983	0.985	0.984
24	123.25	0.800	0.800	0.8
25	121.85	0.735	0.742	0.739
26	120.15	0.655	0.647	0.651
		N_{re} Phase		
27	118.2	0.568	0.570	0.569
28	117.35	0.550	0.547	0.549
29	115.3	0.485	0.483	0.484
30	114.0	0.430	0.431	0.431
31	111.5	0.378	0.375	0.377
32	109.85	0.347	0.349	0.348
33	106.35	0.280	0.279	0.280
34	105.2	0.260	0.258	0.259
35	103.55	0.229	0.227	0.228
36	102.4	0.225	0.221	0.223
37	100.0	0.185	0.184	0.185

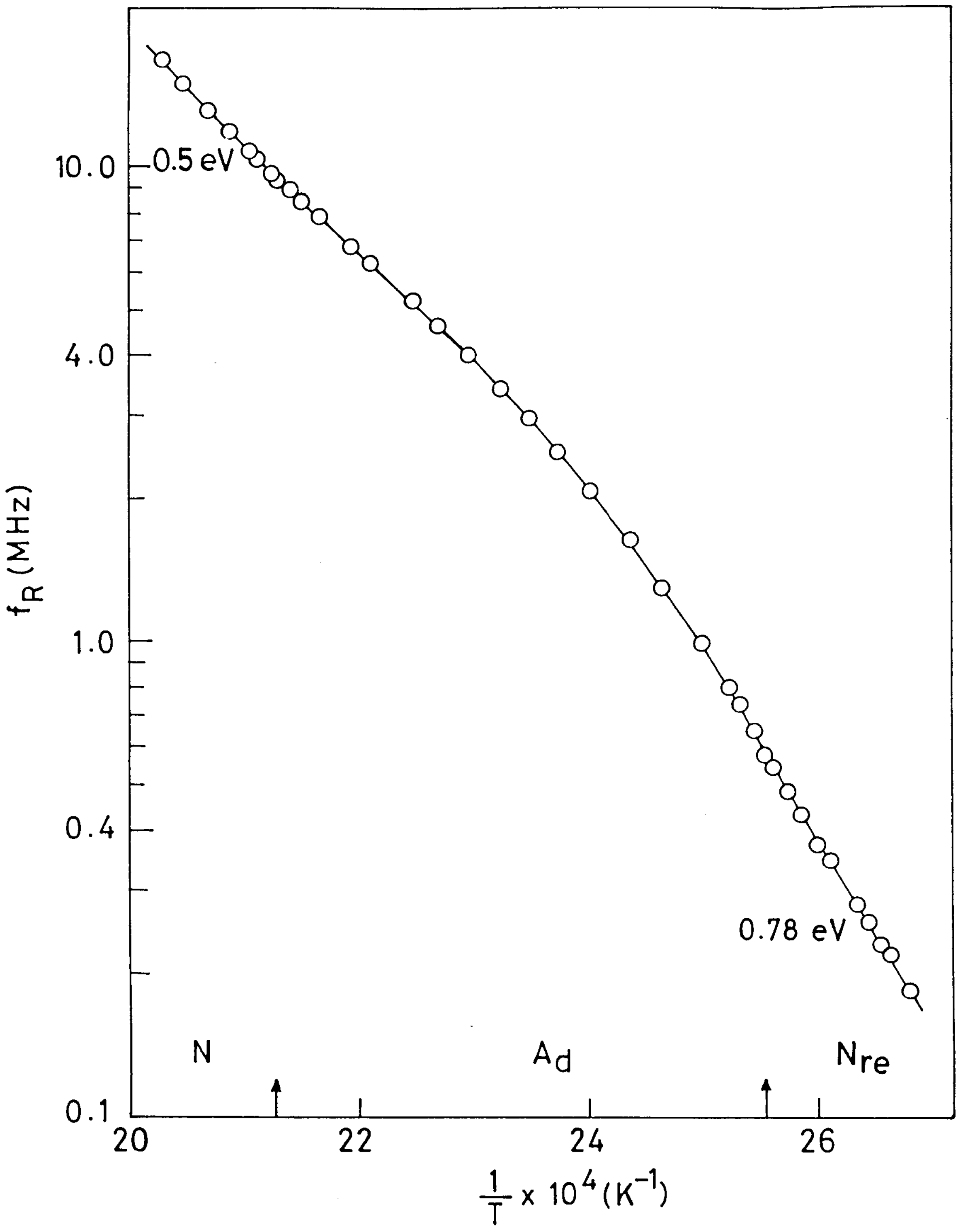


Figure 4.9

The frequency of relaxation f_R vs. 1/T plot of 8OBCBP

Although such a change of curvature can be expected close to another approaching phase (i.e., as a 'precursor effect') such a departure from linearity in the entire A_d range of temperature, which in fact is very large (~80°C), is extremely surprising. Perhaps, a detailed structural study of the A_d phase in this material would help us to understand the reason for this unusual behaviour.

4.3.2. 30 Mole % of 9OBCAB in 8OBCAB

Now we present our dielectric measurements on the binary mixture of 30 mole % 9OBCAB/8OBCAB.

a) Static

Figure 4.10 shows the temperature variation of the dielectric constants $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$ and also of $\Delta\varepsilon$ and the average dielectric constant $\bar{\varepsilon}$. A continuous increase of $\varepsilon_{\parallel}$ with decrease in temperature was found throughout the nematic, smectic A_d and N_{re} phases. However near the reentrant nematic-smectic A_1 (N_{re}-A_1) transition a pronounced decrease in $\varepsilon_{\parallel}$ was observed. This is interpreted as due to the strong increase in the antiparallel correlation in the smectic A_1 phase. These results are in general agreement with those of Legrand et al.[20] on another doubly reentrant single component system: viz., 4-cyanobenzoyloxy-4'-octylbenzoyloxy-p-phenylene (8CBBP).

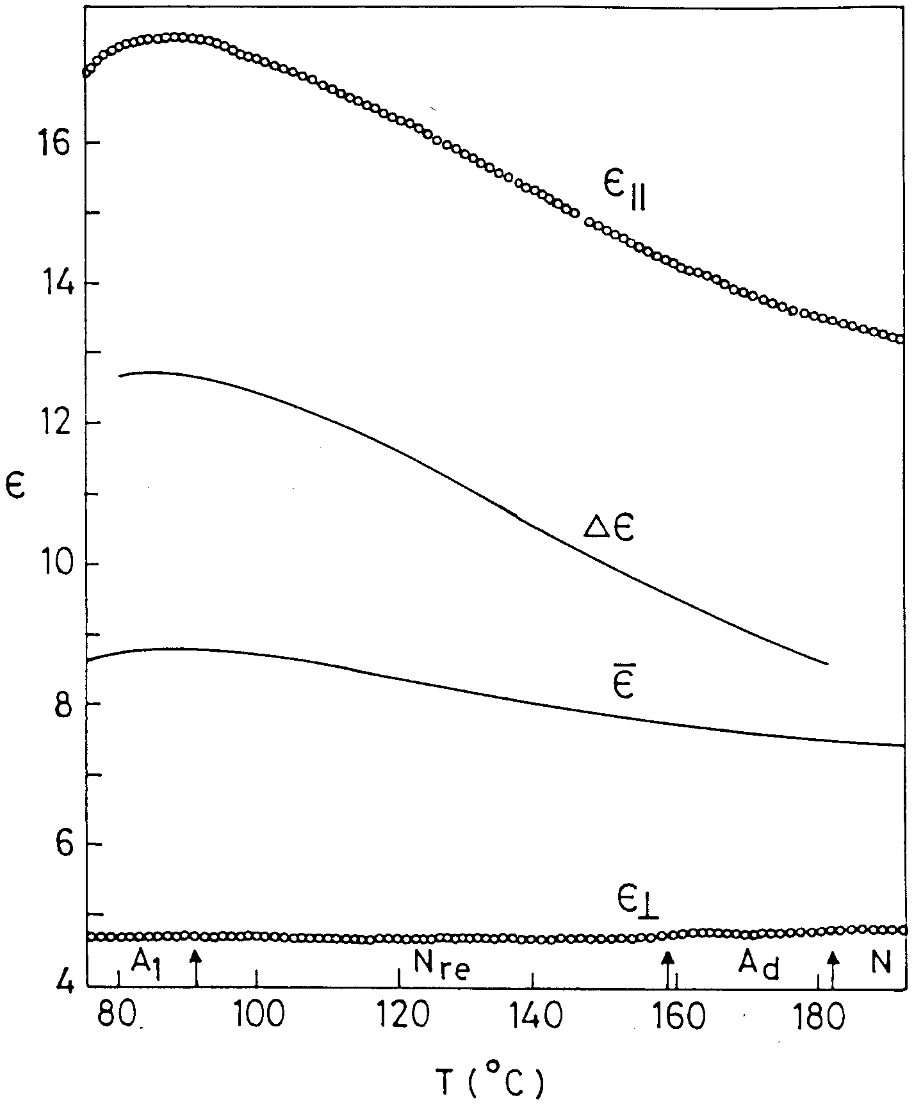


Figure 4.10

The temperature variation of static dielectric constants $\epsilon_{||}$, $\epsilon_{\perp}$ and of $\bar{\epsilon}$ and $\Delta\epsilon$ in N, A_d, N_{re} and A_1 phases of 30 mol % 9OBCAB/8OBCAB mixture.

b) Dispersion

The typical loss curves at a few temperatures in the nematic, smectic A_d, reentrant nematic and A_1 phases are shown in the Fig. 4.11. The variation of the maxima of the loss curves in all the phases reflects the behaviour of $\varepsilon_{\parallel}$. The slight decrease in the maxima near N_{re}-A_1 transition is also clearly seen. The representative Cole-Cole plots in all phases are shown in the Figs.4.12 and 4.13. The frequencies of relaxation (f_R) obtained from loss curves and Cole-Cole plots are listed in the Table 4.4. The plot of f_R versus 1/T is shown in Fig.4.14. This plot is linear in the N and in the A_d phases ($W_N \sim W_{A_d} = 0.44$ eV). However, in the N_{re} phase, the plot is non-linear and changes slope continuously on going towards A_I, In the A_1 phase, the Arrhenius plot is a straight line. We shall now compare the dispersion results on the 9OBCAB/8OBCAB mixture (Fig. 4.1 4) with those on 8OBCBP (Fig. 4.9).

1) On the whole W appears to increase from A_d to N_{re} to A_I. This trend is in accordance with earlier measurements on another doubly reentrant material, viz., 8CBBP.[20]

2) The plot of f_R versus 1/T is linear in the A_d phase only when the temperature range of the phase is small (Fig.4.14). When this range is somewhat large as in the case of 8OBCBP (Fig.4.9), the plot changes slope continuously, the slope increasing with decrea-

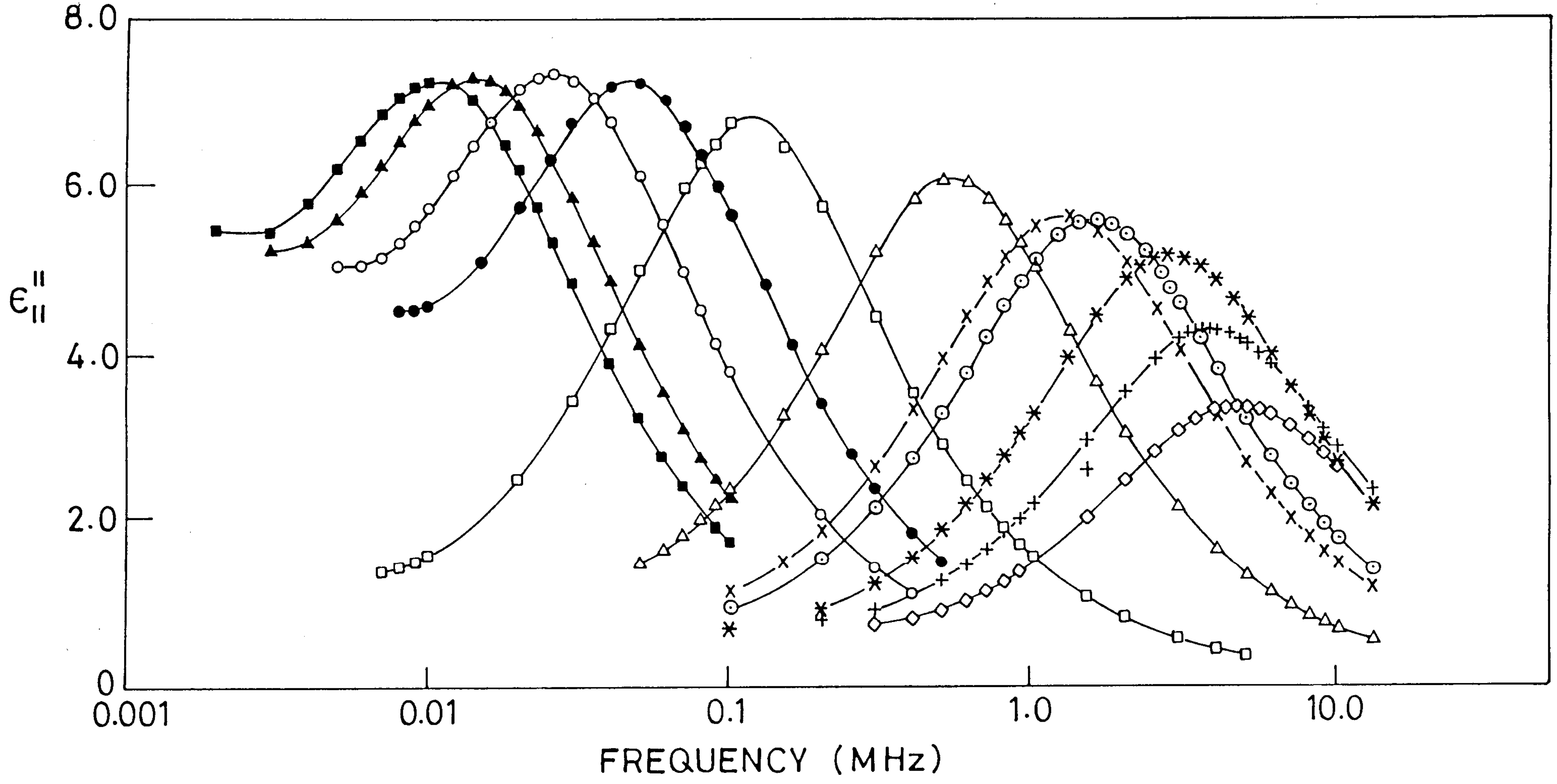


Figure 4.11. The representative loss curves in the nematic (◇ 197.25°C, + 189.8°C), smectic A_d (✱ 176.9°C, ⊙ 162.75°C), reentrant nematic (× 156.6°C, △ 138.4°C, □ 111.5°C, ● 94.75°C) and smectic A_1 (○ 88.5°C, ▲ 81.15°C, ■ 77.85°C) phases of 30 mol % 9OBCAB/8OBCAB mixture.

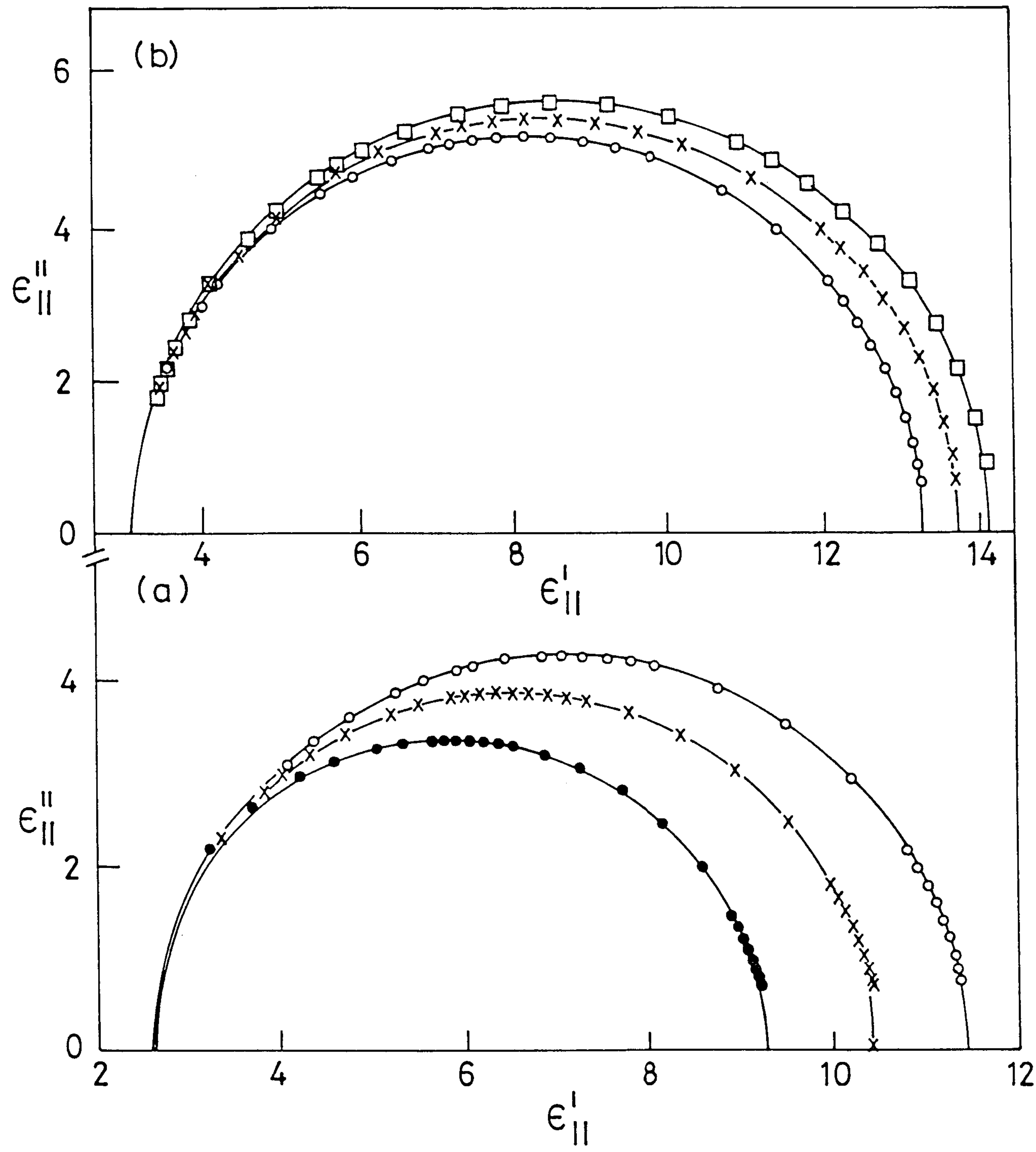


Figure 4.12

The representative Cole–Cole plots in the (a) nematic (● 197.25°C, × 193.25°C, ○ 189.8°C) and (b) smectic A_d (○ 178.9°C, × 173°C, □ 162.75°C) phases of 30 mol % 9OBCAB/8OBCAB mixture.

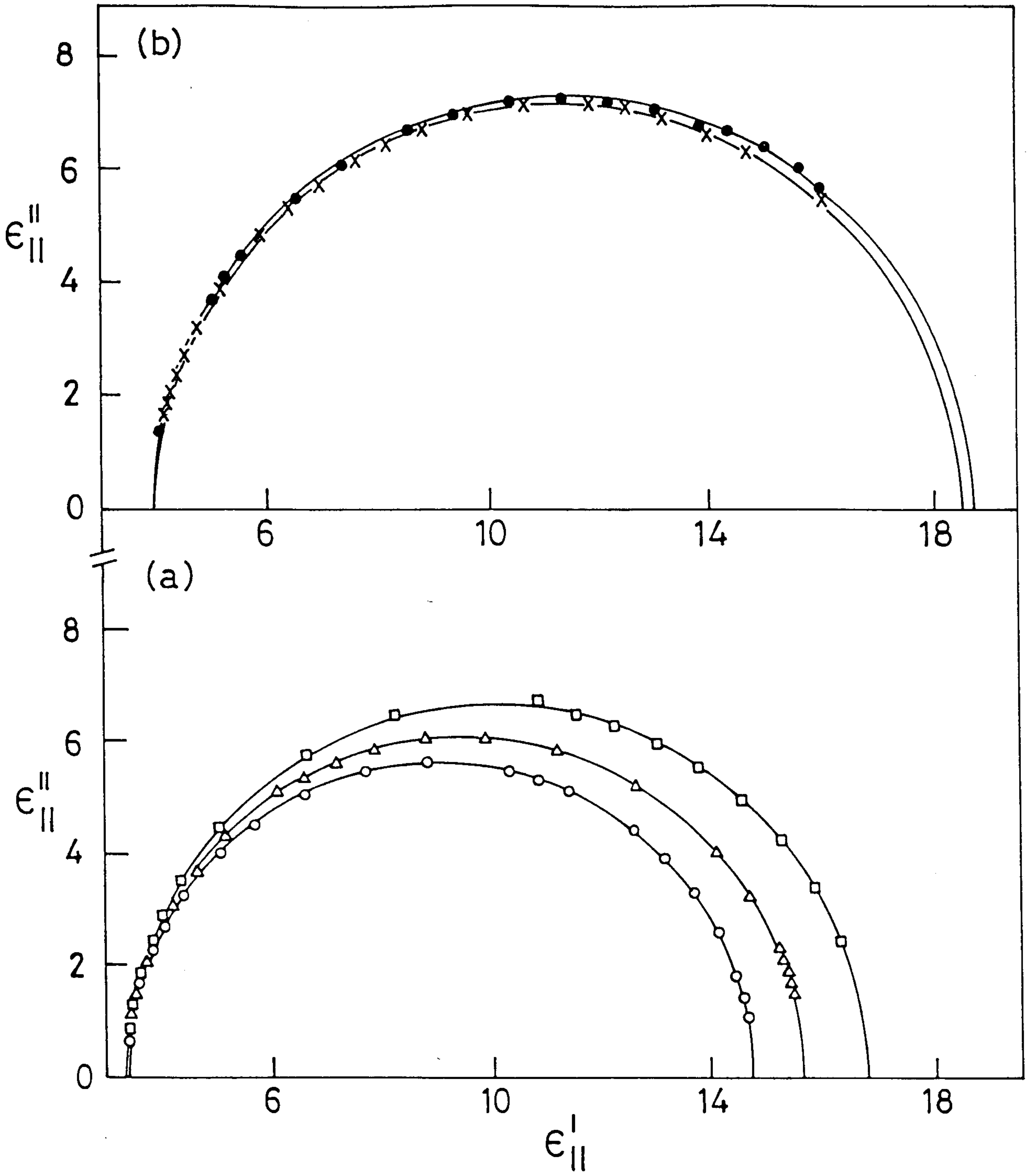


Figure 4.13

The representative Cole-Cole plots in the (a) N_{re} (○ 156.6°C, A 138.4°C, □ 111.5°C) and (b) smectic A_1 (● 88.5°C, x 77.85°C) phases of 30 mol % 9OBCAB/8OBCAB mixture.

TABLE 4.4

Frequency of relaxation (f_R) as a function of temperature for the the binary mixture of 30 mol% 9OBCAB/8OBCAB in the nematic. smectic $A_{d'}$, reentrant nematic and smectic A_1 phases.

S.No.	Temperature (°C)	Frequency of relaxation (in MHz)		Mean f_R
		From loss curve	From Cole-Cole	
		Nematic Phase		
1	198.95	5.2	5.22	5.21
2	196.5	4.8	4.79	4.795
3	192.40	4.4	4.37	4.39
4	189.8	3.85	3.83	3.84
5	187.4	3.70	3.69	3.695
6	186.75	3.5	3.5	3.5
7	184.1	3.42	3.43	3.425
		Smectic A_d		
8	180.70	3.17	3.14	3.16
9	178.9	2.83	2.83	2.83
10	176.85	2.75	2.73	2.74
11	176.6	2.60	2.57	2.59
12	172.95	2.30	2.31	2.305
13	169.3	2.15	2.16	2.155
14	165.75	1.65	1.68	1.67
15	162.75	1.55	1.55	1.55
16	160	1.45	1.46	1.455
		Reentrant Nematic		
17	156.6	1.25	1.24	1.245
18	146	0.750	0.747	0.749
19	138.4	0.525	0.523	0.524
20	131.2	0.391	0.386	0.389
21	123.8	0.255	0.251	0.253
22	118.65	0.202	0.199	0.201
23	111.5	0.115	0.114	0.115
24	100.2	0.065	0.064	0.0645
25	94.75	0.0455	0.044	0.0448
		Smectic A_1		
26	88.50	0.0255	0.023	0.0243
27	86.1	0.021	0.020	0.0205
28	84.3	0.020	0.0187	0.0194
29	81.15	0.014	0.0134	0.0137
30	77.85	0.011	0.0101	0.0106

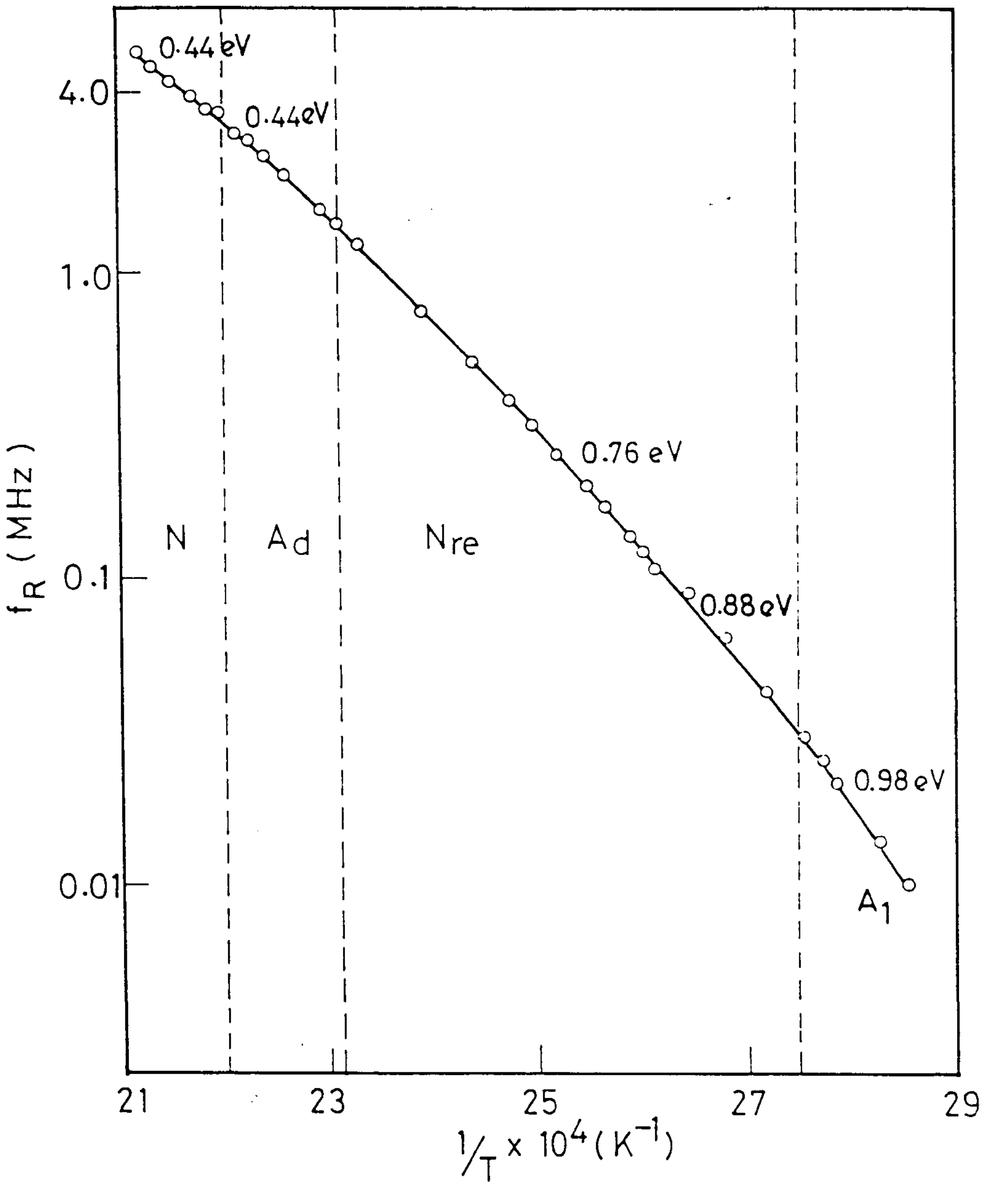


Figure '4.14

The frequency of relaxation f_R vs. 1/T plot for 30 mol % 9OBCAB/8OBCAB mixture.

sing temperature. Exactly similar behaviour is seen in the N_{re} phase also — a straight line plot of f_R vs. 1/T when the range of N_{re} is small (Fig.4.9) and a continuous change of slope when it is large (Fig.4.14). If the change of slope can be regarded as a pre-transitional effect, then such an effect should have been less conspicuous for a larger range while the opposite seems to be the case observed experimentally. A possible explanation could be associated with the fact 'that the reentrant nematic phase, in general, is known to have two types of competing smectic fluctuations — viz., A_1-like and A_d-like, the latter being more prominent at high temperatures while the former is strong at low temperatures. It is conceivable that dielectric dispersion is perhaps strongly influenced by these competing short range order effects leading to a non-linear behaviour of the f_R vs. 1/T plot.

4.3.3. DB9ONO$_2$

Now we present the results of our dielectric investigations on the single component system DB9ONO$_2$, a triply reentrant mesogen.

a) <u>Static</u>

The temperature variation of the static dielectric constants $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ as well as of the dielectric anisotropy $\Delta\varepsilon$ is shown in

Fig. 4.15. It is seen that except at the highest temperature N-A_d transition, both $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ and hence $\Delta\varepsilon$ exhibit a smooth variation through all the other A_d-N transitions. It therefore appears that the dielectric permittivity is not at all affected by the numerous A_d-N transitions occurring in the material. On approaching the A_1 phase $\varepsilon_{\parallel}$ decreases while $\varepsilon_{\perp}$ increases causing thereby a pronounced decrease in $\Delta\varepsilon$. Owing to difficulties in obtaining homogeneous orientation in the C phases we have not made any measurements of $\Delta\varepsilon$ beyond the A_1 phase.*

b) Dispersion

The typical loss curves at a few temperatures in all the phases exhibited by this compound are shown in Figs. 4.16-4.18. Since it was possible to get homeotropic alignment in the C phases, dispersion measurements were carried out in all the lower temperature phases. The representative Cole-Cole plots at a few temperatures in all the phases are shown in the Figs. 4.19-4.21. It is clearly evident from the loss curves and as well as from Cole-Cole plots that there is possibly a second dispersion close to the dispersion discussed here, but at frequencies higher than the maximum frequency (13 MHz) capability of our instrument. The representative Cole-Cole plots clearly show that the second dispersion separates

---

* After completion of these studies on DB9ONO$_2$, it was learnt that Legrand et al.[22] have also studied the dielectric behaviour of the same material. Their results are in good agreement with ours.

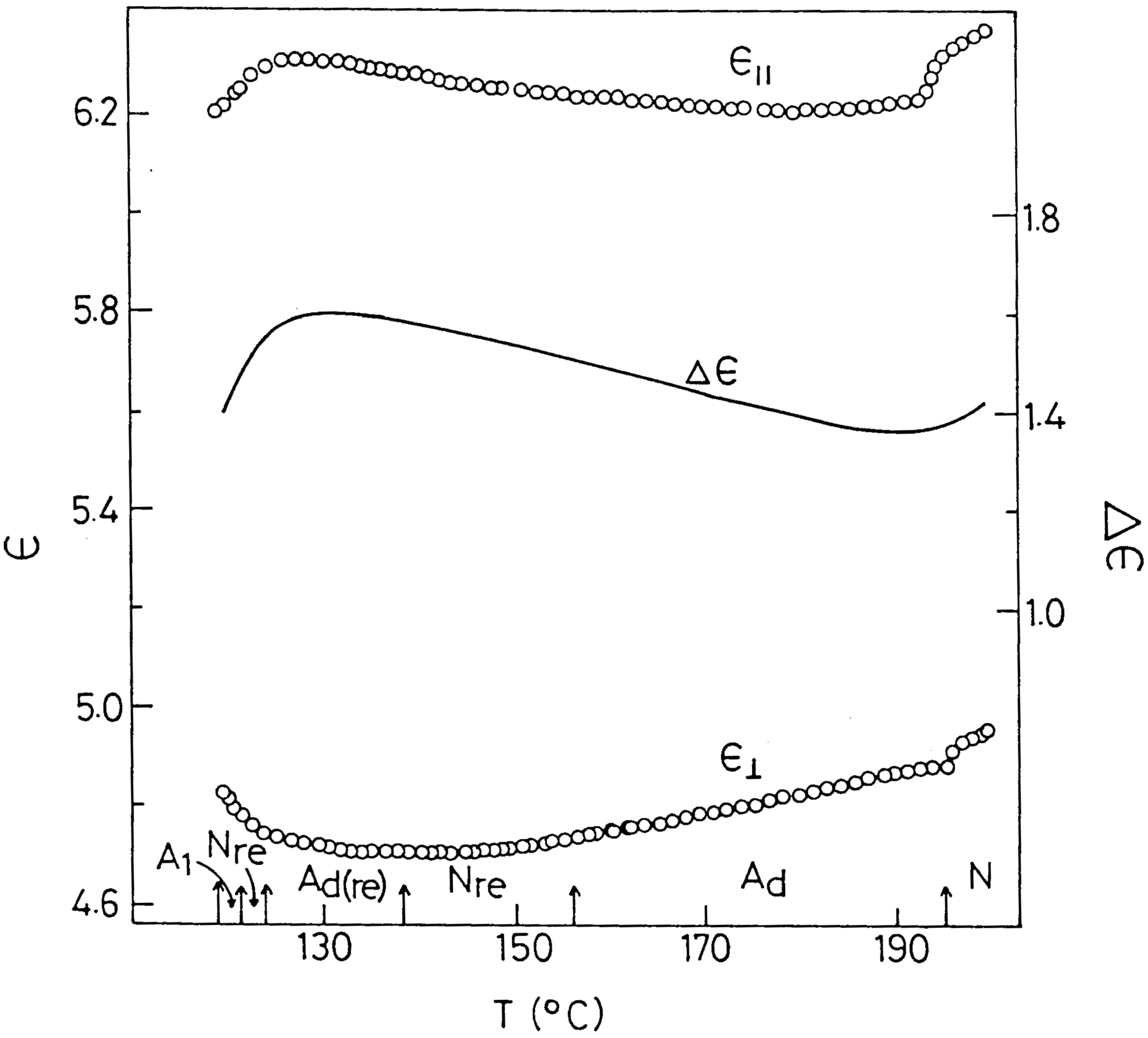
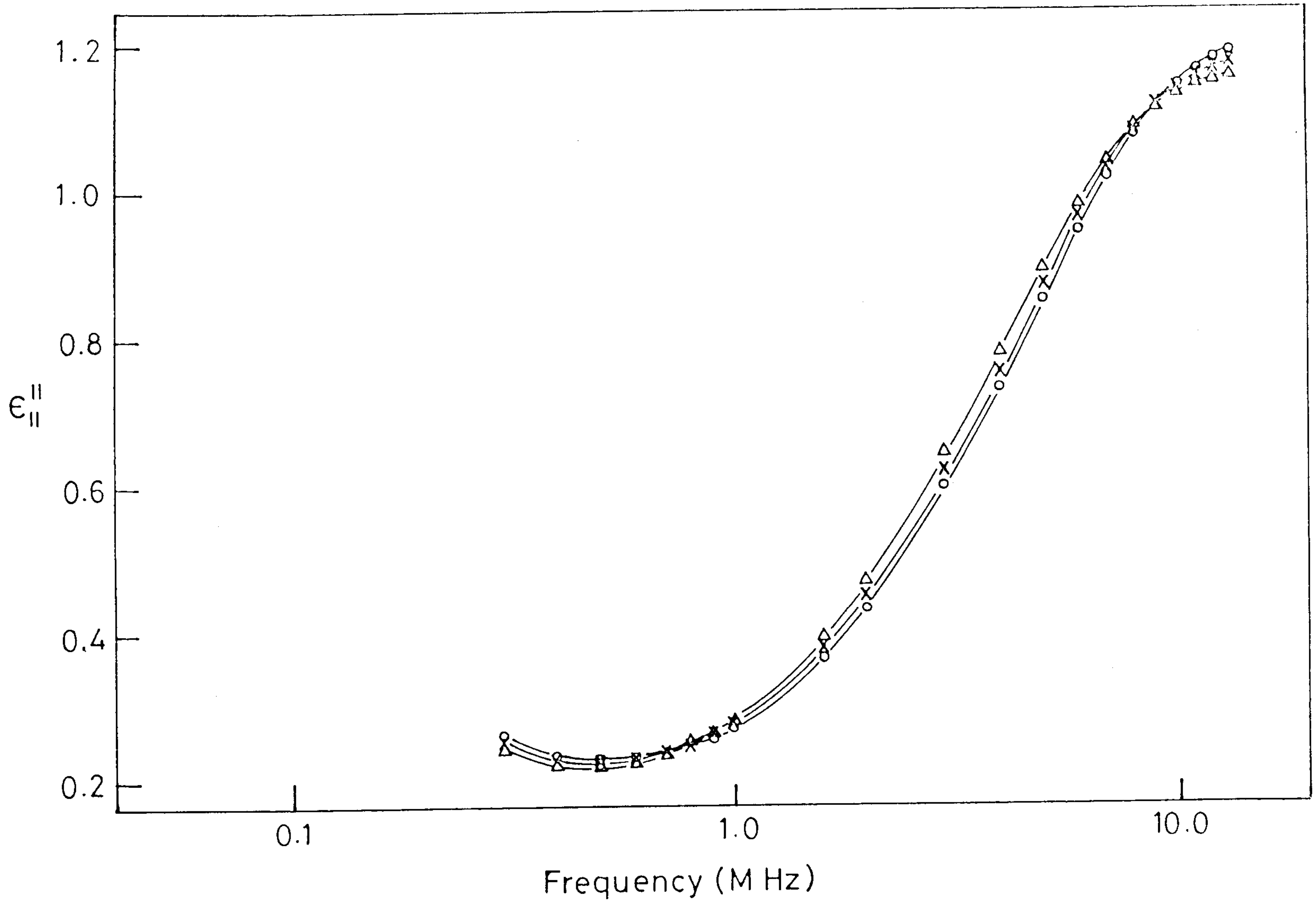


Figure 4.15

The temperature variation of static dielectric constants $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ and the dielectric anisotropy ($\Delta\varepsilon$) in the different phases of DB9ONO$_2$. The arrows indicate transition temperatures.



<u>Figure 4.16</u>. Representative loss curves in the nematic phase (o 202.2°C, × 200.2°C, Δ 197.7°C) of DB9ONO$_2$. The other half of the loss could not be completed because of the frequency limitation of our set up.

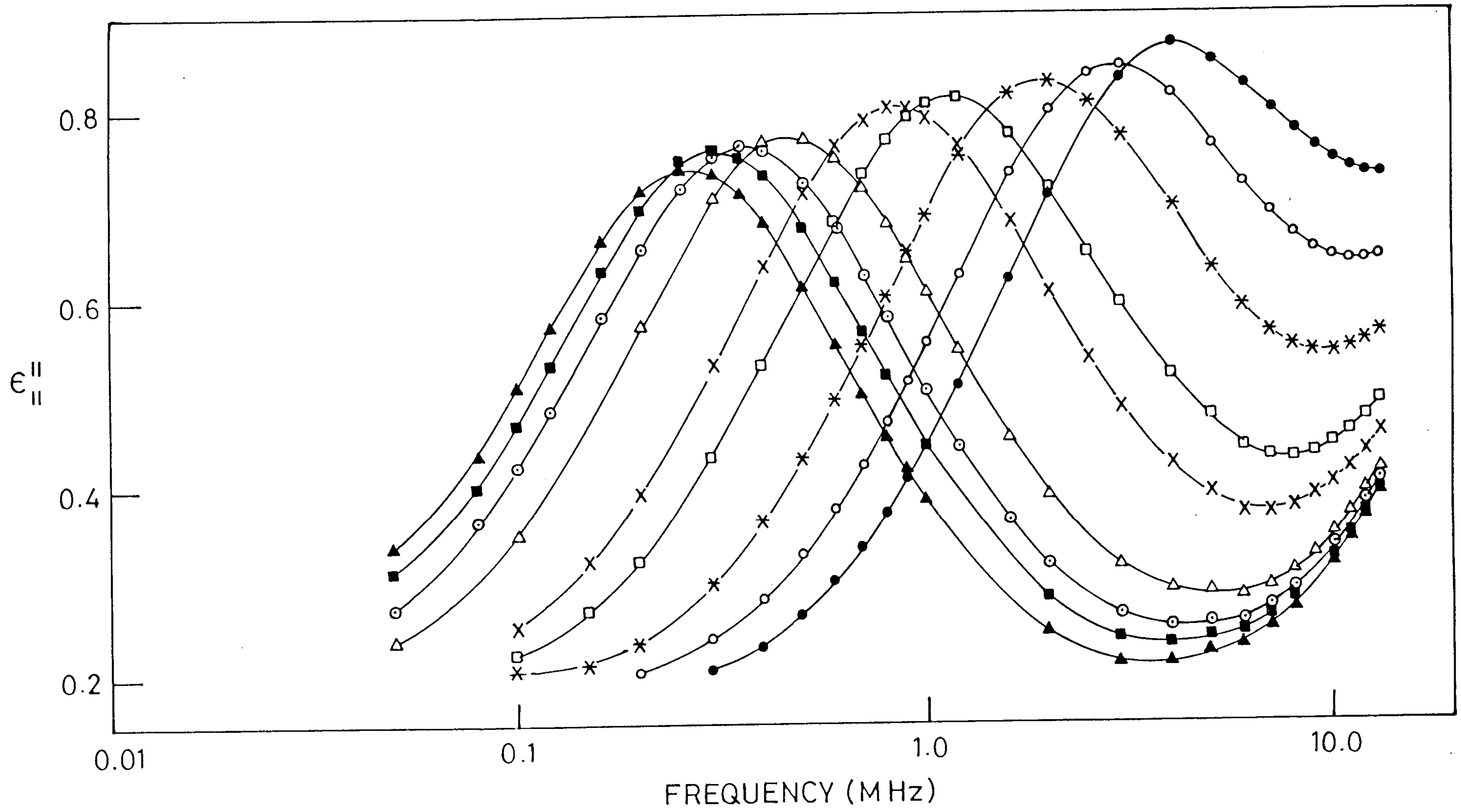


Figure 4.17. Representative loss curves in the A_d (● 168.4°C, ○ 160°C), N_{re} (✱ 151.2°C, □ 140.1°C), $A_{d(re)}$ (× 134.4°C, △ 125.0°C), N_{re} (⊙ 122.6°C, ■ 121.5°C) and A_1 (▲ 120.1°C) phases of $DB9ONO_2$

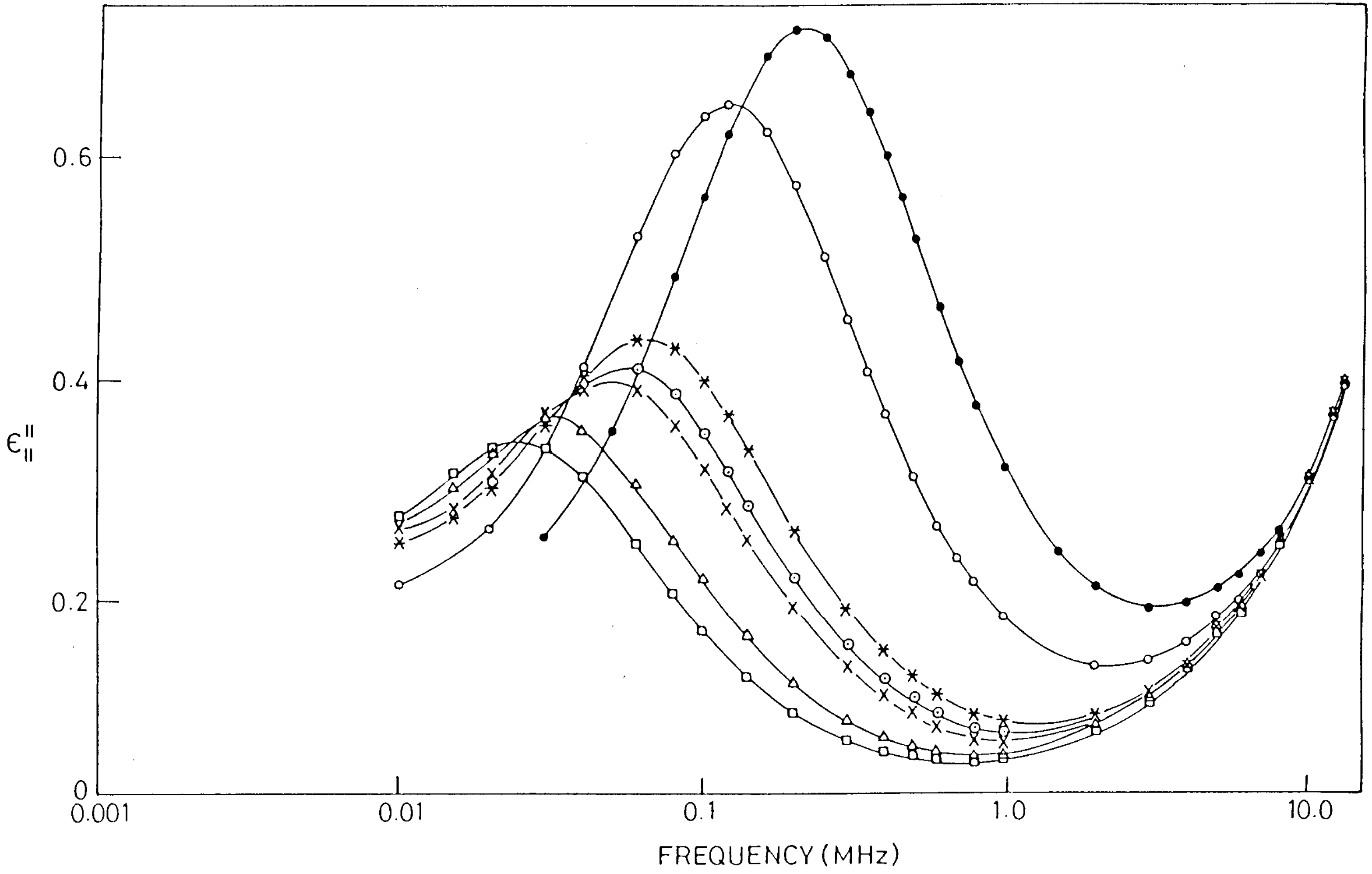


Figure 4.18

Representative loss curves in $\tilde{C}$ (• 117.4°C, o 110°C, ✱ 101.45°C), A_2 (⊙ 99.15°C × 97.5°C) and C_2 (△ 91.65°C, □ 88.65°C) phases of $DB9ONO_2$.

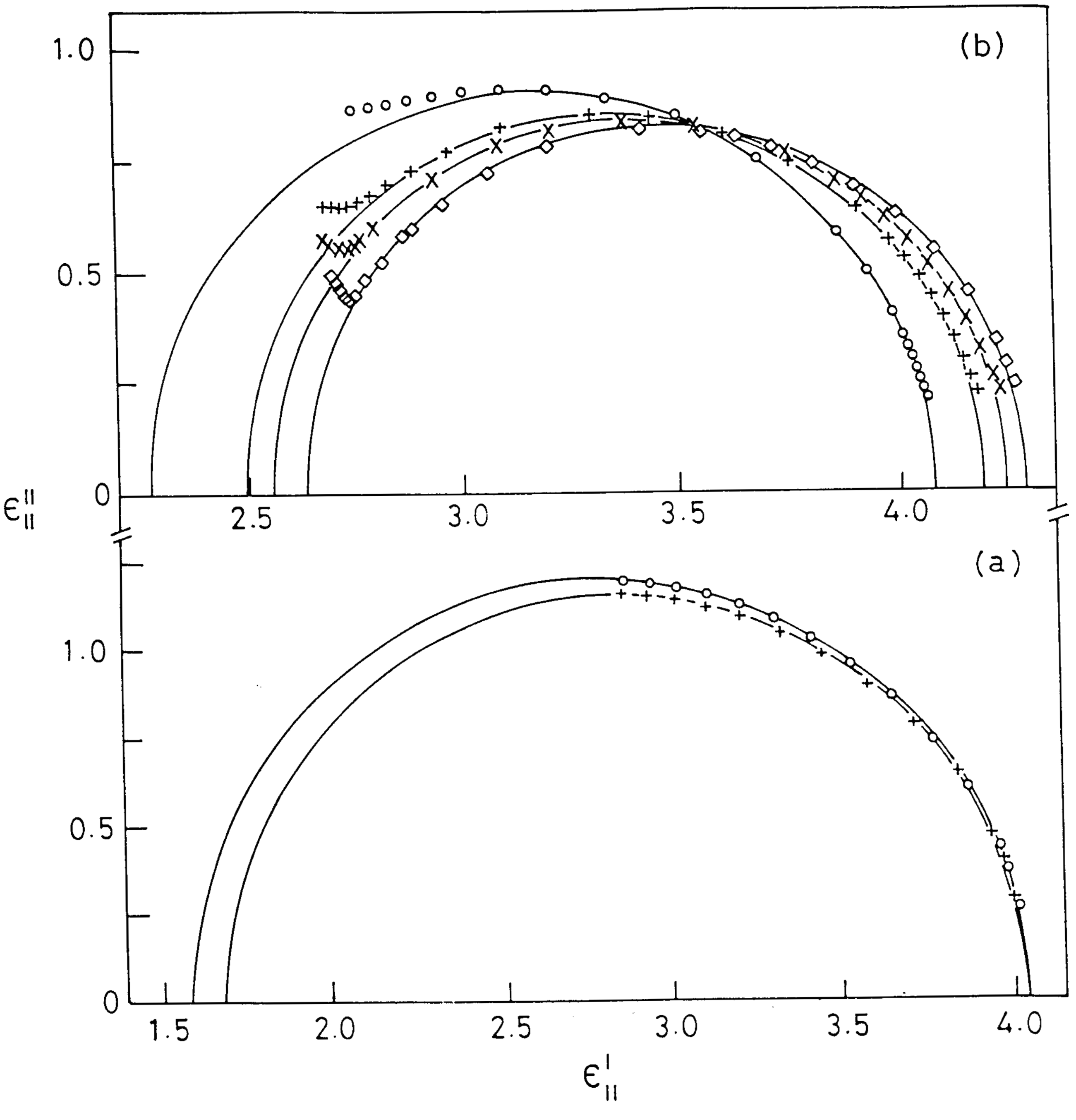


Figure 4.19

Representative Cole-Cole plots in the (a) nematic (o 202.15°C, + 197.7°C), (b) smectic A_d (o 180.2°C, + 160°C) and N_{re} (× 151.2°C, ◇ 140.1°C) phases of $DB9ONO_2$.

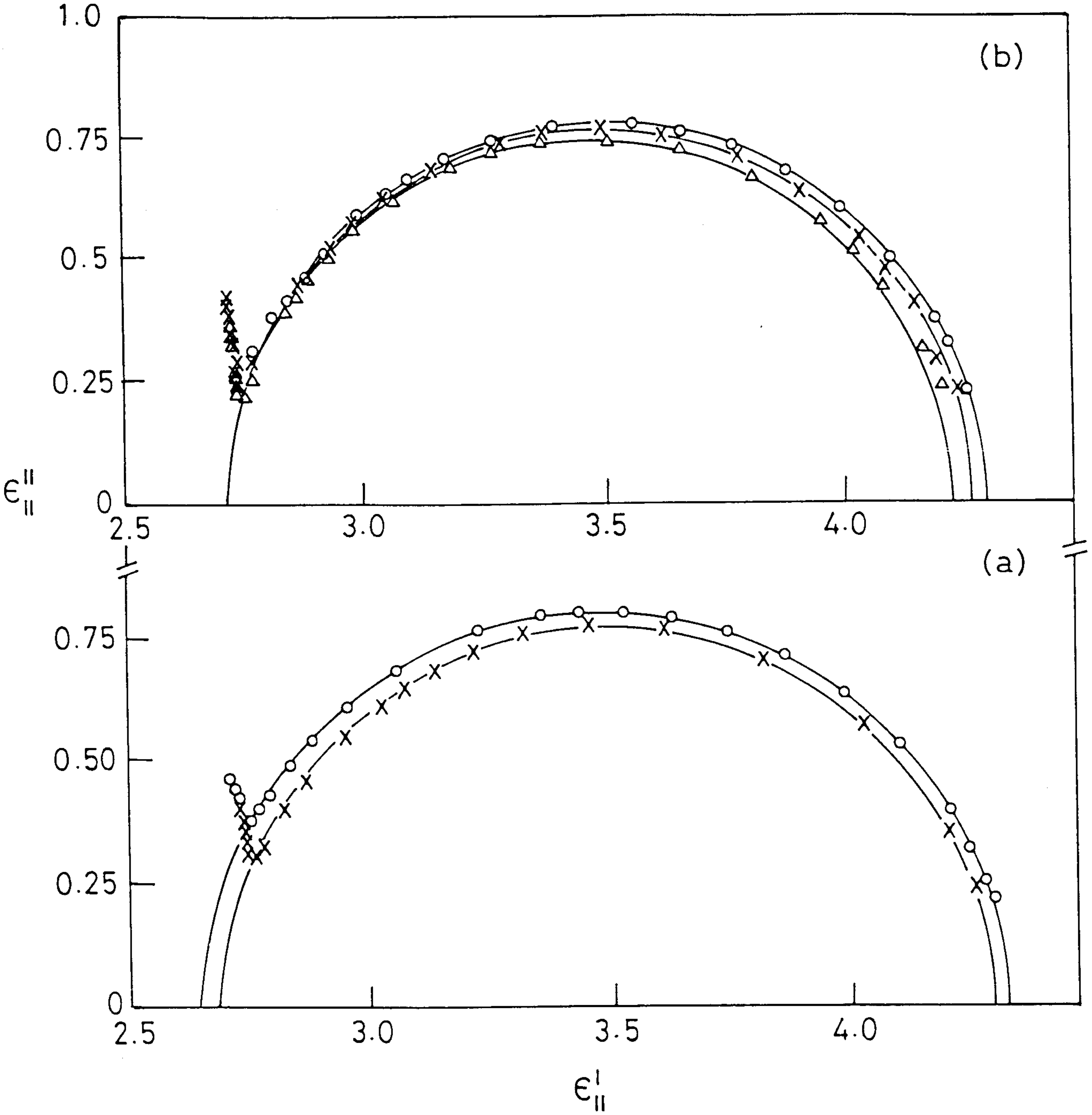


Figure 4.20

Representative Cole-Cole plots in (a) $A_{d(re)}$ (⊙ 134.4°C, × 125°C), (b) N_{re} (○ 124°C, × 121.5°C) and A_1 (△ 120.1°C) phases of DB9ONO$_2$.

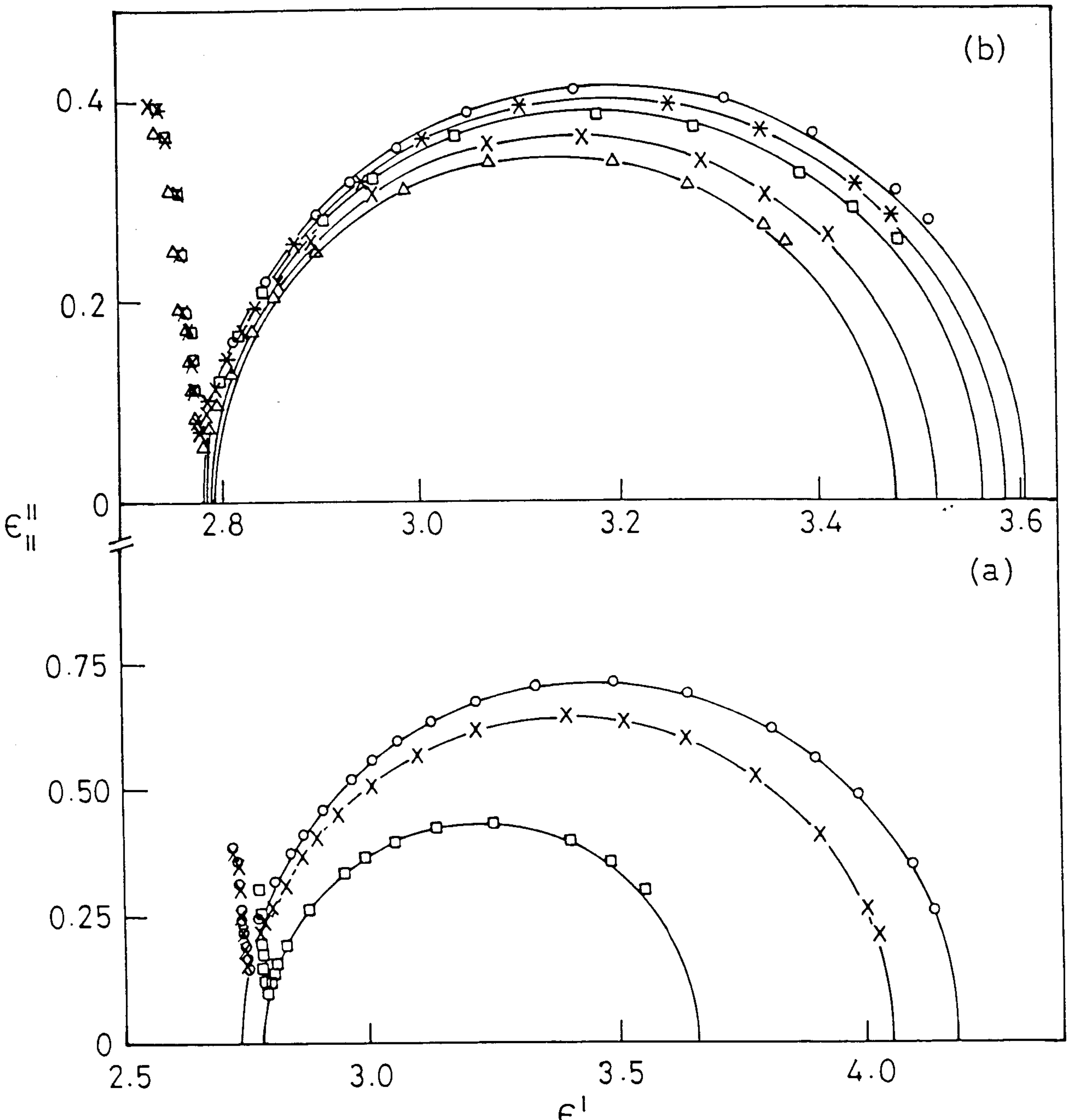


Figure 4.21

Representative Cole-Cole plots in (a) $\tilde{C}$ (○ 117.4°C, X 110°C, □ 101.5°C), (b) A_2 (○ 99.2°C, ✱ 97.5°C) and C_2 (□ 95°C, X 91.7°C, **A** 88.7°C) phases of $DB9ONO_2$.

out more at lower temperatures and as a consequence becomes more pronounced. Our determination of f_R at higher temperatures may have been conceivably affected by the overlapping of the two dispersion regimes at these temperatures. The reason for the second dispersion in all the phases is not clear to us.

The f_R values obtained at various temperatures from the loss curves and as well as Cole-Cole plots (corresponding to the lower frequency dispersion) are listed in Table 4.5. f_R versus $1/T$ plot is shown in Fig.4.22. The activation energies (W) obtained in all the mesophases are listed in the Table 4.6. It is seen that the W value for the lowest temperature N_{re} phase is significantly higher than the W value of the first (or higher temperature) N_{re} phase which in turn is higher than that for the normal nematic phase. Similarly W of the reentrant A_d phase is more than that of the normal A_d phase. Amongst the four A phases that exist for this compound, A_1 has the highest W while the normal A_d has the lowest value.

Thus on the whole, the dielectric anisotropy increases smoothly with decrease of temperature as one goes from N to A_d to N_{re}. This happens regardless of the number of times the nematic phase reenters. (The dielectric anisotropy decreases only in the A_1 phase.) This result would indicate that the dipolar changes accompanying the A_d-N or A_d-N_{re} transitions should be very subtle.

TABLE 4.5

Frequency of Relaxation (f_R) as a function of temperature for DB9ONO$_2$

S.No.	Temperature (°C)	Frequency of relaxation (in MHz)		Mean f_R
		From loss curve	From Cole-Cole	
		Nematic Phase		
1	205.45	-	12.4	12.4
2	204.85	-	12.28	12.28
3	202.15	-	11.84	11.84
4	201	-	11.32	11.32
5	199.50	-	10.94	10.94
6	197.7	-	10.24	10.24
		Smectic A_d		
7	189.15		7.391	7.391
8	185.15		6.695	6.695
9	180.15		5.837	5.837
10	174.1	-	4.754	4.754
11	168.4	4.05	3.856	3.953
12	164.05	3.5	3.58	3.54
13	160	2.95	2.819	2.885
14	157.15	2.55	2.495	2.523
		Reentrant Nematic		
15	154.1	2.25	2.23	2.24
16	151.2	1.975	1.975	1.975
17	148.1	1.7	1.71	1.705
18	145.15	1.46	1.47	1.465
19	142	1.25	1.247	1.249
20	140.1	1.15	1.155	1.153

continued

S.No.	Temperature (°C)	Frequency of relaxation (in MHz)		Mean f_R
		From loss curve	From Cole-Cole	
		Smectic $A_{d(re)}$		
21	137.55	0.990	1	0.995
22	134.4	0.840	0.843	0.842
23	133.15	0.780	0.779	0.780
24	130	0.660	0.647	0.654
25	127.95	0.573	0.579	0.576
26	127.15	0.545	0.547	0.546
27	126	0.500	0.509	0.505
28	125.5	0.490	0.489	0.490
29	124.5	0.453	0.454	0.454
		Reentrant Nematic		
30	124	0.438	0.438	0.438
31	122.6	0.355	0.353	0.354
32	121.5	0.305	0.301	0.303
		Smectic A_1		
33	121.0	0.290	0.293	0.292
34	120.05	0.260	0.262	0.261
35	119	0.240	0.239	0.240
		Smectic $\tilde{C}$		
36	117.4	0.210	0.214	0.212
37	114	0.161	0.162	0.162
38	109.95	0.120	0.121	0.121
39	107	0.095	0.097	0.096
40	104	0.075	0.077	0.076
41	101.45	0.062	0.064	0.063

continued

S.No.	Temperature (°C)	Frequency of relaxation (in MHz)		Mean f_R
		From loss curve	From Cole-Cole	
		Smectic A_2		
42	99.15	0.054	0.055	0.055
43	97.4	0.047	0.0468	0.0469
		Smectic C_2		
44	95	0.04	0.0409	0.0405
45	93.45	0.036	0.0371	0.0366
46	91.65	0.031	0.0319	0.0315
47	88.65	0.0246	0.0246	0.0246

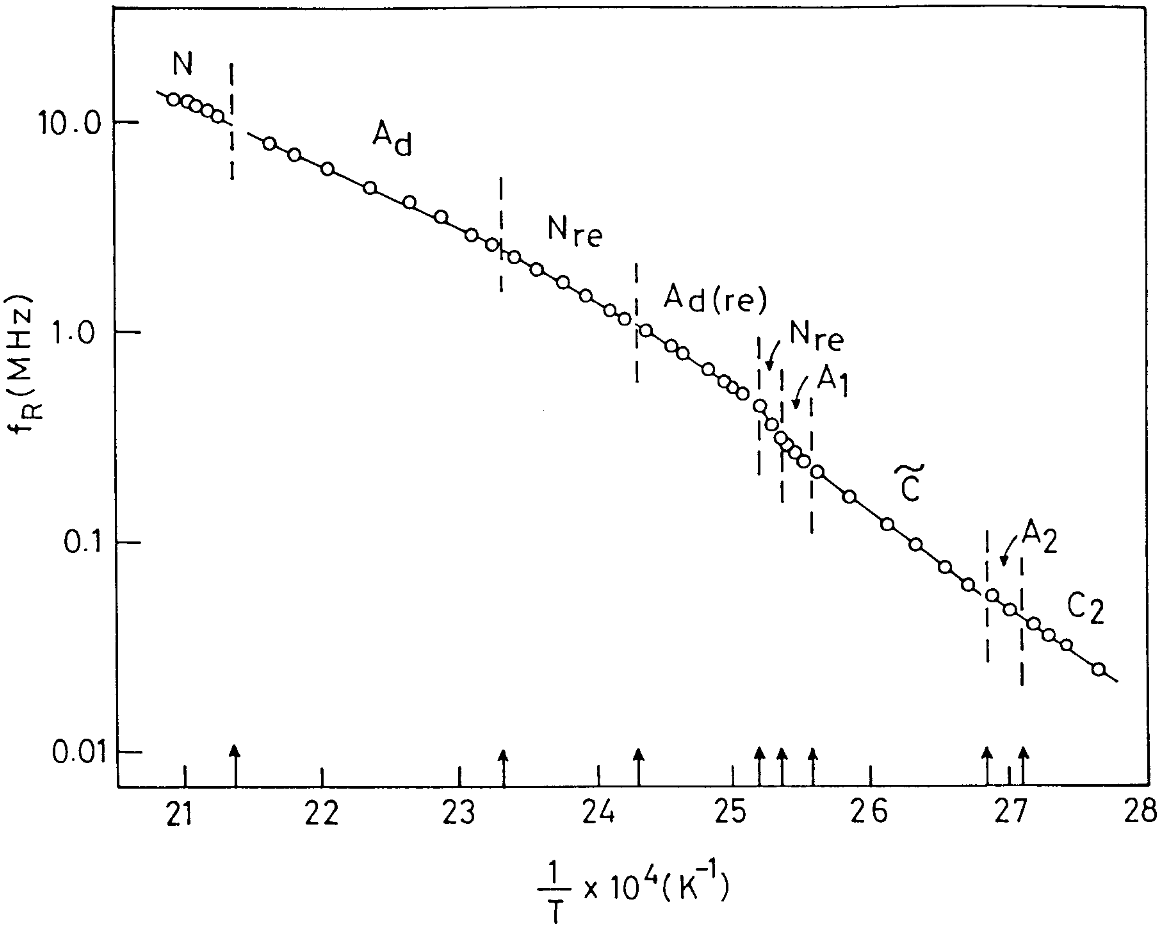


Figure 4.22

Plot of frequency of relaxation f_R vs. 1/T in the different phases of DB9ONO$_2$. The arrows indicate transition temperatures.

TABLE 4.6

Activation energy (W) corresponding to the low frequency dispersion of $\varepsilon_{\parallel}$ in the different phases of DB9ONO$_2$

Phase	N	A_d	N_{re}	$A_{d(re)}$	N_{re}	A_1	$\tilde{C}$	A_2	C_2
W (in eV)	0.54	0.63	0.74	0.87	1.88	1.23	0.97	0.86	0.86

As regards the activation energy W, $W_{N_{re}}$ is always higher than W_N while $W_{A_d} < W_N$, the activation energy being definable only when the temperature range of the phase is small. When this range is large, the plot of f_R versus $1/T$ changes slope continuously and no single value of W can be attributed. The precise reason for this behaviour is not yet clear to us.

There have been several theoretical attempts[23-26] to explain the occurrence of the reentrant nematic phase. Although qualitatively successful, none of these theories have been able to explain all the experimental features exhibited by reentrant mesogens. In the next section we shall briefly discuss the theoretical approach of Longa and de Jeu,[26] and compare the prediction of the theory with experiments with regard to the dielectric properties of reentrant systems.

4.4 SOME COMMENTS ON THEORETICAL WORK CONCERNING THE REENTRANT NEMATIC PHASE

We discussed so far the dielectric permittivities of strongly polar reentrant nematogenic systems. The feature that emerges from the results, regardless of whether the material exhibits one or two reentrant nematic phases, is that $\Delta\varepsilon$ always increases continuously from the high temperature nematic to the lower temperature nematic phase. As mentioned earlier, there have been some theoretical attempts to explain the origin of reentrant nematic behaviour. They are phenomenological and as well as molecular approaches. The phenomenological model[23] of Pershan and Prost which is also referred to as optimum density model makes the hypothesis that reentrant nematic phase occurs because smectic A phase can exist only near 'optimum density. This optimum density model makes two important predictions.

1 There should be doubling of critical exponent associated with correlation length along a line tangential to the parabolic (or elliptical) A-N boundary.

2 The constant density lines in P-T plane should be parallel to the parabolic axis of the P-T boundary.

Although the first prediction has been confirmed by Xray scattering results of Kortan et al.,[27,28] the P-V-T studies by Shashidhar et al.[29] on 8OCB yielded results which are in substantial disagreement with the second prediction of the optimum density model.[23]

From the molecular point of view, only an approximate, qualitative explanation of reentrant behaviour has been possible. The basic idea underlying the molecular model is that because of the antiparallel correlations the molecules form dimers, which are assumed to be somewhat bulgy in the middle (Fig.4.23a). Once the smectic phase is formed the bulgy parts are lined up in a plane,

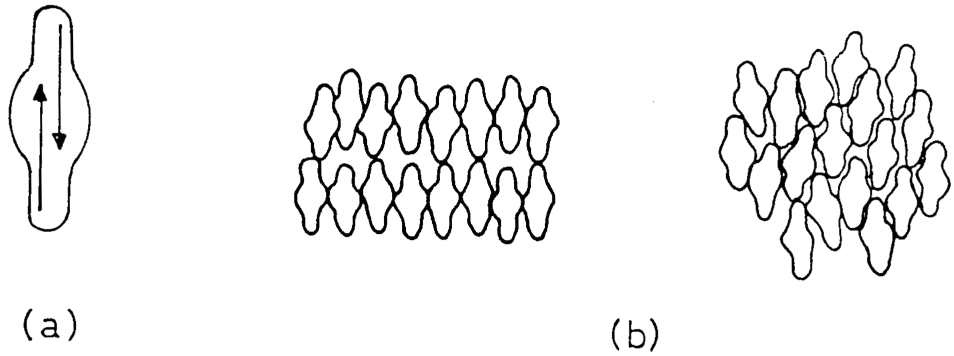


Figure 4.23

Schematic representation of (a) a dimer unit consisting of two antiparallel molecules, (b) the mechanism of destabilisation of the smectic A phase (Ref. 30).

but the alkyl chains cannot fill the rest of the space. With increasing dimer formation (i.e., with decreasing temperature) and also possibly with the stiffening of the end chains, the packing becomes so unfavourable that the A_d phase is destabilized and the nematic reenters (Fig.4.23b). The elements of the model were proposed by Cladis[6,30,31] but a more complete theoretical discussion involving attractive forces and hard core repulsions has been presented by Longa and de Jeu[26] who showed that there can indeed be a lower temperature nematic phase. Qualitatively this is very satisfactory. However, antiferroelectric short range order is a statistical effect, and to look upon the system as a sum of two extreme situations, the perfectly paired dimer with the dipoles compensated and the completely unpaired monomer with the full value of the dipole moment is a rather gross approximation. As emphasized by these authors themselves[26] the quantitative aspects of the model should be treated with caution. This point has been discussed in detail by Chandrasekhar.[32] In the calculations of Longa and de Jeu, the variation of the dimer concentration with decreasing temperature is taken to be of form given in curve 1 of Fig.4.24a, the dimer concentration increasing from about 40%-70% in the A phase. If this were so, the dielectric anisotropy should decrease with decrease of temperature. This point has been illustrated in the case of 8OCB/6OCB mixture.[32] The calculated $\Delta\varepsilon$ drops rapidly with decreasing temperature in the A phase in contrast to what is observed experimentally

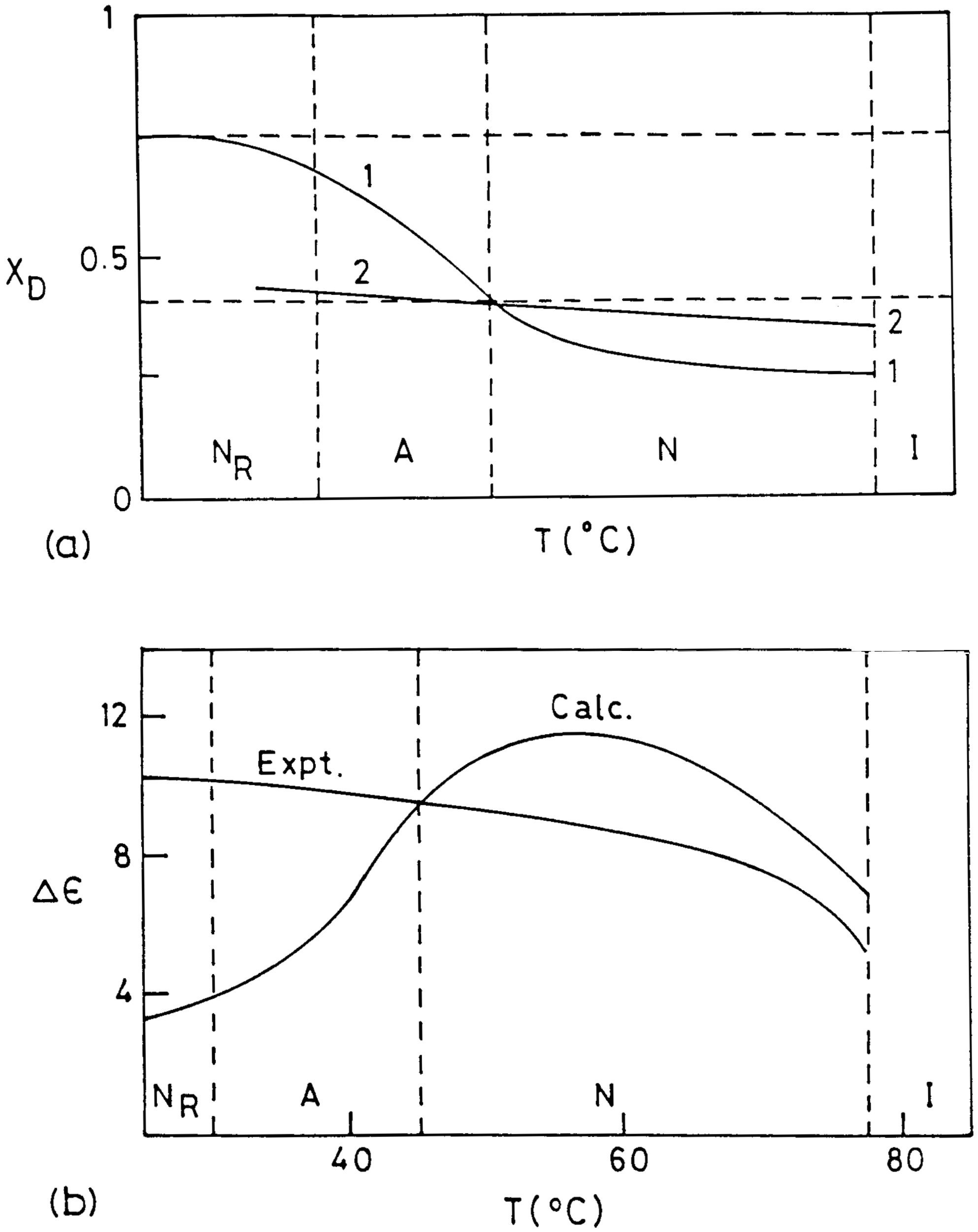


Figure 4.24

(a) Curve 1 : The variation of the dimer concentration through N, A and N_{re} phases assumed in the model of Longa and de Jeu.[26]

Curve 2: Variation of the dimer concentration derived from the experimental dielectric data for 8OCB : 6OCB mixture[21].

(b) Expected form of the dielectric anisotropy ($\Delta\varepsilon$) of the 8OCB : 6OCB mixture calculated from curve 1 of (a). The calculated $\Delta\varepsilon$ decreases rapidly with decreasing temperature in the A phase, in contrast to what is found experimentally (Ref. 32).

by Ratna et al[21] (Fig.4.24b). In fact, the experimental dielectric data require only a very small variation of the dimer concentration with temperature, shown in curve '2' of Fig.4.24a. Another equally serious difficulty has been encountered. It has been shown experimentally that the layer spacing in the A_d phase remains practically constant.[33,34] In order to account for this, the assumption has to be made in the theory that although there is an enormous variation in the dimer/monomer ratio, the monomers just float around in the smecic A layers without affecting the layer spacing. However this is contrary to what is seen experimentally[31,35,36] as illustrated in the smectic A layer spacing versus concentration diagram of a binary mixture of CBOOA (which forms a bilayer smectic) and 4-n-pentylphenyl-4'-n-octyloxybenzoate ($\bar{8}$.O.5) (which forms a monolayer smectic)[35] (see Fig.4.25). There is in fact a striking variation of the layer spacing with concentration. It can therefore be concluded that the occurrence of the reentrant phase involves much more subtle structural changes than expected from the current molecular treatments[26,37] of this phenomenon. Essentially the same conclusions have been drawn by the MIT group[28] from high resolution Xray studies.

Thus it is clear that to look upon the system as a sum of two extreme situations, viz., consisting of interacting dimers and monomers, is too simplistic an assumption. It is perhaps correct

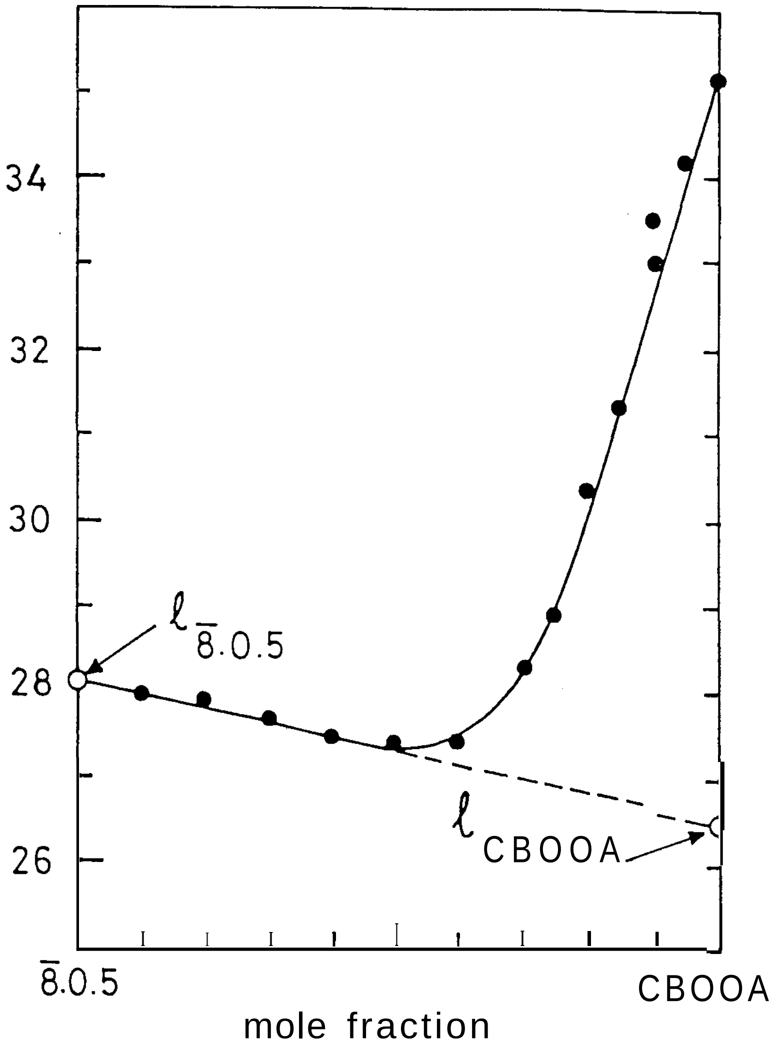


Figure 4.25

The smectic A layer spacing vs. concentration in a binary mixture of CBOOA and $\bar{8}$.0.5 (Ref. 35).

to say that no theory of reentrant nematic phenomenon has been able to explain all the experimentally observed features of reentrant mesogens.

Part II. Studies on Non-Polar Reentrant Mesogens

4.5 INTRODUCTION

In the previous part, we discussed dielectric results on reentrant nematogenic compounds whose constituent molecules possess a strongly polar end group (cyano or nitro). For some years it appeared that reentrant phenomenon is a special feature of compounds with terminal polar groups. The reentrant nematic phase was also observed in mixtures when one of the components of the mixture had a terminal polar group.[31,35,38,39] In principle, reentrant phases can occur in non-polar systems as well. Flonnie Dowell[40] has discussed this possibility in some detail by treating the molecules as hard rigid cores with semiflexible tails and interacting via segmental hard repulsions. In the A phase the molecules are segregated into layers. Dowell showed theoretically that as the tails become more rigid at lower temperatures, layering may become disadvantageous and the A phase can be destabilized. Pelzl et al.[15] observed for the first time the reentrant nematic phase in a mixture of two terminal non-polar compounds. The temperature-concentration diagram (T-X) has been reproduced in the Fig.4.26. In this system

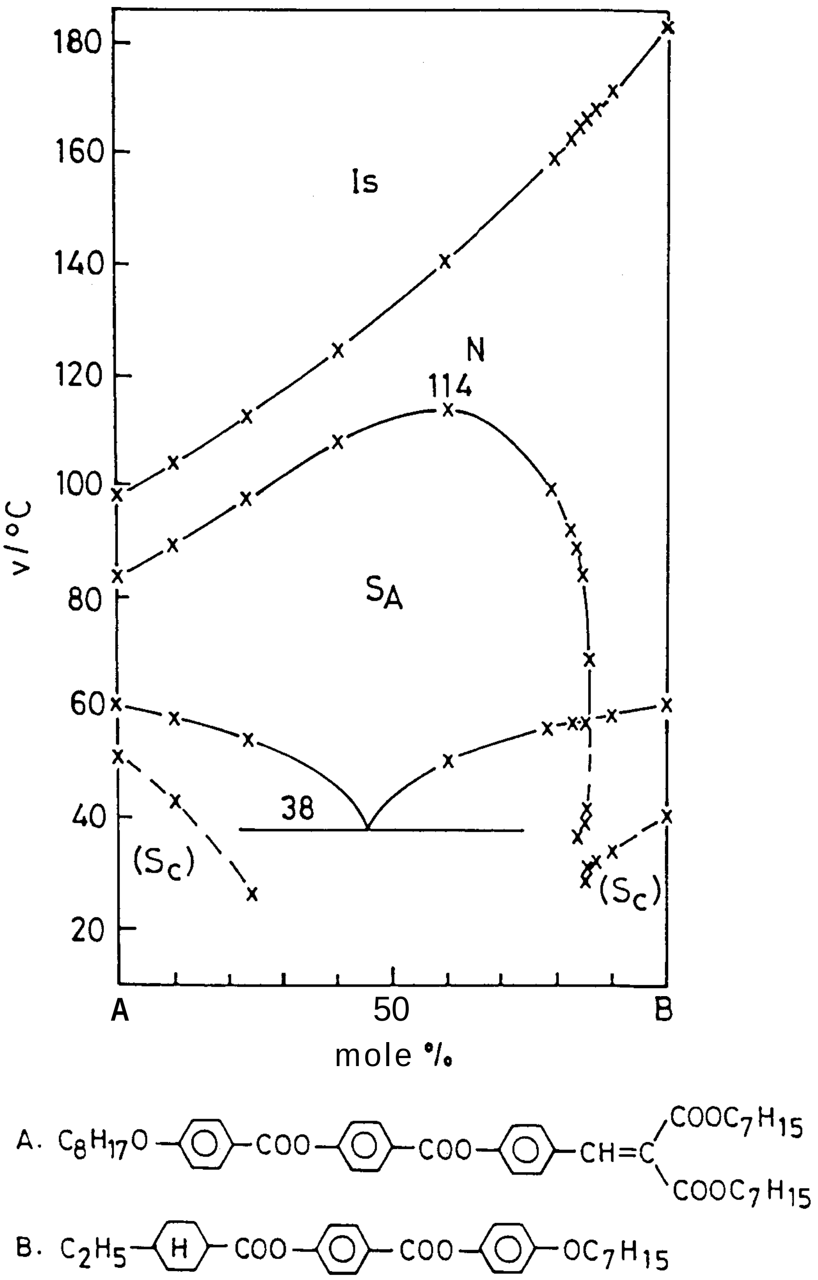


Figure 4.26

The temperature-concentration (T-X) diagram of the binary mixture of the compounds A and B (Ref. 15) the N_{re} phase was found in the supercooled state and crystallized after formation. Diele et al.[16] have found another binary system of terminal-nonpolar compounds in which a stable N_{re} phase exists in a limited concentration region. Very recently Pelzl et al.[41] reported the phase diagrams of nine binary systems whose components are of the terminal-nonpolar type. In all binary systems studied, the first component was a nematogenic compound while the second material exhibited one or more smectic phases.

It is of interest to carry out dielectric studies on reentrant systems of terminal-nonpolar compounds in order to compare and contrast their dielectric properties with those of strongly polar reentrant nematogens.

In this section we present the results of our dielectric studies on a binary reentrant nematogenic mixture of 4-n-heptyloxyphenyl-4-[4-ethyl-cyclohexanoyloxy]benzoate[42] (7OPECB) and n-dodecyl-4-[4-ethoxybenzylidene amino]-α-methyl cinnamate[43] (12EBAMC), both these materials being terminally non-polar. In addition, we have investigated the dielectric properties of one of the constituents of the mixture, viz., 12EBAMC. These results are also presented here.

4.6 MATERIALS AND PHASE DIAGRAM

The binary phase diagram of 12EBAMC in 7OPECB is shown in Fig. 4.27. The chemical structures of the materials are also given in the same figure. It is seen that the N_{re} phase is exhibited over a very narrow region of concentration, viz.,~43-46 mole % 12EBAMC/7OPECB. We have selected for our study a 44 mol % mixture of 12EBAMC in 7OPECB which exhibits a stable N_{re} phase. The transition temperatures of this mixture are

$$K \xrightarrow{50^\circ C} N_{re} \xrightarrow{42^\circ C} A \xrightarrow{68^\circ C} N \xrightarrow{130^\circ C} I$$

We have also studied the compound 12EBAMC whose transition temperatures are given below.

$$K \xrightarrow{69^\circ C} A \xrightarrow{81^\circ C} I$$

4.7 EXPERIMENTAL

The dielectric set up used in this study has already been described in chapter II. In the case of the reentrant nematogenic mixture a magnetic field of 2.4 T was used to obtain the alignments required for the measurement of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$. However, in the case of 12EBAMC which does not have a nematic phase, it was necessary to use suitable surface treatments — octadecyl triethoxy silane was used for homeotropic alignment while polymide resin (ZLI-2650) was used for planar alignment.

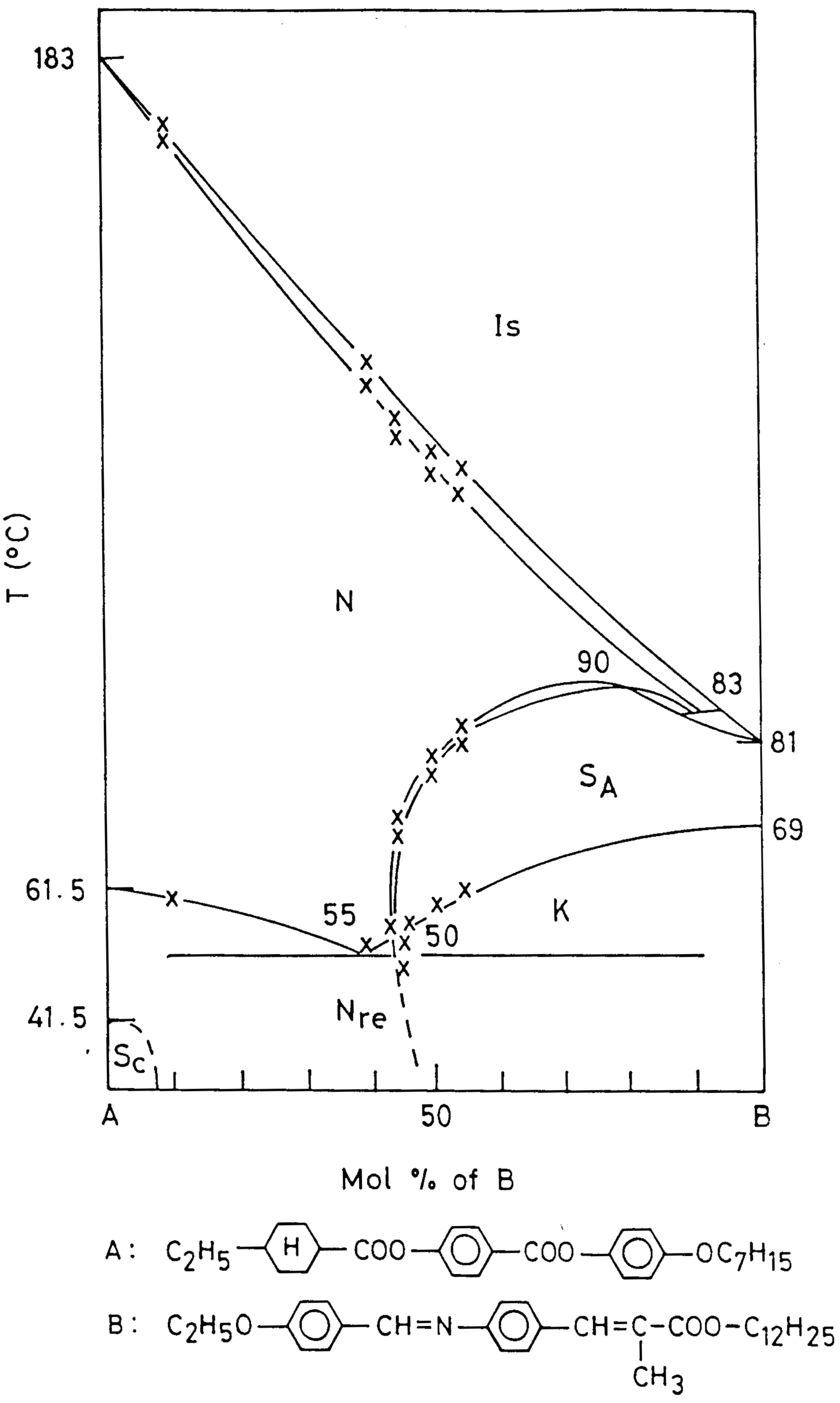


Figure 4.27

The temperature-concentration (T-X) diagram of the binary mixture of the compounds A & B (Ref. 41).

4.8 RESULTS ON 44 MOLE % MIXTURE OF 12EBAMC IN 7OPECB

4.8.1. X-ray

It is of interest to know the type of smectic A phase in reentrant nematic mixture of non-polar materials under discussion. For this purpose, an Xray study was carried out in this laboratory by V.N.Raja[44] on the binary mixture. These studies, conducted using the photographic technique described earlier (chapter III), showed that the d/ℓ ratio at the highest temperature in A_d phase was 1.03. This ratio was found to decrease with decrease in temperature reaching about 1.02 close to A_d-N_{re} transition. (ℓ value in this case is taken by measuring the length of individual components and then calculating the mole fraction of concentrated mixture.) Thus it appears that the A phase of this non-polar reentrant binary mixture has a very small interdigitation. However considering the errors in calculating the molecular length ℓ, it is very difficult to ascertain whether it is a truly partially bilayer or monolayer phase. (We have also investigated A phase of 12EBAMC, one of the constituents of the mixture to investigate the nature of the A phase of this material. These results are presented later.)

4.8.2. Dielectric

We shall now discuss dielectric results on the mixture. Fig. 4.28 shows temperature variation of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ in N, A and

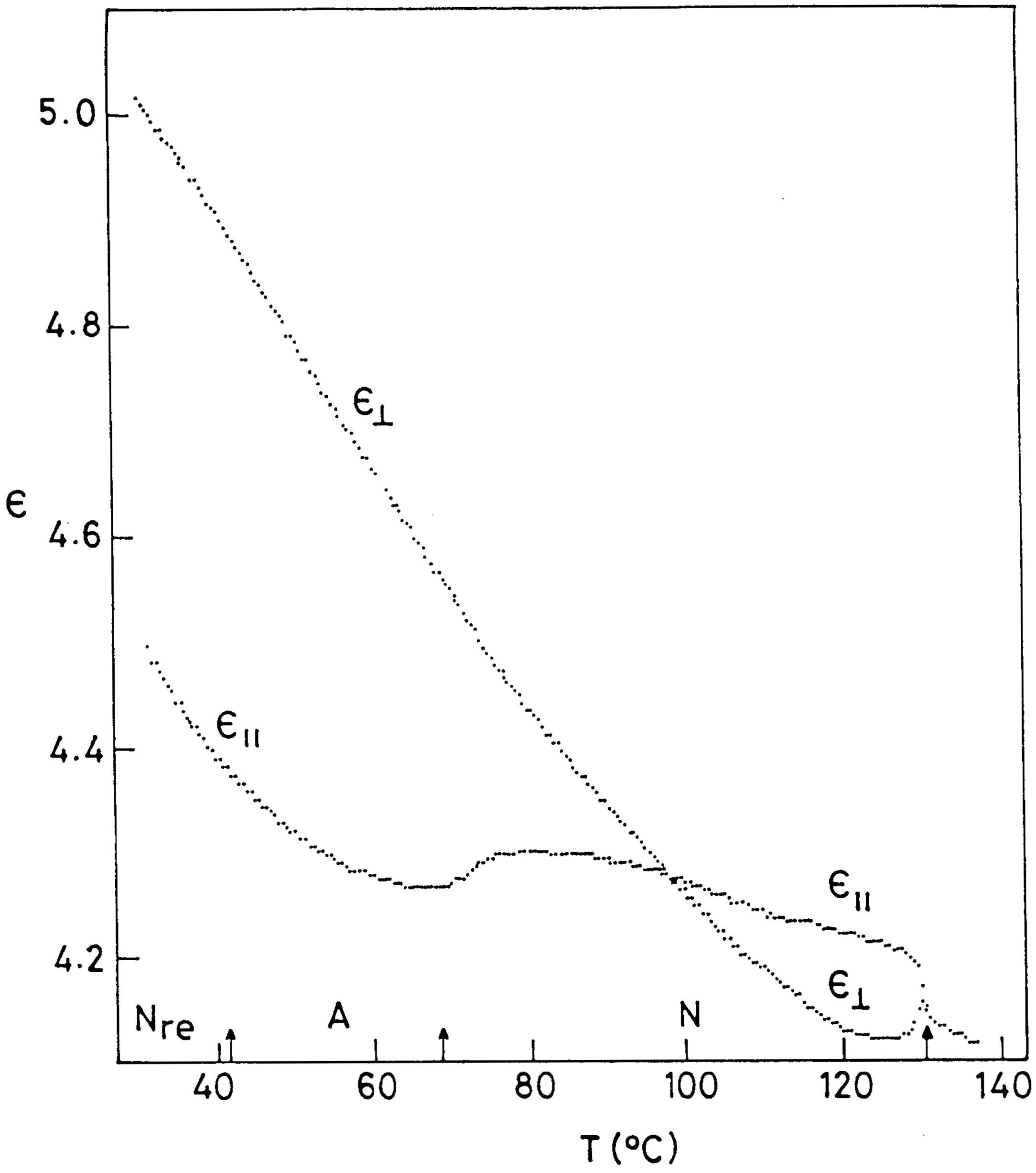


Figure 4.28

The temperature variation of the dielectric constants $\varepsilon_{||}$ and $\varepsilon_\perp$ in the nematic, smectic A and reentrant nematic phases of 44 mol % mixture of 12EBAMC in 7OPECB.

N_{re} phases while $\Delta\varepsilon$ variation is shown in Fig.4.29. Several features are clear from these figures. The mixture exhibits a small positive $\Delta\varepsilon$ in the nematic phase close to the N-I transition but with decrease in temperature, both $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ increase, the rate of increase of $\varepsilon_{\perp}$ is very much steeper than that of $\varepsilon_{\parallel}$. This leads therefore to a change of sign of $\Delta\varepsilon$ at about mid-range of N phase. At the N-A trasition, $\varepsilon_{\parallel}$ shows a slight decrease but on further reduction of temperature, $\varepsilon_{\parallel}$ increases now at a rate faster than the rate of increase exhibited in N phase. In fact, the rate of increase of $\varepsilon_{\parallel}$ with decrease of temperature in N_{re} phase is really the same as that of $\varepsilon_{\perp}$ so much so that $\Delta\varepsilon$ remains saturated at a constant value of ~ -0.5 throughout N_{re} phase. This interesting behaviour of $\Delta\varepsilon$ is completely different from what is generally seen in strongly polar reentrant systems (see e.g., part I). In the case of latter, it is usually observed that $\Delta\varepsilon$ shows a continuous increase from N-A-N_{re} phases. To this extent, dielectric permittivity of non-polar reentrant systems behaves differently.

The reversal of sign of $\Delta\varepsilon$ with decrease in temperature has been observed earlier in a few compounds,[45,46] $\Delta\varepsilon$ changing from a relatively weak positive value near nematic-isotropic transition temperature to a weak negative value at lower temperatures. It turns out that this reversal is accompanied by the occurrence of a smectic A phase at lower temperatures. It has therefore been

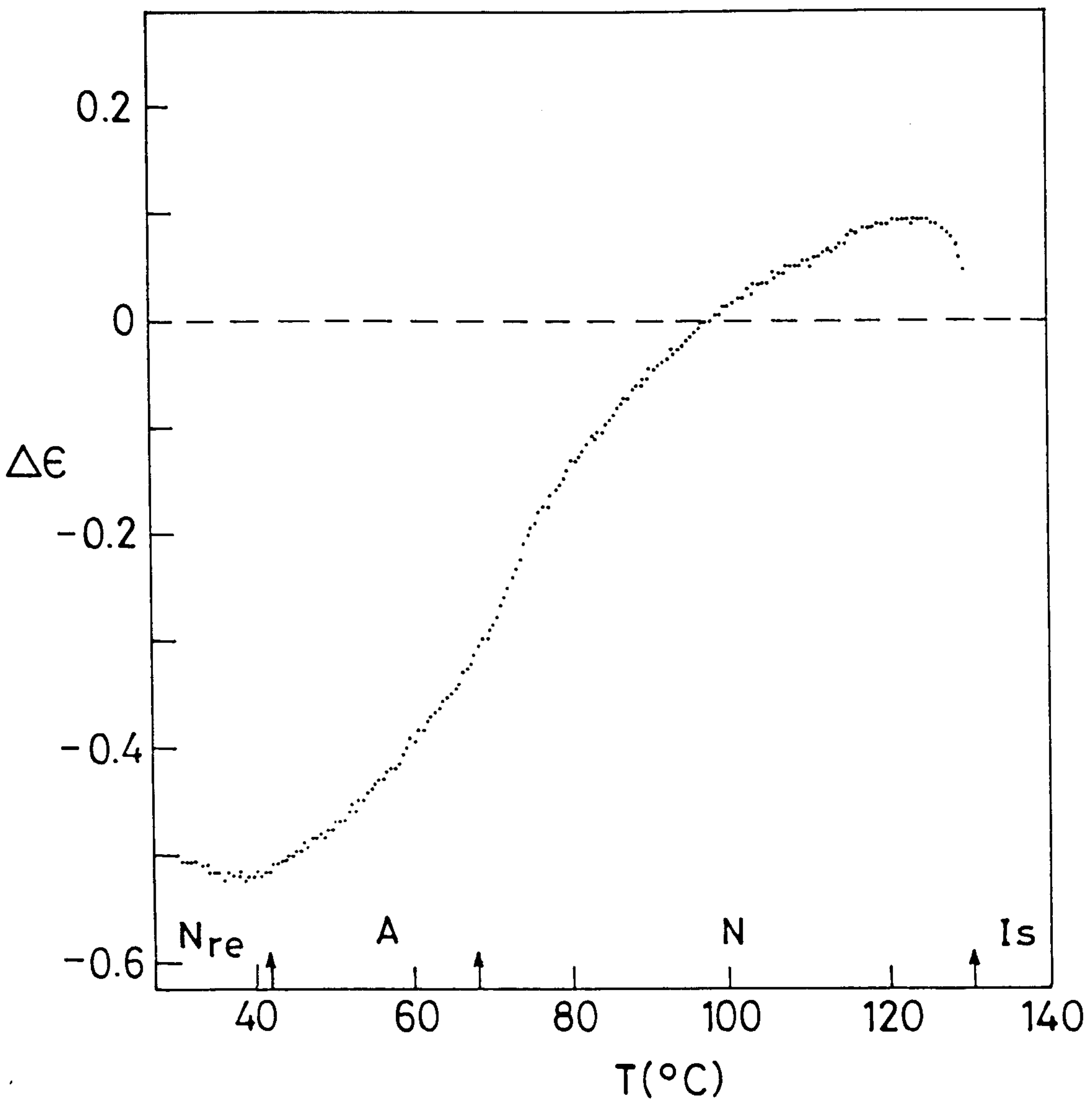


Figure 4.29

The temperature variation of Δε of 44 mol % mixture of 12EBAMC in 7OPECB argued,[45,46] that the smectic layer structure gives rise to a parallel correlation of μ_t, the transverse component of the dipole moment, in addition to the antiparallel correlation of the longitudinal component μ_ℓ, thus resulting in a cross-over of $\Delta\varepsilon$. Another possible explanation was given by Chandrasekhar and Ratna[47] who demonstrated experimentally that there can be a sign reversal of $\Delta\varepsilon$ with decrease in temperature in nematics. They showed that these results are explainable in terms of Maier and Meier[48] mean field theory and therefore the occurrence of the smectic A phase and the consequent dipolar correlations within the smectic layers is not a necessary condition for the sign reversal of $\Delta\varepsilon$. The reason for the sign reversal of $\Delta\varepsilon$ in reentrant non-polar system is also probably explained on the basis of this Maier-Meier theory only. However an exact theoretical calculation is not possible since various parameters necessary to make this calculation are not available for the constituent components of this non-polar reentrant mixture.

4.9 EXPERIMENTAL STUDY ON COMPOUND B (12EBAMC)

As remarked earlier, although Xray studies on reentrant nematic mixture (discussed above) indicate a d/ℓ value slightly greater than 1 in the A phase, it was not possible to say definitely if the A phase of, non-polar reentrant mixture is really of the A_d or A_1 type because of uncertainty in exact determination of the molecular length (ℓ) in the mixture. Since from T-X diagram (see

Fig.4.27) it is clear that the A phase of compound B appears to be the same as that of the reentrant mixture, it is of interest to investigate the nature of the A phase of the B compound, i.e., 12EBAMC. The results of these investigations are presented in this section.

4.1 0 **RESULTS** AND **DISCUSSIONS**

4.10.1 X-ray

Xray studies conducted by V.N.Raja[44] showed that the A phase of 12EBAMC is definitely of A_d type. He found that d/ℓ value is about 1.13 at the highest temperature which decreased to 1.1 1 at the lowest temperature. This appears to be the first instance of observation of A_d phase in a terminally non-polar material.

4.10.2 **Dielectric**

We shall now present the results of dielectric studies on this material. Fig.4.30 gives the plot of dielectric constants $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ in the A phase and ε_{is} in the isotropic phase of 12EBAMC. The temperature variation of $\Delta\varepsilon$ is also shown in the figure. It is seen that ε_{is} increases with decrease of temperature right up to the A-I transition. In the smectic A phase, $\varepsilon_{\parallel}$ decreases steeply with decreasing temperature showing the existence of pronounced dipole-dipole correlations in the A phase. On the other hand, $\varepsilon_{\perp}$,

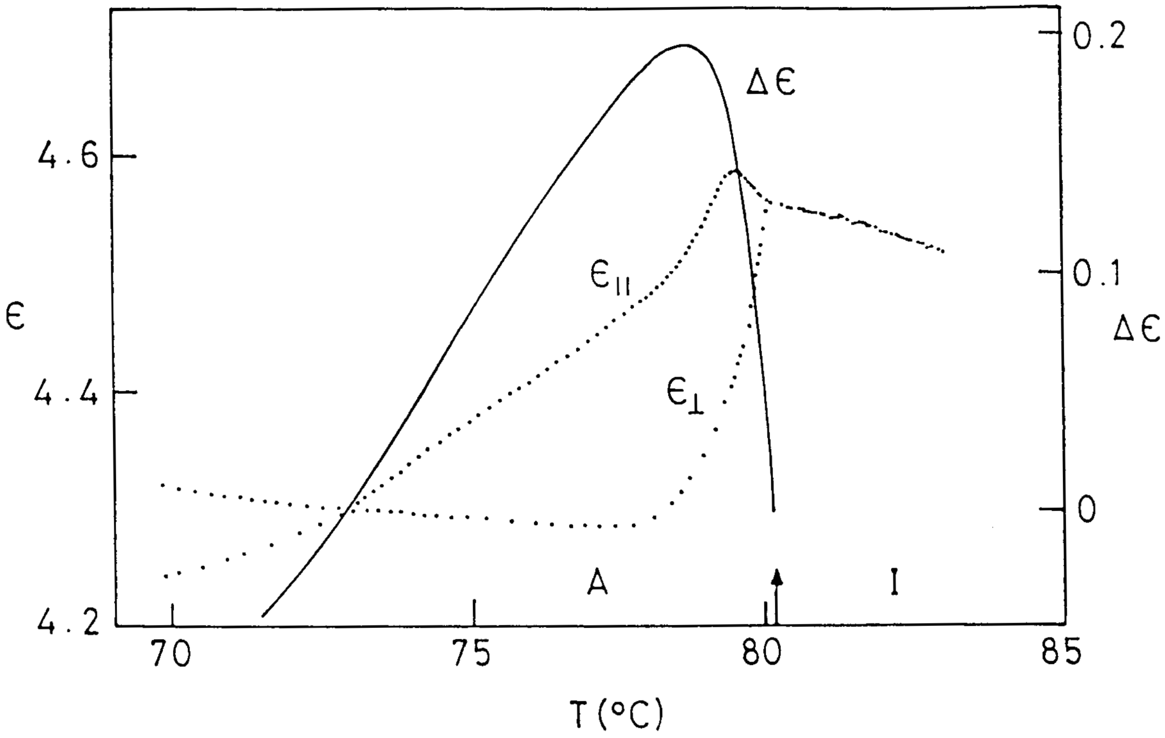


Figure 4.30

The temperature variation of ε_{is}, $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$ and of $\Delta\varepsilon$ for 12EBAMC.

shows only a small increase with decrease of temperature through most of the A phase. Perhaps the most striking feature of the dielectric results is the reversal in the sign of the $\Delta\varepsilon$ (see Fig. 4.30) which occurs at ~ 73°C, i.e., almost in the middle of the range of the A phase. As far as we are aware, this appears to be the first instance of such a reversal in $\Delta\varepsilon$ being seen in a purely smectogenic material, i.e., showing a sequence of transitions K-A-I. There has been an earlier observation[49] of the reversal of sign of $\Delta\varepsilon$ well within the A_d phase, but this occurred close to the A_d-A_2 transition so much so the reversal can almost certainly be associated with the large expansion of the layer spacing which accompanies the A_d-A_2 transition. It is remarkable that in the case of 12EBAMC a reversal is seen within the A_d phase although the layer spacing hardly varies with temperature throughout the A phase. The reason for this is still not clear to us.

Thus the dielectric properties of the terminally non-polar reentrant substances appear to be different from that of strongly polar reentrant mesogens. Further studies on other non-polar reentrant systems would be of considerable interest and would perhaps help to understand the basic mechanism responsible for the reentrant nematic phenomenon.

REFERENCES

1 P.E.Cladis, Phys. Rev. Lett., 35, 48 (1975)

2 A.C.Anderson, W.Reese and J.C.Wheatly, Phys. Rev., 130, 1644 (1963)

3 G. Riblet and K. Winzer, Solid State Commun., 9, 1663 (1971)

4 P.E.Cladis, R.K.Bogardus, W.B.Daniels and G.N.Taylor, Phys. Rev. Lett., 39, 720 (1977)

5 P.E.Cladis, R.K.Bogardus and D.Aadsen, Phys. Rev., **A18**, 2292 (1978)

6 P.E.Cladis, D.Guillon, F.R.Bouchet and P.L.Finn, Phys. Rev., A23. 2594 (1981)

7 F.Hardouin, G.Sigaud, M.F.Achard and H. Gasparoux, Phys. Lett., **71A**, 347 (1979)

8 Nguyen Huu Tinh and H.Gasaparoux, Mol. Cryst. Liq. Cryst. Lett., 49, 287 (1979)

9 N.V.Madhusudana, B.K.Sadashiva and K.P.L.Moodithaya, Curr. Sc., 48, 613 (1979)

10 Nguyen Huu Tinh, F.Hardouin, C.Destrade and A.M.Levelut, J. de Phys. Lett., **43**, L-33 (1982)

11 Nguyen Huu Tinh, F.Hardouin and C.Destrade, J. de Phys., 43, 1127 (1982)

Nguyen Huu Tinh, J.Chim.Phys., 80, 83 (1983)

Nguyen Huu Tinh, F. Hardouin and C.Destrade, J. de Phys., 43, 1127 (1982)

R.Shashidhar, B.R.Ratna, V.Surendranath, V.N.Raja, S.Krishna Prasad and C.Nagabhushan, J. de Phys. Lett., 46, L-445 (1985)

15 G. Pelzl, S.Diele, I.Latif, W. Weissflog, D.Demus, Crystal Research and Tech., 17, K78-K82 (1982)

16 S. Diele, G.Pelzl, I.Latif and D.Demus, Mol. Cryst. Liq. Cryst. Lett., 92, 27 (1983)

17 N.V.Madhusudana and S.Chandrasekhar, Pramana, Suppl. I, 57 (1973)

18 B.R.Ratna and R.Shashidhar, Pramana, 6, 278 (1976); Mol. Cryst. Liq. Cryst., 42, 113 (1977)

19 M.Bock and G.Heppke, Advances in Liquid Crystal Research and Applications, Ed. L.Bata, Pergamon Press, Oxford, 1980, p. 131.

C.Legrand, J.P.Parneix, A.Chapoton, Nguyen Huu Tinh and C.Destrade, J. de Phys. Lett., 45, L-283 (1984)

B.R.Ratna, R.Shashidhar, K.V.Rao, in 'Liquid Crystals', Proc. Int. Conf., Bangalore, December 1979, Ed. S.Chandrasekhar (Heyden, London, 1980), p.135

22 C.Legrand, J.P.Parneix, A.Chapoton, Nguyen Huu Tinh, C.Destrade, Mol. Cryst. Liq. Cryst., 124, 277 (1985)

23 P.S.Pershan and J. Prost., J. de Phys. Lett., 40, L27 (1979).

24 J. Prost, Proc. of the Conf. on Liquid Crystals of One- and Two-Dimensional Order, Garmisch Partenkirschen (Springer-Verlag, Berlin, Heidelberg, New York, 1980), p. 125.

25 A.N.Berker and J.S.Walker, Phys. Rev. Lett., 47, 1469 (1981)

26 L. Longa and W.H.de Jeu, Phys. Rev., A26, 1632 (1982)

27 A.R.Kortan, H.V.Kanel, R.J.Birgeneau and J.D.Litster, Phys. Rev. Lett., 47, 1206 (1981)

28 A.R.Kortan, H.V.Kanel, R.J.Birgeneau and J.D.Litster, J. de Phys., 45, 529 (1984)

29 R.Shashidhar, P.H.Keyes, W.B.Daniels, Mol.Cryst. Liq. Cryst. Lett., 3(6), 169 (1986)

30 P.E.Cladis, in. 'Liquid Crystals', Proc. Int.Conf., Bangalore, 1979, Ed. S.Chandrasekhar (Heyden, London, 1980), p. 105

31 P.E.Cladis, Mol.Cryst.Liq.Cryst., 67, 177 (1981)

32 S.Chandrasekhar, Mol. Cryst. Liq. Cryst., 124, 1 (1985)

33 V.N.Raja and R.Shashidhar (unpublished)

34 D.Guillon, P.E.Cladis and J. Stamatoff, Phys. Rev. Lett., 41, 1598 (1978)

35 B.Engelen, G.Heppke, R.Hopf, F.Schneider, Mol. Cryst. Liq. Cryst. Lett., 49, 193 (1979)

36 S.Diele, U. Baurnister and D.Demus, Z. Chernie, 21, 27 (1981)

37 G.R.Luckhurst and B.A.Timimi, Mol. Cryst. Liq. Cryst. Lett., 64, 253 (1981)

38 G.Pelzl, U. Bottger, D.Demus, Cryst. Res. & Technol., 16, K67 (1981)

39 G.Pelzl, S.Diele, A.Wiegeleben, D.Demus, Mol. Cryst. Liq. Cryst. Lett., 64, 163 (1981)

40 F.Dowell, Phys. Rev., A28, 3526 (1983); Also paper presented at the Tenth Int. Liq. Cryst. Conf., York, July 15-21, 1984

41 G.Pelzl, I. Latif, S.Diele, M. Novak, D.Demus and H.Sackmann, Mol. Cryst. Liq. Cryst., 139, 333 (1986)

42 H.J.Deutscher, M.Korber, H.Altmann and H.Schubert, J. Prakt. Chern., 321, 969 (1979)

43 G.Pelzl and H. Sackmann, Symp. Faraday Soc., 5, 68 (1971)

44 V.N.Raja and R.Shashidhar (to be published)

45 W.H.de Jeu, W.J.A.Goossens and P.Bordewijk, J. Chem. Phys., 61, 1985 (1974)

46 L.Benguigui, J. de Phys., 40, 705 (1979)

47 S.Chandrasekhar and B.R.Ratna, Mol. Cryst. Liq. Cryst. Lett., 82, 193 (1982)

48 W. Maier and G.Meier, Z. Naturforsch, **16a**, 262 (1961)

49 N.R.Njeumo, J.P.Parneix, C.Legrand, N.H.Tinh and C.Destrade, J. de Phys., 47, 903 (1986); also G. Heppke and S.Pfieffer (Private communication).