

## CHAPTER V

### DIELECTRIC STUDIES ON MATERIALS EXHIBITING SMECTIC A-SMECTIC A TRANSITIONS

#### 5.1 INTRODUCTION

It is now well known that materials with strongly polar cyano or nitro end groups exhibit the reentrant nematic phase as well as smectic A polymorphism.<sup>1-4</sup> The first smectic A-smectic A (A-A) transition was observed by Sigaud et al.<sup>5</sup> Since then a number of experimental studies<sup>4,6-9</sup> have been conducted which have led to the observation of the following types of A phases, viz., monolayer ( $A_1$ ) phase, the bilayer ( $A_2$ ) phase, the partially bilayer ( $A_d$ ) phase, the antiphase ( $\tilde{A}$ ), the crenellated phase ( $A_{cre}$ ) and the incommensurate ( $A_{ic}$ ) phase. These different A phases have been unambiguously characterised on the basis of X-ray diffraction patterns exhibited by monodomain samples (Fig.5.1).

It is seen that for the polar  $A_1$  there is a diffraction spot (shown as full circle in Fig.5.1) at a wavevector corresponding to  $2q_0 = 2\pi/\ell$ , where  $\ell$  is the length of the molecule. In addition to this monolayer periodicity generally a diffuse scattering centred around wavevector  $q'_0 (= 2\pi/\ell')$ , where  $\ell < \ell' < 2R$  is also seen. The characteristic pattern of the  $A_2$  phase is the existence of two condensed spots at  $q_0$  and  $2q_0$  corresponding to  $2\ell$  and  $R$  respec-

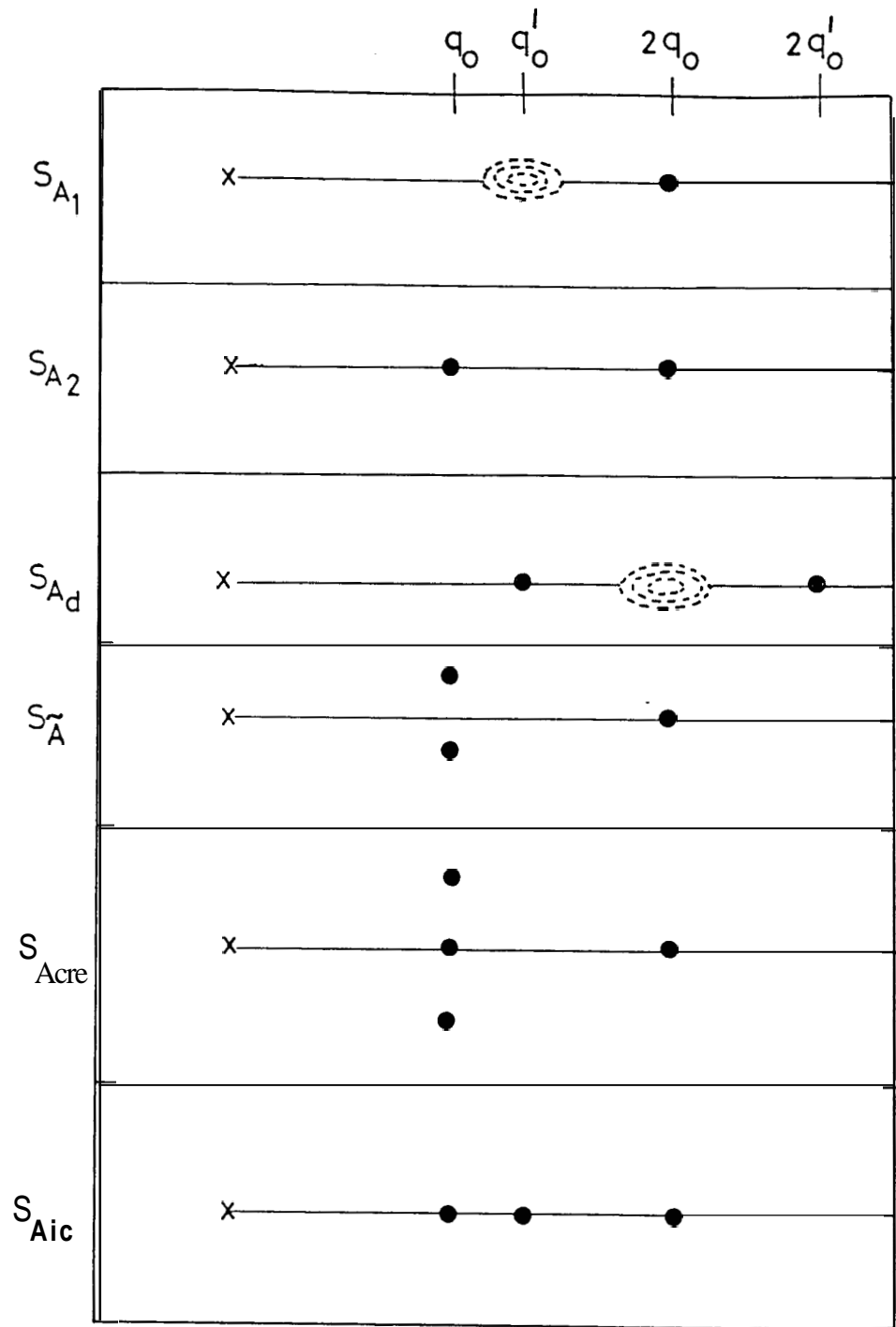


Figure 5.1

Xray diffraction pattern in different smectic A phases. The full circle denotes a condensed spot while the dashed one indicates a diffuse spot (see text).

tively. The partially bilayer  $A_d$  phase exhibits two condensed reflections at  $q'_0$  and  $2q'_0$  and in addition a diffuse monolayer modulation ( $2q_0$ ). It may also be mentioned that the intensity of second harmonic in relation to the intensity of the main reflection is much smaller in the case of  $A_d$  phase than in  $A_2$  phase.  $\tilde{A}$  phase has a condensed spot at  $2q_0$  in addition to two diffraction spots which are split out of the Z axis in a direction perpendicular to it. These spots are symmetrically situated about the  $q_0$  position.  $A_{cre}$  shows an essentially a similar diffraction pattern except that it has different symmetry. Further it shows an additional condensed spot at  $q_0$ . In the case of  $A_{iC}$  phase three condensed reflections are seen at  $q_0$ ,  $q'_0$  and  $2q_0$ .

Before discussing the results of our dielectric studies, we shall briefly summarise the state of art concerning the order of the transition between two polymorphic A phases. The smectic A polymorphism has been successfully explained in terms of a phenomenological model introduced by Prost.<sup>10-13</sup> The nature of the  $A_d$  phase and its relation to  $A_1$  and  $A_2$  phases was addressed to theoretically by Barois et al.<sup>14</sup> Since  $A_d$  and  $A_2$  phases have the same macroscopic symmetry, there cannot be a second order transition between these phases. Barois et al. have predicted that under certain conditions, the first order  $A_d$ - $A_2$  transition can terminate at a critical point (CP) of the gas-liquid type. Indeed such a CP

was recently observed experimentally in the T-X diagram of a binary system.<sup>15</sup>

Essentially the same arguments can be applied to  $A_d-A_1$  transition also. The situation concerning the  $A_d-A_1$  transition has been recently addressed theoretically by Prost and Toner<sup>16</sup> using the dislocation-loop approach. According to them the  $A_d-A_1$  transition boundary can, as in the case of  $A_d-A_2$  transition, terminate at a critical point of gas-liquid type. However when the effect of fluctuations is considered, the theory predicts a nematic island existing at the terminus of the  $A_d-A_1$  transition boundary. So far, experimentally,<sup>17</sup> the nematic island has indeed been seen but not the  $A_d-A_1$  critical point.

In the case of  $A_1-A_2$  transition, the transition can be first order or even second order<sup>18</sup> because of the exact doubling of lattice periodicity.<sup>19</sup> High resolution experimental study<sup>18</sup> on 4-n-hexylphenyl-4'-cyanobenzoyloxy benzoate (DB6CN)/terephthal-bis-4-n-butylaniline (TBBA) systems has shown that this is in fact the case, there being a tricritical point for the  $A_1-A_2$  transition. [Since it is now well known that the smectic A antiphase ( $\tilde{A}$ ) and crenellated smectic A ( $A_{cre}$ ) phase are biaxial, we have not considered the transitions involving these phases.]

Hence, it is clear that there can be a phase transition bet-

ween  $A_d$  &  $A_1$  and  $A_d$  &  $A_2$  phases or there can be a continuous evolution from  $A_d$  to  $A_1$  or  $A_d$  to  $A_2$ . Also, there can be a first or second order phase transition between the  $A_1$  and  $A_2$  phases. A variety of interesting possibilities thus exist concerning A-A transitions. It is of interest to see how the dielectric properties behave near these different kinds of A-A transition. The results of our studies undertaken with this in view are presented in the following sections.

## 5.2 THE $A_d$ - $A_2$ TRANSITION

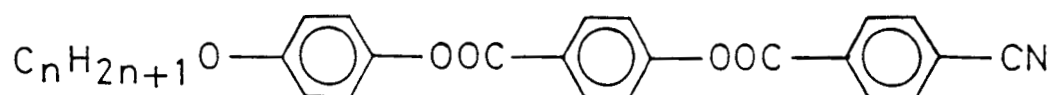
Before discussing the results of our dielectric studies we shall briefly discuss here the results of Xray studies reported on materials which are supposed to exhibit the  $A_d$ - $A_2$  transitions. The first report on the existence of the  $A_d$ - $A_2$  transition in a single component system was by Hardouin et al.<sup>20</sup> They observed that the Xray diffraction pattern in the high temperature A phase was characterised by condensed spot at  $q'=2\pi/R'$ , where  $\ell < \ell' < 2\ell$ ,  $\ell$  being the molecular length. The low temperature A phase showed two different periodicities at wavevectors  $2\pi/\ell$  and  $2\pi/2\ell$ . The former was characterised as partially bilayer smectic A phase ( $A_d$ ) and latter as the bilayer phase ( $A_2$ ). However a detailed study of the layer spacing variation across the  $A_d$ - $A_2$  transition in this material was not carried out. Recently Hardouin et al.<sup>21</sup> reported Xray studies on the eleventh and twelfth members of homologous series

4-n-alkoxyphenyl-4'-(4''-cyanobenzoyloxy)benzoate (nOPCBOB). In another study<sup>22</sup> they reported results of Xray and differential scanning calorimetric (DSC) studies of the n=7 to 13 members of 4-n-alkoxyphenyl-4'-(4''-cyanobenzoyloxy)benzoate (DBnOCN). The structural formulae of these materials are shown in Fig.5.2. Apparently they observed from the Xray studies a jump in the layer spacing at the  $A_d-A_2$  transition for DB7OCN. But for higher homologs no such jump in the layer spacing was observed. Exactly similar results were seen for nOPCBOB, there being a jump in layer spacing for 11OPCBOB, while no such jump was seen for 12OPCBOB. Hardouin et al. concluded from these results the existence of a critical or tricritical behaviour of the  $A_d-A_2$  transition in the temperature-chain length phase diagram.

However more recently Krishna Prasad et al.<sup>23</sup> carried out high resolution Xray studies on DB7OCN and 11OPCBOB. Their experiments were conducted with a very high precision, care being taken to collect data at small intervals of temperature (-100 mK) in the neighbourhood of the expected  $A_d-A_2$  transition. These studies clearly showed that there was **no jump** in the layer spacing at the expected  $A_d-A_2$  transition of either of these materials. It is therefore now clear that neither DB7OCN nor 11OPCBOB exhibits an  $A_d-A_2$  transition, but instead the  $A_d$  phase **evolves continuously** into  $A_2$  phase. The most convincing evidence concerning the exis-

DBnOCN Series

4 - n - alkoxyphenyl - 4' - ( 4'' - cyanobenzoyloxy ) benzoate  
( n = 7 to 13 )



nOPCBOB Series

4 - n - alkoxyphenyl - 4' - ( 4'' - cyanobenzoyloxy ) benzoate  
( n = 11 and 12 )

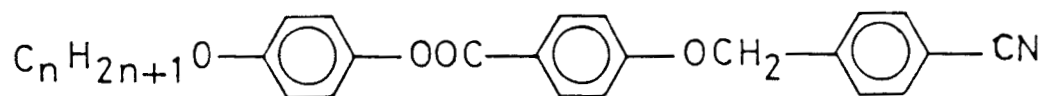


Figure 5.2

Structural formulae of the DBnOCN and nOPCBOB series.

tence of  $A_d-A_2$  transition comes from the Xray results of Somasekhara<sup>24</sup> on the binary system of 4-n-pentylphenyl-4'-cyanobenzoyloxy benzoate (DB5CN) and 4-n-nonyloxybiphenyl-4'-cyanobenzoate (9OBCB). These studies showed a jump in layer spacing of  $\sim 2.6$  Å at the  $A_d-A_2$  transition.

Thus it is now clear that materials are known to exhibit a continuous evolution of  $A_2$  from  $A_d$  as well as a direct first order  $A_d-A_2$  transition. We have chosen for our study **one system** of each kind.

The materials studied are (i) DB7CN which shows continuous evolution from  $A_d$  to  $A_2$  according to Xray results of Raja<sup>25</sup> and (ii) a 65.6 mol % DB5CN/9OBCB which exhibits the  $A_d-A_2$  transition.<sup>24</sup> The structural formulae and the sequences and temperatures of transitions are given in Fig.5.3 and Table 5.1 respectively.

### 5.3 STATIC STUDIES NEAR A-A TRANSITIONS

#### 5.3.1 The $A_d-A_2$ Transition: (a) DB7CN

We shall first discuss the results on DB7CN. The variations of the static dielectric constants in the nematic, smectic  $A_d$  and  $A_2$  phases are shown in Fig.5.4 along with the dielectric anisotropy  $\Delta\epsilon$ . It is seen that in the nematic phase,  $\epsilon_{\parallel}$  as well as  $\epsilon_{\perp}$  show a slight decrease with decrease of temperature. At the nematic-smectic  $A_d$  ( $N-A_d$ ) transition,  $\epsilon_{\parallel}$  shows a steep decrease which



1. 
$$\text{C}_n\text{H}_{2n+1}-\text{C}_6\text{H}_4-\text{OOC}-\text{C}_6\text{H}_4-\text{OOC}-\text{C}_6\text{H}_4-\text{CN}$$

4-n-Alkylphenyl-4'-cyanobenzoyloxybenzoate  
(DBnCN) n = 5 & 7
  
2. 
$$\text{C}_9\text{H}_{19}\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{OOC}-\text{C}_6\text{H}_4-\text{CN}$$

4-n-nonyloxybiphenyl-4'-cyanobenzoate  
(90BCB)
  
3. 
$$\text{C}_4\text{H}_9-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{CH}-\text{C}_6\text{H}_4-\text{C}_4\text{H}_9$$

terephthal-bis-4-n-butylaniline (TBBA)
  
4. 
$$\text{C}_n\text{H}_{2n+1}\text{O}-\text{C}_6\text{H}_4-\text{OOC}-\text{C}_6\text{H}_4-\text{OOC}-\text{C}_6\text{H}_4-\text{NO}_2$$

4-Alkoyloxyphenyl-4'-nitrobenzoyloxy benzoate  
(DBnONO<sub>2</sub>) n = 8 & 10

Figure 5.3

Structural formulae and the abbreviations used for the compounds studied.

**TABLE 5.1**

The sequences and the temperatures of transitions of the systems studied  
(Transition temperatures in °C)

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I	DB7CN
	$I \xrightarrow{234.8} N \xrightarrow{169.4} A_d \xrightarrow{162} A_2$
II	65.6 mol % mixture of DB5CN/9OBCB
	$I \xrightarrow{235} N \xrightarrow{153.6} A_d \xrightarrow{146.6} A_2$
III	10.5 mol % mixture of TBBA/DB5CN
	$I \xrightarrow{253.5} N \xrightarrow{128.3} A_1 \xrightarrow{126.9} A_2$
IV	43 mol % mixture of DB8ONO <sub>2</sub> /DB10ONO <sub>2</sub>
	$I \xrightarrow{224} N \xrightarrow{193.7} A_d \xrightarrow{123.7} A_1 \xrightarrow{119.8} \tilde{C} \xrightarrow{100} A_2 \xrightarrow{98} C_2$

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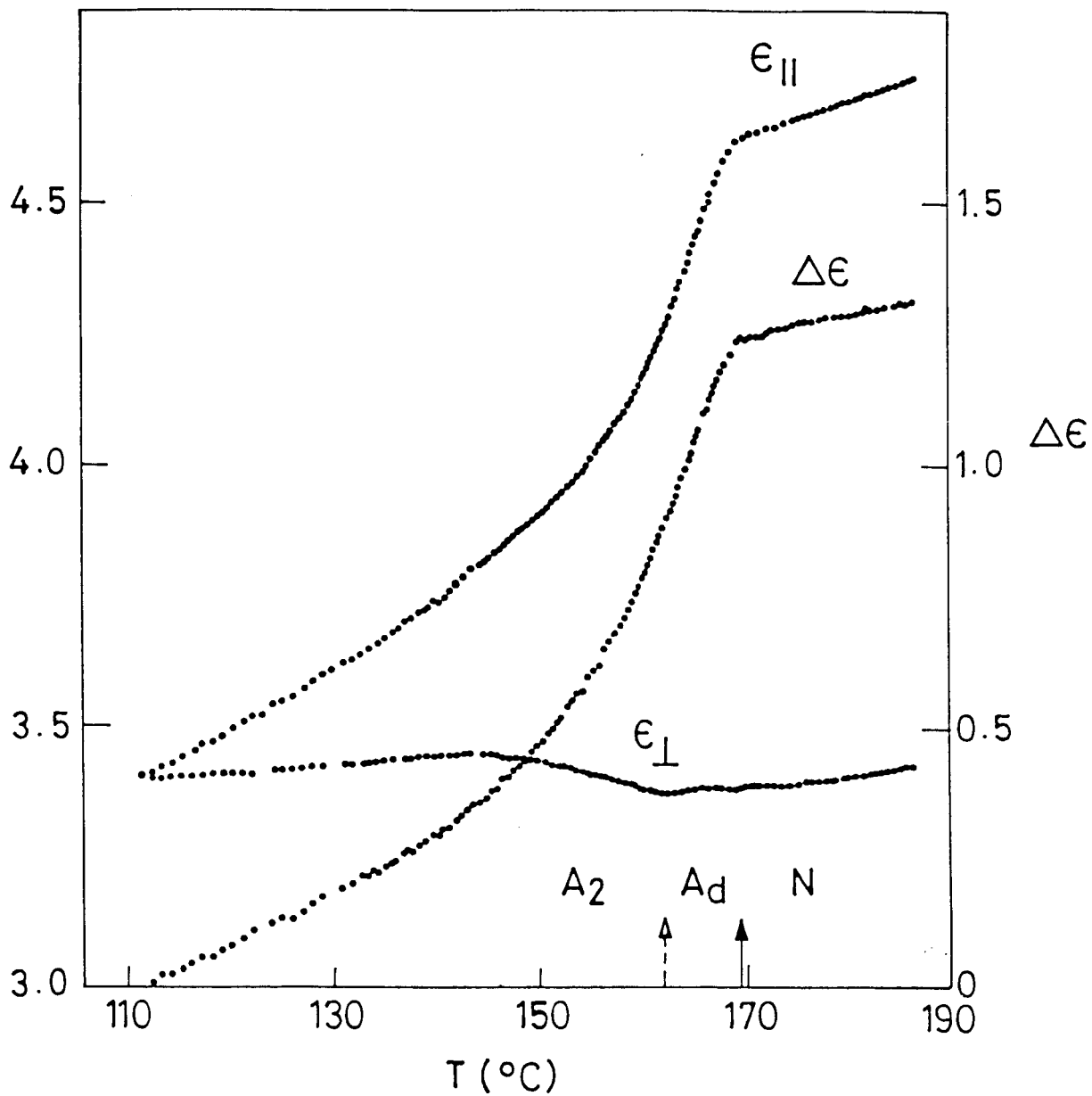


Figure 5.4

Temperature variation of  $\epsilon_{\parallel}$ ,  $\epsilon_{\perp}$  and of  $\Delta\epsilon$  of DB7CN in the nematic, smectic  $A_d$  and  $A_2$  phases.

(Note: The dashed arrow mark corresponds to the expected  $A_d$ - $A_2$  transition from DSC runs.)

continues right through the  $A_2$  phase.  $\epsilon_{\perp}$  on the other hand shows a small increase on going from the  $A_d$  to the  $A_2$  phase. It gets more or less saturated at lower temperatures in the  $A_2$  phase. The steep decrease in  $\epsilon_{\parallel}$  which begins at the N- $A_d$  transition is due to an increase in the cancellation of longitudinal component of dipole moments caused by a head-to-head formation of dipoles. It is interesting that the strong decrease in  $\epsilon_{\parallel}$  occurs in the temperature range in which the layer spacing shows a large expansion on approaching the  $A_2$  phase (see Fig.5.5). These studies therefore suggest that the structural changes that accompany the formation of the dipolar pairs leading ultimately to the  $A_2$  phase are correlated to the dielectric behaviour. It is also interesting to note that  $\epsilon_{\parallel}$  does not show any abrupt change at a temperature at which an  $A_d$ - $A_2$  transition is expected from DSC studies. This can be correlated with the fact that no jump in layer spacing was seen at the expected  $A_d$ - $A_2$  transition. It is also seen from the Fig.5.4 that  $\Delta\epsilon$  decreases strongly with decrease in temperature and reaches a value of almost zero at the lowest temperature in  $A_2$  phase indicating thereby a perfect head-to-head arrangement of dipoles in the  $A_2$  phase at the lowest temperatures. In fact a similar decrease in  $\Delta\epsilon$  has been observed in other systems. Njeumo et al.<sup>26</sup> have reported the variation of dielectric constants in  $A_d$  and  $A_2$  phases of four materials, viz., DB7OCN, DB10OCN, 11OPCBOB and 4-n-

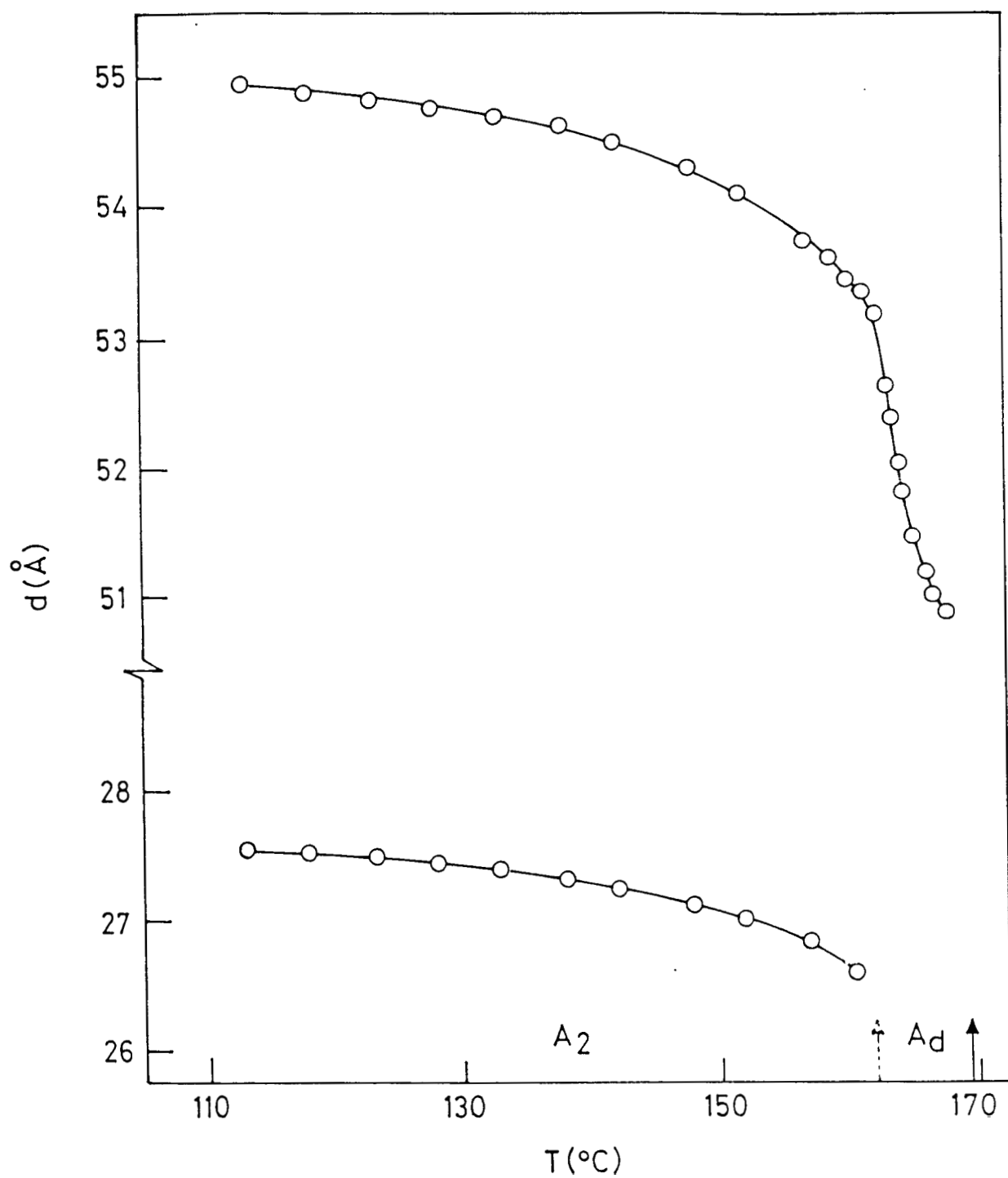


Figure 5.5

Temperature variation of the layer spacing in the  $A_d$  and  $A_2$  phases of DB7CN.

[Note: The dashed arrow mark corresponds to the expected  $A_d - A_2$  transition from DSC runs (Ref. 25)].

decyloxyphenyl-4'-(2-chlorobenzoyloxy)-4"-nitrobenzoate (DB10OCINO<sub>2</sub>). All these materials were initially considered to exhibit an A<sub>d</sub>-A<sub>2</sub> transition. However, as mentioned earlier accurate Xray investigations<sup>23</sup> have now established that in two of these materials, viz., DB7OCN and 11OPCBOB, there is a continuous evolution of A<sub>2</sub> from A<sub>d</sub> as the temperature is decreased. No such Xray data is available for the other two compounds. It is therefore not certain if an A<sub>d</sub>-A<sub>2</sub> transition really exists in these cases.

Njeumo et al.<sup>26</sup> found essentially similar behaviour for both 11OPCBOB and DB10OCINO<sub>2</sub>.  $\epsilon_{\parallel}$  showed a steep decrease with decrease in temperature, the decrease starting from N-A<sub>d</sub> transition itself. The decreasing trend continues into the A<sub>2</sub> phase. On the other hand  $\epsilon_{\perp}$  shows continuously increasing trend throughout A<sub>d</sub> and A<sub>2</sub> phases. This increase in  $\epsilon_{\perp}$  with decrease of temperature could be due to either an increase in hindrance to the molecular reorientation about the long axis or due to an increase in the longitudinal component of transverse dipole moment. It is not possible to conclude which of these is the contributing factor. These variations lead to a change in sign of  $\Delta\epsilon$ —this change seems to occur close to A<sub>d</sub>-A<sub>2</sub> transition in both the cases. The results of Njeumo et al. for DB7OCN and DB10OCN are somewhat similar to our results on DB7CN. In this case,  $\Delta\epsilon$  decreases with decrease in temperature, but does not reverse sign at the A<sub>d</sub>-A<sub>2</sub> transition. Instead it seems

to show a continuous decrease approaching zero only on extrapolating to very low temperatures in the  $A_2$  phase. There have also been some other instances wherein a somewhat large expansion of the layer spacing is accompanied by a reversal in the sign of the dielectric anisotropy.<sup>27,28</sup> Thus on the whole it appears that in materials wherein  $A_2$  continuously evolves from  $A_d$ , there is generally a drastic reduction of  $\epsilon_{\parallel}$  as the  $A_2$  phase is approached accompanied by an increase of  $\epsilon_{\perp}$  (the rate of increase of  $\epsilon_{\perp}$  seems to depend strongly on the material). Consequently, in some cases  $\Delta\epsilon$  goes to zero at the lowest temperatures in the  $A_2$  phase while in some others  $\Delta\epsilon$  changes sign at the expected  $A_d$ - $A_2$  transition temperature.

### 65.6 mol % DB5CN/9OBCB mixture

We shall now discuss the results on the mixture which clearly shows the  $A_d$ - $A_2$  transition. Xray data of Somasekhara<sup>24</sup> is produced in Fig.5.6. It is clear that there is a pronounced jump in layer spacing by about  $2.6 \text{ \AA}$  at the  $A_d$ - $A_2$  transition. Fig.5.7 shows the temperature variation of the static dielectric constants of the mixture. These data have been collected using more precise data acquisition system mentioned in Chapter II. A computer (HP86B) was used to vary the temperature at a constant rate ( $1\text{-}2^\circ\text{C/hr}$ ) as well as to collect the data of  $\epsilon_{\parallel}$  and  $\epsilon_{\perp}$  at temperature interval of about 3 or 4 mK. Since the interest in this material was essen-

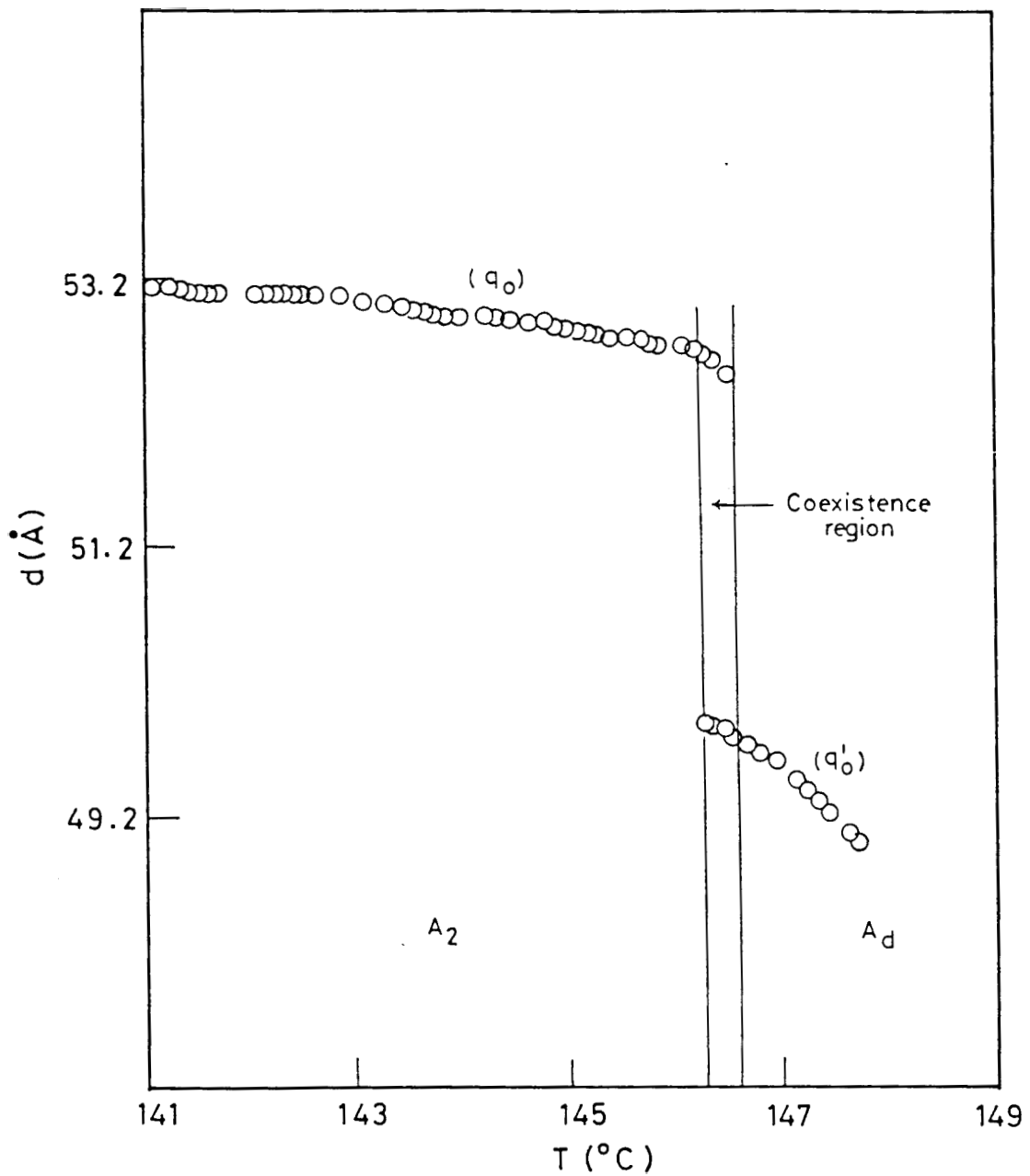


Figure 5.6

Temperature variation of layer spacing corresponding to (001) reflexions in the  $A_d$  and  $A_2$  phases of 65.6 mol % DB5CN/90BCB mixture. The region between the vertical lines shows the coexistence of  $A_d$  and  $A_2$  phases (Ref. 24).



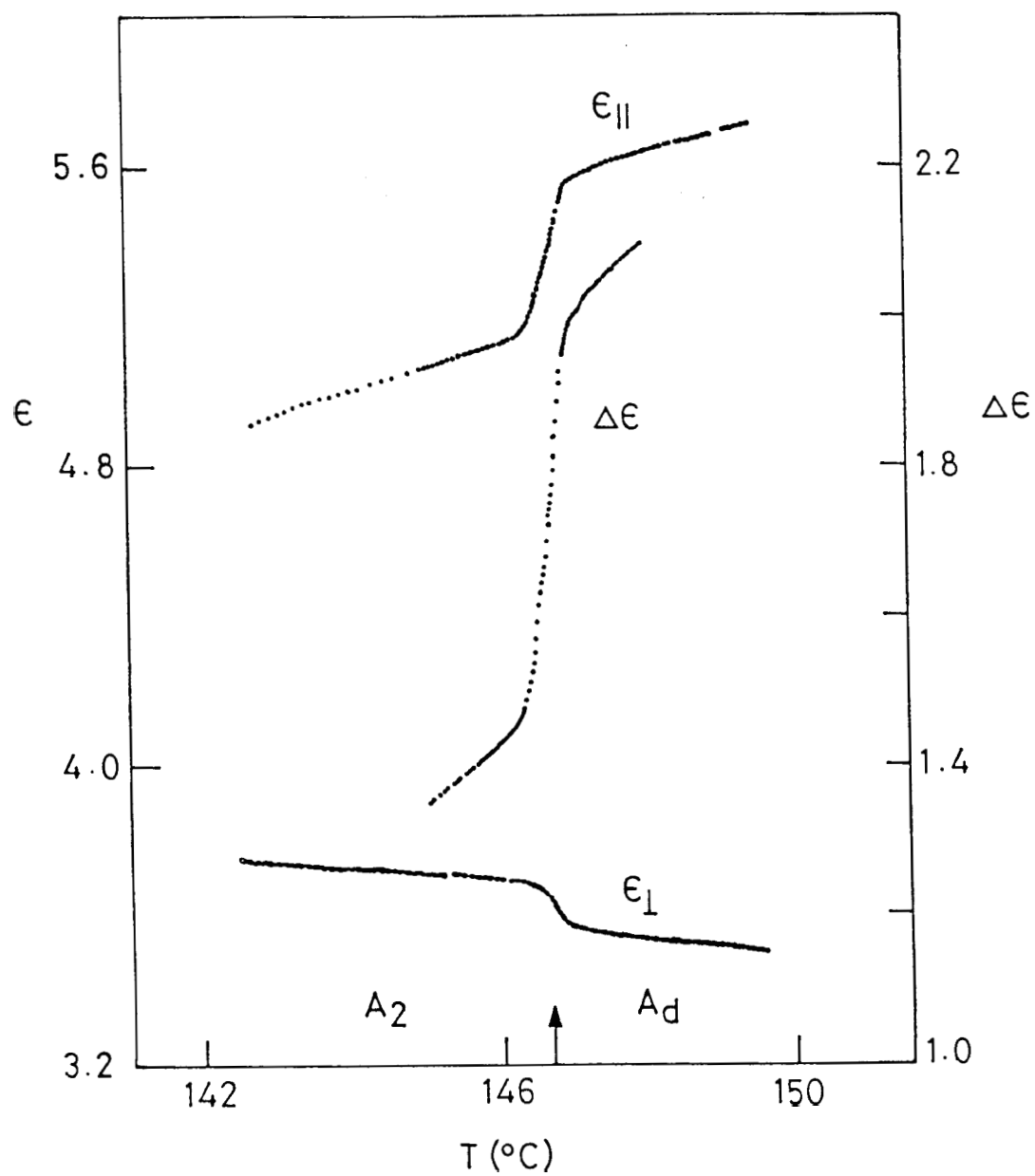


Figure 5.7

Temperature variation of dielectric constants  $\epsilon_{||}$ ,  $\epsilon_{\perp}$  and of  $\Delta\epsilon$  of 65.6 mol % DB5CN/90BCB mixture

tially to see the behaviour of dielectric constants close to  $A_d - A_2$  transition, we have collected data only in the immediate vicinity of the  $A_d - A_2$  transition covering a total temperature range of about  $8^\circ\text{C}$ . The feature of the result is a sharp drop observed at the  $A_d - A_2$  transition. The value of  $\epsilon_{\parallel}$  jumps from about  $-5.6$  to  $-5.1$  at the transition. This is also accompanied by an increase of  $\epsilon_{\perp}$  though the increase is of less magnitude than the decrease of  $\epsilon_{\parallel}$  ( $\epsilon_{\perp}$  changes from  $-3.7$  to  $-3.6$ ). These studies, which constitute the first investigation of a material exhibiting a true  $A_d - A_2$  transition, show that there is a very sharp reduction in  $\Delta\epsilon$  at the  $A_d - A_2$  transition.

### 5.3.2. The $A_1 - A_2$ Transition

The system chosen for the study of  $A_1 - A_2$  transition is 10.5 mol % mixture of TBBA in DB5CN. This mixture has a narrow range of  $A_1$  phase intervening between N and  $A_2$  phases. The structural formulae of the materials are shown in Fig.5.3 while the sequences and the temperatures of transitions are given in Table 5.1.

The variation of the static dielectric constants  $\epsilon_{\parallel}$ ,  $\epsilon_{\perp}$  and also of  $\Delta\epsilon$  in the N,  $A_1$  and  $A_2$  phases are shown in the Fig.5.8.  $\epsilon_{\parallel}$  is more or less independent of temperature in N phase while  $\epsilon_{\perp}$  shows a very small but linear increase with the decrease in

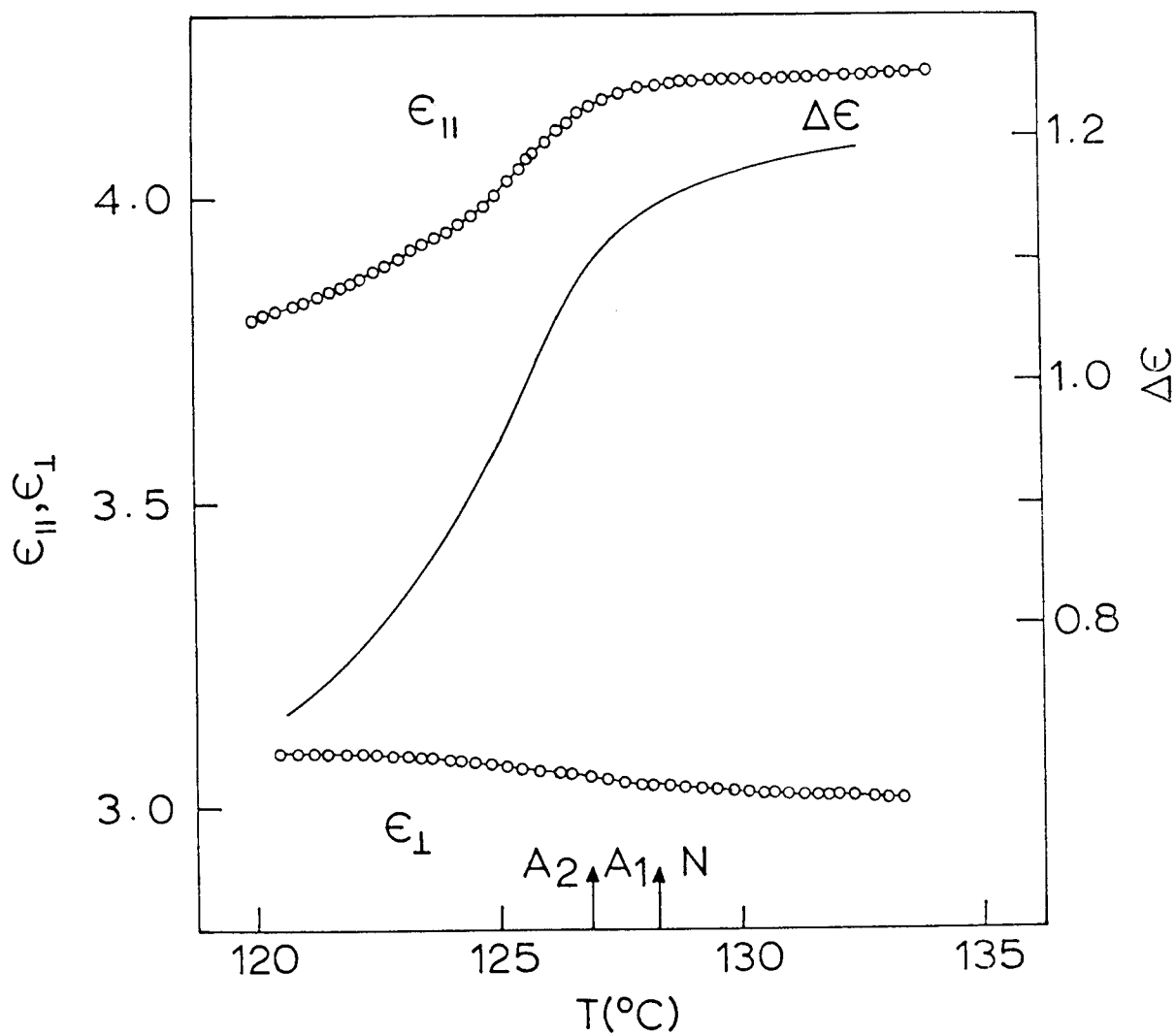


Figure 5.8

The temperature variation of dielectric constants  $\epsilon_{||}$ ,  $\epsilon_{\perp}$  and of  $\Delta\epsilon$  in the nematic, smectic  $A_1$  and  $A_2$  phases of 10.5 mol % TBBA/DB5CN mixture.

temperature. These trends in  $\epsilon_{\parallel}$  and  $\epsilon_{\perp}$  continue right through the N-A<sub>1</sub> transition there being no change at all to signify the existence of the N-A<sub>1</sub> transition. On the formation of the A<sub>2</sub> phase,  $\epsilon_{\parallel}$  shows a steep decrease whilst  $\epsilon_{\perp}$  seems to be unaffected through A<sub>1</sub>-A<sub>2</sub> transition also.  $\epsilon_{\parallel}$  has a value of  $-4.1$  in the A<sub>1</sub> phase near the transition and becomes  $-3.8$  at the lowest temperature in A<sub>2</sub> phase. This variation which is quite pronounced indicating that there is again an increase in the dipole-dipole correlation in the longitudinal direction due to the formation of dipolar pairs which constitute bilayer structure. To this extent, the behaviour of  $\epsilon_{\parallel}$  near A<sub>1</sub>-A<sub>2</sub> transition is similar to that seen at A<sub>d</sub>-A<sub>2</sub> transition. The absence of any change in  $\epsilon_{\parallel}$  on going from N to A<sub>1</sub> phase (the decrease in  $\epsilon_{\parallel}$  commences at A<sub>1</sub>-A<sub>2</sub> transition) indicates that there is no dipolar change on going from N to monolayer A<sub>1</sub> phase. This supports the general idea concerning the polar A<sub>1</sub> phase wherein the dipolar distribution within the layer is, statistically speaking, random, i.e., there is no net correlation between dipoles of two layers. Due to the pronounced decrease in  $\epsilon_{\parallel}$ ,  $\Delta\epsilon$  again shows continuous decrease in A<sub>2</sub> phase.

The only static dielectric studies reported earlier on A<sub>1</sub>-A<sub>2</sub> transition appears to be due to Benguigui et al.<sup>29</sup> They have investigated the variation of  $\epsilon_{\parallel}$  and  $\epsilon_{\perp}$  in 18 mol % mixture of TBBA in DB6CN. They also did not see any pronounced change in  $\epsilon_{\perp}$  at

the  $A_1$ - $A_2$  transition while  $\epsilon_{\parallel}$  showed a somewhat pronounced decrease. They concluded from this that there should be a strong antiferroelectric ordering of dipoles in the  $A_2$  phase. Our results are therefore essentially in agreement with those of Benguigui et al.

It may be pointed out that Xray studies of Chan et al.<sup>18</sup> showed clearly that the  $A_1$ - $A_2$  transition in the TBBA/DB6CN mixture is first order when the range of  $A_1$  phase is very small but second order when this range is somewhat larger. However no detailed Xray data exist on the TBBA/DB5CN system. It may be recalled here that the first observation of  $A_1$ - $A_2$  transition was in fact in TBBA/DB5CN mixtures. These investigations have been restricted to calorimetric studies. There was also an Xray study<sup>30</sup> of this binary system but this was essentially carried out to characterise Xray diffraction patterns of the  $A_1$  and  $A_2$  phases. No detailed studies of the Xray correlation length were carried out and consequently it was not possible to see the range of concentration over which  $A_1$ - $A_2$  transition is first order in the case of TBBA/DB5CN mixture. Density studies<sup>25</sup> conducted on 10.5 mol % TBBA/DB5CN mixture (whose dielectric studies have been described earlier) indicated the absence of any clear jump at  $A_1$ - $A_2$  transition. However these studies were not precise enough to say unequivocally whether this transition is second order or not. It would be of consi-

derable interest to study the dielectric properties of systems exhibiting a tricritical point for the  $A_1$ - $A_2$  transition.

### 5.3.3. The $A_d$ - $A_1$ Transition

The system chosen to study the  $A_d$ - $A_1$  transition is the binary mixture of 43 mol % of 4-octyloxyphenyl-4'-nitrobenzoyloxybenzoate ( $DB8ONO_2$ ) in 4-decyloxyphenyl-4'-nitrobenzoyloxy benzoate ( $DB10ONO_2$ ) whose structural formulae as well as the sequences and temperatures of transitions are given in Fig.5.3 and Table 5.1 respectively. It may be recalled here that the ninth member of the same homologous series ( $DB9ONO_2$ ) is the well known triply reentrant mesogen. The binary system studied exhibits N,  $A_d$ ,  $A_1$ ,  $\tilde{C}$ ,  $A_2$  and  $C_2$  phases. However we have studied the dielectric properties only in the  $A_d$  and  $A_1$  phases — this is because of the high  $A_d$ -N transition temperature which made measurement in the N phase very difficult and the misalignment of the sample which occurs on going over to the  $\tilde{C}$  phase (this precludes any measurements below the  $A_1$  phase).

The variation of static dielectric constants in the vicinity of the  $A_d$ - $A_1$  transition is given in the Fig.5.9. Several interesting features are seen;  $\epsilon_{\parallel}$  and as well as  $\epsilon_{\perp}$  show a very small increase with decrease in temperature in  $A_d$  phase. At the  $A_d$ - $A_1$  transition,  $\epsilon_{\parallel}$  shows a small decrease ( $\sim 0.07$ ) while  $\epsilon_{\perp}$  shows a

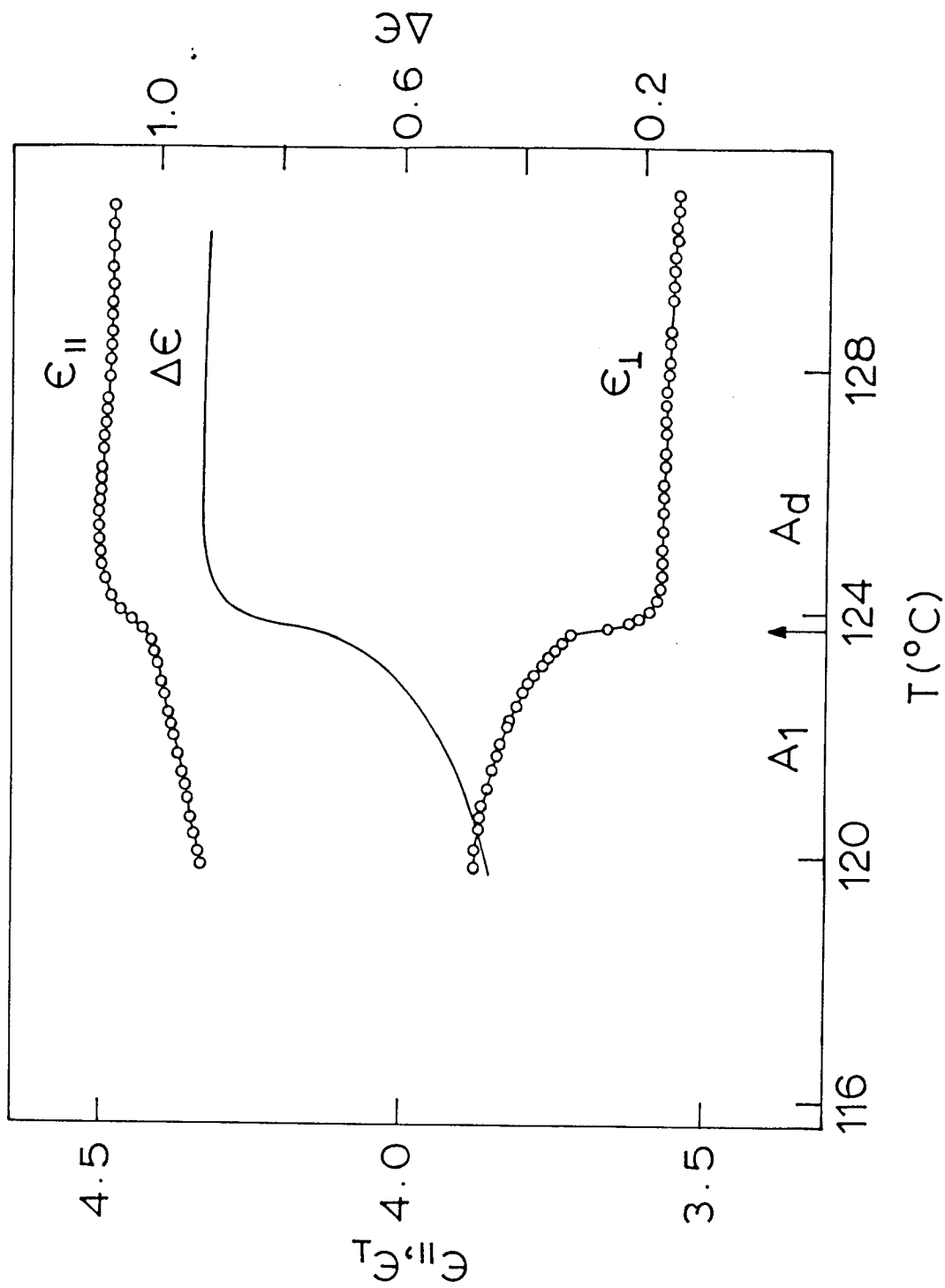


Figure 5.9. Temperature variation of dielectric constants  $\epsilon_{||}$ ,  $\epsilon_{\perp}$  and of  $\Delta\epsilon$  in the smectic  $A_d$  and  $A_1$  phases of 43 mol%  $DB8ONO_2/DB100NO_2$  mixture

more pronounced and sharp increase ( $-0.17$ ). Compared to the  $A_d-A_2$  or  $A_1-A_2$  transition the decrease in  $\epsilon_{\parallel}$  seen on going to  $A_1$  phase from  $A_d$  phase is much less pronounced. The sharp increase in  $\epsilon_{\perp}$  at  $A_d-A_1$  transition is indicative of an increase in hindrance to the molecular reorientation about the long axis on the formation of  $A_1$  phase. The value of  $\epsilon_{\perp}$  in  $A_1$  phase seems to saturate at lower temperatures. Due to the sudden change in  $\epsilon_{\perp}$  and  $\epsilon_{\parallel}$ ,  $\Delta\epsilon$  shows a pronounced drop at the  $A_d-A_1$  transition. These studies which constitute the first measurements on static dielectric constants near an  $A_d-A_1$  transition, show that although there is an increase in antiferroelectric near neighbour ordering on going from  $A_d$  to  $A_1$  phase, this increase is not as pronounced as that seen on going to the  $A_2$  phase (wherein there is head-to-head formation of dipolar pairs). Therefore it can be deduced that compared to  $A_2$  phase, the dipolar heads are more disordered in the  $A_1$  phase.

#### 5.4 DISPERSION STUDIES NEAR A-A TRANSITIONS

##### 5.4.1. The $A_d-A_2$ transition

###### a DB7CN

We shall first present the results of our dispersion measurements in the N,  $A_d$  and  $A_2$  phases of DB7CN in which as already discussed, there is a continuous evolution of  $A_2$  from  $A_d$  phase. The typical loss curves for a few temperatures in the N,  $A_d$  and



$A_2$  phases are shown in Fig.5.10. The striking feature of these curves is the drastic reduction of the maxima of loss curves on going to the  $A_2$  phase. This reflects the behaviour of  $\epsilon_{\parallel}$  which also shows a steep decrease at the  $A_d$ - $A_2$  transition (see Fig.5.4). The representative Cole-Cole plots in the different phases of DB7CN are reproduced in Figs. 5.11 and 5.12. The loss curves as well as the Cole-Cole plots show that there is only a single relaxation process in all the three phases. The frequency of relaxation  $f_R$  values obtained from loss curves and Cole-Cole semicircles are given in Table 5.2. The plot of  $f_R$  vs.  $1/T$  is shown in Fig.5.13 which also shows the activation energy  $W$  in the N,  $A_d$  and  $A_2$  phases. It is clear that  $W_N > W_{A_2} > W_{A_d}$ . The extremely narrow range of  $A_d$  phase makes the value of  $W_{A_d}$  slightly uncertain.

#### b 65.6 Mol % DB5CN/9OBCB Mixture

We shall now present the results on 65.6 mol % DB5CN/9OBCB system which exhibits clear  $A_d$ - $A_2$  transition. The typical loss curves are given in Fig.5.14 while the Cole-Cole plots in Fig. 5.15. The  $f_R$  data obtained from loss curves and Cole-Cole plots are given in Table 5.3. The Arrhenius plot (Fig.5.16) shows that  $W_{A_2} > W_N > W_{A_d}$ . This result is in fact the first study on a material exhibiting the  $A_d$ - $A_2$  transition.

Thus on the whole it can be surmised that  $W_{A_2}$  is always

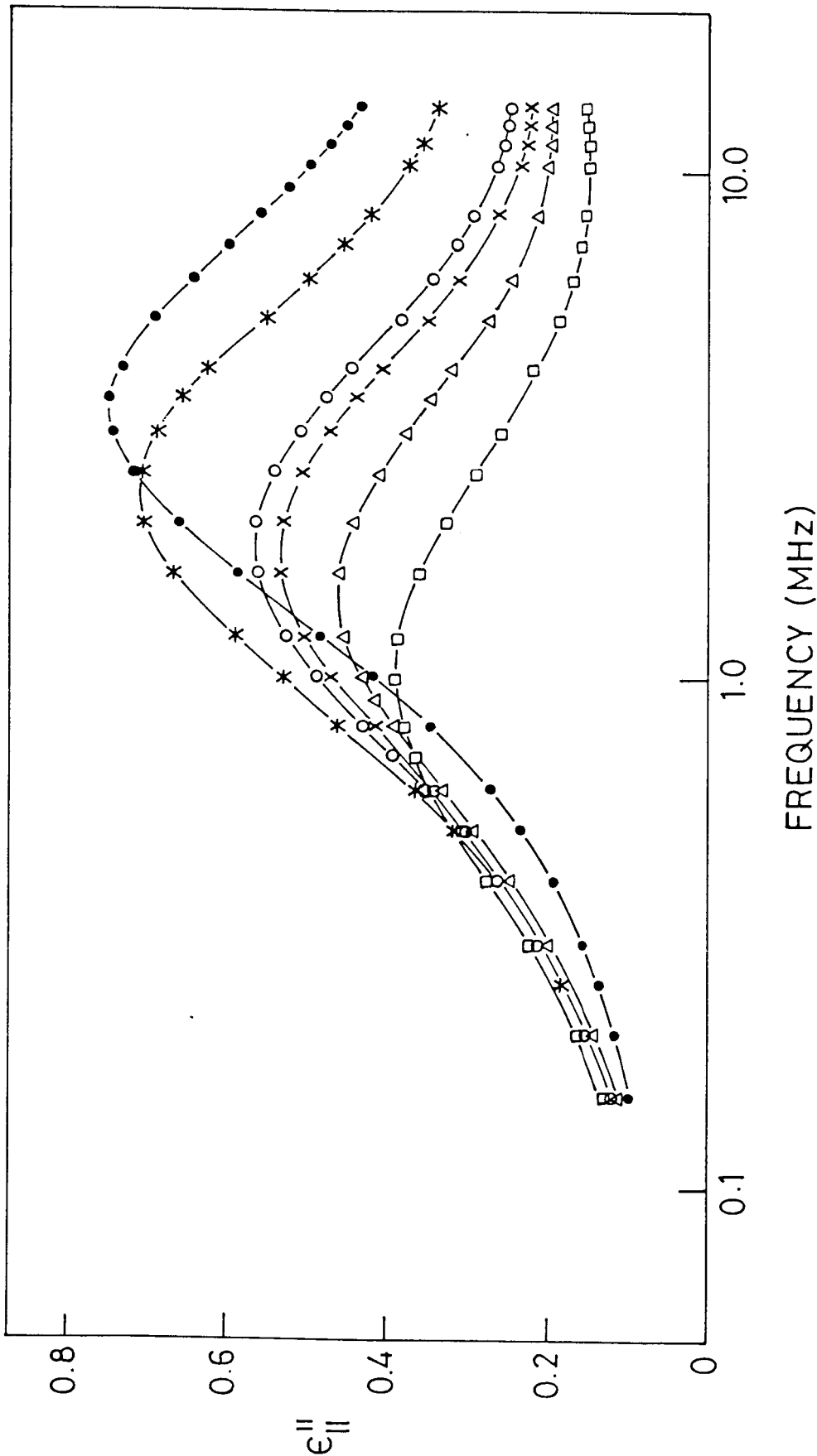


Figure 5.10

Representative loss curves of DB7CN in the nematic (● 185.15°C, ✱ 175.65°C), smectic A<sub>d</sub> (○ 167.9°C) and smectic A<sub>2</sub> (△ 160.7°C, □ 152.65°C) phases.

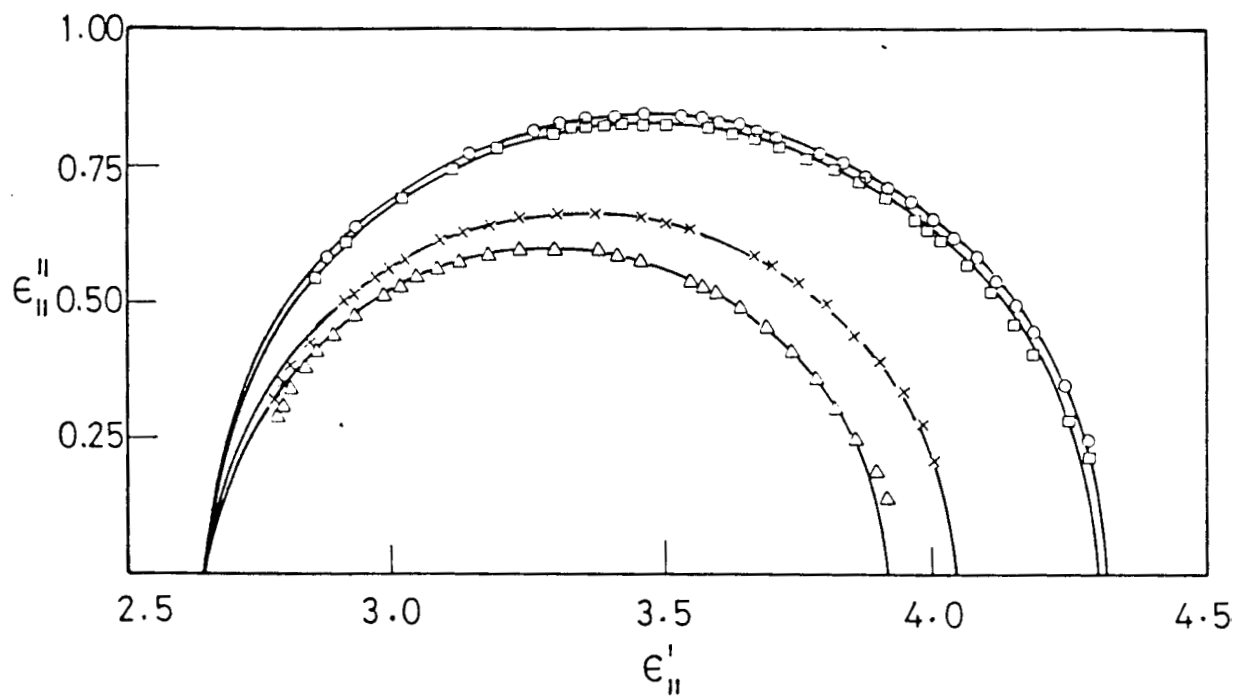


Figure 5.11

Representative Cole-Cole plots of DB7CN in the (a) nematic (● 183.8°C, □ 176.4°C) and (b) smectic  $A_d$  (× 167.2°C, △ 164.6°C) phases.

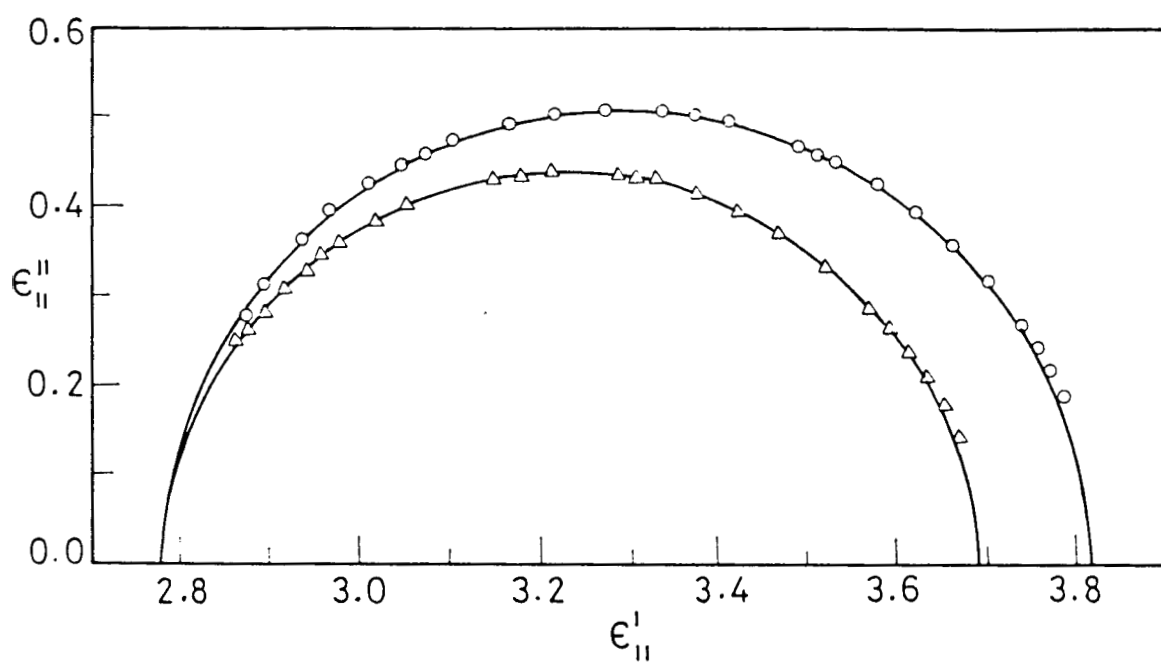


Figure 5.12

Representative Cole-Cole plots in the smectic  $A_2$  phase (  $\bullet$  161.3°C,  $\Delta$  154.2°C) of DB7CN.

TABLE 5.2

Frequency of relaxation  $f_R$  as a function of temperature in the nematic, smectic  $A_d$  and  $A_2$  phases of DB7CN

S.No.	Temperature (°C)	Frequency of relaxation (in MHz)		Mean $f_R$
		From loss curve	From Cole-Cole	
<b><u>N e m a t i c</u></b>				
1	185.15	3.45	3.436	3.443
2	181.85	2.9	2.8	2.85
3	179.1	2.6	2.537	2.569
4	178.2	2.45	2.37	2.41
5	177.0	2.4	2.341	2.371
6	175.55	2.25	2.183	2.217
7	174.4	2.1	2.097	2.099
8	172.8	2.0	2.007	2.004
9	171.5	1.925	1.885	1.905
10	170.8	1.9	1.86	1.88
<b><u>S m e c t i c A<sub>d</sub></u></b>				
11	168.5	1.85	1.796	1.823
12	167.5	1.825	1.772	1.799
13	165.95	1.8	1.732	1.766
14	163.45	1.725	1.66	1.693
<b><u>S m e c t i c A<sub>2</sub></u></b>				
15	160.9	1.625	1.58	1.603
16	159.25	1.525	1.497	1.511
17	157.15	1.425	1.387	1.406
18	155.2	1.275	1.258	1.267
19	153.25	1.175	1.134	1.155
20	152.2	1.15	1.113	1.132
21	151.5	1.1	1.099	1.1
22	149.1	0.970	0.982	0.976
23	146.85	0.900	0.887	0.894
24	144.75	0.820	0.802	0.811
25	142.85	0.740	0.744	0.742

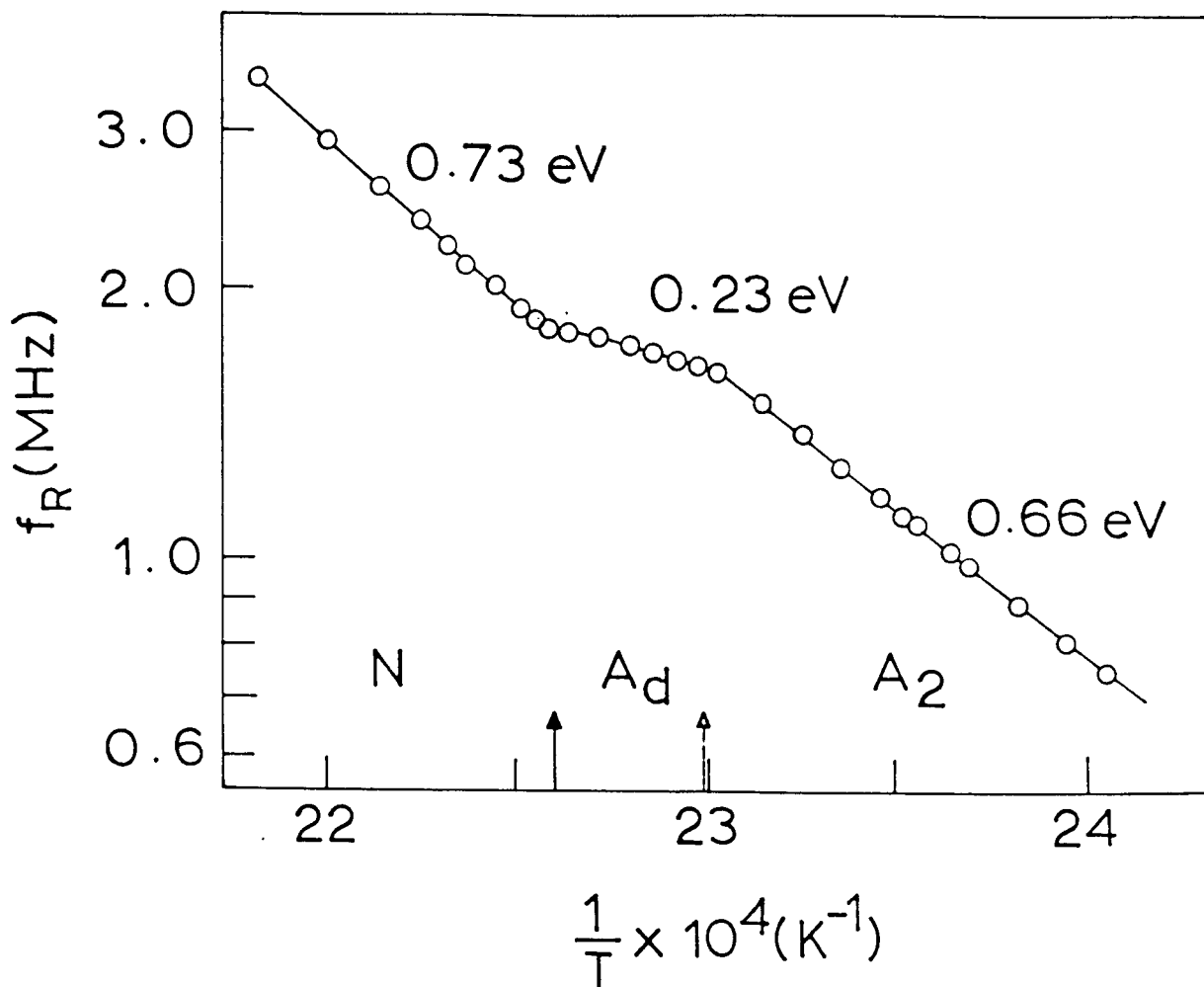


Figure 5.13

$f_R$  vs.  $1/T$  plot of DB7CN. The activation energies are also given. (Note: The dashed arrow mark corresponds to the expected  $A_d-A_2$  transition from DSC runs.)

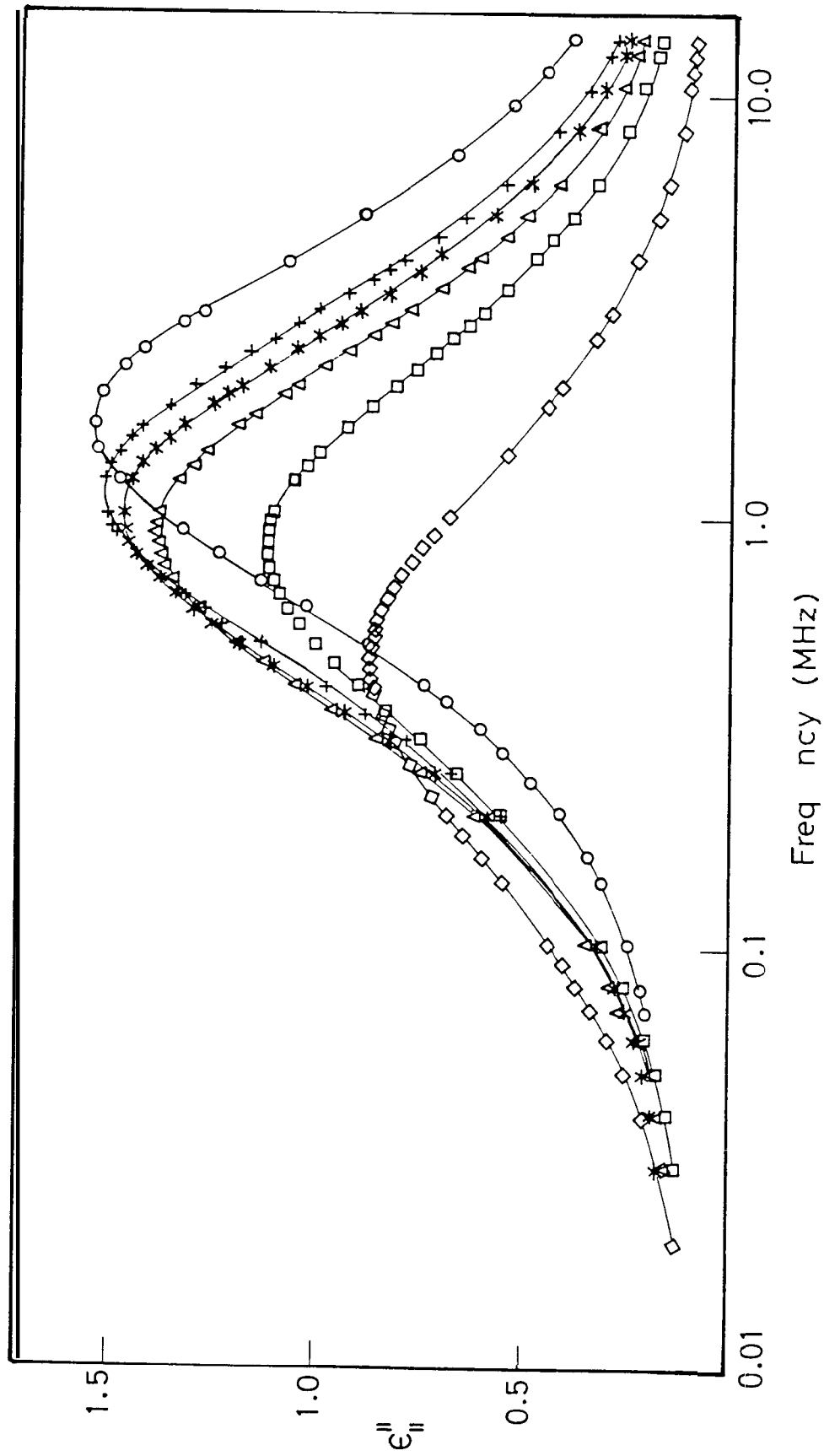


Figure 5.14. The representative loss curves in the nematic (○) 163.7°C, (+) 155°C, smectic A<sub>d</sub> (✱) 151.63°C, A<sub>2</sub> (□) 45°C, ◇ 133.8°C phases of 65.6 mol % D35CN/90E3CB mixture.

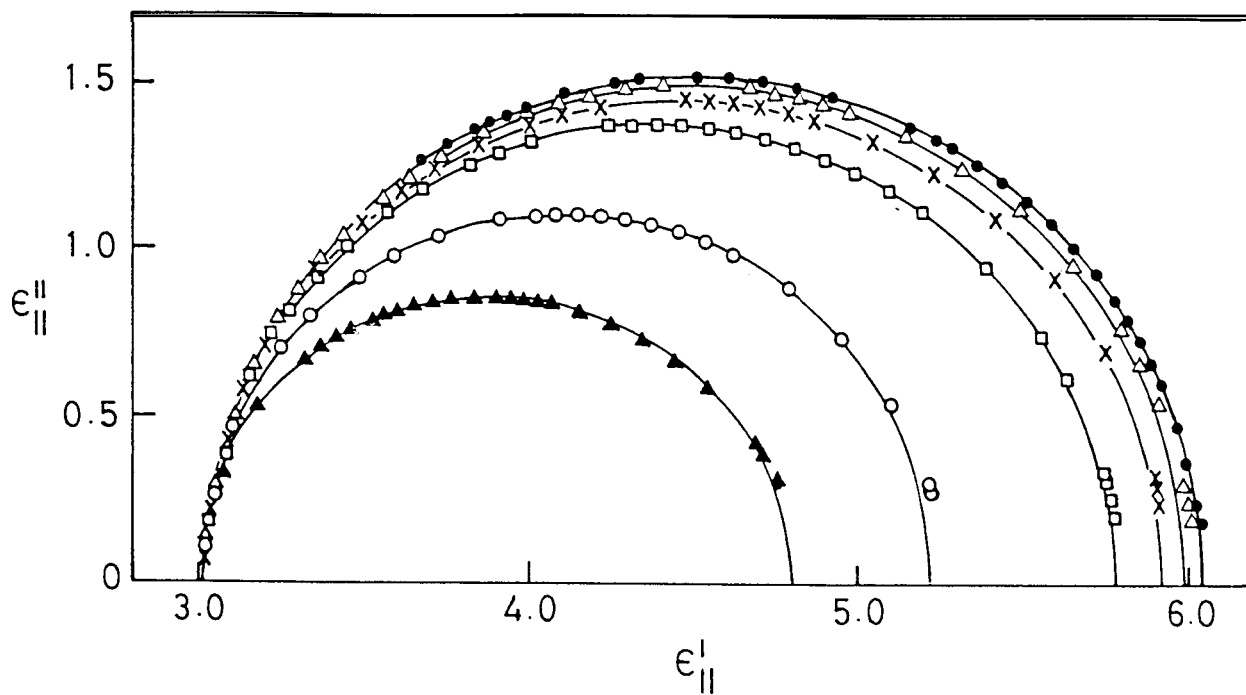


Figure 5.15

The representative Cole-Sole plots of 65.6 mol % DB5CN/90BCB mixture in (a) nematic (● 163.7°C, ▲ 155°C), (b) smectic A<sub>d</sub> (× 151.63°C, □ 148°C) and (c) smectic A<sub>2</sub> (◊ 145°C, ▲ 133.8°C) phases.



**TABLE 53**

Frequency of relaxation  $f_R$  as a function of temperature in  
the nematic, smectic  $A_d$  and  $A_2$  phases of  
65.6 mol % DB5CN/9OBCB mixture

S.No.	Temperature ( $^{\circ}$ C)	Frequency of relaxation (in MHz)		Mean $f_R$
		From loss curve	From Cole-Cole	
<b><u>N e m a t i c</u></b>				
1	163.67	1.6	1.59	1.595
2	162.44	1.5	1.5	1.5
3	160.89	1.425	1.425	1.425
4	159.08	1.325	1.309	1.317
5	157.376	1.225	1.224	1.225
6	156.02	1.165	1.17	1.168
7	154.97	1.1	1.095	1.098
8	154.18	1.075	1.08	1.078
<b><u>S m e c t i c A<sub>d</sub></u></b>				
9	153.3	1.055	1.041	1.048
10	152.69	1.025	1.017	1.021
11	151.63	1	0.995	0.998
12	150.71	0.980	0.972	0.976
13	149.23	0.930	0.921	0.926
14	148.03	0.890	0.882	0.886
15	147.54	0.880	0.873	0.877
16	147.03	0.865	0.858	0.862
<b><u>S m e c t i c A<sub>2</sub></u></b>				
17	146.48	0.860	0.857	0.859
18	146.02	0.855	0.851	0.853
19	145.45	0.840	0.830	0.835
20	145.03	0.830	0.825	0.828
21	144.03	0.790	0.783	0.787
22	143.11	0.755	0.744	0.750
23	141.53	0.690	0.690	0.690
24	140.34	0.650	0.642	0.646
25	137.27	0.550	0.544	0.547
26	133.78	0.455	0.447	0.451

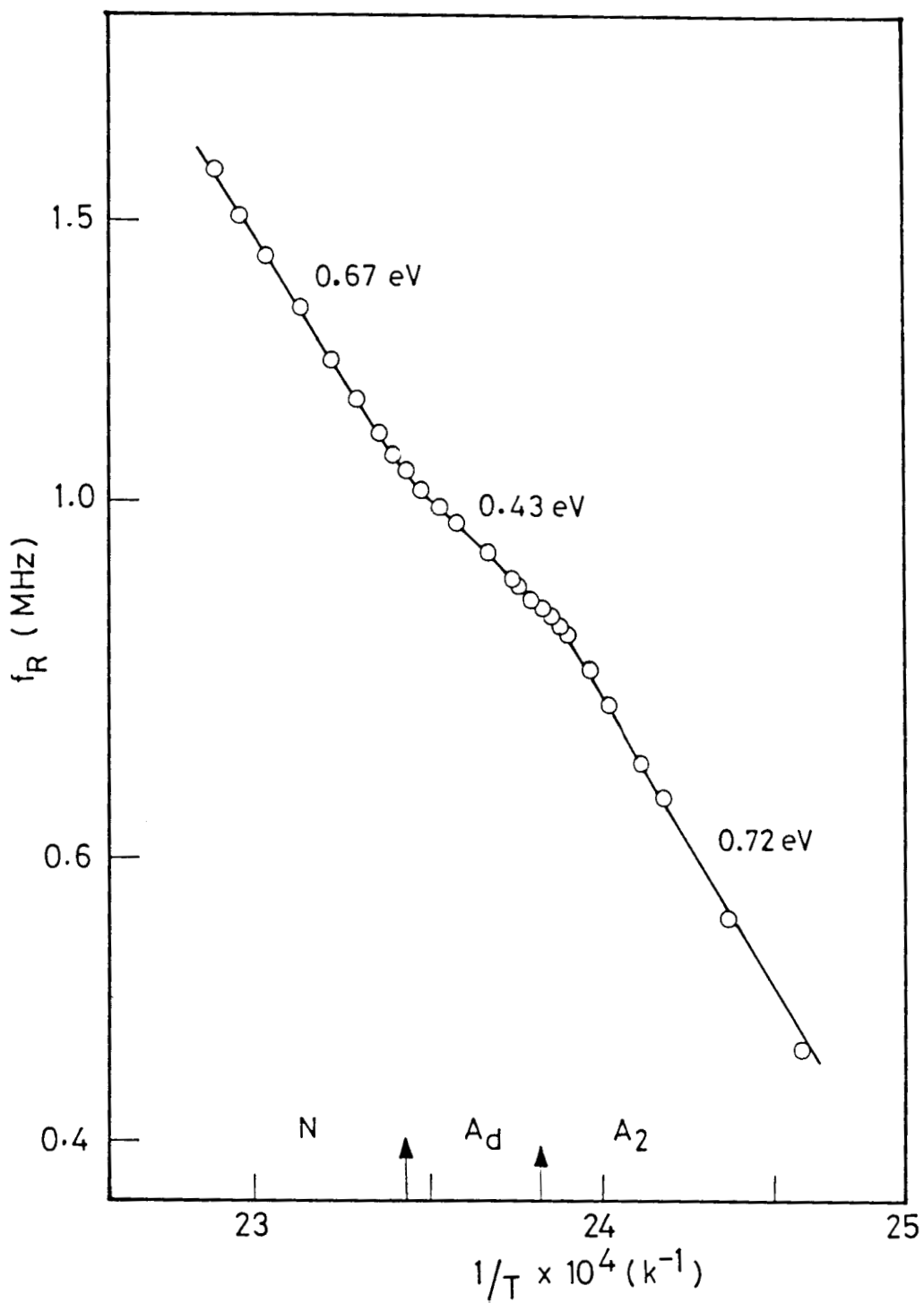


Figure 5.16

$f_R$  vs.  $1/T$  plot in the nematic, smectic  $A_d$  and  $A_2$  phases of 65.6 mol % DB5CN/90BCB mixture

very much greater than  $W_{A_d}$  showing thereby that the reorientation process of the short axis of the molecule is much more hindered in the  $A_2$  phase than in the  $A_d$  phase. Essentially a similar result has been by Njeumo et al.<sup>26</sup> for several systems exhibiting the  $A_d$  and  $A_2$  phases. Considering that at the  $A_d$ - $A_2$  transition of the binary system DB5CN/9OBCB, there is a pronounced jump in layer spacing it was thought worthwhile to see if there is a jump in  $f_R$ , at the transition. With this in view, we collected the data at close intervals near  $A_d$ - $A_2$  transition. However no jump was seen at the transition (Fig.5.16). The higher  $W$  in  $A_2$  phase compared to that in  $A_d$  phase is perhaps an indication of better packing of molecules in bilayer  $A_2$  phase. A study of the comparison of in-plane structure factors of the  $A_d$  and  $A_2$  phases has not been carried out so far and would be of considerable interest.

#### 5.4.2 The $A_1$ - $A_2$ Transition

The representative loss curves and Cole-Cole plots for the 10.5 mol % TBBA/DB5CN system are shown in Figs.5.17-5.19 while the data on  $f_R$  obtained from loss curves and Cole-Cole plots is given in Table 5.4. The plot of  $f_R$  vs.  $1/T$  (Fig.5.20) shows some unusual features.  $W_N$  is found to be the same as in the  $A_1$  phase (0.66 eV) while  $W$  in the  $A_2$  phase is found to be much smaller. Secondly, there is a region of temperature in the  $A_2$  phase (close to the  $A_1$ - $A_2$  transition) in which the data do not fall on the Arrhe-

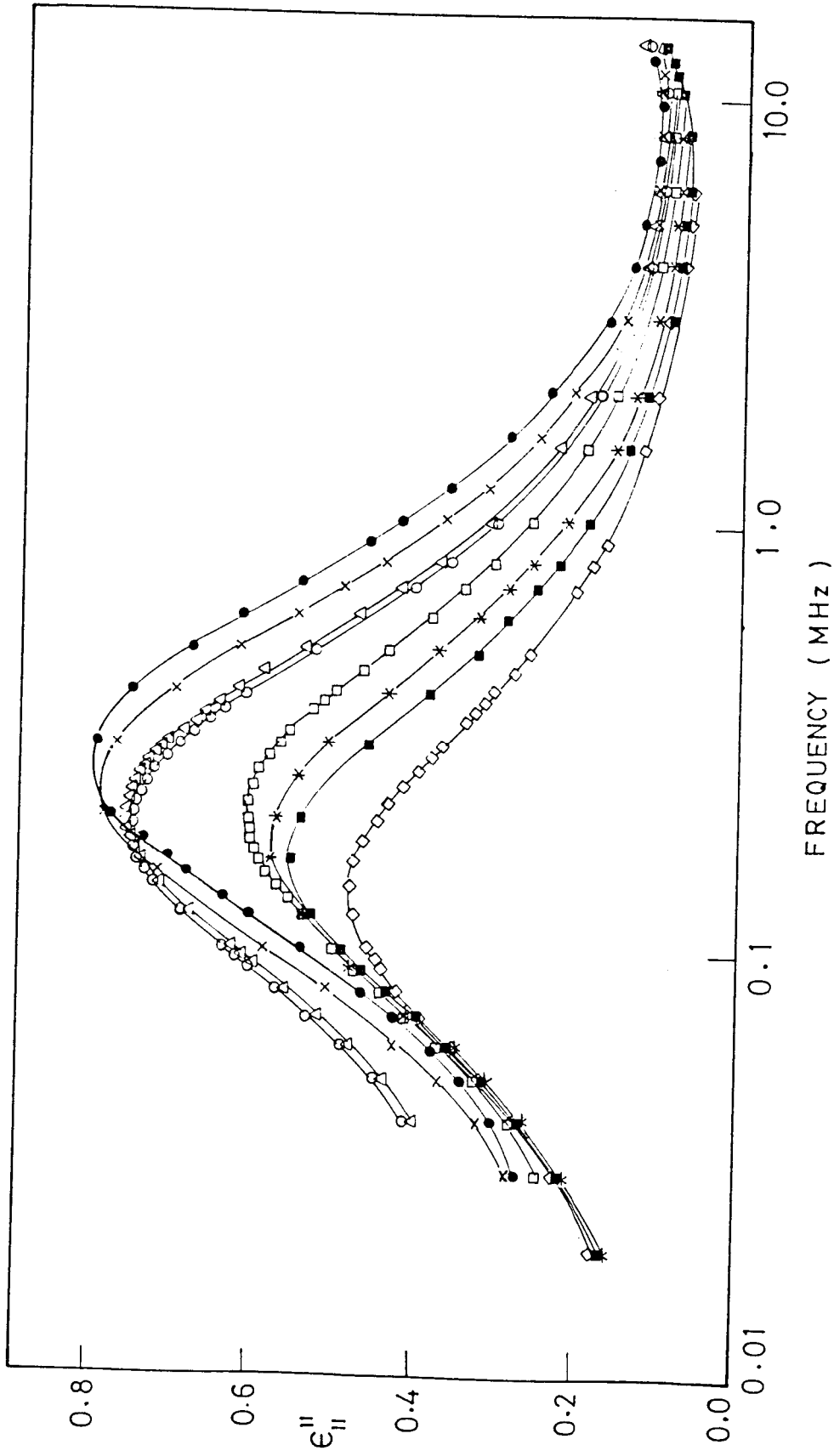


Figure 5.17. Representative loss curves in the nematic (● 136.1°C, × 132°C), smectic A<sub>1</sub> (Δ 127.8°C, □ 123.1°C, \* 118.9°C, ■ 116.6°C, ◇ 112.8°C) phases of 10.5 mol % TBBA/DB5CN mixture.

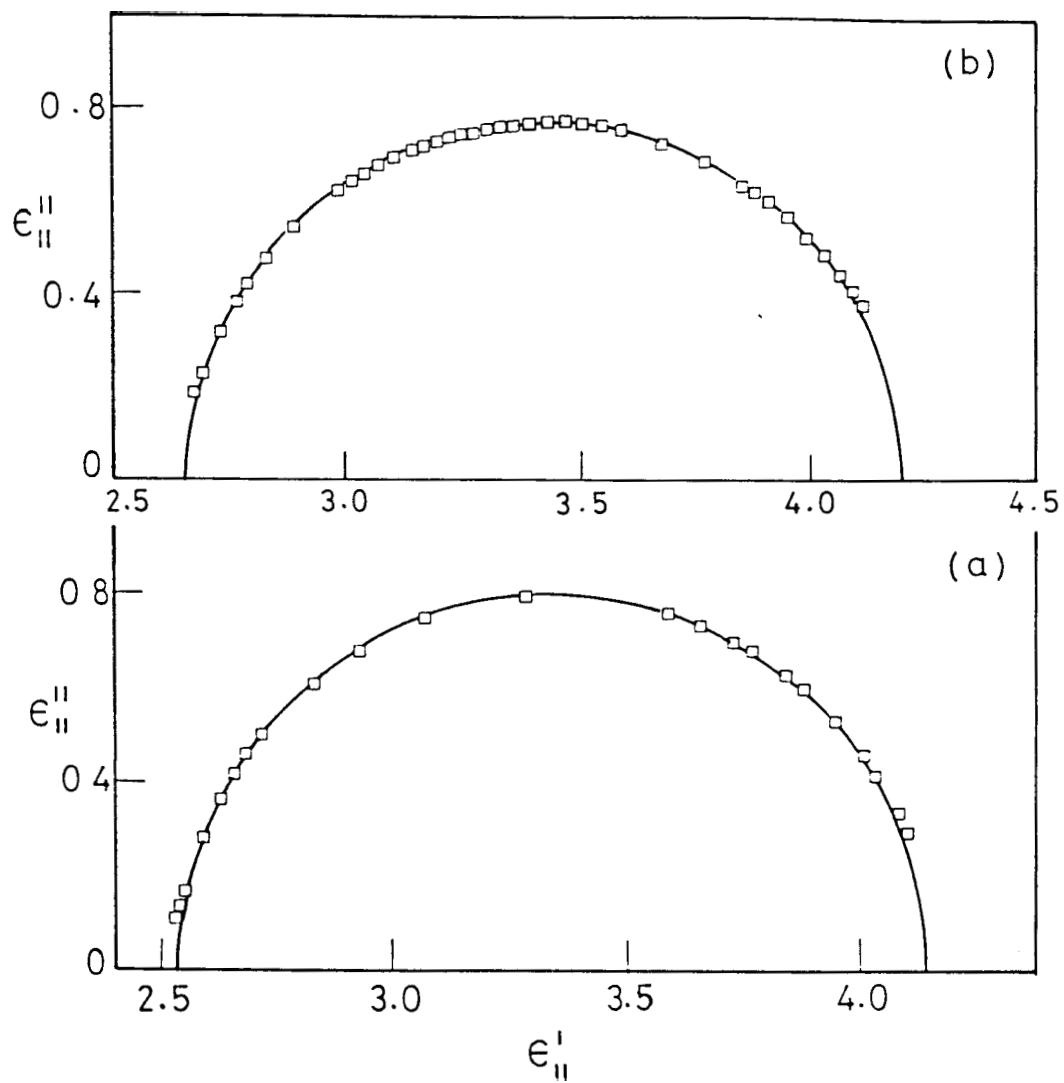


Figure 5.18

Representative Cole-Cole plots in the (a) nematic (136.1°C) and (b) smectic  $A_1$  phase (127.8°C) of 10.5 mol % TBBA/DB5CN mixture.

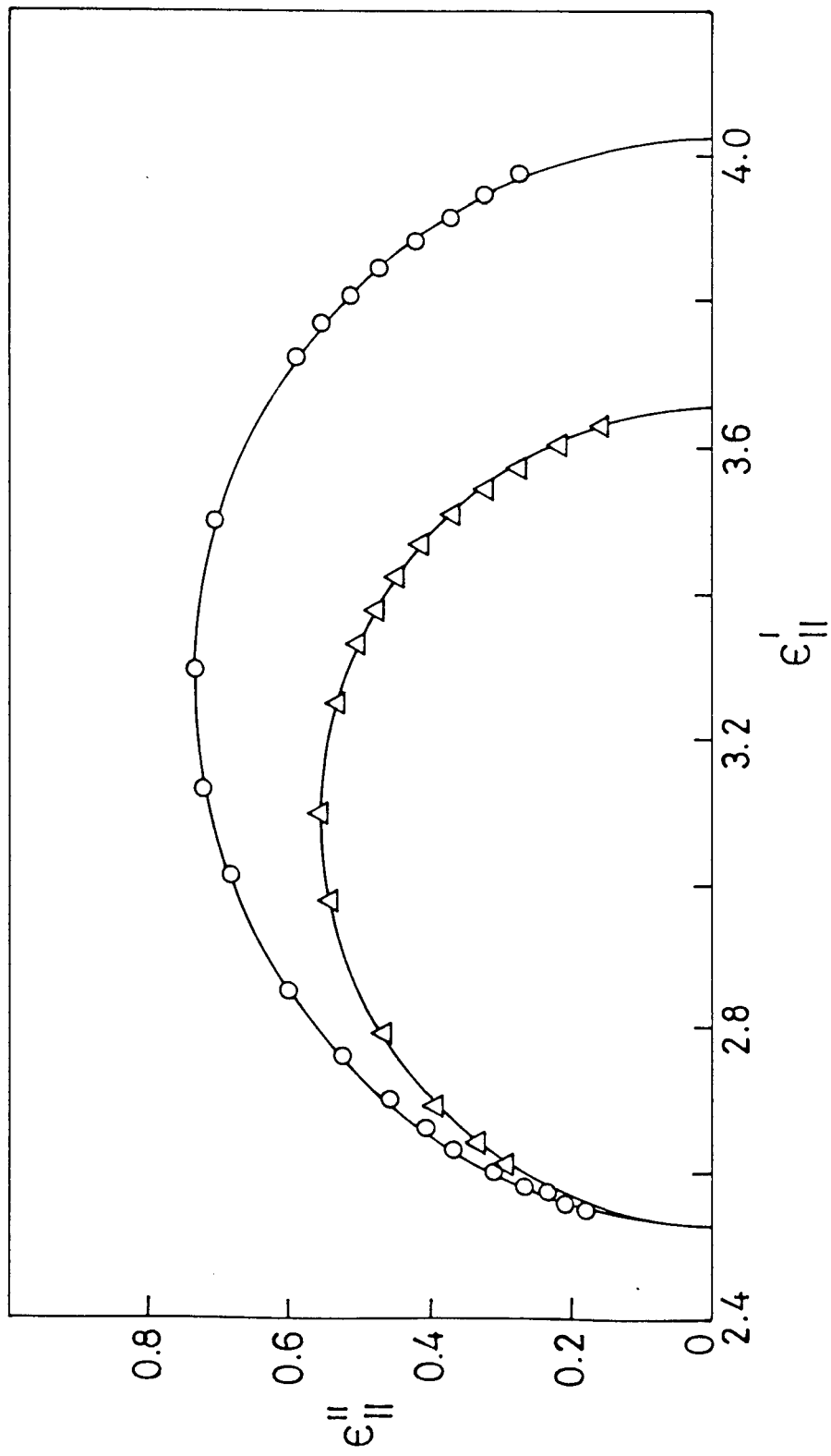


Figure 5.19

Representative Cole-Cole plots in the smectic A<sub>2</sub> phase ( O 125.9°C, Δ 116.6°C) of 10.5 mol % TBBA/DB5CN mixture.

**TABLE 5.4**

Frequency of relaxation  $f_R$  as a function of temperature in  
the nematic, smectic  $A_1$  and  $A_2$  phases of  
10.5 mol % TBBA/DB5CN mixture

S.No.	Temperature (°C)	Frequency of relaxation (in MHz)		hlean $f_R$
		From loss curve	From Cole-Cole	
<b><u>N e m a t i c</u></b>				
1	139.4	0.341	0.331	0.336
2	137.5	0.315	0.310	0.313
3	136.8	0.3	0.299	0.3
4	135.15	0.280	0.280	0.28
5	133.5	0.260	0.260	0.260
6	131.75	0.240	0.238	0.239
7	130.25	0.223	0.223	0.223
8	129.4	0.215	0.216	0.216
9	128.7	0.208	0.206	0.207
10	128.5	0.205	0.204	0.205
<b><u>s m e c t i c A<sub>1</sub></u></b>				
11	128.25	0.203	0.201	0.202
12	128.05	0.200	0.200	0.2
13	127.8	0.198	0.199	0.199
14	127.5	0.193	0.196	0.194
15	127.25	0.192	0.196	0.194
16	126.95	0.192	0.195	0.193
<b><u>s r n e c t i c A<sub>2</sub></u></b>				
17	126.75	0.193	0.194	0.194
18	126.4	0.198	0.197	0.198
19	125.4	0.203	0.204	0.204
20	125.0	0.205	0.205	0.205
21	123.1	0.205	0.204	0.205
22	122.5	0.200	0.198	0.199
23	118.9	0.175	0.177	0.176
24	118.65	0.172	0.174	0.173
25	116.6	0.163	0.161	0.162
26	112.8	0.138	0.137	0.138

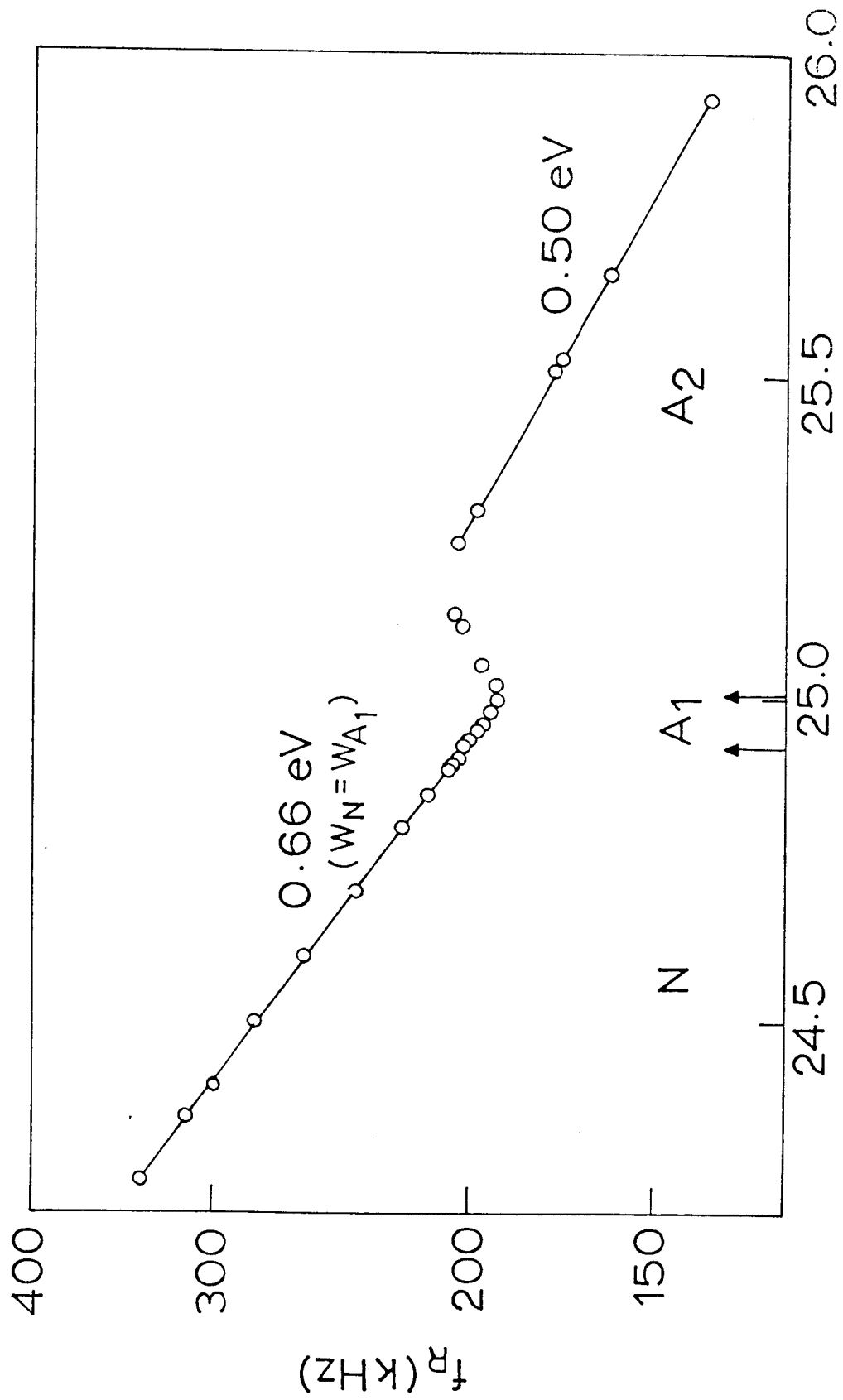


Figure 5.20.  $f_R$  vs.  $1/T$  plot in the nematic, smectic A<sub>1</sub> and A<sub>2</sub> phases of 10.5 mol % TBBA/DB5CN mixture

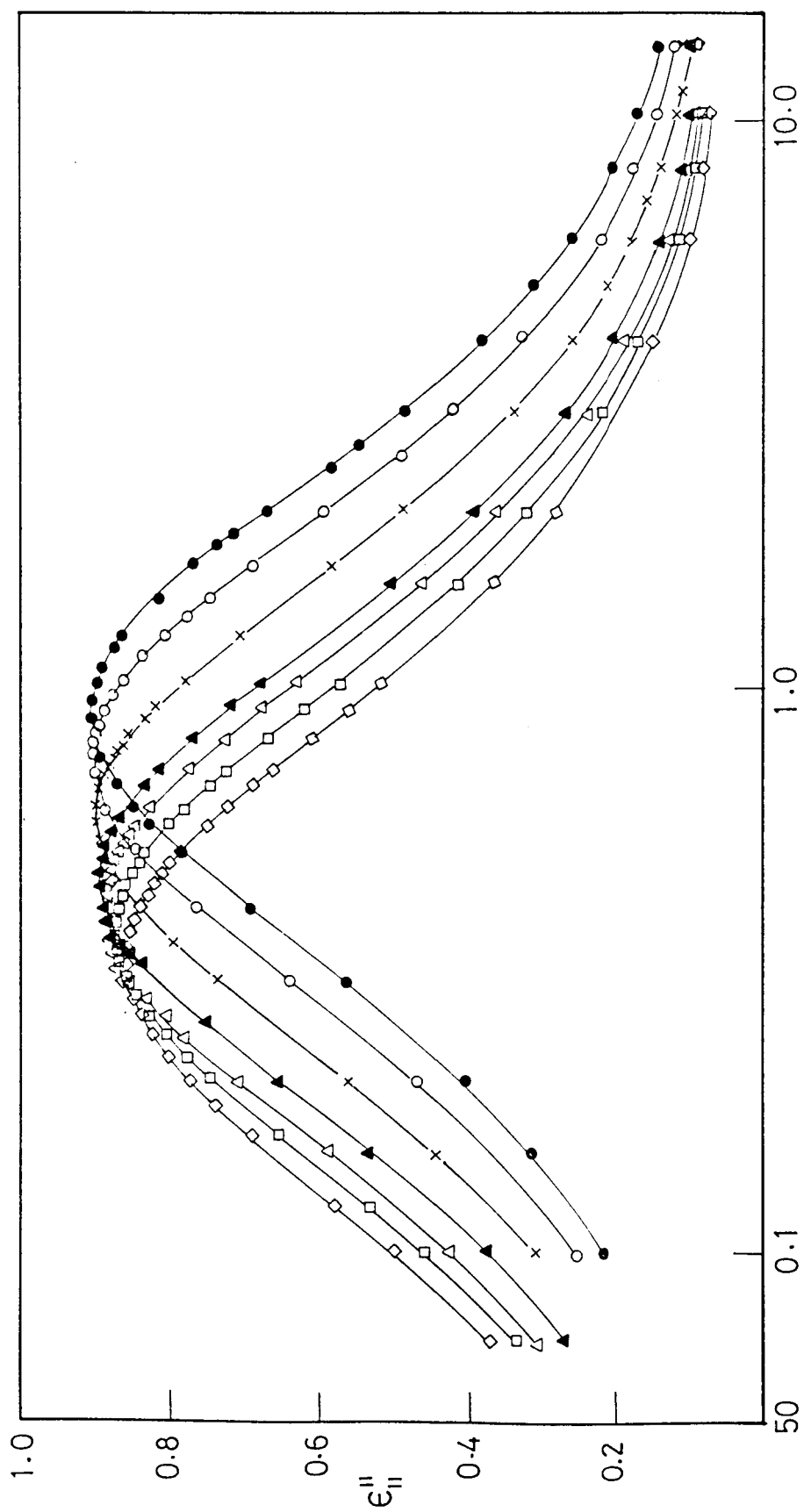


nus plot at all. Thirdly, the extrapolated linear portion of the plot in  $A_2$  phase to  $A_1$ - $A_2$  transition gives a jump in  $f_R$  at  $A_1$ - $A_2$  transition, the relaxation frequency in  $A_2$  phase **being higher** than that of  $A_1$  phase. [The erratic behaviour of the data immediately on the formation of  $A_2$  phase as well as the higher value of  $f_R$  in the beginning of  $A_2$  phase are essentially similar to the behaviour seen near the N- $A_2$  transition in DB5CN (see Chapter III, Section 3.7.1b)]. This result would imply that the head-to-head pairs of dipoles which lead to the bilayer structure of  $A_2$  phase somehow make the reorientation process of a pair of molecules (presumably a mechanism of relaxation in the  $A_2$  phase) easier than the reorientation of a single molecule in the  $A_1$  phase.

It is relevant to recall here the only other dielectric study on the system exhibiting the  $A_1$ - $A_2$  transition—the data of Benguigui and Hardouin<sup>29</sup> on the TBBA/DB6CN system (refer to §5.3.2). Although this study does not give any data in the  $A_1$  phase, it appears to show two relaxations in the  $A_2$  phase. As discussed in chapter III, §3.7.1b none of the subsequent studies on the  $A_2$  phase have shown a second relaxation in any of the materials and therefore the result of Benguigui and Hardouin is perhaps attributable to the difference in chemical nature of the constituent molecules in the mixture. The second dispersion predicted theoretically by Benguigui<sup>31</sup> in  $A_2$  phase is therefore has nor been proved experimentally so far.

### 5.4.3. $A_d - A_1$ Transition

Finally we shall present our dispersion studies near the  $A_d - A_1$  transition in 43 mol % DB8ONO<sub>2</sub>/DB10ONO<sub>2</sub> system. The plots of  $\epsilon''_{\parallel}$  versus frequency, Cole-Cole diagrams and the Arrhenius plot are given in Figs. 5.21-5.24 respectively while the data on  $f_R$  are given in Table 5.5.  $\omega$  in the  $A_1$  phase is found to be substantially larger than that in the  $A_d$  phase. The only previously reported study on the  $A_d - A_1$  transition is due to Benguigui et al.<sup>32</sup> on the binary mixture of 4-octyloxybenzoyloxy-4'-cyanostilbene ( $T_8$ ) in 4-pentyloxybenzoyloxy-4'-nitrostilbene ( $T_5NO_2$ ). 0.75  $T_8/T_5NO_2$  system was shown to exhibit the continuous evolution of  $A_1$  from  $A_d$  phase on the basis of Xray study. The dispersion study of Benguigui et al. seems to show the existence of two relaxations, the strength of one decreasing at the expense of another on going from  $A_d$  to  $A_1$  phase. Benguigui et al. concluded from their results that the A phase with only one possible layer modulation can possess two short-range local orders, the strength of one of the orders becoming less on going to another type of A phase. However, our results on the 43 mol % DB8ONO<sub>2</sub>/DB10ONO<sub>2</sub> system show that there is only a single relaxation process at all temperatures in both  $A_1$  and  $A_d$  phases. It is interesting to note that the constituent molecules of our mixture belong to the same homologous series while the compounds studied by Benguigui et al. have different chemical structures — one of the constituent materials has a cyano



FREQUENCY (MHz)

Figure 5.21

Representative loss curves in the smectic  $A_d$  (● 134.45°C, ○ 131.4°C, × 127.3°C) and smectic  $A_1$  phase (▲ 123.5°C, △ 122.4°C, □ 121.3°C and ◇ 120°C) of 43 mol % DB8ONO<sub>2</sub>/DB100NO<sub>2</sub> mixture.

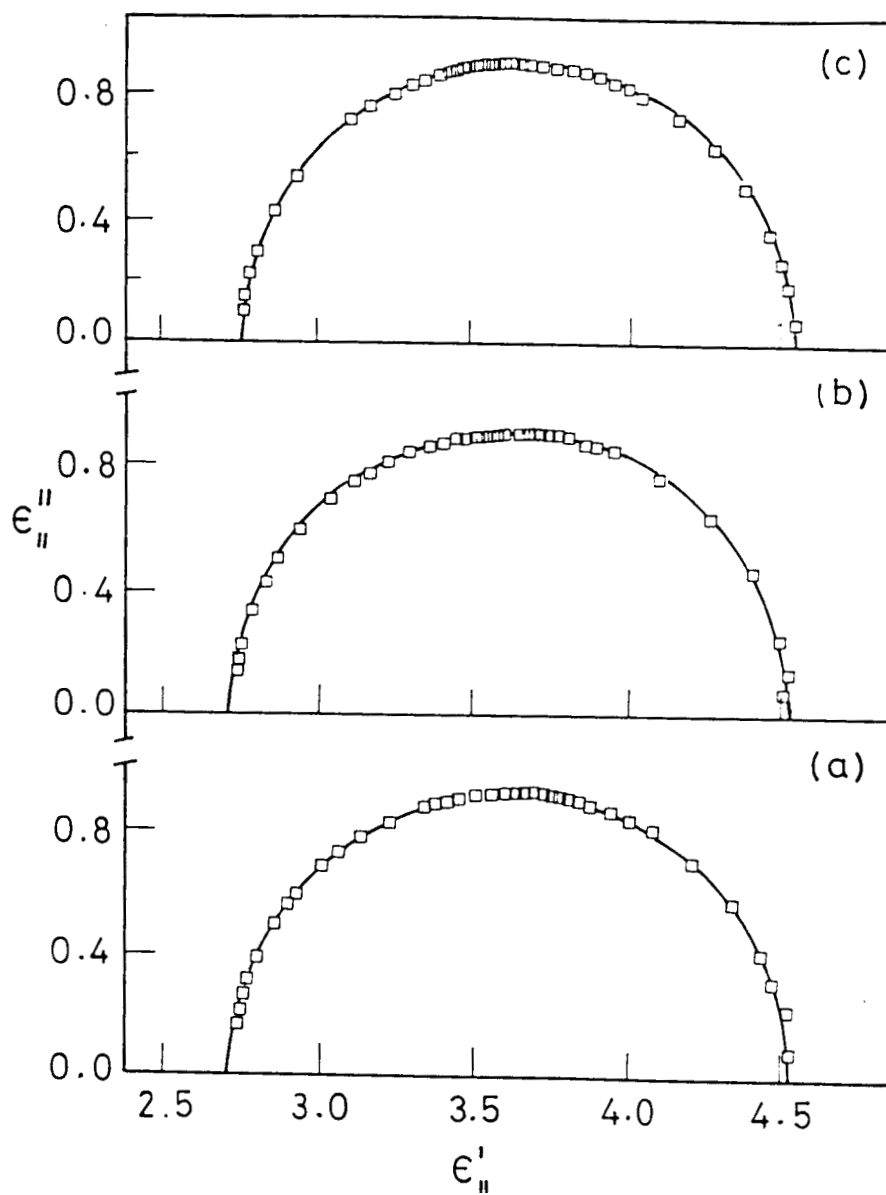


Figure 5.22

Representative Cole-Cole plots in the smectic  $A_d$  phase [(a) 134.45°C, (b) 131.35°C and (c) 124.45°C] of 43 mol % DB8ONO<sub>2</sub>/DB10ONO<sub>2</sub> mixture.

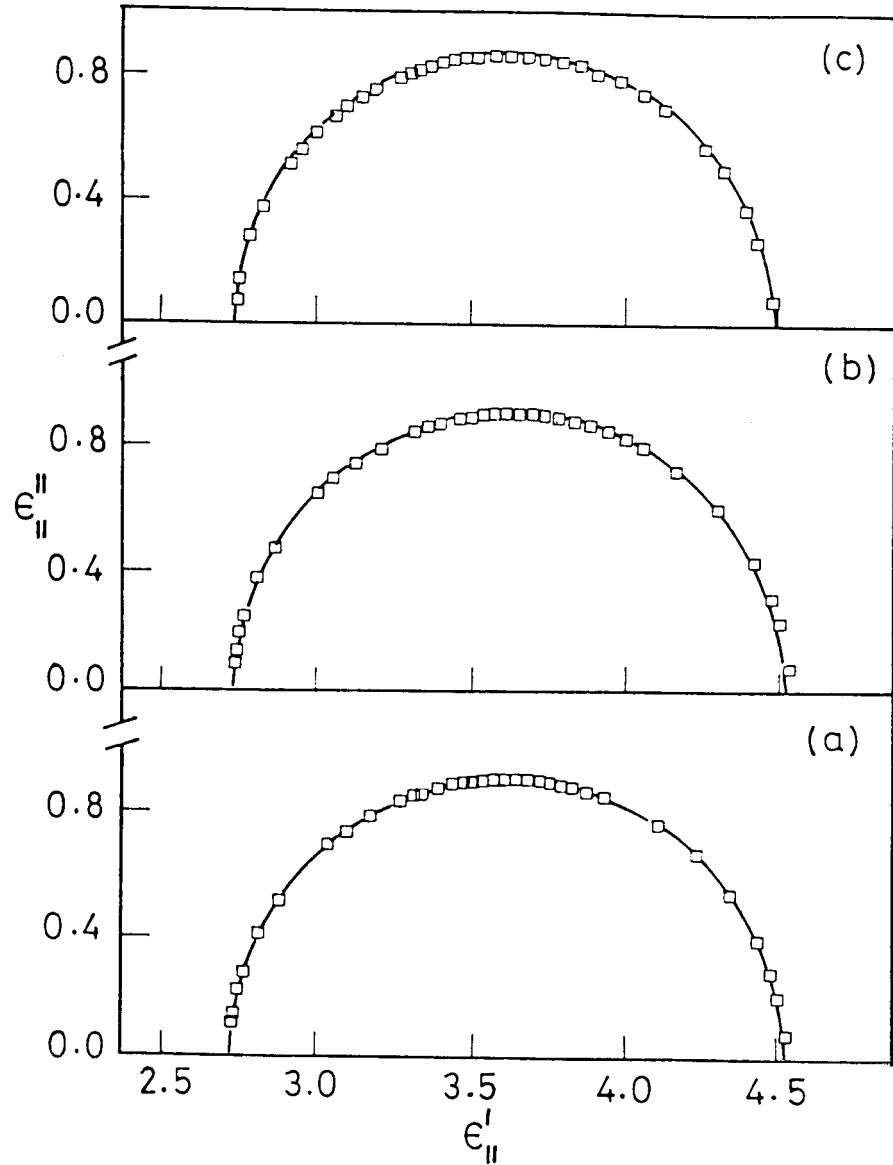


Figure 5.23

Representative Cole-Cole plots in the smectic  $A_1$  phase  
 [(a) 123.4°C, (b) 122.35°C and (c) 120°C] of 43 mol %  
 DB8ONO<sub>2</sub>/DB10ONO<sub>2</sub> mixture.

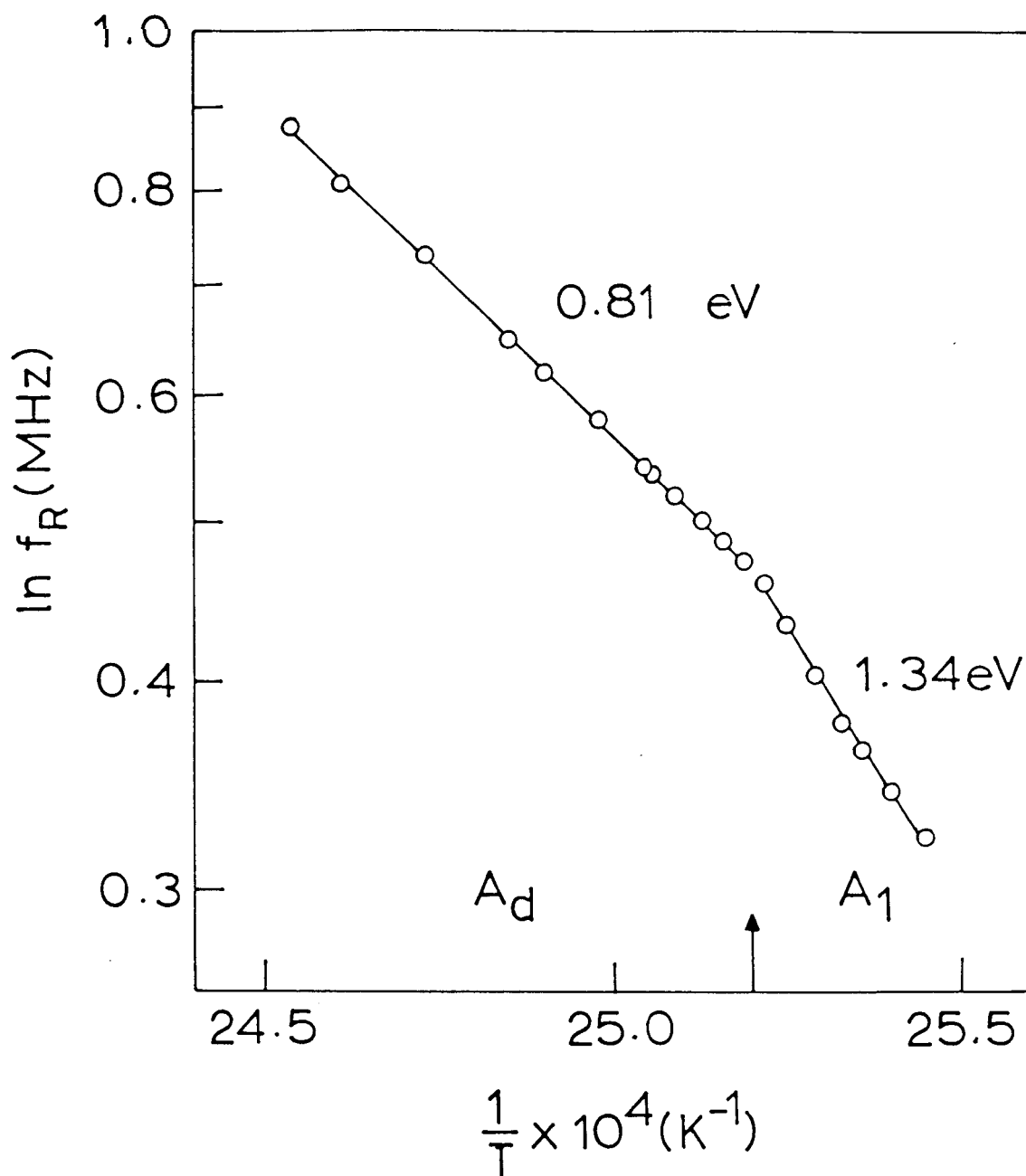


Figure 5.24

Relaxation frequency  $f_R$  vs.  $1/T$  plot in the smectic  $A_d$  and  $A_1$  phases of 43 mol %  $DB8ONO_2/DB10ONO_2$  mixture.

TABLE 5.5

Frequency of relaxation  $f_R$  as a function of temperature in the smectic  $A_d$  and  $A_i$  phases of 43 mol % DB8ONO<sub>2</sub>/DB10ONO<sub>2</sub> mixture

S.No.	Temperature (°C)	Frequency of relaxation (in MHz)		Mean $f_R$
		From loss curve	From Cole-Cole	
<b>Srnectic A<sub>d</sub></b>				
1	134.45	0.880	0.870	0.875
2	133.35	0.805	0.806	0.806
3	131.35	0.730	0.731	0.731
4	129.45	0.650	0.649	0.650
5	128.65	0.620	0.622	0.621
6	127.3	0.560	0.578	0.579
7	126.25	0.540	0.542	0.541
8	125.95	0.535	0.537	0.536
9	125.5	0.520	0.518	0.519
10	124.9	0.500	0.505	0.503
11	124.45	0.488	0.489	0.489
12	123.95	0.475	0.473	0.474
<b>Smectic A<sub>i</sub></b>				
13	123.45	0.460	0.459	0.460
14	122.95	0.435	0.434	0.435
15	122.35	0.403	0.408	0.406
16	121.75	0.380	0.377	0.379
17	121.25	0.365	0.362	0.364
18	120.7	0.345	0.341	0.343
19	120.0	0.323	0.325	0.324

(CN) end group while the other one has a nitro ( $\text{NO}_2$ ) end group. It is therefore conceivable that the two dispersions seen by them could be due to these different types of molecular species.

### 5.5 MICROSCOPIC THEORY OF A-A TRANSITION

A theoretical description of the different types of A phases has been given by Longa and de Jeu<sup>33</sup> by considering the different types of intermolecular interactions. In this section, we shall briefly describe the salient features of their theory.

In their approach, Longa and de Jeu considered the influence of breaking the up-down symmetry of mesogenic molecules on the occurrence of smectic A phases. The constituent molecules are represented by spherocylinders with one point polarizability and one dipole moment, situated on the axis but away from the geometrical center. From estimates of the various types of interactions (dispersion, dipole-induced-dipole, and dipole-dipole) it is found that the occurrence of a ferroelectric  $A_f$  phase consisting of polarized layers is very unlikely. For strongly localized end dipoles an antiferroelectric  $A_2$  phase is favoured, consisting of double layers. A natural consequence of this theoretical description is that once classical (symmetrical) monolayer  $A_1$  phase and polar bilayer  $A_2$  phases are established, an antiferroelectric  $A_1$  phase is also found with a single-layer structure periodicity. (Longa and de Jeu there-



fore clearly distinguished polar  $A_1$  from non-polar  $A_1$ .) However the theory does not make any predictions concerning the dielectric behaviour of the different kinds of A phases.

In summary the studies described in this chapter show that there are interesting differences in the dielectric behaviour near the different types of A-A transitions. A detailed quantitative correlation of these differences with the structural differences as seen by Xray diffraction experiments has not been carried out so far. Such a study would be of considerable interest.

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