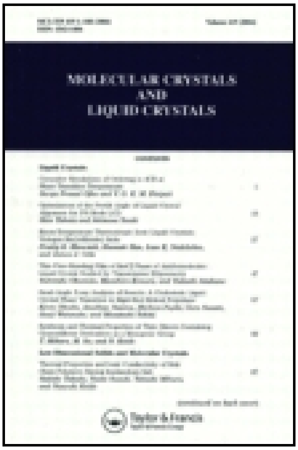

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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ODIC PHASES BETWEEN THE SOLIDS AND THE LIQUID CRYSTALS

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Abstract Normally there exist two separate groups of substances which are intermediate between crystals and liquids. One group forms the so-called plastic crystals (often known as ODIC phases). The other group forms various phases of liquid crystals.
This lecture concerns two substances of the PAA homologous series, in which a mixed sequence was discovered. There are the n=4 and n=5 members of the PAA series. In both substances sequences are : crystal, ODIC crystal, nematic liquid, isotropic liquid. An indication of such a "mixed" behaviour has been obtained in the calorimetry: entropies of fusion are for both substances much lower than those for smaller and larger n. Moreover, the neutron quasielastic scattering experiments as well as the dielectric relaxation measurements show an existance of molecular rotations in the ODIC phases before melting.

INTRODUCTION

It is widely known that there exist phases which are intermediate between crystals and liquids. They appear in two rather distinct groups: plastic crystals, on one hand, and liquid crystals,

on the other. Plastic crystal phases are sometimes called the ODIC (orientationally disordered crystal) ones. In most cases known so far, particular substances exhibit either the sequence crystal phases - ODIC phases - liquid, or the sequence crystal phases - liquid crystal phases - liquid. The former sequence appears when the molecules are nearly globular (eg. $(CH_3)_3CCl$), and the latter one does when the molecules are rod-like (eg. $H_3CO.C_6H_4.NON.C_6H_4.OCH_3$).
This paper provides evidence of the existence of ODIC phases (with fast uniaxial reorientations) between normal crystal phases and liquid crystal ones, corresponding to the sequence: crystal phases - ODIC phases - liquid crystal phases - liquid. These ODIC phases were observed by our Cracow Molecular Crystals and Liquid Crystals Group during a systematic study of seven members of the di-alkoxy-azoxybenzene series (i.e. of $H_{2n+1}C_nO.C_6H_4.NON.C_6H_4.OC_nH_{2n+1}$ with n=1 - 7) by the neutron quasielastic scattering and the dielectric methods; substances with n=4 and n=5 exhibited then a quasielastic component in the neutron scattering pattern and also a dielectric relaxation in the GHz range in the phases below the melting point /1-5/. It has to be pointed out here that the neutron quasielastic scattering method is sensitive to stochastic changes of the positions of protons in the molecule, whereas the dielectric relaxation method is responding to changes of direction of the electric dipole moments.

QNS AND DIELECTRIC BEHAVIOUR OF THE TWO SUBSTANCES IN THE NEMATIC PHASE

The substance with n=4, di-butoxy-azoxybenzene, abbreviated as BOAOB, exhibits the following phase sequence:

$$\mathrm{CrIII} \xrightarrow{+48C} \mathrm{CrII} \xrightarrow{+85C} \mathrm{CrI} \xrightarrow{+104C} \mathrm{N} \xrightarrow{+138C} \mathrm{I},\ /6/.$$

The substance with n=5, di-pentyloxy-azoxybenzene, abbreviated as POAOB, exhibits the phase sequence:

$$\mathrm{CrII} \xrightarrow{+68C} \mathrm{CrI} \xrightarrow{+76C} \mathrm{N} \xrightarrow{+124C} \mathrm{I}\ ,\quad /6/.$$

The neutron quasielastic scattering spectra (abbr. QNS) of the two substances show in the nematic phase typical broad wings, as it is presented in Figs 1 and 2. These wings are interpreted as caused by an internal rotational diffusion in the respective molecules. Reorienting units are the moieties composed of the alkoxy tails coupled with the benzene rings /4/. The C-N bonds i.e. the bonds between the benzene rings and the central NON group serve as the axes around which the reorientation takes place. The reorientational correlation time (τ_1) is ~4.5 ps /1,2/ for both POAOB samples, for the one with deuterated alkoxy tails (d_{22}) and the nondeuterated one (d_0). Since deuteration means masking in the incoherent neutron scattering method, the fact that the correlation time is the same for both samples supports the statement that the alkoxy tails together with the benzene rings form rigid units (at least for the neutron time scale). Similar results were obtained for BOAOB in the nematic phase /5/.

We believe that the reorientational motion we sug-

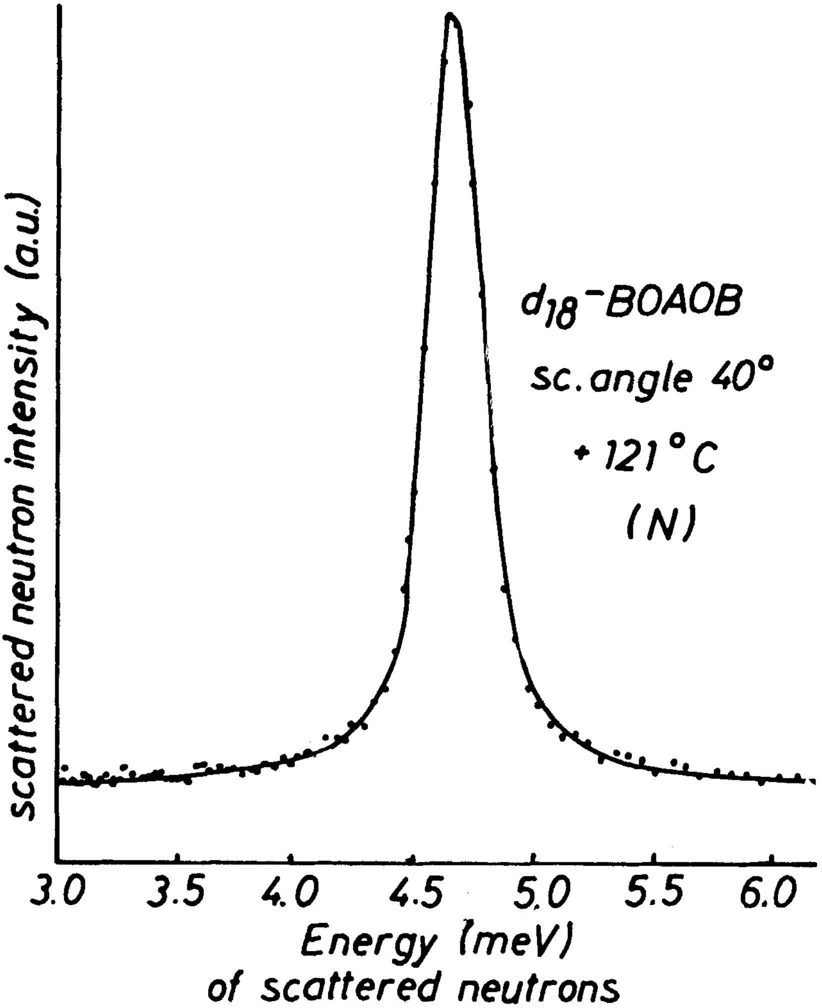

FIGURE 1. QNS spectrum for d_{18}-BOAOB in nematic phase. Solid curve corresponds to a model in which the moieties composed of alkoxy tails coupled with benzene rings perform rotational diffusion around the benzene para axes.

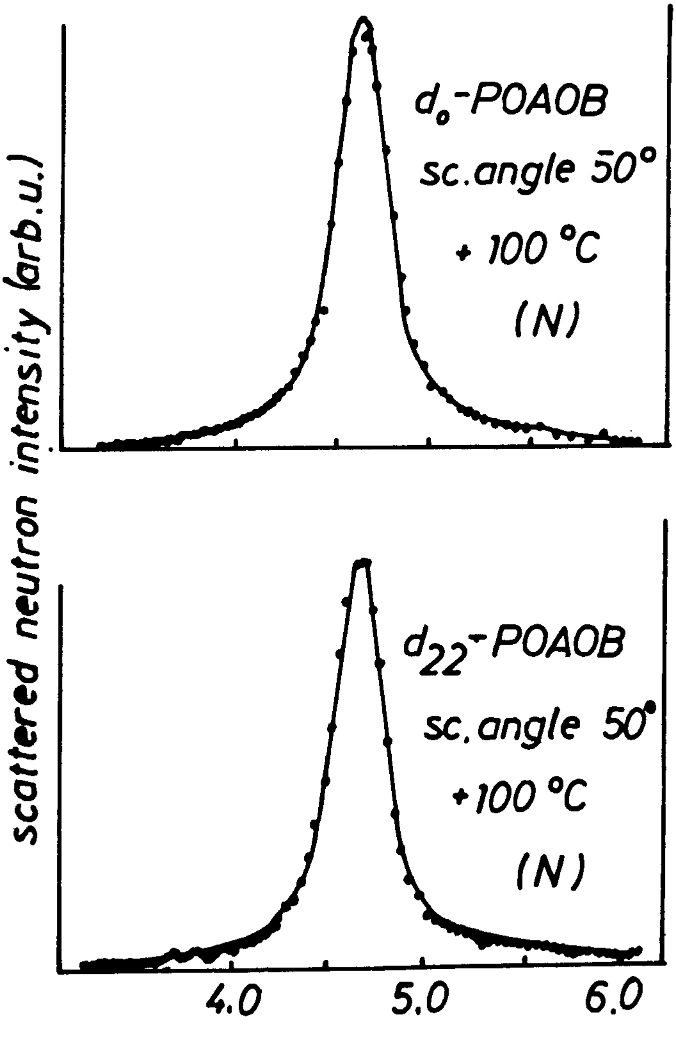

FIGURE 2. QNS spectra for d_0-POAOB and d_{22}-POAOB in nematic phase. Solid curves correspond to a model in which the moieties composed of alkoxy tails coupled with benzene rings perform rotational diffusion around the benzene para axes /1/.

gest is strongly coupled with the reorientational motion of the molecule as a whole around its long axis. This other motion occurs, however, in a different time scale, as will be seen from dielectric measurements.

The dielectric relaxation measurements (abbr.DR) were carried out for the two substances in the nematic phase /1,3,5/. Fig. 3 gives, as an example, the results obtained for POAOB /3/. For the $\vec{E} \parallel \vec{n}$ geometry ($\vec{E}$ is the electric field which causes the polarisation which relaxes and $\vec{n}$ is the nematic director) we can see two relaxation regions; one connected with the reorientation of the molecule around the short and one around the long axis. For $\vec{E} \perp \vec{n}$ only the latter process is seen. Both processes are detected mainly via the perma-

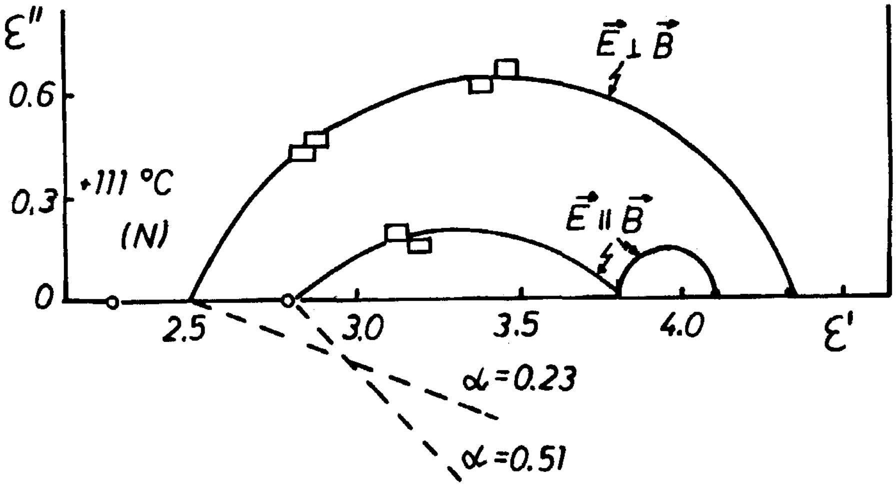

FIGURE 3. The Cole-Cole plots obtained from DR measurements for POAOB, in nematic phase /1/.

nent dipole moment of the NON group. The slow process (reorientation of the whole molecule around the short axis) has a relaxation time between 10^{-7} - 10^{-8}s. The fast process (reorientation of the whole molecule around the long axis) has a relaxation time $\sim$100 ps, hence it definitely is a different process from that responsible for the QNS wings. The parameter α of Fig. 3 differs significantly from 0. This indicates that the relaxation process considered is, in fact, a complicated one.

Similar results were obtained for the BOAOB in the nematic phase /5/. The relaxation time of the slow motion is now $23 \cdot 10^{-9}$s (for +120°C) and that for the fast motion is 53 ps (for the same temperature). The latter value agrees very well with the one reported by Axmann /7/ (57 ps). Again, the fast process observed in DR occurs in a different time scale than that observed in QNS. Like for POAB, we believe that the QNS results are explained by the moieties motion, whereas the DR results correspond mainly to the reorientation of the molecule as a whole around the long axis.

QNS AND DR RESULTS FOR POAOB IN THE SOLID PHASES

Fig. 4 presents examples of the QNS spectra of d_0-POAOB and d_{22}-POAOB in the CrI phase /1,2/. One can see that these spectra have only slightly narrower quasielastic wings than those of Fig.2, corresponding to the nematic phase. The analysis shows that the spectra are now better described

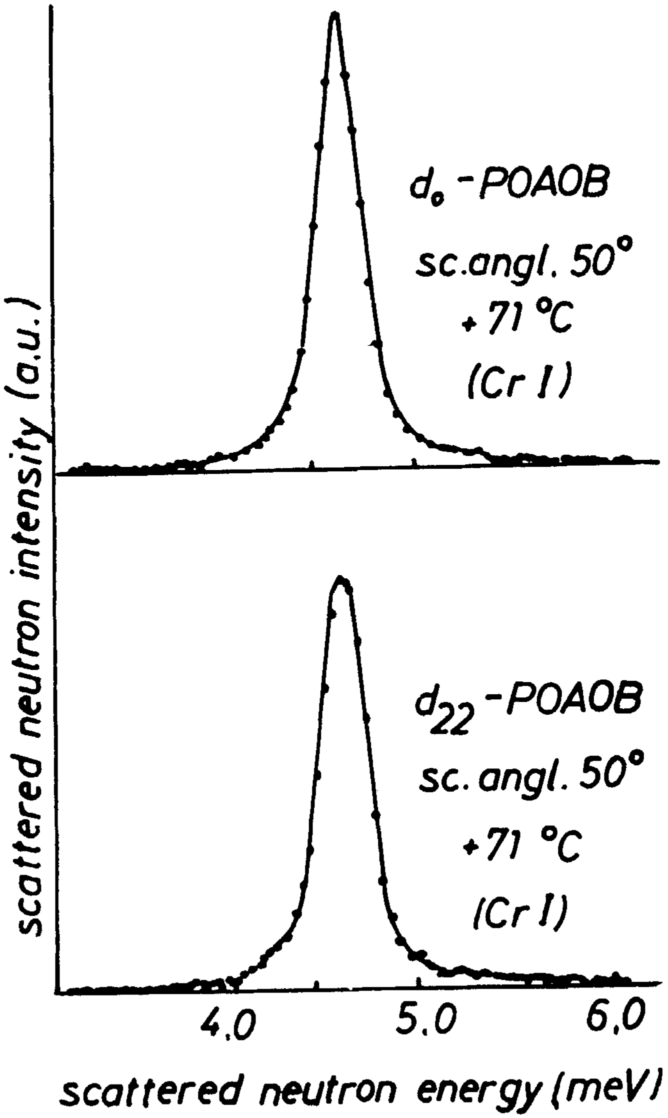

FIGURE 4. QNS spectra for d_0POAOB and d_{22}-POAOB in CrI phase. Solid curves correspond to a model in which the moieties composed of alkoxy tails coupled with benzene rings perform 180° rotational jumps around the benzene para axes /1/.

by the model in which the moieties perform 180° angular jumps than by the model in which they perform a rotational diffusion around the benzene para axes. The correlation time (or rather residence time τ, according to the model) is $\sim$4.5ps /1/, i.e. practically the same as in the nematic phase. Also, there is no difference in the τ-values for the d_{22} and d_0 samples, which (like in the nematic phase) supports the statement that the alkoxy tails form rigid units together with the benzene rings.

It is obvious that the mobilities of molecular moieties, as seen by QNS, are nearly equal in both the nematic and CrI phases; the QNS spectrum for CrII phase, however, cannot be distinguished from the instrumental resolution function. Thus we have to conclude that the reorientational motions in question become seriously hindered or even stop completely at the CrI/CrII transition.

Fig. 5 shows the temperature variation of the DR data /1,3/ obtained when going from the nematic, through CrI, to CrII phase (on cooling) and reverse (on heating). These data also indicate that the molecular mobility exists in the CrI phase. In the case of the DR results, now discussed, this mobility has to be attributed to the whole molecules.

It thus seems natural to conclude that the CrI phase of POAOB is such in which the molecular moieties as well as the whole molecules reorientate fast. As we have seen, the correlation times for the moieties motion are of the order of sever-

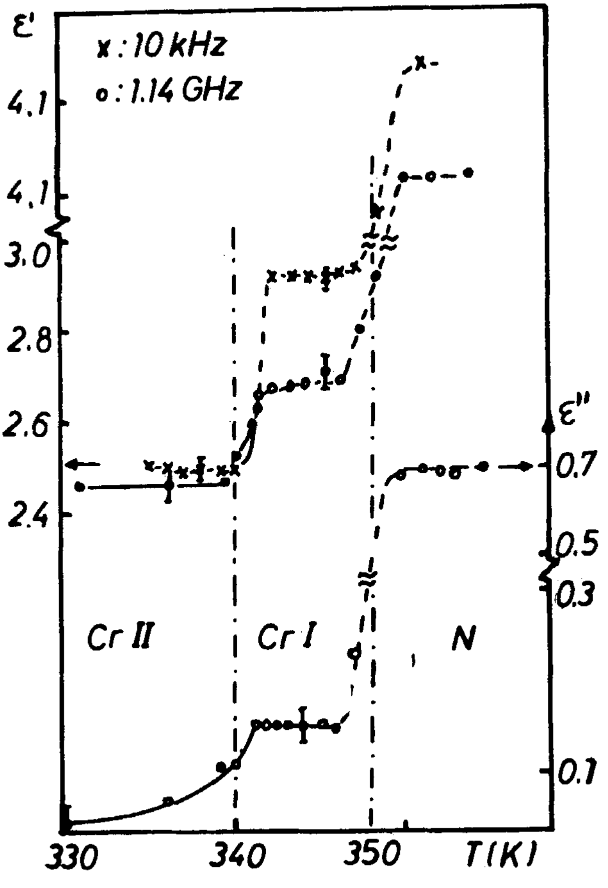

FIGURE 5. Temperature dependence of ε' and ε'' in POAOB /1/.

al ps. The relaxation times for the reorientation of the whole molecule are of the order of 10^{-10}s, since the curves in Fig. 5 correspond to the GHz frequency range. Although the motion of the whole molecules may be quite complicated, it must possess a reorientational character, since both components of the electric susceptibility, ε' and ε'', are detectable.

The CrII phase of POAOB behaves as a normal molecular crystal.

QNS AND DR RESULTS FOR BOAOB IN THE SOLID PHASES

Fig. 6 presents an example of the QNS spectrum of the d_{18}-BOAOB in the CrI phase /5/. This spectrum shows the quasielastic wings, albeit significantly smaller than those in the nematic phase which were shown in Fig. 1. Moreover, the model fitting to this spectrum (and to other spectra obtained for d_{18} and d_0 samples, for various angles) shows that the elastic component is considerably more intense than the model one. We interpret this as an indication that the moieties angular jumps are in the CrI phase of BOAOB restricted to an angle smaller than 180 (very damped librations). Similar results were obtained for the CrII phase, where, the quasielastic wings are still less intense.

Fig. 7 shows some of the DR results obtained for BOAOB /5/. The ε' results are qualitatively similar to those for POAOB. ε' exhibits three steps: one at the CrIII/CrII, another at CrII/CrI and the

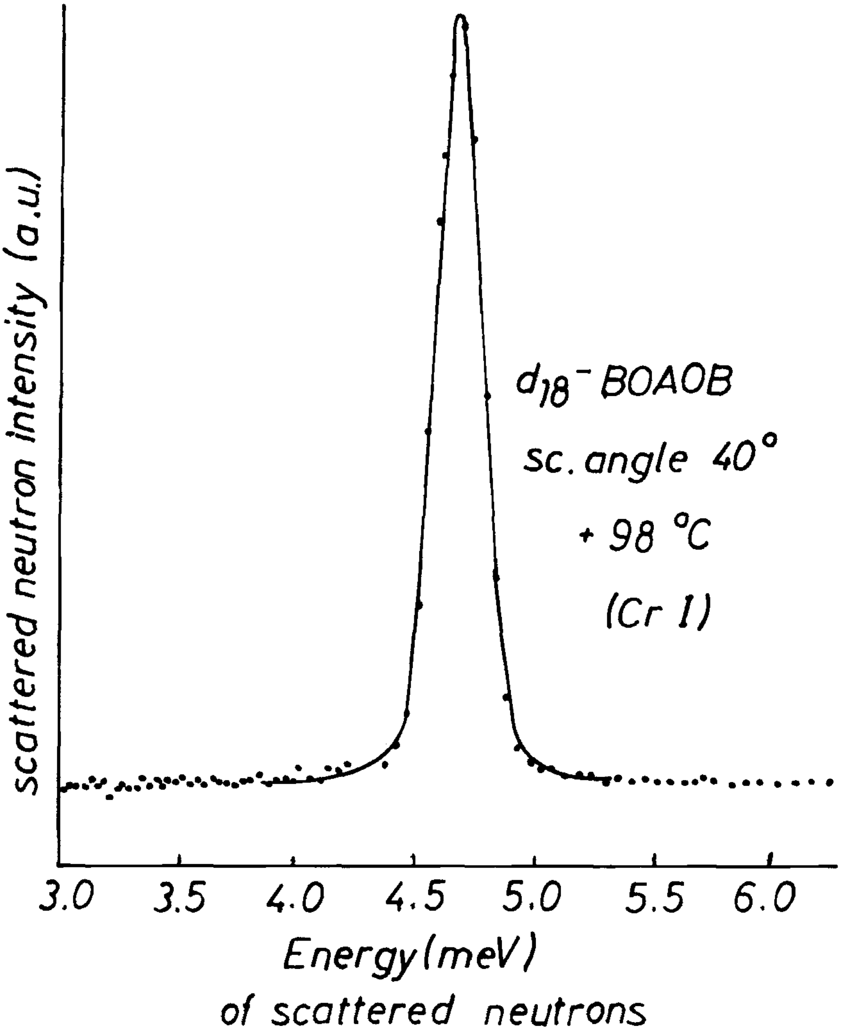

FIGURE 6. QNS spectrum for d_{18}-BOAOB in CrI phase. Solid curve corresponds to a model in which the moieties composed of alkoxy tails coupled with benzene rings perform angular jumps, within an restricted angle smaller than 180°, around the benzene para axes.

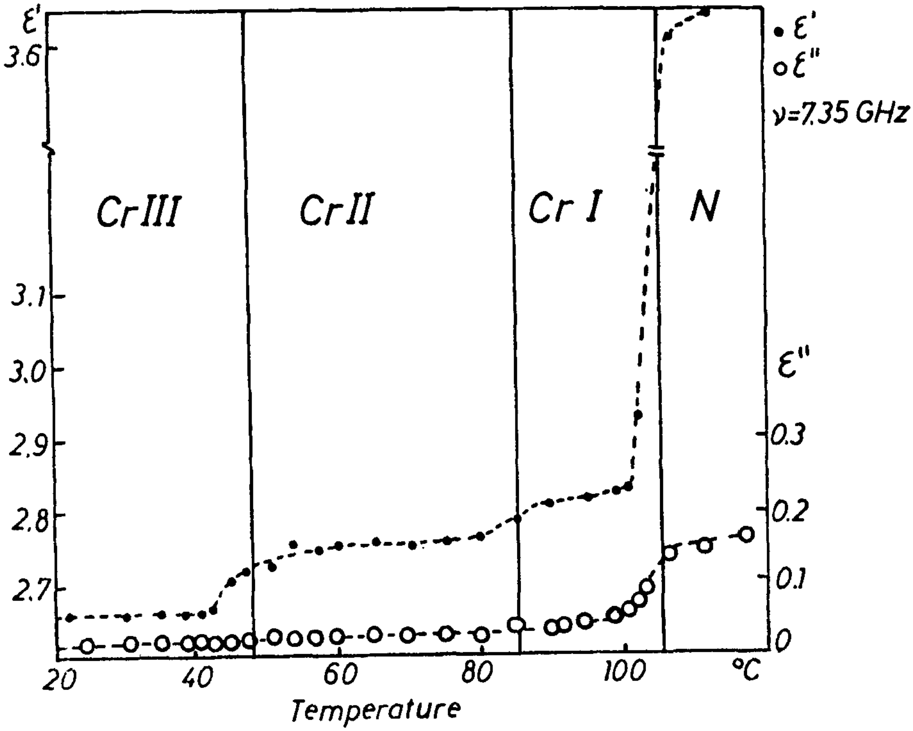

FIGURE 7. Temperature dependence of ε' and ε'' in BOAOB. /5/.

third at CrI/N transitions. This behaviour indicates that the CrII and CrI phases are mobile. The ε''results however are different from those of POAOB. The dielectric losses are very small in the whole range of the solid. The losses show up only when the nematic phase is reached. Therefore, we believe that the ε'' behaviour can be connected with the damped librations of the molecular dipol moment rather than with the reorientation relaxation.

It seems natural to conclude that the CrI and CrII phases of BOAOB are characterized by a large angle and very damped librations both internal (moieties in the molecules) and external (the molecules as wholes). The CrIII phase of BOAOB behaves as a normal molecular crystal.

CONCLUSIONS AND DISCUSSION

Our conclusion is that the CrI phase in POAOB is an ODIC phase, in which the molecules and their moieties perform uniaxial reorientations, whose time scales are 100 ps and several ps respectively. Compared to this, the CrI and CrII phases in BOAOB are only "nearly" ODIC, since they correspond rather to large angle damped librations of the molecules and the moieties. For both substances the axes to reorientations (librations) are close to long axes of the molecules.

It is interesting to note that the existance of such mobile phases could have been expected to show up just for these members of the di-alkoxy-azoxybenzene series (with n=4 and 5), since the melting entropies show, for these members, a pronounced minimum for n=4 and n=5 /1/ (Fig.8). Normally, the melting entropy is much smaller when the melting takes place from the ODIC to fluid phase than when it occurs between a normal crystal and a fluid.

One could perhaps suspect that the mobile phases are some kind of higher order smectics. This, however, seems improbable (at least for POAOB),

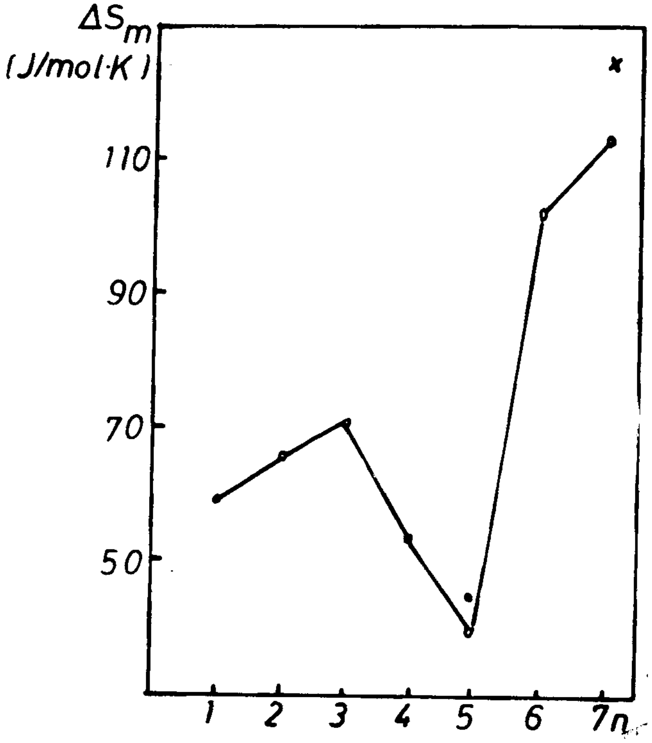

FIGURE 8. Entropies of melting for $H_{2n+1}C_nO.C_6H_4.N_2O.C_6H_4.OC_nH_{2n+1}$ compounds /1/.

since the X-ray diffraction spectrum (for CrI phase) does not show any resemblance to that of smectics. Therefore, we are inclined to say that in the now reported substances the sequences of phases are:

BOAOB: Cr → ODIC II (libr.) → ODIC I (libr.)
→ N → Liq.

POAOB: Cr → ODIC → N → Liq.

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