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Dielectric studies of the hexatic B-smectic A and crystal B-smectic A transitions

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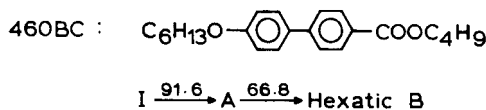
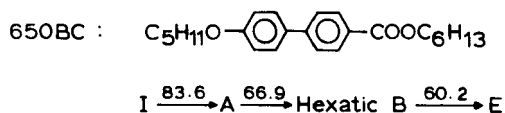
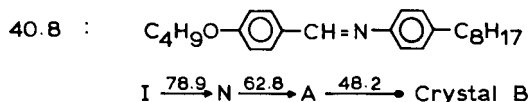
Static dielectric constants, ϵ_{\parallel} and ϵ_{\perp} as well as the low frequency dielectric dispersion of ϵ_{\parallel} have been studied in the vicinity of the hexatic B-smectic A transition in *n*-hexyl-4'-pentyloxybiphenyl-4-carboxylate (65OBC) and *n*-butyl-4'-hexyloxybiphenyl-4-carboxylate (46OBC) and also near the crystal B-smectic A transition in *n*-(4-*n*-butyloxybenzylidene)-4-*n*-octylaniline (4O.8). While the behaviour of the dielectric anisotropy is essentially similar for both transitions, the dispersion results show significant differences.

1. Introduction

The smectic B liquid crystalline phase is known to possess a layered structure with molecules orthogonal to the layer plane and ordered hexagonally within the layer. X-ray studies in the B phase of *n*-(4-*n*-butyloxybenzylidene)-4-*n*-octylaniline (4O.8) showed that the hexagonal order in the B phase involves positional correlations which are three dimensional (3D) and long range [1]. This B phase is therefore now generally known as the 'crystal B' phase. Birgeneau and Litster [2] predicted the existence of another type of B phase consisting of 2D hexatic layers which interact to provide long range 3D bond orientational order. This novel phase, called 'hexatic B', was soon observed in *n*-hexyl-4'-pentyloxybiphenyl-4-carboxylate (65OBC) by Pindak *et al.* [3] who from X-ray studies of free standing films found that the hexatic B phase exhibits short-range in-plane positional correlation but long range 3D six-fold bond orientational order. Since then a number of compounds with a molecular structure similar to 65OBC (for example, 46OBC) have been found to exhibit the hexatic B phase. It has also been shown that the crystal B-A transition in 4O.8 is first order [1, 4] while the hexatic B-A transition in both 65OBC and 46OBC is second order [4, 5]. We have carried out detailed dielectric studies on 4O.8, 65OBC and 45OBC with a view to seeing the difference in the dielectric properties near the crystal B-A and hexatic B-A transitions. We have also measured very accurately the variation of the layer spacing near these transitions.

2. Experimental details

The transition temperature (in °C) of the samples used in the present study are given below:



X-ray diffraction experiments were conducted using a computer controlled Guinier diffractometer (Huber 644). $\text{CuK}_{\alpha 1}$ line was used as the source and a scintillation counter whose angular scans were controlled by a stepper motor served as the detector. A Hewlett-Packard computer (86B) was used to control the angular movement of the detector as well as to acquire and analyse the data. Further details of the X-ray set-up are described elsewhere [6]. The sample filled in a 0.5 mm diameter Lindemann capillary was cooled slowly from the isotropic/nematic phase in the presence of a 2.4 T magnetic field. After obtaining an oriented B phase the sample capillary was transferred to the goniometer head of the diffractometer. X-ray data were then taken by heating the sample. The precision in the layer spacing measurement was $\pm 0.05 \text{ \AA}$ or better, the temperature constancy being $\pm 10 \text{ mK}$.

The dielectric measurements were carried out using a Hewlett-Packard Impedance Analyser (4192 A). The static dielectric constants (ϵ_{\parallel} and ϵ_{\perp}) were measured at 1 kHz while the low frequency dielectric dispersion studies of ϵ_{\parallel} were carried out in the frequency range of 1 kHz–13 MHz. The sample thickness was typically 50–100 μm . A combination of silane coating and 2.4 T magnetic field was used for obtaining the homeotropic alignment needed for ϵ_{\parallel} measurements while only the magnetic field sufficed for ϵ_{\perp} measurement. The static dielectric constants were measured by varying the temperature at a rate of 4–5°C/hour. In the case of the dispersion data the temperature was maintained constant to within $\pm 25 \text{ mK}$.

3. Results

Although high resolution X-ray studies on both 40.8 and 650BC have been reported [1, 3], these investigations were essentially intended to probe the in-plane correlations in the two types of B phases and a detailed study of the layer spacing variation does not appear to have been carried out so far.

We have measured the temperature variation of the layer spacing, d , in the vicinity of the B–A transition in 40.8, 650BC and 460BC. These are given in figures 1–3. For 40.8 (figure 1) we have shown the data not only in the crystal B and A phases but also in the coexistence region. The difference in the wavevectors corresponding to the 001 reflection in the A and B phases being less than 0.3 per cent, the resolution of our set up did not permit us to separate out (as Pershan *et al.* [1] could in their high resolution

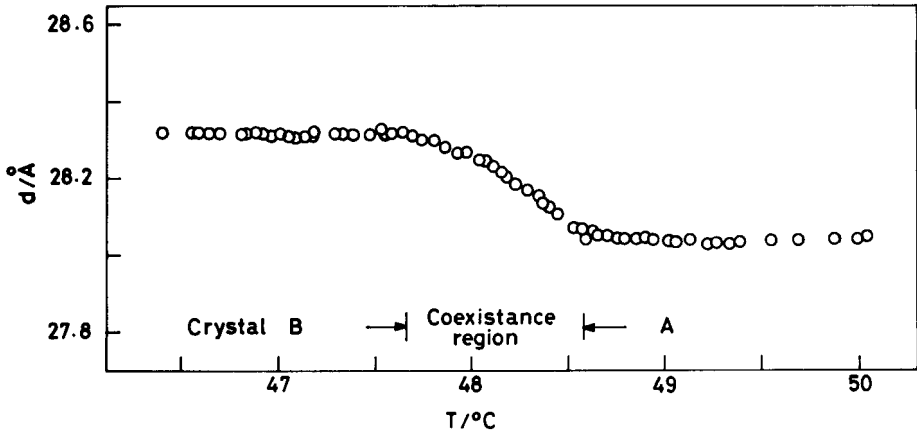


Figure 1. Variation of smectic layer spacing, d , in the neighbourhood of the crystal B-A transition in 4O.8. See text for the explanation of the data in the coexistence region.

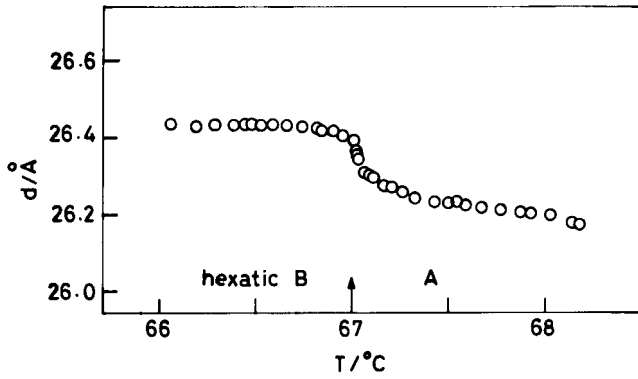


Figure 2. Variation of d with temperature in the vicinity of the hexatic B-A transition in 65OBC.

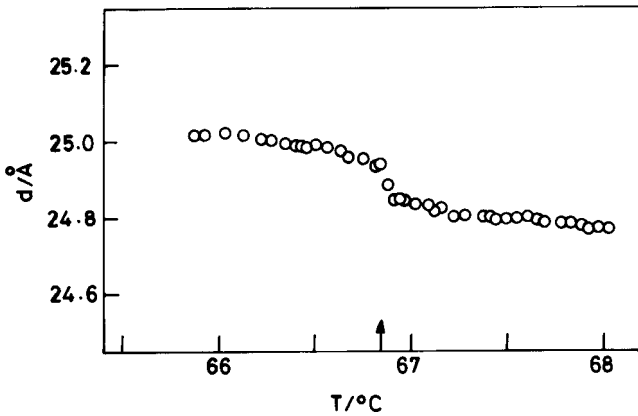


Figure 3. Variation of d with temperature in the vicinity of the hexatic B-A transition in 46OBC.

studies) the two diffraction peaks corresponding to the A and crystal B regions in the coexistence range. Instead we obtained a single but *broader* diffraction peak from which we could evaluate the *average* layer spacing in the coexistence region. Such a broadening of the diffraction maxima was not observed for either 65OBC and 46OBC near the hexatic B–A transition. The layer spacing shows only a very small increase (0.1–0.2 Å) on going from the A to the B phase in all three compounds. It is interesting that, although the changes in the in-plane positional ordering accompanying the crystal B–A and hexatic B–A transitions are drastically different [1, 3], there is hardly any significant difference in the variation of d at the two transitions.

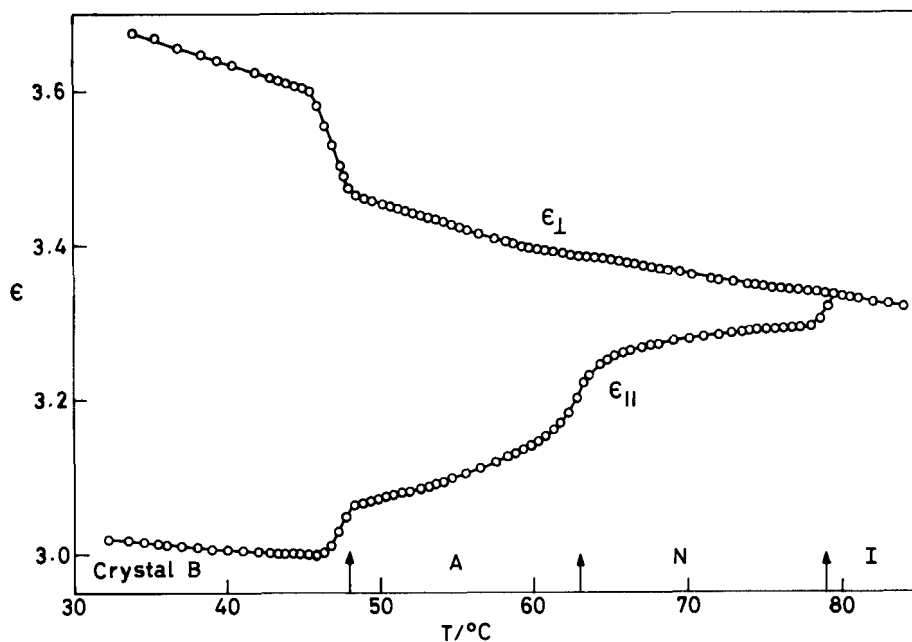


Figure 4. Variation of the static dielectric constants ($\epsilon_{||}$ and ϵ_{\perp}) with temperature in the different phases of 40.8.

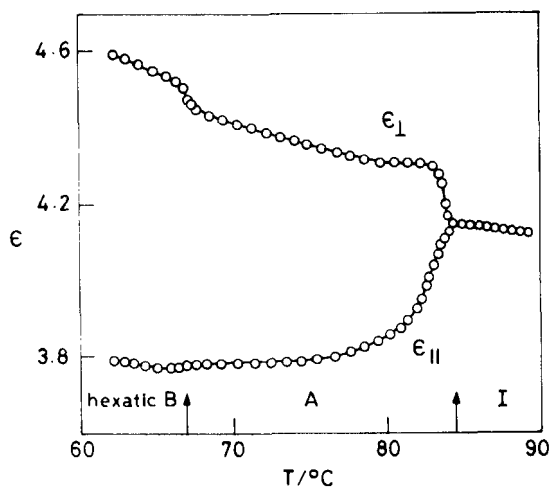


Figure 5. Variation of $\epsilon_{||}$ and ϵ_{\perp} with temperature in the different phases of 65OBC.

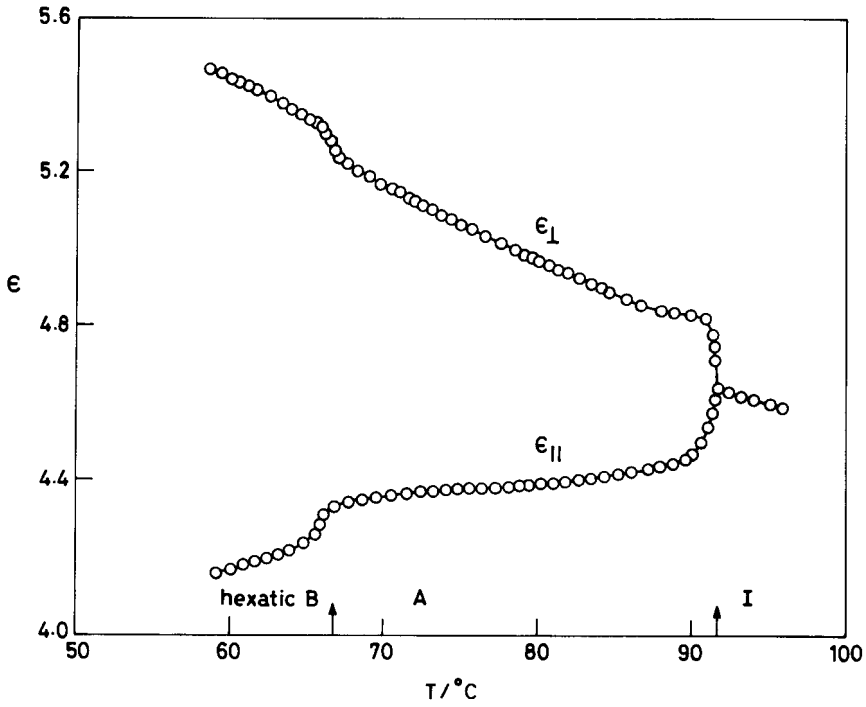


Figure 6. Temperature variation of ϵ_{\parallel} and ϵ_{\perp} in the different phases of 46OBC.

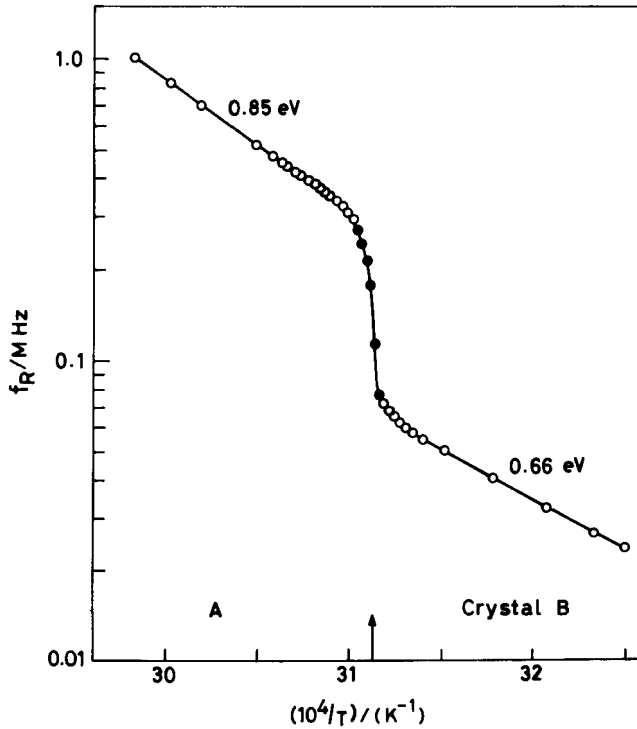


Figure 7. Plot of f_R , the low frequency relaxation of ϵ_{\parallel} , versus $1/T$ in the A and crystal B phases of 40.8. The solid circles denote the temperatures (in the two-phase region) for which the Cole-Cole plots are distorted (see figure 10).

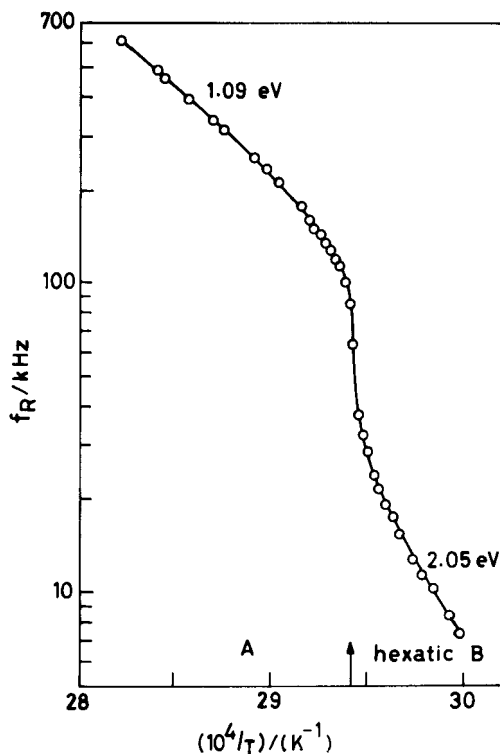


Figure 8. Plot of f_R versus $1/T$ in the A and hexatic B phases of 65OBC.

The variations of ε_{\parallel} and ε_{\perp} with temperature are given in figures 4–6 for 4O.8, 65OBC and 46OBC respectively. The behaviour of both ε_{\parallel} and ε_{\perp} are essentially similar in all the three cases. The dielectric anisotropy $\Delta\varepsilon$ is negative throughout and increases with decrease of temperature. The signature of both the crystal B–A and hexatic B–A transitions is seen as a sudden decrease (increase) in the value of ε_{\parallel} (ε_{\perp}) at the transition.

The frequency of relaxation of ε_{\parallel} , f_R , has been plotted against $1/T$ in the A and B phases of the three compounds in figures 7–9. Special care was taken to acquire data at close intervals of temperature (~ 250 mK) in the neighbourhood of the transition. The activation energies, W , in the A and B phases, evaluated from the linear portions of the f_R versus $1/T$ plot are also given in the same figures. Several interesting features are clear from these diagrams: (i) There is a drastic decrease in f_R (by about a factor of four) on going over from the A to the B phase in all the three compounds. (ii) For 4O.8 the variation of f_R is linear in the A and crystal B phases almost up to the transition temperature (figure 7). In the case of 65OBC and 46OBC, f_R shows marked pre-transitional variations in both A and hexatic B phases, the effect being more pronounced in the hexatic B phases (figures 8 and 9). (iii) The value of W in the crystal B phase of 4O.8 is less than that in the A phase whereas in the case of both 65OBC and 46OBC $W_{\text{hex. B}} > W_A$.

As remarked earlier, data were collected at close intervals of temperature near the B–A transitions in order to see if the first order crystal B–A transition and the second order hexatic B–A transition show any differences in the dielectric dispersion. Figures 10 and 11 show Cole–Cole plots for a series of temperatures near the B–A transition for 4O.8 and 65OBC respectively. It is clear that in 4O.8 the Cole–Cole plot

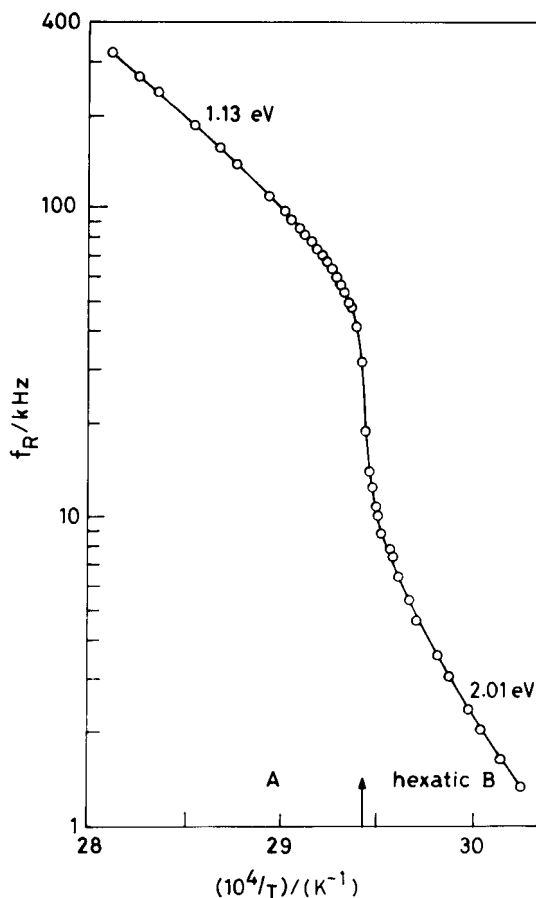


Figure 9. Plot of f_R versus $1/T$ in the A and hexatic B phases of 46OBC.

is a perfect semicircle in the A (figure 10(a)) and crystal B (figure 10(e)) phases, signifying a single relaxation process. However, in the two phase region the plot is not a perfect semicircle (see figure 10(b-d)), the distortion being maximum in the middle of the coexistence region. This is due to the superposition of two relaxation frequencies corresponding to the A and B regions. This effect is similar to the averaging of the layer spacing in the two phase region mentioned earlier. On the other hand it was found that for both 65OBC and 46OBC, the Cole-Cole plot was a perfect semicircle for all temperatures. Representative plots for 65OBC, shown in figure 11, clearly illustrate this. Thus a careful scrutiny of the Cole-Cole plots at temperatures in the close vicinity of the transition shows the differences between the first order crystal B-A and the second order hexatic B-A transitions.

There are some earlier reports [7-10] on the dielectric relaxation studies of compounds exhibiting the B phase. In all these cases a jump in f_R at the A-B transition has been observed. This has been attributed to two factors, namely (1) the increased two dimensional ordering of the centres of molecules within the smectic B layers leading to a greater hindrance to the reorientation of the long molecular axis compared to the A phase, and (2) the first order nature of the A-B transition. We now know from high resolution X-ray scattering studies [1, 3] that in-plane positional ordering of the molecules in the layer is widely different for the crystal B and hexatic B phases. The in-plane correlations extend to at least 14000 Å in the case of crystal

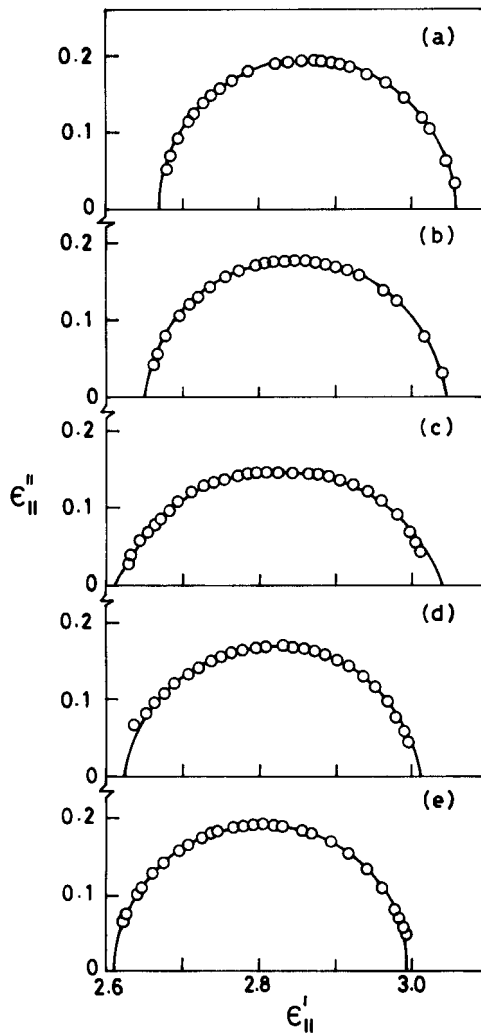


Figure 10. Cole-Cole plots at different temperatures in the vicinity of the crystal B-A transition in 4O.8. (a) A phase, 51.5°C, (b)–(d) two-phase region, 48.3, 48.1 and 47.9°C respectively, (e) crystal B phase, 44.3°C.

B phase while the corresponding value in the hexatic B phase is only about 100 Å. As mentioned earlier, we also know from high resolution a.c. calorimetric studies [5] that the crystal B-A transition in 4O.8 is first order while the hexatic B-A transition in 65OBC and 46OBC is second order. Despite these differences, a jump in f_r of about the same magnitude is seen by us for both crystal B-A and hexatic B-A transitions. This could perhaps be due to the existence of long range bond orientational order in both crystal B and hexatic phases, this being absent in the A phase.

In conclusion our studies show that, although essentially the same behaviour in $\Delta\epsilon$ and f_r is seen at both the crystal B-A and hexatic B-A transitions, the activation energy in the crystal B phase is less than that in the A phase while the opposite is the case for the hexatic B phase. The exact correlation between the structural differences of the crystal B and hexatic B phases and the differences in their dielectric behaviour is still an open question.

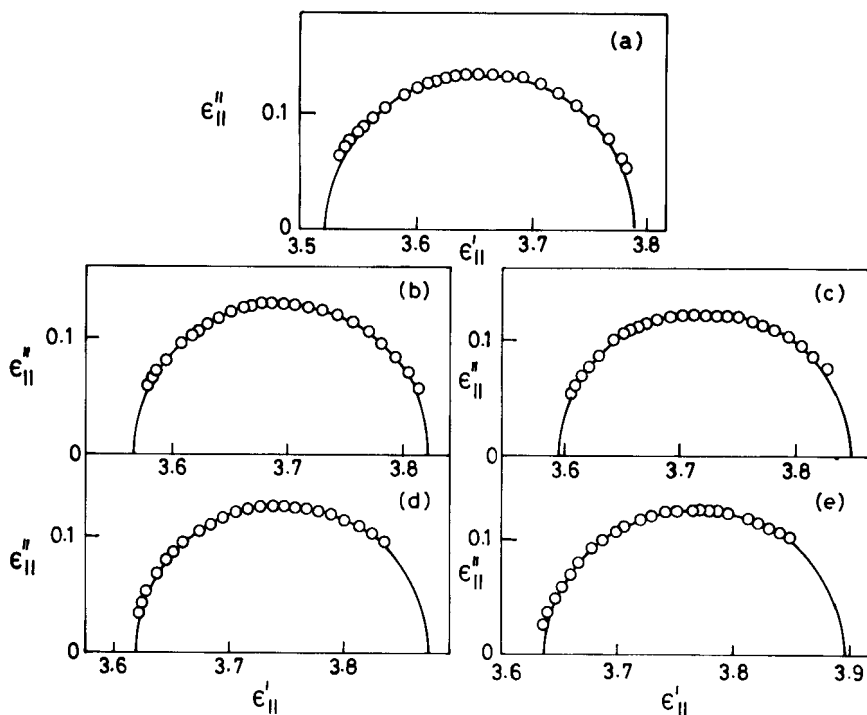


Figure 11. Cole-Cole plots at different temperatures in the vicinity of the hexatic B-A transition in 65OBC. (a) A phase, 71.3°C, (b) A phase, 67.9°C (c)-(e) hexatic B phase, 66.8, 65.6 and 64°C respectively.

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