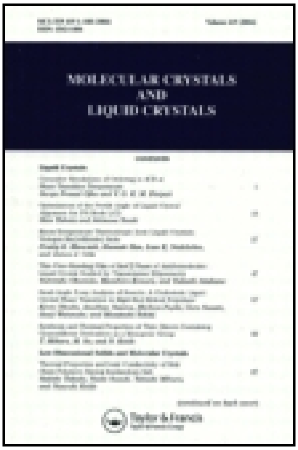

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Dielectric Behavior near a Smectic A_d-Smectic A_2 Critical Point

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Dielectric Behavior near a Smectic A_d-Smectic A_2 Critical Point

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We present precise measurements of the static dielectric constant near the smectic A_d-smectic A_2 critical point in a binary system. Detailed analysis of the data obtained for several mixtures has been done to locate the critical point concentration. Results of a dielectric dispersion study near the A_d-A_2 transition are also presented.

Keywords: A-A transition, critical point, dielectric studies

INTRODUCTION

According to the mean-field theory,[1] the A_d-A_2 transition is identical to the liquid-gas transition and as such can terminate at a critical point. (Hear A_d and A_2 refer to the partially bilayer and bilayer smectic A phases respectively.) More rigorous treatments of the transition have since been proposed.[2,3]

The first experimental observation[4] of the A_d-A_2 critical point was in a binary system of 4-*n*-undecyloxyphenyl-4′-(4″-cyanobenzyloxy) benzoate (or 110PCB0B) and 4-*n*-nonyloxybiphenyl-4′-cyano benzoate (or 90BCB), employing high precision x-ray techniques. Subsequently, high resolution calorimetric studies[5] were conducted on the same system which confirmed the conclusions arrived at from the x-ray studies. In the present paper, we report precise dielectric measurements on the same binary system, which again reveal the critical point in a striking fashion. The results of these measurements are in excellent quantitative agreement with the x-ray and calorimetric experiments.

EXPERIMENTAL

The measurements were carried out using an impedance analyser (HP 4192A). The static dielectric constants ($\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$) were determined at 10 kHz. The low frequency $\varepsilon_{\parallel}$ dispersion studies were done in the frequency range of 1 kHz-13 MHz. The sample (thickness ~ 25 μm) was aligned by cooling it from the nematic phase at a slow rate in the presence of a 2.4T magnetic field. The static measurements were carried out by varying the temperature at a uniform rate of 4–5°C/hour. During any dispersion measurements the temperature was maintained to a constancy of 25 mK. In all we have studied eight binary mixtures, x = 0.55, 0.59, 0.63, 0.65, 0.68, 0.72, 0.80, 0.90 in addition to the pure compound 110PCB0B. Here x indicates the mole fraction of 110PCB0B in the mixture.

RESULTS AND DISCUSSION

Figures 1 and 2 show the temperature variation of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ in the A_d and A_2 phases, for x = 0.63 and 0.80. Whereas, x = 0.63 shows a steep change in $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ across the transition (~120.7°C), x = 0.80 shows a much smoother variation with change of temperature. Previous x-ray studies[4] had identified x = 0.642 as the critical point concentration. Thus, x = 0.63 should show a first-order transition while x = 0.80 a continuous evolution without any phase transition. The clear difference between the curves for these two concentrations does indeed reflect this.

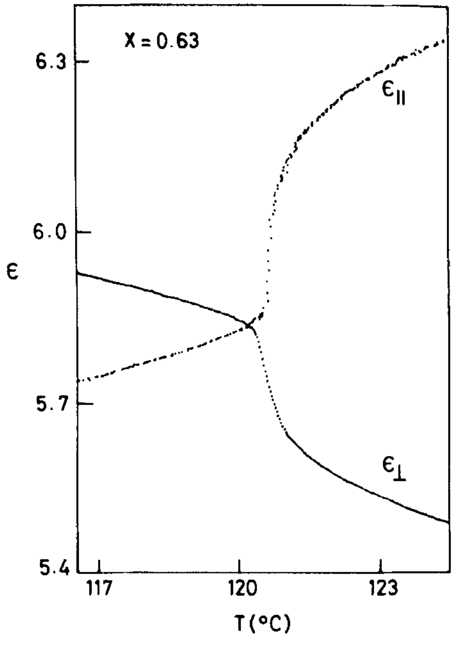

FIGURE 1 Temperature variation of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ for x = 0.63.

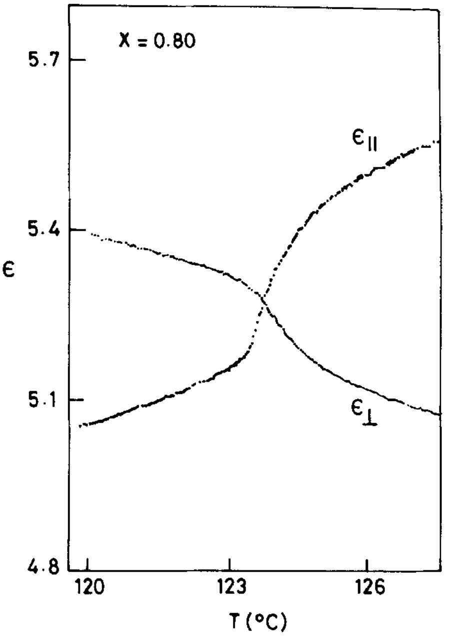

FIGURE 2 Plot of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ as a function of temperature for $x = 0.80$.

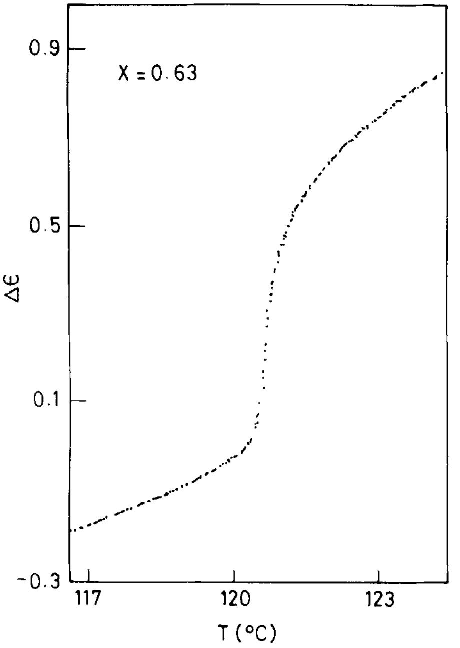

FIGURE 3 The variation of the dielectric anisotropy $\Delta\varepsilon$ with temperature for $x = 0.63$.

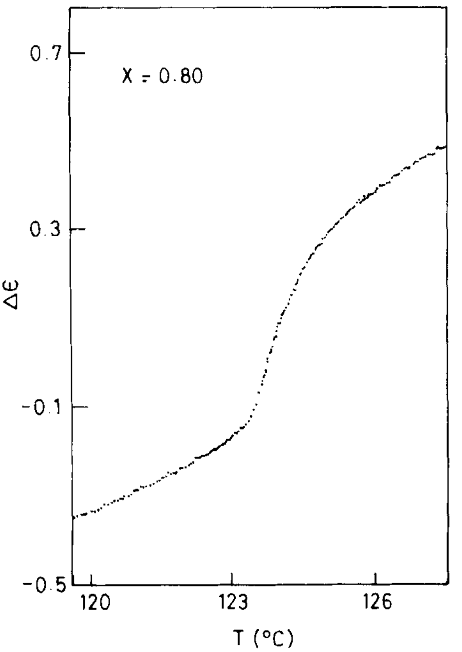

FIGURE 4 Δε versus temperature for $x = 0.80$.

As seen in Figures 1 and 2, there is a cross-over in the values of $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ near the transition. This feature has been observed for all the concentrations studied, though the relative thermal variation of $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ depends on the concentration. This effect is clearly shown up in the plots (Figures 3 and 4) of the dielectric anisotropy ($\Delta\varepsilon = \varepsilon_{\|} - \varepsilon_{\perp}$) as a function of temperature. Although the steepness of the $\Delta\varepsilon$ variation near the transition shows a concentration dependence, it was not significant enough to locate the critical point accurately.

In order to locate the critical point precisely we have proceeded as follows: The data of $\Delta\varepsilon$ versus T has been fitted to an expression of the form

$$\Delta\varepsilon = A^{\pm} t^{B} + C(T - T_c) + D \tag{1}$$

where $t = (T - T_c)/T_c$; A, B, C and D are constants.

It may be noted that a similar expression for the variation of specific heat was predicted by the one-loop model.[2] Expression (1) describes the data very well for all the mixtures studied. Figure 5 below shows the data and the fit for a representative mixture, $x = 0.63$. For comparison, we reproduce here the x-ray data of $x = 0.642$ for which a similar fit has been done (Figure 6) by Jeong et al.[5]

Using the fit parameters we have plotted in Figure 7, the thermal variation of $\Delta\varepsilon/\Delta T$ for three different mixtures, viz., $x = 0.55$, 0.63 and 0.72. We observe firstly that the peaks resemble very closely the specific heat curves[5] obtained near the critical point, and secondly that the height of the peak is much larger for $x = 0.63$ than for $x = 0.55$ or 0.72. The peak heights obtained in this manner are

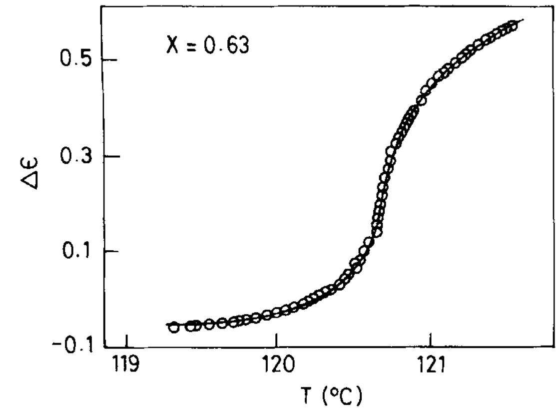

FIGURE 5 Plot showing the fitting of Δε to Equation (1); circles are measured points and solid line the fitting.

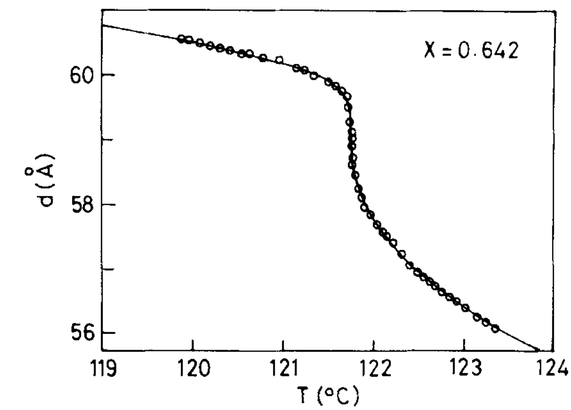

FIGURE 6 Fitting of the smectic layer spacing d to an expression similar to Equation 1 (from Reference 5).

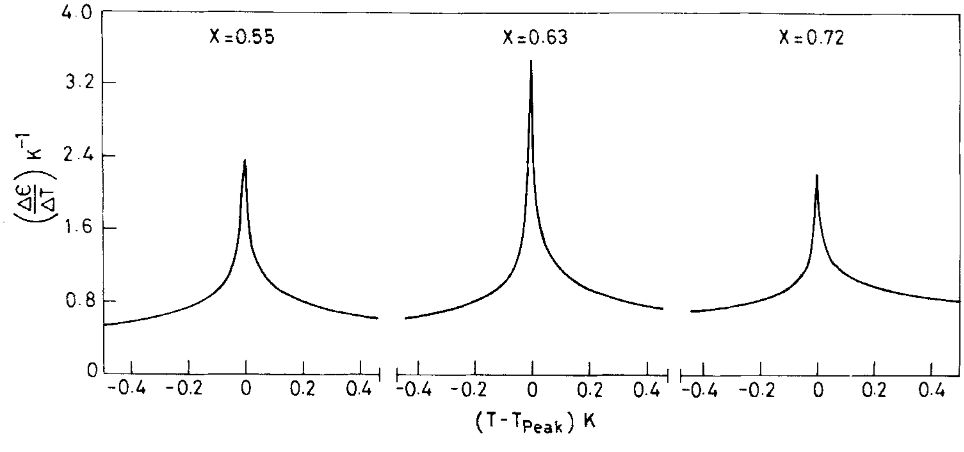

FIGURE 7 Plot of $\Delta\varepsilon/\Delta T$ as a function of reduced temperature $T - T_{peak}$ for the three concentrations $x = 0.55$, 0.63 and 0.72.

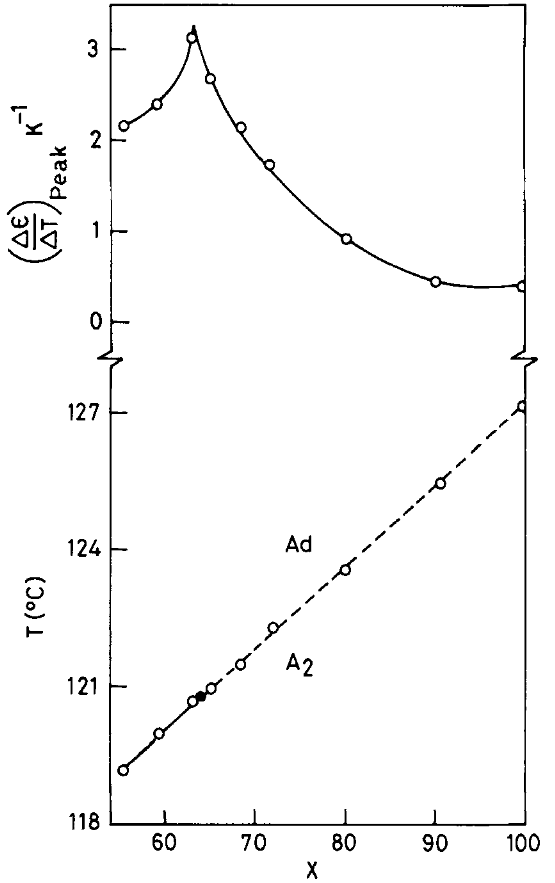

FIGURE 8 Top panel: Peak height of $\Delta\varepsilon/\Delta T$ versus $T - T_{peak}$ curves plotted as a function of x. Bottom panel: Partial phase diagram of the binary system 110PCBOB + 90BCB. Solid line denotes the A_d-A_2 transition boundary while the dashed line represents the locus of "inflection points" in the supercritical region. The filled circle denotes the critical point estimated from peak height plots of $\Delta\varepsilon/\Delta T$ curves.

plotted in Figure 8 as a function of x. It is seen that the peak height value increases from either side (lower as well as higher concentrations) on approaching the critical point concentration, which has been found to be $x = 0.64$, in excellent agreement with the value obtained from x-ray[4] and calorimetric[5] measurements.

DISPERSION STUDIES

The frequency of relaxation of $\varepsilon_{||}$, f_R has been plotted (Figure 9) in the A_d and A_2 phases of the mixture $x = 0.63$. The results show that there is no drastic change in the f_R values between the A_d and A_2 phases. This probably explains the observation of a single relaxation even in the transition region contrary to the expected coexistence of two relaxations at a first-order transition. However, the activation

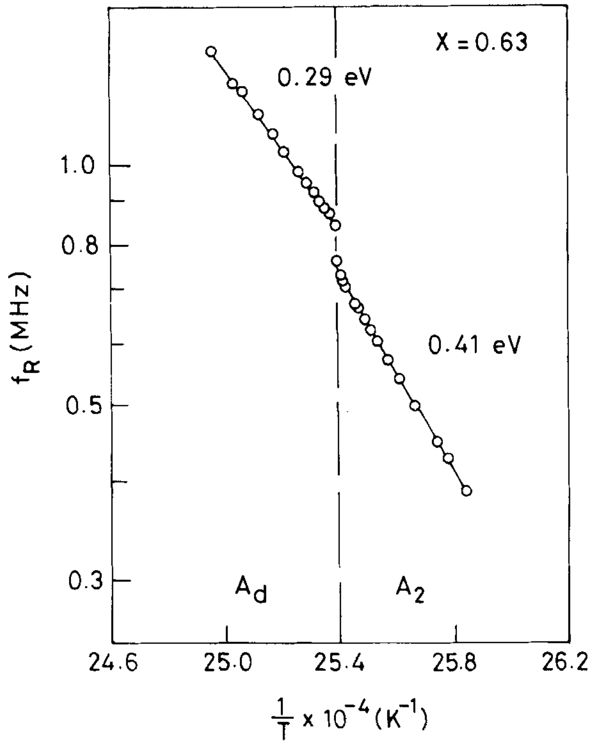

FIGURE 9 f_R versus $1/T$ plot for $x = 0.63$.

energies, W, in the A_d and A_2 phases, evaluated from the linear portions of the f_R versus $1/T$ plot are quite different; $W_{A_d} = 0.29$eV and $W_{A_2} = 0.41$eV, i.e., $W_{A_2} > W_{A_d}$. Similar features were seen in an earlier study[6] on a different material showing a A_d-A_2 transition.

In conclusion, we have carried out for the first time precise dielectric studies near the A_d-A_2 critical point. Data analysis has led to the identification of the critical point to be very near to $x = 0.64$ in excellent agreement with the values determined previously by x-ray and calorimetric methods. Measurements are in progress on another binary system which shows[7] the A_d-A_2 critical point in the temperature-molecular length phase diagram. The results of these studies will be published separately.

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