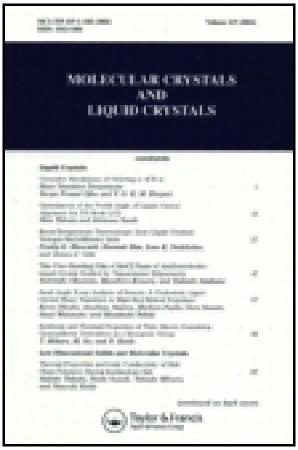

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Effect of Smectic Ordering on the Dielectric Properties of Reentrant Nematic Mixtures[†]

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We have measured the static dielectric constants $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ as well as the low-frequency dispersion of $\varepsilon_{\parallel}$ for mixtures of two eutectic compositions exhibiting a reentrant nematic phase over a range of concentration. The dielectric properties of a nematic mixture, whose concentration is close to the critical concentration (C_{cr}) at which the smectic phase appears, are found to be markedly different from those for a concentration far away from C_{cr}. This can be understood as being due to an increase in the smectic like ordering in the nematic phase as the critical concentration is approached.

INTRODUCTION

Since the discovery of the reentrant nematic phase,[1] a variety of experiments have been performed to understand the nature of this phase. The phenomenon of reentrance has been observed only in strongly polar compounds in which there is significant antiparallel ordering of the molecules. These antiparallel molecular correlations are best revealed in the dielectric properties. An extension[2] of the Maier-Meier theory[3] to include the short range antiparallel correlations predicted a small increase in the mean permittivity ($\bar{\varepsilon}$) at the nematic to isotropic transition point. Dielectric measurements on a number of cyano compounds[4,5,6] confirmed this prediction

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[†] Presented at the Ninth International Liquid Crystal Conference, Bangalore, 1982.

and showed further that the antiparallel correlations increase with decrease of temperature,[7,8] the increase being greater in the presence of smectic ordering.

EXPERIMENTAL

The two eutectic compositions (C_1 and C_2) have three components each. The chemical structure of the constituent components are given in Table I along with the ratios in which they are mixed. The phase diagram is shown in Figure 1. Measurements were carried out for three concentrations, *viz.*, C_1, C_3 (50 mole % of C_2 in C_1) and C_4 (60 mole %).C_1 and C_3 exhibit only a nematic phase whereas C_4 exhibits, in addition, smectic A and reentrant nematic phases. The transition temperatures of the mixtures are given in Table II.

The static dielectric constants were measured at 1592 Hz using a Wayne Kerr B642 bridge. The low frequency dispersion of $\varepsilon_\parallel$ was measured using a Wayne Kerr B602 (100 kHz–10 MHz) RF bridge and a Hewlett-Packard 4800A (5 Hz–500 kHz) vector impedance meter. The alignments of the samples (50–150 μm thick) were achieved by a 15 kGauss magnetic field.

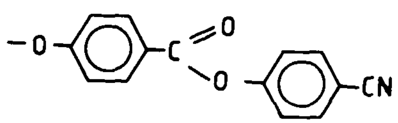
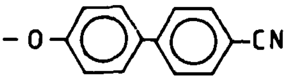
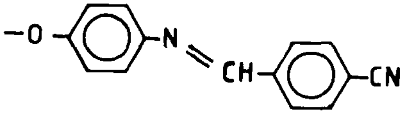
RESULTS AND DISCUSSION

1. Static dielectric constants

The temperature dependence of the static dielectric constants $\varepsilon_\parallel$, $\varepsilon_\perp$ in the mesophases and ε_{is} in the isotropic phase of C_1, C_3, and C_4 are

TABLE I

Molecular structure and mole fraction of the components of C_1 and C_2

C_1	C_2	
C_8H_{17} – $X = .157$	C_9H_{17} – $X = .134$	
C_7H_{15} – $X = .494$	C_8H_{17} – $X = .552$	
C_7H_{15} – $X = .349$	C_8H_{17} – $X = .314$	

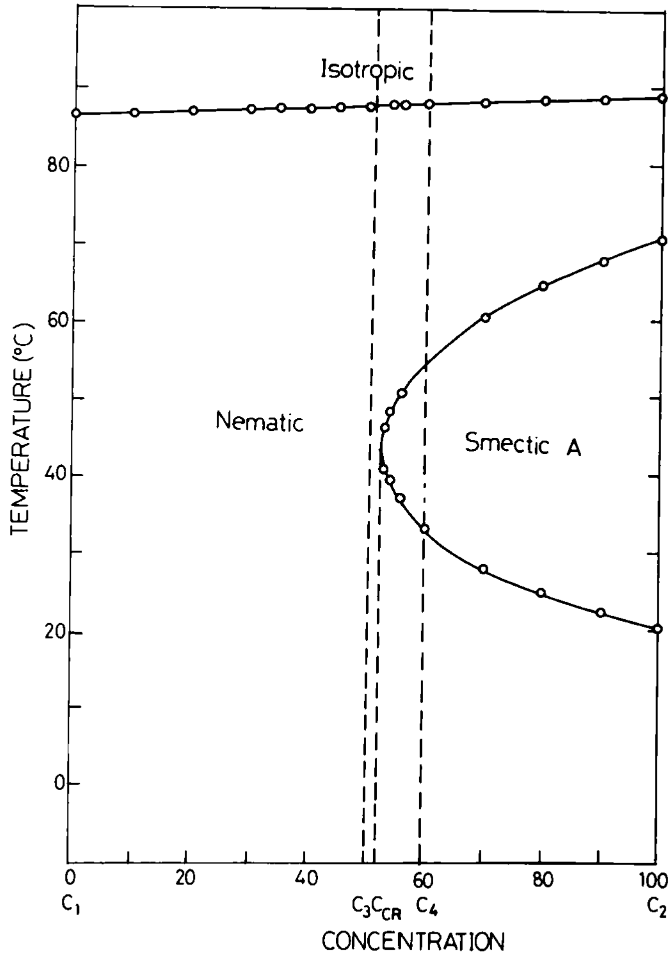


FIGURE 1 Phase diagram of the eutectic compositions C_1 and C_2. Concentration is given in weight per cent of C_2 in C_1. The concentrations for which the dielectric studies have been made are C_1, C_3 and C_4.

TABLE II

Transition temperatures in °C of the mixtures studied

	C		N_{Re}		S_A		N		I
C_1	•	32.0	–		–		•	86.4	•
C_2	•	35.4	•	20.2	•	70.6	•	88.7	•
C_3	•	26.9	–		–		•	87.5	•
C_4	•	26.6	•	32.8	•	54.1	•	87.8	•

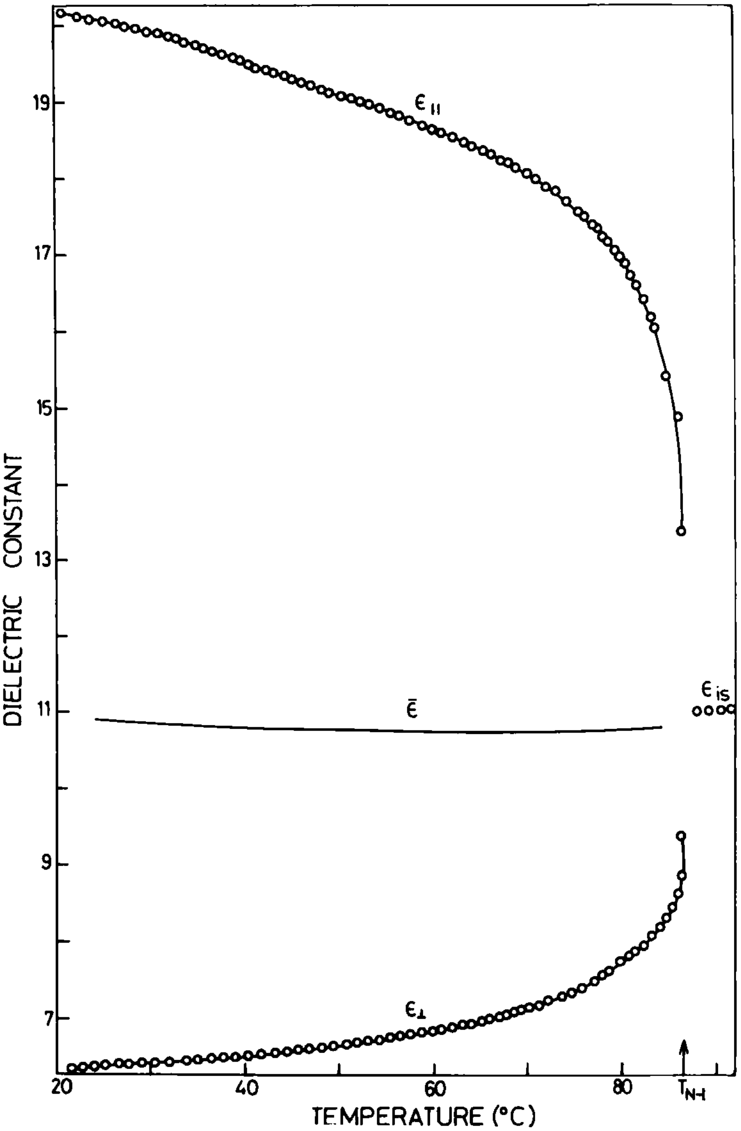


FIGURE 2 Static dielectric constants of $C_1 \cdot \varepsilon_{is} - \bar{\varepsilon}_{min} = 1.8\%$.

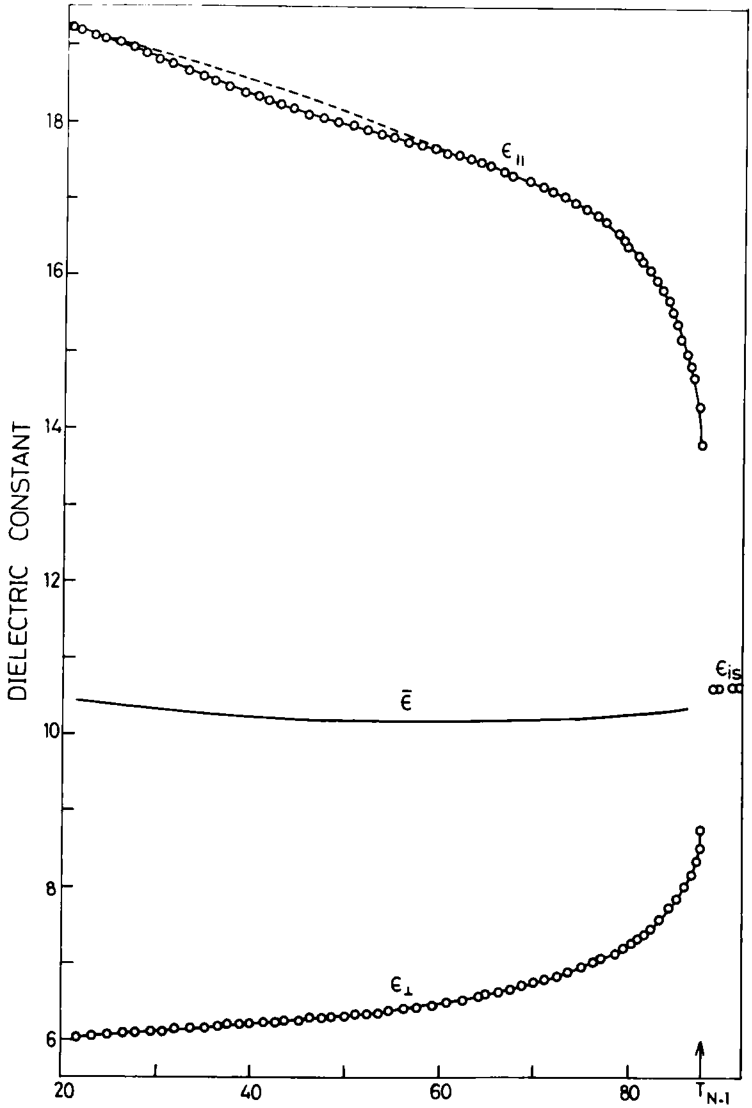


FIGURE 3 Static dielectric constants of $C_3 \cdot \varepsilon_{is} - \bar{\varepsilon}_{min} = 3.8\%$.

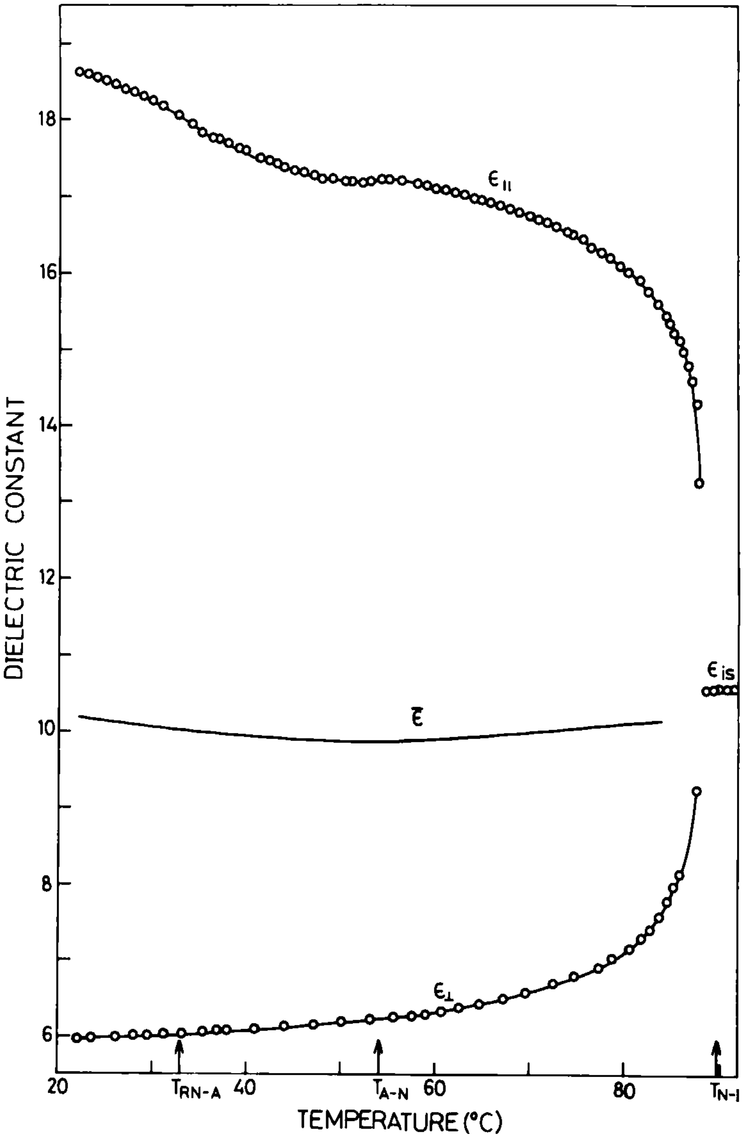


FIGURE 4 Static dielectric constants of C_4 · $\varepsilon_{is} - \bar{\varepsilon}_{min} = 6.4\%$.

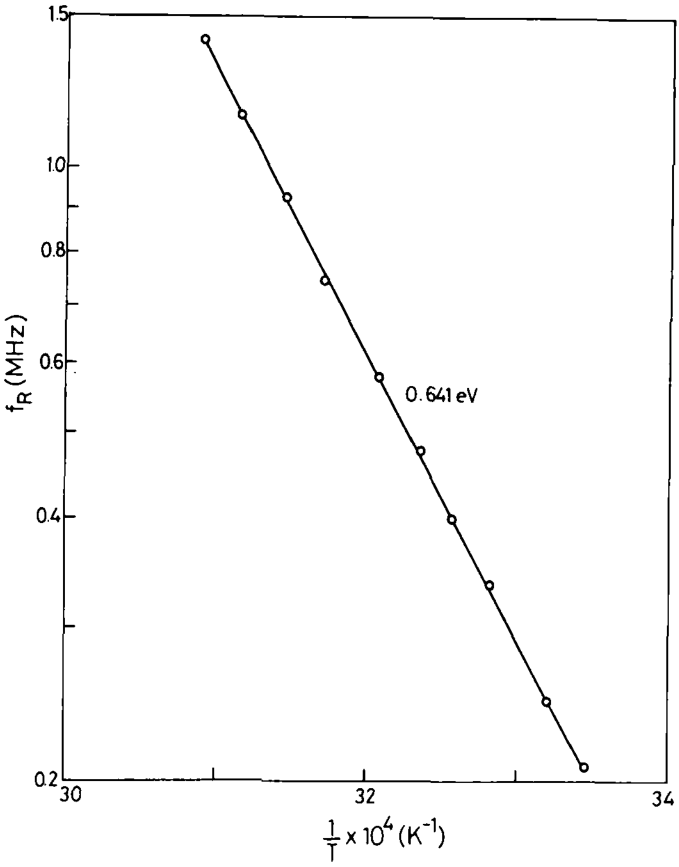


FIGURE 5 $\ln f_R$ vs 1/T for C_1.

shown in Figures 2–4, respectively. The temperature variation of $\bar{\varepsilon} = (\varepsilon_\parallel + 2\varepsilon_\perp)/3$ calculated from the measured values of $\varepsilon_\parallel$ and $\varepsilon_\perp$ is also shown in the same diagrams. The shape of the $\varepsilon_\perp$ *vs* temperature curve is identical in all the three mixtures, whereas the shape of the $\varepsilon_\parallel$ curve is different. In the case of C_1, $\varepsilon_\parallel$ appears to continuously increase with decrease of temperature. But $\bar{\varepsilon}$ shows a minimum, the difference between the minimum value of $\bar{\varepsilon}$ and ε_{is} at the transition being ~1.8%. On the other hand, C_3 shows a minimum in $\varepsilon_\parallel$. (The dashed line in Figure 3 is the

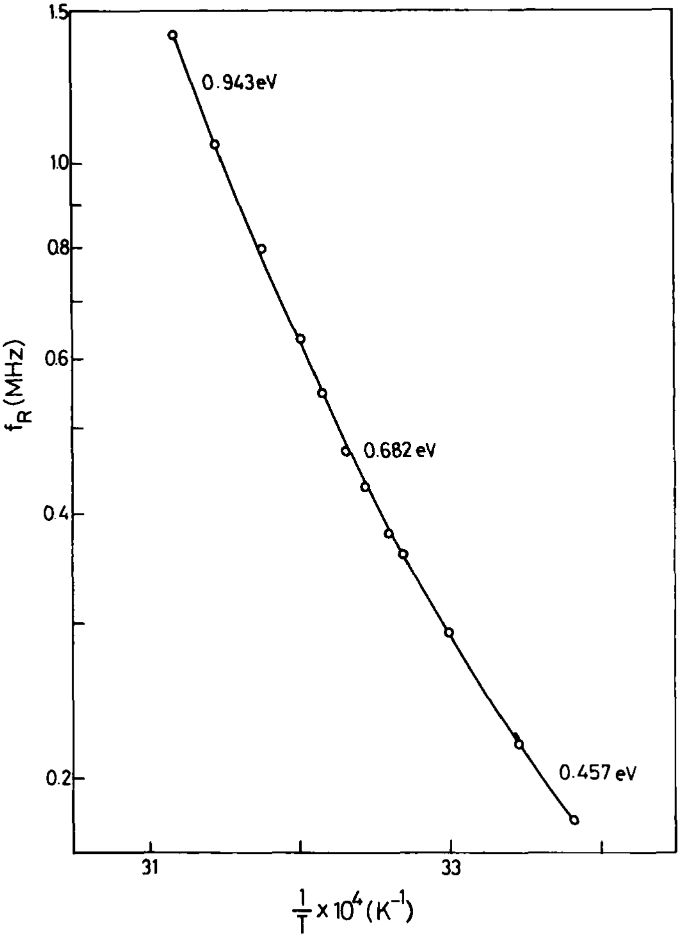


FIGURE 6 ln f_R vs 1/T for C_3.

$\varepsilon_{\|}$-curve for C_1 superimposed to make the shallow minimum perceptible.) Also the difference between ε_{is} and $\bar{\varepsilon}_{min}$ has increased to 3.8%. These differences between C_1 and C_3 are obviously due to the smectic-like ordering being higher in C_3 by virtue of its proximity to the critical concentration C_{cr} at which smectic A appears. The conductivity anisotropy measurements[9] on the same mixtures also showed (i) that the strength of the smectic ordering in the nematic mixtures increases as the critical concentration C_{cr} is approached, and (ii) that the smectic ordering goes through a maximum with respect to temperature. Similar results have also been observed for other binary liquid crystal systems.[10]

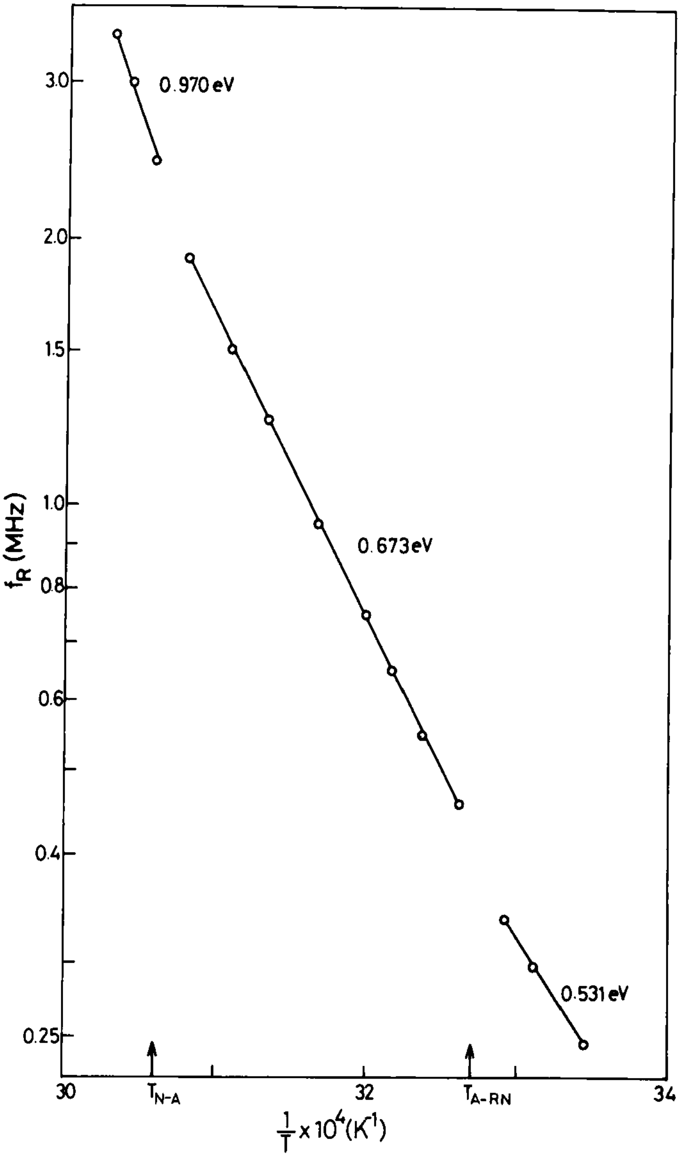


FIGURE 7 ln f_R vs 1/T for C_4.

In mixture C_4, $\varepsilon_\parallel$ decreases by a small amount at the nematic-smectic A transition temperature (T_{AN}) just as in any other strongly polar compound exhibiting a smectic A phase, e.g., 4′-*n*-octyl-4-cyanobiphenyl[8] (8 CB). However, instead of just decreasing with further decrease of temperature as in 8 CB, $\varepsilon_{\parallel}$ starts increasing again. This could be due to the decreasing smectic ordering at these temperatures as shown by the conductivity measurements. The density measurements[11] on the 65% mixture show that this increase in $\varepsilon_{\parallel}$ cannot be due to the increase in the density alone. The difference between ε_{is} and ε_{min} for this mixture is $\approx 6.4\%$. Thus we find that higher the strength of the smectic ordering deeper is the minimum of $\bar{\varepsilon}$.

2. Dispersion of $\varepsilon_{\parallel}$

The relaxation frequencies for C_1, C_3 and C_4 were measured over approximately the same temperature range and the respective Arrhenius plots are shown in Figures 5–7. The activation energy in the high temperatuare nematic phase (W_N) is greater than that in the reentrant nematic phase (W_{RN}) (see figure 7) whereas for some other reentrant compounds[12] we had found $W_{RN} > W_N$. Lack of viscosity data on these compounds makes it difficult for us to comment on this difference. For the mixture C_3, the plot of $\ln f_R$ *vs* 1/T is a curve with a continuously varying slope. Interestingly if we determine slopes for this curve at temperatures corresponding to the middle of the three mesophases of C_4, the values obtained are close to the activation energies of the corresponding mesophases of C_4. On the other hand, for C_1 we get only a single straight line with an activation energy of 0.64 eV. The variation of W with temperature in C_3 (or the lack of it in C_1) is a consequence of the larger variation in the smectic ordering in C_3 as compared to C_1. This clearly shows that the relaxation is governed by the short range order rather than the long range order.

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