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Short range order in the isotropic phase of antiferroelectric liquid crystals

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Optical activity measurements in the isotropic phase of two antiferroelectric liquid crystal systems in which the chirality can be varied reveal unusual behaviour of the short range order. In one system the phase sequence as the chirality is increased is smectic A, smectic C_A^*, and smectic Q. In the other system the phase sequence is smectic C*, smectic C_A^*, and smectic Q as the chirality is increased. The short range order of the isotropic phase behaves similarly for these systems, showing mean field behaviour at low chirality and far above the phase transition, but deviating from this behaviour significantly as the chirality is increased and the phase transition is approached. These optical activity results indicate how different is the short range order in the isotropic phase for these antiferroelectric liquid crystal systems and demonstrates the crucial role played by chirality. Past theoretical work that includes smectic-like fluctuations in the calculation of short range order in the isotropic phase is capable of qualitatively explaining these results.

1. Introduction

Investigation of the short range orientational order in the isotropic phase of liquid crystals has a long history of leading to important new understanding, both of the phases themselves and of the phase transitions between them. De Gennes was the first to write out a phenomenological expression for the free energy density in the isotropic phase of a chiral liquid crystal, keeping terms up to second order in the order parameter tensor $S_{\alpha\beta}$ and its derivatives,

$$g(S,T) = g_{iso} + \frac{1}{2}a(T)S_{\alpha\beta}S_{\alpha\beta} + \frac{1}{2}L_1(\nabla_\alpha S_{\alpha\beta})(\nabla_\alpha S_{\alpha\beta}) + \frac{1}{2}L_2(\nabla_\alpha S_{\alpha\gamma})(\nabla_\beta S_{\beta\gamma}) - q_0 L_1 \varepsilon_{\alpha\beta\gamma}\nabla_\gamma S_{\alpha\mu}S_{\beta\mu} \quad (1)$$

where $a(T) = a_0(T - T^*)$ is a temperature dependent constant and L_1 and L_2 are temperature independent phenomenological constants [1]. T is the absolute temperature, T^* is the absolute temperature of a second order transition, and q_0 is the chirality. In the chiral nematic phase, q_0 is equal to 2π divided by the pitch. This mean field framework was used to analyse magnetic birefringence and light scattering measurements in the isotropic phase of a nematic liquid crystal ($q_0 = 0$), confirming the temperature dependence of $a(T)$ and measuring the correlation length of the fluctuations in the isotropic phase [2–4].

The free energy density given in equation (1) was formulated in a more convenient way by Brazovskii and co-workers. First, the free energy was written in momentum space with $S_m(q)$ representing the Fourier amplitude of the spatially varying order parameter tensor. The index m runs from -2 to $+2$, with each representing a basis structural mode or basis tensor. The $m = \pm 2$ modes represent planar helical structures of opposite handedness, the $m = \pm 1$ modes represent conical helical structures of opposite handedness, and the $m = 0$ mode represents a non-chiral or nematic-like structure. The resulting mean field free energy can be written

$$g(S(q),T) = g_{iso} + \sum_{m=-2}^{+2}\left\{a(T) - mbq_0 q + \left[b + \frac{c}{2}(4 - m^2)\right]q^2\right\}|S_m(q)|^2 \quad (2)$$

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where b and c are temperature independent phenomenological constants and q_0 is again the chirality, but is defined to be 4π divided by the pitch in the chiral nematic phase [5, 6]. This theoretical framework was applied to the blue phases by Hornreich and Shtrikman [7, 8], and in turn was used extensively by experimentalists investigating the blue phases. One recent example of this is the light scattering study of Koistinen and Keyes, in which they measured both the chirality of the fluctuations and the correlation length in the isotropic phase of a chiral liquid crystal near a critical point between the isotropic phase and the third blue phase (BP_2III) [9].

Another measurement in the isotropic phase that has been analysed using this same theoretical framework is optical activity. In fact, optical activity measurements were crucial to the discovery of the critical point mentioned above [10]. Starting wih the free energy density given in equation (2), the optical activity due to the short range order of the isotropic phase is

$$\phi = \frac{\pi k_B q_0}{12\epsilon_0 \lambda^2 \sqrt{a_0 b}} \left[1 + \frac{c}{2b}\right]^{-3/2} \frac{T}{(T - T_1^*)^{1/2}} \qquad (3)$$

where k_B is Boltzmann's constant, ϵ_0 is the permeability of free space, and λ is the wavelength of the light in the sample [11]. T_1^* is a slightly different second order transition temperature from T^*. The temperature dependence of the optical activity has been shown to follow this prediction in many cases, the first verification being by Cheng and Meyer [12]. The chirality dependence of equation (3) has also been verified, but only in a recent experiment [13].

The experiments that have attracted the most interest have been those in which the optical activity did not follow the prediction of the theory. The first example of this was in the highly chiral systems with the BP_2III phase. Instead of diverging according to equation (3) as the temperature decreases to the transition temperature, the optical activity peaks and even decreases slightly just before the transition [14]. Continued experimentation revealed that a critical point between BP_2III and the isotropic phase was the reason for the behaviour. The second example was optical activity measurements in the isotropic phase above a twist grain boundary (TGB_A) phase [15]. Again, instead of continuing to diverge as the temperature is decreased to the transition, the optical activity reaches a maximum and remains at that value for several degrees just above the transition. Differential scanning calorimetry shows a weak, broad peak in this region and X-ray diffraction shows a similar weak, broad peak, indicating that smectic layers are weak but present in this region just above the TGB_A phase [16]. Whether a new phase exists in this region, or whether this behaviour is due to the effect of smectic fluctuations in the isotropic phase, is an open question.

Recent measurements of the optical activity in the isotropic phase of several smectic compounds revealed that a deviation from mean field behaviour is not unusual. A plateau in the optical activity just above the transition to a smectic C* phase was observed and a temperature dependence of the optical activity in the isotropic phase never seen before was reported just above an antiferroelectric or ferrielectric phase [17].

Both theoretical and experimental work has shown that smectic fluctuations have an effect on the short range order of the isotropic phase. This can be understood theoretically by adding terms to the nematic free energy that account for (1) the nematic–smectic transition utilizing a smectic order parameter, and (2) coupling between the nematic and smectic order parameters [18–22]. The prediction of this theoretical approach is that the short range order should follow mean field behaviour except for a region very close to the transition, where it can deviate in either direction depending on the sign of the coupling term. The strength of the deviation depends on the width of the nematic phase, with the deviation being stronger the narrower the nematic phase. Experimental verification of a deviation of this type (in one direction only) has come from Kerr effect measurements [18, 22] and light scattering measurements [19, 21, 23].

Although this work on smectic fluctuations has been done for non-chiral systems, it is not difficult to extend the basic idea to chiral systems and predict that the scattering of circularly polarized light should show the same deviation [24]. Interestingly enough, the direction of this deviation in the isotropic phase just above the transition to a twist grain boundary phase is opposite from that observed in non-chiral systems. Clearly the negative deviation of both the intensity of light scattering and the optical activity are due to a change in the short range orientational order. Significant deviations of this sort should not be surprising in compounds with a transition from a smectic phase to the isotropic phase. In this case, the transition to the isotropic phase involves the loss of both orientational (nematic) and positional (smectic) order, so the fluctuations in the isotropic phase should be much more complicated than when a nematic or chiral nematic phase is present. It should be kept in mind, however, that the presence of a smectic phase without a nematic phase does not ensure that the optical activity in the isotropic phase deviates from mean field theory predictions. Two measurements on the same chiral compound with a smectic A to isotropic phase transition show that the optical activity in the isotropic phase can be fitted extremely well by mean field theory [15, 25].

To illustrate the effect of smectic fluctuations on the optical activity in the isotropic phase, a simple calculation based on past theoretical work can be used. The basic result of this theory is that the temperature dependent coefficient in front of the square of the order parameter in the free energy expression is 'renormalized' by the smectic fluctuations. This 'renormalization' takes on different forms depending on the exact nature of the calculation. But all involve an additional term in which the temperature dependence is some negative power of the temperature [18–20]. Picking the term with the proper sign gives a 'renormalized' coefficient

$$a(T) = a_0(T - T^*_{NI}) + \frac{\mu}{(T - T^*_{SI})^{1/2}} \qquad (4)$$

where μ is a coefficient related to the strength of the coupling and T^*_{NI} and T^*_{SI} are the second order transition temperatures associated with the nematic–isotropic and smectic–isotropic transitions, respectively. The effect of this 'renormalization' on the inverse light scattering intensity, which is proportional to $a(T)$, and the optical activity, which is given by equation (3), is shown in figure 1 for a single set of values of T^*_{NI} and T^*_{SI} and three values of μ/a_0. Both the inverse light scattering intensity and the optical activity dependences in figure 1 are similar to the experimental data for some chiral smectic systems [15, 17, 24].

The molecular interactions in an antiferroelectric smectic phase may differ from the molecular interactions in ferroelectric smectic phases. In antiferroelectric phases the molecules in neighbouring layers are no longer parallel on average, a fact that may be reflected in the short range order of an isotropic phase directly above such a phase. Since smectic fluctuations in general are known to affect the short range orientational order of the isotropic phase, the question of whether antiferroelectric order affects it differently must be asked. This question, plus past experiments showing extremely unusual behaviour in some smectic systems [17], were the two motivations for this investigation of two antiferroelectric systems.

At low chirality the two systems possessed different smectic phases below the isotropic phase, either the smectic A or smectic C* phase; these phases gave way to the smectic C^*_A and smectic Q phases at higher chirality in both systems. The smectic C^*_A phase is the antiferroelectric version of the chiral smectic C phase. The director alternates from one side of the tilt angle cone to the other in going from one layer to the next, while slowly precessing around the tilt angle cone. The smectic Q phase for these two compounds is a twist grain boundary phase in which the grain boundaries are arranged to give tetragonal symmetry with a lattice constant on the order of 10 nm [26]. The optical activity for both of these systems followed mean field behaviour at low chirality and far above the transition at higher chirality, but deviated in a new but systematic way over a large range of temperature near the transition when the chirality was high. The deviation can be qualitatively explained by the previous work on the effects of smectic fluctuations, but as was true for the previous work on chiral systems, the deviation is toward a reduction in the effects due to fluctuations relative to the prediction of mean field theory.

2. Experiment and results

The first system investigated was a four-ring ester with two chiral centres [27]. The highly chiral isomer, (*S*,*S*)-M7BBM7, can be mixed with the racemic mixture, *rac*-M7BBM7, to form mixtures with varying chirality. The racemic mixture possesses the smectic C_A, smectic A, and isotropic phases with increasing temperature, while the (*S*,*S*) isomer shows the smectic C^*_A, smectic Q, and isotropic phases as the temperature increases. The

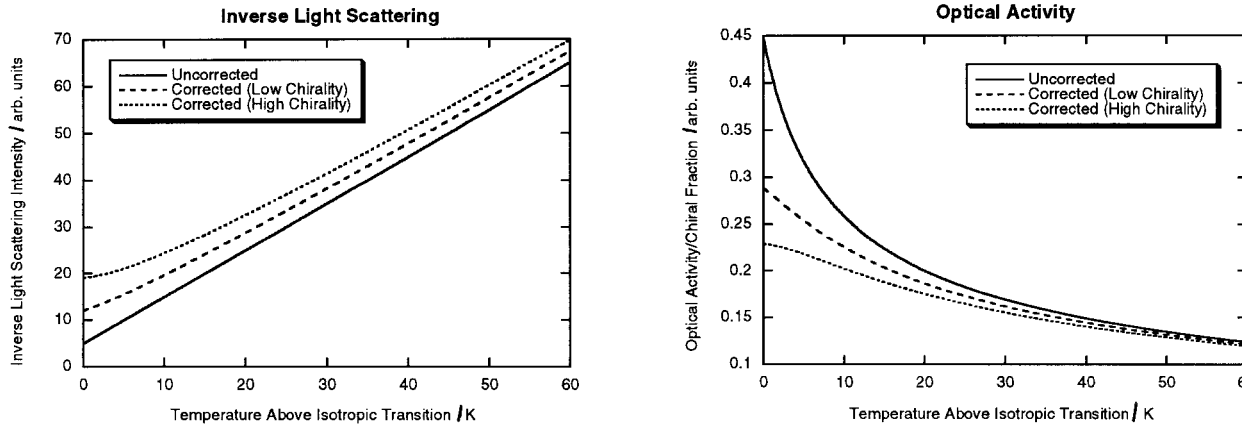

Figure 1. Theoretical effect of smectic fluctuations on the inverse light scattering intensity and the optical activity. In all cases $T_C - T^*_{NI} = 5$ K and $T_C - T^*_{SI} = 8$ K. Solid line: $\mu/a_0 = 0$; dashed line: $\mu/a_0 = 20$ K$^{3/2}$; dotted line: $\mu/a_0 = 40$ K$^{3/2}$.

transition to the isotropic phase is from the smectic A phase for chiral fractions between 0 and roughly 0.35, from the smectic C_A^* phase for chiral fractions between about 0.35 and 0.85, and from the smectic Q phase for chiral fractions above approximately 0.85. One unusual aspect of this system is that the racemic mixture melts to the isotropic phase around 145°C, whereas the (*S*,*S*) isomer's isotropic transition occurs around 85°C, about 60°C lower. The phase diagram for this mixture and the structure of (*S*,*S*)-M7BBM7 are shown in figure 2 [27].

The second system studied was a three-ring Shiff's base compound with two chiral centres [28]. The highly chiral isomer, (*R*,*R*)-M7TAC was mixed with a racemic mixture of another compound in the homologous series, *rac*-M10TAC. This mixture was chosen because the transition to the isotropic phase occurs at about 130°C for all chiral fractions. The transition to the isotropic phase is from the smectic C* phase for chiral fractions from 0 to about 0.4, from the smectic C_A^* for chiral fractions between roughly 0.4 and approximately 0.9, and from the smectic Q phase for chiral fractions above 0.9. The phase diagram for this mixture, as obtained by a contact preparation, and the structure of the compounds are shown in figure 3 [28].

The samples were contained between two glass slides separated by a 0.125 mm mylar spacer; all of this was placed inside an Instec mK1 hot stage. The temperature was controlled to the nearest mK and all experiments were performed with increasing temperature. The optical activity was measured by computer control of a rotation stage, together with a Faraday modulator and lock-in detection. The light source was a HeNe laser operating

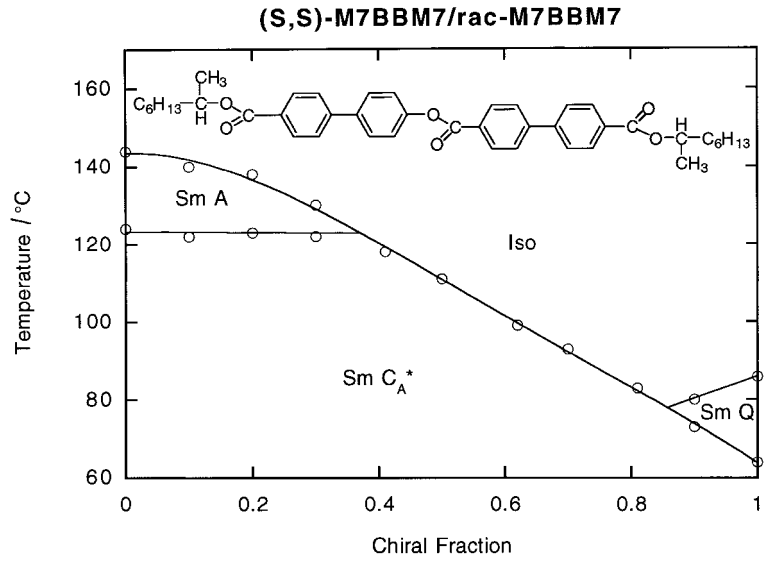

Figure 2. Phase diagram and structure for the (*S*,*S*)-M7BBM7/*rac*-M7BBM7 system. The racemic mixture contains equal amounts of the four isomers.

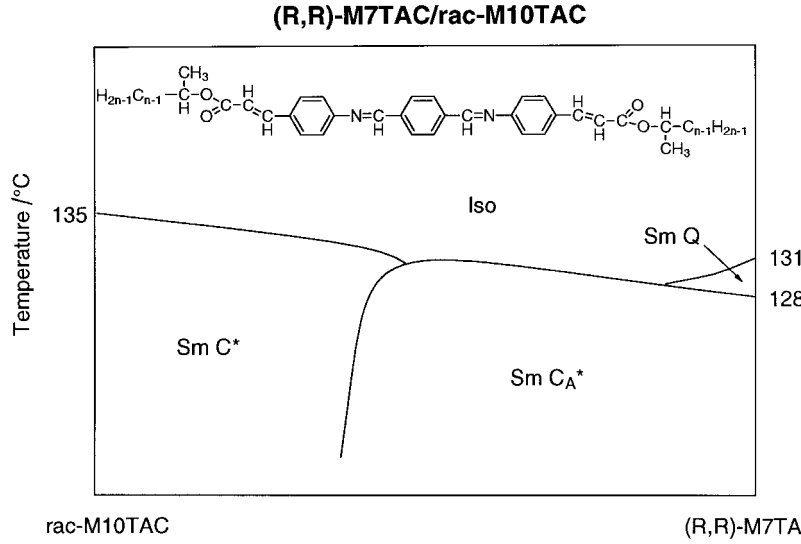

Figure 3. Phase diagram (contact preparation) and structure for the (*R*,*R*)-M7TAC/*rac*-M10TAC system. The racemic mixture contains equal amounts of the (*R*,*R*)-M7TAC and (*S*,*S*)-M7TAC isomers and twice this amount of the (*R*,*S*)-M7TAC isomer.

at 633 nm. This measurement system has been described previously [10]. Since these systems in general react sluggishly to changes of temperature, all measurements of the optical activity were taken after the sample had been at the new temperature for five minutes.

The optical activity of the M7BBM7 system for five different chiral fractions is shown in figure 4. It can be seen that although the optical activity at very high temperatures has the form predicted by mean field theory, the temperature dependence changes at lower temperatures, especially for the higher chiral fraction mixtures. Also, the isotropic phase transition occurs at very different temperatures for different chiral fraction mixtures. The solid line in figure 4 is a fit of the mean field theory to the data for the 0.1 chiral fraction mixture. The fit is quite good, indicating that mean field theory is capable of explaining the optical activity of the isotropic phase in this system when the chirality is very low.

To see more clearly the deviation from mean field theory as the chirality is increased, figure 5 shows the optical activity data divided by the chiral fraction. If all mixtures followed mean field theory, the data for all five chiral fractions would fall on top of each other [12, 13]. This clearly occurs at the highest temperatures, but the data fall below the mean field values as the temperature is decreased. This reduction of the optical activity/chiral fraction is greater the higher the chiral fraction.

The optical activity data for the MnTAC system are shown in figure 6, where again five different chiral fractions have been investigated. The data cover roughly the same temperature interval for all mixtures in these compounds, but none of them exhibit a behaviour that

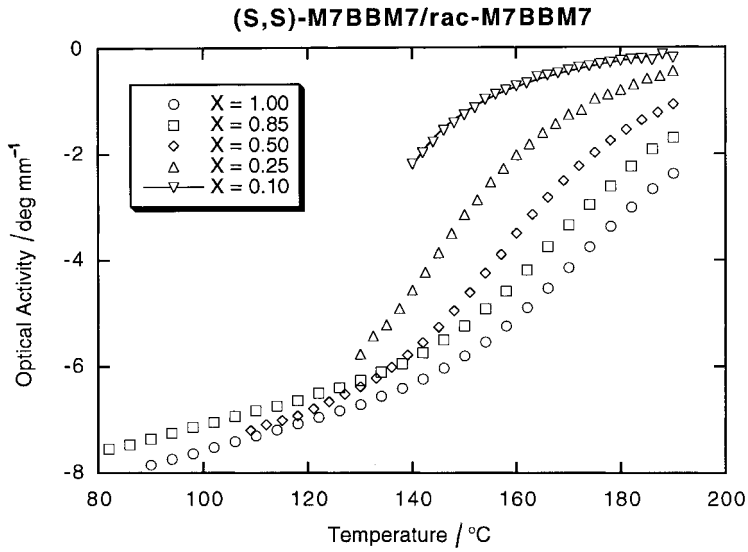

Figure 4. Optical activity in the isotropic phase for five chiral fractions of the M7BBM7 system. X denotes chiral fraction; the wavelength of the light is 633 nm. The solid line is a fit of mean field theory, equation (3), to the $X = 0.1$ data.

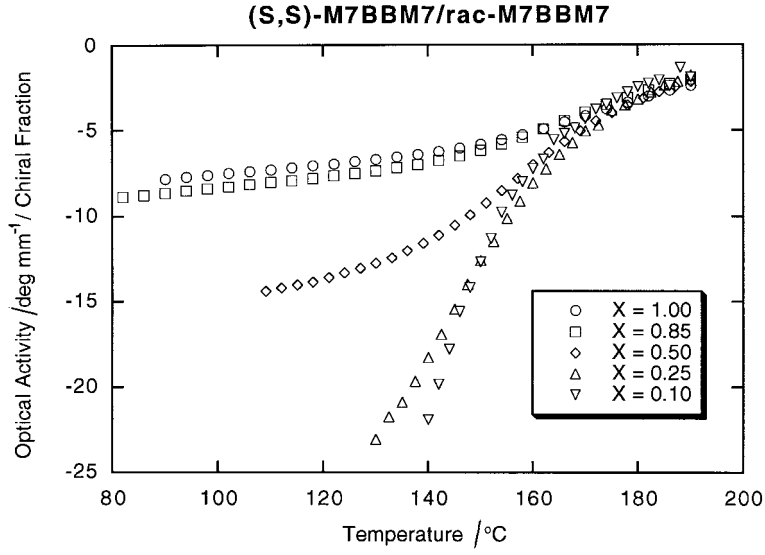

Figure 5. Optical activity divided by chiral fraction for the M7BBM7 system. The wavelength of the light is 633 nm. Mean field theory predicts that the data for all five chiral fractions should fall on top of each other.

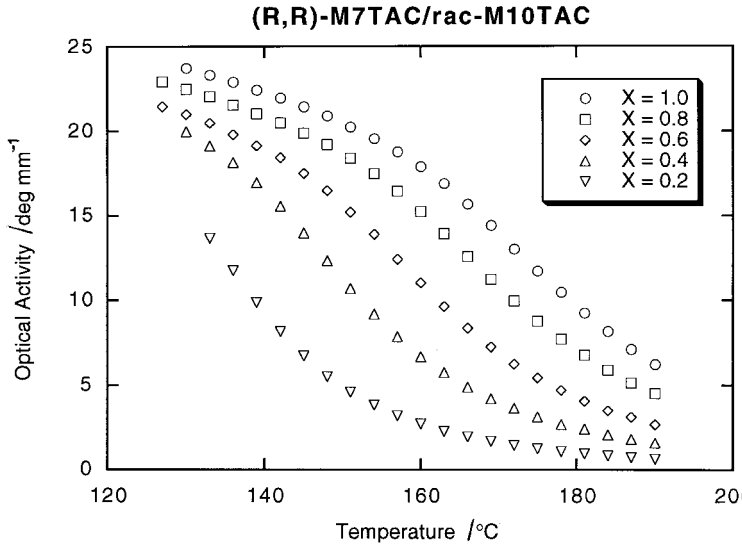

Figure 6. Optical activity in the isotropic phase for five chiral fractions of the (*R*,*R*)-M7TAC/*rac*-M10TAC system. *X* denotes chiral fraction; the wavelength of the light is 633 nm.

follows the prediction of mean field theory. The optical activity data divided by the chiral fraction are shown in figure 7. Notice once again that the data tend to fall on top of each other at high temperatures, but deviate from each other at lower temperatures. The higher the chiral fraction, the greater the reduction of the optical activity/chiral fraction.

3. Discussion

The optical activity/chiral fraction data for both of these systems are similar to the theoretical temperature dependences of figure 1. This indicates that the deviation from mean field behaviour in these systems may be due to the effect of smectic fluctuations in the isotropic phase. Smectic fluctuations cause an increase in the pitch (hence a decrease in chirality) in chiral nematic liquid crystals [29], so it is likely that this is also the case for the chiral fluctuations in the isotropic phase. Such a decrease in chirality would cause the light scattering intensity for chiral modes and the optical activity/chiral fraction to decrease, which is exactly what is observed.

The results show a strong correlation between the onset of antiferroelectric ordering in the liquid crystal phase and the deviation from mean field theory of the optical activity in the isotropic phase. From figure 5, it is clear that at a chiral fraction of 0.25, the deviation is not large, unlike at a chiral fraction of 0.5 where the deviation is extremely significant. It is probably no coincidence that the non-chiral smectic A gives way to the antiferroelectric smectic C_A^* at a chiral fraction around 0.35. Likewise, the deviation from mean field theory for the MnTAC system is already significant at a chiral fraction of 0.4 (see figure 7), which is the region where the ferroelectric smectic C* phase gives way to the antiferroelectric

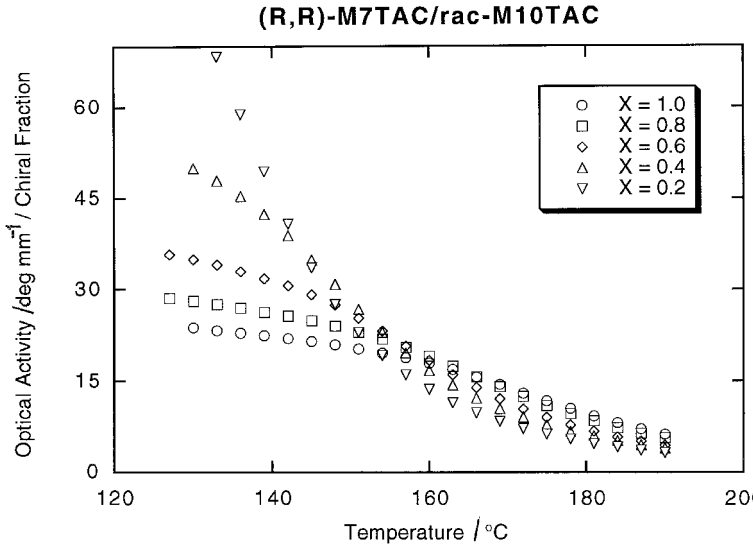

Figure 7. Optical activity divided by chiral fraction for the (*R*,*R*)-M7TAC/*rac*-M10TAC system. The wavelength of the light is 633 nm. Mean field theory predicts that the data for all five chiral fractions should fall on top of each other.

smectic C_A phase. Thus in these two systems it is safe to say that antiferroelectric ordering in the liquid crystal phase is linked to the breakdown of mean field theory in the isotropic phase.

The other interesting aspect of the results is that the optical activity becomes nearly linear with temperature near the isotropic–smectic transition when the chirality is high. This effect is more pronounced in the M7BBM7 system due to the depression of the liquid crystal transition with an increase in chirality. This type of behaviour is reminiscent of what happens to the optical activity in the isotropic phase above a TGB_A phase. For the TGB_A compound, X-ray scattering and calorimetry measurements indicate that a small amount of orientational and positional order is present just above the transition to the isotropic phase. An interesting question is whether some degree of order can be detected in the isotropic phase of these antiferroelectric systems. If so, one must then ask if there is a relationship between the presence of this order and the depression of the liquid crystal phase transition. Alternatively, is there some sort of 'isotropic' phase different from the canonical isotropic phase and does the temperature range of this 'isotropic' phase increase at the expense of the smectic phase as the chirality is increased?

4. Conclusions

Clearly more theoretical work is required to understand the short range order in the isotropic phase above chiral smectic phases. Additional experimental investigations of systems such as these are also necessary, hopefully to establish the nature of the order and the presence or absence of additional phase transitions. The results presented here can be thought of as a first organizing principle. The short range order in the isotropic phase of some antiferroelectric systems can be explained by simple mean field theory; but an increase in chirality and the subsequent establishment of smectic phases with long range antiferroelectric order changes the short range orientational order in the isotropic phase from its mean field value. The greater the chirality, the greater this change. Finally, the build-up of smectic fluctuations in the isotropic phase is capable of explaining these changes, at least qualitatively.

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