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High pressure study of the cholesteric/smectic C* phase transition of 4-*n*-hexyloxyphenyl-4′-(2″-methylbutyl)biphenyl-4-carboxylate (CE3)

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The cholesteric (Ch)/smectic C* (S_C^*) phase transition of CE3 has been studied up to 2 kbar and 115°C by a light reflection method. In contrast to the cholesteric/smectic A phase transition, which can cross over from first to second order at elevated pressure, the Ch/S_C^* transition of CE3 was found to remain first order. This result is in agreement with most theoretical predictions. The pretransformation on the cholesteric side of the Ch/S_C^* transition is influenced only weakly by increasing pressure. Because of the high viscosity of the smectic C* phase corresponding results could not be obtained on the smectic side of the transition.

1. Introduction

As expected theoretically and observed experimentally the cholesteric (Ch)/smectic A (S_A) phase transition can be first or second order. In the case of the cholesteric (Ch)/smectic C* (S_C^*) and nematic/smectic C phase transitions, the situation has been somewhat different up till now: most of the theoretical studies predict a first order phase transition (see, e.g., [1–4]), although a few theories also permit a second order transition (see, e.g., [5]). Experimental work done so far, at atmospheric pressure, points to a first order transition (see, e.g., [6, 7]).

We have demonstrated experimentally, using the example of cholesteryl myristate, that the Ch/S_A transition can cross over from being first to second order at high pressure [8]. For that reason we have now studied the phase transition Ch/S_C^* of 4-*n*-hexyloxyphenyl-4′-(2″-methylbutyl)biphenyl-4-carboxylate (CE3) at elevated pressure. At atmospheric pressure CE3 has a first order Ch/S_C^* transition.

2. Experimental

The purity of CE3 was checked by thin-layer chromatography and found to be good. The Ch/S_C^* phase transition temperature of CE3 at atmospheric pressure was determined by a Leitz polarizing microscope and the corresponding transition enthalpy by a Perkin-Elmer DSC 2.

The phase transition Ch/S_C^* was observed at elevated pressure by a light reflection method [9], which not only allows the determination of the phase transition data but also the observation of pretransitional effects during the same measurement. Furthermore we can always distinguish between a cholesteric and a smectic C* phase, because both phases have a different characteristic reflection band (see later).

3. Results

At atmospheric pressure the selective light reflection of the CE3 cholesteric phase was found, by Lim and Ho [10], to be in the visible spectral region. We should

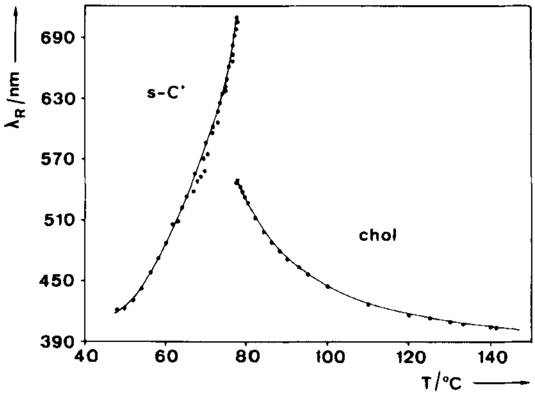

Figure 1. Wavelength of maximum light reflection, λ_R, of the CE3 cholesteric and smectic C* phase versus temperature, T, at atmospheric pressure.

therefore have a good chance of observing the Ch/S_C^* phase transition at elevated pressure by our light reflection method [9].

To be sure that the Ch/S_C^* transition is first order at atmospheric pressure we had to examine whether the wavelength of maximum light reflection, λ_R, which is proportional to the pitch of the cholesteric helix [11], has a finite value at the phase transition or whether it diverges to infinity [8]. Since this is not clearly stated in [10], we have repeated the determination of the temperature dependence of λ_R; the result is shown in figure 1. Undoubtedly the last λ_R of 550 nm which could be measured in the cholesteric phase is a breaking-off value: a further decrease of the temperature caused the intensity of the corresponding reflection band to become zero without a change in the wavelength. Accordingly, the Ch/S_C^* transition of CE3 is first order at atmospheric pressure. This is consistent with the comparatively large transition enthalpy of 1·30 kJ mol^{-1} (cf. 1·17 kJ mol^{-1} reported in [10]).

The light reflection of the smectic C* phase can also be measured. The reproducibility of the wavelength of maximum reflection, λ_R, is however, unsatisfactory. The main reason for it may be the very high viscosity of the smectic phase which hinders the molecular orientation. λ_R is about 690 nm at the phase transition to the cholesteric phase (cf. figure 1). The shape of the reflection band in the smectic C*

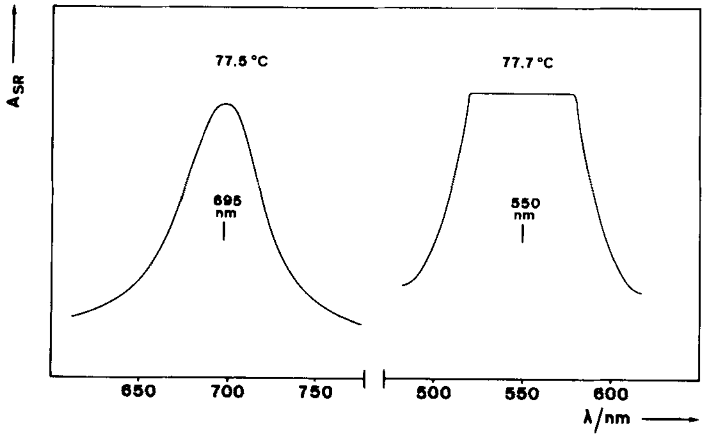

Figure 2. Quasi-absorption, A_{SR}, caused by the selective light reflection of the CE3 cholesteric (77·7°C) and smectic C* (77·5°C) phase versus wavelength, λ.

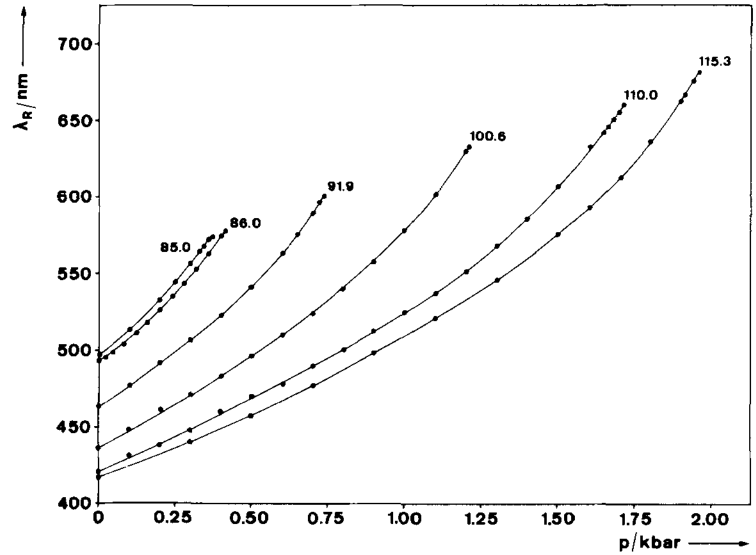

Figure 3. Wavelength of maximum light reflection, λ_R, of the CE3 cholesteric phase versus pressure, p, at various temperatures (the temperature is given, in °C, on the curves).

phase is different from that in the cholesteric phase. For comparison, both kinds of bands are shown in figure 2 (left-hand side, S_C^*; right-hand side, Ch).

We then performed light reflection measurements at elevated pressure in order to find out whether the order of the Ch/S_C^* transition can be altered by the application of pressure. In figure 3 λ_R is plotted versus pressure, p, for six different temperatures in the cholesteric phase. λ_R is always discontinuous at the Ch/S_C^* transition. The last λ_R value before the transition is denoted by λ_t.

As we can see in figure 4, λ_t shifts linearly to longer wavelengths with increasing transition pressure, p_t. It is important to note that λ_t depends only weakly on pressure. A pressure variation of 2 kbar changes λ_t only by about 130 nm (cf. figure 4). The course of all isotherms is remarkably similar, although the temperature increases from 85·0 to 115·3°C. In order to examine this more precisely, the slopes of the isotherms just before the occurrence of the phase transition were evaluated: in all cases a value of about 0·26 nm bar^{-1} was obtained.

Nothing is known so far about the pressure dependence of the smectic C* pitch. Since the de Vries λ_R–pitch relationship [11] for the cholesteric phase is also valid for

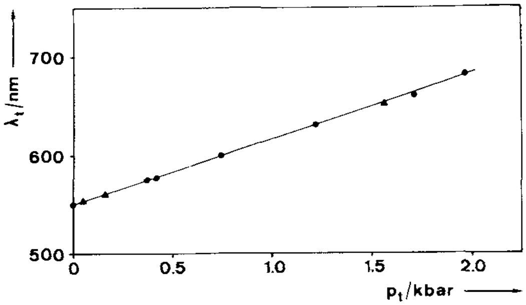

Figure 4. Wavelength of maximum light reflection at the phase transition cholesteric/smectic C*, λ_t, of the CE3 cholesteric phase versus phase transition pressure, p_t (circles, obtained with increasing pressure; triangles, obtained with decreasing pressure).

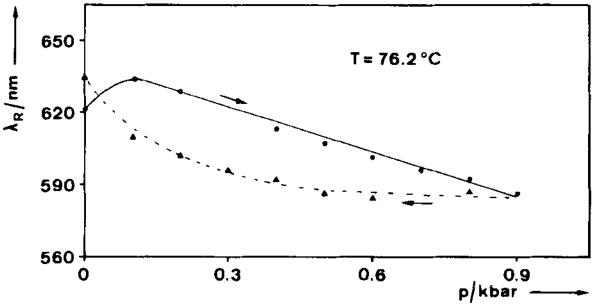

Figure 5. Wavelength of maximum light reflection, λ_R, of the CE3 smectic C* phase versus pressure, p, at 76·2°C (circles, obtained with increasing pressure; triangles, obtained with decreasing pressure).

the smectic C* phase (light incidence parallel to the helix axis) [12], we have also performed light reflection measurements at elevated pressures in the smectic C* phase. In doing so we had to accept, however, the low reproducibility of the λ_R measurements. Figure 5 presents λ_R data on CE3 for a typical isothermal pressure run (76·2°C). The run starts with a λ_R value of 621 nm. On an initial increase of pressure by about 100 bar, λ_R increases to 635 nm and then decreases linearly to 586 nm at 900 bar. (In order to avoid crystallization the application of pressure was stopped there, since the region of existence of the smectic C* phase is very small.) Subsequent lowering of the pressure does not influence λ_R at first. Only at about 400 bar does λ_R increase, and it finally reaches 635 nm at atmospheric pressure. Extrapolation of the solid straight line to atmospheric pressure yields a value of λ_R between 640 and 645 nm

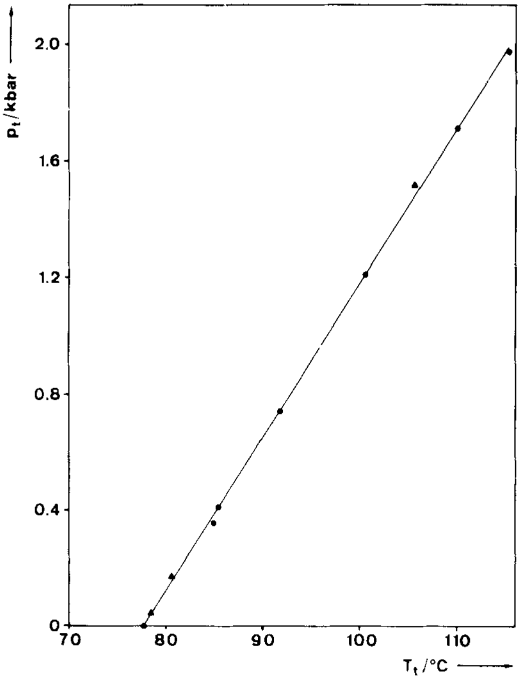

Figure 6. Phase equilibrium line cholesteric/smectic C* of CE3. Phase transition pressure, p_t, versus phase transition temperature, T_t (circles, obtained with increasing pressure; triangles, obtained with decreasing pressure).

which is approximately equal to that measured at the end of the pressure run (635 nm). The application of pressure at the beginning of the run seems to generate the equilibrium value of λ_R. The very high viscosity of the smectic C* phase is probably responsible for the hysteresis behaviour of λ_R with decreasing pressure. The latter effect is not accompanied by changes in linewidth and shape of the reflection band. There is no doubt that increasing pressure reduces the pitch of the smectic C* phase. The mean value of $-0{\cdot}06\,\mathrm{nm\,bar^{-1}}$ for the linear decrease of λ_R with pressure obtained from several runs can be accepted as an approximate value for the pressure dependence of the pitch.

Finally, we have tried to study the behaviour of λ_R in the vicinity of the transition to the cholesteric phase, but the low reproducibility of the measurements did not allow us to obtain precise results. The reproducibility of the last λ_R measurable in the smectic C* phase was, however, somewhat better. This λ_R of about 660 nm was found to be the same within ±20 nm along the coexistence curve. Therefore the pressure dependence of λ_t of the smectic C* phase can only be very weak.

The transition to the cholesteric phase is sharply detected by the change in shape of the reflection band (cf. figure 2). The first λ_R values which can be measured with decreasing pressure in the cholesteric phase are plotted in figure 4. They are on the straight line which was drawn on the basis of the break-off values in the cholesteric phase obtained with increasing pressure. The p_t, T_t coordinates of all λ_t values were used to determine the Ch/S_C^* coexistence curve of CE3; $T_t = 76{\cdot}8°\mathrm{C}$ at atmospheric pressure was also obtained microscopically. Figure 6 shows a linear relationship between phase transition pressure, p_t, and temperature, T_t.

4. Discussion

In principle conclusions can be drawn from λ_R measurements for smectic C* phases on the pretransformation to the cholesteric phase. Because of the low reproducibility of the λ_R values in this work we are unable to discuss this point. As far as we know there are no theoretical predictions about pretransitional effects for this direction of the transition. In contrast to the smectic side of the Ch/S_C^* transition, we can give precise information on the pretransformation of the cholesteric side. This pretransformation consists of the formation of smectic-like clusters, which cause an increase of the pitch of the cholesteric helix and thus also of λ_R.

For a second order Ch/S_C^* transition as well as a Ch/S_A one, the pitch and λ_R should diverge to infinity when approaching the smectic phase. For the Ch/S_A transition this phenomenon was observed by us some time ago [8]. The divergence can occur at atmospheric pressure or only at elevated pressure. The latter means that the phase transition is first order at atmospheric pressure and crosses over to second order at a higher pressure. The corresponding cross over point on the phase transition curve is called a tricritical point. Cholesteryl myristate (CM) is a convincing example of this behaviour [8]. At atmospheric pressure CM shows only a small pretransitional effect as the smectic A phase is approached. The breaking-off value of λ_R at the transition point λ_t is < 400 nm; accordingly the cholesteric helix is unwound only weakly. As we can see in figure 7, λ_t increases rapidly with increasing transition pressure, p_t. The p_t coordinate of the tricritical point is easily obtained by extrapolation of $\lambda_t = f(p_t)$ to $\lambda_t = \infty$: $p_t = 0{\cdot}82\,\mathrm{kbar}$ ($T_t = 98{\cdot}6°\mathrm{C}$). From this $p_t(T_t)$ condition onwards λ_R diverges to infinity, which means that the helix is entirely unwound at the Ch/S_A phase transition; this is now second order [8].

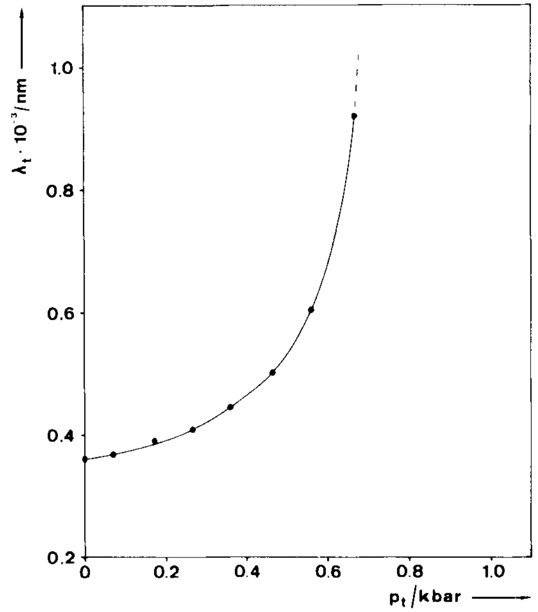

Figure 7. Wavelength of maximum light reflection at the phase transition cholesteric/smectic A, λ_t, of the CM cholesteric phase versus phase transition pressure, p_t.

As for the Ch/S_A transition of CM the Ch/S_C^* transition of CE3 shows a clear, but not a very strong, pretransitional effect at atmospheric pressure. The cholesteric helix is only unwound to a small extent (cf. figure 1: $\lambda_t < 600$ nm). Whereas the pretransitional behaviour of CM is extremely sensitive to increasing transition pressure and temperature [8], that of CE3 undergoes no distinguishable change (cf. figure 3). It is true that the λ_t of CE3 increases weakly with transition pressure (cf. figure 4), but the slope of the λ_R–p isotherms close to the transition is nearly the same. This is not like the Ch/S_A transition of CM, where λ_t becomes infinite within 0·82 kbar (cf. figures 4 and 7). Following the Ch/S_C^* transition curve upwards all the λ_t values determined are breaking-off values. That means that the Ch/S_C^* transition of CE3 remains first order, in contrast to the Ch/S_A transition of CM. This result is in agreement with most of the theoretical predictions (see, e.g., [1–4]).

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