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Phase transition sequence in the chiral compound 10FHBBBM7* studied by Raman scattering

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Integrated Raman intensity of the stretching mode of the phenyl rings as a function of temperature has been studied in order to determine the phase sequence in a new liquid crystalline compound. It is shown that the Raman technique provides the identification of the phase transitions, although some of them were not observed by macroscopic techniques. In particular, two ferrielectric phases were found from Raman measurements between the SmC* and the $\mathrm{SmC}^*_\mathrm{A}$ phases, while by DSC and by dielectric measurements only one phase could be detected. A detailed Raman study under d.c. electric field has shown that in this compound the Raman intensity is weakly influenced by the appearance of disclination lines.

1. Introduction

It is well known that chiral smectic liquid crystals can exhibit a rich variety of polar phases and the complete identification of the phase sequence is of great importance when studying these compounds. Many macroscopic techniques have been used for this purpose, namely, differential scanning calorimetry (DSC), comiscibility between like phases [1], texture observations, dielectric measurements, the temperature scan method (TSM) [2], etc. In contrast, raman scattering is a microscopic technique which has proven to be a useful method to determine the orientational order of the individual molecules in liquid crystals. The orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ of nematics were successfully obtained from polarized Raman studies [3]. Recently, Raman scattering has been proposed for the identification of the phase transitions of a liquid crystalline compound displaying a ferroelectric–ferrielectric–antiferroelectric phase sequence [4].

As was shown by Jen *et al.* [3], for each of the molecular vibrations there is a Raman polarizability tensor $\boldsymbol{\alpha}'$ that is essentially unchanged in the molecular frame when the compound exhibits phase transitions from the isotropic to any of the liquid crystalline phases. The $\boldsymbol{\alpha}'$ tensor is a microscopic property of the molecule and local field corrections are needed to connect the macroscopic properties to the microscopic ones. Since the local field corrections depend on the short range correlations between molecules, which are not significantly different in liquid crystalline phases, it was assumed that $\boldsymbol{\alpha}'$ can be treated as a 'dressed' molecular polarizability tensor which already includes the local field corrections. The three (or more) phenyl rings of the molecule (the latter assumed to be a cylindrical rod) make a major contribution to the optical response and, obviously, their stretching direction is parallel to the molecular long axis. In particular, for the Raman active stretching mode of phenyl rings (localized near $1600\,\mathrm{cm}^{-1}$), the Raman tensor $\boldsymbol{\alpha}'_\mathrm{m}$ has the diagonal form

$$\boldsymbol{\alpha}'_\mathrm{m} = \boldsymbol{\alpha}\begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

where the molecular long axis is taken along z, and the y axis is parallel to both the smectic layers and the glass plates of the sample. This Raman tensor is usually strongly anisotropic, so that $a, b \ll 1$. The approach considered above is also valid in the case of chiral liquid crystals with a helicoidal structure, since, as was pointed out by Farhi *et al.* [4], the azimuthal angle φ varies

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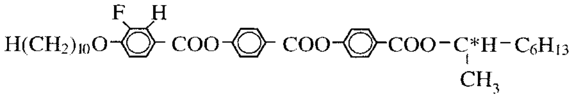
continuously as a function of z. As the size of the sample area used in Raman scattering is significantly larger than the pitch of the helix, the azimuthal angle can be considered as homogeneously distributed.

The integrated Raman intensity of the stretching mode of phenyl rings can be used as a probe of the orientational order at phase transitions from SmA* to polar phases where the tilt angle θ appears, and the Raman tensor acquires non-diagonal components in the axes previously chosen.

The present contribution reports a detailed Raman study of the orientational order in the new liquid crystalline compound 10FHBBBM7* [(*R*)-4-(1-methylheptyloxycarbonyl)phenyl 4-(4-decyloxy-3-fluorobenzoyloxy)-benzoate], which has the chemical formula [5]:



The results obtained confirm the usefulness of this technique for the study of the phase sequences in liquid crystals.

2. Experimental

DSC and texture observations suggested the following phase transition sequence [5]:

$$\mathrm{Cr} \xrightarrow[37.8]{89\,^{\circ}\mathrm{C}} \mathrm{SmC}_{\mathrm{A}}^{*} \xrightarrow[0.013]{101.8\,^{\circ}\mathrm{C}} \mathrm{SmC}_{\mathrm{FI}}^{*} \xrightarrow[0.029]{103.4\,^{\circ}\mathrm{C}} \mathrm{SmC}^{*} \xrightarrow[0.243\ddagger]{112.8\,^{\circ}\mathrm{C}}$$

$$\mathrm{SmC}_{\alpha}^{*} \xrightarrow{113.3\,^{\circ}\mathrm{C}} \mathrm{SmA}^{*} \xrightarrow[5.04]{127\,^{\circ}\mathrm{C}} \mathrm{I} \quad \mathrm{kJ\ mol^{-1}}$$

The liquid crystal was filled by capillarity into 25 µm planar glass cells (E.H.C. Co., Japan) coated with ITO in order to perform dielectric measurements or apply an electric field. The samples were placed in a hot stage and the temperature was controlled by a Lakeshore DRC-93CA temperature controller, using a chromel–alumel thermocouple as a thermometer. The accuracy was better than 0.1 K.

Raman spectra were recorded in a back scattering geometry using a Jobin Yvon T64000 spectrometer equipped with a micro-Raman set up and a CCD detector. The 514.5 nm line of an argon laser (Coherent INOVA 90) was used as exciting source. The laser power was kept low to avoid sample degradation or local overheating. To eliminate the polarization anisotropy of the monochromator, Raman spectra were recorded for zz and yy components by rotation of the sample through the angle 90°. The spectrometer was also calibrated by measuring the well-known depolarization ratio of benzene lines at 1600 cm^{-1}.

To obtain good alignment of the molecules in the sample, a low frequency (between 10 and 30 Hz) and high amplitude electric field (≈ 1 V µm^{-1}) was applied in the high temperature range of the SmC$_{\alpha}^{*}$ phase for ≈ 30 min. All measurements were performed on cooling from the SmA* phase. For Raman measurements, a well aligned domain was previously selected and the direction of its optical axis was oriented relative to the direction of polarization of the laser light using transmission optical microscopy. Raman measurements were performed simultaneously with dielectric measurements, in order to determine phase transition temperatures unambiguously.

3. Results and discussion

The temperature dependence of the complex dielectric constant ($\varepsilon' - i\varepsilon''$) obtained at 100 Hz on cooling is shown in figure 1 (*a*). The anomalies presented by ε' and ε'' give a clear indication of the existence of several polar phases, namely SmC$_{\mathrm{A}}^{*}$, SmC$_{\mathrm{FI}}^{*}$, SmC* and SmA* phases, as suggested by the DSC technique. Polarization hysteresis loops confirmed the polar character of each phase. The vertical lines depicted in figure 1 (*a*) indicate the temperature range of the different phases. The transition temperatures deviate somewhat from those determined by DSC, due to different calibration of the equipment used and different scanning rates.

The SmC*–SmC$_{\mathrm{FI}}^{*}$ and the SmC$_{\mathrm{FI}}^{*}$–SmC$_{\mathrm{A}}^{*}$ phase transition temperatures can be easily determined from figure 1 (*a*) and correspond to 104°C and 102°C, respectively. The inverse of ε' as a function of the temperature, shown in the inset of figure 1 (*a*), presents a small anomaly in the slope of $1/\varepsilon'(T)$ at about 113.9°C, which corresponds to the SmC$_{\alpha}^{*}$–SmC* phase transition. Moreover, at this temperature there is an anomaly in the polydispersive coefficient of the system, which is associated with the appearance of a strong contribution of the Goldstone mode that is responsible for the huge increase of ε' below 113.9°C.

$\varepsilon'(T)$ measurements do not provide evidence for the SmA*–SmC$_{\alpha}^{*}$ phase transition, but taking into account the temperature dependence of the spontaneous polarization ($\mathbf{P}_{\mathrm{s}}$) and of the optical tilt angle ($\theta_{\mathrm{optical}}$) presented in figure 1 (*b*), this phase transition is presumed to occur at ≈ 114.7°C.

The saturation polarization and the optical tilt angle were calculated from analysis of polarization and of optical hysteresis loops, respectively. Both $\mathbf{P}_{\mathrm{s}}$ and $\theta_{\mathrm{optical}}$ are averaged, macroscopic quantities obtained under fully unwound conditions. This is one reason why their temperature behaviour is regular and in general inadequate to indicate the presence of phase transitions other than SmA*–SmC$_{\alpha}^{*}$. Nevertheless, in our study a step in $\mathbf{P}_{\mathrm{s}}(T)$ and a slight change in the derivative $\mathrm{d}\theta_{\mathrm{optical}}/\mathrm{d}T$ can also be seen in figure 1 (*b*) at the SmC$_{\mathrm{FI}}^{*}$–SmC$_{\mathrm{A}}^{*}$ phase transition.

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‡0.243 kJ mol^{-1} is the sum of the enthalpies for the SmC*–SmC$_{\alpha}^{*}$ and the SmC$_{\alpha}^{*}$–SmA* phase transitions.

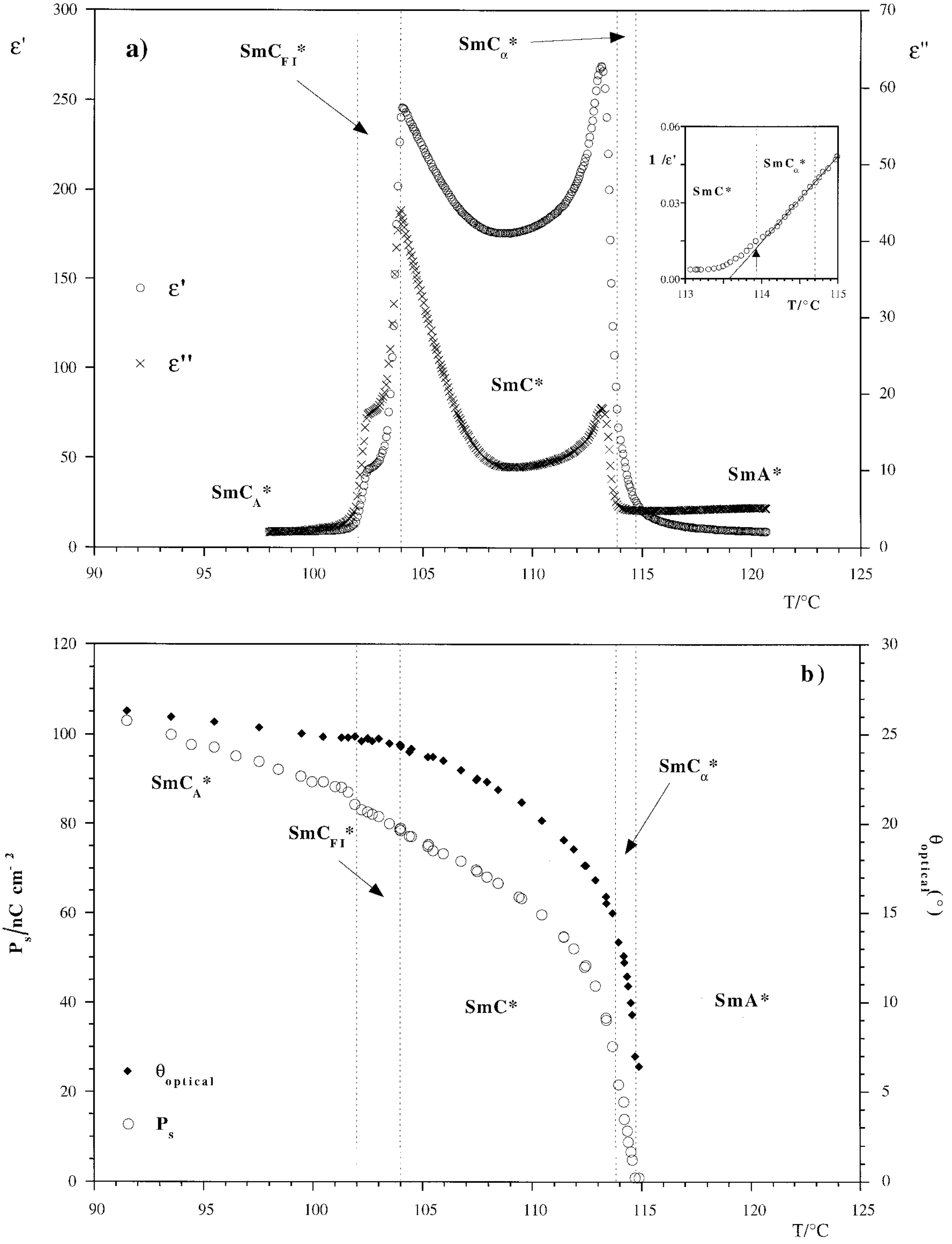

Figure 1. (*a*) Temperature dependence of the dielectric constant, obtained at 100 Hz. The insert shows the behaviour of $1/\varepsilon'(T)$ near the SmC$_\alpha^*$–SmC* phase transition. (*b*) Temperature dependence of the spontaneous polarization ($\mathbf{P}_s$) and of the optical tilt angle ($\theta_{\mathrm{optical}}$).

In the Raman spectra of 10FHBBBM7*, the stretching mode of the phenyl rings appears as a doublet at 1602 and 1615 cm^{-1}. The summarized integrated intensity of the doublet was obtained from a two-Lorentzian fitting procedure performed for each spectrum recorded. The Raman tensor of this mode shows a strong anisotropy in the paraelectric SmA* phase, where the I_{zz}/I_{yy} ratio has been found to be equal to ≈ 16. As was shown by Kim *et al.* [6], in the case of a uniaxial Raman tensor with, in addition, $a = b \ll 1$, the Raman intensity of the C–C stretching mode of phenyl rings provides information about the average orientation of the molecular long axis. Moreover, the I_{zz} Raman intensity is nearly proportional to the fourth power of cos θ, where θ is the spontaneous tilt angle of the molecules.

The temperature dependence of the I_{zz} normalized Raman intensity observed in 10FHBBBM7* is shown in figure 2, where the values of $\cos^4(\theta_{\text{optical}})$ are also plotted for comparison. $\text{Cos}^4(\theta_{\text{optical}})$ was calculated from the direct tilt angle measurements presented in figure 1 (*b*). In contrast to the temperature behaviour of θ_{optical}, which provides clear evidence only for the transition from the SmA* to the first polar phase, the normalized Raman intensity presented in figure 2 exhibits small but detectable anomalies, some of them associated with the different phase transitions and others not easily identified due to some scattering of the data.

A deviation of the normalized I_{zz} intensity from unity in the SmA* phase a few degrees above the SmA*–SmC$_\alpha^*$ phase transition, is probably caused by pretransitional fluctuations of the director from the layer normal, resulting from long-axis fluctuations of the molecules. Furthermore, the Raman intensity of the 1602, 1615 cm^{-1} doublet for the $yz(zy)$ component is non-zero in the SmA* phase, which may also be seen as evidence of pretransitional fluctuations (see figure 3).

In the SmC$_\alpha^*$ phase and in the high temperature region of the SmC* phase, the I_{zz} Raman intensity is nearly proportional to $\cos^4\theta$, as predicted. However, in the low temperature region of the SmC* phase, I_{zz} exhibits a non-regular temperature dependence, in contrast to the optical measurements of the tilt angle and deviates from a $\cos^4\theta$ law. In the region of the SmC$_{\text{FI}}^*$ and SmC$_{\text{A}}^*$ phases, agreement between the optical and Raman data is also imperfect (figure 2). Similar difference between Raman and optical measurements, namely a higher value of the tilt angle obtained from the Raman data, was also observed in the C8 tolane compound [4]. One reason for the deviation of I_{zz} from a $\cos^4\theta$ dependence is that the condition $a = b \ll 1$ assumed above is rather poorly fulfilled in SmC$_{\text{A}}^*$, SmC$_{\text{FI}}^*$ and the low temperature range of SmC* phases, as is suggested by the temperature behaviour of the $R_0 = I_{zz}/I_{yy}$ ratio plotted in figure 4. Moreover, the domain structure in SmC$_{\text{FI}}^*$ and SmC$_{\text{A}}^*$ phases may induce deviations of the smectic layer alignment from the polarizing directions previously selected in the paraelectric SmA* phase; therefore some decrease in the Raman intensity is expected. The drop in the I_{zz}

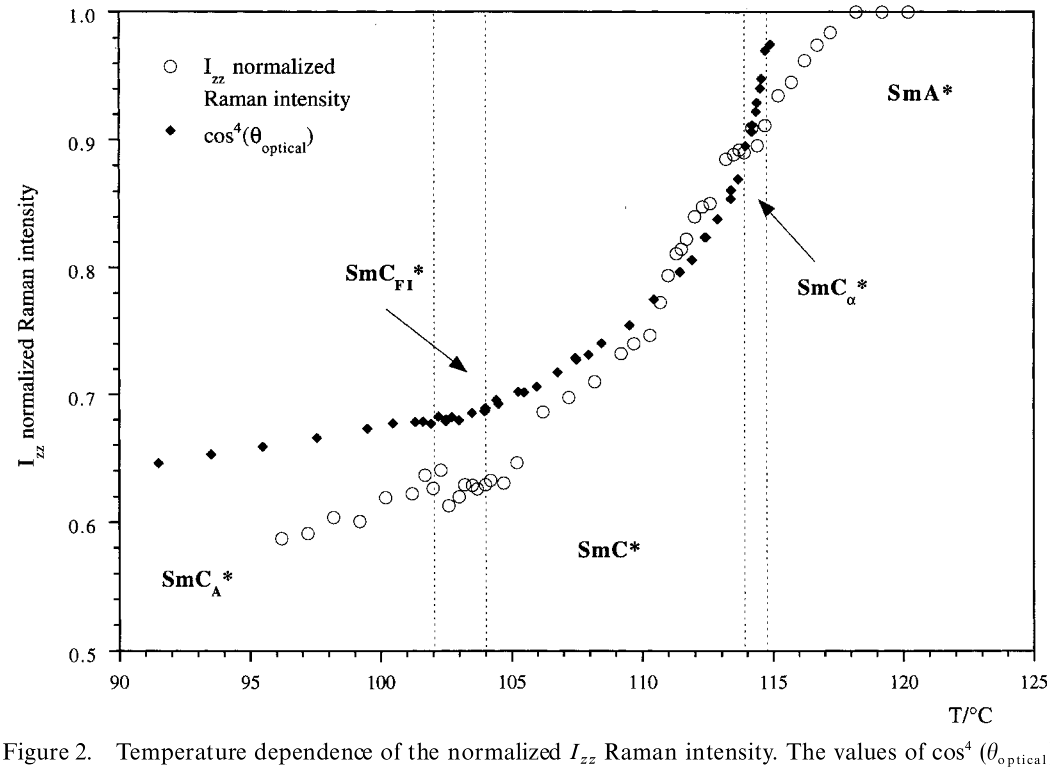

Figure 2. Temperature dependence of the normalized I_{zz} Raman intensity. The values of $\cos^4(\theta_{\text{optical}})$.

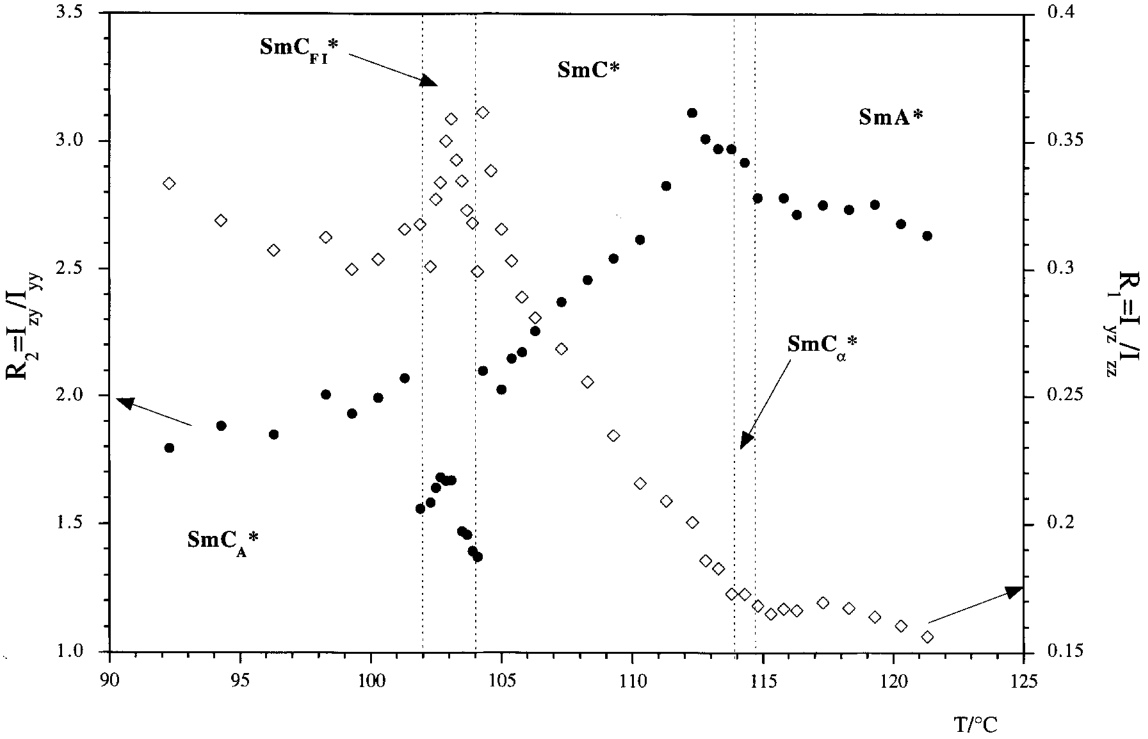

Figure 3. Temperature dependence of the ratios $R_1 = I_{yz}/I_{zz}$ and $R_2 = I_{zy}/I_{yy}$.

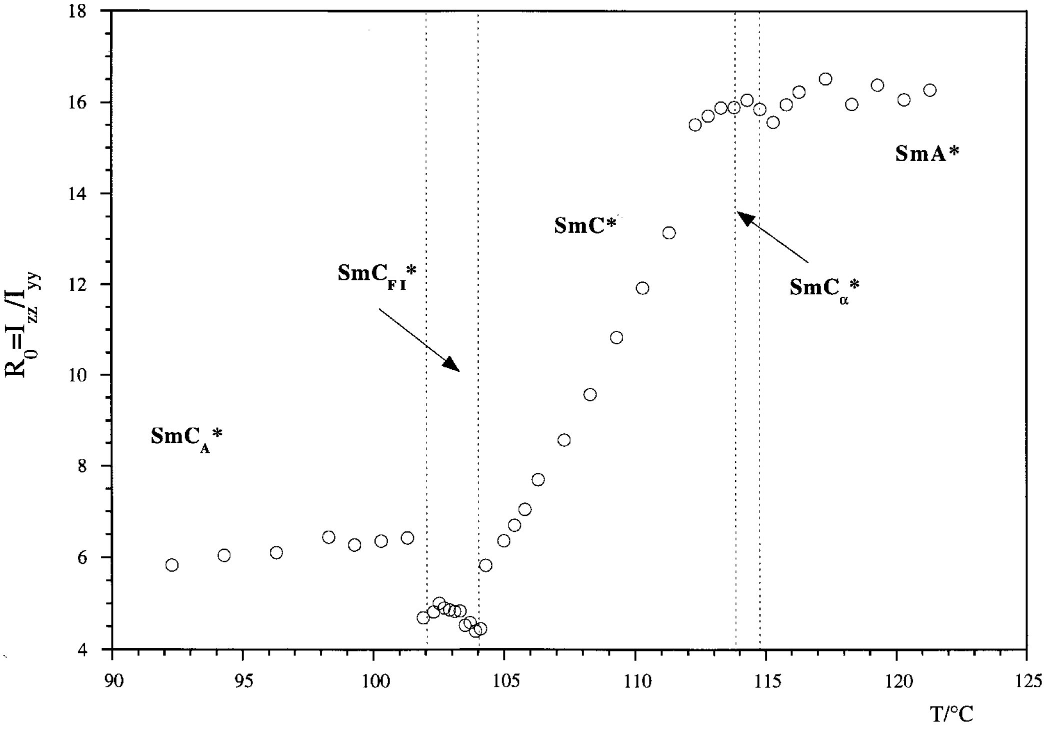

Figure 4. Temperature dependence of the ratio $R_0 = I_{zz}/I_{yy}$.

Raman intensity at ≈ 105.7°C (figure 2) coincides with the appearance of disclination lines observed directly during the micro-Raman measurements. These defect lines were observed to be nearly perpendicular to the previously achieved alignment, so the latter may be disturbed by their appearance. Nevertheless, good optical contrast of the domain used in the Raman measurement between parallel and crossed polarizers was always observed.

The scattering of the data is minimized by taking the ratios $R_1 = I_{yz}/I_{zz}$ and $R_2 = I_{zy}/I_{yy}$. These ratios are plotted in figure 3 as a function of the temperature. On cooling, a significant increase of R_1 and of R_2, in the temperature range of the SmC$^*_\alpha$ phase, is associated undoubtedly with an increase in the tilt angle in this phase, see also figure 1(*b*). Nevertheless no firm conclusions concerning the SmA*–SmC$^*_\alpha$ and the SmC$^*_\alpha$–SmC* phase transition temperatures can be reached.

The phase transitions SmC*–SmC$^*_{\mathrm{FI}}$ and SmC$^*_{\mathrm{FI}}$–SmC$^*_{\mathrm{A}}$, detected by DSC and dielectric measurements, could not be confirmed from the optical measurements of the tilt angle. The last phase transition was revealed from a weak anomaly in the DSC measurements and a shoulder in the dielectric susceptibility, see figure 1(*a*). In contrast, the depolarization ratios $R_1 = I_{yz}/I_{zz}$, $R_2 = I_{zy}/I_{yy}$ and $R_0 = I_{zz}/I_{yy}$ presented in figures 3 and 4, respectively, allowed the unambiguous determination of the above mentioned phase sequence, since well defined abrupt changes have been found at 104°C and 102°C. Moreover, the R_1 and R_2 ratios exhibit a well-defined two-step behaviour within this temperature interval, with a clear change of slope between 104°C and 102°C. This result points very clearly to the existence of two narrow, distinct ferrielectric phases, SmC$^*_{\mathrm{FI}_1}$ and SmC$^*_{\mathrm{FI}_2}$. The intermediate SmC$^*_{\mathrm{FI}_2}$–SmC$^*_{\mathrm{FI}_1}$ phase transition was detected neither by DSC [5] (transitions between ferrielectric phases usually give small enthalpy values) nor by the dielectric measurements (a poorly resolved shoulder can be lost in the temperature dependence of ε', which changes significantly in the narrow temperature interval from SmC* to SmC$^*_{\mathrm{A}}$). However, the Raman data presented in figure 3 provides evidence for the two ferrielectric phases.

Figure 4 shows that the R_0 ratio presents minimum values exactly in the ferrielectric region (between 102°C and 104°C), then increases abruptly at the transition to the SmC$^*_{\mathrm{A}}$ phase and remains constant on further cooling. Both R_1 and R_2 ratios also exhibit anomalies in the same region. A similar behaviour was also observed in the C8 and C10 tolane compounds [4], where the drop in I_{zz} and the enhancement in I_{yy} were interpreted as being caused by a large number of defects, including disclination lines within the ferrielectric phase.

Disclination lines (often called 'dechiralization lines' or 'unwinding lines') result from the incompatibility of two structures, a helicoidal structure in the bulk of the sample and a homogeneous, unwound structure close to the glass plates. At zero electric field, on cooling, these lines appear in the ferroelectric region at least two degrees before the transition to the ferrielectric phase both in the C10 Tolane [7] and 10FHBBBM7* compounds. They exhibit good optical contrast throughout the ferrielectric phase and are not visible in the SmC$^*_{\mathrm{A}}$ phase.

To estimate the influence of disclination lines on the Raman intensity for the compound 10FHBBBM7*, we have also measured the integrated Raman intensity, I_{zz}, as a function of an applied d.c. field. The typical behaviour is shown in figure 5. The applied d.c. field was increased until a fully unwound state was achieved and the disclination lines were observed to disappear completely. As can be seen from figure 5, the effect of the appearance (or disappearance) of disclination lines is very weak for 10FHBBBM7*. The weak increase in the I_{zz} intensity under a d.c. field observed in the ferroelectric phase (see figure 5(*a*)) can be explained by a decrease in the tilt angle fluctuations. In the ferrielectric region, the I_{zz} intensity exhibits only scattering around an average constant value, up to the unwound state. As shown in figure 5(*b*), the disclination lines disappear when the applied field is higher than 0.12 V μm^{-1}. In the antiferroelectric phase, where the tilt angle is saturated and the temperature is considerably lower, tilt angle fluctuations seem to be negligible and no variation of Raman intensity was found on increasing the d.c. field up to the unwound state, see figure 5(*c*). Further increase of the I_{zz} Raman intensity on decreasing the field is caused by the improved alignment of the sample, since the electric field applied to unwind the helix in this phase was very high.

4. Conclusion

Raman spectroscopy has proven to be a powerful technique to determine the phase sequence of chiral liquid crystals. At least one of the measured ratios R_1, R_2 and R_0 shows an anomaly at the SmC$^*_\alpha$–SmC*, SmC*–SmC$^*_{\mathrm{FI}}$ or SmC$^*_{\mathrm{FI}}$–SmC$^*_{\mathrm{A}}$ phase transitions, which are not visible from the optical measurements of the tilt angle. The anomalies observed by Raman scattering are in good agreement with the phase transition sequence determined from texture observation, DSC and dielectric measurements.

In the temperature interval of the ferrielectric region 102–104°C, the R_1 and R_2 ratios present a two-step behaviour, with a well-defined change in slope between those temperatures. This fact leads us to conclude that the compound 10FHBBBM7* presents two distinct ferrielectric phases, although the transition SmC$^*_{\mathrm{FI}_2}$–SmC$^*_{\mathrm{FI}_1}$ was not detected by DSC.

Taking into account the ensemble of results, we suggest that the sudden variation of the R_1 and R_2 ratios in the middle of the ferrielectric region is probably caused by a molecular rearrangement. Consequently, two ferrielectric phases were proposed in the temperature region where the transformation from ferroelectric to antiferroelectric

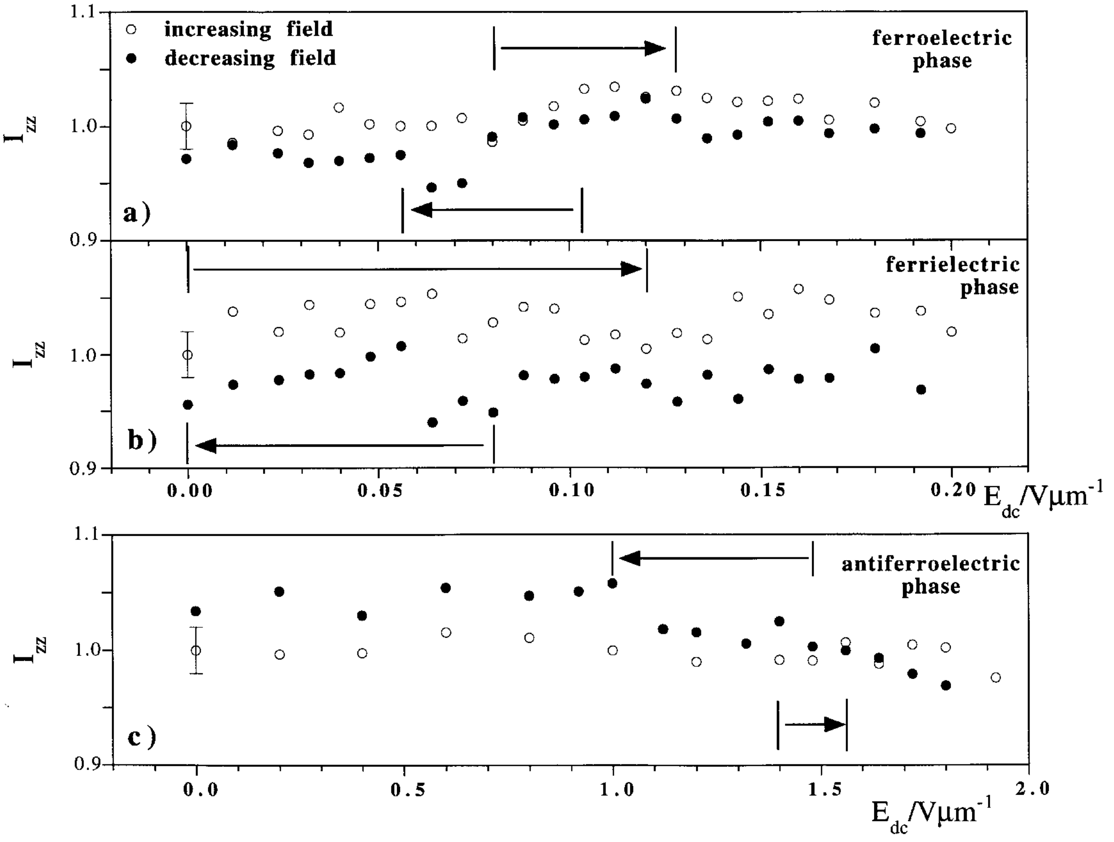

Figure 5. Typical behaviour of the I_{zz} normalized Raman intensity as a function of applied d.c. field in the (*a*) ferroelectric, (*b*) ferrielectric and (*c*) antiferroelectric phases. The vertical lines show the regions where disclination lines were observed. The arrows, → and ←, indicate increasing and decreasing fields, respectively. A typical error bar is indicated in each case.

order occurs. Such a transformation implies considerable alterations of the orientation of the molecules, causing abrupt changes of the R_1 and R_2 ratios in the narrow temperature interval between the ferroelectric and the antiferroelectric states.

It is known [4] that disclination lines may bring dramatic changes in Raman measurements, because they can induce changes in the local electric field [4]. However, the conductivity of the samples may be high enough to compensate (or reduce considerably) the electrical charge carried by 2π-disclinations (π-disclinations are not charged [7]). The results obtained in 10FHBBBM7* as a function of the d.c. field show that the effect of disclination lines is very weak in this compound.

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