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Studies of the field-induced alignment of the SmA phase using deuterium NMR spectroscopy have revealed a complex pattern of behaviour when the director is initially orthogonal to the aligning field. Here we report the electric field-induced alignment of the SmA director using time-resolved deuterium NMR when the aligning electric field ***E*** *is at an angle with the magnetic field* ***B*** *of the spectrometer which is considerably smaller than 90°; here the director is initially aligned parallel to the magnetic field. The dynamics of the electric field-induced alignment of the director for the smectic phase of 4-α,α-d_2-octyl-4′-cyanobiphenyl (8CB-d_2) was investigated at two angles between* ***B*** *and* ***E*** *of roughly 45° and 54.5° the so-called magic angle, at different electric field strengths and also at two temperatures, 305.1 K and 302.6 K. The dynamics of the SmA director alignment of 8CB-d_2 was monitored by measuring the deuterium NMR spectrum as a function of time. The results for the 45° and 54.5° geometries revealed, in contrast to the complex dynamics of alignment of*

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the SmA director observed for the 90° geometry, a much simpler pattern of relaxation. Here the director appeared to be aligned almost as a monodomain. In general, for either of the two geometries employed here, the ultimate angle of alignment the director achieves relative to ***E*** *depends on the electric field strength. Lowering the temperature by just 2.5°C from 305.1 K to 302.6 K has a dramatic effect on the rate of director relaxation presumably because of the large increase in the combined rotational viscosity and the elastic energy effects of the SmA phase with decreasing temperature. Furthermore for the 45° geometry at 302.6 K, the SmA sample separates on relaxation ultimately into two domains with different alignment angles.*

Keywords: Smectic A; electric field-induced alignment; deuterium NMR

INTRODUCTION

The smectic A phase is characterised by the presence of long range, one dimensional translational order giving rise to a layered structure in which the director is parallel to the layer normal. A monodomain SmA sample can, in principle, be obtained by the application of an aligning field of sufficient strength. When the direction of the aligning field is then changed, the orientation of the director, **n**, will be changed and the layered structure will have to be re-established orthogonal to the new direction. This is clearly a more complex process than for the alignment of the nematic phase. When the direction of the aligning field is changed by 90°, the pattern of the alignment process was revealed to be very complex both from magnetic [1] and electric field-induced investigations [2]. One of the advantages of using an electric field in investigating the SmA alignment dynamics is the ability to change the rate of alignment by varying the electric field strength and hence the torque exerted on the director. The main features of the electric field-induced alignment of the SmA in the orthogonal geometry (i.e. the aligning field is applied at 90° relative to the initial director orientation) were found to be [2]:

1. The existence of an induction period which could vary from a few minutes to several hours depending on the electric field strength.
2. The smectic directors do not align uniformly, that is as a monodomain, but adopt a range of orientations which depends on the field strength.
3. At high electric field strengths when the rate of alignment is fast a switch from the initial director orientation to the final director orientation (essentially parallel to the electric field) is observed without apparently any intermediate director orientations.
4. At intermediate values of the electric field strength, intermediate director orientations are observed with a curious cut-out from $\sim 40°$ to

90° with the final director orientation locked at two orientations: one essentially parallel to the electric field and the other $\sim 10°$ from this.
5. At low values of the electric field strength a continuous distribution of director orientations is formed.
6. The existence of a threshold voltage has also been observed [3].

In view of this complexity in the alignment dynamics of the SmA phase for the 90° geometry (which could be caused by the degeneracy in the path the director could take to align at 90° to the initial orientation: from 0° to 90° or equivalently from 0° to 270° as shown, for example in the complex alignment dynamics of the nematic phase of 5CB [4]) we wanted to know how the director alignment process proceeds when the aligning field is at an angle which is considerably less than 90°.

In this investigation we have, therefore, chosen two geometries in which the aligning field (the electric field) makes an angle relative to the initial field (which is the magnetic field of the NMR spectrometer) of $\sim 45°$ and $\sim 54.5°$ (the magic angle; this value was chosen simply to be greater than 45° since for nematics it is predicted theoretically that the alignment pathway is complex [5]). Here we present the results of a study of the effects of varying the electric field strength for these two non-orthogonal geometries on the rate and pattern of alignment of the SmA phase. We also look at the effect of varying the temperature on the dynamics of director alignment.

The alignment process was monitored by deuterium NMR spectroscopy which is a particularly useful method for determining the director orientation because it also allows the director distribution to be determined. For a uniformly aligned uniaxial liquid crystalline sample, that is one described by a single director, **n**, a group of equivalent deuterium nuclei gives, when ignoring dipolar couplings, a deuterium NMR spectrum which is a quadrupolar doublet whose separation is $\Delta\nu(\theta)$, where θ is the angle between the director and the magnetic field, **B**. The value of the quadrupolar splitting $\Delta\nu(\theta)$ at any given temperature depends on θ according to

$$\Delta\nu(\theta) = \Delta\nu(0°)(3\cos^2\theta - 1)/2, \tag{1}$$

where $\Delta\nu(0°)$ is the splitting when the director is parallel to **B**. The quadrupolar splitting, $\Delta\nu(0°)$, depends on the orientational order of the CD_2 group as well as on the deuterium quadrupolar tensor; however it is not necessary to know the form of this dependence in order to determine the director orientation from the observed quadrupolar splitting. For a monodomain sample the variation of $\Delta\nu(\theta)$ with the angle θ is shown in Figure 1. However, when the director distribution is non-uniform new spectral features appear corresponding to specific director orientations since the overall NMR spectrum is the sum of all sub-spectra from the

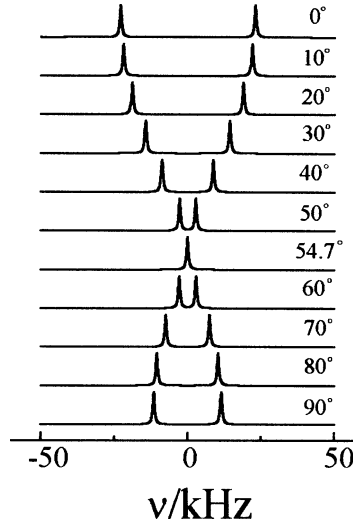

FIGURE 1 The angular variation of the quadrupolar splitting $\Delta\nu(\theta)$ for a uniformly aligned director. θ is the angle between **n** and **B**.

different director orientations. Figure 2 illustrates these spectral features as the director distribution becomes progressively broader and, in the limit of a random planar director distribution, the characteristic 2D powder spectrum is observed.

In this study we use a thin film of the liquid crystal 4-α,α-d_2-octyl-4′-cyanobiphenyl (8CB-d_2) which has a nematic and a smectic A phase and is

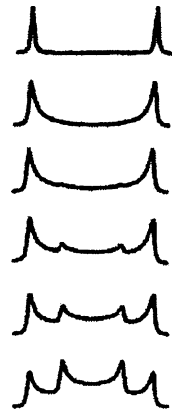

FIGURE 2 The broadening of NMR lines as the distribution of director orientations becomes progressively non-uniform within a plane.

specifically deuteriated in the α-position of the chain. The director **n** of 8CB-d_2 in the nematic phase will align parallel to the spectrometer magnetic field because of the positive anisotropy, $\Delta\chi$, in the diamagnetic susceptibilty. This director alignment will be preserved when the sample is cooled into the SmA phase so that a monodomain SmA is produced. As the liquid crystal is a thin film confined between two glass plates that are usually placed parallel to **B**, such a smectic alignment would produce a monodomain sample in a book-shelf geometry in which the layers are orthogonal to the glass surfaces [2]. However, in this study we incline the cell to **B** to produce the non-orthogonal geometry which we use here (see Figure 3a). The alignment of the smectic layers now produces a monodomain in which the layers are inclined at an angle with respect to the glass surface (see Figure 3a).

This initial alignment of the director is changed by switching on an electric field **E** normal to the glass plates but making an angle α (see Figure 3b) relative to **B** and the original director. If **E** is sufficiently strong to overcome the magnetic torque exerted on the director, the constraining effect of the SmA structure, the surface forces and elastic effects then the director will be forced to align towards the electric field direction. For this to happen the material should have a positive anisotropy in the dielectric permittivity, $\Delta\varepsilon$, as in 8CB. The deuterium NMR spectrum is then used to monitor how the director aligns towards the electric field direction.

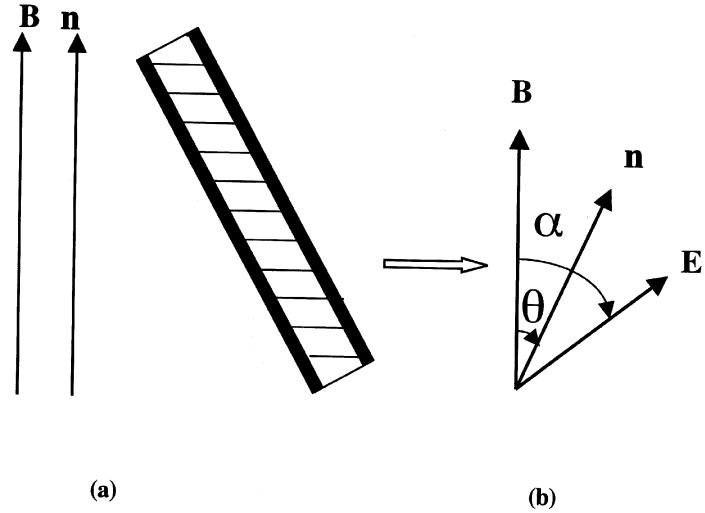

FIGURE 3 Experimental geometry: (a) At $\mathbf{E} = 0$, the cell is positioned at an angle to the magnetic field, **B**, the director, **n**, is parallel to **B**. The smectic layers are orthogonal to **B** (b) After **E** is switched on; **E** makes an angle α with **B**; at any time the director makes an angle θ with **B**.

EXPERIMENTAL

The preparation of the specifically deuteriated 4-α,α-d_2-octyl-4′-cyanobiphenyl (8CB-d_2) has been described before [1]; the transition temperatures were found to agree with literature values ($T_{NI} = 313.8$ K and $T_{SmAN} = 306.8$ K) [6].

The construction of the cell and its filling as well as the arrangement of the cell in the NMR spectrometer has been described elsewhere [2]. The cell gap is 56.8 μm. An amplifier and a function generator were used to provide a 10 kHz sinusoidal AC electric field across the cell. The cell is initially held in the NMR spectrometer so that the glass plates are aligned parallel to the magnetic field and the goniometer set at 0°. The final alignment of the cell is carried out by switching the electric field on (a high enough field of 1.4 MVm^{-1} to align the director completely along the electric field) while the sample is in the nematic phase. The cell is then rotated using the goniometer until a doublet is obtained which gives the desired value of α according to Eq. (1). Two geometries were used with α values of $\sim 45°$ and $\sim 54.5°$. Here we present the results at two temperatures of 305.1 K and 302.6 K for both geometries. The electric field strength used in these experiments varied from 1.3 MVm^{-1} to 0.80 MVm^{-1} (corresponding to an applied voltage across the cell of ~ 74 to 45 V_{RMS}). The spectra were recorded using a JEOL Lambda 300 spectrometer which has a magnetic flux density of 7.05 T. The spectra were obtained using a quadrupolar echo pulse sequence with a 90° pulse of 6 μs and interpulse delay of 40 μs. The number of free induction decays (FID) used to produce spectra with good signal to noise was 6500–7000. The acquisition time is ~ 4 min which places an upper limit on the rate of director dynamics which can be studied. The procedure for a typical SmA director alignment experiment is the same as has been described before [2].

RESULTS AND DISCUSSION

We will give the results for the two geometries at 305.1 K first and then those at 302.6 K.

Results at 305.1 K

(a) 45° Geometry:

We carried out measurements at the following field strengths: 0.8, 0.9, 1.0, 1.1, 1.2 and 1.3 MVm^{-1}. Typical spectra, recorded as a function of time during the process of alignment of the SmA director, are shown in Figures 4

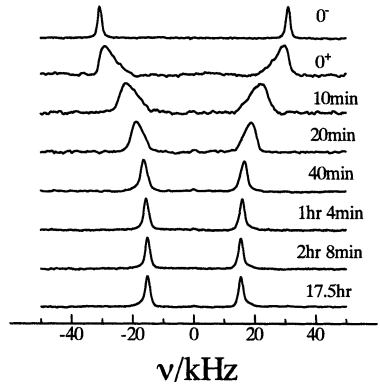

FIGURE 4 Spectra recorded as a function of time for the cell at $T = 305.1\,K$ and $E = 1.2\,MVm^{-1}$ for the 45° geometry.

and 5 for two values of the electric field strength namely $1.2\,MVm^{-1}$ (relatively fast rate of alignment) and $0.8\,MVm^{-1}$ (relatively slow rate of alignment).

In Figure 4, we see that the spectrum prior to switching the electric field on, at time $t = 0^-$ (i.e. immediately before switching E on), consists of two sharp lines (linewidth at half height of $\sim 1.7\,kHz$) and a quadrupolar splitting of $\Delta\nu(0°) = 61.8\,kHz$. The spectrum at $t = 0^+$ (i.e. immediately after switching E on) shows a splitting $\Delta\nu \sim 59\,kHz$ (corresponding to a value of $\theta = 10.2°$) but the lines are broader ($\delta\Delta\nu$(½ height) $\sim 6\,kHz$). The broadening of the lines is associated with a distribution of director orientations which is present during the period of spectral acquisition. It is

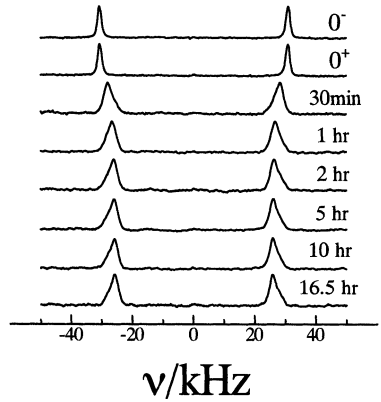

FIGURE 5 Spectra recorded as function of time for the cell at $T = 305.1\,K$ and $E = 0.8\,MVm^{-1}$ for the 45° geometry.

possible to estimate the width of the distribution in the director orientations on the basis of Eq. (1). If the distribution function is centred on θ and has a width $\delta\theta$, then in the limit of small $\delta\theta$ the associated range of quadrupolar splittings, $\delta\Delta\nu(\theta)$, is obtained from Eq. (1) as [7]

$$\delta\Delta\nu(\theta) = (3/2)\,\Delta\nu(0^\circ)\sin 2\theta\,\delta\theta. \tag{2}$$

This range corresponds approximately to the line broadening resulting from the distribution of director orientations. From the additional broadening (above that when $\theta = 0^\circ$) in the spectral linewidth at $t = 0^+$, we can estimate the width in the director distribution as $\delta\theta \sim 8.5^\circ$ centred at $\theta = 10.2^\circ$. The spectrum at $t = 10$ min, shows the director has now moved to an orientation at which $\theta = 26^\circ$. The lines are still broad but the distribution in the director orientations has narrowed now to $\delta\theta \sim 4^\circ$. At $t = 20$ min θ reaches a value of $\sim 31^\circ$ and the lines narrow further corresponding to $\delta\theta \sim 2^\circ$.

At $t = 40$ min, the value of θ has changed by only a few degrees to $\sim 34^\circ$ although the lines have sharpened further to give $\delta\theta \sim 0.5^\circ$. From then only very small changes in θ are observed. At $t = 17.5$ h, the final director orientation has $\theta = 35.5^\circ$ with sharp spectral lines having a linewidth of ~ 1.8 kHz and a sharp distribution in the director orientation of $\delta\theta < 0.1^\circ$.

In contrast to the relatively fast alignment rate at $E = 1.2\,MVm^{-1}$, the results in Figure 5 for the slow SmA director alignment rate at $E = 0.8\,MVm^{-1}$ show sharp spectral lines at $t = 0^+$ indicative of a narrow director orientational distribution during the first 4 min of the alignment process following switching the electric field on. The director achieves an orientation of $\theta = 2.5^\circ$ at $t = 0^+$. However, at $t = ½$ h the lines are somewhat broad corresponding to a director width $\sim 2.5^\circ$ and $\theta \approx 14^\circ$. For the remainder of the alignment process the lines remain somewhat broad but the director orientation distribution gradually narrows from $\delta\theta \sim 2^\circ$ at $t = 1$ h to $\sim 1.3^\circ$ after 16.5 h. During this time the director orientation changes gradually from $\theta = 17.5^\circ$ at $t = 1$ h to a final value of 19.4° after 16.5 h.

(b) 54.5° geometry:

Measurements were carried out at the following values of E: 1.1, 1.0, 0.9 and $0.85\,MVm^{-1}$. Figures 6 and 7 show typical spectra recorded as a function of time during the alignment of the SmA director for $E = 1.1$ and $0.85\,MVm^{-1}$, respectively.

The pattern of alignment of the director for this magic angle geometry is essentially similar to that found for the 45° geometry. Thus from Figure 6 at $E = 1.1\,MVm^{-1}$, the spectrum at $t = 0^+$ shows broad spectral lines at an average value of $\theta \approx 8^\circ$ with a lineshape suggesting a distribution of director

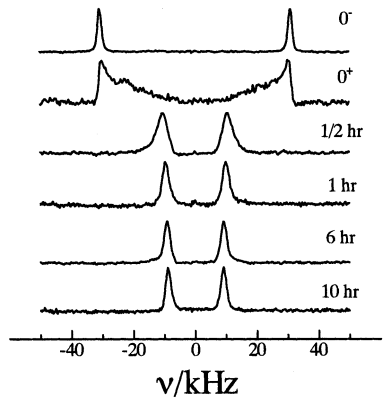

FIGURE 6 Spectra recorded as function of time for the cell at $T = 305.1\,K$ and $E = 1.1\,MVm^{-1}$ for the magic angle geometry.

orientations at values of θ from $\sim 8^\circ$ to values less than the magic angle (since there is no intensity in the middle of the spectrum showing a single peak expected for the magic angle). The spread in director orientations is approximately 13.5°. At $t = 1/2\,h$, the spectral lines have sharpened considerably to give a director distribution with $\delta\theta \sim 1.3^\circ$. For the rest of the run, the lines continue to narrow while the director orientation changes slightly reaching a value for θ of 43.4° at $t = 10\,h$ with sharp lines broadened slightly, corresponding to $\delta\theta \sim 0.3^\circ$. For the lowest rate of alignment investigated here at $E = 0.85\,MVm^{-1}$ (see Figure 7) the spectral lines are sharp at $t = 0^+$ with the director orientation changing by a few degrees to

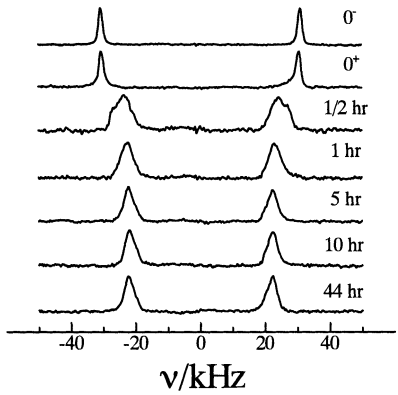

FIGURE 7 Spectra recorded as function of time for the cell at $T = 305.1\,K$ and $E = 0.85\,MVm^{-1}$ for the magic angle geometry.

$\theta = 4.4°$. At t = 1/2 h, the lines have broadened noticeably to give a director distribution with $\delta\theta \sim 4.4°$ at an average director orientation of $\theta = 22.8°$. At t = 1 h, the director orientation now has $\theta = 25°$ and the distribution of director orientations has narrowed to a value of $\delta\theta \sim 2.3°$.

After the passage of 5 h, the director orientation remains basically little changed at $\theta = 25.6°$ and the lines narrow slightly corresponding to $\delta\theta \sim 1.6°$. This situation remains unchanged even after 44 h. Thus at t = 44 h, $\theta = 25.5°$ and $\delta\theta \sim 1.6°$. Hence at this relatively low value of E, the rate of alignment of the director is slow with an associated small distribution in the director orientations ($\sim 2°$) which persists throughout the alignment process.

2. Results at 302.6 K

(a) 45° Geometry:

At the lower temperature of 302.6 K, the spectrum at $t = 0^-$ is a doublet with quadrupolar splitting $\Delta\nu(0°)$ of 64.4 kHz and sharp lines with a width of ~ 1.5 kHz.

The alignment experiments were carried out at the electric field strengths: 1.3, 1.2 and 1.1 MVm^{-1}. The results at these three field strengths appear to be similar in that the rate of alignment is much slower than at T = 305.1 K so that the spectra at $t = 0^+$ are sharp with no change in

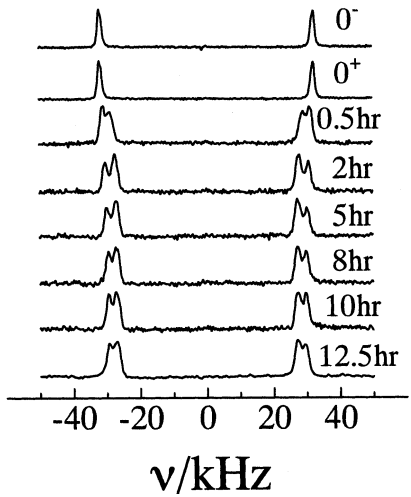

FIGURE 8 Spectra recorded as a function of time for the cell at T = 302.6 K and E = 1.3 MVm^{-1} for the 45° geometry.

orientation (i.e. θ is unchanged at $\sim 0°$). Furthermore, two quadrupolar splittings develop with time and remain for the rest of the experiment even 12 to 18 h after the electric field, E, is switched on. Typical spectra recorded as a function of time for $E = 1.3\,MVm^{-1}$ are given in Figure 8. The spectral lines for the spectrum at $t = 0^+$ are sharp. At $t = ½$ h, two quadrupolar splittings appear. These two splittings correspond to two domains with different director orientations at $\theta_1 \approx 9.4°$ and $\theta_2 \approx 14.8°$ (less intense). The two splittings are observed for the rest of the experiment. Even after 12½ h, the two director orientations have only increased slightly to $\theta_1 = 14°$ and $\theta_2 = 19°$. It is possible that one of the domains is due to parts of the sample close to the glass surfaces while the other is associated with that in the middle of the cell. The final angle reached by the director at $E = 1.3\,MVm^{-1}$ at this temperature is just $\theta = 19°$ compared with $\theta = 38°$ at the same field strength at 305.1 K. Similar differences in the final value of θ reached at this temperature are observed at the other field strengths as compared to the behavior at 305.1 K.

(b) 54.5° Geometry:

The alignment experiments were carried out at the following values of the field strengths E: 1.3, 1.2 and $1.1\,MVm^{-1}$. Initially the alignment pattern appears similar to that observed for the 45° geometry in that the spectra are sharp at $t = 0^+$ with $\theta = 0°$. However, in contrast with the results for the 45° geometry, we do not observe the development with time of two stable director domains, but rather asymmetric lines. There is a hint of the presence of two domains in the time evolution of the spectra during the director alignment at $E = 1.3\,MVm^{-1}$ (see Figure 9). Thus at $t = ½$ h, the lines are somewhat broad with $\theta \approx 14.8°$ and with a spread in the distribution of director orientations $\delta\theta \sim 3.6°$. At $t = 1½$ h the spectrum shows some further splitting with the main peaks giving $\theta = 26°$ and the other less intense peaks giving an orientation of $\theta = 21°$. This second splitting is observed up to $t = 2½$ to 3 h after which the lines sharpen progressively. Thus at $t = 5$ h, $\theta = 31°$ and the director distribution now narrows to $\delta\theta \sim 1.3°$. At $t = 12\,½$ h, the value of $\theta = 31.7°$ and the director distribution is now $\sim 1°$ wide.

(c) The Final Director Orientation

For experiments at both temperatures and for the 45° and 54.5° geometries and for all of the values of the electric field strength E used in this work, the director achieves its final orientation usually within 2 to 3 h after the electric field is switched on. The value of this final orientation depends on E. Figures 10 (a) and (b) show the values of the final director orientation for the 45° and the magic angle geometries, respectively and for results at 305.1 K and 302.6 K. It is clearly apparent from Figure 10 that reducing the

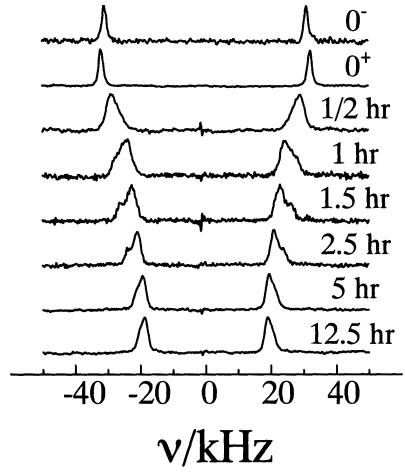

FIGURE 9 Spectra recorded as a function of time for the cell at $T = 302.6\,K$ and $E = 1.3\,MVm^{-1}$ for the magic angle geometry.

temperature by just 2.5°C has a drastic effect on reducing (to less than half) the value of the final director orientation presumably because of the large increase in the combined viscoelastic effects on the behaviour of the SmA phase on lowering the temperature[8–10]. The variation of the final value of θ with E is seen from Figure 10 to be non-linear and the values of θ should eventually saturate at $\sim 45°$ and $\sim 54.5°$ (for the two geometries) but only at much higher values of E than those used in this work. It is also apparent from Figure 10 that the rate of change of θ with E is larger for the 54.5° geometry than for the 45° which implies that the effective torque on the director is larger for the magic angle geometry

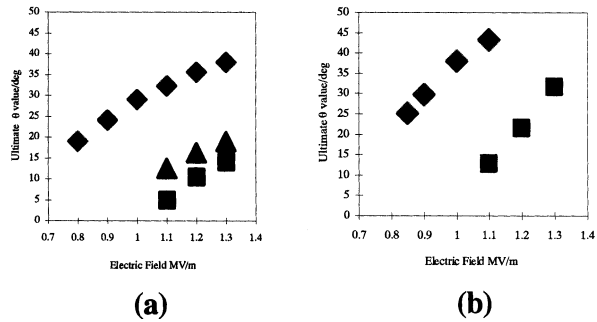

FIGURE 10 The change of the final director orientation with the electric field strength, E, (a) for the 45° geometry and (b) for the 54.5° geometry, for the temperatures of 305.1 K (◆) and 302.6 K (▲ and ■).

than for the 45° geometry (which is consistent with the values calculated for the nematic phase under similar conditions [11–13]).

CONCLUSIONS

We can summarise the main features of the results for the electric field-induced alignment of the SmA director for the two geometries employed here (the 45° and the magic angle) and at the two temperatures (305.1 and 302.6 K) as follows:

1. The director alignment follows an almost monodomain relaxation path. The final angle of alignment achieved by the director depends on the field strength, E. Similar monodomain relaxation behaviour has been observed for the alignment of the director of nematic 5CB, for example [11–13].
2. Lowering the temperature by just 2.5°C appears to have a dramatic effect both on the rate of alignment and on the final angle of alignment. Presumably this is due to the effect of lowering the temperature on the viscoelastic behaviour of the SmA phase.
3. The rate of change of the final angle of alignment with E is higher for the magic angle geometry than for the 45° geometry. We conclude that the effective torque acting on the director for the conditions of our experiments must be larger than that for the 45° geometry (consistent with the observations for the nematic phase [11–13]).
4. For the 45° geometry the SmA sample separates as the relaxation proceeds into two domains with different alignment angles. One of the domains could originate from parts of the sample close to the glass surfaces and the other from parts in the middle of the sample.
5. For the magic angle geometry we also observe some separation into two domains during the time evolution of the alignment. These domains, however, appear to merge together later either because they are not stable enough or because the lines in the spectra are not so well resolved and so they appear as merged.
6. The director in the final state is clearly shown to be inclined at an angle with respect to **B**. What is not clear is the state of organisation of the smectic layers, i.e. whether they are uniformly inclined or not. The mechanism by which the layers could be induced, in our experiment, by the electric field, to align at an inclined angle relative to **B** could proceed in a manner similar to that described by Ribotta and Durand [10] in which, in response to a compressive stress normal to the SmA layer structure, the layers tilt through a series of small steps where the molecules in the layer first tilt and then the layers rearrange to an angle relative to the initial layer alignment in order to preserve the SmA layer

thickness. The dynamics of this process is controlled by the motion of structural defects present in the layers [10,14].

7. Our measurements alone cannot provide us with information about the layer organisation or the presence of defects, types of defects, their concentration and their rate of propagation. A direct way of observing the state of the smectic layer during the alignment process would be to use a time-resolved X-ray scattering techniques. This requires a high intensity X-ray beam in combination with a field (magnetic or electric) to initially align the SmA layers and a means by which to suddenly change the angle of the aligning field and then to monitor the dynamics of realignment. This is clearly not an easy experiment to set up. More readily, perhaps, is to carry out simultaneous NMR and polarized microscopy. This latter technique will help to detect defects and how they evolve and propagate during the alignment process. Such a system is already under construction.

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