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On the Problem of the Alignment of Smectics Using Magnetic Fields

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Smectic alignment via magnetic fields was studied using Sn-119 Mossbauer Effect (ME) spectroscopy. A sample of *p*-(11-trimethyltin) undecyloxybenzylidene-*p*′-*n*-butylaniline (Sn-UBBA) was aligned by cooling from the isotropic phase to the smectic B phase in a magnetic field. A liquid crystalline glass was formed by rapid cooling to 77 K where it was studied with the ME as a function of the magnetic field strength (H) for the orientation angle $\theta = 0°$. The data indicated that the boundary layers of the disc-shaped sample were aligned perpendicular to the disc faces. Further, for $\theta = 0°$ ($H \parallel$ to the gamma beam direction) the effective thickness of the boundary layer was determined to be $\lambda = 0.369/(1 + 0.153\, H^{1.54})$ mm. The effect of the misalignment on the apparent values of the order parameter and the lattice contribution to the nuclear vibrational anisotropy of the Mossbauer nucleus are discussed. Some suggestions for more accurate analysis of the experimental data derived from orientational studies of smectics are given.

INTRODUCTION

The phenomenon of alignment of nematics with the help of magnetic fields (Freedericksz transition) is well known and the relevant theory is well developed.[1-6] In contrast not much work has been done regarding the effect of magnetic fields on smectics. In the case of a smectic A phase Rapini[7,8] found that the maximum tilt angle from the original direction of the director remains very low at twice the critical field. A different kind of magnetic transition of planar cholesteric structures was proposed by Helfrich[9] and a generalized treatment of this transition was developed by Hurault.[10] This theory can be extended to the case of

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the smectic A phase. On the basis of this extension one can expect an undulation of the planes to occur at a critical field of $H_c = 20$ kGauss, for a 1 cm thick sample, (H_c is proportional to $d^{-1/2}$, where d is the sample thickness). This transition proved to be a ghost transition. From among the various configurations treated by Parodi,[11] the most probable is the one in which the transition region is made up of periodic boundary grains, Figure 1. For a thickness of 1 cm he predicts that $H_c \sim 10^4$ Oe. Gosciansci *et al.*[12] have experimentally confirmed the occurrence of this transition at several degrees below the nematic to smectic A transition temperature. It is evident that this kind of configuration is consistent with the structure of the smectic B phase, since it does not require any bends or any other high strain disinclinations of the planes.

The following section includes a description of the Sn-bearing smectic liquid crystalline material used in these experiments and the technique used to form the smectic glass. In addition, the dependence of the thickness of the boundary layers aligned by the surfaces on the external magnetic field is discussed.

EXPERIMENTAL

The liquid crystalline compound used in this study was *p*-(11-trimethyltin)undecyloxy-benzylidene-*p*′-*n*-butylaniline (Sn-UBBA) which exhibits the following phases:[13]

$$\begin{tikzcd}
\text{Crystal} \arrow[r, "315.3\text{-}315.6\ \mathrm{K}", "{H = 5.70\ \mathrm{Kcal/mole},\ S = 18.1\ \mathrm{cal/mole/^\circ C}}"'] & \text{Smectic B} \arrow[r, shift left, "332.6\ \mathrm{K}"] \arrow[d, "315.6\ \mathrm{K}"] & \text{Smectic C} \arrow[l, shift left, "{H = 0.656,\ S = 1.97}"] \arrow[r, shift left, "340.9\ \mathrm{K}"] & \text{Isotropic Liquid} \arrow[l, shift left, "{H = 1.98,\ S = 6.74}"] \\
\text{Glass} \arrow[u] & \text{Supercooled Smectic B} \arrow[l, "T_g"'] & &
\end{tikzcd}$$

For this study we made a disc-shaped sample of Sn-UBBA by enclosing it in a teflon washer (11 mm in diameter and 1 mm thick) with mylar windows. The sample was aligned, with orientation angle $\theta = 0°$ (θ is the angle between the liquid crystal director or equivalently the magnetic field and the normal to the sample disc which was parallel to the direction of the Mossbauer γ-ray beam) in the following way. First the sample was heated to about 10–15° C above the smectic C—isotropic

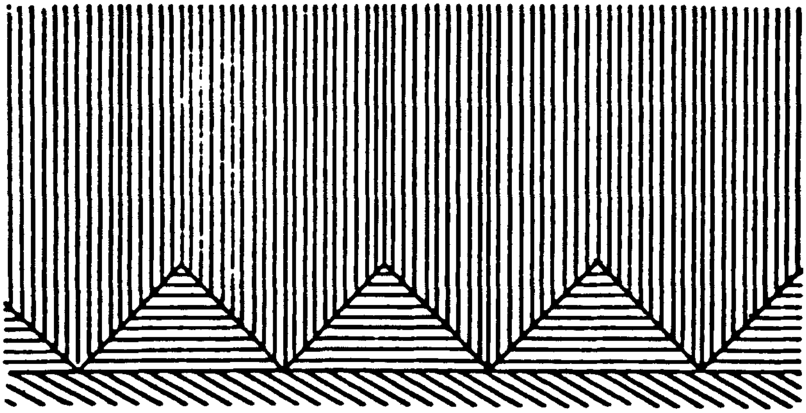

FIGURE 1 The configuration of periodic boundary grains described in Ref. 11. This is the most probable configuration of the smectic A phase, for the geometry shown, under the influence of a magnetic field. The parallel continuous lines denote the smectic planes. The figure is not drawn to scale.

liquid transition temperature. After being kept there for more than 20 minutes, it was cooled down to room temperature in the presence of the field generated by a 9 inch Magnion magnet. Subsequently the sample was securely mounted on the sample supporting rod and immersed in the liquid nitrogen of an Andonian (Option 0-24/7M-H) Mossbauer absorber cryostat. Thus a liquid crystalline glass of Sn-UBBA was formed. The spectra of glasses aligned with different intensities of the magnetic field were accumulated using a Mossbauer spectrometer which has been described elsewhere.[14] The Mossbauer spectra were fitted to a single Lorentzian line using a Burroughs 5500 computer.

RESULTS AND DISCUSSION

In the static case, one tries to align the liquid crystalline samples by distorting the existing structure with the application of a magnetic field. The case which is of most interest in this work is the dynamic case, in which the distortion occurs as the compound is cooled from the melt to the lowest temperature smectic phase, in the presence of a magnetic field.

It should be pointed out that despite the fact that prior to this work the existence of a nematic phase was considered essential for the alignment of a smectic liquid crystal by cooling from the melt in the presence of a magnetic field,[15-17] this does not seem to be as important as claimed. From the results of our experiments on tin bearing samples of Sn-UBBA and *p*-(11-trimethyltin)undecyloxybenzylidene-*p*′-*n*-octylaniline (Sn-UBOA)[18] one can infer considerable alignment, despite the fact that they do not have a nematic phase.

We should point out that the effect of the misalignment in the determination of the order parameter is evidently important. It is also important in the determination of the lattice contribution to the nuclear vibrational anisotropy ϵ_L. Consider the following equation

$$\frac{A(\theta)}{A(0)} = \exp(\epsilon_L \sin^2 \theta) + C \tag{1}$$

which is applicable to the case of perfect planar alignment of a smectic *A* or *B* liquid crystalline glass (when the intramolecular contribution to the nuclear vibrational anisotropy ϵ_M is small). Here $A(\theta)$ is the ME intensity corresponding to the orientation angle θ. *C* is a constant which accounts for the fact that the $A(0)$ values are not known with zero statistical uncertainty.[17] Misalignment causes the ratio $A(90)/A(0)$ to approach unity and has the effect of causing the measured value of ϵ_L to be too low in magnitude. Thus since the penetration region is a function of the magnetic field intensity *H*, the effective value of ϵ_L is a function of *H* and the values of ϵ_L and the order parameter S determined in Mossbauer experiments (with the present status of the theory)[14,17] represent lower limits of the real values of these quantities.[18]

As can be seen from Figure 2 which gives the absorption area vs. *H* data, for the $\theta = 0°$ orientation of pure Sn-UBBA, the alignment is achieved in an asymptotic way with increasing magnetic field. (The sample which yielded the data in Figure 2 did not meet the "thin absorber" criterion for Mössbauer experiments. Subsequent experiments with samples of similar thickness, however, showed that the experimental $A(90)/A(0)$ value differs from the ratio of absolute fractions by less than 3%[18,19]). Therefore, there is considerable competition between forces from the sample boundaries and from the magnetic field. In the case of periodic boundary grains, Parodi found that in the case of the smectic *A* phase, above a critical magnetic field $H_c \simeq 9$kOe, for a sample of thickness equal to 1 cm, the bulk of the sample is aligned by the magnetic field, but two thin layers of thickness λ, adjacent to the plates are not aligned. He found that:

$$\lambda^2 = \frac{4 f''_c}{X_a H^2} \tag{2}$$

where f''_c is a dislocation core energy and X_a is the magnetic anisotropy of the material.

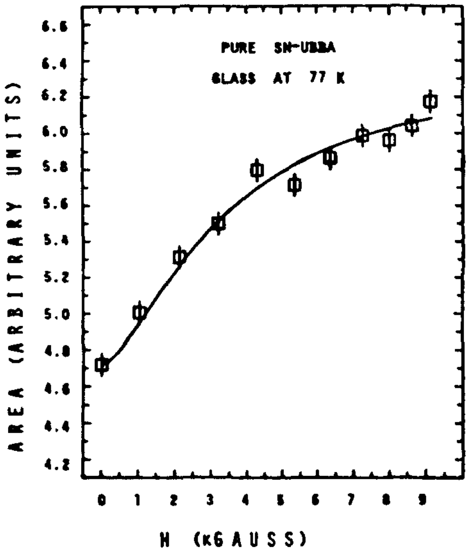

FIGURE 2 The area under the Mossbauer peak vs. field intensity H for pure Sn-UBBA in the glass phase, at 77 K, for $\theta = 0°$. The solid line results from the fitting of Eq. (3) to the area under the Mossbauer spectrum peak vs. H data, assuming that x is given by Eq. (7).

Without claiming to fully understand the phenomenon of the alignment of the smectic phases in the dynamic case, we will try to approximate the relation between λ and H in this case. For this we assumed that the alignment was complete in the middle of the sample, and we disregarded the effect of the washer surface. Thus we essentially have a configuration like the one of Figure 3. In this case, as in Ref. 17, the bulk of the sample is aligned with the director $\hat{n}$ normal to the windows, but in the two thin layers adjacent to the windows, $\hat{n}$ is parallel to the windows. In this case, as in Ref. 17, the recoil-free fraction (rff) is the highest for the $\theta = 0°$ orientation, while its value for the unoriented glass (at the same temperature) is close to the rff of the $\theta = 90°$ orientation. Thus the area under the Mossbauer peak (which in the small thickness approximation is proportional to the recoil free fraction) is given by the relation:

$$A = 2xf(90) + (1 - 2x)f(0) \tag{3}$$

thus

$$x = \frac{A - f(0)}{2[f(90) - f(0)]} \tag{4}$$

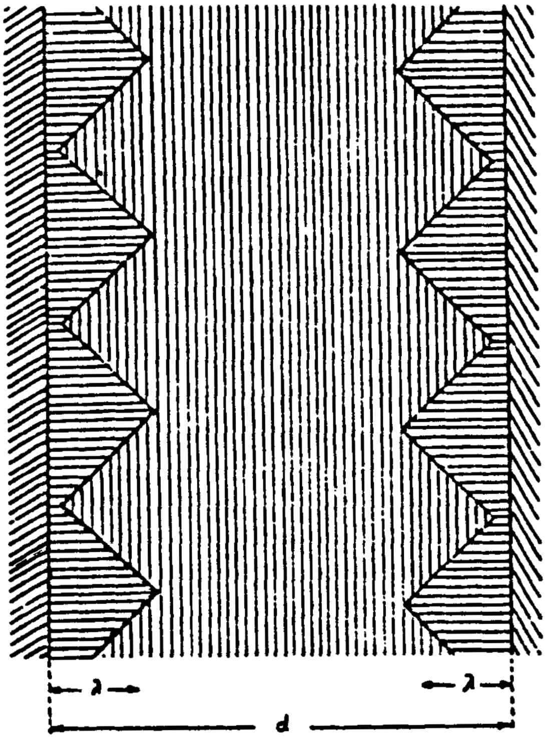

FIGURE 3 The most probable configuration of the smectic liquid crystalline glass samples, which were aligned by cooling the sample from the melt in the presence of a magnetic field (for $\theta = 0°$). The parallel continuous lines represent the smectic planes. In contrast to Figure 1, in this case the long axes of the molecules are parallel to the mylar windows of the cell near the windows. The figure is not drawn to scale.

where $x = \lambda/d$, d is the sample thickness, and $f(0)$ and $f(90)$ are the normalized peak areas for perfect alignment of the sample at $\theta = 0°$ and $\theta = 90°$, respectively. Thus one can calculate x provided that good approximations for $f(0)$ and $f(90)$ are available. Then these values of x can be fitted to a "reasonable" function $x(H)$. It is evident that for the geometry of our samples, which is approximated by Figure 3, if one neglects the effect of the washer surface, a function of the form:

$$x = \frac{1}{B_1 H^c} \tag{5}$$

where B_1 and c are constants, would not be valid, since for $H \rightarrow 0$, $x \rightarrow \infty$, while in reality the maximum value of x is equal to 0.5. To alleviate this discrepancy we added a constant to the denominator of Eq.

(5), which resulted in the following:

$$x = \frac{1}{E + B_1 H^c} \tag{6}$$

or

$$x = \frac{x_0}{1 + B H^c}. \tag{7}$$

This form is more appropriate for the geometry of our samples. Here $x_0 = 1/E$ is equal to the value of x for $H = 0$, and $B = B_1/E$. As good approximations of $f(0)$ and $f(90)$ we took the ME intensity values at $\theta = 0$ and $\theta = 90°$, respectively, for the highest fields attainable with our magnets.

The result of the fitting of Eq. (7) to the experimental data is shown in Figure 2. It corresponds to $x_0 = 0.369$, $B = 0.153$ and $c = 1.540$. This least squares fit was accomplished with the use of the Gauss–Seidel method for the solution of a system of simultaneous equations. Since the sample thickness is approximately 1 mm, we finally get: $\lambda = 0.369/(1 + 0.153\, H^{1.54})$ mm.

The problem of whether the quantities x_0, B, and c depend on the orientation angle θ remains to be investigated. We should point out that in the case of the Freedericksz transition of nematics, the critical field H_c has been found to be θ-dependent.[12] Similarly, the deviation from the original direction of the director, at a certain point of the sample, under the influence of the magnetic field is θ-dependent. To check this problem one can measure the θ-dependence of the ME intensity:

$$A = 2xf(90) + (1 - 2x)f(\theta). \tag{8}$$

Similar considerations should be taken into account when one deals with the area ratio of the two transitions of a quadrupole split doublet. In that case we have:

$$\frac{A_\pi(\theta)}{A_\sigma(\theta)} = \frac{2x\, f_\pi(90) + (1 - 2x)\, f_\pi(\theta)}{2x\, f_\sigma(90) + (1 - 2x)\, f_\sigma(\theta)} \tag{9}$$

where $A_\pi(\theta)/A_\sigma(\theta)$ is the ratio of the apparent (experimental) areas for the π and σ transitions, respectively. $f_\pi(\theta)$ and $f_\sigma(\theta)$ are the corresponding parameters for the perfect planar alignment of the whole sample. After $f(\theta)$ and $f_\pi(\theta)/f_\sigma(\theta)$ are known one can use the formula given in Ref. 14 to connect the $f(\theta)$ vs θ and $f_\pi(\theta)/f_\sigma(\theta)$ vs θ data to the order parameter S, the intramolecular contribution to the nuclear vibrational anisotropy ϵ_M and the intermolecular contribution to the nuclear vibrational anisotropy ϵ_L.

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