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HAL Id: jpa-00246311
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Submitted on 1 Jan 1991

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Short Communication

Tilt angle determinations in chiral and nonchiral smectic C phases using dielectric absorption spectroscopy

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(Received 19 September 1990, accepted in final form 26 November 1990)

Abstract. — The temperature dependence of the tilt angle in the smectic C phase has been determined using a novel method based on dielectric absorption measurements in the smectic A and C phases, of both chiral and non-chiral compounds. The appropriate expressions for evaluating this tilt angle \( \theta \) from dielectric absorption spectra are derived. The critical exponent for the tilt angle obtained by the dielectric method was found to be in good agreement with results from optical methods.

1. Introduction.

One of the characteristic features of the smectic C phase is the tilt angle \( \theta \) of the director with respect to the smectic layer normal [1]. The temperature dependence of \( \theta \) in the ferroelectric \( C^* \) phase is of particular interest, because of its importance as primary order parameter. It is the tilt in the \( C^* \) phase, coupled with the lack of mirror-symmetry due to chirality, that gives rise to ferroelectricity [2]. Different techniques have been used for tilt angle measurements, for instance optical methods [3, 4], X-ray diffraction [5, 6], nuclear magnetic resonance [7], electron spin resonance [8], and dielectric measurements [9-11]. The dielectric method described in reference [9] is based on dielectric absorption measurements at different angles between the measuring electric field and orienting magnetic field. Fitting the experimentally measured dielectric absorption to a numerically calculated function deduced from a multi-domain model yielded an estimation of tilt angle. The method presented in reference [10] enabled determination of tilt angle from measurements of the three components of the dielectric tensor in the C phase. In these measurements a magnetic field was used in order to separate the dielectric tensor components. A determination of tilt angle from the intensities of dielectric absorption obtained at low (kHz range) and high (\( \approx 1 \) GHz) frequencies was given. The measurements were performed when the electric field was applied parallel to the orienting magnetic field, and later also with orthogonal fields. Using these experimentally measured absorption intensities the dielectric relaxation correlation functions (derived from a multi-domain model) were evaluated. The model enabled calculation of
the correlation functions at different $\theta$ from $0^\circ$ to $90^\circ$. Thus, from the calculated value of the correlation function obtained from the experimental results one can get the corresponding value of tilt angle. The different dielectric methods described for tilt angle measurements has so far included the use of a magnetic field, a complication which prevents it from being frequently used for tilt angle determinations. The present work, however, presents a convenient method to calculate $\theta$ using the maximum values of $\varepsilon^{\prime\prime}_{||}$ $(\varepsilon^{\prime\prime}_{||}(\text{max}))$ measured on a homeotropically aligned A phase cooled to the C (or $C^*$) phase without the use of a magnetic field. Such an orientation is e.g. employed for obtaining $\varepsilon_{||}$ when measuring the dielectric anisotropy $\Delta \varepsilon$ ($\Delta \varepsilon = \varepsilon_{||} - \varepsilon_{\perp}$). Thus, additional preparations are not necessary in order to determine $\theta$, but it suffices to measure $\varepsilon^{\prime\prime}_{||}(\text{max})$ at different temperatures in the A and $C^*$ phases. It is worth pointing out that the present method is a development of the method given in reference [11].

2. Theory.

It is well known that in the A phase the parallel components of the dipole moment $\mu_{||}$ have a tendency to adopt an antiparallel correlation [12], which explains the drop in the value of the parallel component of the static dielectric constant $\varepsilon_{||}$ at the nematic - smectic A phase transition. This value $\varepsilon_{||}$, according to Debye's equation, is directly related to $\varepsilon^{\prime\prime}_{||}(\text{max})$; thus $\varepsilon^{\prime\prime}_{||}(\text{max})$ is a measure of the dipolar correlation.

The evaluation of $\theta$ from dielectric absorption measurements is based on the following assumptions:

1) in the A phase, it is assumed that $\varepsilon^{\prime\prime}_{||}(\text{max})$ decreases linearly with decreasing temperature in a small temperature interval. The decrease in values of $\varepsilon^{\prime\prime}_{||}(\text{max})$ with decreasing temperature is due to the enhanced anti-parallel correlation of $\mu_{||}$ within the smectic layer;

2) in the C (and $C^*$) phase, we assume that the anti-parallel correlation of the moments $\mu_{||}$ has the same temperature dependence as in the A phase. This means that if the measuring electric field in the C phase was allowed to follow the direction of the director, the measured $\varepsilon^{\prime\prime}_{||}(\text{max})$ will be just an extrapolation of that in the A phase. The values of $\varepsilon^{\prime\prime}_{||}(\text{max})$ in the C phase obtained by extrapolation from the A phase will be denoted as $\varepsilon^{\prime\prime}_{||}(\text{max})_A$. However, the measured values of $\varepsilon^{\prime\prime}_{||}(\text{max})$ in the C phase will be denoted as $\varepsilon^{\prime\prime}_{||}(\text{max})_C$;

3) in the C phase, any additional decrease in $\varepsilon^{\prime\prime}_{||}(\text{max})_C$ is attributed to the tilt and not to an increase in the anti-parallel correlation;

4) the tilt in the C phase is totally attributed to the director, while the layers are assumed to keep their orientation from the A phase.

As shown in figure 1, we define the coordinates $xyz$ as the principal axes of the dielectric tensor, whereas the coordinates $x' y' z'$ refer to the laboratory frame. Note that the measuring electric field $E$ is along the $y'$ direction and makes an angle $\theta$ with the director $n$.

The complex dielectric constant $\varepsilon^*$ measured with the field in the $y'$-direction is obtained by the following tensor transformation

$$
\varepsilon_{||}^{\prime\prime} = T \varepsilon^{(p)*} T^T
$$

where

$$
\varepsilon^{(p)*} = \begin{pmatrix}
\varepsilon_{xx}^{(p)*} & 0 & 0 \\
0 & \varepsilon_{||}^{(p)*} & 0 \\
0 & 0 & \varepsilon_{zz}^{(p)*}
\end{pmatrix}, \quad (\varepsilon^{(p)*} = \varepsilon_{yy}^{(p)*})
$$

(1b)
The symbol $p$ stands for principal axes, and $T$ is the transformation matrix between the two coordinate systems, its transpose denoted as $T^T$. Performing the tensor transformation, equation (1) can be rewritten as

$$
\varepsilon_{||}^p = \begin{pmatrix}
\varepsilon_{xx}^{(p)} \cos^2 \theta + \varepsilon_{||}^{(p)} \sin^2 \theta & \left(\varepsilon_{||}^{(p)} - \varepsilon_{xx}^{(p)}\right) \sin \theta \cos \theta & 0 \\
\left(\varepsilon_{||}^{(p)} - \varepsilon_{xx}^{(p)}\right) \sin \theta \cos \theta & \varepsilon_{xx}^{(p)} \sin^2 \theta + \varepsilon_{||}^{(p)} \cos^2 \theta & 0 \\
0 & 0 & \varepsilon_{xx}^{(p)}
\end{pmatrix}
$$

(2)

Since we are measuring in the $y'$-direction, we are interested in the $y'y'$-element of the matrix in equation (2), which we denote by $\varepsilon_{||}^p_C$,

$$
\varepsilon_{||}^p_C = \varepsilon_{xx}^{(p)} \sin^2 \theta + \varepsilon_{||}^{(p)} \cos^2 \theta
$$

(3)

The real and imaginary parts of equation (3) can be written as

$$
\varepsilon_{||}^p_C = \varepsilon_{xx}^{(p)' \, \sin^2 \theta + \varepsilon_{||}^{(p)' \, \cos^2 \theta}
$$

(4a)

$$
\varepsilon_{||}^p_C = \varepsilon_{xx}^{(p)'' \, \sin^2 \theta + \varepsilon_{||}^{(p)'' \, \cos^2 \theta}
$$

(4b)

The term $\varepsilon_{xx}^{(p)''}$ in equation (4b) corresponds to the absorption due to molecular rotation around the long-axis. This absorption is usually observed in the GHz and high MHz regions of the dielectric spectra [11]. The term $\varepsilon_{||}^{(p)''}$ corresponds to molecular rotation around the short-axis, with a dielectric absorption usually in the kHz regime. Since our dielectric measurements are performed in the kHz range, the first term in equation (4b) gives no contribution to the measured $\varepsilon_{||}^p_C$. In equation (4a) both terms, however, contribute over the whole frequency range. It is possible to determine the contribution of each term provided an orienting field is used (for instance a
magnetic field), a complication which we can avoid in our novel method. Therefore we are going to restrict our discussion to the imaginary part, which for low frequencies can be written as

$$\varepsilon''_{||C} = \varepsilon''_{||(p)} \cos^2 \theta$$  \hspace{1cm} (5)

According to assumption number 2, the maximum value of the dielectric absorption ($\varepsilon''_{||}$) in the C phase measured in the $y'$-direction is denoted as $\varepsilon''_{||}(\text{max})_C$, and the corresponding value of $\varepsilon''_{||}$, obtained by extrapolation from the values in the A phase, is denoted as $\varepsilon''_{||}(\text{max})_A$. From equation (5), $\theta$ can be written as

$$\theta = \cos^{-1} \left( \frac{\varepsilon''_{||}(\text{max})_C}{\varepsilon''_{||}(\text{max})_A} \right)$$  \hspace{1cm} (6)

3. Experimental.

The chemical formula of the investigated substances has the general form

$$\text{C}_n\text{H}_{2n+1} \rightarrow \text{O} \quad \text{C} \quad \text{O} \quad \text{O} \quad \text{C} \quad \text{C}_2\text{H}_5$$

For $n = 8$, the transition temperatures are

Solid 48.0° (C* 43.0°) A* 59.0° Isotropic

For $n = 10$, the substance, which in this case is a racemic mixture, has the transition temperatures

Solid 45.9° C 48.9° A 63.2° Isotropic

We are going to use the symbols C8 and C10 for the first and second compound, respectively. For both compounds, the C phase can be supercooled to about 30° C.

The dielectric absorption measurements were made using an HP 4192 impedance analyzer (5Hz - 13 MHz). The cell consists of two conducting glass plates separated by mylar spacers of 50 μm thickness. The measuring electric field was applied in a direction parallel to the director in the A phase, and it makes an angle $\theta$ equal to the tilt angle in the C phase. The cell was calibrated using standard liquids (Cyclohexane and chloroform). A typical plot of the measured $\varepsilon''_{||}$ over a relatively wide frequency range ($10^2 - 10^7$Hz) is shown in figure 2. A discussion of the correction procedures needed when determining the $\varepsilon''$-values will be published elsewhere.

4. Results and discussion.

An example of the measured temperature dependence of $\varepsilon''_{||}(\text{max})$ in the A* and C* phases of the C8 compound is shown in figure 3a. In the A* phase a clear linear behaviour of $\varepsilon''_{||}(\text{max})$ with temperature is found. According to assumption number 2 this line was extrapolated to the C* phase. At any temperature $T$ in the C* phase, any point on this line is denoted as $\varepsilon''_{||}(\text{max})_A$. At the
Fig. 2. — Frequency dependence of $\varepsilon''$ of the C8 compound in the A* phase. The dielectric spectrum can be divided into three regions: at low frequencies (< 2 kHz), the ionic contribution is dominating, in the middle part (≈ 200 kHz) the absorption peak is due to molecular rotation around the short axis, and in the high frequency region (> 2 MHz) the contribution to $\varepsilon''$ is mainly due to the resistance of the ITO conducting layer.

A* — C* phase transition, $\varepsilon''(\max)_C$ reveals a deviation from the linear behaviour. This decrease is attributed only to the tilt of the director. A similar behaviour of the racemic compound is shown in figure 4. The temperature dependence of the calculated values of $\theta$ for the C8 compound is shown in figure 3b. The values are compared with the data obtained by an optical method [13]. A maximum difference of about 4° in the C8 and 2° in the C10 compounds was found.

Tilt angle values reported in the literature (for a given compound) are dispersed depending on the method used [14, 15]. The same method may also give different values for different measuring geometries [15]. For instance the values of $\theta$ reported by Martinot-Lagarde et al. [15] for DOBAMBC measured by X-ray are found to be smaller than the optically determined by 2-5°. For the same compound, using an optical method the measured tilt angle on planar orientation gives a value less than that for homeotropic geometry by 5°. From their study of the tilt angle for different C* materials they observed that the tilt angle measured on homeotropic geometry is always larger than the tilt angle deduced from planar orientation. This is in agreement with our dielectric method which is carried out on a homeotropically aligned sample, giving larger tilts than the optically measured in a planar orientation. It seems that the homeotropic geometry gives more accurate results than the planar, irrespective what probing method is used. This is partly due to the fact that in homeotropic samples, the smectic layer orientation is well defined, while in planar geometry this is not the case. Also, surface effects more easily lead to director distortions in planar geometry, which influence the determination of the correct inherent tilt angle. This is consistent with results reported by Druon and Wacrenier [11] where dielectric absorption measurements made on the two measuring geometries gave a difference of 6°.

All different tensors describing the anisotropic molecular properties may have different axes [14], which also influences the comparison between optical and dielectric tilt angle. Our results (Fig. 3b) show that the dielectric values are higher, indicating that the dielectric indicatrix is tilted with respect to the optical indicatrix, thus resulting in a larger tilt angle.

The temperature dependence of $\theta$ is found to obey the power law

$$\theta \approx (T_C - T)^\beta$$

(7)

where $\beta$ is a critical exponent. A plot of log $\theta$ vs. log $(T_C - T)$ for C8 is shown in figure 5.
Fig. 3. — (a) Temperature dependence of the measured dielectric absorption maximum $\varepsilon''_{||}(\text{max})$ in the A* and C* phases. (b) Temperature dependence of the tilt angle $\theta$ obtained from dielectric measurements compared with results from the optical method.

Fig. 4. — The measured dielectric absorption $\varepsilon''_{||}(\text{max})$ as a function of temperature in the A and C phases.
Values of $\beta$ from both dielectric and optical methods are in good agreement with each other. For C8, $\beta$ (dielectric) = 0.29 and $\beta$ (optical) = 0.28. For C10, $\beta$ (dielectric) = 0.30 and $\beta$ (optical) = 0.30. The uncertainty of the calculated $\beta$ values is equal to 0.03. According to the theory of the A-C transition by de Gennes [17], the temperature dependence of $\theta$ is expressed by the power law with $\beta = 0.35$. From the experimental results reported in literature, it is difficult to say if $\beta$ generally agrees with the mean field approximation ($\beta = 0.50$) or the non-classical approach ($\beta = 0.35$). Experimental values of $\beta$ vary between 0.25 and 0.5 [15, 17-19] depending on the measuring method and the temperature interval from $T_C$. The critical exponent reported in reference [15] for DOBAMC depends very much on the measuring method: X-ray determinations yielded $\beta = 0.35$, while optical measurements gave $\beta = 0.42$ and 0.44, for planar and homeotropic orientations respectively.

Acknowledgements.

This work has been supported by the National Swedish Board for Technical Development under grant No. 84-3638, and by the Swedish National Research Council under Grant No. 84-3693.

References


Cet article a été imprimé avec le Macro Package "Editions de Physique Avril 1990".