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Anisotropic Correction Factors in the Evaluation of Nematic Order Parameters from Polarized Fluorescence Measurements

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Formulas allowing the determination of the order parameters of the nematics by fluorescence measurements are obtained. The anisotropy of the local field, of the losses on the boundary surfaces, of the aperture of the registered fluorescence emission and of the absorption of the exciting light is taken into account. The experimental results confirm the necessity of correction for this anisotropy.

Usually the anisotropy of the local field is taken into account when investigating the order of the nematic liquid crystals by optical methods.[1-3] Up to now, for these investigations made by means of fluorescence measurements,[4-6] the anisotropy of the local field has not been taken into account.

The present paper considers the case for the determination of the order parameters $\langle P_2 \rangle = 1/2 \langle 3 \cos^2 \theta - 1 \rangle$ and $\langle P_4 \rangle = 1/8 \langle 35 \cos^4 \theta - 30 \cos^2 \theta + 3 \rangle$ by polarization fluorescence measurements of fluorescent substances inserted in small quantities in the nematic liquid crystal. The anisotropy of the local field and of the light losses on the boundary surfaces liquid crystal-glass is taken into account.

For achieving the purpose, the model shown by us[7] has been accepted, at $\alpha = \beta = 0$ and γ and $\eta = 0$ or $\pi/2$, i.e. the optical axis of the sample is directed along axis z of the accepted co-ordinate system $Oxyz$, while the exciting and fluorescence light is polarized along y or z. The liquid crystal layer, placed between glass plates, lies in the plane yOz. An admixture absorbing in a region that is free of liquid crystal absorption is incorporated in the mesogene. We

assume that this admixture does not violate the alignment of the liquid crystal and it is aligned in the same manner. As in Refs. 5 to 7 the depolarization of fluorescence light due to thermal motion of probe molecules is not taken into account. The optical properties of the sample are described in the frames of single dipole approximation.[7] Taking into account the results from, Ref. 7, the intensity of the measured fluorescence emission J_{ij}^m with correction for the local field anisotropy and the anisotropy of the losses on the boundary surfaces will be:

$$J_{ij}^m \sim (n_j/n_i)D_i\Omega_j K_i^e K_j (f_{ii}^e)^2 (f_{jj})^2 J_{ij} \quad i,j = y,z \tag{1}$$

where the indices i,j show the polarization of the exciting and fluorescence light respectively; D_i is a correction for the absorption anisotropy of the exciting light, defined by corresponding measurements;[7] Ω_j—a correction for the anisotropy of the angular aperture of the registered fluorescence light,[7] proportional to $1/n_j^2$. K_i^e and K_j are corrections for the anisotropy of the losses on the boundary surfaces liquid crystal-glass, respectively for the wave length of the exciting and fluorescence light. According to Ref. 8 they have the form $K_i^e = 4n_g^e n_i^e/(n_g^e + n_i^e)^2$ and $K_j = 4n_g n_j/(n_g + n_j)^2$, where $n_y = n_\perp$ and $n_z = n_\parallel$ are refractive indices of the ordinary and the extraordinary beam in the liquid crystal, and n_g—of the glass, respectively with index e for the exciting light and without index for the fluorescence emission. f_{ii}^e and f_{jj} are the components of the local field tensor, respectively for the exciting and the fluorescence light, and the tensor f is diagonal,[3] i.e. $f_{xx} = f_{yy} = f_\perp$ and $f_{zz} = f_\parallel$.

$$J_{ij} \sim \int_0^{2\pi}\int_0^{\pi/2} I_{ij}(\theta,\varphi) f(\theta) \sin\theta \, d\theta \, d\varphi$$

is a function of the order parameters.[7]

The solution of the Eq. (1) with respect to $\langle P_2\rangle$ and $\langle P_4\rangle$ gives the formulas:

$$\langle P_2\rangle = \frac{1 + A - 4B}{1 + 4A + 8B}, \qquad \langle P_4\rangle = \frac{1 - 6A + 3B}{1 + 4A + 8B} \tag{2}$$

where

$$A = \frac{J_{zy}^m (n_g + n_\perp)^2 (f_\parallel)^2}{J_{zz}^m (n_g + n_\parallel)^2 (f_\perp)^2}, \quad B = \frac{J_{yy}^m D_z (n_g^e + n_\perp^e)^2 (n_g + n_\perp)^2 (f_\parallel^e f_\parallel)^2}{3 J_{zz}^m D_y (n_g^e + n_\parallel^e)^2 (n_g + n_\parallel)^2 (f_\perp^e f_\perp)^2}$$

It is assumed that the refractive indices participating in (2) are known or are obtained by corresponding measurements.

For determining the ratio f/f in (2) we use the results from[9] and after some transformations we get:

$$\frac{f_\parallel}{f_\perp} = \frac{n_\parallel^2 - 1}{n_\perp^2 - 1} \cdot \frac{1 - \langle P_2\rangle(\gamma_\parallel - \gamma_\perp)/(\gamma_\parallel + 2\gamma_\perp)}{1 + 2\langle P_2\rangle(\gamma_\parallel - \gamma_\perp)/(\gamma_\parallel + 2\gamma_\perp)} \tag{3}$$

where $\gamma_{\parallel}$ and $\gamma_{\perp}$ are the polarizabilities along and perpendicular to the long axis of the nematic molecule.

We assume like other authors,[10,11] that the ratio $(\gamma_{\parallel} - \gamma_{\perp})/(\gamma_{\parallel} + 2\gamma_{\perp})$ does not change during the phase transition. This is confirmed by the fact that for EBBA (the nematic used in the present work) this ratio at $\lambda = 633$ nm is one and the same for the crystal[10] and the isotropic state.[12] This assumption allows to use values for $\gamma_{\parallel}$ and $\gamma_{\perp}$ for the solid state of the mesogen.

It deserves to be noted that $f_{\parallel}/f_{\perp}$ depends on $\langle P_2 \rangle$ and at substitution of (3) in (2) $\langle P_2 \rangle$ appears in the right hand part of (2) which seriously embarrasses the expression of the order parameters through the rest values. This imposes the determination of $\langle P_2 \rangle$ to be done by some suitable iterative method. For our concrete purposes we have used the regula falsi,[13] and for the zero-order approximation of $\langle P_2 \rangle$ we have accepted the value obtained by method.[7]

Formulas (2) give a possibility to determine the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ taking into account the anisotropy of the local field, of the losses on the boundary surfaces, of the angular aperture of the registered light and of the absorption of the exciting light.

With a view to illustrate the influence of these factors on the values of the measured order parameters, determination of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ have been done in the temperature range of the nematic phase of EBBA. The substance *p*-dimethylamino-*p*-nitrostylbene with concentration 0,02% was used for the fluorescent admixture. This compound was used for similar measurements[4,7] and it satisfies our requirements.[4,14] The homogeneous alignment of the sample was achieved by using glass plates covered with a golden layer obtained by vacuum evaporation at an angle of 60° by the method of Janning.[15] The measurement of the intensities J_{ij}^{m} was carried out by means of set up apparatus described in Ref. 7. The values of the used intensities J_{ij}^{m} represent average values from five measurements.

In Figure 1 are given the dependences of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ as a function of $T_c - T$. The values obtained by the method given in, Ref. 7 i.e. corrected only for the absorption anisotropy of the exciting light and the anisotropy of the angular aperture of the registered fluorescence, are given with a broken line. The curves given with a dot-dashed line are obtained by using formula (2) at $f_{\parallel} = f_{\perp}$, i.e. assuming an isotropic local field and taking into account the anisotropy of the losses on the boundary surfaces. The dependences given with a continuous line are obtained on the basis of formula (2), i.e. taking into account the anisotropy of the local field as well.

These experimental results show the significant dependence of the obtained values of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ in the temperature range of the nematic phase of EBBA from the anisotropy of the considered factors. This shows the necessity of taking into account this anisotropy at determining the order parameters by fluorescence measurements.

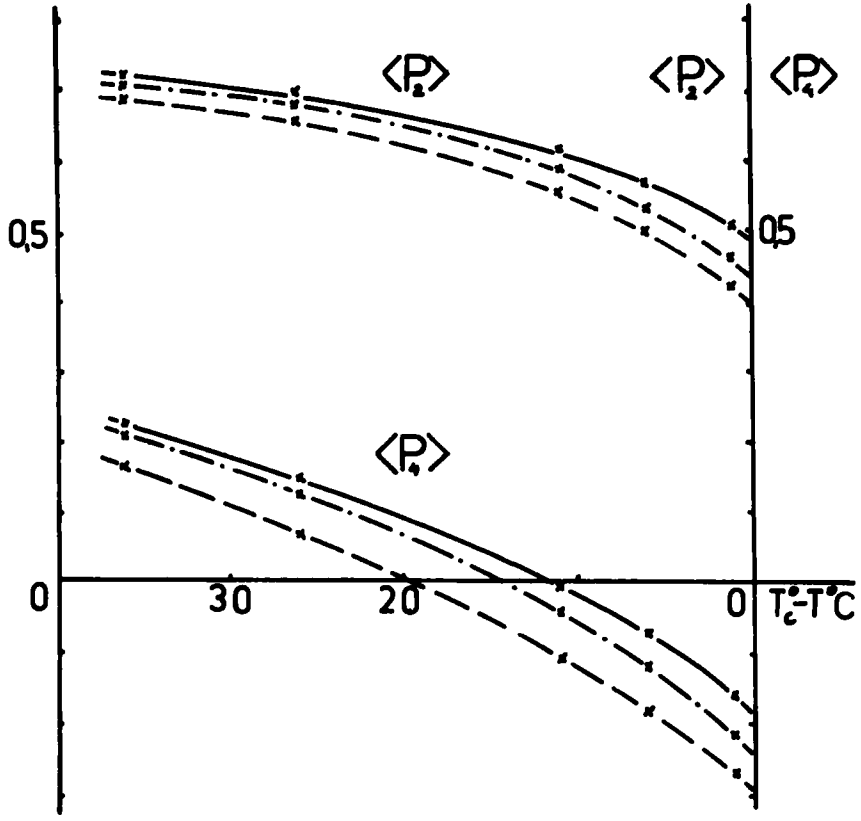

FIGURE 1 Temperature dependences of the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ of the nematic EBBA.

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