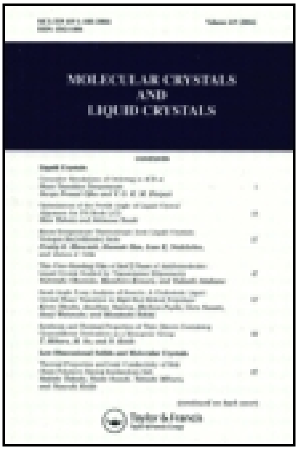

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NMR Spectral Patterns in Magneto-Aligned Biaxial Liquid Crystals

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NMR Spectral Patterns in Magneto-Aligned Biaxial Liquid Crystals

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Unique NMR spectral patterns can be obtained from biaxially ordered smectic phases where only one of the principal axes of the time averaged nuclear spin interaction is aligned by the magnetic field. It is shown how the asymmetry parameter of the interaction can be obtained directly from edge singularities in these patterns.

INTRODUCTION

Many smectic liquid crystalline materials are easily aligned by an applied magnetic field.[1] This is particularly true when the material possesses a nematic phase at a higher temperature, where upon cooling the material in the presence of the field, the smectic phases may also be aligned. If the smectic phase is a biaxial one, it is normally expected that the magnetic field can only align one axis (director) of the sample. In the case of the time averaged quadrupole interaction, the biaxiality will often show itself in terms of a motionally induced asymmetry parameter.[2,3] In this case only the principal z-axis of the interaction may be aligned whereas the x and y axes are totally random. Such a case will produce a unique spectral pattern consisting of edge singularities.

An example is the smectic G phase reported in a recent article by Barbara and Dailey.[4] Observing the deuterated solvent $CDCl_3$ dissolved in n-(4-n-hexyloxybenzylidene)-4-n-hexylaniline (60,6) a new type of spectral pattern obtained from a magneto-aligned sample is reported. In this paper we show the calculation of the shape of this spectral pattern based on a sample alignment as described above. The angular dependence of this shape and the positions of the singularities as the principle z axis is oriented at different angles in the magnetic field is calculated. Further, it is shown how the asymmetry parameter can be obtained directly from the positions of the edge singularities.

THEORY

In the case of the Zeeman perturbed quadrupole interaction for a nucleas of spin 1 such as deuterium, two spectral lines appear at frequencies given by the expression:[5]

$$\nu = \pm\frac{3}{4}\nu_Q\left\{\left(\frac{3}{2}\cos^2\theta_0 - \frac{1}{2}\right) + \frac{\eta}{2}\sin^2\theta_0\cos 2\phi_0\right\} \qquad (1)$$

where θ_0, ϕ_0 are the polar angles giving the direction of the magnetic field in principal x, y, z axes frame of the time averaged electric field gradient; $\nu_Q = eQV_{zz}/h$ is the coupling constant with V_{zz} the time averaged electric field gradient along the z-axis and $\eta = (V_{xx} - V_{yy})/V_{zz}$ the motionally induced asymmetry parameter with the transverse electric field gradients defined such that $|V_{xx}| \leq |V_{yy}| < |V_{zz}|$.

We are interested in the case where the z-axis is aligned relative to the direction of the magnetic field (fixed value of θ_0) but that there is a random distribution of orientation of V_{xx} and V_{yy} (random distribution of ϕ_0). In this case it is convenient to express Eq. (1) in terms of dimensionless quantity $\omega = 2\nu/3\nu_Q$ whereby

$$\omega = \pm(\alpha + \beta\cos 2\phi_0) \qquad (2)$$

where $\alpha = (1 + 3\cos 2\theta_0)/8$ and $\beta = \eta(1 - \cos 2\theta_0)/8$. The spectral pattern $G(\omega)$ can be calculated from the equation[5]

$$G(\omega) = G_0 d\phi_0/d\omega = \frac{G_0}{2\beta}\left[1 - \left(\frac{\omega - \alpha}{\beta}\right)^2\right]^{-1/2} \qquad (3)$$

where G_0 is a constant. As seen from Eq. (3) the pattern will consist of edge singularities at values of $\omega = \pm|\alpha + \beta|$ and $\pm|\alpha - \beta|$. The spectral pattern is illustrated in Figure 1 which shows the positions of the edge singularities for $\theta_0 = 90°$ and $\eta = 0.3$.

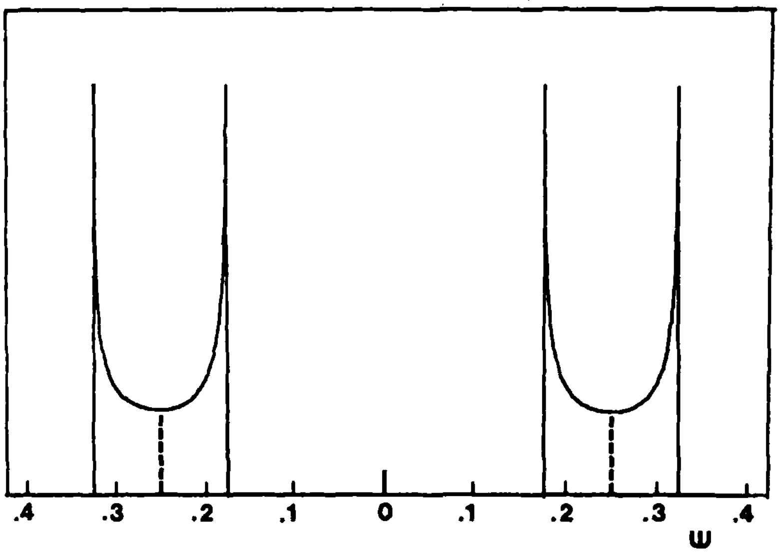

FIGURE 1 Biaxial spectral pattern illustrated for the model outlined in the text where $\eta = 0.3$ and $\theta_0 = 90°$.

The angular dependence of the splittings between the singularities, $\Delta\omega_1 = 2|\alpha - \beta|$, $\Delta\omega_2 = 2|\alpha + \beta|$ are illustrated in Figure 2 for a value of $\eta = 0.3$. It is seen that the center line between the two singularities follows $2|\alpha|$ which is the $|P_2(\cos\theta_0)|$ dependence.

Experimentally, $|\Delta\omega| = |\Delta\nu(\theta_0)/\Delta\nu(\theta_0 = 0)$ where $\Delta\nu$ is the splitting between either the inner or outer singularities. The above model can easily be checked by the angular dependence of $\Delta\omega$ whereby:

$$|\Delta\omega_1| = \frac{1}{4}|(1 - \eta) + (3 + \eta)\cos 2\theta_0| \tag{3a}$$

$$|\Delta\omega_2| = \frac{1}{4}|(1 + \eta) + (3 - \eta)\cos 2\theta_0|. \tag{3b}$$

DISCUSSION

The simple theory described above appears to explain quite well most features of the spectral pattern observed by Barbara and Dailey. The presence of the edge singularities as indicated in Figure 1 is evident. Furthermore, the angular dependence of the splittings between the singularities fits well with Eq. (3). Not explained by the theory above are the unequal intensities of the edge singularities between the $\phi_0 = 0$ and

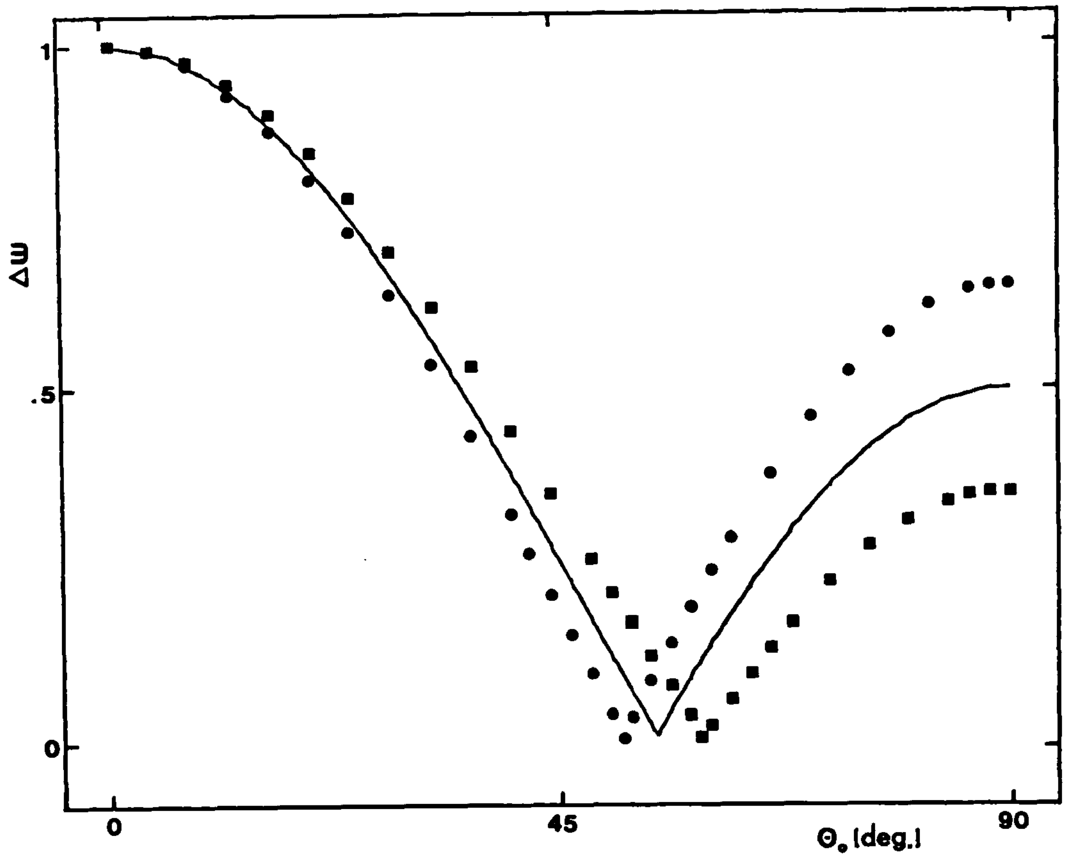

FIGURE 2 The angular dependence of the splitting; $\Delta\omega_1$, circles and $\Delta\omega_2$, squares, is illustrated for $\eta = 0.3$. The continuous line represents $|P_2(\cos\theta_0)|$.

$\phi_0 = 90$ orientations clearly present in the $CDCl_3$ (60,6) data. This suggests that the orientation of the x and y principal axes are not totally random. There is evidence for this in that the relative intensities appear to be affected by the rate of cooling.[4] Further experimental studies in other materials or perhaps sample containers might be helpful to clarify this important point.

Acknowledgments

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