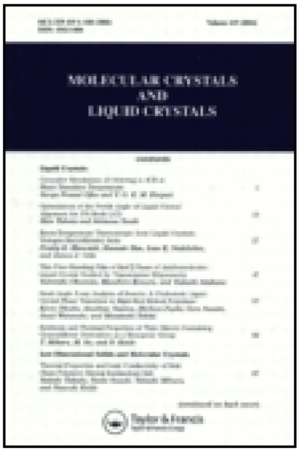

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Note on the NQR Measurement of Biaxial Order Parameters in Liquid Crystals

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NOTE ON THE NQR MEASUREMENT OF BIAXIAL ORDER PARAMETERS IN LIQUID CRYSTALS**

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ABSTRACT. It is shown, for the case of nuclear spin 1, that pure nuclear quadrupole resonance (NQR) detects only the <u>square</u> of the particular biaxial order parameter which gives rise to the tilt angle in some models of the smectic C phase. As a consequence, pure NQR does not provide a sensitive test of these models.

Seliger et al.[1] have recently studied the molecular orientational order in a smectic C liquid crystal by a pure quadrupole resonance (NMR) experiment involving the spin 1 N^{14} nucleus. We point out here that this type of experiment detects only the <u>square</u> of the (small) biaxial order parameter which gives rise to the tilt angle in some models of the smectic C phase.[2,3] Thus, pure NQR does not provide a sensitive test of these models.

The spin 1 pure NQR spectrum consists of a doublet centered at frequencey $\omega_1 \propto |V_3|$, with splitting $\propto \eta\omega_o$, where

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$$\eta = |(V_1 - V_2)/V_3| \qquad (1)$$

and V_i are the principal values of the (time averaged) electric field gradient tensor $\bar{\underset{\approx}{V}}$ at the nuclear site, $|V_3| > |V_1|, |V_2|$.[4,5] Since $\underset{\approx}{V}$ is traceless, we have $V_1+V_2+V_3 = 0$

Let the unit vector $\underset{\sim}{e}$ denote the direction of the long molecular axis. In the molecular theory of liquid crystals one introduces the frame $\hat{x},\hat{z},\hat{y}$ defined as the principal axes of the order matrix $\underset{\approx}{Q} = \langle \underset{\sim}{e}\,\underset{\sim}{e} - \underset{\approx}{1}/2\rangle$:[6]

$$\underset{\approx}{Q} = S(\hat{z}\,\hat{z} - \underset{\approx}{1}/3) + \Delta(\hat{x}\,\hat{x} - \hat{y}\,\hat{y}); \qquad (2)$$

S is the usual Maier-Saupe order parameter ($S \sim 0.5$) and Δ is a (small) biaxial order parameter which vanishes in uniaxial phases. $\hat{z}$ is the nematic axis or director and $\hat{x}$ may be taken as the C_2 axis in the smectic C phase.

The time averaged tensor $\bar{\underset{\approx}{V}}$ in the smectic C phase will not in general be diagonal in the frame $\hat{x},\hat{z},\hat{y}$, but will be given by an expression of the form

$$\bar{\underset{\approx}{V}} = a\hat{z}\hat{z} + b\hat{y}\hat{y} + c(\hat{z}\hat{y} + \hat{y}\hat{z}) + d\hat{x}\hat{x}, \qquad (3)$$

with $a+b+d = 0$. Without loss in generality, we may assume $a>0$.[7] In uniaxial phases $c=0$ and $b=d= -a/2$. Only the quantity c depends on (and is proportional to) the specific biaxial order parameter which determines the tilt angle in the smectic C models of References 2 and 3.[8] The quantities a,b,d depend on S and various other orientational order parameters.[8] Given that S is much larger than the other order parameters, one has, as a rule,[9]

$$b \approx d \approx -a/2. \qquad (4)$$

$$|c| \ll a.$$

It is seen from Eq. (3) that for $c \neq 0$ the frame which diagonalizes $\bar{\underset{\approx}{V}}$ is obtained by rotating the axes x,y through an angle of order c/a about the x axis. Accordingly, one of the principal values of $\bar{\underset{\approx}{V}}$ is d and the other two are the roots $\lambda_{\pm}$ of the determinantal eigenvalue equation

$$\begin{vmatrix} a-\lambda & c \\ c & b-\lambda \end{vmatrix} = 0;$$

i.e.,

$$\lambda_{\pm} = \{a+b\pm[(a-b)^2 + 4c^2]^{1/2}\}/2. \qquad (5)$$

By relation (4), $a-b \sim 3a/2 >> |c|$, so we may expand (5) to second order in c/a, with the results,

$$\lambda_{\pm} = \begin{cases} a+c^2/(a-b) \\ b-c^2/(a-b) \end{cases}.$$

Clearly, $V_3 = \lambda_+$, and the asymmetry parameter is given by

$$\eta = \left|\frac{d-\lambda_-}{\lambda_+}\right| \approx \left|\frac{d-b}{a} - \frac{2d}{a-b}\,\frac{c^2}{a^2}\right|, \qquad (6)$$

correct to second order in c/a.

Eq. (6) shows that the asymmetry parameter η varies with the square of c/a and is independent of c/a to first order. As a consequence, pure NQR is insensitive to the type of "rotational freeze out" invoked by the smectic C models of Refs. 2 and 3.

NQR measurements with an applied magnetic field whose direction can be varied with respect to the liquid crystal director frame can detect c/a to the first power.[5,8] One such experiment has been done recently[10] and it was found that $c/a \sim 10^{-2}$. This exceedingly small value of c/a does not support the models of references 2 and 3.

A different derivation of (6) and a more detailed consideration of the quantities a,b,c,d is to be presented elsewhere by one of the authors.[11]

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7. By Eq. (1), it makes no difference whether we find the principal values of $\underset{\approx}{V}$ or of $-\underset{\approx}{V}$.
8. See the second of References 3 above.
9. In principle, the relations (4) might be disobeyed in accidental cases for which the coefficient (proportional to $\underset{\sim}{e}\cdot\underset{\approx}{V}\cdot\underset{\sim}{e}$) multiplying S in the quantity a is very small. For a cylindrically symmetric quadrupole field $\underset{\approx}{V}$, for example, $\underset{\sim}{e}\cdot\underset{\approx}{V}\cdot\underset{\sim}{e} \approx 0$ if the major axis of $\underset{\approx}{V}$ makes an angle very close to 54°44' with $\underset{\sim}{e}$. Experimentally, the failure of relations (4) would be revealed by a very small value of the mean absorption frequency ω_o.
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