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Publisher: Taylor & Francis

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## Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

http://www.tandfonline.com/loi/gmcl16

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

A. Wulf <sup>a</sup> & J. W. Doane <sup>b a</sup>

<sup>a</sup> Department of Applied Mathematics, Research School of Physical Sciences, The Australian National University, Canberra, A.C.T., 2600, Australia

<sup>b</sup> Department of Physics and Liquid Crystal Institute, Kent State University, Kent, Ohio, 44242, U.S.A. Version of record first published: 20 Apr 2011.

To cite this article: A. Wulf & J. W. Doane (1978): Note on the NQR Measurement of Biaxial Order Parameters in Liquid Crystals, Molecular Crystals and Liquid Crystals, 41:5, 115-118

rarameters in Eigend Crystals, Molecular Crystals and Eigend Crystals, 41.5, 115-

To link to this article: <a href="http://dx.doi.org/10.1080/00268947808070281">http://dx.doi.org/10.1080/00268947808070281</a>

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Mol. Cryst. Liq. Cryst. Vol. 41 (Letters), pp. 115-118 © 1978, Gordon and Breach Science Publishers Ltd. Printed in the United States of America

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

A. WULF\*
Department of Applied Mathematics, Research School of Physical Sciences, The Australian National University, Canberra, A.C.T. 2600, Australia and J.W. DOANE
Department of Physics and Liquid Crystal Institute, Kent State University, Kent, Ohio 44242 U.S.A.

(Submitted for Publication December 30, 1977)

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. 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<sup>14</sup> 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.<sup>2,3</sup> 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  $\omega_1^{~\alpha}~|V_3^{~}|$ , with splitting  $\alpha$   $\eta\omega_0^{~}$ , where

Permanent address: Centro de Fisica, Instituto Venezolano de Investigaciones Cientificas (IVIC), Apartado 1827, \*\*Caracas 101, Venezuela.

One of us, JWD, acknowledges the support of the National Science Foundation Grant DMR-76-21365.

$$\eta = |(V_1 - V_2)/V_3| \tag{1}$$

and  $V_{i}$  are the principal values of the (time averaged) electric field gradient tensor  $\overline{V}$  at the nuclear site,  $|V_3| > |V_1|, |V_2|.4,5$  Since  $\sum_{\infty}^{\infty}$  is traceless, we have  $V_1 + V_2 + V_3 = 0$ 

Let the unit vector 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  $Q = \langle e \ e - 1/2 \rangle$ :  $Q = S(\hat{\hat{z}} \ \hat{z} - 1/3) + \Delta(\hat{x} \ \hat{x} - \hat{y} \ \hat{y});$ 

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

S is the usual Maier-Saupe order parameter (S  $\sim$  0.5) and  $\Delta$  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  $\overline{V}$  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

 $\bar{V} = a\hat{z}\hat{z} + b\hat{y}\hat{y} + c(\hat{z}\hat{y} + \hat{y}\hat{z}) + d\hat{x}\hat{x},$ with a+b+d=0. Without loss in generality, we may assume a>0. 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,

$$b \approx d \approx -a/2.$$
 (4) 
$$|c| \ll a.$$

It is seen from Eq. (3) that for  $c \neq 0$  the frame which diagonalizes  $\vec{V}$  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  $\bar{V}$  is d and the other two are the

roots 
$$\lambda_{+}$$
 of the determinantal eigenvalue equation 
$$\begin{vmatrix} a - \lambda & c \\ & & \\ c & b - \lambda \end{vmatrix} = 0;$$

i.e.,

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

By relation (4),  $a-b \sim 3a/2 \gg |c|$ , 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  $\eta$  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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- By Eq. (1), it makes no difference whether we find the principal values of V or of -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 e·V·e) multiplying S in the quantity a is very small. For a cylindrically symmetric quadrupole field V, for example, e·V·e ≈ 0 if the major axis of V makes an angle very close to 54°44' with e. Experimentally, the failure of relations (4) would be revealed by a very small value of the mean absorption frequency ω.
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