^{14}N-^{1}H Nuclear Double Resonance in Biaxial Liquid Crystals

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There has been considerable interest recently in the nature of the local orientational order in the biaxial smectic liquid crystalline phases. According to the Meyer-McMillan theory(1) the tilting of the molecules with respect to the smectic planes in the smectic C and the smectic H phases is connected with a freezing out of the "isotropic" rotational motion of the molecules around their long axes due to the anti-parallel anti-ferroelectric like ordering of the "outboard" molecular dipoles(1). The discovery of ferroelectricity in chiral smectic C phases(2), where the in plane spontaneous polarization seems to arise from a small, but non-vanishing parallel ordering of molecular dipoles - and a resulting rotational bias - has lend further support to this model. The freezing out of the molecular rotations around their long axes is however not a necessary condition for the occurrence of biaxiality in smectic systems and alternative models have been formulated(3) where the tilt takes place while the molecules are still freely rotating.

The experimental evidence for the local orientational order predicted by the Meyer-McMillan theory(1) in achiral biaxial smectics has been so far either inconclusive or negative.

In this paper we report what we believe to be the first direct check on the anisotropy of rotation of the out-board molecular dipoles in the smectic C and the smectic H phases. The experiment was performed via a determination of the asymmetry parameter

$$\eta = \frac{V_{XX} - V_{YY}}{V_{ZZ}}$$

of the electric field gradient (EFG) tensor at the ^{14}N sites in TBBA and represents the first nuclear quadrupole resonance (NQR) study of any smectic system.

The measurements were performed with the help of a proton-nitrogen nuclear double resonance technique, involving magnetic field cycling . The results for TBBA in particular are:

Solid II(20°C): e^2Qq/h = 4220 KHz; η = 0,260
Sm H-V(91°C) : e^2Qq/h = 1170 KHz; η = 0.70
Sm C (150°C) : e^2Qq/h = 1010 KHz; η = 0,08
Sm A (185°C) : e^2Qq/h = 810 KHz; η = 0

The data show that the electric field gradient tensor at the ^{14}N sites deviates from cylindrical symmetry in the biaxial Sm C and Sm H phases whereas it is cylindrically symmetrical in the uniaxial Sm A phase. The maximum value of the orientational order parameter $\langle \cos \psi \rangle$ = 0.025 for the Sm C and 0.18 for the Sm H phase. This suggests that in the Sm C phase the molecular tilt induces the rotational bias and not vice versa, whereas in the supercooled Sm H phase the situation is different and the results can be interpreted within the Meyer-McMillan Model.

References

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3. See, for instance, P.G.de Gennes, The Physics of Liquid Crystals, Clarendon Press, Oxf. (1974) and references therein