

times that of the free-rotor molecules. This is still faster than the rate due to H_{dd}^{inter} , and thus it is probably this mechanism which determines the conversion rate of the ordered molecules, giving a ($T=0$) conversion time on the order of a year.

One of us (A.J.B.) is grateful to Professor M. Bloom for interesting him in this problem. We would also like to thank Professor I. F. Silvera, Professor A. B. Harris, and Mr. M. Sprik for helpful comments on the manuscript.

¹O. Runolfson and S. Mango, Phys. Lett. **28A**, 254 (1968).

²J. E. Piott, Ph.D. thesis, University of Washington, 1971 (unpublished).

³P. van Hecke and L. van Gerven, Physica (Utrecht) **68**, 359 (1973).

⁴R. F. Code and J. Higginbotham, Can. J. Phys. **54**, 1248 (1976).

⁵K. P. Wong, J. D. Noble, M. Bloom, and S. Alexander, J. Magn. Res. **1**, 55 (1969).

⁶W. Press, J. Chem. Phys. **56**, 2597 (1972).

⁷W. Press and A. Kollmar, Solid State Commun. **17**, 405 (1975).

⁸A. J. Nijman and N. J. Trappeniers, to be published.

⁹A. J. Nijman, Ph. D. thesis, University of Amsterdam (to be published).

¹⁰H. Kapflla and W. Gläser, Phys. Lett. **31A**, 158 (1970).

¹¹H. M. James and T. A. Keenan, J. Chem. Phys. **31**, 12 (1959).

¹²T. Yamamoto, J. Chem. Phys. **48**, 3193 (1968).

¹³H. Yasuka, T. Yamamoto, and Y. Kataoka, Prog. Theor. Phys. **41**, 859 (1969).

¹⁴Y. Kataoka, K. Okada, and T. Yamamoto, Chem. Phys. Lett. **19**, 365 (1973).

¹⁵A. J. Berlinsky, Phys. Rev. B **12**, 1482 (1975).

¹⁶G. J. Vogt and K. S. Pitzer, J. Chem. Phys. **63**, 3667 (1975).

¹⁷I. Ozier and K. Fox, J. Chem. Phys. **52**, 1416 (1970).

¹⁸T. K. Bose, J. S. Sochanski, and R. H. Cole, J. Chem. Phys. **57**, 3592 (1972).

¹⁹I. K. Snook and T. H. Spurling, Trans. Faraday Soc. **68**, 1359 (1972).

²⁰T. Nagamiya, Prog. Theor. Phys. **6**, 702 (1951).

Orientalional Order in Biaxial Liquid Crystals

J. Seliger, R. Osredkar, V. Žagar, and R. Blinc
J. Stefan Institute, University of Ljubljana, Ljubljana, Yugoslavia
 (Received 15 November 1976)

¹⁴N nuclear-quadrupole-resonance data show that the electric-field-gradient tensor at the ¹⁴N sites in terephthal-*bis*-butylaniline deviates from cylindrical symmetry in the biaxial smectic-*C*, smectic-*H*, and smectic-*VI* phases whereas it is cylindrically symmetrical in the uniaxial smectic-*A* phase. The results suggest that in the smectic-*C* phase the molecular tilt induces the rotational bias and not vice versa, whereas in the smectic-*H* phase the situation is different and the results may be interpreted within the Meyer-McMillan model.

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 antiparallel, antiferroelectriclike 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 nonvanishing parallel ordering of molecular dipoles—and a resulting rotational bias—, has lent 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 formulated³ 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 theory¹ in achiral biaxial smectics has been so far either inconclusive or negative. Proton⁴ and deuteron⁵ magnetic resonance measurements in terephthal-*bis*-butylaniline (TBBA) as well as x-ray⁶ and quasielastic neutron scattering⁷ data have all been interpreted in terms of rapid and nearly or completely "isotropic" rotational motion of the molecules around their long axes. Only a recent magnetic resonance experiment⁸ on the terminal methyl-group deuterons in *n*-heptyl-

d30-oxyazoxybenzene was interpreted as indicative of a small rotational freeze-out with $\langle \cos\phi \rangle \approx 0.01$.

In this Letter we report what we believe to be the first direct check on the anisotropy of rotation of the outboard molecular dipoles in the smectic-C and the smectic-H phases. The experiment was performed via a determination of the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ 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. For free rotation, the largest principal value, V_{zz} , will point along the long molecular axis and the EFG tensor will be axially symmetric: $V_{xx} = V_{yy}$, $\eta = 0$. Any anisotropy in the molecular motion around the long molecular axes will destroy the axial symmetry of the ^{14}N EFG tensor resulting in a finite η and the appearance of three ^{14}N pure NQR lines, $\nu_1 = \frac{3}{4}K(1 + \eta/3)$, $\nu_2 = \frac{3}{4}K(1 - \eta/3)$, $\nu_3 = \nu_1 - \nu_2$, instead of the single nonzero one for $\eta = 0$. Here $K = e^2qQ/h$ is the ^{14}N quadrupole coupling constant and $eq = V_{zz}$.

The advantage of the present approach is the following: (i) The measurement of the orientational order is performed directly at the sites of the outboard dipoles and not at the benzene rings or hydrocarbon tails where the molecular motion might be different from that at the dipolar sites. (ii) The deviations of the ^{14}N EFG tensor from cylindrical symmetry are determined via a frequency measurement so that—in view of the relatively large quadrupole moment Q of the nitrogen—even a small anisotropy and local orientational ordering can be detected. (iii) No oriented monodomain samples are necessary thus avoiding errors due to misalignment effects.

The measurements were performed with the help of a proton-nitrogen nuclear double resonance technique, involving magnetic field cycling.⁹ Typical ^{14}N NQR spectra are shown in Fig. 1 for the smectic-A, the smectic-C, the smectic-H, and the smectic-VI phases. The results are as follows: for solid II (20°C),

$$e^2qQ/h = 4220 \text{ kHz}, \quad \eta = 0.26;$$

for smectic VI (91°C),

$$e^2qQ/h = 1170 \text{ kHz}, \quad \eta = 0.70;$$

for smectic H (134.5°C),

$$e^2qQ/h = 1020 \text{ kHz}, \quad \eta = 0.24;$$

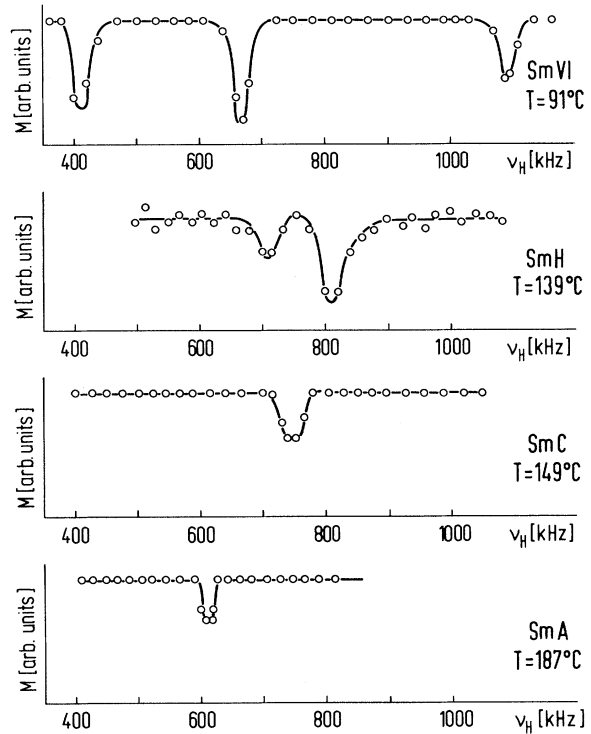


FIG. 1. ^{14}N NQR spectra in the smectic-VI, smectic-H, smectic-C, and smectic-A phases of TBBA.

for smectic C (150°C),

$$e^2qQ/h = 1010 \text{ kHz}, \quad \eta = 0.08;$$

for smectic A (185°C),

$$e^2qQ/h = 810 \text{ kHz}, \quad \eta = 0.$$

As can be seen from Fig. 2, the center of the ^{14}N line continuously shifts towards lower frequencies as the temperature is increased in the smectic-C phase. In the same temperature range the linewidth first increases and then decreases with increasing temperature. In view of the long nitrogen spin-lattice relaxation time the anomalous linewidth in the smectic-C phase can be understood only if the spectra consist of two overlapping ^{14}N lines, ν_1 and ν_2 , with a finite spacing due to a nonzero value of η . This means that the ^{14}N quadrupole coupling constant continuously decreases with increasing temperature, while the asymmetry parameter η exhibits a maximum in the middle of the smectic-C phase (Fig. 3). On going from the C to the H phase, η jumps by nearly a factor of ten (Fig. 3), while it attains a still higher value ($\eta = 0.70$) in the VI phase.

The fact that the ^{14}N EFG tensor in the biaxial smectic-C and smectic-H phases is—in contrast

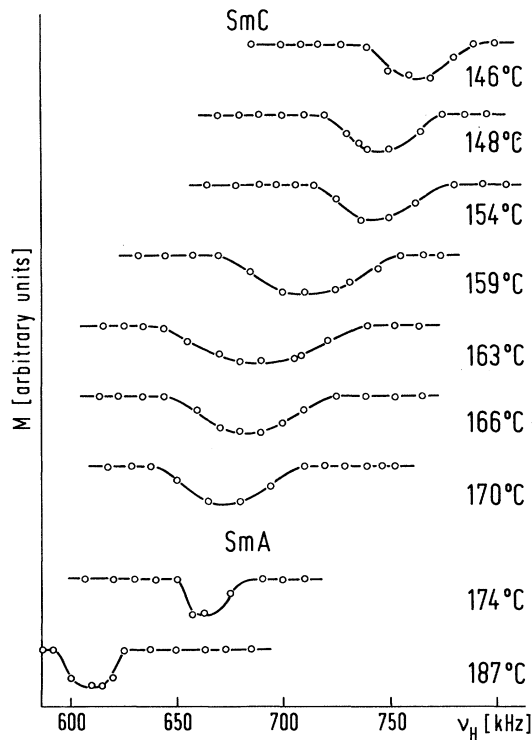


FIG. 2. Temperature dependence of the proton-nitrogen NQR double resonance line shape in the smectic-C phase of TBBA.

to the uniaxial smectic-A phase—not cylindrical symmetric demonstrates that the onset of the tilt is connected with the occurrence of an anisotropy in motion of the two outboard dipoles around the long molecular axes in achiral TBBA. Such an anisotropy is absent in the smectic-A phase. The anisotropy cannot be due to a linear coupling between the tilt and an in-plane spontaneous polarization^{2,10}—as in ferroelectric² chiral smectic-C and smectic-H phases—since in achiral smectic-C systems such a term is forbidden by symmetry. A linear coupling of the tilt with the in-plane antipolarization \vec{P} is however allowed by symmetry.

Group theory does not tell us what is the driving force of the orientational ordering, i.e., whether the tilt induces the antipolarization or the antipolarization induces the tilt. To discriminate between these two possibilities, let us now try to estimate the magnitude of the local orientational order parameters and analyze the temperature dependence of e^2qQ/h and η .

From the fact that the C-N=CH-C group is planar it follows that one ($V_{x_0x_0}$) of the principal axes of the ^{14}N EFG tensor in the solid phase of

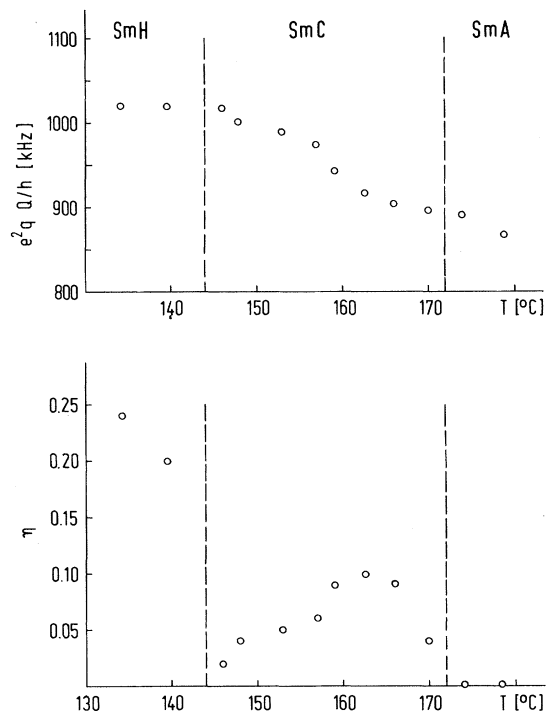


FIG. 3. Temperature dependence of the ^{14}N quadrupole coupling constant e^2qQ/h and the asymmetry parameter η in the smectic-A, smectic-C, and smectic-H phases of TBBA.

TBBA must be perpendicular to this (y_0z_0) mirror plane. The nonzero elements of the ^{14}N EFG tensor in the molecular frame are thus $V_{x_0x_0}$, $V_{y_0y_0}$, $V_{z_0z_0}$, and $V_{y_0z_0}$, where z_0 is the direction of the long molecular axis. These elements are specified by the ^{14}N data in the solid phase and the direction of the largest principal axis of the ^{14}N EFG tensor, which is from other Schiff's bases known^{11,12} to lie in the y_0z_0 plane and make an angle of about 60° with the z_0 axis. Transforming from the molecular x_0, y_0, z_0 frame into a frame $\xi, \eta, \zeta \parallel z_0$, where the ξ and η axes rotate around the ζ axis—or, what is the same, jump between n equilibrium orientations with $n \geq 3$ in a potential $U(\varphi) = U(-\varphi)$, where φ is the angle between ξ and x_0 —we find the instantaneous ^{14}N EFG tensor as

$$V_{\xi\xi} = -\frac{1}{2}V_{z_0z_0} + \frac{1}{2}(V_{x_0x_0} - V_{y_0y_0})\cos 2\varphi, \quad (1a)$$

$$V_{\eta\eta} = -\frac{1}{2}V_{z_0z_0} - \frac{1}{2}(V_{x_0x_0} - V_{y_0y_0})\cos 2\varphi, \quad (1b)$$

$$V_{\zeta\zeta} = V_{z_0z_0}, \quad (1c)$$

$$V_{\eta\xi} = V_{y_0z_0}\cos\varphi, \quad (1d)$$

where $\varphi = \varphi(t)$. This model seems to describe the results in the smectic-VI and smectic-H phases.

To take into account the possibility of anisotropic fluctuations of the long molecular axis in the smectic-C phase, we make still another transformation from the ξ, η, ζ frame to an x, y, z frame, where z is normal to the smectic planes, $x \parallel \vec{P}$, and y is parallel to the C_2 axis. Designating with

$\theta = \theta(t)$ the angle between the z axis and the instantaneous direction of the long molecular axis and with $\phi = \phi(t)$ the angle between the projections of the average and the instantaneous directions of the long molecular axis on the smectic (xy) plane, we find the time-averaged value of the ^{14}N quadrupole coupling constant as

$$e^2qQ/h = (eQ/h)V_{z_0z_0} \left(\langle \frac{3}{2} \cos^2\theta - \frac{1}{2} \rangle + \frac{3}{2} \langle \sin^2\theta \cos^2\phi \rangle \right), \quad (2a)$$

and the asymmetry parameter as

$$\eta = \frac{1}{2} [(V_{x_0x_0} - V_{y_0y_0})/V_{z_0z_0}] \langle \cos 2\varphi (1 + \cos^2\theta) \cos 2\phi \rangle + \frac{3}{2} \langle \sin^2\theta \cos 2\phi \rangle - \langle \sin\theta \cos\theta \cos\phi \rangle^2. \quad (2b)$$

Since the asymmetry parameter in the smectic-C phase as well as the tilt angle¹³ is small we have here neglected terms quadratic in $\langle \cos\phi \rangle$ and $\langle \cos 2\varphi \rangle$ as well as third-order terms in $\sin\theta$. These expressions seem to describe rather well the experimentally observed monotonic decrease in e^2qQ/h with increasing temperature in the smectic-C and smectic-A phases, where the second term in (2a) vanishes, as well as the maximum in η in the middle of the smectic-C phase. $V_{z_0z_0}$ expressed in frequency units equals ≈ 1020 kHz.

Introducing $\langle \theta^2 \rangle = \theta_0^2 + \langle \delta\theta^2 \rangle$, where θ_0 is the mean tilt angle, we find for small fluctuations in θ the following simplified relations:

$$e^2qQ/h \approx (eQ/h)V_{z_0z_0} (1 - \frac{3}{2} \langle \delta\theta^2 \rangle), \quad (3a)$$

$$\eta \approx [(V_{x_0x_0} - V_{y_0y_0})/V_{z_0z_0}] \langle \cos 2\varphi \cos 2\phi \rangle + \frac{3}{2} \langle \delta\theta^2 \cos 2\phi \rangle. \quad (3b)$$

Because of the linear coupling between the tilt and the antipolarization, the orientational order parameter $\langle \cos 2\varphi \rangle$ should be proportional to the tilt, $\langle \cos 2\varphi \rangle = \alpha \theta_0$. Thus the first term in expression (3b) is monotonically decreasing with increasing temperature. The second term in (3b) is, on the other hand, responsible for the observed maximum in η . In the low-temperature part of the smectic-C phase, $\langle \cos 2\phi \rangle \approx 1$ and η increases with increasing temperature because of the increase in $\langle \delta\theta^2 \rangle$. At higher temperatures η decreases as $\langle \cos 2\phi \rangle \rightarrow 0$, so that there has to be a maximum in between.

The maximum value of $\langle \cos 2\varphi \rangle$ in the smectic-C phase can be estimated from the value of η right above the smectic-H-smectic-C transition where $\langle \cos 2\phi \rangle \approx 1$. Here $\langle \delta\theta^2 \rangle \rightarrow 0$ and since $(V_{x_0x_0} - V_{y_0y_0})/V_{z_0z_0} \approx 2$, we find, from the observed value of η , $\langle \cos 2\varphi \rangle_{\text{max}} \approx 0.025$. For a polar deformation of the hexagonal potential hindering the rotation of a given dipole around the long molecular axis, we have

$$\langle \cos\varphi \rangle = \langle \cos 2\varphi \rangle = W - W_1. \quad (4)$$

Here $W = W_6$ is the occupation probability for the preferred orientation of an outboard dipole on a given sublattice, and $W_1 = W_2 = W_3 = W_4 = W_5$ is the occupation probability for the other five sites.

The above values for $\langle \cos\varphi \rangle$ and $\langle \cos 2\varphi \rangle$ are

smaller than the ones expected on the basis of the McMillan theory.¹ Thus it seems that the tilt induces the antipolarization in the smectic-C phase of TBBA rather than vice versa.

The situation may be different in the smectic-H and -VI phases. Here the values of η are so large that they cannot be due to anisotropic fluctuations of the long molecular axes but rather to a large degree of local orientational ordering. By a diagonalization of the time-averaged tensor [(1a)-(1d)] and assumption (4) we find from the experimental data in the H phase $\langle \cos\varphi \rangle = \langle \cos 2\varphi \rangle \approx 0.12$. This value of the orientational order parameter is so large that it does not contradict the McMillan model.¹

¹R. J. Meyer and W. L. McMillan, Phys. Rev. A **9**, 899 (1974).

²R. J. Meyer, L. Liebert, L. Strzelecki, and P. Keller, J. Phys. (Paris), Lett. **36**, L-69 (1975).

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

⁴Z. Luz and S. Meiboom, J. Chem. Phys. **59**, 275 (1973).

⁵Z. Luz, R. C. Hew, and S. Meiboom, J. Chem. Phys. **61**, 1758 (1974); B. Deloche, J. Charvolin, L. Liebert, and L. Strzelecki, J. Phys. (Paris), Coll. **36**, C-1 (1975).

⁶A. M. Levelut and M. Lambert, C. R. Acad. Sci., Ser. B **272**, 1018 (1971).

⁷H. Hervet, F. Volino, A. J. Dianoux, and R. E. Lechner, J. Phys. (Paris), Lett. **35**, L-151 (1974); H. Hervet, F. Volino, A. J. Dianoux, and R. E. Lechner, Phys. Rev. Lett. **34**, 451 (1975).

⁸J. W. Doane, in Proceedings of the Seventh International Liquid Crystal Conference, Kent, Ohio, August 1976 (to be published).

⁹J. Seliger, R. Blinc, H. Arend, and R. Kind, Z. Phys. **B25**, 189 (1976).

¹⁰R. Blinc, Phys. Status Solidi (b) **70**, K29 (1975).

¹¹J. Seliger, M. Mali, R. Osredkar, and R. Blinc, J. Chem. Phys. **65**, 2887 (1976).

¹²Unpublished work from this laboratory.

¹³R. A. Wise, D. H. Smith, and J. W. Doane, Phys. Rev. A **7**, 1366 (1973); T. R. Taylor, S. L. Aurora, and J. L. Ferguson, Phys. Rev. Lett. **25**, 722 (1970).

Self-Consistent Structure of Metallic Hydrogen*

David M. Straus† and N. W. Ashcroft

Laboratory of Atomic and Solid State Physics and Materials Science Center, Cornell University, Ithaca, New York 14853

(Received 23 November 1976)

A calculation is presented of the total energy of metallic hydrogen for a family of face-centered tetragonal lattices carried out within the self-consistent phonon approximation. The energy of proton motion is large and proper inclusion of proton dynamics alters the *structural* dependence of the total energy, causing isotropic lattices to become favored. For the dynamic lattice the structural dependence of terms of third and higher order in the electron-proton interaction is greatly reduced from static lattice equivalents.

Perturbation theory has been moderately successful in accounting for the structural dependence of the *static* energy in many simple crystalline metals.^{1,2} In this method, the structural energy is obtained by expansion in orders of the effective conduction-electron-ion interaction (or pseudopotential), the expansion usually being truncated at the lowest term and resulting in what is referred to as the second-order band-structure energy. For perfect lattices, this term reduces to a relatively simple sum over the sites of the reciprocal lattice.

In the case of metallic hydrogen, the electron-ion (electron-proton or electron-deuteron) interaction is exactly known, and it is partly for this reason that this system has attracted theoretical attention.³⁻⁷ Within the static-lattice approximation, perturbation theory for the structural energy has been carried through to fourth order,⁷ and extensive scans of "Bravais lattice space" have been carried out in an attempt to determine, at zero pressure, the structures with lowest static energy.³ In the latter calculations (which were at third order), Broyman *et al.*³ concluded that static metallic hydrogen would take up structures which are so highly anisotropic that near the zero-pressure metastable density they would become "liquidlike" in certain crystal directions upon inclusion of the proton dynamics.

Since the ionic mass in metallic hydrogen is

small, one expects on quite general grounds that the ionic degrees of freedom can play a rather significant role in determining the structure with lowest overall energy. It is known^{3,7} that energy differences between different structures are small—much smaller, for example, than the estimate of the energy bound up in the zero-point motion of the protons. Evidently, what is required is a calculation of structural energies carried out self-consistently for various lattices disturbed by the presence of phonons. The purpose of this Letter is to report on the outcome of such an investigation: We have completed a series of calculations within the self-consistent harmonic phonon approximation^{8,9} (SCHA) for a representative family of face-centered tetragonal (fct) Bravais lattices in their ground states at a density¹⁰ of $r_s = 1.36$ [with $\frac{4}{3}\pi(r_s a_0)^3 = n^{-1}$, n being the electron density N/Ω]. Two important results emerge: First, the inclusion of ion dynamics radically alters the structural dependence of the energy so that, in the family which we consider, it is the *isotropic* lattice (fcc) that is ultimately favored. Second, by the inclusion of ion dynamics in the perturbation theory, the structural sensitivity of the terms *higher* than second order is greatly reduced from that appropriate to the static theory.

The arguments go as follows: To second order in the electron-proton interaction, the total *ground-state energy* per proton in the self-con-