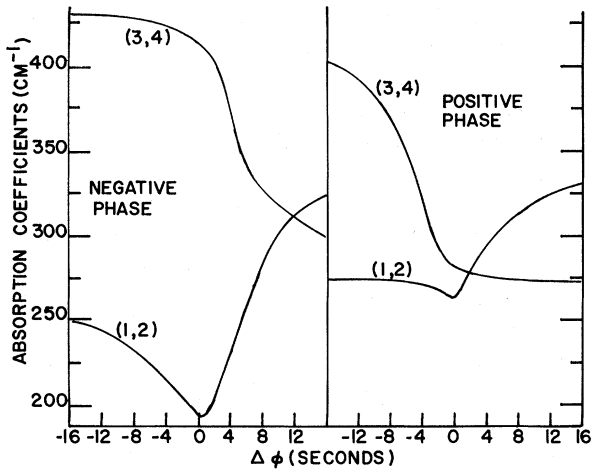

FIG. 4. Relative excitations of modes of propagation. Calculated for negative and positive phase products.

negative structure-factor phase triplets should yield different spatial distributions of diffracted intensity in n-beam diffraction. I have observed such phase effects repeatedly in perfect crystals of germanium and ammonium dihydrogen phosphate as well as in the relatively imperfect crystal of aluminum oxide discussed above. Analysis of Eq. (2) shows that the effects of a change of the phase product on the diffraction process are maximized when all three structure factors are equal to one another, and vanish if one of the structure factors equals zero. The phase effects should therefore be detected as readily when all three structure factors are "weak," as when all are "strong." The extent to which these effects can be detected in imperfect crystals, such as are usually used for crystal-structure analysis, or in noncentrosymmetric crystals remains to be determined.

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Orientational Order in Biaxial Liquid Crystals: The Smectic-VI and -*H* Phases

F. Volino
Groupe de Dynamique des Phases Condensées, Laboratoire de Cristallographie, Université des Sciences et Techniques de Languedoc, Place E. Bataillon, 34060 Montpellier Cedex, France
and
A. J. Dianoux
Institut Laue-Langevin, Centre de Tri, 38042 Grenoble Cedex, France
(Received 9 May 1977)

The ^{14}N nuclear-quadrupole resonance (NQR) data of Seliger *et al.* on the smectic-VI and -*H* phases of terephtal-*bis*-butylaniline are reanalyzed and compared to neutron results. For the smectic-VI phase, both methods lead to remarkably consistent conclusions, but do not differentiate between possible models. For the *H* phase, the NQR results are consistent both with a model permitting weak orientational order around the long axis and with a model permitting uniform rotation around the long axis plus (anisotropic) fluctuations of this axis. The latter is more realistic since it agrees with the neutron results while the former does not.

In a recent Letter,[1] ^{14}N nuclear-quadrupole resonance (NQR) data on terephtal-*bis*-butylaniline (TBBA) have been presented and analyzed in terms of rotational models for the molecular motions. Concerning the smectic-*H* phase, it is concluded that the results may be interpreted within the Meyer-McMillan theory[2] which predicts the existence of a polar orientational ordering around

the long axis. Concerning the VI phase, the authors suggest that the situation may be similar. These conclusions are at variance with those extracted from neutron quasielastic scattering (NQES) data, namely (i) that in the H phase, in addition to uniform (i.e., no orientational order) rotation around the long axis,[3,4] this axis fluctuates about its equilibrium position[5] and (ii) that in the VI phase, although the existence of a polar orientational ordering cannot be excluded, a more probable model is the one where the molecules are allowed to flip by π around their long axis.[6]

This Letter is an attempt to clarify this situation. From a critical analysis of the NQR data, we show that, due to the fact that one parameter of the problem [namely the angle u between the largest principal axis of the ^{14}N electric-field-gradient (EFG) tensor and the "long molecular axis"] is not sufficiently well known (and it is not sure that it can really be), the models suggested by the NQES results are also qualitatively and semiquantitatively consistent with NQR data.

We use the same notations, and make the same hypothesis concerning the symmetry properties of the EFG tensor in the molecular frame, as in Ref. 1. From the NQR data one extracts the modulus of the largest principal value of the EFG tensor $|eq|$ and the asymmetry parameter η. Let $|eq_0|$ and η_0 be the corresponding values in the solid phase. Since the molecular motions increase with temperature, the modulus of the averaged principal values of the EFG tensor (and in particular that of the largest one) are expected to decrease (for isotropic spherical rotation, all are zero). Consequently, we can define a reduction by $r = |eq/eq_0|$. Thus, each NQR spectrum yields the two quantities r and η. The experimental results relevant for our present purpose are those corresponding to the smectic-VI and -H phases at 91 and 134.5°C, namely those with $r = 0.277$ and $\eta = 0.70$, and those with $r = 0.242$ and $\eta = 0.24$, respectively.[1]

We consider first uniaxial models where the molecules can rotate in a noncylindrical, symmetrical potential V. The nonzero components of the corresponding average (and not instantaneous[1]) EFG tensor are given by Eqs. (1a)–(1d) of Ref. 1 where $\cos\varphi$ and $\cos 2\varphi$ have been replaced by their average. These components depend on the models through $\langle\cos\varphi\rangle$ and $\langle\cos 2\varphi\rangle$ and on $|eq_0|$, η_0, and u through $V_{x_0x_0}, \ldots, V_{y_0z_0}$. Under the assumption that the measured values of $|eq_0|$ and η_0 in the solid are of pure intramolecular origin, the only parameter left to fit models is u.[7] The value of u is known to be about 60°.[1] However, even if u were precisely known in the solid phase (for example, from a similar NQR experiment on a monocrystal) it would not necessarily be the same in the other phases since the concept of "long molecular axis" may also change slightly because of an increasing number of possible molecular conformations, as the temperature rises. With this in mind we shall show now that it is sufficient to choose u in a range of less than ± 4° around 60° and allow it to change by 3° from the H to the VI phase to change radically the result of the analysis. To do this, we have numerically diagonalized the EFG tensor given by Eqs. (1a)–(1d) of Ref. 1, labeling $\lambda_1, \lambda_1, \lambda_3$ the eigenvalues such that $|\lambda_1| \leq |\lambda_2| \leq |\lambda_3|$ and defining $r = |\lambda_3/eq_0|$ and $\eta = |(\lambda_2 - \lambda_1)/\lambda_3|$, as usual. We have used three models: the model of Ref. 1 (model A) and the models used in Refs. 4 and 6, namely a Meyer-McMillan–type model with $V = V_1(\varphi) \propto \cos\varphi$ (model B) and a model with $V = V_2(\varphi) \propto \cos 2\varphi$ (model C). (In fact, model A is a rough approximation of model B.) For each of them, $\langle\cos\varphi\rangle$ and $\langle\cos 2\varphi\rangle$ are related as follows: $\langle\cos\varphi\rangle = \langle\cos 2\varphi\rangle$ for model A,[1] $\langle\cos\varphi\rangle = I_1(\gamma')/I_0(\gamma')$ and $\langle\cos 2\varphi\rangle = I_2(\gamma')/I_0(\gamma')$ for model B (the I_i are modified Bessel functions and γ' the connecting parameter),[5,6] and $\langle\cos\varphi\rangle \equiv 0$ for model C.[6] An example of the results is shown in Figs. 1 and 2 where we have plotted r and η vs $\langle\cos\varphi\rangle$ (models A and B) or $\langle\cos 2\varphi\rangle$ (model C) for $u = 60.0°$ (apparently the value used in Ref. 1). The corresponding experimental values of r and η for the VI and H phases are also shown. These results call for a few comments. The most important one is linked to Fig. 1. It is seen that the experimental r values are greater, but *very near* the minimum value r_I corresponding to the uniform (i.e., no order) rotation. Since r_I (and all the curves) are expected to vary with u, it is of prime importance here to know the corresponding variation. This is easily calculated and we have

$$r_I = \tfrac{1}{4}|(3+\eta_0)\cos 2u + 1 - \eta_0| . \quad (1)$$

This function is shown in the inset of Fig. 1 together with the experimental values of r and the conclusion is drawn immediately. For the smectic-VI phase, choosing $u < 62.2°$, then, there is some hope to find a uniaxial model which would fit the data. For the smectic-H phase which is more controversial, the situation is similar for $u < 60.8°$, and a uniaxial model may also work. However, for $u > 60.8°$, r_I is greater than the ex-

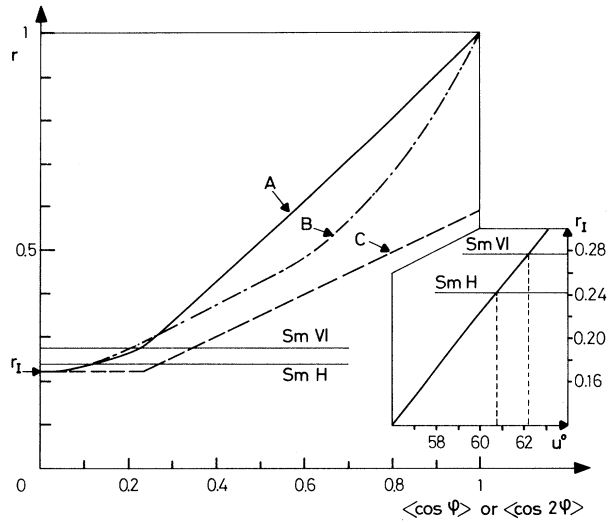

FIG. 1. Plot of the reduction parameter r as a function of the order parameter $\langle\cos\varphi\rangle$ (models A and B) or $\langle\cos 2\varphi\rangle$ (model C) for the uniaxial models discussed in the text, for $u = 60.0°$. In the inset is shown the variation of r_I (value of r for $\langle\cos\varphi\rangle = \langle\cos 2\varphi\rangle = 0$) vs u [Eq. (1)]. The experimental values for the smectic-VI phase at 91°C and the smectic-H phase at 134.5°C are also shown.

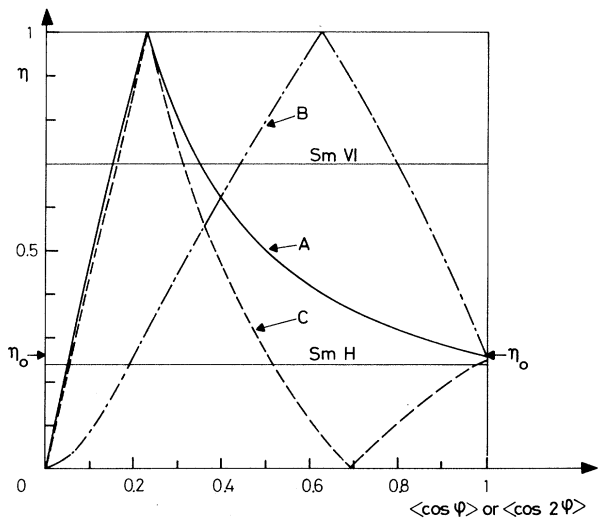

FIG. 2. Plot of the asymmetry parameter η as a function of the order parameter $\langle\cos\varphi\rangle$ (models A and B) or $\langle\cos 2\varphi\rangle$ (model C) for the uniaxial models discussed in the text for $u = 60.0°$. The experimental values for the smectic-VI phase at 91°C and the smectic-H phase at 134.5°C are also shown. Note that the fact that η for $\langle\cos 2\varphi\rangle = 1$ (model C) is very near η_0 is only fortuitous.

perimental value and any purely uniaxial model will then be impossible. Physically, this means that in this case, the motion has to be more "isotropic" than uniaxiality, a situation which can be realized for example with additional fluctuations of the long axis. In this case, to explain a nonzero value of η, it is sufficient to assume that these fluctuations are anisotropic, an assumption which is not unreasonable in a tilted phase.

We have first looked for solutions with the uniaxial models A, B, and C by allowing u to vary by $\pm 5°$ around 60°. We must first note that there is no solution for $u = 60.0°$. In particular for model A in the H phase for which Fig. 1 yields $\langle\cos\varphi\rangle \approx 0.12$ (the value of Ref. 1) but Fig. 2 only 0.05. The solutions are summarized in Table I. For the H phase we find a solution of the Meyer-McMillan type, as expected from the analysis of Ref. 1, but corresponding to order parameters which are significantly smaller than predicted by the Meyer-McMillan theory.[2] No solution corresponding to the C model is found. For the VI phase on the contrary, the three models can work, with values of the order parameters comparable with those deduced from the NQES data.[6] The reasons why we believe that model C is the most probable are discussed in Ref. 6.

We have then looked for a solution for the H phase with a model permitting uniform rotation around the long axis plus fluctuations of this axis. We have thus rotated the EFG tensor given by Eqs. (1a)–(1d) of Ref. 1, with $\langle\cos\varphi\rangle = \langle\cos 2\varphi\rangle = 0$ taking as z axis the normal to the smectic planes. We have assumed that the polar (θ) distribution is peaked at θ_0 and that the azimuthal (φ) distribution is of the Meyer-McMillan type as for the above-mentioned model B. This means that $\langle\cos\varphi\rangle$ and $\langle\cos 2\varphi\rangle$ are related through the same parameter γ'. For the practical calculation, we have assumed small fluctuations of θ around θ_0 as in Ref. 1, writing $\theta = \theta_0 + \delta\theta$. The parameters of the model are thus $\langle\delta\theta^2\rangle^{1/2}$, $\langle\cos\varphi\rangle$, and

TABLE I. Values of the parameter u and of the order parameter for the purely uniaxial models A, B, and C, which best fit the ^{14}N NQR data in the smectic-VI and -H phases of TBBA.

Phase	Model	u	Order parameter
VI(91°C)	A	57.1°	$\langle\cos\varphi\rangle = 0.26$
	B	56.2°	$\langle\cos\varphi\rangle = 0.31$
	C	60.6°	$\langle\cos 2\varphi\rangle = 0.33$
H(134.5°C)	A	60.6°	$\langle\cos\varphi\rangle = 0.056$
	B	59.0°	$\langle\cos\varphi\rangle = 0.17$
	C		No solution

θ_0 to be determined with three pieces of data namely r, η, and the tilt angle ω. The tilt angle is indeed expected to be different from θ_0, and given by

$$\tan\omega = \langle|\tan\theta|\rangle\langle\cos\varphi\rangle , \quad (2)$$

as can be easily inferred from geometrical considerations.

Choosing $u = 64°$, with $r = 0.242$, $\eta = 0.24$, and $\omega = 28°$ (the values for 134.5°C) we have found the following solution: $\theta_0 = 31.2°$, $\langle\delta\theta^2\rangle^{1/2} = 22°$, $\langle\cos\varphi\rangle = 0.97$ corresponding to $\langle\Delta\varphi^2\rangle^{1/2} \approx 14°$. This corresponds to an average amplitude fluctuation of the axis of about 20°, a value which is fairly consistent with what was estimated from the NQES results.[5] The fact that η decreases while r remains practically constant when the temperature is increased in the H phase is easily accounted for by an increase of the azimuthal fluctuation amplitude. For 139°C, we have found $\langle\delta\theta^2\rangle^{1/2} \approx 22°$ and $\langle\cos\varphi\rangle \approx 0.94$ corresponding to $\langle\Delta\varphi^2\rangle^{1/2} \approx 20°$.

In conclusion, for the VI phase, the present NQR and NQES results are quite consistent with one another but both do not allow discrimination between the various models. Model C is favored from other considerations.[6] For the H phase, the NQR results are consistent either with a uniaxial model with weak orientational ordering, or with a model permitting uniform rotation around the long axis and fluctuation of this axis. In this case, the latter should be favored since it agrees with the NQES results while the former does not.[3-6]

Finally, concerning the smectic-C phase, since the situation is essentially the same as in the smectic-H phase, there is clearly no need to invoke any orientational order around the long axis to explain the corresponding NQR data.[1] This will be discussed in detail in a forthcoming paper.

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Exact Relation between the Solid-on-Solid Model and the XY Model

H. J. F. Knops
Instituut voor Theoretische Fysika, Universiteit Nijmegen, Nijmegen, The Netherlands
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An exact relation is established between the solid-on-solid model describing the growth of crystals and the classical XY model. Application of this relation to a special case leads to an exact correspondence between the XY model and the Coulomb gas which matches with the relation obtained by Kosterlitz in the strong-coupling limit.

Recently there has been a growing interest in the existence and nature of a roughening transition which might describe the sudden loss of a sharp interface in Monte Carlo simulations[1,2] of crystal growth. The interface in these simulations is described by the so-called solid-on-solid (SOS) model in which the possibility of "overhangs" above the interface are ruled out so that the interface is conveniently described in terms of integers h_j denoting the number of adatoms at the jth lattice position of the interface. The interaction, which will be assumed here to be of nearest-neighbor type, is expressed in terms of height differences of adjacent columns as

$$H = \sum_{\langle i,j\rangle} V(h_i - h_j) . \quad (1)$$

Originally[3,4] the possibility of a roughening