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Macroscopic and local orientational orders in nematic glass

V. K. Dolganov
Institut of Solid State Physics, Russian Academy of Sciences, 142432, Chernogolovka, Moscow district, Russia

R. Fouret, C. Gors, and M. More
Laboratoire de Dynamique et Structures Des Matériaux Moléculaires, Université de Lille I, UFR de Physique, 59655 Villeneuve d'Ascq, France

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X-ray diffraction has been measured at different stages of the transition from a glassy to a partially ordered $C1$ phase of *p*-methoxybenzyliden-*p*'-*n*-butylaniline. The measurements were performed on oriented samples for various orientations of the director of the liquid crystalline structure with respect to the scattering wave vector. The transition presents both a translational and an orientational ordering of the molecules. The variations of the macroscopic orientational order parameter $\langle P_2 \rangle$ with the range of the molecular correlation length are reported. The change of $\langle P_2 \rangle$ at the transition is associated with a short-range orientational order in the glassy state. The dependence of the local orientational order parameter $\langle P_2^l \rangle$ upon the correlation length has also been determined and this is the first experimental demonstration of the interdependence of the orientational and positional order.

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I. INTRODUCTION

The rapid cooling of a liquid crystal may lead to the formation of a glassy state [1]. In the case of nematic liquid crystals, the glassy state is characterized by a translational disorder, which is a common characteristic feature of the amorphous state, and a macroscopic orientational order characteristic of the nematic phase. As a rule, the heating of the glassy state above the glass-transition temperature, leads to the formation of a metastable crystalline structure. The study of the short-range molecular order in the glassy state and its change during the transition to a crystalline phase is one of the urgent problems of the physics of disordered structures. Both the translational and orientational molecular order are modified during the transition. Unlike amorphous materials, the change in the orientational order in a glassy liquid crystal (GLC) can be determined by diffraction measurements independently of the change in the translational order. It is thus possible to investigate both types of structural disorders per se, and the formation of the crystalline phase upon heating the glassy state. In this paper we present such investigations for the typical nematic *p*-methoxybenzyliden-*p*'-*n*-butylaniline (MBBA).

During recent years, the structure, solid-state polymorphism, molecular, and intermolecular dynamics of MBBA have been widely studied [2–8]. The rapid cooling of MBBA from the nematic phase (296–317 K) leads to the formation of the so-called $C0$ glassy state phase ($T_g = 202$ K). The $C0$ structure is similar to that of the nematic liquid crystal. It was established that the sequence of phase transitions when heating $C0$ depends on the heating rate. At a relatively high rate (> 1 K min^{-1}), the GLC transforms into a supercooled liquid crystalline state (at about 202 K), and a so-called $C3$ phase is formed during further crystallization (at 215 K). A slow heating of the GLC or the prolonged exposure of the sample in the vicinity of the glassy-transition temperature causes the formation of the $C1$ phase.

The transformation of the nematic $C0$ structure into phases $C1$ or $C3$ also presents substantially different behaviors. The transition to the $C3$ phase immediately leads to the occurrence of an ordered crystalline state. The transition $C0$ to $C1$ proceeds after some time delay and the continuous evolution of the diffraction pattern, which depicts the change of the molecular order, can be observed in the vicinity of T_g where the molecular mobility is low.

Some studies of the formation of an ordered state in the vicinity of T_g have considered that the transformation $C0$-$C1$ is first-order-like and the kinetics of the transformation of smectic layers has been investigated [9]. In this paper, we consider the transition as a progressive change of the translational and of the orientational ordering of molecules. Diffraction measurements have been made for an oriented MBBA sample at different stages of the transition from the glassy state to the $C1$ phase. The measurements performed for various directions of the wave vector $\mathbf{Q}$ with respect to the director $\mathbf{n}$ were used to investigate the transformations of both the orientational and the translational order, and to determine the dependence of the translational order parameter on the size of the domains of the correlated molecular arrangement.

II. EXPERIMENT

X-ray diffraction measurements were carried out with the apparatus described in an earlier paper [6]. The incoming x-ray beam ($\lambda = 1.5406$ Å) is monochromatized by the $(10\bar{1}1)$ Bragg reflection of a curved quartz monochromator. The diffracted intensity was detected by a curved linear position sensitive multidetector in the range

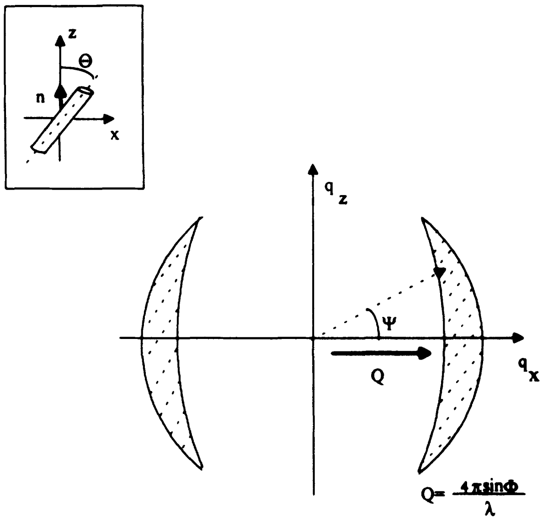

FIG. 1. A schematic x-ray diffraction pattern of a liquid crystal. The director **n** is along q_z. The molecular geometry is shown in the inset. Θ is the molecular tilt angle.

($3° \leq 2\Phi \leq 120°$) of the scattering angle, with an electronic resolution of 0.03°. A cryostat [10], with a controlled (± 0.1 K) temperature, was used for the low temperature measurements. The liquid crystal was introduced inside a Lindeman glass capillary of diameter 1 mm and length 10 mm and centered on the vertical axis of a goniometer head. The sample in its nematic state was oriented in a magnetic field (0.8 T) perpendicular to the glass capillary axis. After cooling into liquid nitrogen, the capillary was introduced into the previously cooled cryostat, so that the director lays in the horizontal scattering plane. The diffraction measurements were carried out for different orientations of the director with respect to the incident x-ray beam; this was achieved by rotating the sample through fixed angles Ψ with respect to the vertical axis (Fig. 1).

The orientational order parameter in GLC, $\langle P_2 \rangle = \frac{1}{2}(3\langle \cos^2\Theta \rangle - 1)$ (where Θ is the angle between the director and the long molecular axis) depends on the cooling rate and was found to vary between 0.8 [2] to 0.45 [11]. The sample was placed in a thin wall capillary and cooled by immersion in liquid nitrogen. The cooling rate thus achieved from the start of the cooling to the hardening of the sample is about 10 K s^{-1}. In the measurements reported here, a reproducible value of 0.62 was obtained for $\langle P_2 \rangle$. This value is close to that of the orientational order parameter in the nematic state. It can be assumed that at least part of the long-wave orientational fluctuations freeze along with the freezing of the molecular order. The relaxation time for the fluctuations, already large at room temperature [12], increases strongly during the cooling.

Below 201.5 K, the transformation rate of the unstable glassy state is too low for a practical measurement of the transition to $C1$. At higher temperatures, x-ray scattering data show that the transformation is occurring. The transformation rate is highly dependent on the temperature at 202 K the transition time is about 8 h and, at 205 K it is only a few minutes. The structure at various degrees of advancement of the transformation was measured by aging the sample at 202 K and quenching it at 170 K to freeze the state of the sample. The first aging was performed for 2 h. The aging and quenching cycle was repeated until the transition to the $C1$ phase was completed. At 170 K, diffraction measurements were performed every 200 s at various fixed orientations of the director.

Figure 2 shows diffraction patterns recorded at some stages of the transition from $C0$ to $C1$. Figure 3 presents the maximum intensity of the main peak as a function of the rotation angle Ψ of the director.

III. DISCUSSION

The position of the main diffraction peak characterizes the intermolecular distance d between the long molecular axes. The half-width of the diffraction peak is related to the size of the regions of coherent scattering, i.e., the correlation length of the local order. The angular distribution $I(\Psi)$ reflects the orientational distribution of long molecular axes with respect to the director. During a transition, d is practically not changed ($d = 4.31$ Å in $C0$ and $d = 4.35$ Å in $C1$) but $I(\Psi)$ and the half-width of the diffraction peak $I(Q)$ decrease substantially ($\Delta Q = 0.22$

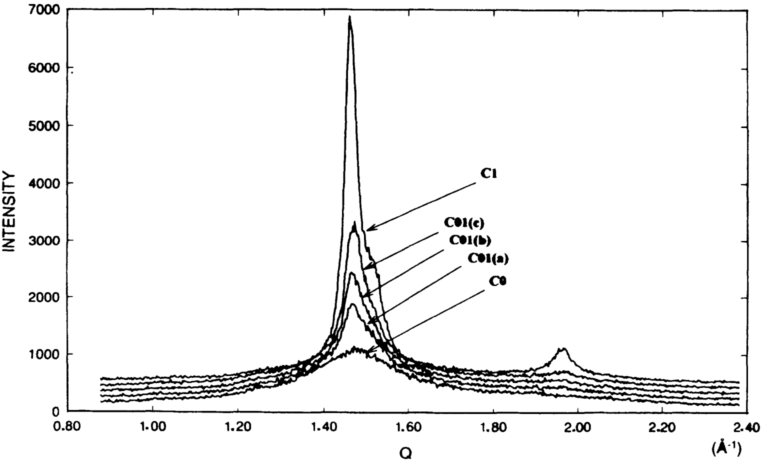

FIG. 2. The x-ray diffraction pattern for the $C0$ and $C1$ phases and at different stages of the transition from $C0$ to $C1$: [$C01$ (1), $C01$ (b), $C01$ (c)]; $Q = 4\pi \sin\Phi/\lambda$ and 2Φ is the diffraction angle.

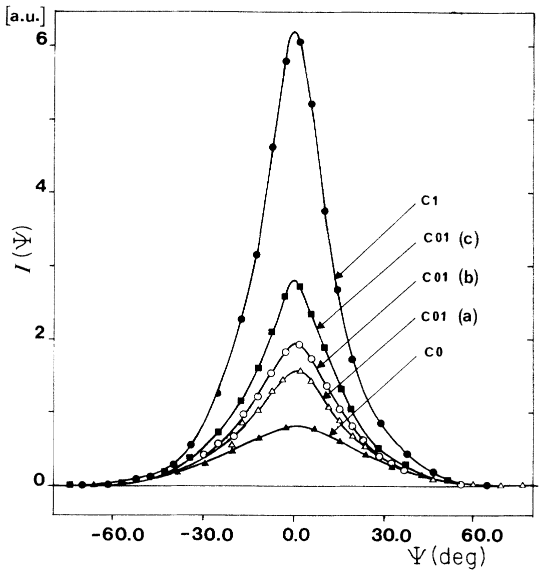

FIG. 3. The distribution of x-ray intensity of the maximum of the diffraction crescent as a function of the rotation angle Ψ of the director.

Å^{-1} in C0 and $\Delta Q = 0.043$ Å^{-1} in C1). The diffraction curves in the intermediate states [C01 (a), C01 (b), and C01 (c), Fig. 3], as well as in results obtained earlier [3], cannot be represented in the form of a linear superposition of the initial C0 and final C1 states. During the transition, there is a progressive evolution of $I(\Psi)$, which reflects the change of both translational (Fig. 2) and orientational (Fig. 3) molecular order.

According to the commonly accepted model for x-ray diffraction of nematic liquid crystals [13,14], the molecules can be assumed to form microdomains or clusters of quasiperfectly aligned molecules. The distribution function of domains may be approximated by the orientational distribution function (ODF) for a molecular singlet. The angular intensity distribution $I(\Psi)$ and the ODF are related by an integral equation [13,14]. The integral equation for any type of distribution function was solved by Deutsch [15,16]. From these results and considering that the measured intensity distribution reported here has a maximum at $\Psi = 0$, and a relatively small width thus satisfying the condition for the Maier-Saupe case [12], the intensity distribution can be assumed identical to the ODF [compare Figs. 2(a) and 2(b) in [16]]. Thus, in light of Deutsch's work, Vainshtein's model [17], which has been considered earlier as an empirical approximation, can be used to calculate $\langle P_2 \rangle$ for our measurements.

The domains of coherent scattering were estimated from a simple polydomain model. To describe the orientational order, it is assumed that each small monodomain contains a few ordered molecules (at least ten molecules [13]) and that neighboring domains scatter incoherently. The actual diffraction profile $I(Q)$ depends on the shape and size of the domains. The half-width at half maximum of the diffraction ring is always proportional to the inverse of the averaged monodomain size L^{-1}, which is estimated from the half-width ΔQ of diffraction curves using the relation $L = 5.6/\Delta Q$ Å [17]. Figure 4 shows the curves of the calculated order parameters $\langle P_2 \rangle$ for the C0 phase and $\langle P_2^d \rangle$ for the molecular clusters at different stages of the transformation C01 (a), C01 (b), C01 (c), C1 versus the correlation length $R = \frac{1}{2}L$ calculated using the data of Figs. 2 and 3. The increase of the domain sizes is coupled with a substantial increase in the orientational order. It should be emphasized that R characterizes a domain size and that the quantities $\langle P_2 \rangle$ and $\langle P_2^d \rangle$ are related to the degree of orientational order of the sample. If the number of domains of a given orientation was proportional to the number of molecules with that orientation, then the orientational distribution and $\langle P_2 \rangle$ (Fig. 4) would remain constant. A probable cause for the enhancement of $\langle P_2 \rangle$ is the existence of a short-range orientational order.

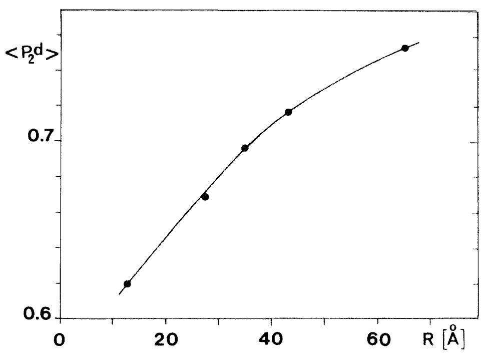

FIG. 4. Variation of the order parameter $\langle P_2^d \rangle$ with the correlation length R at various stages of the transformation between C0 and C1.

A more comprehensive approach is achieved when the short-range orientational order is taken into account. Figure 5 schematically shows the structure of a nematic liquid crystal. Angles Θ, Θ', and Θ'' are defined in Fig. 5. The orientational order of small regions of size L may be characterized by the local orientational order parameter $\langle P_2^l \rangle = \frac{1}{2}(3\langle \cos^2\Theta'' \rangle - 1)$ and the local director $\mathbf{n}^l$, where Θ'' is the angle between $\mathbf{n}^l$ and the long axis of each molecule, and by $\langle P_2^n \rangle = \frac{1}{2}(3\langle \cos^2\Theta' \rangle - 1)$ where

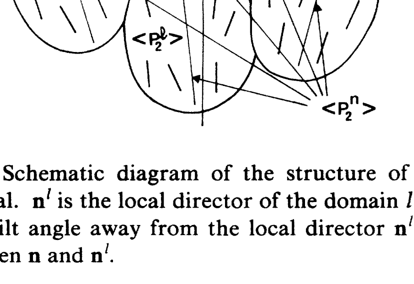

FIG. 5. Schematic diagram of the structure of a nematic liquid crystal. $\mathbf{n}^l$ is the local director of the domain l. Θ'' is the molecular tilt angle away from the local director $\mathbf{n}^l$. Θ' is the angle between $\mathbf{n}$ and $\mathbf{n}^l$.

$\cos\Theta' = (\mathbf{n}\cdot\mathbf{n}^l)$. The values of $\langle P_2^l \rangle$ and $\langle P_2^n \rangle$ depend on the size of the region in which the local orientational order parameter is determined. The short-range order leads to the facts that $\langle P_2^l \rangle$ is greater than $\langle P_2 \rangle$ and $\langle P_2^n \rangle$ is lower than 1. When L is increased to a macroscopic size, $\langle P_2^l \rangle$ tends to $\langle P_2 \rangle$ and n^l tends to the director of the liquid crystal. It is reasonable to suggest that during the transition, the direction of long molecular axes in a domain is determined by the local director in the corresponding region of GLC. In this case $\langle P_2^d \rangle$ characterizes the ordering of the local director $\mathbf{n}^l$ with respect to the director $\mathbf{n}$ of the liquid crystal ($\langle P_2^d \rangle = \langle P_2^n \rangle$). This provides an explanation for the increase of $\langle P_2^d \rangle$ when regions of coherent scattering and domain sizes are increasing.

A simple expression to estimate the value of the local orientational order $\langle P_2^l \rangle = \langle P_2 \rangle / \langle P_2^d \rangle$ can be obtained from the relations between $\cos^2\Theta$, $\cos^2\Theta'$, and $\cos^2\Theta''$. The values of $\langle P_2^l \rangle$, thus determined, are shown in Fig. 6 in terms of their dependence on R. With the assumptions made in the model used to describe the orientational order, $\langle P_2^l \rangle$ is nearly equal to 1 when R is equal to the size of the region of coherent scattering in the glassy state, roughly 13 Å. In fact, $\langle P_2^l \rangle$ should be somewhat less than 1; however, that does not lead to a qualitative change in the dependence of $\langle P_2 \rangle$ upon R.

It is commonly accepted at present that correlations between neighboring molecules exist in nematic and glassy states. Phenomenological models and computer-made structural calculations show these correlations [12,19]. The effects of short-range order have been observed experimentally in the isotropic liquid near the transition to a liquid crystal and the correlation lengths of orientational modes have been determined [12,19]. To date, x-ray diffraction and optical methods in the nematic state have only yielded results on the macroscopic orientational order parameter. Our data show that the local orientational order extends to a significant distance (about 60 Å) (cf. Fig. 4). This ordering must be taken into account in a microscopic model of disordered structures and, furthermore, many of the macroscopic properties can depend on the local correlations.

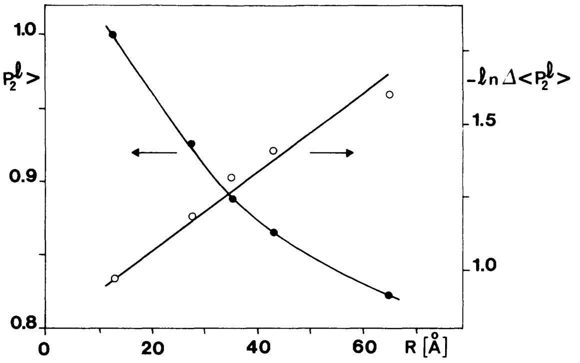

FIG. 6. The dependence of the local order parameter $\langle P_2^l \rangle$ on the correlation length R, $\Delta\langle P_2^l \rangle = \langle P_2^l \rangle - \langle P_2 \rangle$.

We have presented measurements at various stages of the evolution of the translational and orientational order during the transition from the glassy to the ordered $C1$ state. The change of $\langle P_2 \rangle$ at the transition can be explained by the existence of the short-range orientational order in the glassy state. We present results on the variation of the local order parameter with the correlation length [18].

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[1] G. Chistyakov and B. K. Vainshtein, Kristallografiya **8**, 570 (1963) [Sov. Phys. Crystallogr. **8**, 458 (1964)].

[2] V. K. Dolganov, Fiz. Tverd. Tela (Lengingrad) **21**, 2629 (1979) [Sov. Phys. Solid State **21**, 1513 (1979)].

[3] V. K. Dolganov, L. A. Novomlinski, and I. M. Shmyt'ko, Fiz. Tverd. Tela (Leningrad) **23**, 2427 (1981) [Sov. Phys. Solid State **23**, 1418 (1981)].

[4] V. K. Dolganov, N. Kroo, L. Rosta, E. F. Sheka, and J. Szabon, Mol. Cryst. Liq. Cryst. **127**, 187 (1987).

[5] A. V. Beluskin, V. K. Dolganov, I. Natkaniec, and V. G. Simkin, Mol. Cryst. Liq. Cryst. **150B**, 187 (1987).

[6] G. Pepy, R. Fouret, M. More, and L. Rosta, Liq. Cryst. **5**, 571 (1987).

[7] P. Derollez, M. Bee, C. Gors, R. Fouret, and A. J. Dianoux, J. Chim. Phys. **86**, 2001 (1989).

[8] R. Boese, M. Yu Antipin, M. Nussbaumer, and D. Blaser, Liq. Cryst. **12**, 431 (1992).

[9] C. Gors, T. Mansare, M. More, and G. Verven (unpublished).

[10] G. Odou and D. Naviez, Spectra 2000 **17**, 49 (1987).

[11] N. Kirov and M. Fontana, Mol. Cryst. Liq. Cryst. (Lett.) **56**, 195 (1980).

[12] P. G. De Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, (1974).

[13] A. J. Leadbetter and E. K. Norris, Mol. Phys. **38**, 669 (1979).

[14] A. J. Leadbetter, in *The Molecular Physics of Liquid Crystal*, edited by G. R. Luchurst and G. W. Gray (Academic, London, 1979).

[15] M. Deutsch, Phys. Rev. Lett. **64**, 697 (1990).

[16] M. Deutsch, Phys. Rev. A **44**, 8264 (1991).

[17] B. K. Vainshtein, *Diffraction of X-Rays by Chain Molecules* (AN SSSR, Moscow, 1963).

[18] V. A. Belyakov, E. I. Demikov, V. E. Dmitrienko, and V. K. Dolganov, Zh. Eksp. Teor. Fiz. **89**, 2035 (1985) [Sov. Phys. JETP **62**, 1173 (1985)].

[19] S. Chandrasekhar, *Liquid Crystals* (Cambridge University Press, Cambridge, England, 1975).