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Structural study of the liquid-crystal analog of the vortex liquid phase in type-II superconductors

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Abstract. – We propose a high-resolution X-ray study of the twisted liquid crystalline phase appearing between the Twist Grain Boundary smectic A phase (TGB$_A$) and the usual cholesteric liquid crystal N*. The structure of this new phase has been proposed as a liquid of screw dislocations in a smectic A matrix, analogous to the liquid of magnetic vortices found in type-II superconductors in between the ordered Abrikosov lattice and the normal conductor phase. Our data show that the smectic correlation length is consistent with the existence of dislocations, hence supporting the theory of Kamien and Lubensky.

Introduction. – An elegant analogy between superconductors (SC) and smectic liquid crystals (LC) was built up in 1972 when de Gennes [1] pointed out the formal similarity between the Landau-Ginzburg Hamiltonians describing the normal to superconductor transition (NC-SC) in a magnetic field on the one hand and the chiral nematic to smectic A phase transition (N*-SmA) on the other hand. In both cases, the broken symmetry is described by the onset of a two-dimensional XY order parameter. The equivalence of the two formalisms allowed to associate to each physical variable of the superconductor problem its exact counterpart in the liquid-crystal world. The nematic director field $\boldsymbol{n}$ for instance, describing the average direction of the long axis of rodlike molecules, is analogous to the magnetic vector potential $\boldsymbol{A}$, whereas chirality plays the role of an external magnetic field.

Two differences were noticed though: i) Interestingly, the Ginzburg criterion predicted that the effect of fluctuations should be different. The critical domain was expected to be broad for the non-chiral N-SmA transition whereas the NC-SC transition was essentially mean field. Indeed, experiments confirmed that non-trivial critical exponents were measured at the N-SmA transition [2]. ii) Unlike its SC homolog, the N-SmA Landau-Ginzburg Hamiltonian contains a non–gauge-invariant term $1/2\ K_1(\mathrm{div}\,\boldsymbol{n})^2$, corresponding to the elastic energy of a splay deformation of the director field. Consequently, the behaviour of some physical observables such as the correlation lengths cannot be simply extrapolated from the SC model but can be calculated from gauge transformation theories [3].

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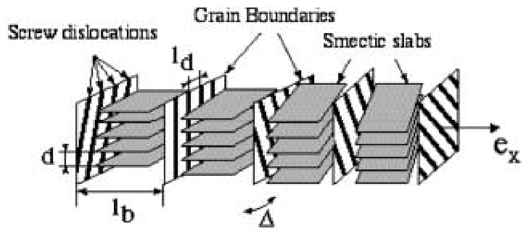

Fig. 1 – Sketch of the helical structure of the TGB_A phase. Slabs of SmA material of thickness l_b are regularly stacked in a helical fashion along an axis $\boldsymbol{e}_x$ parallel to the smectic layers. Adjacent slabs are connected by a twist grain boundary made of parallel screw dislocation of average separation l_d.

In the early days, all experimental observations on liquid crystals were consistent with the so-called type-I behaviour of superconductors. In particular, the LC counterpart of the well-known Meissner effect was the expulsion of twist at the first-order N^*-SmA transition and no intermediate phase was observed. A more spectacular illustration of the analogy was proposed in 1988 when Renn and Lubensky [4] worked out the theoretical structure of an intermediate phase that should show up in the type-II limit. This new phase, analogous to the flux phase of SC, was called twist grain boundary (TGB) phase. A twisted lattice of screw dislocations was proposed as the counterpart of the Abrikosov lattice of magnetic vortices. Amazingly, the complex structure of the TGB phase, shown in fig. 1, was experimentally discovered shortly afterwards [5] and carefully characterised subsequently [6–8]. For the first time, the analogy had shown a strong predictive power. In the meantime, high-T_c superconductors had been discovered and extensively studied [9]. High-T_c superconductors are essentially type II, and unlike low-T_c superconductors, their critical domain is broad and the effects of fluctuations are important. In this respect, TGB phases are more closely related to high-T_c superconductors through the analogy. Thermal fluctuations can cause the regular Abrikosov vortex lattice to melt, hence producing an entangled flux liquid in which the flux lines are on average parallel to a common direction [10]. Dissipation occurs when an applied electric field produces flux flow, unless vortex pinning generates a disordered but static vortex-glass phase [11]. The observation of the LC analog of the disordered vortex states (liquid or glass) would of course constitute another strong evidence of the importance of the analogy. Kamien and Lubensky [12] have proposed a structure for the LC vortex-liquid phase in which the screw dislocations exhibit no long-range positional order, but are arranged in a helical fashion to form a cholesteric LC. We use the subscript L to denote this new twisted phase N^*_L. As in the SC case, it is important to notice that the N^*_L phase has locally the order parameter of the low-temperature phase but the macroscopic symmetry of the high-temperature phase. It differs from the usual cholesteric phase by the existence of a strong local smectic A order.

High-resolution calorimetric studies have been used to investigate the phase diagram of several LC series with a SmA-TGB_A-cholesteric sequence [13, 14]. The calorimetric data are consistent with the existence of the N^*_L phase in an intermediate region between the TGB_A and cholesteric phases (*i.e.*, supercritical behaviour of the N^*_L-cholesteric transition) but give no information about the structure. Navailles *et al.* [6] have revisited this phase sequence with a synchrotron study in oriented samples and found that the organisation of the TGB_A phase as a regular stack of well-defined smectic A slabs was lost in the intermediate region, although the local smectic A order was still strong. This was consistent with the disordered state of the Kamien-Lubensky KL model for the N^*_L phase, but also with a simple TGB_A-cholesteric transition as described in [4].

The present work is focused on the validity of screw dislocations model. Indeed, in a conventional cholesteric phase, the space distribution of the molecules is liquid-like and the notion of screw dislocations is meaningless. In a nematic or cholesteric with short-range smectic A order, the correlation lengths of the smectic order parameter $\xi_{\mathrm{Sm}_\parallel} = \xi_{\mathrm{Sm}}$ and $\xi_{\mathrm{Sm}_\perp} = b\xi_{\mathrm{Sm}}$ are finite (the subscripts $\parallel$ and $\perp$ denote, respectively, directions parallel and perpendicular to the layer normal, and the anisotropy factor b is of order few units [15]). The maximum length of any object that has the local topology of a dislocation cannot exceed ξ_{Sm}. In the KL model for the N^*_L phase, the cholesteric twist is produced as in the ordered TGB_A phase by a finite density of screw dislocations. The average distance l between these dislocations can be simply estimated from the TGB_A model [4]: $l \approx l_d \approx l_b \approx \sqrt{dP/2\pi}$, in which d is the smectic layer thickness, P is the helical pitch, and l_d, l_b are defined in fig. 1. The KL model of a cholesteric twist produced by a set of screw dislocations hence requires that ξ_{Sm} should be significantly longer than l. We present in this paper an experimental determination of the correlation length $\xi_{\mathrm{Sm}_\parallel}$ by high-resolution X-ray diffraction.

Experimental setup. – X-ray scattering experiments were performed on the BM32 beam line at the European Synchrotron Radiation Facility (ESRF). With the selected energy of 18 keV, corresponding to a wavelength of 0.69 Å, the incident beam intensity was around 10^9 photons/second. The final beam size was $50 \times 300\,\mu\mathrm{m}^2$ (V × H) at sample position hence fixing the resolution in reciprocal space to $7.9 \cdot 10^{-4}\,\text{Å}^{-1}$ (two-theta axis angular width set to 0.005 deg). In order to improve the resolution to $3 \cdot 10^{-4}\,\text{Å}^{-1}$ (0.002 deg), the front and back slits were closed in a second step. The scattered X-rays were recorded on a low background scintillation detector located at about 700 mm from the sample. The two-stage oven was mounted on the three-circle goniometer and the temperature of the sample was controlled to a precision of ± 10 mK. No evidence of any phase coexistence was found at the SmC^*-TGB_A transition (two Bragg peaks of different wave vectors would be clearly visible here) upon heating by 0.1 °C steps. This rules out temperature gradients larger than 0.1 °C across the irradiated area. The sample cell was mounted vertically (*i.e.*, perpendicular to the beam) with the average helical axis of the TGB phase parallel to the X-ray beam. Diffraction along the smectic layer normal was then probed via theta–two-theta scans.

The liquid-crystal compound was the (S) enantiomer of the $n = 10$ homolog of the series of 3-fluoro-4[(S)-1-methylheptyloxy]-4(4-alkoxy-23-difluorobenzoyloxy) tolane ($10\mathrm{F}_2\mathrm{BTF}_2\mathrm{O}_1\mathrm{M}_7$ for short). The transition temperatures have previously been studied by high-resolution calorimetry [13] and the phase sequence (from smectic to isotropic (I)) appears to be

$$\mathrm{Sm}C^*(99.7\,^\circ\mathrm{C})\mathrm{TGB}_A(102.85\,^\circ\mathrm{C})\mathrm{N}^*_L(106.71\,^\circ\mathrm{C})\mathrm{N}^*(115.7\,^\circ\mathrm{C})\mathrm{I}.$$

Well-aligned liquid-crystal cells were prepared from two glass plates. Planar boundary conditions were obtained by spin-coating the inner surface of the glass plates with a polymer solution (polyvinyl alcohol in water) which was then unidirectional buffed with an appropriate velvet cloth. Absorption of X-rays by glass was reduced by etching the outer surface of the glass plates with hydrofluoric acid to a thickness of about 50 μm. Parallel cells were assembled with calibrated spacers (two 20 μm parallel gold wires 3 mm apart). All cells were filled by capillarity in the isotropic phase and the quality of the alignment was checked before the X-ray run by optical observation using a polarising microscope. For all 4 sample cells studied, the alignment procedure was the following: the temperature was set to $T = 120\,^\circ\mathrm{C}$ in the isotropic phase during 3 min, then the sample was cooled down slowly (1 °C/min) to $T = 102\,^\circ\mathrm{C}$ in the TGB_A phase. In order to stabilise the system, the sample was left in the TGB_A phase for several minutes. In order to compare our measured temperatures with the temperature sequence taken from the high-resolution calorimetry [13], the SmC^* to TGB_A phase transition was located in X-ray measurements and used as a reference temperature. The recorded temperature always fell within a few tenth of degree from the high-resolution calorimetry reference.

Results and discussion. – The experimental procedure consisted in studying the lineshape of the smectic Bragg peak as a function of temperature: a sharp smectic reflexion and a broad Lorentzian shape are expected, respectively, in TGB_A and N^* phases. It is our assumption that in the intermediate range of temperatures, the transition from TGB_A to N_L^* phase should appear as a weak broadening of the smectic reflexion associated to the reduction in the underlying smectic correlation length. The continuous evolution from N_L^* to N^* should be accompanied by a further increase of this width eventually leading to a complete loss of smectic order.

Figure 2 presents X-ray data recorded for the direct beam (instrumental resolution) and for three different temperatures corresponding to the expected location of the TGB_A, N_L^*, and N^* phases. Those data are presented together with fitted curves obtained using Levenberg-Marquardt algorithm: the direct beam is adjusted assuming a Gaussian shape plus constant background while other data are fitted with a background and the convolution product between the experimental resolution function, whose parameters are fixed by the direct beam analysis, and a Lorentzian. A Lorentzian shape is indeed expected in the N^* phase and, from the analogy with superconductors, such a shape is also expected in the N_L^* region where the correlation function of the order parameter should decay exponentially [16]. On the other hand, in the TGB_A phase [4], the observed Bragg peak is broader than the instrumental resolution. The fact that it is not resolution limited originates from both the finite size of single-crystal domains (polycrystallinity) and the Landau-Peierls instability and a refined shape analysis, as was done for smectics in [17], should be performed. Unfortunately, data accuracy does not allow, here, to discriminate between this refined analysis and a Lorentzian shape. We therefore opted for a single-analysis method (Lorentzian shape) throughout the different phases. This ensures that a change of the measured linewidth (if any) at the TGB_A-N_L^* transition corresponds to a real change, *i.e.* is not generated by a change of the fitting function.

Figure 3 plots the full width at half-maximum (FWHM) of the Lorentzian peak as a function of temperature, as deduced from data and fitting procedure presented in fig. 2, and assuming for error estimation a standard deviation on scattered intensity as the square root of the intensity. It must be noted that plotted data correspond to different liquid-crystal cells together with heating and cooling temperature scans. An excellent reproducibility can be

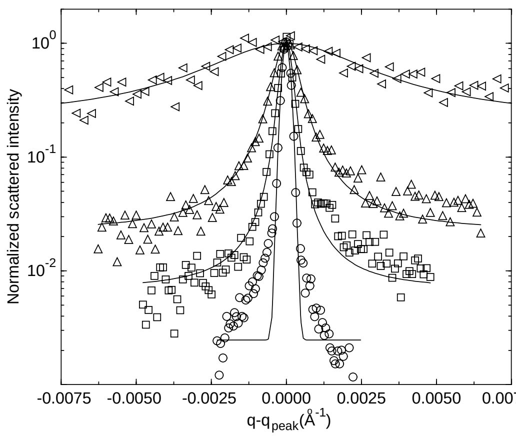

Fig. 2 – Normalised scattered intensity *vs.* wave vector in the different phase regions of $10F_2BTF_2O_1M_7$. $\circ$ direct beam (instrumental resolution), $\square$ TGB_A, $\triangle$ N_L^*, $\triangleleft$ N^*. Solid lines correspond to fitted functions as described in the text.

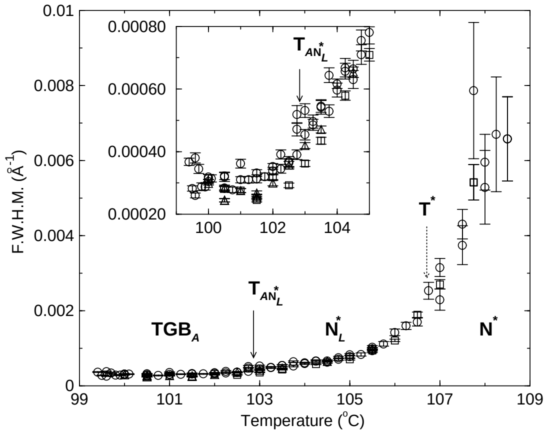

Fig. 3 – Lorentzian peak full width at half-maximum *vs.* temperature for $10F_2BTF_2O_1M_7$. Inset: close-up on the TGB$_A$-N$_L^*$ transition region. Arrows correspond to peak locations in high-resolution calorimetry [13]. Different symbols refer to different samples.

observed that rules out, for instance, any problem of radiation damage on our samples.

The width of the peak is observed to increase continuously with temperature, slowly, first, and then much more rapidly with FWHM becoming very large when the N* region is reached. However a close-up on the first, almost flat, portion of the data plot shows very clearly that this increase in FWHM, denoting a weakening in the smectic order, only starts above 102 °C. This temperature corresponds i) to the very sharp peak observed at $T_{\mathrm{AN}_L^*} = 102.85\,°\mathrm{C}$ in high-resolution calorimetry experiments [13] revealing the existence of a weakly first-order phase transition that melts the TGB$_A$ lattice and ii) to the smearing-out of the Bragg ring reported in ref. [6] revealing the loss of regular helical arrangement of the smectic A slabs. Although the peak is not resolution limited below 102 °C, as explained earlier, no broadening at all is observed until this temperature is reached. Above 102.85 °C, the increasing broadening results from the decrease of the smectic correlation length that we expect in the N$_L^*$ phase. We believe that the experimental results reported in refs. [6, 13] and in the present work now constitute a consistent set of data that strongly support the existence of a liquid crystal analog to the liquid vortex phase in superconductors.

N$_L^*$ and N* share the same symmetry and therefore should really be considered as a single phase. High-resolution calorimetry measurements [13] show nevertheless a broad and rounded heat capacity peak separating these two regions. This peak is presumably associated with the change in the short-range order with N$_L^*$ keeping a strong local smectic order while this latter is eventually lost in the N* region. Qualitatively, such a change can be expected to occur when the very notion of screw dislocation and, hence, of a twist produced by a finite density of screw dislocations, is becoming meaningless. This occurs when the correlation length ξ_{Sm} of the underlying smectic order is becoming shorter than the mean distance l between dislocations. This distance l can be evaluated in N$_L^*$ using a TGB-like description. In the TGB structure, the layer normal rotates by a finite angle Δ across a grain boundary (see fig. 1). This angle is related to the thickness l_b of the smectic slabs and to the distance l_d between screw dislocations in a grain boundary through: $d/2l_d = \sin(\Delta/2)$ and $l_b/P = \Delta/2\pi$. Taking $l = l_b \approx l_d$ as expected from theoretical prediction [4] and experimental measurements [6], taking the helical pitch P from optical determinations [18] and the smectic period d from diffraction measurements [19], one ends with $l \approx 200$ Å in the N$_L^*$ to N* region. Our criteria on the validity domain of a screw dislocations liquid-phase description leads now to FWHM $= 2/\xi_{\mathrm{Sm}} \approx 2/l$ and therefore FWHM $\approx 0.01\,\text{Å}^{-1}$. In fig. 3, it can be inferred that such a width occurs around 108-109 °C. This is in reasonable agreement with the position of the heat capacity peak ($T^* =$ 106.71 °C), considering in addition that this peak extends over several degrees in temperature.

Conclusion. – In this paper, we have presented high-resolution X-ray scattering data providing structural information on the twisted liquid-crystalline phase N_L^* that corresponds, in the superconductor analogy, to the liquid of magnetic vortices. The measured evolution of the smectic correlation length ξ_{Sm} with temperature shows a change in behaviour around 102 °C in agreement with the location of the transition temperature, from TGB_A to N_L^*, as deduced from calorimetry experiments [13]. Moreover, we have shown that our data on $\xi_{\mathrm{Sm}}(T)$ are consistent with the liquid of screw dislocations description in the N_L^* temperature region. Beyond the elegance of the analogy, evidenced here, between liquid crystals and superconductors, it must be noted that liquid crystals provide a direct mean to measure the correlation function of the order parameter: a possibility that we hope will trigger new interactions with the superconductor community.

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