Periodic In-Layer Director Modulations Responsible for the Stripe Texture Formation in Chiral Smectic-*C* Phase

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Periodic modulations of the director inside the smectic layer were identified as being responsible for a stripe texture formation in free suspended films of the chiral smectic-*C* phase with the helix along the smectic layer normal, spontaneously unwound. Monotonous increase of the stripe periodicity with the increasing film thickness agrees with a theoretical model. A 2D modulated pattern observed in thick films was found to be related to the molecular chirality.

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The reduced symmetry of the tilted chiral smectic phase allows the appearance of the spontaneous twist of the c vector along the smectic layer normal, a bend of the c vector (splay of an electric spontaneous polarization) in the smectic layer, and a twist of the smectic layers [1]. The c vector is defined by the projection of the molecular director onto the smectic layer plane. Small space modulations of director and layer deformations are described by linear gradient terms [1]

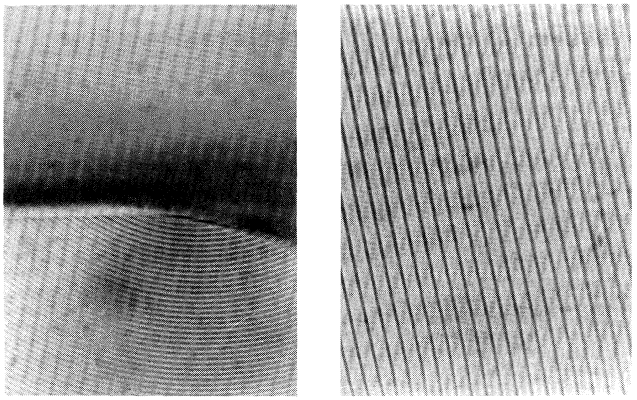
$$D_1\,\partial\Omega_z/\partial x + D_2\,\partial\Omega_x/\partial x + D_3\,\partial\Omega_z/\partial z\,, \qquad (1)$$

where Ω_z (so called azimuthal angle) denotes rotation of the c vector around the z axis parallel to the layer normal and Ω_x is the rotation of the layer normal. The chiral elastic constants are denoted as D_i, for racemate $D_i = 0$ $(i = 1,2,3)$. Usually only the last term leads to an observable effect to the well-known helioelectric structure of the smectic-C^* (Sm-C^*) phase. The second term, which is important when screw dislocation walls are present in the sample [1], can be recognized as being connected with the formation of the twist grain boundary phase (TGB) [2]. The detailed analysis of the first term [3,4] shows that it governs the in-plane director modulations leading, for the strong chirality limit, to the structure with the disclination lines or walls at which the azimuthal angle Ω_z changes discontinuously. The experimental evidences for periodic in-plane modulations driven by the term $D_1\,\partial\Omega_z/\partial x$ are scarce. The only documented cases are appearances of the "converging" schlieren texture in the droplets of Sm-I phase [3] and the dim stripe texture in thin films of the Sm-C^* phase [5]. Both textures do not show the predicted periodic system of defects, and thus are significantly different from that reported in this Letter.

We believe that in strongly chiral materials, under special circumstances, if the part of the free energy related to the helioelectric structure was significantly diminished, the in-plane regularly modulated phase with the net of defects can emerge. The conditions of strong chirality but suppressed formation of the helix, hereafter called z helix, seem to be conflicting. However, the substances exhibiting spontaneous helix twist inversion [6] and relatively high spontaneous polarization P_s, which reflects their strong chirality, are the best candidates for intended studies. With these materials one can ensure the existence of a temperature interval at which the director modulation along the layer normal has long periodicity compared to the sample thickness. In the regime of suppressed z helix, the in-plane modulation can still remain strong since the molecular interactions, which are responsible for the in-layer and interlayer director modulations, can be generally very different.

For our studies we choose compounds of two homologous series of the lactic acid derivatives, denoted as H $m/10$ and Cl $m/5$ where m is the number of carbons in the alkoxy chain attached to the chiral center. They exhibit the broad temperature range Sm-C^* phase and the strong chirality, as evidenced by their high value of P_s. In planar samples $\sim$25 μm thick the helix twist becomes unwound in a region about 10 K around a temperature T_i defined as the region center, the helix handedness being opposite on both sides of this temperature region [7]. For comparison, we have also studied the MHPOBC compound, in which the helix twist inversion occurs in the antiferroelectric Sm-C_A^* phase [8].

In experiments, free suspended films, drawn across a hole a few millimeters in diameter, were used. In this geometry almost ideal sample alignment with the smectic layers parallel to the film surface can be obtained. The textures were observed using the polarizing microscope equipped with a hot stage. The sample thickness was estimated as a distance at focusing the upper and lower film surfaces. Above the helix twist inversion temperature T_i (between 80 and 120 °C for all studied compounds [7]) a smooth homeotropic texture, typical for the Sm-C^* phase, was observed. When the temperature T_i was approached, a stripe texture abruptly appeared [see Fig. 1(a)]. On further cooling, in compounds of both homologues series, Cl $m/5$ and H $m/10$, the stripe texture persisted until recrystallization that usually occurred around 40 °C. The frequently observed schlierenlike stripe pattern and the lack of optical activity suggest that the z helix was not



(a) (b)

FIG. 1. (a) The texture at the transition between the homeotropic and stripe phase in Cl 8/5 at 82 °C, the stripe periodicity $d = 1.3$ μm; (b) the stripe texture in MHPOBC at 80 °C, $d = 2.5$ μm. The lower and upper lines mutually shifted by $d/2$ are visible in a different contrast.

restored. The stripe periodicity was determined from the diffraction of the laser light (630 nm) on the stripe pattern.

A similar result, i.e., the abrupt appearance of the stripe texture around the T_i temperature, was obtained also in the antiferroelectric Sm-C_A^* phase of MHPOBC [see Fig. 1(b)]. In this material the stripe texture exists from ~85 to 75 °C. The homeotropic texture and the significant optical activity above and below this range evidenced the existence of the z helix.

The stripes are also visible with nonpolarized light, confirming that they are formed by arrays of defects. Careful microscopic studies show that there are two systems of stripes existing near the upper and lower surfaces of the film, which are mutually shifted by half of the stripe distance [see Fig. 1(b)].

The stripe periodicity d is controlled mainly by two factors, by the chirality of the system and the sample thickness. The first factor can be related to the value of P_s [9], and its influence can be studied by choosing substances differing in P_s. For the same film thickness of 10 μm the stripe periodicity $d \sim 1-1.5$ μm was found with compounds of the Cl $m/5$ homologue series, for which $P_s \sim 200-300$ nC/cm^2 in the studied temperature interval [7], $d \sim 3$ μm with H $m/10$ compounds, for which $P_s \sim 100-200$ nC/cm^2 [7], and $d \sim 2.5$ μm with MHPOBC, where $P_s \sim 80-100$ nC/cm^2 between 60 and 80 °C [10].

In all studied compounds the stripe period increases as the film thickness increases (see Fig. 2). The stripes do not appear in films thinner than ~5 μm, i.e., containing less than ~1500 smectic layers. On the other hand, the striped pattern observed in Ref. [5], which shows continuous director rotation without any defects, appears in samples from several hundred down to ~60 layers thick. The nonzero optical rotation in the ~5 μm thick samples observed when the system departs from the inversion temperature suggests that the z-helical structure

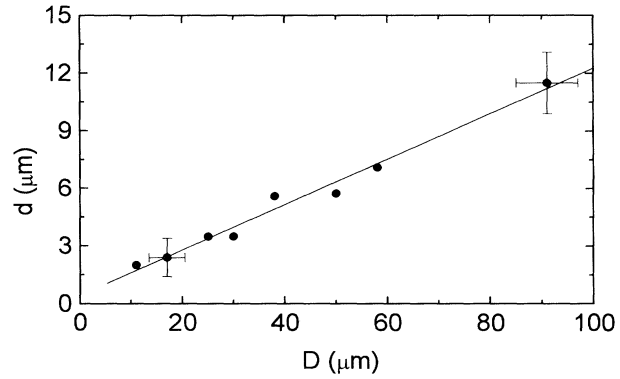


FIG. 2. Thickness dependence of the stripe periodicity d in Cl 8/5 doped with 10% of a nonchiral Sm-C. The nonchiral dopand was used to increase d for easier microscopic measurements. The line is the fit to the theoretical solution $d(D)$.

is at least partially restored. In thin samples strong light scattering due to rapid fluctuations in the director field was usually detected around the T_i temperature. Moreover, in compounds of Cl $m/5$ homologue series the stripe periodicity wave vector q was found to increase critically with increasing temperature (see Fig. 3), suggesting a weakly first order transition between the phases with the order parameter modulation propagating along the layer normal and perpendicular to the layer normal. On the contrary, in MHPOBC the q wave vector is almost insensitive to the temperature changes (see inset in Fig. 3).

The chiral part of the elastic energy related to the in-plane c-vector modulations in the ferroelectric Sm-C^* phase can be described [1,3,4] by the Landau expression $g \sim D_1 \mathrm{rot}(\vec{c})_z$. Introducing fixed coordinates x and y and the vector $c = [c_0 \cos \Omega_z(x), c_0 \sin \Omega_z(x)]$, which is uniform in y but modulated in x, the free energy density

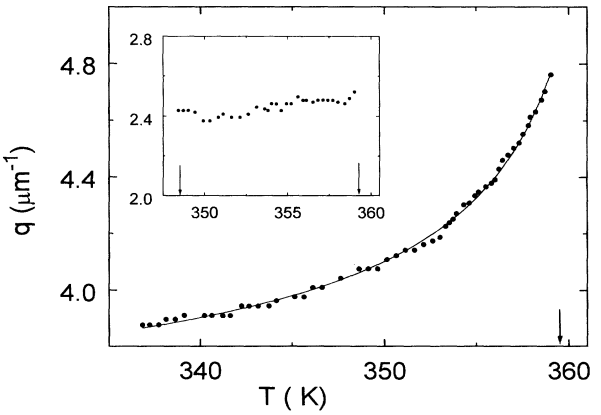


FIG. 3. Temperature dependence of the stripe periodicity wave vector q in Cl 8/5 measured in ~10 μm thick film. The line is a power law fit with the critical exponent 0.5. In the inset the temperature dependence of q in MHPOBC is shown. The arrows indicate transition temperatures between the stripe and homeotropic textures.

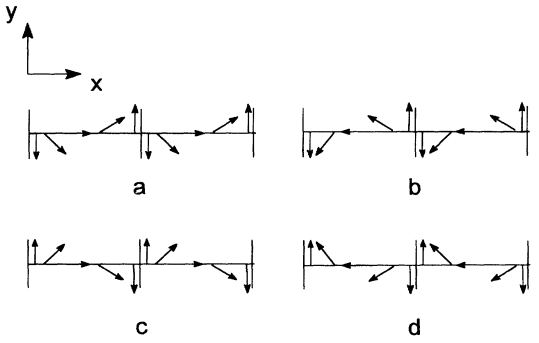


FIG. 4. Possible surface domains for the opposite chiralities. (a),(b) For $D_1 > 0$ and (c),(d) for $D_1 < 0$.

g is reduced to

$$g \sim -D_1 \cos\Omega_z \, \partial\Omega_z/\partial x \,. \tag{2}$$

The chiral term (2) significantly lowers the elastic free energy of the system when the azimuthal angle Ω_z changes by an angle smaller than π along the x axis and then jumps on the defect, which has to be formed. For $D_1 > 0$, two kinds of domains, symmetrical under π rotation around the z axis, minimize the free energy (2); those are domains where $d\Omega_z/dx > 0$, $-\pi/2 < \Omega_z < \pi/2$ or $d\Omega_z/dx < 0$, $\pi/2 < \Omega_z < 3\pi/2$. For the opposite chirality, $D_1 < 0$, the domains where $-\pi/2 < \Omega_z < \pi/2$, $d\Omega_z/dx < 0$, or $\pi/2 < \Omega_z < 3\pi/2$, $d\Omega_z/dx > 0$ are possible (see Fig. 4). Domains formed for the opposite chirality can be converted into each other by mirror reflection through the plane normal to the smectic layer.

A model for 3D molecular order in the in-layer modulated phase had to assume the observed shifted positions of defects at the opposite film surfaces [see Fig. 1(b)]. Thus the model described in Refs. [3,4] with walls propagating through the whole sample thickness has to be modified. A possible director field in the free suspended film of the Sm-C^* phase is presented in Fig. 5. It supposes a c-vector structure with in-plane modulated surface layers. The c vector in domains near the upper and lower film surfaces rotates in opposite directions, which is, as explained in Fig. 4, permitted for the same sense of chirality. The modulated surface domains are separated by π walls terminated by π disclinations at a distance h from the surface. The domains at the opposite surfaces have to be connected by a director twist along the layer normal (z axis) over a distance $D - 2h$, where D is the total film thickness. The π disclinations near both surfaces have the same sign, which is responsible for the mutually shifted positions of defects near the upper and lower surfaces. In the case of disclinations with opposite sign, the π walls could be simply connected and the structure of Langer and Sethna was obtained [3].

The director field structure shown in Fig. 5 is rather complicated, and in this contribution it will be approximated by a simplified model. The regular in-plane rotation by $\Delta\Omega_z$ between the walls can be

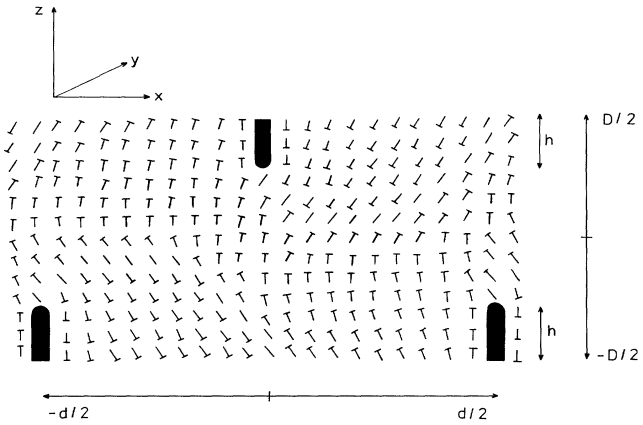


FIG. 5. The director modulation in the free suspended film of the thickness D in ferroelectric Sm-C phase. The in-plane modulation between the walls of height h has periodicity d. The director azimuthal angle Ω_z varies continuously by π between the walls and jumps by π at the walls. The surfaces are connected by the director twist along the smectic layer normal.

expressed as $\varphi_+(x) = \Delta\Omega_z(x/d - 1/2)$ in the interval $x \in (0_+, d/2)$, $\varphi_+(x) = \Delta\Omega_z(x/d + 1/2)$ for $x \in (-d/2, 0_-)$, and $\varphi_-(x) = \Delta\Omega_z(1 - x/d)$ for $x \in (-d/2, d/2)$, φ_+ and φ_- corresponding to the upper and lower surfaces, respectively. The twist in the sample bulk, i.e., for $z \in (-D/2 + h, D/2 - h)$, is $\psi(x,z) = [\varphi_+(x) - \varphi_-(x)]z/(D - 2h)$. The free energy density f can be written as a sum of terms related to the in-plane director modulation and the director twist along the layer normal [1]:

$$f = \tfrac{1}{2}B_1(\partial\Omega_z/\partial x)^2 + \tfrac{1}{2}B_3(\partial\Omega_z/\partial z)^2 - D_1 \cos\Omega_z(\partial\Omega_z/\partial x) \,. \tag{3}$$

The total energy W (per unit length in the y direction) is the integral of f over the sample thickness D and sample dimension L in the x direction. Then $W = LD\overline{w}$ with $\overline{w} = (\int_0^D dz \int_{-d/2}^{d/2} f \, dx + 2h\gamma)/dD$. The energy $2h\gamma$ of two walls of the height h situated at the period d (γ is the wall self-energy per unit surface) is included in W. Then

$$(D/B_1)\overline{w} = \pi^2(D + 4h)/6d^2 + 13\pi^2\beta^2/24(D - 2h) - 4q_x h/d \,, \tag{4}$$

where $\beta^2 = B_3/B_1$, $q_x = D_1'/B_1$, and assuming $\Delta\Omega_z = \pi$. The parameter D_1' is defined as $D_1' = D_1 - \gamma/2$.

The gain of energy with respect to the homogeneous state is possible if $\overline{w} < 0$. The last relation can be fulfilled only when $D_1' > 0$, similarly as in Ref. [3]. The equilibrium condition $(D/B_1)\partial\overline{w}/\partial d = 0$ gives the linear dependence $d = \pi^2(D + 4h)/12q_x h$, which can be fitted, with the use of the relation $\overline{w} < 0$, to the experimentally found film thickness dependence of the stripe periodicity $d(D)$ shown in Fig. 2. The condition $\overline{w} = 0$ gives a critical film thickness D_c, below which the stripe texture does not appear. For the fit we have used the experimental value of $D_c \sim 5$ μm. The fitting

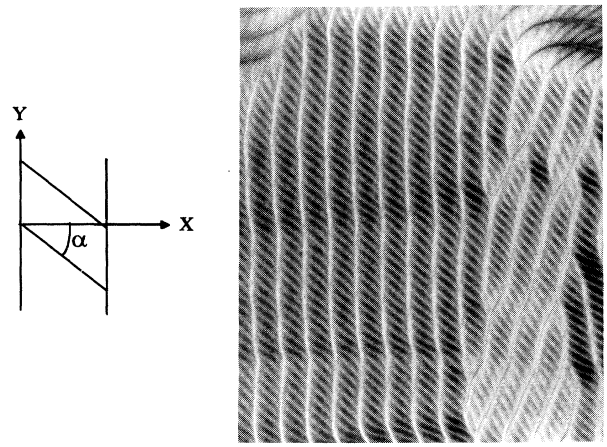


FIG. 6. The secondary domains formed in thick film of R-enantiomer. The sign of the inclination angle α between the primary and secondary stripes is determined by the molecular chirality (see the text).

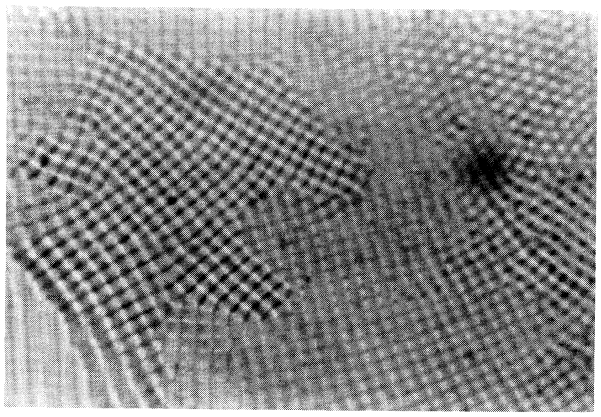


FIG. 7. The 2D patterns observed in the temperature gradient. The consecutive hexagonal→square→stripe texture transitions are observed under the temperature decrease.

parameters are $\beta \sim 2.8$, $B_1/D_1' \sim 0.13$ μm, and $h \sim 0.9$ μm, which yields $D_1'/B_3 \sim 0.95$ μm^{-1}. Near the helix inversion temperature the helicoidal pitch $p_z = 2\pi/q_z$ is greater than the sample thickness D, i.e., $p_z \geq D$. Then for $D > D_c$ (except for $D \approx D_c$) it is $D_1'/B_3 > 2\pi/D > q_z$ and thus $D_1 > B_3 q_z = D_3$. The relation $D_1 > D_3$ is in accordance with the fact that the stripe domains emerge close to the helix inversion temperature where the elastic constant D_3 driving the z-helix formation sufficiently decreases with respect to D_1 responsible for in-plane modulation.

It should be noted, however, that the present model of director structure is very simplified. In more elaborate models properties of π disclinations terminating the π walls and the π walls themselves should also be taken into account.

In thick samples more complex textures other than a 1D array of defects were also observed. In samples thicker than ~20 μm, the second generation of fine stripes with smaller periodicity was observed (see Fig. 6). The orientation of these additional stripes is tilted with respect to the primary ones by the angle α, which is approximately 40° in MHPOBC and 50° in Cl 8/5. The angle α does not change significantly with the temperature. The sets of the secondary stripes focused at upper and lower surfaces are mutually perpendicular, which corresponds to their equal orientations under the film reversion. At each of the interfaces only one kind of inclined secondary domains, with angle α positive or negative is observed, depending on the molecular chirality. As a result, the texture lacks the inversion symmetry. As we observe the 2D pattern at the upper surface of the film, for S-enantiomers the domains with $\alpha > 0$ appear. For the R-enantiomer the opposite domain with $\alpha < 0$ appears. In addition to the pattern without inversion symmetry, a hexagonal lattice of defects similar to the structure proposed in Ref. [4], or a square pattern were observed (see Fig. 7).

In conclusion, we reported the first nonambiguous evidence for the existence of the ferroelectric and antiferroelectric Sm-C^* phase with an in-plane modulated order parameter. The phase is formed in free suspended films of materials in which the helix along the smectic layer normal is spontaneously unwound. The presence of the walls, in our model located near the film surfaces, agrees with theoretical predictions [3,4]. Some of the 2D texture patterns are related to the molecular chirality.

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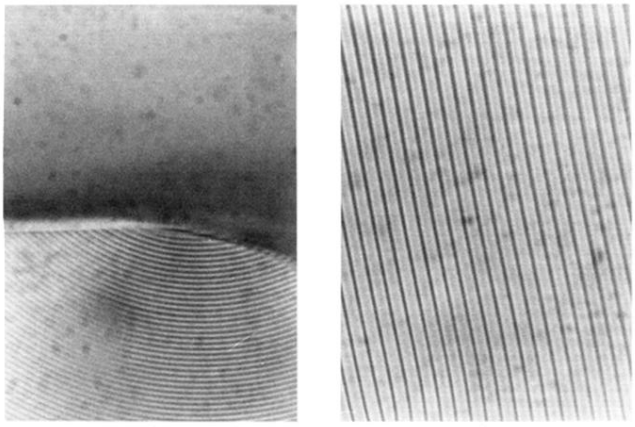
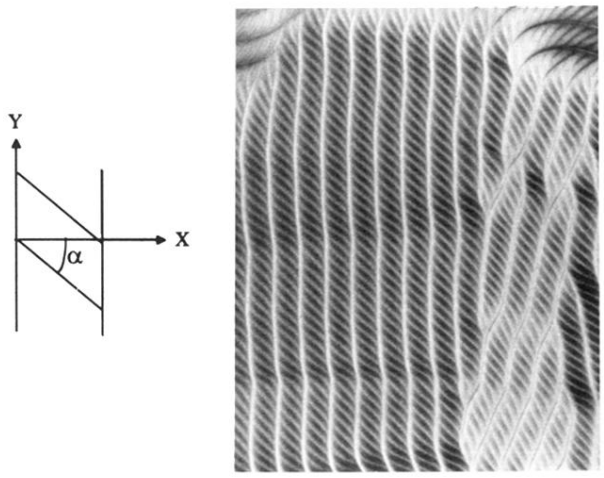
[1] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon Press, Oxford, 1993).
[2] S. R. Renn and T. C. Lubensky, Phys. Rev. A **38**, 2132 (1988).
[3] S. A. Langer and J. P. Sethna, Phys. Rev. A **34**, 5035 (1986).
[4] G. A. Hinshaw and R. G. Petschek, Phys. Rev. A **39**, 5914 (1989); G. A. Hinshaw, R. Petschek, and R. A. Pelcovits, Phys. Rev. Lett. **60**, 1864 (1988).
[5] E. Demikhov, Europhys. Lett. **25**, 259 (1994).
[6] J. W. Goodby, P. Styring, A. J. Slaney, J. D. Vuijk, J. S. Patel, C. Loubser, and P. L. Wessels, Ferroelectrics **147**, 291 (1993).
[7] M. Kašpar, E. Gorecka, H. Sverenyák, V. Hamplová, M. Glogarová, and S. A. Pakhomov, Liq. Cryst. (to be published).
[8] A. D. L. Chandani, E. Gorecka, Y. Ouchi, H. Takezoe, and A. Fukuda, Jpn. J. Appl. Phys. **28**, L1265 (1989).
[9] J. W. Goodby, J. Mater. Chem. **1**, 307 (1991).
[10] M. Glogarová, H. Sverenyák, A. Fukuda, and H. Takezoe, Liq. Cryst. **14**, 463 (1993).



(a) (b)

FIG. 1. (a) The texture at the transition between the homeotropic and stripe phase in Cl 8/5 at 82 °C, the stripe periodicity $d = 1.3\ \mu$m; (b) the stripe texture in MHPOBC at 80 °C, $d = 2.5\ \mu$m. The lower and upper lines mutually shifted by $d/2$ are visible in a different contrast.



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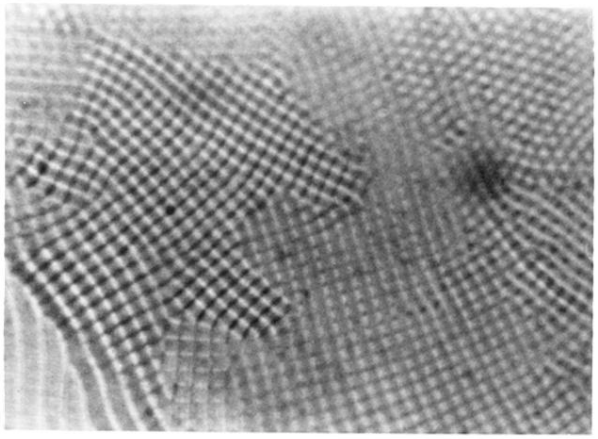

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