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R. Hosemann [a] & B. Müller [a]
[a] Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, 33, Faradayweg, 4-6

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Paracrystalline Lattices in Mesophases and Real Structures

R. HOSEMANN and B. MÜLLER

Fritz-Haber-Institut der Max-Planck-Gesellschaft
Berlin 33
Faradayweg 4-6

Abstract—The structure of liquid crystals to some extent can be understood as mesophases (C. Hermann). Unfortunately, by the statistical group theory only a small number of partially amorphous, partially crystalline structures (so-called *a,z*-structures) can be described. It is shown that the concept of paracrystals not only contains more of such " *a,z*-structures " but a large variety of more or less distorted lattices, which are not of the *a,z*-type. This is illustrated by Fraunhofer patterns with a He–Ne-Laser of two-dimensional models of paracrystalline point structures. Some further examples of solids with paracrystalline lattices on the atomic and colloidal scale are given.

1. Introduction

If molecules in solution are asymmetrically shaped and/or flat and not too small, they often build up mesomorphic or liquid-crystalline phases, which strongly depend on temperature, composition, and concentration. In the pioneer-work of Zocher (1927) the light optical properties of such phases with reference to their structures are discussed. By the application of group theory Hermann (1931) derived eighteen structures. The amorphous-like, disordered character of these structures is taken into consideration by " statistical ", " reciprocal " and " direct " translations S, R, D. Only (RD) corresponds to the translation of conventional crystallography. Hereby a classification into 9 translation types of mesophases is possible. Bernal and Fankuchen (1941) refer to this work and Mabis (1961) fully explains it—again with coloured illustrations. Unfortunately, Hermann's concept only takes into account fully distorted (" amorphous ")

or fully crystalline components of translation (so called *a,z*-structures).

In nature we mostly meet with intermediate cases. It is the aim of this paper to point out that the concept of paracrystalline lattices (Hosemann (1950)) can fill this gap. With the help of Fraunhofer patterns of two-dimensional models it will be shown, that there exists beyond Hermann's concept a much larger number of varieties for disordered structures.

2. The paracrystalline lattice

The cell edge vectors $\mathbf{a}_k$ ($k = 1, 2, 3$) of a primitive paracrystalline lattice statistically and independently fluctuate around a mean value $\bar{\mathbf{a}}_k$.

$$\bar{\mathbf{a}}_k = \int \mathbf{x}\, H_k(\mathbf{x})\, dv_x \tag{1}$$

$H_k(\mathbf{x}$ is the a-priori distance distribution function of $\mathbf{a}_k$. If it corresponds to next neighbors, it is called " coordination statistic " $H_k(\mathbf{x})$. The standard deviation of $\mathbf{a}_k$ in the direction of $\mathbf{a}_i$ ($i = 1$, 2, 3) is defined by

$$\Delta x_{ki} = \left[\frac{1}{\bar{a}_i^2}\int (\mathbf{x} - \bar{\mathbf{a}}_k, \bar{\mathbf{a}}_i)^2 H_k(\mathbf{x})\, dv_x\right]^{1/2} \tag{2}$$

The standard deviation Δx_{ki} relative to $\bar{a}_i$ is defined by the nine g_{ki}-values‡ (Fig. 1).

$$g_{ki} = \frac{\Delta x_{ki}}{\bar{a}_i} \tag{3}$$

If all nine $g_{ki} = 0$ the perfect crystalline lattice is established. Otherwise the diffraction reflections are broadened more and more with larger scattering angle and finely merge into each other.

‡ For sake of simplicity we suppose, that the three coordination vectors $\bar{\mathbf{a}}_1$, $\bar{\mathbf{a}}_2$, $\bar{\mathbf{a}}_3$ are orthogonal and the main axes of the fluctuation tensors of the three $H_k(\mathbf{x})$ are parallel to them.

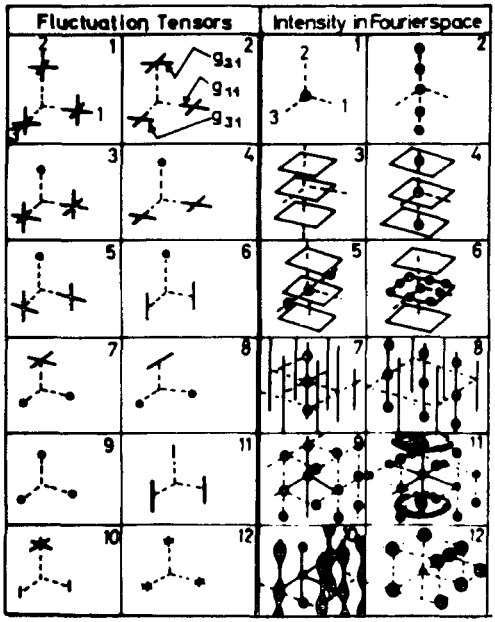


Figure 1. Hermann's Mesomorphic Translation Types 1–9 and some real paracrystalline structures.

Principal tensor axes of the coordination statistics $H_k(\mathbf{x})$ for the nine mesophases of Hermann and three real structures 10–12 (left hand side) and their Fourier transforms (schematically, on the right).

Let n_{ik} be the number of reflections in the direction i, which evidently are separated from their next neighbors in the direction k. Their maximum is at least 20% higher than the minimum between them. Then the relation holds (cf. Hosemann–Bagchi (1962)):

$$n_{ik} = \frac{0.3}{g_{ki}} \tag{4}$$

This equation will be explained by many examples in section IV. Applying the paracrystalline theory to noncrystalline substances it was found to be convenient, to introduce the classification of Table 1.

From Table 1 it can be seen, that in nature not only paracrystalline lattices with lattice constants of some Å exist (Hosemann,

TABLE 1 Degree of distortion g_{ik}

g_{ik}	Class	Application to
0	*z* (zero)	crystal
<2%	*v* (very small)	atomic orionic lattices in high polymers alloys, spinels etc.
2–5%	*s* (small)	
5–10%	*m* (medium)	macrolattices in natural and synthetic linear high polymers
10–20%	*l* (large)	liquids
>20%	*a* (amorphous)	some glasses, and liquids at higher temperature

Preisinger, Vogel (1966)), but for larger motifs (e.g. fibers) cell edges of 100 Å or more (Hosemann–Bagchi (1962)). Synthetic linear polyethylene with monomers of some atoms mostly builds up superlattices with "periods" of about 100 Å and more (Hosemann–Lemm–Wilke (1967)). The X-ray scattering of soaps and lipids in solution (Luzzati *et al.*, 1958) and the light scattering of cholesteric phases (Rhodes, Stein, Chu and Porter, 1968) give evidence of much larger periodicities up to microns. We therefore distinguish between three orders of magnitude for the lattice dimension:

TABLE 2 Dimension of the lattice constants a_k

a_k	Class	Type of lattice
1–10 Å	*i*	atomic, *i*onic
10–1000 Å	*c*	colloidal dimension
>1000 Å	*o*	light *o*ptical dimension

3. Hermann's Translation Types of Mesophases and Real Structures

From the classification of Table 1 one obtains for each of the nine g_{ik}-values six different possibilities, hence at all about $6^9 \sim 10^6$ different lattice-structures. In Table 3 those are collected which are important with respect to Hermann's classification. Besides structures No. 5 and 8 they are statistically identical with respect to directions 1 and 3, hence can be described by five independent g_{ik}-values:

$$g_{11} = g_{33};\ g_{12} = g_{32};\ g_{13} = g_{31};\ g_{21} = g_{23};\ g_{22} \qquad (5)$$

Pyrocarbon is similar to DDR, but with curved, not planar ($0k0$) netplanes. Polyacrylonitril (Hosemann–Lindenmeyer (1963)) has besides much smaller fluctuations, similarities with RRD, hot stretched polyethylene with SSR, and collagen with SSD. The most important difference is, that large distortions of class *a* (Table 1) don't occur in all these real structures. In other words the mesophases are a black-and-white picture (distortions of type *z* and *a*) of nature. We call them *a,z*-structures. The black–white structure No. 10, and many others, can't be found in Hermann's mesophases. In Fig. 1 a schematic illustration in a three-dimensional perspective both in physical and Fourier space is given for all these structures.

4. Two-dimensional Models and Their Fraunhofer Patterns

The Fraunhofer diffraction camera used for Figs. 2–13 consists in the well-known way of two lenses (with 1.20 m and 80 cm focal-length on both sides of the model). A parallel lightbeam of a He–Ne-Laser (LAS-101 He–Ne-Laser, EOA, Palo Alto California) was focused by a lens with 1 cm focal length to the focal point of the 80 cm focal length lens to illuminate quite uniformly the 80 cm lens (4 cm diameter).

The point lattice models automatically were drawn by means of a Computer (Z 23, Zuse KG) and a graphomat (Zuse KG, Z 64)

TABLE 3

Structure No.	Symbol (Hermann)	g_{11}, g_{33}	g_{12}, g_{32}	g_{31}, g_{13}	g_{23}, g_{21}	g_{22}	Fig.	Example
1	SSS	*a*	*a*	*a*	*a*	*a*	2	scattering of Rayleigh (1880)
2	SSR	*a*	*z*	*a*	*a*	*z*	3	turbostratic with amorphous lamellae (Warren (1949))
3	SSD	*a*	*a*	*a*	*z*	*z*	4	nematic uncorrelated
4	SS(RD)	*a*	*z*	*a*	*z*	*z*	5	nematic with orthogonal smectic correlation
5	RDS	*a z*	*a*	*a z*	*z*	*z*	3, 6	nematic with parallel smectic correlation
6	RRD	*z*	*a*	*z*	*z*	*z*	6	nematic monodisperse
7	DDR	*z*	*z*	*z*	*a*	*z*	7	graphitic, plane I
8	DR(RD)	*z*	*z*	*z*	*a z*	*z*	7, 8	graphitic, plane II
9	(RD) (RD) (RD)	*z*	*z*	*z*	*z*	*z*	8	crystalline
10		*z*	*a*	*a*	*a*	*z*	9	a new *a*, *z* structure
10a		*v*	*s*	*v*	*s*	*s*	10	pyrocarbon (*i*)
11		*z*	*l*	*z*	*v*	*m*	11	polyacrylonitrile (*i*)
12		*v*	*v*	*v*	*v*	*v*	12	ammonia catalyst (*i*)
13		*m*	*l*	*m*	*m*	*m*		cold stretched polyethylene (*c*)
14		*m*	*s*	*m*	*m*	*s*		hot stretched polyethylene (*c*)
15		*m l*	*s m*	*l*	*s*	*v*	13	β-keratin (*c*)
16		*m l*	*v m*	*l*	*v*	*v*		collagen (*c*)

on 32×32 cm^2 paper. Negatives 2.4×2.4 cm^2 were photographed on Agfa–Gevaert films 0.80 P. The developer G 8 c of Agfa–Gevaert was used, to obtain opaque screens with very small transparent circles (diameter 85μ). Each model consisted of 3100 points (E. Mallow, 1968).

Each two-dimensional coordination statistic $H_1(x)$ and $H_2(x)$ consisted of 55×55 equidistant point functions. Lattice point by lattice point one of these 55^2 different values was drawn from a lottery box and given to the computer, which row by row and column by column pointed the distorted lattice of a so-called " ideal paracrystal " (cf. Hosemann–Bagchi, 1962).

Pictures of these two-dimensional models are given in Figs. 2–13. We will now describe them and their Fraunhofer patterns and compare them with the three-dimensional structures of Fig. 1. In Table 4 eq. (4) is applied to the models: $n_{21} = 5$ for instance means, that in the vertical direction 2, five discrete reflections $(0k)$ (the (0,0) reflection excluded) exist, which are distinguishable from the horizontal neighbors $(1k)$ and $(\bar{1}k)$ in the direction 1 (see Fig. 1).

TABLE 4

Structure No.	1	2, 5	3	4	5, 6	7, 8	8, 9	10	10a	11	12	15
Fig.	2	3	4	5	6	7	8	9	10	11	12	13
$g_{11}(\%)$	28	28	28	28	0	0	0	0	0	0	10	9
$g_{12}(\%)$	28	0	28	0	28	0	0	28	17	30	10	0
$g_{21}(\%)$	28	28	0	0	0	17	0	28	17	0	10	9
$g_{22}(\%)$	28	0	0	0	0	0	0	0	0	12	10	0
n_{11}	1	1	1	1	∞	∞	∞	∞	∞	∞	3	3
n_{21}	1	∞	1	∞	1	∞	∞	1	2	1	3	∞
n_{12}	1	1	∞	∞	∞	2	∞	1	2	∞	3	3
n_{22}	1	∞	∞	∞	∞	∞	∞	∞	∞	3	3	∞

The model of Fig. 2 with all $g_{ik} = 28\%$ gives rise to a diffraction for all $n_{ik} = 1$, hence only the reflection (0,0) exists, all other ones are diffuse. The diffraction pattern offers no wide angle interferences, though a strongly distorted lattice exists.

In the model of Fig. 3 horizontal equidistant straight lines exist. Hence $g_{12} = g_{22} = 0$. But the distances within the lines strongly vary ($g_{11} = a$) and the rows are much shifted against each other in the horizontal direction ($g_{21} = a$). According to eq. 4 only $n_{22} = n_{21} = \infty$ hence only reflections ($0k$) are crystalline like, ($1k$) and ($\bar{1}k$) are just visible, all other ones are diffuse.

In Fig. 4 straight vertical lines with equidistant points along the column exist ($g_{22} = g_{21} = 0$), all other g_{ik} are quite large. Now according to eq. (4) $n_{22} = n_{12} = \infty$ hence an infinite large number of horizontal reflection lines exists, which consist of series of overlapping reflections ($n_{11} = 1$, $n_{21} = 1$).

In Fig. 5 only $n_{11} = 1$, all other $n_{ik} = \infty$. Hence outside of the reflections ($0k$) horizontal lines exist. Only the reflections ($\bar{1}k$), ($1k$) are just separable from one of their neighbors.

In Fig. 6 only $n_{21} = 1$, all other $n_{ik} = \infty$. Now crystalline reflections (h,0) exist and all other reflections besides of (01) and ($0\bar{1}$) are smeared out to sharp horizontal lines. If $n_{12} = 2$ and all other $n_{ik} = \infty$ (Fig. 7) we have the pattern of Fig. 6 turned by 90° and the reflections ($\bar{2}$ k), ($\bar{1}$ k), (0 k), (1 k), (2 k) are separated from all neighbors, but only ($0k$) absolutely crystalline. Figure 8 with all $g_{ik} = 0$ gives the well known crystalline case. In Fig. 9 $n_{12} = n_{21} = 1$, all other $n_{ik} = \infty$. Hence the reflections (0 k), (h 0) are sharp along the k- and h-direction, respectively, but diffuse in the other dimensions. This is an example of an a,z-structure which can not be found in Hermann's mesophases. But it, in principle, is realized in nature in the case of pyrocarbon (see Fig. 10). Some two-dimensional structures with either $g_{ik} = z$ or $g_{ik} = a$ ("a,z structure") correspond to Hermann's three-dimensional mesophases, others do not.

As shown in Table 4, Fig. 2 fits with structure 1, Fig. 3 with structure 2, Fig. 4 with structure 3, Fig. 5 with structure 4, Fig. 6 with structure 6, Fig. 7 with structure 7 and Fig. 9 with structure 10 if in Fourier space we built up the same intensity function in the (2,3) plane as in (2,1).

In structure 1 there exists only the reflection (000), all around totally diffuse (Rayleigh-scattering), in structure 2 crystalline

($0k0$) reflections, all others totally diffuse, in structure 3 the (000) reflection surrounded by sharp layer planes ($0k0$), in structure 4 crystalline ($0k0$) reflections surrounded again by sharp layer planes ($0k0$), structure 6 crystalline ($h0l$) reflections, all other ones partially along sharp ($0k0$)-planes, totally diffuse in the h- and l-directions, structure 7 with crystalline ($0k0$) reflections and sharp lines ($h0l$) parallel to k and finally the three-dimensional point function of Ewald (1940) in structure 9.

All these mesophases have in common (cf. Fig. 1) that the statistical parameters in the (2,3) netplane are the same as in (2,1). Structure 5 on the other hand along (2,1) looks like Fig. 4, along (2,3) like Fig. 6. Hence only crystalline reflections (001) exist, all other reflections are totally smeared out in h and l directions to sharp planes orthogonal to k. This is pointed out in the perspective three-dimensional drawing on the right hand side of fig. 1. Structure 8 in the (2,1) netplane is crystalline like Fig. 8, in the (2,3) netplane like Fig. 6, turned by 90°. Now crystalline reflections ($hk0$) exist and straight lines ($h0l$) parallel k (see Fig. 1).

All the above mentioned mesophases are discussed in the paper of Mabis (1961). But as noted above many other important a,z-structures cannot be defined by Hermann's concept. Figure 9 gives a two-dimensional example, mentioned as structure 10 in Table 3 and Fig. 1. If one introduces not extreme g_{ik} values z, a but medium ones, this structure is represented in nature for instance in pyrocarbon (structure 10a of Table 3 and Fig. 10). As seen from Table 3 $g_{12} = g_{32} = s$; $g_{11} = g_{33} = v$; $g_{31} = g_{13} = v$ hence the slightly distorted and curved netplanes orthogonal to direction 2 exist with slightly fluctuating distances ($g_{22} = s$) and shifted against each other ($g_{23} = g_{21} = s$).

The reflections ($h0l$) are smeared out with ($h1l$), ($h2l$) but sharp orthogonal to k, the reflexions ($0k0$) are crystalline like (cf. Warren (1941)).

Other examples of medium g_{ik}-values are given in the structures 12–16. The index i (c) according to Table 2 indicates, that the lattices under consideration are in atomistic or colloidal scale.

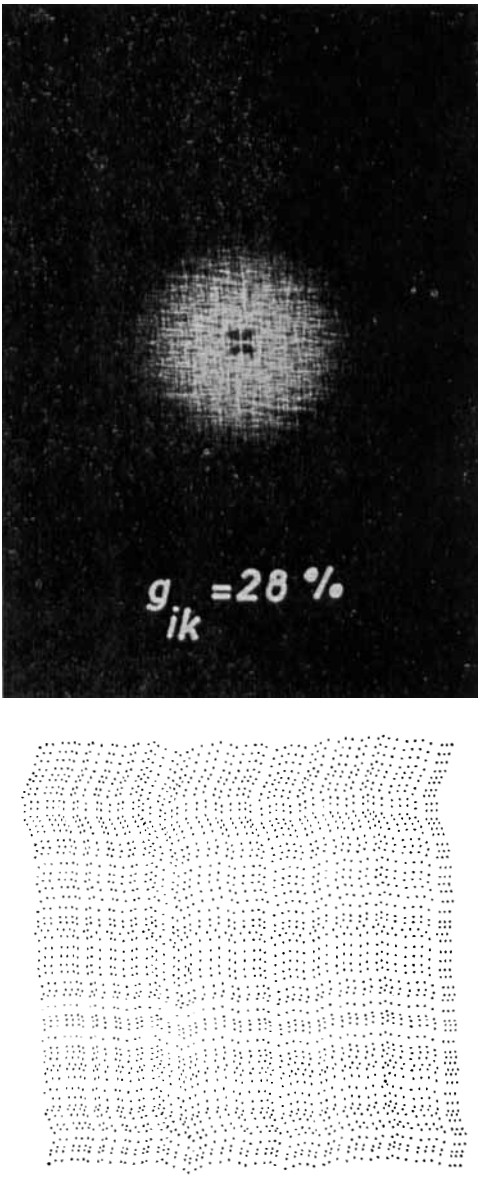
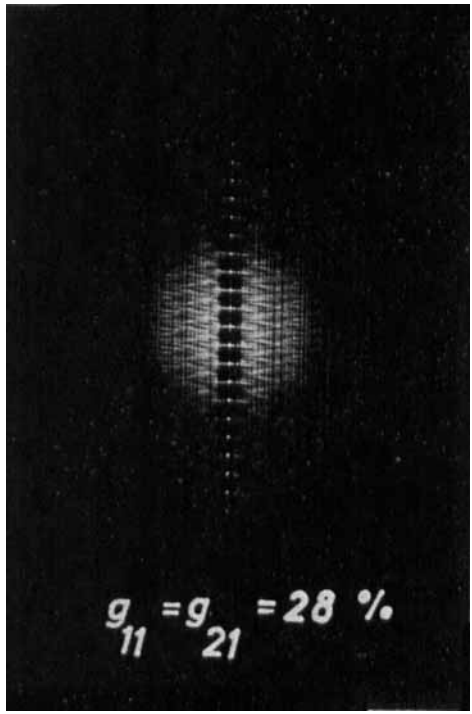


Figure 2. Structure 1. Totally amorphous lattice SSS



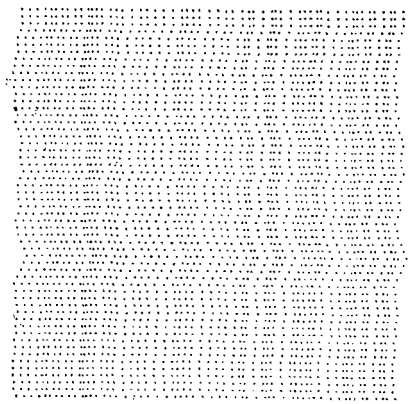


Figure 3. Two-dimensional model of the mesophase SSR, if the horizontal axis has the same features as the axis orthogonal to the drawing plane.

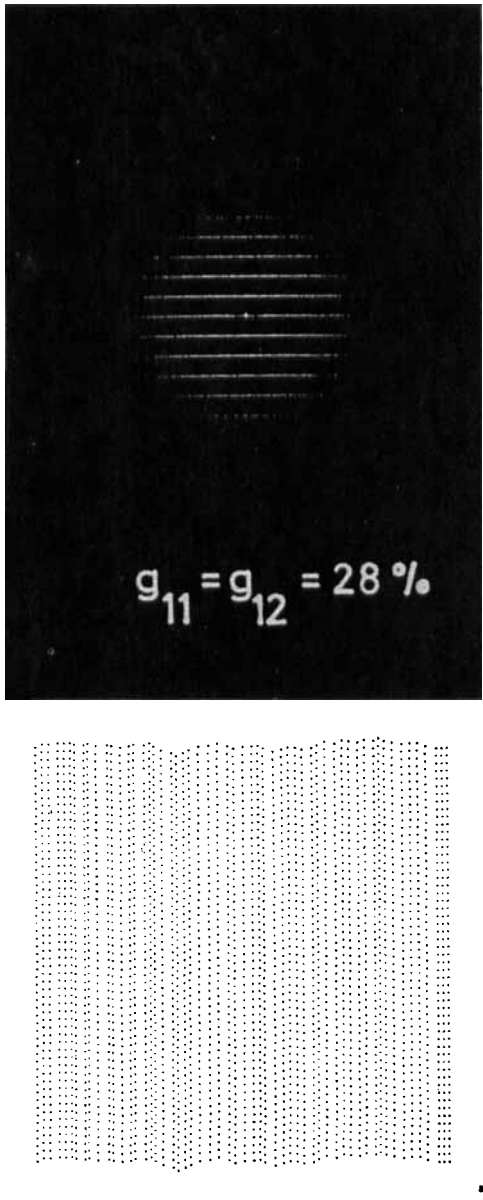


Figure 4. Structure 3. Two-dimensional model of the mesophase SSD under the same assumption of Fig. 3.

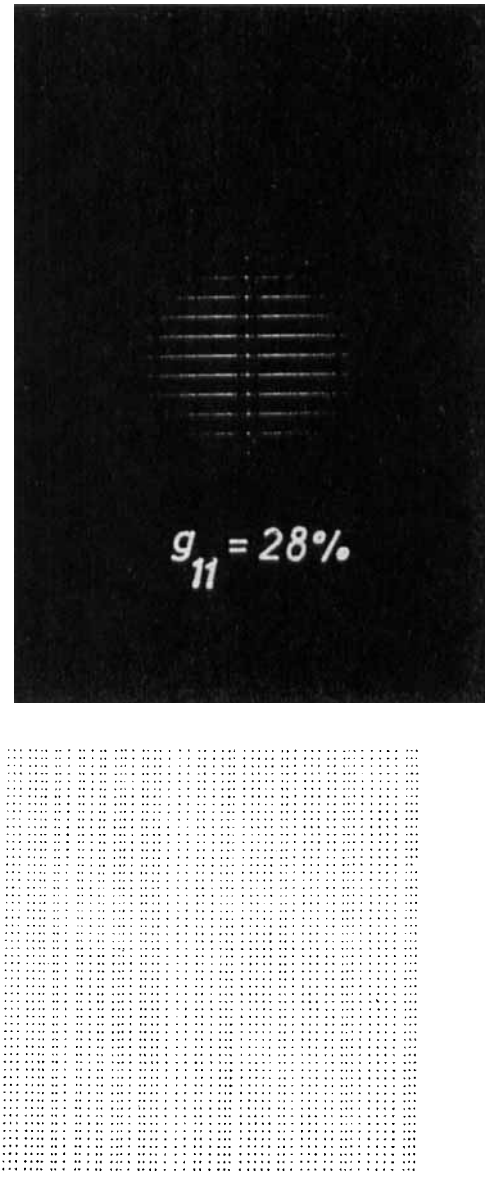


Figure 5. Structure 4. Two-dimensional model of the mesophase SS(RD) under the same assumption of Fig. 3.

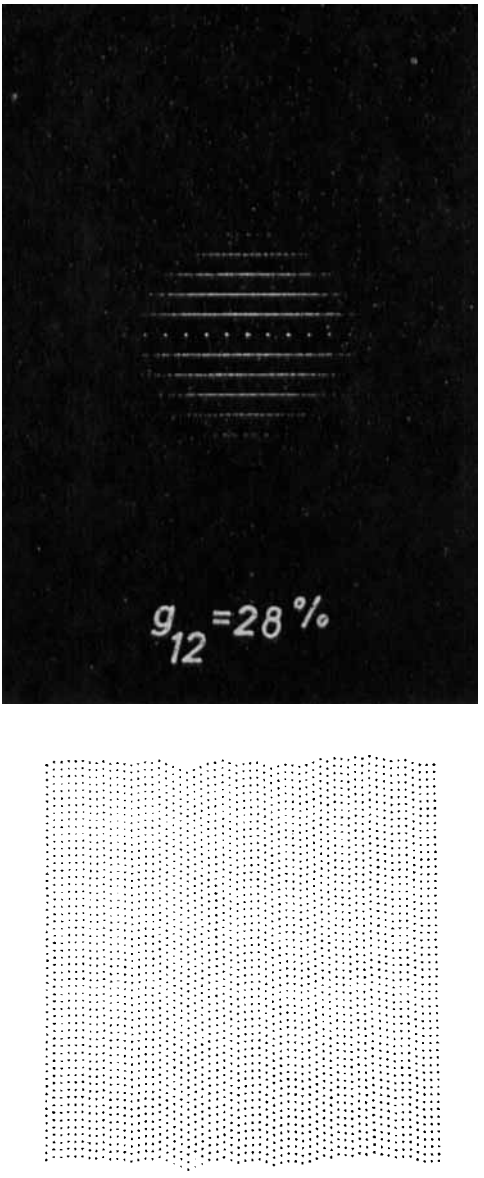


Figure 6. Structure 6. Two-dimensional model of the mesophase RRD under the same assumption of Fig. 3.

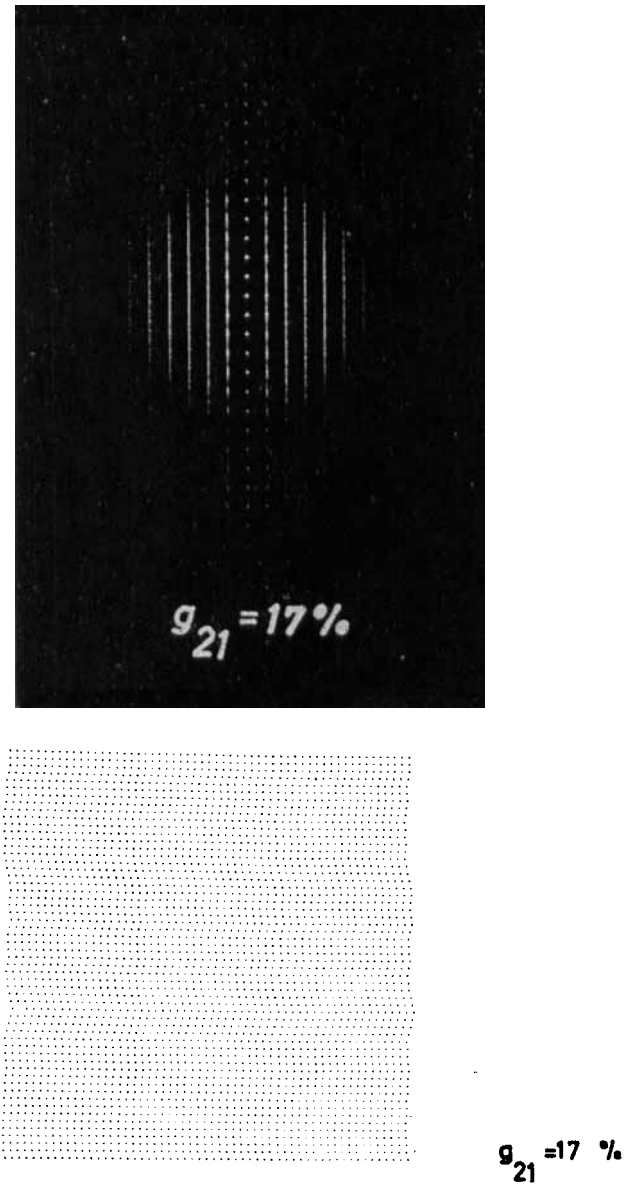
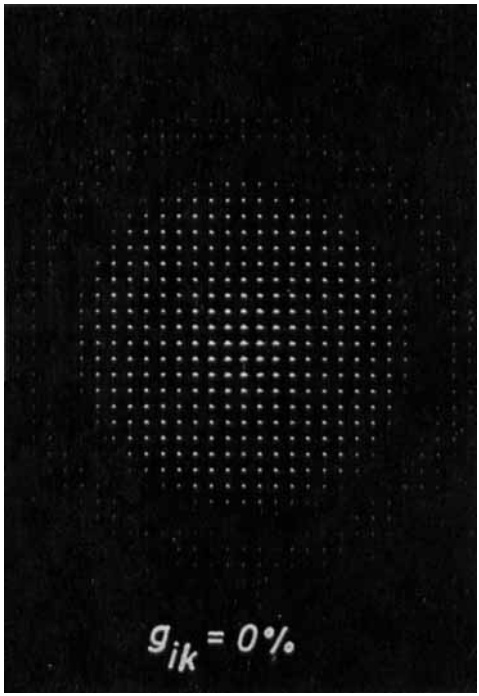


Figure 7. Structure 7. Two-dimensional model of the mesophase DDR under the same assumption of Fig. 3.



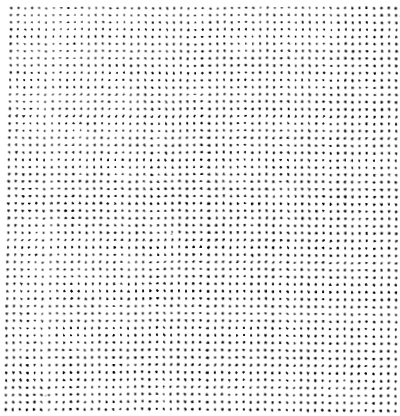


Figure 8. Structure 9. Crystalline case (mesophase ((DR) (DR) (DR)).

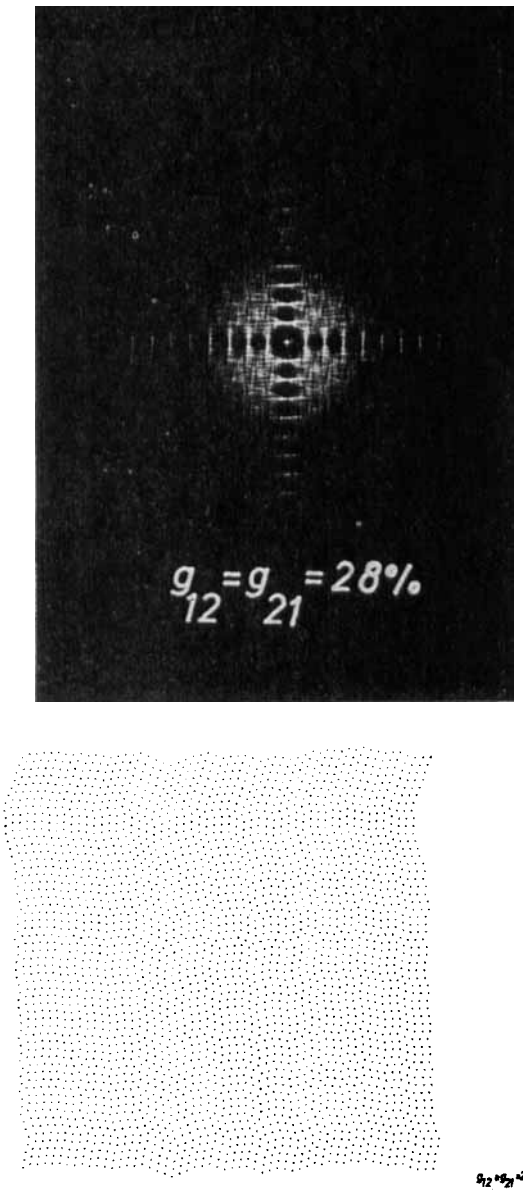
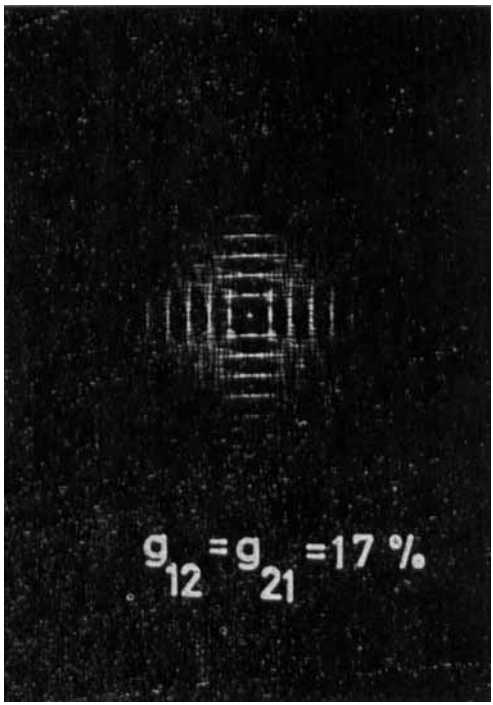


Figure 9. Structure 10. An example of a three-dimensional new a-z-structure (see Fig. 1).



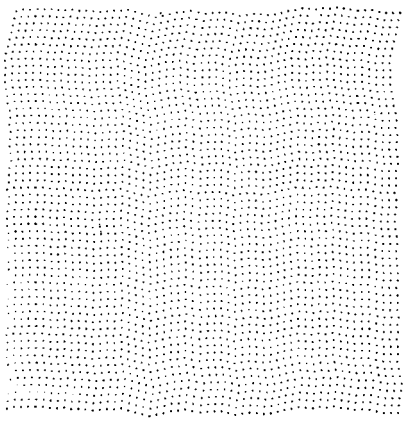


Figure 10. Structure 10a. Paracrystalline distortions of the same type of Fig. 9. Example for pyrocarbons.

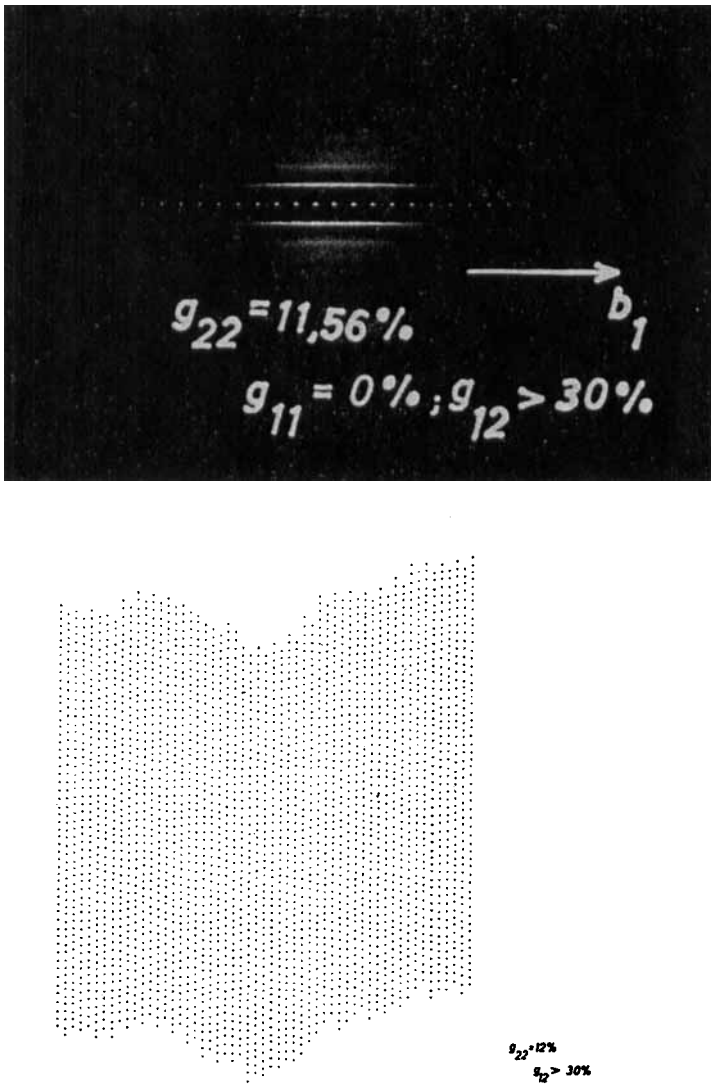


Figure 11. Structure 11. Example for the molecular lattice of polyacrylonitril.

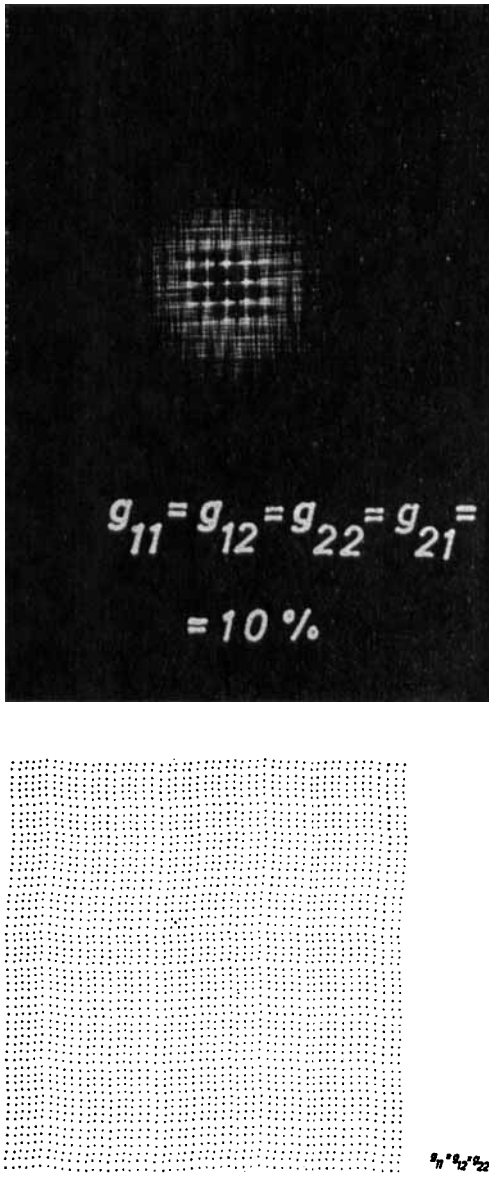
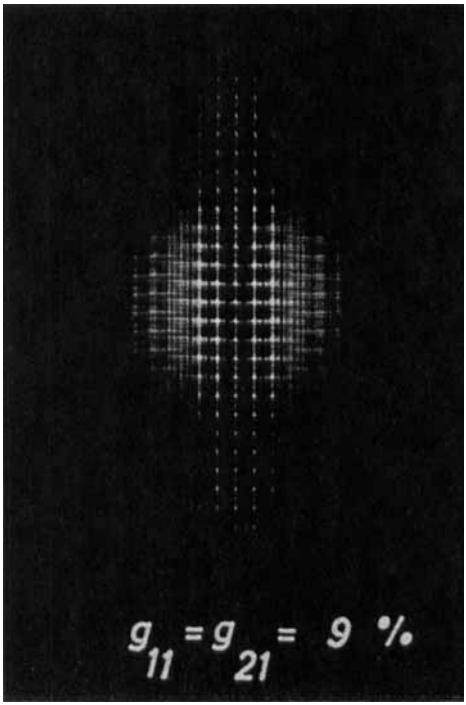


Figure 12. Structure 12. Example for the atomistic lattice of ammonia catalyst.



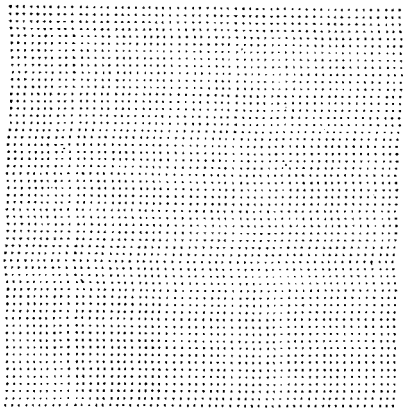


Figure 13. Example of the macrolattice (c) of β-keratin.

See for detail Hosemann–Lindenmeyer (1963), Hosemann–Preisinger–Vogel (1966) and Hosemann–Lemm–Wilke (1967).

To this moment we could not work out an example of liquid crystals since their lattices are of type *o* (Table 2). Here one must discuss lattices in the domain of the visible light, which only can be studied by diffraction of light. How to do this is pointed out in the paper of Rhodes, M.B., Stein, R. S., Chu, W., Parker, R. S. (1968). We are in the first stage of exploring a new branch of science.

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REFERENCES

Bernal, I. D. and Fankuchen, I., *J. Gen. Physiol.* **25**, 111 (1941).
Hermann, C., *Z. Krist.* **79**, 186, and 337 (1931).
Hosemann, R., *Zs. Phys.* **128**, 1 and 465 (1950).
Hosemann, R. and Bagchi, S. N., "Direct Analysis of Diffraction by Matter". North Holland Publ. Comp., Amsterdam (1962).
Hosemann, R. and Lindenmeyer, P. *J. Appl. Phys.* **34**, 42 (1963).
Hosemann, R., Preisinger, A. and Vogel, W. *Ber. d. Bunsenges. f. phys. Chem.* **70**, 6, 796 (1966).
Hosemann, R., Lemm, K. and Wilke, W., *Mol. Cryst.* **1**, 333 (1967).
Luzzati, V., Mustrachi, H. and Skoulios, A. *Disc. Farad. Soc.* **25**, 43 (1958).
Mabis, A. J., *Acta Cryst.* **15**, 1152 (1961).
Mallow, E., Diploma F. U. Berlin-Dahlem "Untersuchung parakristalliner Strukturen an lichtoptischen Modellen" (1968)
Rayleigh, Lord, *Phil. Mag.* **10**, 73 (1880).
Rhodes, M. B., Stein, R. S., Chu, W. and Porter, R. S. Light Scattering Studies of Orientation Correlation in Cholesteryl Esters, ONR Techn. Rep. No. 112 (1968) Polymer Research Institute, University of Mass., Amherst. (1968).
Warren, B. E., *Phys. Rev.* **59**, 693 (1941).