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Crystals of Higher Order and their Relation to Other Superphases

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Two examples have been observed of an orthorhombic crystal type, composed of particles of dimensions about 10^{-6} to 10^{-4} cm separated by water layers of the same order of magnitude. The particles themselves are small crystals, likewise of orthorhombic shape, at least to a first approximation. Like the cubic crystals of certain viruses and similar systems, they belong to the same type of phase as the smectic and nematic 'tactosols' and the amorphous 'coacervates'.

In order to distinguish phases of this type from those composed of molecules in immediate contact, they might be named *phases of higher order* or *superphases*. Their equilibrium is mainly determined by the surface charges and their counterions. The influence of temperature is small. Such phases with translation periods (smectic or crystalline) exhibit iridescence instead of X-ray interference.

The new orthorhombic crystals are obtained from the iridescent smectic tactosols of ferric chloride hydrolysate and of tungstic acid by a treatment that diminishes the distance between the particles. In the smectic state the crystal leaflets are distributed at random around the main axis. They reveal their orthorhombic oblong shape only at short distance in the supercrystals by arrangement in a three-dimensional periodic lattice.

Phases of higher order in general

The condensed phases considered as examples in classical thermodynamics are statistically or periodically homogeneous. Homogeneity is the equality of all samples cut out from the system. In view of the discontinuous structure of all matter, the sample must be large enough to satisfy this condition to a certain degree, and the 'homogeneity region' must include a sufficient number of atoms or molecules to characterize the phase structure. Consequently, the decision whether homogeneity exists or not is somewhat arbitrary, and may depend upon the magnitude of the dimension considered. For instance, it may be that macro- and microscopic investigation indicates a homogeneous crystallized, smectic or nematic* phase, whereas electron-microscopic or X-ray investigation reveals that the system is composed of phase particles or macromolecules of colloidal dimensions (10^{-7} to 10^{-4} cm) separated by water layers of the same order of magnitude. We call such phases *phases of higher order* or *superphases*. They differ from the normal molecular phases, not only in nature and dimension of the structural units, but also in the forces which determine the equilibrium. Consequently, their physicochemical behaviour differs from that of normal dense molecular phases, where the Born repulsion together with the thermal movement and the London – van der Waals attraction are the determining factors. In the superphases, the 'long range' forces of the surface charges and their counterions – and perhaps the remainder of the van der Waals forces – determine the equilibrium between the particles (Zocher, 1925; Zocher & Jakobsohn, 1929; Michaeli, Overbeck & Voorn, 1957). This equilibrium depends upon the concentration and the nature of the free ions, especially the *p*H, whereas the influence of temperature is generally small. The particular role of the water is the consequence of its high dielectric constant, which makes high surface charges and thick double layers possible.

The first examples of phases of higher order were discovered by Zocher (1925) and called *tactosols*. (Zocher & Jakobsohn, 1929). They represent the nematic and smectic variety. Threadlike particles of vanadium pentoxide, for instance, unite in parallel positions to a water-including anisotropic phase, which is separated from the more dilute isotropic mother liquor by sharp interfaces. The droplets (*tactoids*) of this type of superphase, surrounded by the isotropic *atactosol* are spindle-shaped (Figs. 1–4). This shape indicates only that besides the surface tension, which as a scalar cannot be anisotropic, the elastic forces – produced by the deformation of the anisotropic interior – are also

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* The terms *smectic* and *nematic*, introduced by Friedel (1922), refer to the only two well known types of mesophases or 'liquid crystals'. In the smectic state, often found in soaps, the long molecules are arranged in parallel positions in equidistant planes. According to this structure, there exist one translation period in the direction of the infinite-fold symmetry axis and two rotation periods of 180 or 360° around any pair of perpendicular axes parallel to the equidistant planes. In the nematic state, occurring in *p*-azoxyanisole and similar substances, the rod-shaped molecules are likewise in parallel positions, but there is no translation period and the molecules may glide freely also in the direction of the main axis, not being limited to parallel planes. Only the two rotation periods exist as in the smectic state. Enantiomorphic (optically active) substances in this state, like cholesteryl esters, may exhibit light interferences according to a torsion around an axis perpendicular to the main axis, with a period of the wavelength of light. The reflexion is, of course, enantiomorphic (circularly polarized) and is completely different in nature from the iridescence of smectic or crystalline superphases.

of noticeable influence*. The latter are insignificant in the case of air bubbles and of the low molecular nematic phases, forming spherical droplets in the amorphous phase. The compact nematic tactosol does not differ very much from the low-molecular nematic phases, exhibiting the same discontinuities of orientation. Fig. 5 shows two pairs of the most frequent type of inhomogeneity, symbolized by Friedel (1922) as +1 and −1 (*cf.* Zocher & Birstein, 1929; Zocher & Török, 1960*b*).

The droplets of atactosol included by tactosol – the *atactoids* – are similarly shaped to the tactoids (Fig. 6).

A smectic superphase built up by disc-shaped particles is formed by the hydrolysis of dilute ferric chloride (Zocher, 1925; Zocher & Heller, 1930; Heller, 1935) and in tungstic acid sols (Zocher & Jakobsohn, 1929). The discs are arranged in large sheets in parallel positions at uniform distances. The period is of the dimension of about the wavelength of visible light, and thus produces a vivid iridescence which is easily observed from the bottom of the vessel with a mirror. The brilliant reflexion reminds one of the metallic lustre of some tropical butterflies, which is also produced by multiple periodic structures. The droplets of the smectic tactosol are cylindrical, exhibiting the iridescence on the base.

Another example of nematic superphase was observed in benzopurpurine (Zocher, 1925; Zocher & Jakobsohn, 1929), and yet another was discovered in the tobacco mosaic virus with the uniform rodlets in hexagonal dense packing (Bernal & Fankuchen, 1941). Zocher & Török (1960*a*,*b*, 1962 and unpublished work) observed the nematic superphases of γ-AlOOH (böhmite) and that of β-FeOOH. Probably a tactosol also exists in the haemoglobin of blood sickle disease.

The separation of amorphous condensed superphases from solutions of proteins and other organic colloids by charge diminishing agents was first observed by Ostwald & Köhler (1927) and thoroughly studied by Bungenberg de Jong & Kruyt (1929). These authors called them *coacervates*, *i.e.* accumulations, in order to stress the difference from the normal low-molecular condensed amorphous phases and from the coagulated sediments, leaving open the question as to whether they are to be considered as phases at all.

Crystals of the same type of phases (*supercrystals*) have already been shown to exist in two symmetry classes; those of the tobacco mosaic virus are hexagonal (Oster, 1950), and those of the *Tipula* iridescent virus (Klug, Franklin & Humphreys-Owen, 1959) and of monodisperse high polymer suspensions (Luck, Klier & Wesslau, 1963) are cubic. In the two latter cases the crystal lattice is equivalent to the dense packing of spheres [space group *Fm*3*m* (O_h^5)]. The crystal periods are of the dimensions of the wavelength of light and cause striking iridescent colours. The particles of *Tipula* iridescent virus are indeed icosahedra, but at the relatively long distance the deviation from a sphere is without influence upon the arrangement. The latex particles are spheres to a good approximation.

Recently we found a new type of supercrystal starting from the smectic superphases, the 'iridescent layers', of ferric chloride hydrolysate (Zocher, 1925) and of tungstic acid (Zocher & Jakobsohn, 1929; Löw-Beer, 1935). In both cases the smectic superphase described above is transformed into orthorhombic crystals [space group *Pmmm* (D_{2h}^1)] by the diminution of the distance between the particles. The asymmetry of the shape in the plane of the small crystals, which are evidently rectangular leaflets, is without effect at long distance, but becomes significant on closer mutual approach: being distributed at random in relation to the main axis in the smectic state, they are forced into the periodic parallel position of a crystal lattice.

The transition from the smectic to the crystalline superphases

Ferric chloride hydrolysate

In earlier experiments (Zocher & Heller, 1930) it was observed that the iridescent layers often occur in ferric chloride solutions of about 30 mmol.l^{-1} at room temperature in the course of several months, or more rapidly at 50–60 °C. As reaction vessels, we used simple Pyrex bottles with ground-glass stoppers and the thinnest possible bottoms, so that we could study the reflexions from the sediment from below with a magnification of *ca.* 200. The iridescent layers are not always formed and are invariably accompanied by a great amount of a non-iridescent brown turbid mass.

The iridescent layers are deposited in the lowest part of the bottles, in a circular groove. They may exhibit different colours, varying from red of the first order to red of the second order*. In most cases they show green of the second order. The microscope shows that the reflecting areas are often interrupted by more or less parallel curved dark lines (Figs. 7 & 8) without preferential direction. Eventually they converge and end in small dark patches. Single lines may also vanish within a bright area. These dark lines are probably discontinuities resulting from the encounter of two independently grown parts of the layer with an irregular structure at the borders. Oblique illumination in effect shows a convex curvature of the reflecting layer in the vicinity of the dark lines. The perpendicularly reflected light is not polarized, if the illuminating light is natural; the reflexion of polarized light does not show noticeable depolarization. The limits of the iridescent layer against the non-reflecting dark brown liquid or the lighter brown turbid sediment are sharp curved lines.

Newly formed reflecting layers show a very vivid Brownian scintillation caused by the rotation of the leaflets around an axis in the plane of the stratification.

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* *Cf.* also Bernal & Fankuchen (1941).

* The order of the interference colour is determined by the variation of the reflected wave-length with the angle between the ray and the reflecting surface.

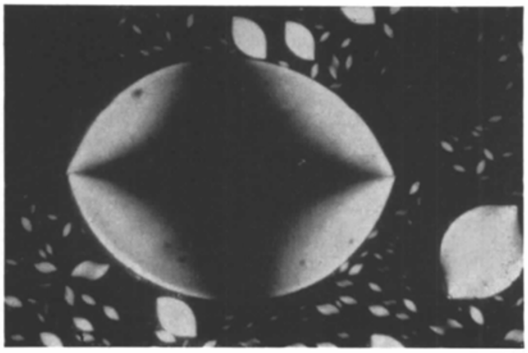

Fig. 1. Vanadium pentoxide, simple droplet ('tactoid'), symmetric position, crossed polarizers (× 105).

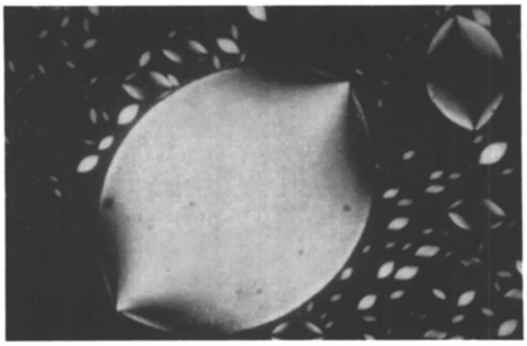

Fig. 2. The same under 45°.

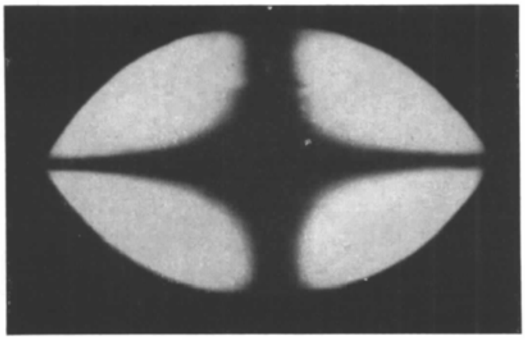

Fig. 3. γ-AlOOH (boehmite), as Fig. 1 (× 105).

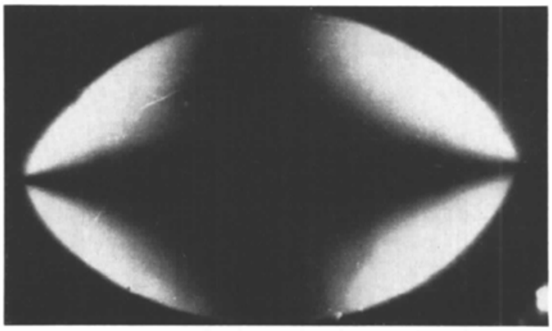

Fig. 4. Tobacco mosaic virus as Fig. 1 (× 240).

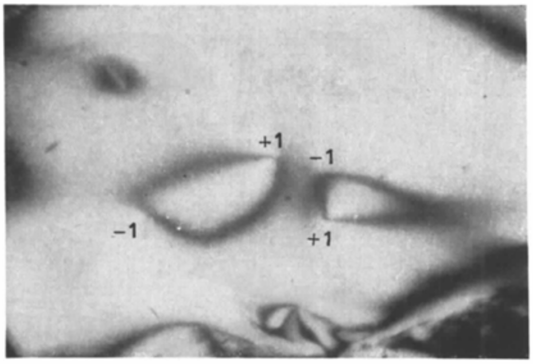

Fig. 5. γ-AlOOH, compact mass with two pairs of orientation inhomogeneities (+1) and (−1); (× 40).

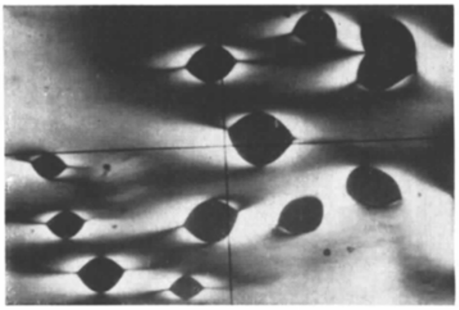

Fig. 6. Vanadium pentoxide, compact mass including 'atactoids' (× 40).

Figs. 1 to 6. Nematic phases of higher order

Fig. 7. $FeCl_3$ hydrolysate, smectic, reflected light, green of second order (×405).

Fig. 9. $FeCl_3$ hydrolysate, crystals of higher order, twinned, reflected light, green and yellow of first order, light vector parallel to the short side (×405).

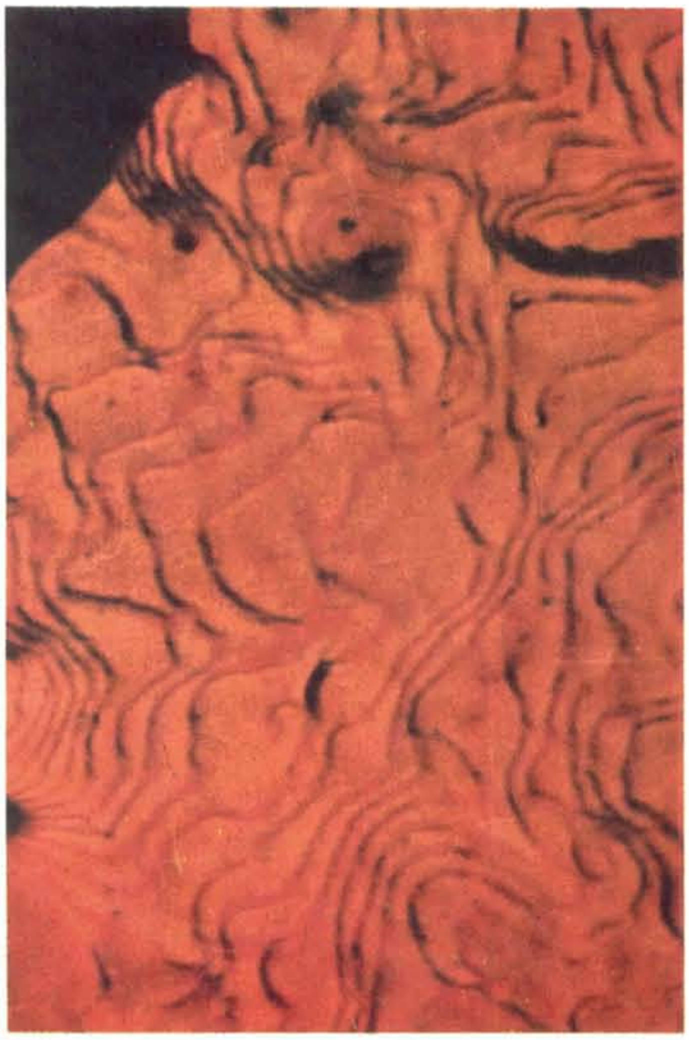

Fig. 8. The same as Fig. 7, red of first order.

Fig. 10. The same as Fig. 9, light vector parallel to the long side. The isotropic, brown reflecting, mostly striated parts are probably transformation products of crystals of higher order.

Figs. 7 to 10. Smectic and crystalline phases of higher order

In the course of time, the intensity of the movement diminishes, but it is readily re-established by agitation and new sedimentation, if the iridescent layers are not coagulated by some impurity or by their own electrolyte.

In order to obtain a more stable iridescent sediment, the more or less clear upper part of the solution was removed and substituted by distilled water until the dilution corresponded to 20 times the original value. After agitation, a new sediment resulted, which showed a green reflexion, similar to the previous one. However, the variation with the angle of incidence showed that it was no longer a green of the second order, but a green of the first order. This signifies that the distance between the layers diminished, so that the optical period amounted only to one half of the original value. This is rather unexpected, since dilution in general raises the distances between colloidal particles. However, the liquid formed by the hydrolysis of ferric chloride is strongly acidic and the surface charge may be lower in a liquid of higher *p*H. In fact, the *p*H was raised from 1·5 to 3 or more by dilution.

Yet more surprising was the result of the microscopic examination: the layers now exhibit a strongly anisotropic reflexion, being brilliant green for one vibration and bright yellow for the other. The whole reflecting sediment is mosaic-like, composed of green and yellow areas, each green changing into yellow and each yellow into green by rotating the polarization filter by 90°. The different parts are separated by sharp borders parallel to the two main light vibrations, often including rectangular or square areas. Oblique lines are often neatly composed by staircase-like alternating parts. Thus, the behaviour is that of perpendicularly twinned crystals (Figs. 9–12).

If the vibration transmitted by the polarizer is perpendicular to the groove at the bottom of the bottle, containing the sediment as a narrow long sickle, the greater part is green. In each case almost all parts are orientated with their optical anisotropy parallel or perpendicular to the length of the groove. This orientation certainly originates from the streaming along the groove, which is easily caused by any movement of the vessel. Therefore the vibration of the yellow reflexion is probably parallel to the length of the primary crystal leaflets.

It may also happen that this sediment occurs as a mass of a great number of isolated small rectangular particles surrounded by the atactosol (Fig. 13). The vibration of the green reflexion is then parallel to the length, and that of the yellow is parallel to the short side. The appearance is exactly that of a crystalline sediment.

Indeed the whole behaviour of this iridescent sediment, its anisotropy and the perpendicular twinning, can only be understood as the formation of 'supercrystals' analogous to those of the *Tipula* iridescent virus, but differing in symmetry: they are orthorhombic instead of cubic. In the two cubic examples of supercrystals, the crystallization is determined by geometric conditions of the groupment without the influence of any shape asymmetry of the elementary particles.

The nature of the elementary rectangular leaflets has not yet been completely cleared up. Like other authors (Heller, Kratky & Novotny, 1936), we have not succeeded in separating the iridescent material from the preponderating mass of covering turbid brown sediment. The X-ray interferences obtained from the sediment were mostly those of β-FeOOH, in old samples of α-FeOOH. The β modification is tetragonal (Mackay, 1960) and therefore unable to form rectangular leaflets. The α modification, goethite, is orthorhombic, but its birefringence is too weak to produce the great difference of colour. The wavelength of the highest intensity is, for example, for the one vibration $\lambda_1 = 585\ \text{m}\mu$ and $\lambda_2 = 540\ \text{m}\mu$ for the other. The two optical periods hence are:

$$\lambda_1/2 = 292{\cdot}5 = 1{\cdot}33w + n_1x \quad \text{and}$$
$$\lambda_2/2 = 270 = 1{\cdot}33w + n_2x$$

where w and x are the thickness of the water layer and of the leaflets respectively, n_1 and n_2 are the two refractive indices in the leaflets, and 1·33 is the refractive index of water.

The lower limit of relative birefringence is obtained by putting $w = 0$:

$$\frac{n_1 - n_2}{n_1 + n_2} = \frac{22{\cdot}5}{562{\cdot}5} = 0{\cdot}04\,.$$

The refractive indices of goethite are 2·26, 2·50 and 2·39; hence the highest relative birefringence $(n_1 - n_2)/(n_1 + n_2) = 0{\cdot}03$ is certainly too low. Lepidocrocite, γ-FeOOH, has refractive indices 1·94, 2·20 and 2·51. In the case in which the vibration perpendicular to the layer is that of the greatest refraction – the earlier observations (Zocher, 1925) in fact indicated a strong positive birefringence of the smectic layers – the ratio $(n_1 - n_2)/(n_1 + n_2)$ equals 0·063. Lepidocrocite therefore is well able to produce the observed strong difference of the optical period. Supposing the crystal leaflets to be lepidocrocite, one can calculate their thickness, $x = 85\ \text{m}\mu$, and that of the water layer, $w = 76\ \text{m}\mu$. And supposing that in the smectic state, which reflects the second order yellow green ($\lambda \simeq 550\ \text{m}\mu$), the average ordinary refractive index of the layer is $n_0 = \sqrt{(2{\cdot}210 \times 1{\cdot}94)} = 2{\cdot}065$, the thickness of this water layer results as $w = (550 - 85 \times 2{\cdot}065)/1{\cdot}33 = 280\ \text{m}\mu$.

Lepidocrocite is also known as a product of laboratory reactions. In a series of experiments in which ferric nitrate was hydrolysed we also obtained lepidocrocite as an abundant sediment, easily identified by X-rays. But no iridescent layers could be observed. These are indeed bound to a uniform shape and size, obtained perhaps only in the presence of chloride ions. Thus, the idea may not be far-fetched that the elementary particles are basic chloride FeOCl, which was likewise observed in the hydrolysis of solutions of ferric chloride (Heller, Kratky & Novotny, 1936). Unfortunately, the refractive indices of these crystals, having a crystal lattice similar to that of lepidocrocite, are not known. It is only known that the double refraction is strong.

Tungstic acid

The second example of a smectic superphase is that of tungstic acid. These iridescent layers are easily investigated microscopically with high power objectives in vessels with a thin cover-glass as bottom. The particles are often oblong leaflets with two arcs as limits. In old samples they are always rectangles of a length of a few microns and a width of more or less one micron. The thickness is less than 0·1μ, according to optical behaviour – the lowest interference colour is blue I, $n=2{\cdot}25$ – and the number of particles per cm^3 (Bergmann, Löw-Beer & Zocher, 1938). Only one of the three dimensions is in the proper colloidal range, and thus the particles are on the limit at which the formation of well-ordered superphases may be expected. The thermal movement is low and the influence of gravitation is already considerable.

The thickness of the water layers is easily diminished by the addition of salts in low concentration (Bergmann, Löw-Beer & Zocher, 1938).

The sample we selected as object was 6 years old and still showed a very brilliant iridescence. The interference colour varied from the green of the third order in the centre to the red of the third order on the border, where the total thickness was smaller. By addition of sodium chloride solution we diminished the period and with it the order of interference colour of the sediment formed in a cylindrical vessel with a coverglass bottom. The microscope showed that the sediment consisted of rectangular leaflets of 3 to 4μ length and about 1μ width.

When the concentration of sodium chloride is raised to 0·25 mmol.l^{-1}, the interference colour of the reflexion from the bottom continuously diminishes from the third order through the second to the red of the first order. The microscope showed (Fig. 14) that the densely packed small rectangles are always parallel to the bottom, twinkling intensely in consequence of the rotatory Brownian movement around an axis in the plane. The azimuth of their length-edge is distributed at random in the reflecting plane corresponding to the structure of a smectic tactosol. On concentration to 1·0 mmol.l^{-1}, the colour changes to orange, yellow and green. At the same time, ranks of several parallel rectangles appear, resembling crosswise striped ribbons. Their frequency increases and the number of particles included in one group also increases. Neighboring groups are parallel or perpendicular to one another and soon the appearance of the layer is that of wickerwork (Fig. 15). Finally, the uniformly orientated regions grow, consisting of parallel rows of parallel rectangles. This disappearance of the 'twinning' may be caused equally by an unavoidable shaking, which furnishes the free energy for breaking the wrong orientations, or, on the other hand, by the slow increase of the salt concentration, which raises the energy of binding in the parallel position. Finally, we found uniform areas of about 0·1 mm in diameter, arranged in a homogenous lattice (Fig. 16). This means that some thousands of crystals are arranged in rank and file, with an incessant thermal motion, the particles twinkling brilliantly in their places – a very fascinating appearance indeed.

The grouping is to be considered as a crystal, since it has a three-dimensional periodicity, each elementary crystal leaflet being situated above one in the lower rank. This is to be expected from the fact that a rank, consisting of many leaflets, has as a whole not sufficient thermal energy to get out of the energy minima of its position. The observations on single pairs (Hachisu & Furusawa, 1963) show the 'pile formation' very neatly. The two lattice periods in the plane are easily measured in the microscope as $a=1{\cdot}1\mu$ and $b=3{\cdot}5\mu$. The perpendicular period c is certainly less than 0·1μ, the result obtained neglecting the thickness of the crystal leaflets.

It is clear that the periodically striated layers must act as optical gratings of 7300 and 23000 lines per inch. Indeed, the corresponding interferences can be observed macroscopically as brilliant coloured dots.

In contrast to the strong colour difference of the polarized reflexion in the case of ferric chloride hydrolysate, tungstic acid does not show any noticeable difference. This is to be expected, since the birefringence for the two vibrations parallel to the leaflets is only $2{\cdot}26-2{\cdot}24=0{\cdot}02$. The refraction of the vibration perpendicular to the leaflets is 2·09. Since the thickness of the leaflets is less than 0·1μ, the path difference is $0{\cdot}2\times0{\cdot}02\mu=0{\cdot}4$ mμ, a difference too small to be observed.

Conclusion

The observations described show unmistakably that a phase may be composed of two phases of smaller homogeneity regions. In particular, water layers, thick enough to be considered as water phase, may include small crystals or other particles aggregated to supercrystals or a smectic, nematic or amorphous superphase, according to the geometrical characteristic of the particle shape and the concentration.

The forces producing the superphase are certainly based upon the surface charges and double layers. The particles included in the water may be macro or giant molecules, viruses or perhaps even larger elements such as bacteria.

The existence of long-range forces is essential to the 'supercrystallization' and other formations of superphases. Certain aggregation types as, for instance, the dense packing of spheres or a fiber structure, may occur also in the dry state, without the possibility of a phase equilibrium, as the result of capillary contractions during drying or by dense coagulation. Such objects, not corresponding to a thermodynamic equilibrium,

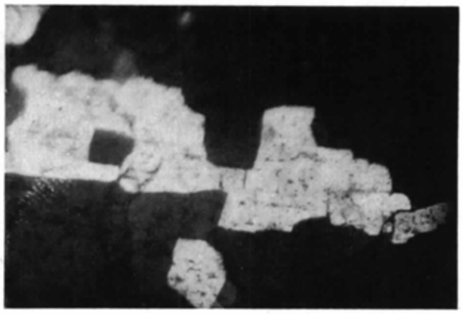

Fig. 11

Fig. 12

Figs. 11 and 12. The same as Figs. 9 and 10. Perpendicular twin borders; strong yellow filter, dark parts green, light parts yellow (× 300).

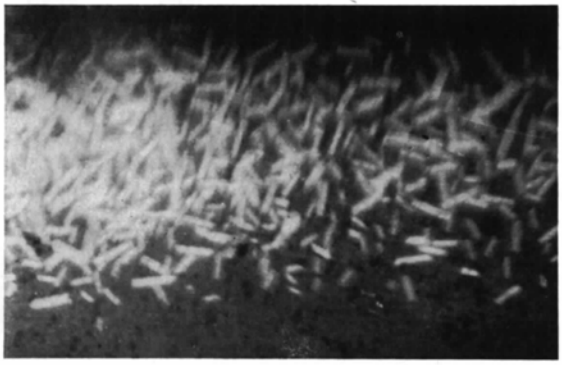

Fig. 13. $FeCl_3$ hydrolysate, isolated crystals, light vector parallel to the short side, brighter reflexion yellow, darker green (× 300).

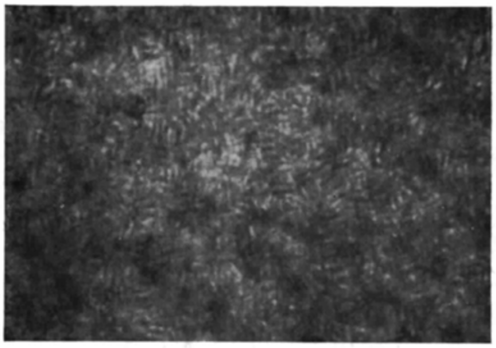

Fig. 14. Tungstic acid, smectic phase of higher order, reflected light red of the first order, not polarized (× 730).

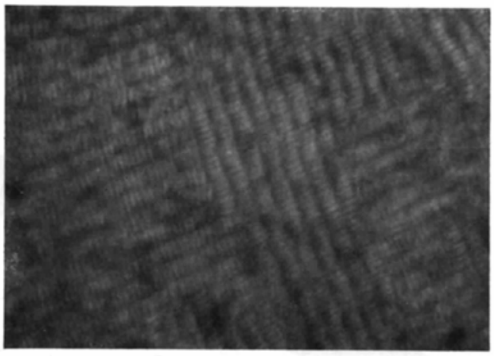

Fig. 15. Tungstic acid crystals of higher order, twinned, unoplarized, reflected light green first order (× 730).

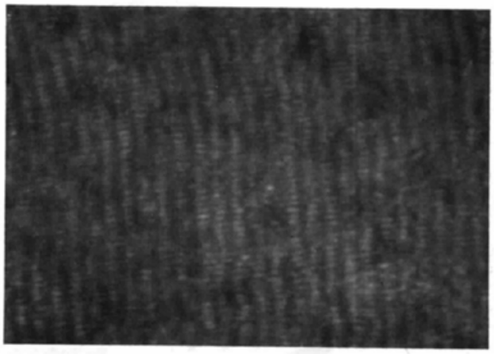

Fig. 16. Homogeneous crystal of higher order; as Fig. 15.

Figs. 11 to 16. Crystalline phases of higher order.

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are not to be considered as crystals or as nematic phases *etc.*

Considering the relatively thick water layers in the phases of higher order, probably permitting only the transmission of rather coarse asymmetries, it appears to be doubtful whether one could expect to find many space groups other than $Fm3m$ (O_h^5), $Pmmm$ (D_{2h}^1) or $P6/mmm$ (D_{6h}^1).

In the case of tetragonal leaflets, for example, the transition energy smectic $\rightleftharpoons$ tetragonal is probably too low to allow for the existence of the corresponding crystals of the space groups $P4/mmm$ (D_{4h}^1). Special types of aggregation may then be produced by long range forces on account of geometric reasons only or of shape anisotropy with one or two (equal or different) dimensions comparable to the distance. The other kinds of asymmetry (Zocher & Török, 1953, 1954) may appear at short distances in one, two or all three directions, when the forces between surface charges and counter ions pass into the normal van der Waals forces. In spite of this restriction, the long range forces involved in the formation of superphases may be important in the formation of biological structures too.

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The Absolute Atomic Scattering Factor of Iron

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X-ray intensity measurements of the 110 reflexion from a carbonyl iron powder, using monochromatic Mo $K\alpha$ radiation, were carried out on an absolute basis by direct intensity measurement of the incident beam. Effects of preferred orientation, porosity, and surface roughness were shown to be negligible. No contamination of specimens was found during storage for over one year under normal laboratory conditions. The absolute experimental scattering factor, $f(110)$, of iron was found to be only 1·7% lower than the theoretical value for a free atom in the ground state. By combining this result with relative measurements made by one of the authors (T.P.), it was shown that the difference completely vanishes at $\sin\theta/\lambda = 0{\cdot}5$ Å^{-1}. This result contrasts with the measurements of Batterman, Chipman & DeMarco.

Introduction

In recent years, X-ray diffraction measurements have been undertaken to obtain information about the electron distribution in the transition metals of the iron group; these metals are especially interesting because of their incompletely filled 3*d* shell. Several authors (Batterman, Chipman & DeMarco, 1960; Cooper, 1962) have found that on a relative scale the experimental scattering factors agree with theoretical predictions for the free atom in the ground state, but that they are about 4–5% lower on an absolute scale. How-