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OPTICS AND STRUCTURE OF THREE-DIMENSIONAL SPHERULITES

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INTRODUCTION (by J. D. H. D.)

The present paper gives the results of further investigation of artificial three-dimensional spherulites and related aggregates.[1] Financial help, received from the Penrose Fund of the Geological Society of America, to defray part of the expenses, and research facilities placed at our disposal by Stanford University, are gratefully acknowledged. Sincere thanks are tendered to Dr. G. Tunell for a critical reading of the manuscript.

Most of the laboratory work was done jointly by the two authors in the Summer of 1934. A first draft of the paper was then prepared. The manuscript, however, owing to alterations and additions, was not completed until March 1936, and Dr. Morse's illness at that time prevented him from seeing it in its final form. I, therefore, wish to take full responsibility for whatever errors or inaccuracies may be found in this paper.

Dr. H. W. Morse passed away on March 12, 1936 at the age of 63. May I be permitted to express at this place my deep admiration for his character as a man and as a scientist. His driving enthusiasm for art, literature, music, and drama, as well as for scientific research or professional duties, his serene philosophy, modesty, and kindness, made him a man of the highest type. Working with him has been a lasting source of inspiration, a thrilling experience, a great privilege. It is with a distressed emotion that I pay this tribute to his memory and express my profound gratitude for all I owe him.

METHOD OF PREPARATION

Artificial spherulites and related aggregates are prepared by allowing a concentrated solution of one salt to diffuse into a gel containing a dilute solution of another salt able to combine with the first by metathesis, and to form a compound of slight solubility. A great many substances can be grown in spherulitic form by this process; they are mentioned in our second paper. The present article, however, deals mostly with carbonates.

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[1] Previous papers:

Morse, H. W., and Donnay, J. D. H., Calcite artificielle obtenue par diffusion dans un gel: *Bull. Soc. franç. Minér.*, vol. **54**, pp. 19–23, 1931.

Morse, H. W., Warren, C. H., and Donnay, J. D. H., Artificial spherulites and related aggregates: *Am. Jour. Sci.*, vol. **23**, pp. 421–39, 1932.

Morse, H. W., and Donnay, J. D. H., Spherulite optics: *Am. Jour. Sci.*, vol. **23**, pp. 440–61, 1932.

Morse, H. W., Donnay, J. D. H., and Ott, Emil, Composition and structure of artificial spherulites: *Am. Jour. Sci.*, vol. **25**, pp. 494–8, 1933.

Morse, H. W., and Donnay, J. D. H., Artificial spherulites: *Am. Mineral.*, vol. **18**, pp. 66–7, 1933.

The gel used is gelatine in most preparations. Other gels have also been tried and proved satisfactory: agar, sodium silicate (water glass), fruit jellies, etc. Small spherulites have even been obtained in pure water by the same process of diffusion.

The best results are obtained with a commercial gelatine, previously washed and purified. However careful this process of purification, foreign ions seem to be unavoidable. The diffusion of barium chloride into a gelatine containing sodium carbonate usually yields a certain amount of optically positive spherulites, with low birefringence, together with negative spherulites, with high birefringence. Since only one substance should be expected from the double decomposition in progress, the other form may be thought to be due to impurities in the gelatine. This point was settled by an x-ray examination of the two forms present in different preparations; the negative one gave a powder picture identical with that of the expected carbonate, the positive one was proved to be a sulfate of the same metal (strontium, barium, lead). This explains the repeated observation that the positive form is more frequent in preparations obtained in a gel containing a higher percentage of gelatine. Gels ranging from 2 *per cent.* to 40 *per cent.* in gelatine content have been used; the higher the gelatine content, the more abundant were the positive spherulites, because of the larger amount of impurities in the gel.

An aqueous solution of gelatine, containing SO_4 ions, might be expected to precipitate, say, barium sulfate when a solution of barium chloride is allowed to diffuse into it. This was found not to be the case; the sulfate precipitates only in the presence of a carbonate in the gel (action of a protective colloid?).

The range of concentration of the two salts present may vary somewhat. We used 0.1N to 1.0N for the diffusing solution and 0.02N to 0.05N for the salt in the gel. The gel is allowed to set in a tube, placed vertically, and the concentrated solution is poured over it. The diffusion progresses downwards. The precipitation takes place in successive layers, obeying the law of rhythmic precipitation. Slight differences are observed in the form of the aggregates appearing in the lower layers (front of the diffusion) and in the upper layers (back of the diffusion). Differences in the rate of feeding of the growing aggregates by the diffusing substance probably account for this observation.

A great variety of forms are obtained in this manner. Their longest dimension is of the order of magnitude of 100μ. They can be washed out of the gelatine, dried, and mounted for optical examination under the microscope. They are always three-dimensional objects, sometimes perfect spheres. This point needs to be emphasized because the word "spherulite" is often used in the literature to designate two-dimensional radiate crystallizations grown between glass slip and cover glass. Such spherulites actually are discs, in which the fibers radiate from the center like the spokes of a wheel. The latter have been extensively studied (Wallerant, Gaubert, Lacroix, Popoff) and it must be recognized that they afford much better material for investigation. An eminent example of this type of work is found in Boris Popoff's paper[2] on the modifications of malonamide and resorcine, whose optical properties are very carefully described and illustrated by exquisite plates.

Several papers have appeared in recent literature on the subject of three-dimensional spherulites. They seem to be of interest to a wide range of people. For instance, a botanist, A. Wieler, published an article on it last year.[3] A book by C. J. Peddle on "Defects in glass" (kindly brought to my attention by Mr. W. J. Kirkpatrick) devotes a number of pages to descriptions of spherulitic crystallizations in industrial glasses,[4] which will be of interest to all geologists acquainted with the paper by L. V. Pirsson dealing with spherulites in an artificial lava flow.[5]

Description of Some Typical Forms

In the preparation of artificial three-dimensional spherulites by diffusion and metathesis in gelatine and jellies, a large number of apparently different types of crystalline aggregates have been found, either alone or along with regular spheres. These aggregates assume the most capricious forms and, at first sight, seem to justify the view taken by those crystallographers who regard such unusual crystallizations as accidental. In his book *Trachten der Kristalle*, Tertsch writes:

> We shall not consider here spherulites, ice-forms, crystal threads or hairs, sinter forms, and the like, since in these cases we have to deal with aggregates, whose external appearance (*habit* in the inexact sense of the term) is not a result of forces innate in the individual crystals, but a consequence of the more or less accidental aggregation of numerous individuals.

This statement is representative of a fairly common attitude towards aggregates.

Although it may possibly be true that some of the forms mentioned by Tertsch actually are accidental in origin, careful observation of our preparations shows convincingly that most, if not all, of our artificial aggregates belong to a well defined type of crystallization. The latter is

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[2] Popoff, Boris, Sphärolithenbau und Strahlungskristallisation: *Latv. Farm. Žurn.*, **1934**, pp. 1–48, February 1934.

[3] *Kolloid-Zeitschrift*, vol. **70**, p. 79, 1935.

[4] Published by Glass Publications, Ltd., Talbot House, Arundel Street, Strand, *London* W.C.2. **1927**,

[5] *Am. Jour. Sci.*, (4), vol. **30**, p. 97, 1910.

characterized by sub-radiate to radiate arrangement of fibrous units whose component particles have the triperiodic crystalline structure.

The various forms we observed differ only from each other by their external shape, which is conditioned by the number of fibers entering its composition, that is to say by the more or less advanced stage of growth.

Sheaves.—Certain forms are bundles of fibers, somewhat divergent at both ends. We call them sheaves. They occur in preparations of a large number of substances (barium and strontium carbonates, calcium oxalate, etc.).

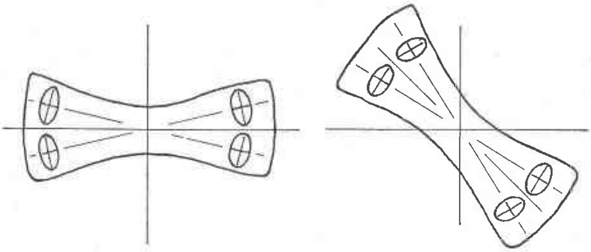

FIG. 1 FIG. 2

FIGS. 1–2. Behavior of a sheaf between crossed nicols. Sheaf in parallel position with respect to the nicols, in Fig. 1; sheaf at 45° to the nicols, in Fig. 2.

This is one of the first steps toward a radiate structure. When such an aggregate is examined between crossed nicols, a broad dark cross appears when the length of the sheaf is placed parallel to the vibration direction of one of the nicols; the four quadrants are faintly visible, they compensate as do negative spherulites (in the case of carbonates, *e.g.*), interference colors going up in two opposite quadrants and down in the other two quadrants. When the stage is rotated until the sheaf has its elongation at 45° to the nicols, the black cross disappears and so do the quadrants. The whole aggregate shows either addition or subtraction as the test plate is inserted. The sign of its elongation is negative, as should be expected from the preceding test in parallel position. This behavior is easily explained (Figs. 1 and 2).

When the sheaf lies in parallel position on the stage of the microscope (Fig. 1), the ellipses cut by a horizontal plane in the index ellipsoid of the negative fibers, although very slightly inclined on the sheaf axis, are inclined in opposite directions with respect to the ellipse of the test plate. In other words, the ellipses of the fibers have their major axes either almost parallel or almost perpendicular to the major axis of the ellipse of the test plate. Addition and subtraction, respectively, will take place, although the effect is not as clearly marked as it would be if these fiber ellipses were at 45° to the principal directions of the nicols (as is the case in the quadrants of the *spherulitic figure*).[6] Still it is sufficient to be discernible.

When the length of the sheaf lies at 45° to the nicols, the ellipses of the fibers have their major axes parallel or almost parallel to one of the axes of the test plate ellipse. Hence, either addition only (as in the case of the Fig. 2) or subtraction only will take place. This can also be visualized if the half sheaf be considered as a detached sector of a complete spherulite. In the first sketch (Fig. 1) the sheaf behaves like a horizontal diametral region (EW diameter) of the spherulitic figure (hence the cross and quadrants); in the second sketch (Fig. 2) the sheaf behaves like the central part of two opposite quadrants (NW and SE) of the spherulitic figure (hence the uniform addition of colors).

The interference colors of the two ends of the sheaf and also the movement of the dark lines when the quartz wedge is inserted (with monochromatic light) indicate that the sheaf bulges at both ends and permits one to obtain a fairly good idea of the external shape (the black lines in the wedge test are like moving "contour lines" giving approximately the thickness at each point).

Opening sheaves.—Such forms are found in barium carbonate and other substances, but are best shown in our preparations of calcium oxalate, where all degrees of "opening" of the sheaves may be seen.

Barium carbonate preparations in which widely opened sheaves occur also contain doublets and spherulites. The doublets look like two portions of spheres attached together.

The interference figure of the opened sheaves, obtained in parallel light, is very similar to that of a perfect spherulite. The more "open" the sheaf, the more striking the resemblance.

Near-spheres.—A widely opened sheaf gives the appearance of a sphere. Viewed under the microscope, it looks like a circle with a line drawn across a diameter, as it were, showing the region where the two growing ends of the sheaf have met.

In many cases, the result is a "doublet," in which the external shape of the two halves is close to spherical; these are viewed as two portions of circles united by a common chord, the size of the two portions being either the same or slightly different, the length of the chord being more or less different from a diameter.

It should be explicitly stated at this point that the words "opening sheaves" and the like, used in the foregoing descriptions, are not to be

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[6] The use of this term has been suggested in our third paper to designate the interference figure of a spherulite, obtained in parallel light and between crossed nicols. The figure consists of concentric rings of equal retardation and a dark cross; it is analogous to the convergent light figure exhibited by a uniaxial crystal cut perpendicularly to the optic axis; the law of spacing of the rings, however, is different.

taken literally. No actual "opening" takes place in the sense of fibers moving apart from one another; the apparent opening is due to further growth of new fibers at an angle to the old ones.

A series of sketches (Fig. 3) indicate the more common forms observed in the preparations.

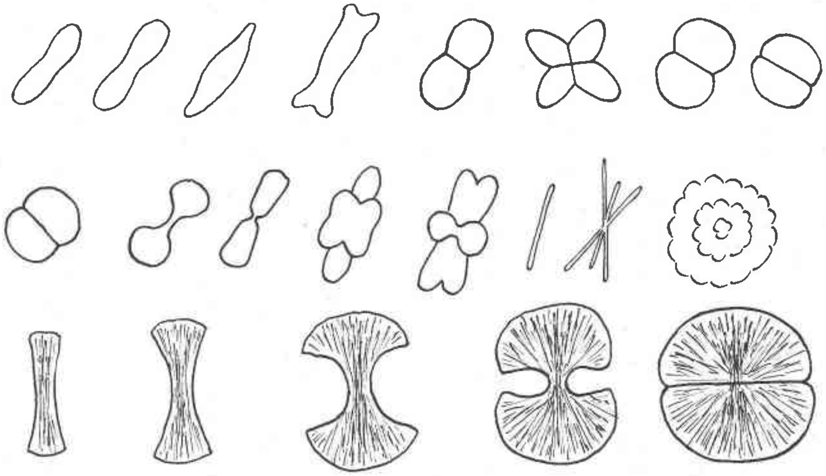

Fig. 3. Sketches of the more common forms observed in the preparations.

Mechanism of Formation of Spherulitic Structures

When one tries to visualize the process of formation of spherulitic aggregates, the first idea that naturally comes to one's mind is that a spherulite must grow by simultaneous crystallization of fibers radiating from a common center in all directions with equal speed. Such a mechanism would obviously lead to a spherical shape of the aggregate at every moment during the growth. It is a "working hypothesis" in the sense that it will account for the phenomena observed on "perfect spherulites," that is to say those spherical aggregates which, in parallel light between crossed nicols, exhibit the "spherulitic figure" with ideal perfection. None of our observations can invalidate this hypothesis as a possible mechanism for such truly spherical aggregates. The explanation, however, cannot apply to the other forms described (sheaves, doublets, and the like). The growth of the latter would have to be explained by some entirely different process. Hence it would follow that the same chemical compound, which is found to assume different shapes in the same preparation, could almost indifferently adopt two (or more) different mechanisms of aggregate growth under apparently identical

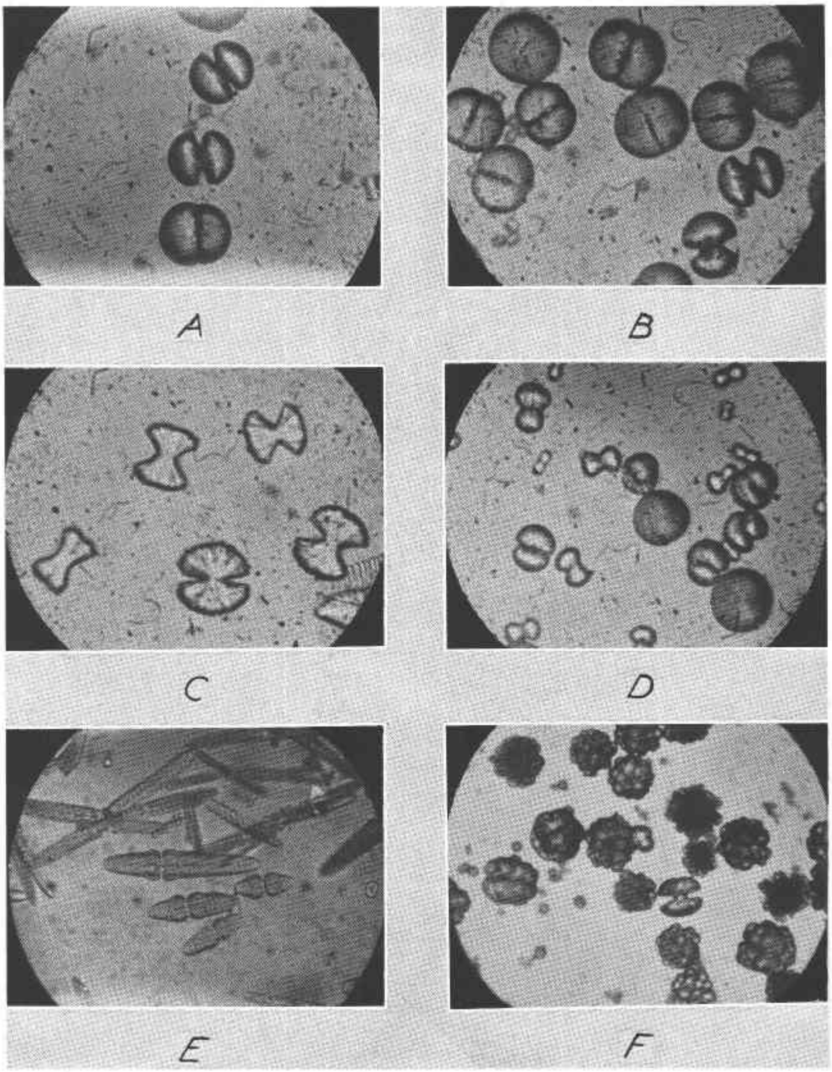

Plate I

A—Strontium carbonate, widely opened sheaves or near-spheres. ×295.

B—Strontium carbonate, same preparation as A. Mostly near-spheres and spheres showing the "waist line". Note that the size of the aggregate increases with the perfection of the sphere. ×295.

C—Calcium oxalate forms, showing gradational transitions between sheaf and near-sphere. Note how further growth results in "opening" the sheaf like a double fan. Also note that the size of the aggregate increases as the "opening" progresses. One of our best photographs to substantiate our hypothesis as to the formation mechanism of such aggregates. ×295.

D—Barium carbonate, similar forms. ×295.

E—Barium carbonate, slender sheaves and doublets of several shapes, more or less elongated. The internal structure is fibrous and radiate. ×70.

F—Barium carbonate forms, resembling mulberries. Although the external shape is rather irregular, only roughly spherical, the forms also belong to the general class of radiate aggregates. ×96.

experimental conditions. This objection to a hypothesis of "isotropic growth" may not be irrefutable, yet it seems to offer a real difficulty.

Forms such as those found side by side in one and the same preparation of calcium oxalate (Fig. C, Plate I) can be interpreted as successive stages of spherulitic growth. The five aggregates shown in the photograph exhibit various degrees of "opening" of the sheaf and the more "opened" sheaves are larger than the less "opened" ones (in the ratio of 9 to 7, as measured on the two extreme cases in the photograph). Although these two facts combined will probably be considered sufficient by most geologists to warrant the interpretation of the various forms as successive stages, it is well to keep in mind just how much experimental evidence sustains the inference. We do not wish to revive the polemics that once divided "creationists" and "evolutionists," and shall simply state that, even if the inference be not fully substantiated, it at least is a working hypothesis leading to an unexpected, yet plausible, formation mechanism, valid for both sheaves and spheres.

In this conception the crystallization radiating from a center or nucleus must be considered as being possible in a limited solid angle only. We have no data on the angle of aperture of such a cone of radiating fibers, but it is obvious that a 360° aperture (crystallization radiating in all directions) is incompatible with the formation of sheaves. The latter is best explained by assuming an acute angle of aperture for the cone of possible radiating crystallization. The direction in which growth starts can reasonably be expected to be conditioned by the crystallographic properties of the substance. It should be the direction of fastest growth. This would account for the early stages of growth (fibers and fiber bundles). It must also be postulated, as a characteristic property of radiate crystallization, that every point at the surface of the growing cone of fibers can act as a new starting point for further radiating growth, the spatial extent of the latter being controlled by the possible angle of aperture of the cone, on the one hand, and by the mechanical obstruction of preëxisting fibers, on the other. As growth proceeds new fibers will appear to "branch out," that is to say will be formed at an angle to the older ones, and radiating from points already reached by the latter. The sheaf, hence, "opens" at both ends, in fan-like manner, until spherical shape is reached or, at least, approximated (doublets, near-spheres), when the feeding of the crystallizing aggregate gives out.

The shape of the intermediate stages will depend on the angle of aperture of the radiating crystallization. Figure 4 shows one-half of a meridional section of a growing sheaf, where the angle of aperture is arbitrarily taken equal to 50° for the cone of first radiation and equal to 14° for the successive radiations. Dashed curves indicate successive outer surfaces. The velocity of growth is taken as constant (the same from all centers). When growth has proceeded sufficiently the "drooping" fibers issuing from the two ends of the sheaf will meet along a plane perpendicular to the axis of the sheaf (Fig. 4). The external appearance will undergo a radical change at this stage, passing as it does from a bundle to a near-sphere. The outer surface may be considered to be one of revolution around the axis CD of the sheaf. It never becomes rigorously spherical, although it can approximate a sphere very closely. The reason for this is well shown in Fig. 4; the outer boundary, in the meridional section, is a curve composed of "raccording" arcs of circles with decreasing radii from the "polar regions" (at both ends of the axis of revolution) to the "equator," where the curve cusps in. The revolution surface must therefore show an equatorial constriction, which gradually becomes smoothed out (less and less reëntrant) as growth goes on. This feature has been repeatedly observed on near-spheres in our preparations. It was so striking that we used to refer to it as "the waist

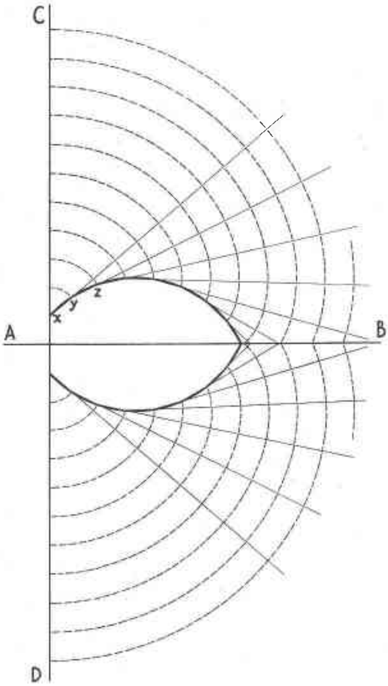

FIG. 4. Meridional section of a spherulite (one-half only) explaining the hypothesis as to its formation mechanism.

line," in informal conversation, long before conceiving any possible theoretical explanation for it.

Will the center of a completed spherulite enclose a hollow region "walled in" by the fibers coming from both ends of the sheaf and meeting in the "waist line"? This would appear to be a logical consequence of our hypothesis. The shape of such a cavity, if it does exist, is easily visualized. The successive centers of radiation X, Y, Z, · · · (Fig. 4) are immediately seen to lie on an arc of a circle, as a necesssary consequence of the mode of construction. This holds true for both the upper and the lower half of the sheaf. The lower half is the mirror-image of the upper in the equatorial plane AB. Hence the two arcs, upper and lower, have equal radii but different centers, and enclose a spindle-shaped area (shown in the meridional section, Fig. 4). Revolution of the latter around the axis CD of the sheaf generates the required surface of the cavity, which would look like the mould of a doubly umbilicated disc tapering off bluntly on its edge.

We have no experimental evidence in support of the existence of such a central cavity. If it does actually occur it must be small as compared with the size of the encasing spherulite, since in the vast majority of cases the spherulitic figure (parallel light, crossed nicols) shows no irregularity in the central region. It is more likely that the cavity is filled in by later growth. The example of calcium oxalate is suggestive in that respect since it shows (Fig. C, Plate I) that the empty space between the opening ends of the sheaf becomes narrower as growth proceeds.

Popoff's "Zweiblatt" in Three-Dimensional Spherulites

Since such transverse fibers as would be required to fill the hypothetical central cavity are not seen in the early stages (fiber bundles) they must either start growing later or else grow more slowly than the fibers parallel and sub-parallel to the axis of the sheaf. The idea of a difference in the velocity of growth is in accord with the crystallographic properties of a substance. It furthermore agrees with the experimental results obtained by B. Popoff in some two-dimensional spherulites. Popoff describes, and gives beautiful photographs of, a central region having the shape of a double leaf, which he calls "Zweiblatt."

The Zweiblatt is of course a plane figure, since the preparation is grown between glass slip and cover glass. Popoff calls attention to this fact and suggests that the central body may have a surface of revolution, so that the "double leaf" (Zweiblatt) seen in his preparations would be the meridional section of a "double bud" (doppeltknospenförmige Gestalt). The double bud is conceived as generated by the revolution of the double leaf around its long axis (AB, Fig. 5). Notice that the surface generated by the revolution of the double leaf around an axis CD, perpendicular to the length of the leaves, is a doubly umbilicated disc similar (although not identical) to the one we discussed above as a consequence of our hypothesis of a limited, constant angle of possible radiating crystallization.

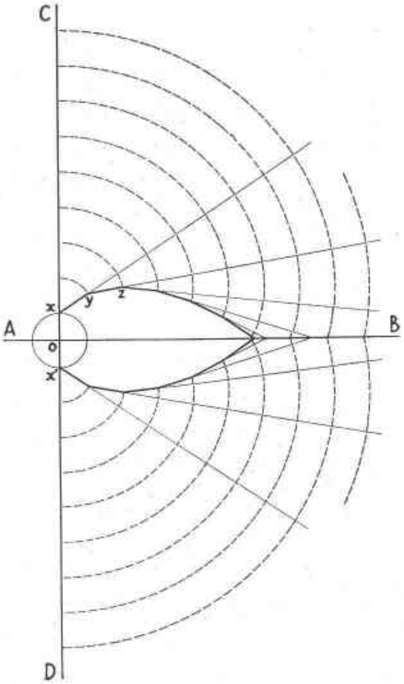

Fig. 5. Popoff's construction of the "Zweiblatt" curve (one-half only).

Popoff's elegant explanation of the shape of his Zweiblatt rests on the following assumptions: (1) The nucleus of the spherulite first grows in all directions with equal speed v_1 until a sphere is formed; the radius of this sphere may be extremely small but cannot be zero, otherwise the construction of the Zweiblatt curve (see above) would fail. (2) Two points, located at the extremities XX' of a privileged diameter of the initial sphere, then act as center points for radiating crystallization, which proceeds at a speed v_2, slightly greater than v_1, while the initial sphere keeps on growing radially at speed v_1. The crystallographic orientation of the nucleus determines the diameter XX' as that of fastest growth. (3) Every point reached by radiating crystallization is

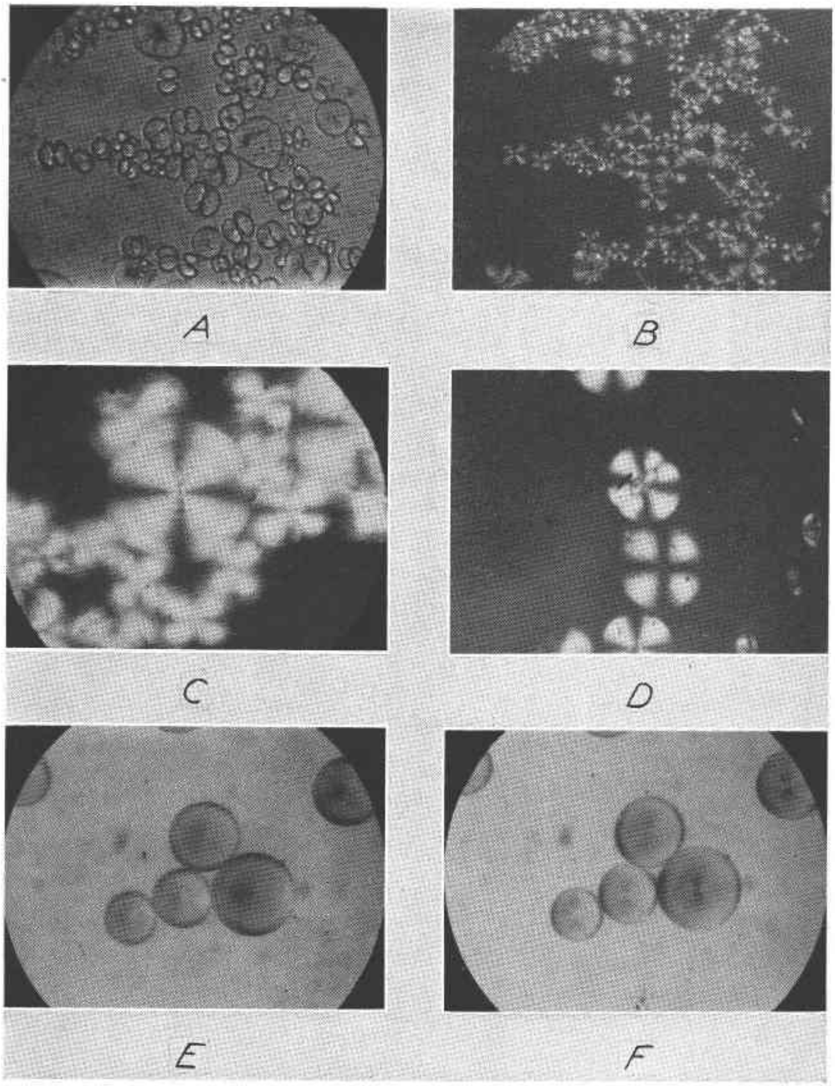

Plate II

A—Calcium carbonate forms, ranging from more or less opened doublets to near-spheres and spheres. Note how the "waist line" persists through all stages; some spheres, otherwise perfect, show it as a diameter. Notice one hollow radiating aggregate (such forms have been observed by Cross in natural spherulites). ×167.

B—Same as A, crossed nicols, parallel light. See gradations between perfect spherulitic figure and interference figures shown by doublets.

C—Calcium carbonate preparation containing occasional fairly regular spherulites, but mostly near-spheres and doublets. Note effect of external shape on interference figure and fibrous radiate structure, apparent from spherulitic cross. Crossed nicols, parallel light. ×167.

D—Strontium sulfate. The near-sphere in center shows the "zweiblatt." Crossed nicols, parallel light. ×500.

E—Barium carbonate. Perfect spherulites showing the optical distortion. Lower nicol only, tube somewhat lowered. ×96.

F—Same as E, upper nicol only, tube somewhat lowered. The distortion is seen in opposite diameters, in photos E and F.

capable of acting as a new starting point for further radiation (this point was proved experimentally by Popoff). Radiating crystallization need not proceed in all directions, but only in a cone of "sufficient aperture." Popoff's construction yields a curve very similar to the observed Zweiblatt (see Fig. 5). It is as follows. From X as a center strike an arc with radius v_2, from O as a center strike an arc with radius $2v_1$, the intersection of the two arcs is a point, Y, of the curve. Likewise Z is the intersection of an arc struck from Y as a center with radius v_2 and another arc from O with radius $3v_1$. And so on. Symmetrical branches of the curve will appear in the four quadrants and eventually meet on line AB.

From the construction just described, it appears that the central body of a three-dimensional spherulite is more likely to be a "disc" than the "double-bud" suggested by Popoff.

One of our photographs of strontium sulfate (Fig. D, Plate II) shows a doublet exhibiting the near-spherical shape, the equatorial constriction, and a central body. As far as we know, this is the first example of a central body in a three-dimensional spherulite. Compensation by means of the usual 1st order red plate indicates that the outer portion of the spherulite is optically positive, whereas the center is optically negative. It follows that the orientation of the crystalline particles along the fiber is different in the central body and in its encasing near-sphere. This difference of fiber orientation is known in two-dimensional spherulites, where it can be easily proved. In our case, however, we must reckon with another possibility, namely that the core be strontium carbonate and the shell strontium sulfate. The two salts, as has been explained above, have been found to occur together in the same preparation. We have been unable to rule out this last explanation; the diameter of the spherulite with a central body being 20 microns. We can only report the suggestive similarity of the central body shown in our photograph with Popoff's Zweiblatt.

We will now turn our attention to some of the optical phenomena displayed by spherulitic aggregates.

INTERFERENCE FIGURE IN PARALLEL LIGHT

As to the interference figure shown by the aggregates in parallel light between crossed nicols, it varies of course with the external shape, but the phenomenon is essentially the same as in a perfect spherulite. The "rings" of equal retardation are not as perfectly circular, but they are still visible in a great many cases. The "sign" of the figure is obtained as in a spherulite by examining the motion of the rings when a quartz wedge is inserted.

In a previous paper (*Spherulite optics*), we have shown that the movement of lines in the center of a spherulitic figure is the same as in the interference figure of a uniaxial crystal cut perpendicularly to the optic axis, and viewed in convergent light. This remark was sufficient to give an idea of the phenomenon in the case of perfect spheres. Since the phenomena are less plainly displayed in aggregates whose shapes depart sometimes widely from the spherical form, the analogy with the uniaxial convergent light figure becomes rather remote.

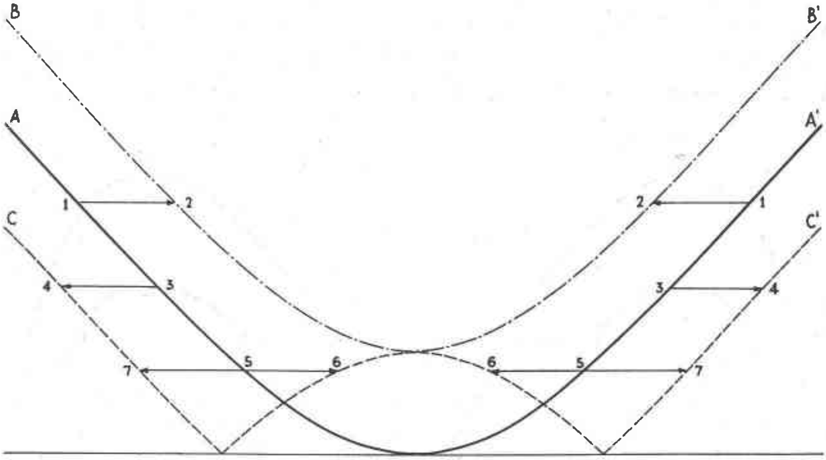

FIG. 6. Meridional section of the retardation surface in the interference figure (crossed nicols, convergent light) of a uniaxial crystal cut perpendicularly to the optic axis (curve AA′). The same, after inserting a test plate in additive position (curve BB′). The same, after inserting a test plate in subtractive position (curve CC′). Motion of isochromatic rings shown by arrows, when a quartz wedge is used instead of the test plate.

The retardation curve[7] for the uniaxial figure is shown in figure 6. A uniaxial crystal is cut normally to the O.A. and examined in convergent light. The concentric circles are cut by a diametral line; the graph shows the retardation at each point along that line, *i.e.*, the value of the retardation (path-difference) is plotted against the distance from the center of the interference figure. The curve obtained has approximately the shape shown in Fig 6. The retardation increases from zero at the center of the figure, symmetrically on either side, as shown by

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[7] The equation of this curve can be found in our third paper, equation (13). Its derivation was based on the known theorem: the interference figure is similar in shape to the figure obtained on the upper face of the crystal slice if the light source is supposed to be a point on the lower face of the slice.

curve AA′. When a test plate is inserted in additive position, the curve of retardation becomes BB′, since the retardation is increased at each point by the same amount, namely the retardation of the test plate. When the same test plate is used in subtractive position, the retardation is shown by the curve CC′. Note that retardations are always considered in absolute value so that there will now be a ring of zero retardation from which the retardation increases both outward and inward. The motion of the lines when a quartz wedge is inserted is shown by the arrows on the graph; in the case of addition, the ring numbered 1 shrinks into 2 (all rings shrink); in the case of subtraction, the outside rings expand (3, for instance, goes into 4), but the inside rings move both in and out (ring 5 contracts to 6 and expands to 7).

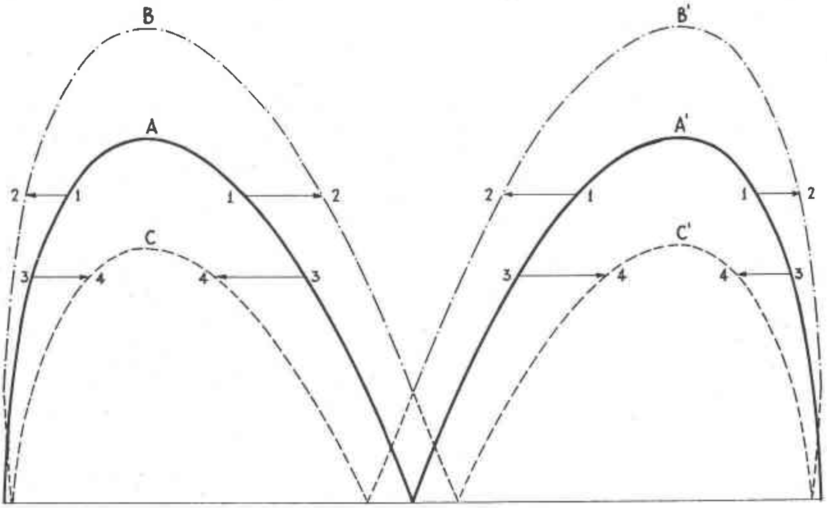

Fig. 7. Meridional section of the retardation surface in the spherulitic figure (crossed nicols, parallel light) of a perfect spherulite (curve AA′). The same, after inserting a test plate in additive position (curve BB′). The same, after inserting a test plate in subtractive position (curve CC′). Motion of isochromatic rings shown by arrows, when a quartz wedge is used instead of the test plate.

The retardation in a perfect (spherical) spherulite will now be considered (Fig. 7). The curve AA′ shows the retardation across a diameter in a spherulite. The two maxima indicate the ring of maximum retardation (see third paper). When the wedge is inserted in additive position, the two concentric rings of retardation 1 move away from the ring of maximum retardation; when the wedge is used in subtractive position, the two rings move towards the ring of maximum retardation (for instance, rings marked 3 go into 4). The inner rings (smaller than the ring of maximum retardation) shrink or expand like those of a uniaxial figure; the outer rings show the opposite effect.

If one keeps the above observation in mind, it is fairly easy to understand the figures shown by irregular (not spherical) aggregates, in which the line of maximum retardation is not a perfect circle and does not lie at exactly the same distance from the center as in a spherulite.

Optical Distortion of the Circular Outline of a Spherulite

Perfect spherulites (perfect in the sense that they are very close to spherical), such as we have obtained in our artificial preparations, appear as true circles when viewed under the microscope in ordinary light.

In polarized light, however, certain spherulites show an appreciable amount of shading at the two ends of the NS (or EW) diameter (Figs. E and F, Plate II). This effect results in the appearance of two dark crescents giving the optical illusion of a shortening of the diameter that connects them. The outline of the perfect spherulite, in such cases, is no longer circular but elliptical. The optical effect is due to the radiate structure of the spherulite since the latter is the cause of the fact that the plane polarized light (vibrating NS, for instance) will be transmitted through the spherulite with different velocities along the NS and the EW diameters. In other words, the index of refraction effective at the ends of the EW diameter is different from that effective at the ends of the NS diameter. Depending upon the value of the refractive index of the mounting medium, the relief at the ends of the NS and EW diameters will be more or less different, hence the observed effect.

It is clear that the Becke test may give opposite results at the ends of the NS and EW diameters, if the index of the mounting medium is intermediate between the two indices of the spherulite effective at these two places. This has already been observed by Spangenberg[8] for natural spherulites. This effect was thought to be susceptible of application to the measurement of the indices of the spherulitic substance by Spangenberg, who did not make any discrimination between the indices of the fiber and those of the substance constituting the fiber. The method, however, will only permit the determination of fiber indices; it can give no indication as to the indices of the substance entering the constitution of the fiber.

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[8] *Centralbl. Min.*, **1920**, pp. 406–14.

The facts of observation.—Consider artificial spherulites of strontium carbonate. The identity of the spherulitic substance with strontianite has been proved by an earlier x-ray study (see fourth paper). Strontianite is slightly biaxial but can be considered uniaxial for our purpose; its indices (as given by Larsen) are: $n_\epsilon = 1.520$, $n_\omega = 1.667$. The fiber indices have been measured on splinters of the spherulites. The first measurements (previously reported) gave: $n_e = 1.516$, $n_o = 1.593$. The values of fiber indices apparently are apt to vary for, on repeating the measurements, we found: $n_e = 1.5095$, $n_o = 1.5955$. The following experiments, therefore, should be made on spherulites from the same crop, whose fiber indices have been previously determined. The spherulites are examined in different mounting media, in polarized light (lower nicol only, light vibrating NS).

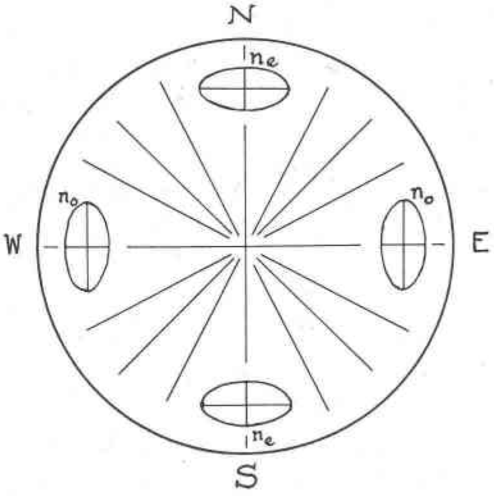

FIG. 8. Outline of a spherulite, as viewed under the microscope. Explanation of the optical distortion observed when a spherulite is embedded in a liquid whose refractive index is intermediate between the fiber indices.

Canada balsam.—Embedded in Canada balsam (index *ca.*1.54), the spheres show the following effects.

When the tube of the microscope is raised, the Becke line goes in the spherulite at the ends of the EW diameter and out (*i.e.*, towards the medium) at the ends of the NS diameter. The ingoing line (EW) is followed by the dark crescents mentioned above. When the tube is lowered, the effect is reversed; the Becke line goes out EW and in NS, again followed by the dark crescent in the latter case.

The explanation of these observations is found in the following sketch

(Fig. 8), which shows the effective ellipses of the fibers of the spherulite. By "ellipse" we mean the ellipse cut through the ellipsoid of indices by a plane section parallel to the wave-front. The fibers are negative ("length fast"), hence the effective index, for light vibrating NS, is n_e at the ends of the NS diameter and n_o at the extremities of the EW diameter. Now the index of Canada balsam is higher than n_e and lower than n_o; hence the observed effects.

That the fiber indices, not the crystal indices, are the important factor in the explanation must be proved, since in the case of Canada balsam the index of the mounting medium is comprised between the two crystal principal indices (n_ϵ and n_ω) as well as between the two fiber principal indices (n_e and n_o), and no conclusion can be drawn as to which are effective.

Index liquids.—A first liquid is chosen, whose index lies between the principal indices of the crystal, though not between those of the fiber. Let n be the index of the liquid. We have, in this case $n_e<n_\epsilon<n_o<n<n_\omega$.

The Becke test shows no difference in the behavior of the NS and the EW diameters. On raising the tube, the bright line goes out of the spherulite; on lowering the tube, the fringe goes in; and in both cases the motion of the line is concentric to the outline of the spherulite. There is a difference of relief, higher NS than EW, in our experiment because our liquid has an index equal to 1.62 and consequently $n-n_e>n-n_o$.

A second liquid is then used, whose index (designated here by n') is such that we have the relation $n_e<n'<n_\epsilon<n_o<n_\omega$. In this case, the index of the liquid lies in between the fiber indices, but not in between the crystal indices. If the fiber indices are the controlling factor, the difference in the Becke test according to the direction (either NS or EW) of the diameter should be observed here. This is found to be so. When the tube is raised, the Becke fringe goes out NS and in EW; the reverse appears when the tube is lowered. In both cases, the black crescents follow the bright line in its inward motion.

Upper nicol only.—Similar effects are obtained when only the upper nicol is used. Strontium carbonate spherulites, embedded in Canada balsam, show a Becke line moving towards the spherulite NS when the tube is raised, EW when it is lowered. This is the reverse of what has been observed when the lower nicol only is used.

The explanation is that light is polarized by the spherulite. Along the NS diameter, for instance, the ordinary light is polarized in two directions at right angles, one NS (parallel to the fiber axis), the other EW (normal to the fiber axis). The same is true for the EW diameter of the spherulite. The upper nicol only lets EW vibrations through; hence, n_o for the NS diameter and n_e for the EW diameter. It will be remembered that the effective indices, with the lower nicol only, were n_e and n_o, respectively, for the NS and the EW diameters of the spherulite.

When other mounting media are used, similar observations can be made. With a liquid of index 1.66, for example, the effect is the same as with the lower nicol only, in the sense that the Becke test is concentric; the higher relief, however, is now EW $(n-n_e)$ instead of NS.

Practical conclusion.—The fiber indices can be approximately determined by embedding the spherulite in various media. As long as the motion of the Becke fringe is different EW and NS, the index of the medium lies between the principal indices of the fiber. When the Becke test is concentric to the outline of the spherulite, the index of the medium is either higher or lower than both principal indices of the fiber.

Such tests can have no bearing on the determination of the indices of the crystals constituting the fibers.

SPHERULITIC STRUCTURE THEORY

The spherulitic figure, observed in parallel light between crossed nicols, is susceptible of a quantitative explanation (see previous paper on *Spherulite optics*). This explanation rests upon consideration of the splinter (fiber or fiber-bundle) as the unit of the radiate structure.

The value of the retardation R in a spherulite is here assumed to be directly proportional to the diameter $2r$ of the sphere; the ratio $R:2r$ is plotted for each ring (monochromatic light) against the radius of the ring. This yields the experimental curve. A theoretical curve is obtained from the assumption that the fiber-bundle (splinter) is a uniaxial entity with its own indices; the theoretical values of $R:2r$ are functions of these fiber indices only; the latter are measured by immersion methods and their values, introduced in the expression of the retardation, permit plotting of the theoretical curve, which is found to check with the experimental curve.

This treatment is the first step in the explanation of spherulitic structure. All the assumptions made in the theoretical treatment are justified by facts. The radiate structure is seen in crushed spherulites, which break into sectors; it is also observed between crossed nicols in parallel light, since it is the cause of the spherulitic dark cross. That the fiber-bundle should behave like a uniaxial entity, with its optic axis parallel with the elongation of the fibers, is justified by the fact that no third index can be measured across the fiber, so that both principal indices normal to the elongation of the fiber must be equal or sufficiently close to each other to warrant the assumption; the fiber structure, as revealed by x-ray studies, points to the same conclusion.[9] The helicoidal arrangement of crystal particles along the axis of the fiber, well known in two-dimensional spherulites, would give the same statistical average for the refractive index transverse to the fiber as a random arrangement in all directions but the fiber-length.

The treatment is quite satisfactory insofar as the fiber is considered the structural unit. The indices of the fiber, however, differ from those of the natural mineral of the same chemical composition. This discrepancy demands further explanation. The next step in the investigation should be the elucidation of the fiber structure.

Various working hypotheses.—The discrepancy between the fiber indices and the indices of the corresponding natural mineral could be accounted for by polymorphism. The fiber, in this case, would be a new modification of the known mineral. Such an hypothesis was considered. It has been disposed of by our x-ray study of artificial spherulites, which showed that the fiber is composed of the known modification.

Other explanations must now be considered. Alteration of the values of the refractive indices may be due to the orientation of the component crystals of the known mineral constituting the fiber. Since the presence of some interstitial material (water, gelatine?) has been ascertained in spherulites, form-birefringence (Form Doppelbrechung) is another factor that may be held responsible for the observed lowering of indices.[10]

Orientation of Component Crystals Along Spherulitic Fibers

The question of crystal orientation in spherulites has been studied by

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[9] Quoting Bragg, W. L.: "If a bundle of asbestos fibres is placed in the path of an x-ray beam, a pattern is obtained similar to that of an ordinary crystal rotation-photograph. Apparently the fibres all have one crystal axis along the fibre-length, while being oriented in all directions around this axis," (*Zeit. Krist.*, vol. **74**, p. 254, 1930).

[10] The values of the refractive indices of strontianite have been given, together with the values measured, by immersion methods, on fibers of strontium carbonate spherulites. Other data are as follows.

For barium carbonate spherulites,

fiber indices: $n_e=1.511$, $n_o=1.615$,
also $n_e=1.519$, $n_o=1.615$;
witherite indices: $n_\epsilon=1.529$, $n_\omega=1.6765$.

For calcium carbonate spherulites,

fiber indices: $n_e=1.485$, $n_o=1.599$,
aragonite indices: $n_\epsilon=1.530$, $n_\omega=1.6825$,
calcite indices: $n_\epsilon=1.486$, $n_\omega=1.658$.

In the above list, strontianite, witherite, and aragonite are considered uniaxial since their index ellipsoid approximates an ellipsoid of revolution. The inaccuracy resulting from the approximation is less than the errors of measurements.

Jansen.[11] His x-ray results confirm the statement of Bragg, quoted above, and justify the assumption we had used in our theory of spherulite optics, *viz.*, that the fiber behaves like an optically uniaxial entity. Jansen finds that a spherulite fiber is made up of crystals, each of which has only one direction (always the same) fixed with respect to the fiber axis; and that, except for that restriction, the crystal may have any orientation (one degree of freedom, rotational). In the cases studied by Jansen, the crystal direction that lies along the fiber axis is a crystallographic axis of the crystal. A complete theory, however, should also consider other possible cases. From an optical standpoint, all cases would be covered by considering the problem as follows:

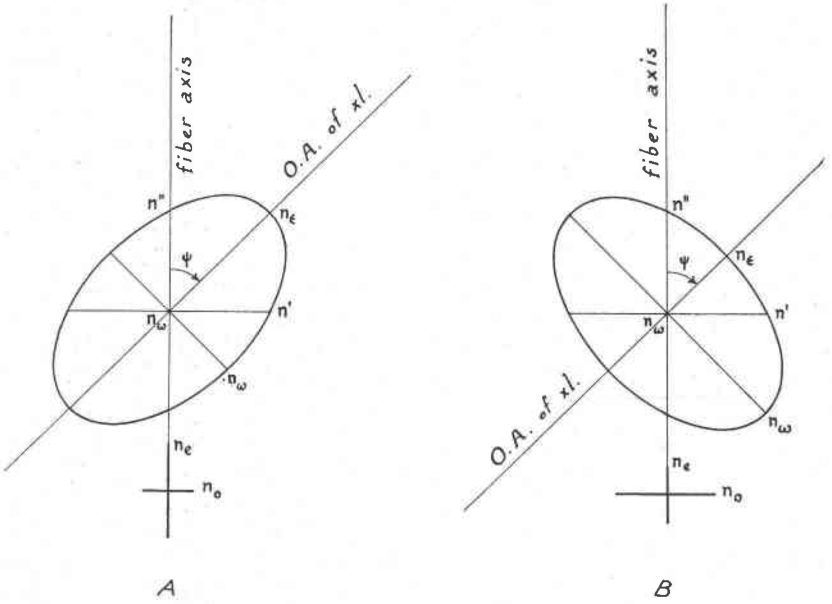

FIG. 9. Orientation of component crystals along the fiber axis. Positive crystal (A); negative crystal (B). Explanation of the relation between the fiber indices (n_e and n_o) and the crystal indices (n_ϵ and n_ω).

(1) Uniaxial crystals—the optic axis of the crystal makes an angle ψ with the fiber axis, and ψ may vary from 0° to 90°.

(2) Biaxial crystals—the direction of the fiber axis makes an angle ψ' with one of the optic axes and an angle ψ'' with the other. Both angles may vary from 0° to 90°. Optically the result is the same whether the fiber axis makes an angle ψ' with the first optic axis and an angle ψ''

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[11] Jansen, Wilhem: Röntgenographische Untersuchung über die Kristallorientierung in Sphärolithen, *Zeit. Krist.*, vol. **85**, pp. 239–70, 1933. (Bibliography of 26 titles.)

with the second optic axis, or an angle ψ'' with the first and an angle ψ' with the second. This is due to the symmetry of the triaxial ellipsoid.

Analytical treatment in the case of uniaxial crystals.—The problem is as follows. To find the indices n_e and n_o of a uniaxial fiber made up of uniaxial crystals with indices n_ϵ and n_ω, the angle between the fiber axis and the optic axis of the crystal being ψ, an angle that varies from 0° to 90°.

Consider the cross-section of the ellipsoid of the component crystal by a plane passing through the fiber axis and the optic axis of the crystal (Fig. 9). Call n'' the index parallel to the fiber axis, represented by the radius vector of the "ellipse of section" making an angle ψ with the principal semi-axis n_ϵ; designate by n' the radius vector of the same ellipse at right angles to n''. The equation of the ellipse in polar coordinates gives immediately

$$n' = \frac{n_\omega n_\epsilon}{\sqrt{n_\epsilon^2 \cos^2 \psi + n_\omega^2 \sin^2 \psi}}.$$

Using the same approximation as in our second paper (*Spherulite optics*), we may write instead of the above formula

$$n' = n_\omega \cos^2 \psi + n_\epsilon \sin^2 \psi \tag{1}$$

and we also have, in like manner,

$$n'' = n_\epsilon \cos^2 \psi + n_\omega \sin^2 \psi. \tag{2}$$

The indices of the fiber are

$$n_e = n'' \quad \text{and} \quad n_o = \frac{n' + n_\omega}{2},$$

or, after substitution,

$$n_e = n_\epsilon \cos^2 \psi + n_\omega \sin^2 \psi, \tag{3}$$

$$n_o = \tfrac{1}{2}(n_\epsilon \sin^2 \psi + n_\omega \cos^2 \psi + n_\omega). \tag{4}$$

The latter may be written as follows

$$n_o = \frac{n_\epsilon + n_\omega}{2} \sin^2 \psi + n_\omega \cos^2 \psi. \tag{5}$$

The *fiber birefringence* (or "spherulitic birefringence") is found to be, in terms of the *crystal birefringence* and the angle ψ,

$$n_e - n_o = \frac{n_\epsilon - n_\omega}{2} (3 \cos^2 \psi - 1). \tag{6}$$

This expression is obtained by means of the equations (3) and (5). Note the occurrence of the second spherical harmonic $(3\cos^2\psi-1)$, encountered in other problems in physics.

The formulae numbered from (1) to (6) hold good for both positive and negative crystals (Figs. 9, A and 9, B, respectively); the birefringence of a positive crystal is positive $(n_\epsilon > n_\omega)$, that of a negative crystal is negative $(n_\epsilon < n_\omega)$.

Discussion of equation (6).—(1) For $\psi=0$, $n_e-n_o=n_\epsilon-n_\omega$. The fiber birefringence is equal to the crystal birefringence, both in magnitude and in sign, when the direction of the crystal lying along the fiber axis is the optic axis. Example: quartzine, according to Correns and Nagelschmidt.[12]

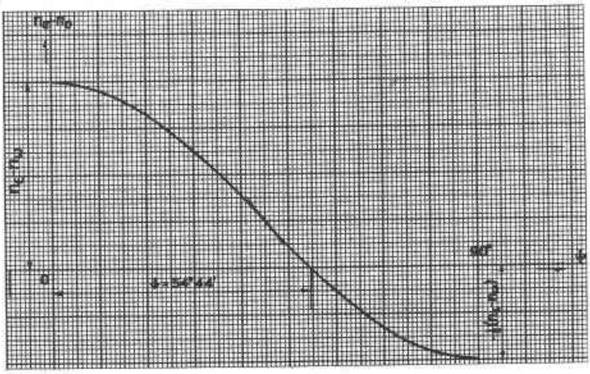

FIG. 10. Variation of the value of the fiber birefringence (n_e-n_o) with orientation of component crystals along fiber axis. The abscissa is the angle ψ between the axis of the fiber and the optic axis of the component crystal. The graph expresses equation (6), derived in the case of uniaxial crystals.

(2) For $\psi=90°$, $n_e-n_o=-\frac{1}{2}(n_\epsilon-n_\omega)$. The fiber birefringence is equal to one half the crystal birefringence and the sign is reversed when the optic axis of the constituent crystal is at right angle to the fiber axis. Example: chalcedony, where the fiber is made up of quartz crystals with either one of two horizontal crystallographic directions (*i.e.*, directions normal to the *c*-axis) oriented along the fiber length (*x*-ray results of Correns and Nagelschmidt).

(3) When the angle ψ varies from 0° to 90°, the fiber birefringence varies according to the law expressed by equation (6), passing from $(n_\epsilon-n_\omega)$ to $-\frac{1}{2}(n_\epsilon-n_\omega)$. There is a value of ψ for which the fiber bi-

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[12] Correns, Carl W., and Nagelschmidt, Günter: Über Faserbau und optische Eigenschaften von Chalzedon, *Zeit. Krist.*, vol. **85**, pp. 199–213, 1933.

refringence is zero; it is found from the condition $3\cos^2\psi-1=0$, which gives $\cos\psi=\frac{1}{3}\sqrt{3}$ and $\psi=54°44'$. This is the crystallographic angle "cube:octahedron." The physical meaning of this is that it would be possible to build up optically isotropic fibers by means of birefringent crystals, uniaxial positive or negative, of any birefringence whatsoever, under the sole condition that the angle between the optic axis of each component crystal and the fiber axis be 54°44′. This unexpected conclusion, however, is a consequence of the use of the approximate equation of the ellipse, introduced in equation (1). If the correct equation of the ellipse is used, the angle ψ for which the fiber birefringence is zero, has different values in positive and negative crystals; the two values are astride 54°44′, from which they depart but slightly in most cases. It must also be kept in mind that the present theory takes no heed of form-birefringence, the influence of which will be considered further on.

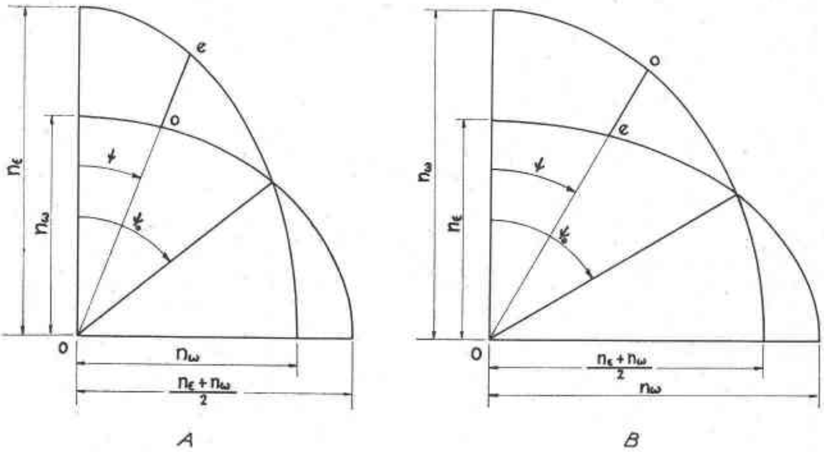

FIG. 11. A graphic way of finding the fiber indices (n_e and n_o) in terms of the crystal indices (n_ε and n_ω) and the angle ψ at which the optic axis of the component crystal is inclined to the fiber axis. Positive crystals (A); negative crystals (B).

The curve expressed by equation (6) is plotted in rectangular coordinates on Fig. 10. It gives the value of the fiber birefringence (n_e-n_o) for any angle ψ comprised between 0° and 90°. The graph holds for positive and negative crystals; in the former case, the arrow on the ordinate axis indicates its positive direction; in the latter case, the same arrow marks its negative direction.

A graphic method of finding n_e and n_o, the fiber indices, in terms of n_ε and n_ω, the crystal indices, and ψ, the angle between the optic axis of the crystal and the fiber axis, is shown in Fig. 11. Inspection of these graphs yields the following information:

In the case of positive crystals (Fig. 11, A), n_e can decrease from n_ϵ to n_ω, but can never be smaller than n_ω; n_o can increase from n_ω to $\frac{n_\epsilon+n_\omega}{2}$, but can never exceed the latter value. Likewise, in the case of negative crystals (Fig. 11, B): n_e can increase from n_ϵ to n_ω but not any more, n_o can decrease from n_ω to $\frac{n_\epsilon+n_\omega}{2}$ but no further.

The values of n_e and n_o are not independent; their mutual dependence is shown by the graphs: when one increases, the other decreases.

As to fiber birefringence, n_e-n_o, the graphs show that it can retain the sign of the crystal birefringence $n_\epsilon-n_\omega$ and decrease from $(n_\epsilon-n_\omega)$ to 0, or can have the opposite sign and increase from 0 to $\frac{n_\epsilon-n_\omega}{2}$ in absolute value. Note that the fiber birefringence can never exceed the crystal birefringence when the sign is retained, also that the fiber birefringence cannot exceed one half of the crystal birefringence (in absolute value) when the sign is reversed.

The values $n_e-n_o=\frac{1}{2}(n_\epsilon-n_\omega)$ and $n_e-n_o=-\frac{1}{2}(n_\epsilon-n_\omega)$ occur for $\psi=35°16'$ (the complement of the angle "cube:octahedron") and $\psi=90°$ respectively.

Remark.—A more exact solution of the determination of the fiber indices in terms of the crystal indices may easily be derived in the case of uniaxial crystals. In the preceding treatment, we have used the approximation generally found in text books on crystal optics.

For instance, for positive crystals:

$$n_e = \frac{n_\omega n_\epsilon}{\sqrt{n_\epsilon^2 \sin^2\psi + n_\omega^2 \cos^2\psi}} \quad \text{and} \quad n_o = \frac{2}{\pi} n_\omega F_1,$$

where F_1 is the complete elliptic integral of the 1st class,

$$F_1 = \int_0^{\pi/2} \frac{d\xi}{\Delta(\xi)}, \quad \text{with } \Delta(\xi) = \sqrt{1 - c^2 \sin^2\xi}, \quad c^2 = \frac{n'^2 - n_\omega^2}{n'^2},$$

and

$$n' = \frac{n_\omega n_\epsilon}{\sqrt{n_\epsilon^2 \cos^2\psi + n_\omega^2 \sin^2\psi}}.$$

This solution, however, is only of mathematical interest because such accuracy is not required in our problem.

Biaxial crystals.—This case is somewhat more complicated than that of uniaxial crystals. We shall simply outline the procedure to be followed.

The radius vector determined in the triaxial ellipsoid by the direction of the fiber axis (making two given angles with the optic axes) is computed in terms of the three principal indices and the two angles ψ' and ψ''. This is the value of the fiber index parallel with the fiber elongation, n_e. Then the two half-axes of the ellipse cut through the ellipsoid by a plane normal to the fiber axis are computed (the formulae solving this problem may be found in Fletcher's *Indicatrix*, for instance); the half-sum of these two indices is equal to the fiber index normal to the elongation of the fiber, n_o.

That such cases need be taken into consideration is evident since they are known in nature. The orientation of the crystal with respect to the fiber axis in fairly large spherulites of feldspars is given in the literature as the edge [100] along the fiber length. Since, in the cases studied in this paper, the index ellipsoid of the substances considered approximates an ellipsoid of revolution, there was no need for developing the theory of biaxial component crystals.

Comparison between theory and experimental data.—Consideration of the crystal orientation along the fiber is insufficient to account for the change in the values of the refractive indices apparently brought about by the aggregate structure.

The example of strontium carbonate spherulites (optically negative) will serve to demonstrate the lack of agreement between the theory and the measurements.

The indices of the strontianite crystals (negative) constituting the fiber are: $n_\epsilon = 1.520$, $n_\omega = 1.667$, as n_α is taken for n_ϵ and $n_\beta = n_\gamma$ for n_ω.

If n_ϵ is assumed to be oriented along the fiber length, the fiber indices n_e and n_o should be, according to the above theory, $n_e = n_\epsilon = 1.520$, $n_o = n_\omega = 1.667$.

The measured values, one will recall, were $n_e = 1.5095 - 1.516$, $n_o = 1.5955 - 1.593$.

If we assume that n_ϵ is perpendicular to the fiber axis, the fiber birefringence should be positive, with $n_e = n_\omega = 1.667$, $n_o = \frac{1}{2}(n_\epsilon + n_\omega) = 1.593$. Neither the indices nor the optic sign checks with the observations.

Can n_ϵ be oriented at an angle ψ to the fiber axis that would account for the values of the measured indices? Substituting in the equation (6) the value of the strontianite birefringence (-0.147) for $n_\epsilon - n_\omega$ and that of the fiber birefringence $(-0.086$ or $-0.077)$ for $n_e - n_o$, we get $\psi = 31°44'$ or $\psi = 34°18'$, according to the value adopted for the fiber birefringence. If we set ψ equal to $31°44'$ or $34°18'$ in equations (3) and (5), we reach respectively the following sets of values for the fiber indices: $n_e = 1.561$, $n_o = 1.647$; and $n_e = 1.567$, $n_o = 1.643$.

It is plain, therefore, that some other factor, besides the crystal orientation along the fiber, must be taken into account in order to explain the lowering of the refractive indices. Let us consider the effect of form birefringence.

FORM BIREFRINGENCE

Form birefringence is an important case of accidental birefringence, accidental in the sense that it is not due to the anisotropy resulting from (non isometric) crystallinity.

It is well known that isotropic particles may build up an anisotropic fiber, which behaves either like a positive uniaxial or like a negative uniaxial entity (so-called "rod birefringence" and "plate birefringence" respectively). The formulae have been established by Wiener[13] on the basis of the electromagnetic theory of light; they have been applied by colloid chemists (Ambronn and Frey, Wächtler[14]). Anisotropic particles (rods or plates) may, in like manner, build a fiber with a "form birefringence," which is algebraically added to the original birefringence of the fiber.

The condition for the existence of form birefringence is that the fiber be composed of two media, the particles of which must be smaller than the wave length of light. In their explanation of the structure of chalcedony spherulites, Correns and Nagelschmidt have postulated that this condition was satisfied. Our previous x-ray study of artificial spherulites (Morse, Donnay, Ott) gave us the order of magnitude of the crystalline particles in the aggregate—ranging from 10^{-3} to 10^{-5} cm. A number of these particles must be smaller than the wave length of light. As to the presence of another medium, interstitial between the crystal particles, it is to be expected that spherulites grown in gelatine will contain some interstitial medium (gelatine, water, or possibly air). Johnston, Merwin, and Williamson[15] have reported the retention of as much as 4 per cent (by weight) of water by artificial spherulites of calcium carbonate. Moreover the results of specific gravity determinations on our artificial spherulites cannot be accounted for without the presence of some foreign medium, less dense than the substance of the spherulite. We therefore feel justified in considering form birefringence as a possible agent effective in the lowering of the indices.

It is difficult to give a quantitative treatment of the action of form birefringence in the present instance because neither the percentage amount nor the refractive index of the interstitial medium can be determined accurately.

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[13] *Abhandlungen d. Sächs. Ges. d. Wiss., math.-phys. Kl.*, **1912.**

[14] Wächtler, Maximilian, Über die Doppelbrechungserscheinungen in Kolloiden, *Fortschr. d. Min., Krist. u. Petr.*, vol. **12,** pp. 119–192, 1927. Bibliography of 91 titles.

[15] Johnston, J., Merwin, H. E., and Williamson, E. D., The several forms of calcium carbonate: *Am. Jour. Sci.*, (4) vol. **41,** pp. 473–512, 1916.

The problem can be attacked in the following manner. First assume the orientation of the crystals with respect to the fiber axis; assumption to be guided by the habit of the crystal. Compute the indices of the fiber (n_e, n_o) in terms of the indices of the crystal (n_ϵ, n_ω) by means of the formulae (3) and (5), derived in the preceding section. Compare the "original birefringence" ($n_e - n_o$) with the "total birefringence" ($n_\parallel - n_\perp$), which is the difference of the measured indices of the fiber. This comparison will enable one to decide whether the "form birefringence" should be positive or negative. If it is found to be positive, for instance, the fiber must be a bundle of rods or needles; this affords a check on the assumption for the crystal orientation. Finally, solve Wiener's two equations for the *index of the interstitial medium* and its *percentage by volume.* Since we have two unknowns and two equations, there is no way of checking the results. Further progress will depend on devising an experimental technique of determining the volume percentage of the medium and its index of refraction.

The comparison of birefringences, mentioned in the above paragraph, is made by using the formula

$$B_{\text{total}} = B_{\text{original}} + B_{\text{form}}.$$

In this formula the original birefringence, B_{original}, of the fiber represents the birefringence that the fiber possesses owing to the anisotropy of its crystalline component particles; it has also been called "own birefringence" (Eigendoppelbrechung) by chemists; it is a function of the indices n_ϵ and n_ω of the component crystals; this function was designated by ($n_e - n_o$) in equation (6). The form birefringence, B_{form}, of the fiber, on the other hand, depends on the shape and arrangement of the component particles of the fiber, together with the presence of an interstitial medium; form birefringence exists even in a fiber composed of isotropic particles and an isotropic medium. The total fiber birefringence, B_{total}, should agree with the values derived from the measurements of the fiber indices; we shall designate it by ($n_\parallel - n_\perp$) in the following formulae, $n_\parallel$ and $n_\perp$ being the theoretical values that should agree with the measured fiber indices (given in footnote 7, where they were designated by n_e and n_o).

Wiener's formulae may be written as follows, in the case of positive form birefringence:

$$n_\parallel^2 = (1 - x)n_e^2 + xy^2,$$

$$n_\perp^2 = y^2 \frac{(2 - x)n_o^2 + xy^2}{(2 - x)y^2 + xn_o^2},$$

in which $n_\parallel$ and $n_\perp$ are the indices of the splinter (fiber), n_e and n_o the indices of the fiber as resulting from the orientation of crystal particles,

y the index of the interstitial medium, and x the fraction of unit volume occupied by the interstitial medium (so that there is $100x$ per cent of medium by volume).

For negative form birefringence the formulae become, with the same notation,

$$n_{\parallel}^2 = \frac{n_e^2 y^2}{(1 - x)y^2 + x n_e^2},$$

$$n_{\perp}^2 = (1 - x)n_o^2 + xy^2.$$

Comparison between theory and experimental data.—Even when the action of form birefringence is taken into account, in addition to that of crystal orientation along the fiber, a comparison between the theoretical results and the measurements is disappointing.

One case only might be considered somewhat satisfactory, *viz.*, that of calcium carbonate spherulites. Here, however, the determination of which modification of calcium carbonate occurs in the spherulites presents an additional difficulty. The very careful work of Gibson, Wyckoff, and Merwin[16] has shown that calcium carbonate can occur in spherulitic form in two modifications: vaterite A and vaterite B, which they have proved to be identical with calcite and μ-$CaCO_3$, respectively. They have not found any spherulites made of aragonite. The observations we have made on our spherulites of calcium carbonate do not fit the properties of either vaterite A (=calcite) or vaterite B (=μ-$CaCO_3$). The measured indices of the fiber are $n_{\parallel} = 1.485$, and $n_{\perp} = 1.599$; these values are decidedly too low for vaterite B; the value of $n_{\parallel}$ is above the maximum value recorded for vaterite A by Johnston, Merwin, and Williamson (1916), although that of $n_{\perp}$ falls within the range of measurements of these authors. The fibers have a negative elongation, like fibers of vaterite A. The cobalt nitrate test (Meigen reaction) unquestionably yielded the lilac coloration (supposed to be characteristic of aragonite), like vaterite B. An x-ray powder picture, kindly taken for us by Dr. Hoard, gave the calcite pattern, like vaterite A; on reëxamination of the sample under the microscope, however, it was found that the spherulites, while retaining their external spherical form, had recrystallized into large, irregular areas of calcite; it is quite possible that this recrystallization may have taken place before the x-ray photograph was obtained, because several weeks elapsed before Dr. Hoard took his picture. At all events, the lowering of the refractive indices cannot be explained on the basis of form birefringence and crystal orientation, if the spherulites are made of calcite. The explanation is, on the other

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[16] Gibson, R. E., Wyckoff, R. W. G., and Merwin, H. E., Vaterite and μ-calcium carbonate: *Am. Jour. Sci.*, (5), vol. **10**, pp. 325–333, 1925.

hand, fairly plausible if the spherulites are supposed to be composed of aragonite crystals, as will be shown presently.

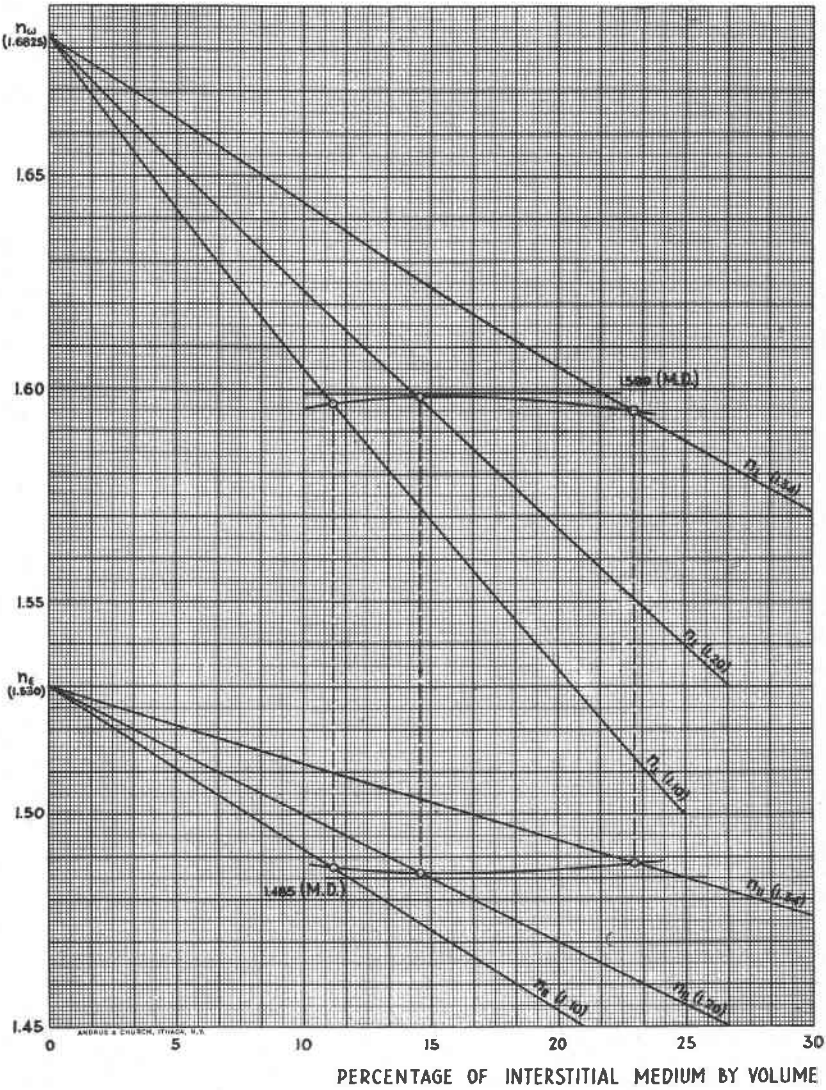

FIG. 12. Action of form birefringence in aragonite spherulites. Curves showing the lowering of the fiber indices ($n_\perp$ and $n_\parallel$) with increasing percentage of interstitial medium. Three pairs of curves are drawn, the index of the medium being taken as 1.34, 1.20, and 1.10, respectively.

The measured values of the fiber indices, obtained by Johnston, Merwin, and Williamson (1916) for spherulites of vaterite *A* (=calcite), are satisfactorily accounted for by the theory.[17]

Lowering of indices in spherulitic fibers composed of aragonite crystals.—Let us apply the foregoing theory to spherulites made of aragonite crystals, forming fibers separated by a varying percentage of interstitial medium, for several values of the refractive index of the medium. Plotting the index against the percentage of interstitial medium, we shall obtain two families of curves, one for $n_\perp$ and one for $n_\parallel$, the index of the medium changing from curve to curve in each family.

The indices of aragonite are: $n_\alpha = 1.530$, $n_\beta = 1.680$, and $n_\gamma = 1.685$. We consider aragonite crystals to approximate uniaxial crystals with the following indices: $n_\epsilon = 1.530$, $n_\omega = 1.6825$. The acicular habit of aragonite (parallel with the *c*-axis) suggests the assumption that the fibers are made up of crystals oriented with their *c*-axis parallel to the fiber length. Since the orientation of the component crystals is random except for that one restriction, the fiber results in a uniaxial entity with the indices: $n_e = n_\epsilon = 1.530$ and $n_o = n_\omega = 1.6825$. The measured indices of the fiber are: $n_\parallel = 1.485$ and $n_\perp = 1.599$. The theory should account for the lowering of the indices from 1.530 to 1.485 and from 1.6825 to 1.599, respectively. The fiber birefringence, which *a priori* should be 0.153 (=original birefringence), only amounts to 0.114 (=total birefringence). These figures are absolute values, since these birefringences are negative. We thus find that the form birefringence must be positive and equal to 0.039, in order to satisfy the relation $-0.114 = -0.153 + 0.039$. Two structures are possible: rods or plates, parallel to the fiber axis. Our assumption as to the orientation of crystals in the fiber is one of them (rods).

Plot the values of $n_\parallel$ and $n_\perp$ given by Wiener's formulae against x, the percentage by volume of the medium, for several values of the index y of the medium (1.34, 1.20, 1.10). The curves obtained are almost straight lines, showing only a slight concavity upwards (Fig. 12). Now the measured values of $n_\parallel$ and $n_\perp$ should be found on the same vertical (*i.e.*, for a given percentage of interstitial medium) on corresponding curves (*i.e.*, curves drawn for the same value of the index of the medium). The graph will show that the measured values of the fiber indices lie nearly on the same vertical for 15 *per cent.* by volume of an interstitial medium with index 1.20. Owing to the observed variability in the refractive indices of the fibers, the following figures may also be considered in satisfactory agreement with the measurements: 20 *per cent.* of a medium

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[17] Donnay, J. D. H., La biréfringence de forme dans la vaterite: *Annales Société géol. Belgique*, **1936** (in press).

with index 1.30, 23 *per cent.* of a medium with index 1.34. The last figures account for a lowering of the indices to values that depart from the meas-

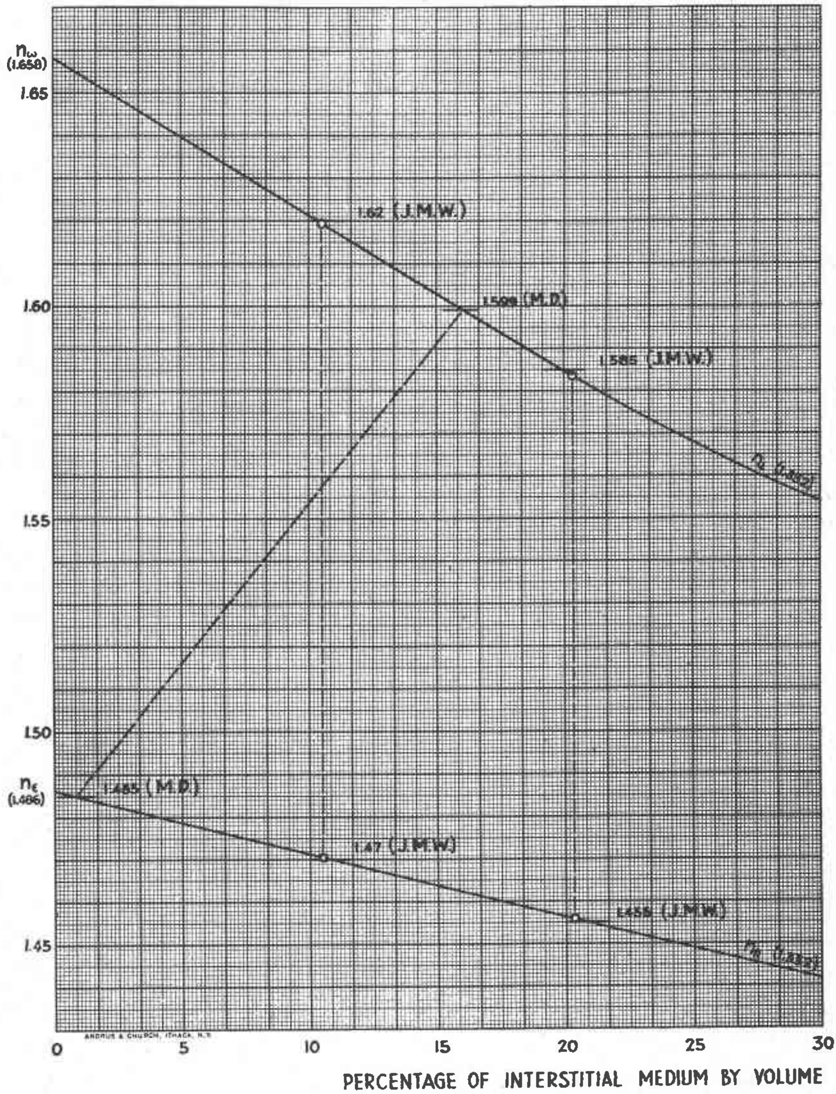

FIG. 13. Action of form birefringence in calcite (=vaterite A) spherulites. Curves showing the lowering of the fiber indices ($n_\perp$ and $n_\parallel$) with increasing percentage of interstitial medium (water, index taken as 1.332). Index measurements by Johnston, Merwin, and Williamson (1916) shown by their initials.

ured ones by less than 4 in the third decimal place. Such results are reasonably in accord with what could be expected.

Lowering of indices in spherulitic fibers composed of calcite crystals.—If we repeat the calculations for spherulitic fibers of calcite (= vaterite A) we get the curves shown in Fig. 13. The fibers are supposed to be built up of calcite crystals oriented with their optic axis parallel to the fiber length. The form birefringence is positive.

Johnston, Merwin, and Williamson (1916) give two sets of values for the fiber indices: 1.62 and 1.47 (in the test, page 488, *op. cit.*), 1.585 and 1.455 (in the footnote, same page). They write that the latter were obtained in one case only. For the more usual material, they report (*op. cit.*, p. 489) the presence of about 10 *per cent.* (by volume) of interstitial medium, "mainly water."

The agreement with the theory is perfect. The curves, drawn for an index of the medium equal to 1.332, show that the values which lie on the same vertical between 10 and 11 *per cent.* by volume of the medium depart from the measured values (1.47 and 1.62) by less than 2 in the third decimal place. Again for the values obtained in the isolated case (1.455 and 1.585), theoretical values not off by more than a few units in the third place are seen to lie on the vertical corresponding to 20 to 21 *per cent.* by volume of the medium.

The same figure shows that the fiber indices we have measured on our $CaCO_3$ spherulites cannot be accounted for if calcium carbonate occurs in the calcite modification.

Lowering of indices in fibers of strontium carbonate spherulites and barium carbonate spherulites.—Similar curves have been plotted for strontium carbonate fibers and for barium carbonate fibers. The results are disappointing. In neither case is it possible to account for the lowering of the indices by means of the above theory.

Strontium carbonate fibers have measured indices of 1.510 and 1.595, while strontianite has the indices 1.520 and 1.667. It is striking fact that the low index, $n_{\parallel}$, is lowered much less than the high index, $n_{\perp}$. We have tried crystal orientations that would lead to positive or negative form birefringences; we also tried to consider strontianite as the "medium" interstitial between the gelatine as well as the more obvious conception of strontianite crystals separated by the gelatine; in no case can the facts be reconciled with the theory.

The same conclusion holds for barium carbonate fibers. It is reasonable to suppose, then, that some other factor, besides crystal orientation along the fiber and form birefringence, must intervene in the alteration of the values of the indices.

Similar phenomena in fibrous minerals.—In his recent paper on ishkyldite,[18] Syromyatnikov presents interesting speculations on the optical properties of fibrous minerals. He attempts to explain the properties of α-chrysotile and ishkyldite by means of the Wiener theory. Quoting him:

> The intermediate medium for this mineral (α-chrysotile) is probably the absorbed water, filling the interstices between the elementary fibers. Its refringence must be lower than that of chrysotile. The integral index of refraction will lie between the refractive index of water and that of chrysotile. *As the fibers of chrysotile are continuous throughout their length, the refractive index N_g must remain constant and independent of the surrounding medium.* Hence, we shall be interested chiefly in the optic vector across the length of the fiber.

The statement, which we have placed in italics in the above quotation, shows clearly that Syromyatnikov was facing the same difficulty as we are, when trying to explain the fact that the refractive index parallel to the fiber length, $n_\parallel$, is very little lowered by the action of the interstitial medium.

Conclusion.—If Syromyatnikov's statement with respect to the value of $n_\parallel$ is correct, it will provide an easy way out of our difficulty. The splinters of our spherulites are also made of fibers continuous throughout their length, and hence $n_\parallel$ should not be lowered to any great extent, whereas $n_\perp$ would be the lowered value of n_o resulting from the presence of the interstitial medium.

One last possibility is that the spherulites are in a state of strain, resulting from their mode of preparation in gelatine. One fact of observation (reported in our second paper) is that some spheres break up, when rubbed, with almost explosive violence. This is true of lead sulfate especially, but has also been noticed in spherulites of calcium carbonate. This is taken to indicate that the spherical aggregate is under strain. Now strain will induce additional "accidental birefringence," the refractive indices being altered still further. We have not attempted to give this last factor a quantitative expression, fearing that the mathematical treatment involved would be beyond our competence.

The good agreement found between the theory and the experimental data of Johnston, Merwin, and Williamson, in the case of vaterite *A*, may be explained by the fact that their spherulites, grown in aqueous solutions, were not in a state of strain, and hence no additional accidental birefringence was involved.

SUMMARY

The paper presents the results of further study of the shape and the optical properties of artificial spherulites and related aggregates, grown by diffusion and metathesis in gelatine.

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[18] Syromyatnikov, F. V., Ishkyldite, a new structural variety of chrysotile: *Am. Mineral.*, vol. **21**, pp. 48–54, 1936.

Although these aggregates may vary widely in external shape, most of them belong to one and the same type of "aggregation," due to radiating crystallization. An hypothesis is advanced as to the mechanism of formation of spherulitic structures, *viz.*, that a continuous branching out of fibers makes an aggregate look like a sheaf "opening" at both ends, in fan-like manner, as growth proceeds until spherical shape is attained or, at least, approximated. The hypothesis rests on the observation of a series of forms interpreted as transitional stages. The central "Zweiblatt," described by Popoff in two-dimensional spherulites, finds its counterpart in our three-dimensional structures (in one case).

The *spherulitic figure* (x-nicols, parallel light) is compared with the interference figure observed (x-nicols, convergent light) in a uniaxial crystal cut at right angle to the optic axis. The circular outline of spherulites, viewed in plane polarized light, appears elliptically distorted when the refractive index of the mounting medium falls between the principal indices of the fibers. Contrary to Spangenberg's idea this optical effect can give no information on the indices of the crystals constituting the fibers.

The optical unit of the structure is the fiber, which behaves as a uniaxial entity. Its refractive indices, however, differ from those of the crystalline species that builds up the fiber. Various factors are considered to explain this discrepancy: crystal orientation along the fiber, form birefringence, and accidental birefringence due to strain.

Errata in Previous Paper

Am. Jour. Sci., vol. **23**, 1932, page 427, line 6, read $n_\gamma = 1.615$, $n_\alpha = 1.511$, instead of 1.677 and 1.529.

ibid., page 431, signs of anglesite, barite, celestite, should be (+) instead of (−).