XXVI. *On the Remarkable Phenomenon of Crystalline Reflexion described by* Prof. Stokes. *By* Lord Rayleigh, *Sec. R.S.**

The phenomenon in question is that exhibited by certain crystals of chlorate of potash, consisting of a peculiar internal coloured reflexion. The following, stated very briefly, are its leading features as described by Stokes† :—

(1) If one of the crystalline plates be turned round in its own plane, without alteration of the angle of incidence, the peculiar reflexion vanishes twice in a revolution, viz. when the plane of incidence coincides with the plane of symmetry of the crystal.

(2) As the angle of incidence is increased the reflected light becomes brighter and rises in refrangibility.

(3) The colours are not due to absorption, the transmitted light being strictly complementary to the reflected.

(4) The coloured light is not polarized. It is produced indifferently whether the incident light be common light or light polarized in any plane, and is seen whether the reflected light be viewed directly or through a Nicol's prism turned in any way.

(5) The spectrum of the reflected light is frequently found to consist almost entirely of a comparatively narrow band. When the angle of incidence is increased, the band moves in the direction of increasing refrangibility, and at the same time increases rapidly in width. In many cases the reflexion appears to be almost total.

Prof. Stokes has proved that the seat of the colour is a narrow layer, about a thousandth of an inch in thickness, in the interior of the crystal; and he gives reasons for regarding this layer as a twin stratum. But the phenomenon remains a mystery. "It is certainly very extraordinary and paradoxical that light should suffer total or all but total reflexion at a transparent stratum of the very same substance, merely differing in orientation, in which the light had been travelling, and that, independently of its polarization."

From the first reading of Prof. Stokes's paper, I have been much impressed with the difficulty so clearly set forth. It seemed impossible that a combination of two surfaces merely could determine either so copious or so highly selected a reflexion. If light of a particular wave-length is almost totally reflected, what hinders the reflexion when the wave-

* Communicated by the Author.
† Proc. Roy. Soc. Feb. 1885.

length is altered, say, by one twentieth part? Such a result may arise from the interference of two streams under a relative retardation of many periods; but in that case there are necessarily a whole series of wave-lengths all equally effective. The prism should reveal a number of bright bands and not merely a single band. The selection of a particular wave-length reminds one rather of what takes place in gratings; and I was from the first inclined to attribute the colours to a periodic structure, in which the twins alternate a large number of times. Such a view explains not only the high degree of selection, but also the copiousness of the reflexion.

Partly with a view to this question, I have discussed in a recent paper* the propagation of waves in an infinite laminated medium (where, however, the properties are supposed to vary continuously according to the harmonic law), and have shown that, however slight the variation, reflexion is ultimately total, provided the agreement be sufficiently close between the wave-length of the structure and the half wave-length of the vibration. The number of alternations of structure necessary in order to secure a practically perfect reflexion will evidently depend upon the other circumstances of the case. If the variation be slight, so that a single reflexion is but feeble, a large number of alternations are necessary for the full effect, and a correspondingly accurate adjustment of wave-lengths is then required. If the variation be greater, or act to better advantage, so that a single reflexion is more powerful, there is no need to multiply so greatly the number of alternations; and at the same time the demand for precision of adjustment becomes less exacting. The application of this principle to the case of an actual crystal, supposed to include a given number of alternations, presents no difficulty. At perpendicular incidence symmetry requires (and observation verifies) that the reflexion vanish; but, as the angle of incidence increases, a transition from one twin to the other becomes more and more capable of causing reflexion. Hence if the number of alternations be large, the spectrum of the reflected light is at first limited to a narrow band (whose width determines in fact the number of alternations). As the angle of incidence increases, the reflexion at the centre soon becomes sensibly total, and at the same time

* "On the Maintenance of Vibrations by Forces of Double Frequency, and on the Propagation of Waves through a Medium endowed with a Periodic Structure," Phil. Mag. Aug. 1887.

the band begins to widen *, in consequence of the less precise adjustment of wave-lengths now necessary. At higher angles the reflexion may be sensibly total over a band of considerable width. All this agrees precisely with Prof. Stokes's description of the case considered by him to be typical. The movement of the band towards the blue end of the spectrum is to be attributed to the increasing obliquity within the crystal, as in the ordinary theory of thin plates.

It thus appears that if we allow ourselves to invent a suitable crystalline structure, there need be no difficulty in explaining the vigour and purity of the reflexion; but such an exercise of ingenuity is of little avail unless we can at the same time render an account of the equally remarkable circumstances stated in (1) and (4). When the incidence is in the plane of symmetry, no reflexion takes place. As Prof. Stokes remarks, this might be expected as regards light polarized in the plane of symmetry; but that there should be no reflexion of the other polarized component is curious, to say the least. Not less remarkable is it that when the incidence is in the perpendicular plane, the reflected light should show no signs of polarization. The phenomenon being certainly connected with the doubly refracting property, we should naturally have expected the contrary.

The investigation of the reflexion from a twin-plane, contained in the preceding paper (pp. 246 *et seqq.*), shows, however, that the actually observed results are in conformity with theory. In the plane of symmetry there should be no reflexion of either polarized component, at least to the same degree of approximation as is attained in Fresnel's well-known formulæ for isotropic reflexion. As regards light reflected in the perpendicular plane, theory indicates that if the incident light be unpolarized, so also will be the reflected light. Again, the intensity of the (unanalyzed) reflected light should be independent of the polarization of the incident. So far there is complete agreement with the observations of Prof. Stokes. But there is a further peculiarity to be noticed. Theory shows that in the act of reflexion at a twin plane, *the polarization is reversed*. If the incident light be polarized in the

* It should be observed that if the spectrum be a prismatic one, there is a cause of widening which must be regarded as purely instrumental. According to Cauchy's law $(\mu=A+B\lambda^{-2})$,

$$\delta\mu=-2B\lambda^{-3}\delta\lambda;$$

so that if the band correspond in every position to a given relative range of λ, its apparent width (reckoned as proportional to $\delta\mu$) will vary as λ^{-2}. In a diffraction-spectrum this cause of widening with diminishing λ would be non-existent.

plane of incidence, the reflected light is polarized in the perpendicular plane, and *vice versâ*. When I first obtained this result, I thought it applicable without reservation in the actual experiment, and on trial was disappointed to find that the reflected light was nearly unpolarized, even when the incident light was fully polarized, whether in the plane of incidence or in the perpendicular plane. When, however, the *angle of incidence was diminished*, the expected phenomenon was observed, provided that the original polarization were in, or perpendicular to, the plane of incidence. If the original polarization were oblique, the reflected light was not fully polarized, even though the angle of incidence were small*.

Further consideration appeared to show that the loss of polarization usually observed could be explained by the depolarizing action of the layer of crystal through which the light passes, both on its way to the reflecting plane and on its return therefrom. As is shown in the preceding paper, this depolarizing action does not occur when the angle of incidence is small, and the polarization in, or perpendicular to, the plane of incidence. It seems scarcely too much to say that the theory not only explains the laws laid down by Stokes, but also predicts a very peculiar law not before suspected†.

The theory, as so far developed, is indeed limited to incidences in the two principal planes. It could probably be treated more generally without serious difficulty; but there seems no reason to suppose that anything very distinctive would emerge. It is not unlikely that the intensity would prove to be proportional to the square of the sine of the angle between the planes of incidence and of symmetry. If this theory be accepted—and I see no reason for distrusting it—the brilliant reflexion cannot be explained as due to a single twin stratum. The simplest case which we can consider is when the angle of incidence is small and the polarization in or perpendicular to the plane of incidence. There is

* Whatever the angle of incidence, the arrangement of crossed nicols may sometimes be conveniently applied in order to isolate the light under investigation from that reflected at the front surface of the crystalline plate. In the observations described in the text the crystal was mounted with Canada balsam between thick plates of glass, so that there was no difficulty in observing separately the various reflexions. At small angles of incidence the coloured image is at its brightest when the analyzing nicol is so turned that the white image (reflected from the glass) vanishes, and *vice versâ*, the incident light being polarized in, or perpendicularly to, the plane of incidence.

† The wording of Prof. Stokes's description is perhaps a little ambiguous, but I gather that he did not examine the result of a *simultaneous* operation of polarizer and analyser.

then sensibly but one wave reflected at the first twin plane. On the arrival of the transmitted wave at the hinder surface of the twin stratum, a second reflexion ensues, similar to the first, except for the reversal of phase due to the altered circumstances. The relation to one another of the two reflected waves is exactly the same as in the ordinary theory of thin plates, and does not appear to admit of the production of anything unusual. I think we may even go further, and conclude that in conformity with our theory it is impossible to find an explanation of the brilliant and highly selected reflexion, unless upon the supposition that there is a repeated alternation of structure.

The optical evidence in favour of the view that there are a large number of twin planes thus appears to be very strong; the difficulty is rather to understand how such a structure can originate. And yet if we admit, as we must, the possibility of the formation of one twin plane, and of two twin planes at a very small distance asunder *, there seems nothing to forbid a structure regularly periodic, which may perhaps be due to causes vibratory in their nature.

It would undoubtedly be far more satisfactory to be able to speak of the periodic structure as a matter of direct observation, and it is to be desired that some practised microscopist should turn his attention to the subject. *Ex hypothesi*, we could not expect to see the ruled pattern upon a section cut perpendicularly to the twin planes, as it would lie upon, or beyond, the microscopic limit. I have tried to detect it upon a surface inclined to the planes at a very small angle, but hitherto without success.

In the absence of complete evidence it is proper to treat the views here put forward with a certain reserve; but it is perhaps not premature to consider a little further what may be expected to result from a structure more or less regular. If the periodicity be nearly perfect, the bright central band in the spectrum would be accompanied by subordinate bands of inferior and decreasing brilliancy. If the angle of incidence be small, so that the aggregate reflexion is but feeble, each stratum may be considered to act independently, and the various reflected waves to be simply superposed. The resultant intensity will depend of course upon the phase relations. At the centre of the band the partial reflexions agree in phase, and the intensity is a maximum. As we leave this point in either direction, the phases begin to

* This is the simplest supposition open to us, when, as in most of the coloured crystals, the parts on either side of a very thin lamina are similarly oriented.

separate. When the alteration of wave-length is such that the phases of the reflected waves range over a complete cycle, the resultant vanishes, and a dark band appears in the spectrum. The same thing occurs whenever the relative retardation of the extreme components amounts to a complete number of periods. At points approximately midway between these, the resultant is a maximum, but the values of the successive maxima diminish *. Near the central band, where (when the number of alternations is great) a considerable fraction of the incident light is reflected by the system of layers, this way of regarding the matter may cease to be applicable, for then the anterior and the posterior layers act under sensibly different conditions.

Apart from the magnitude of the complete linear period, something will depend upon the manner in which it is divided between the twins. The most favourable, as it is also perhaps the most probable, arrangement is that in which the thicknesses are equal. In that case every partial reflexion may agree in phase. If the thicknesses, though regular, are unequal, we may first form the resultant for contiguous pairs, and then consider the manner in which the partial resultants aggregate.

It will be seen that even if the thicknesses of the twins are equal, there are still *two* ways in which a regularly laminated crystal may vary, as compared with the single kind of variation open to a simple twin stratum. These are the magnitude of the linear period, and the number of periods. Comparison of a number of coloured crystals † seems to favour the view that there are important differences of constitution, even when the colour is the same at a given incidence.

In many cases the appearances are such as to suggest that the periodicity is imperfect. A little irregularity might alter or obliterate the subordinate bands, while leaving the central band practically unaffected. Sometimes there is evidence of two or more distinct periods, each sustained through a number of alternations. If the period were subject to a gradual change, the central band in the spectrum of the reflected light would be diffused, even at small angles of incidence. The

* The case is similar to that of the distribution of brightness in the neighbourhood of a "principal maximum," when light of given wave-length is diffracted by a grating.

† For a rich collection of such crystals I am indebted to Mr. Muspratt. He informs me that, though the result of a second crystallization from comparatively pure liquids, the coloured crystals are but rarely found when the chlorate is produced by the magnesium process.

mere broadening of the band might be due to fewness of alternations; but this case would be distinguished from the other by the accompanying feebleness of illumination.

On the whole, the character of the reflected light appears to me to harmonize generally with the periodical theory. One objection, however, should be mentioned. It might be supposed that the total number of twin planes was as likely to be odd as to be even. In the former case the layers of crystal on either side of the thin lamina (which is the seat of the colour) would be of opposite orientations. In many crystals the character of the twinning is difficult of observation, but I have not noticed any instance of *brilliant coloration* answering to this description. So far as it goes this argument is in favour of the simple stratum theory; but, in view of our ignorance as to how the twin planes originate, it can hardly be considered decisive.

I have also examined a number of what appeared to be simply twinned crystals, kindly sent me by Mr. Stanford, of the North British Chemical Works. The light reflected from the twin plane is not easily observed on account of its feeble character, at least when, as in the experiments now referred to, the incidence is limited by the requirement that the light must enter the crystal at a face parallel to the twin plane. Using, however, the method described by Prof. Stokes (§ 13), I was enabled to separate the reflexions at the twin plane from those at the external surfaces of the crystal. A narrow slit admitted sunlight into the dark room, and was focused upon the crystal by a good achromatic object-glass*. When the obliquely reflected light was examined with a hand magnifier, a ghost-like image corresponding to the twin plane could usually be detected. As the crystal was rotated in its own plane, this image *vanished twice during the revolution*.

It is worthy of notice that there is an evident difference both in the brightness and quality of the reflected light obtained from different crystals, even though apparently simply twinned. This suggests that, instead of a single twin plane, there may sometimes be in reality 3, 5, or a higher odd number of such in close juxtaposition. In other specimens, affording similar reflexions, the principal thicknesses on either side of a very thin layer are undoubtedly of the same kind, so that the number of twin planes must be even. Here, again, the reflected light exhibited marked differences, when various crystals were examined. In none of those now referred to could the light reflected from the thin layer be observed without very special arrangements.

* I did not succeed in my first trials when I employed a common lens.

In these experiments the light entered and left the crystal by a face parallel to the twin planes. In one specially well-formed and apparently simply twinned crystal I was able to observe a much more oblique reflexion from the internal surface or surfaces. The light here entered and left the crystal by cleavage faces making a large angle with the reflecting planes, and thus under conditions widely different from those considered hitherto, and in the latter part of the preceding theoretical discussion. Three reflected images were seen, all completely polarized (the original light being unpolarized), two in one direction and the third in the opposite direction. These images are coloured, and present tolerably discontinuous spectra, giving rise to a suspicion that the twin plane is not really single. These observations were made without special arrangements by merely examining the reflected images of a candle-flame, when the crystal was held close to the eye.

I have made many experiments on the crystallization of chlorate of potash in the hope of tracing the genesis of the coloured crystals, but without decisive results. Besides the usually small but highly coloured crystals, found by Stokes, I have obtained many larger ones in which the reflexion is feebler and less pure. These appear to be distinct from the exceedingly thin plates which at the early stage of crystallization swim about in the solution. Mounted in Canada balsam the crystals in question show colours of varying degrees of brightness and purity; and under these circumstances the effect can hardly be due to the action of the external surfaces (in contact with the balsam). The light disappears twice during the revolution of the plates in azimuth, just as in the case of the more highly coloured specimens. It seems natural to suppose that the reflexion takes place from twin surfaces relatively few in number, and perhaps less regular in disposition. Altogether the existence of these crystals favours the view that fully formed colour is due to a large number of regular alternations.

Some interesting observations bearing upon our present subject have been recorded by Mr. Madan*. Transparent crystals, free from twinning, were heated on an iron plate to the neighbourhood of the fusion-point. During the heating no change was observable, but "when the temperature had sunk a few degrees a remarkable change spread quickly and quietly over the crystal-plate causing it to reflect light almost as brilliantly as if a film of silver had been deposited on it." Subsequently examined, the altered crystals are found to

* "On the Effect of Heat in changing the Structure of Crystals of Potassium Chlorate," 'Nature,' May 20, 1886.

"reflect little light at small angles of incidence, but at all angles greater than about 10° they reflect light with a brilliancy which shows that the reflexion must be almost total. ..... When the plate is turned round in its own plane, two positions are found, differing in azimuth by 180°, in which the crystal reflects no more light than an ordinary crystal under the same conditions. In these cases the plane of incidence coincides with the plane of crystallographic symmetry."

Mr. Madan worked with comparatively thick (1 millim.) plates, from which the associated twin had been removed by grinding. In repeating his experiments I found it more convenient to use thin plates, such as may be obtained without difficulty from crystallizations upon a moderate scale, and which appear to be free from twinning*. There seems to be little doubt that the altered crystals are composed of twinned layers. Except in respect of colour, there is no difference between the behaviour of these crystals and that of the brilliantly iridescent ones described by Stokes. If light be incident at a small angle, and be polarized in or perpendicularly to the plane of incidence, the polarization of the reflected light is the *opposite* to that of the incident.

The only difference that I should suppose to exist between the constitution of these crystals and that of the iridescent ones is, that in the former case the alternations are irregular, and also probably more numerous. Mr. Madan conceives that there are actual cavities between the layers in the heated crystals, comparing them to films of decomposed glass †. It is, however, certain that no closeness of contact could obviate the optical discontinuity at a twin plane; and there is besides a marked experimental distinction between the cases in question. It is easy to observe, and was, I think, observed by Brewster, that the application of water to a film of decomposed glass destroys the effect. The water insinuates itself

* It is not clear why composite crystals free from included mother-liquor should suffer disruption upon heating. A line drawn on the twin plane would tend to expand equally, to whichever crystal it be considered to belong.

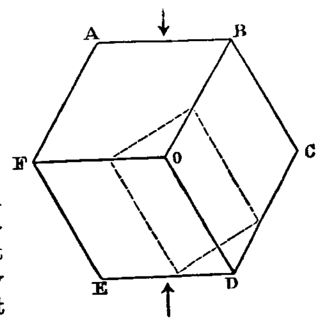
† "Although a large amount of light must escape reflexion at a single cavity, yet if the transmitted rays encountered a large number of precisely similar and similarly situated cavities at slightly lower levels in the crystal, the sum of the partial reflexions would produce an effect almost equivalent to a total reflexion of the original incident ray, and a corresponding deficiency in the amount of light transmitted through the whole plate. The brilliancy of the colours in the light reflected from the well-known films of decomposed glass is accounted for in precisely the same way, and the successive separate films of glass can be easily seen under a microscope at the edges of the compound film, where they only partially overlap."

into the cavities, and greatly attenuates the reflecting power. If a corresponding experiment be tried, by wetting the edge of one of Mr. Madan's crystals with saturated solution of the salt, no change is observed to ensue.

Whether there are cavities or no, the fact that during the preparation the silvery reflexion does not set in until the crystal has sensibly cooled is of great interest. I have found that if a crystal in which the silvery lustre has already been produced be reheated, the lustre disappears, to return again upon a fall of temperature. The operation may be repeated any number of times.

The existence of twin strata in Iceland spar was observed by Brewster*, and Reusch † has shown that such strata can be induced artificially by suitably applied pressure (fig. 1) in rhombs originally homogeneous. The planes of these strata truncate the polar edges, *i. e.* the edges which meet symmetrically at the obtuse trihedral angle (O). Being desirous of examining whether the reflexion from these strata would conform to the law deduced from theory, I submitted a rhomb to the treatment prescribed by Reusch with the effect of developing several exceedingly thin twin laminæ (four or five at least) in close juxtaposition.

Fig. 1.



When light is reflected from these strata in a plane perpendicular to the edge (O D) which they truncate, the brilliancy is considerable. But the observation which I wished to make required that the plane of incidence should be perpendicular to this, so as to include the truncated edge and the optic axis. Without much difficulty it was proved that in this plane *the reflexion vanished*, reviving on either side as the plane of incidence deviated a little from the plane of symmetry. The observation was facilitated by immersing the crystal in a small cell containing water or bisulphide of carbon, the twin strata being horizontal, and the plane of symmetry parallel to two of the sides of the cell.

* Treatise on Optics, 1853, p. 349.
† Pogg. *Ann.* t. xii. p. 448 (1867).