

On the polarisation and spectral character of the iridescence of potassium chlorate crystals

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1. Introduction

In a series of three recent papers in these *Proceedings*, we described and discussed the results of studies made with material selected from the rather extensive collection of iridescent crystals of potassium chlorate at our disposal. In particular, we dealt with the spectral character and polarisation of the iridescence of five selected crystals the optical behaviour of which indicated a high degree of regularity in their structure. Since then, we have made observations with a dozen other crystals of the same kind over a wider range of azimuths and obliquities of incidence than previously. A fairly complete picture of the phenomena has emerged from these studies. It is proposed in the present paper to describe our findings and to illustrate the same by a new set of spectrograms obtained with a typical specimen.

2. Some theoretical considerations

Potassium chlorate is a strongly birefringent crystal and the reflections which give rise to the iridescence owe their origin to the fact that the alternate layers of the polysynthetically twinned crystal are orientated differently from the rest. It might seem in these circumstances that a theoretical treatment of the problem would be very complicated. Fortunately, however, there are circumstances which considerably simplify the situation. In the first place, all the layers in the polysynthetic crystal have a common symmetry plane and a common axis perpendicular to it which coincides with the direction of maximum optical polarisability. Then again, while potassium chlorate is actually a biaxial crystal, its optical behaviour is not very different from that of an uniaxial crystal. In dealing with the problem, therefore, one can use the phraseology appropriate to an uniaxial crystal, and speak of an ordinary and an extraordinary beam, the directions of vibration in which are determined by the position of the optic axis

(which is the direction of least polarisability) relatively to the direction of the wave-normal.

A beam of unpolarised light incident on the face of the crystal divides upon entry into two beams of light, viz., the ordinary and the extraordinary beams polarised in perpendicular planes. In the particular case when the directions in which these beams traverse the crystal lie in the symmetry plane, the ordinary and the extraordinary beams retain their character as such in their entire course through the crystal. In such a case, of course, there is no reflection at the twin-plane boundaries. So long as the directions of propagation do not deviate largely from the symmetry plane, we are justified as a first approximation in assuming a similar situation to subsist, viz., that an ordinary beam remains an ordinary one and an extraordinary beam as extraordinary throughout. Similar assumptions may also be made in the same circumstances about the beams of light arising from the internal reflections. In other words, it will be assumed that light reflected as an ordinary or as an extraordinary beam retains this character until its final emergence from the crystal.

As has already been shown in the second of our earlier papers, the state of polarisation of a light beam traversing the crystal and reflected at a twin-plane boundary changes from the ordinary to the extraordinary and vice versa in the act of reflection, irrespectively of the angle of incidence, provided that the directions of the incident and reflected beams do not deviate greatly from the plane of symmetry, and the reflections are in consequence very weak. More generally, an ordinary beam is reflected both as an extraordinary and as an ordinary beam, while similarly an extraordinary beam is reflected both as ordinary and as extraordinary. The strength of the second component relatively to the first in each case would be determined jointly by the azimuth and by the obliquity of incidence, and may reach considerable values if the azimuthal angle as well as the angle of incidence are large.

3. Spectral character of the reflections

Thus, in general, we have four sets of reflected beams generated at each of the twinning plates in the crystal and finally emerging from it. For convenience we can refer to them as the $o-o$, $o-e$, $e-o$ and $e-e$ reflections, the first letter indicating the state of polarisation in the incident light and the second in the reflected light. In general, also, the total optical path traversed in all these four cases would be different, and hence the wavelength for which the intensity of reflection is a maximum at any given angle of incidence, would be different for these four beams. Thus, in general, we should have four different reflection maxima in the spectrum; all the four would be plane-polarised, but in different ways. Since the ordinary index is substantially greater than the extraordinary index, it follows that the $o-o$ reflection maximum would have the greatest wavelength of the four and that the

$e-e$ reflection maximum would have the smallest. Between them would lie the $o-e$ and the $e-o$ reflection maxima.

An explanation is necessary here to indicate why the positions of the $o-e$ and the $e-o$ reflection maxima in the spectrum would not in general be identical. The direction of minimum optical polarisability in potassium chlorate makes an angle of 38° with the normal to the surface of the plate. The refractive index of the ordinary ray is approximately independent of the directions of the incident and reflected beams within the crystal. But this is not the case in respect of the extraordinary index, which would be greater for the incident beam and less for the reflected beam or vice versa according as the light is incident on one side or the other of the normal to the plate. The position in this respect is reversed when we consider the alternate layers of the twinned crystal, since in the latter the direction of minimum polarisability is situated on the opposite side of the normal. There is thus a compensation which would be complete if the alternate layers in the polysynthetically twinned crystal are of equal thickness. In such a case the total optical paths for the $o-e$ and the $e-o$ reflected beams would be identical, and instead of a quartet of reflection maxima in the spectrum we would in general have only a triplet. There is no reason however for assuming that the periodic twinning of the crystal is always or even frequently of the special type referred to above. A regular periodic twinning is consistent with the alternate layers being of different thickness. In such a case it would follow that the total optical path for the $o-e$ reflection is greater than the path for the $e-o$ reflection, or vice versa.

4. Some consequences of the theory

The considerations set forth above have several verifiable consequences. In the first place, if the azimuth of incidence is 90° , i.e., if the plane of incidence be normal to the plane of symmetry and the reflections are hence of maximum intensity, the incident and reflected beams lie symmetrically on either side of the normal, and hence the $o-e$ and the $e-o$ paths are necessarily identical irrespective of the angle of incidence and the nature of the twinning. Hence it follows that in this particular azimuth and irrespective of the angle of incidence, the $o-e$ and the $e-o$ reflections would overlap and the quartet of reflection maxima would be reduced to a triplet.

A second verifiable consequence of the theory is the effect of rotating the crystal in its own plane through two right angles. As the result of such rotation, the directions of travel of the incident and reflected beams with reference to the orientations of the optic axis within each layer of the crystal would be reversed. Hence the $o-e$ and the $e-o$ reflection maxima should also reverse their positions in the spectrum and such reversal should take place in a continuous manner, the two reflections approaching each other and coinciding when the azimuthal angle is 90° , and thereafter separating again when the crystal is rotated further. That an interchange between the $e-o$ and the $o-e$ reflections is thus brought about would

be indicated by a corresponding interchange in the plane of polarisation of these reflection maxima in the spectrum.

Another verifiable consequence is that the separation of the $o-e$ and the $e-o$ reflections of the spectrum would vary from specimen to specimen and in particular cases actually vanish, whereas the $o-o$ and the $e-e$ reflections would be widely separated in the spectrum in all cases, and their planes of polarisation would not be reversed when the crystal is turned round through 180° .

It follows from what has been stated earlier that the $o-o$ and $e-e$ reflections would vanish completely if the azimuth of incidence is nearly coincident with the plane of symmetry, and this is irrespective of the angle of incidence. Thus, for such azimuths, the quartet of reflections would reduce to a doublet the components of which would be polarised in perpendicular planes, the separation of the components also varying from specimen to specimen. The separation of the doublets should also increase with the angle of incidence. But the simultaneous spectral widening of the reflection maxima would not be very conspicuous in view of the small reflecting power at such azimuths of incidence.

Observed at nearly normal incidence, the $o-o$ and the $e-e$ components would vanish in all cases. If in addition the azimuth of observation is 90° , the $o-e$ and the $e-o$ components would also coincide. Thus instead of a quartet of reflection maxima, we would obtain a single and fairly sharply defined maximum in the spectrum. At more oblique incidences, the $o-o$ and the $e-e$ components would make their appearance; for any given angle of incidence, their intensity would be greatest when the azimuth of observation is 90° , whereas they would vanish when the azimuthal angle is 0° as already remarked. At intermediate azimuths, they may be expected to be visible but less conspicuously. When the azimuth of incidence is 90° , the $o-e$ and the $e-o$ components would appear overlapping each other in the same position. Hence at this azimuth the single sharp maximum which is seen at nearly normal incidence alters into a triplet when the incidence is made more oblique.

From what has been stated above, it follows that neither at an azimuth 0° nor at an azimuth 90° would the quartet of reflection maxima indicated by the theory be observable. The most favourable case for viewing it is when the azimuth of incidence is neither too small nor too large, and the incidence should also be fairly oblique, as otherwise the separation of the $o-e$ and the $e-o$ components may be too small to be detectable.

5. Description of the spectrograms

The various features set forth above are illustrated in the series of spectrograms reproduced as figures 1 to 4 in plate I and as figures 1 to 4 in plate II. These were recorded with a crystal which at nearly normal incidence exhibited a highly monochromatic iridescence at $\lambda 5665$ with a spectral width of about 25 A.U. A

reflection of higher order is recorded at the same incidence at $\lambda 4280$ while a reflection of lower order comes into view at the extreme red end of the spectrum at oblique incidences. From these facts it is readily deduced that the reflection at $\lambda 5665$ is of the third order. The actual values of the azimuthal angle of incidence (ϕ) measured from the plane of symmetry and of the obliquity of incidence (θ) measured from the normal to the surface are indicated against each of the spectrograms in the figures.

Figure 1 in plate I reproduces a series of seven spectrograms taken at an azimuthal angle of about 5° , the angle of incidence increasing in steps from 5° to 65° . It will be seen that the reflection maximum is recorded as a doublet the components of which drift apart from each other and also towards shorter wavelengths with increasing obliquity. If the increasing dispersion of the instrument in the region of shorter wavelength is taken into account, it will be seen that there is hardly any increase in the spectral width of each component with increasing obliquity of incidence. Fairly large exposures of the order of half an hour had to be given to record the doublets. This exposure, though considerable, fails to bring out the true secondary spectrum. Figure 2 in the same plate exhibits the polarisation of the doublet. The two spectrograms in the figure were recorded with equal exposures, a nicol being placed in front of the slit of the spectrograph with its vibration directions respectively vertical and horizontal. It will be seen that in the one case the component on the longer wavelength side has been extinguished while in the other the component on the shorter wavelength side has disappeared. Figure 3 in the same plate exhibits the reversal in the position of the two components produced by rotating the crystal through 180° in its own plane, the arrangements being otherwise identical with those used for recording figure 2.

Figure 4 in plate I shows the typical quarter spectrum. It will be seen that the two central components are both much wider and much more intense than the two outer ones. The latter indeed remain quite sharp even at oblique incidences whereas the former have widened out notably. A whole series of subsidiary maxima can be distinctly seen in the spectrograms recorded at the more oblique incidences. In the same figure the central doublet of the reflection of the higher order has come out weakly in two of the spectrograms, and it will be seen that they are much sharper and more clearly separated than in the lower order reflection.

The seven spectrograms reproduced as figure 1 in plate II were recorded at an azimuthal angle of 60° . It will be seen that the increased azimuthal angle has brought about a notable increase in the intensity of the outer components as well as a diminution in their sharpness. Likewise, the two central components have broadened out so much so that at moderate obliquities they are hardly separated from each other. The separation is however clearly seen in the second order reflection appearing near the violet end of the spectrum. At the more oblique incidences the two central components though greatly broadened, are clearly separated. They are however so broad that they have masked the outermost

components. The secondary maxima are clearly seen in many of the spectrograms.

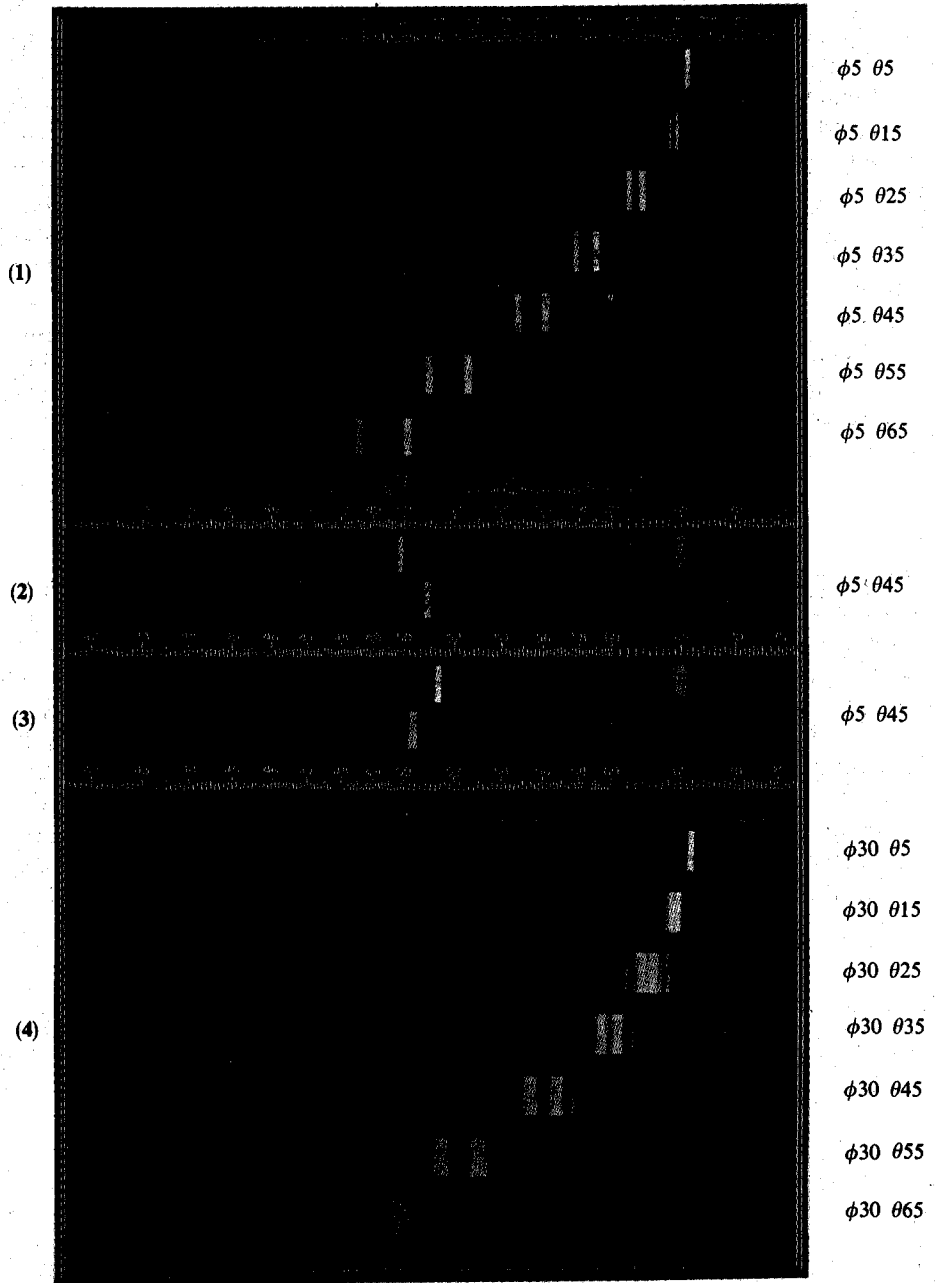
Figure 4 in plate II shows the triplet spectrum recorded at an azimuthal angle of 90° . The appearance of the outer components and the increase in their intensity and width as well as of the central component at increasing obliquities of incidence are clearly shown. Figure 2 in the same plate exhibits the polarisation of the outer components of the triplet and the lack of polarisation in the central component. The spectrograms shown in that figure were recorded by placing a nicol in front of the slit of the spectrograph with its vibration directions respectively vertical and horizontal and giving equal exposures. Figure 3 was recorded under identical conditions except that the crystal was turned round in its own plane through 180° . It will be noticed that the components have now *not* interchanged their positions.

6. Summary

It is shown from theoretical considerations and confirmed by the spectrograms reproduced in the paper that the sharply defined monochromatic reflection observed at nearly normal incidences splits up into a quartet in the general case of any arbitrary azimuth and obliquity of incidence. The outer components disappear thereby reducing the quartet into a doublet when the azimuthal angle is small. But if the azimuthal angle be 90° the two central components merge and the quartet reduces to a triplet. When the crystal is rotated in its own plane the two central components of the quartet come together, overlap and move out again in the same direction, thereby giving rise to a reversal of their polarisation characters. They owe their origin to the alternate layers of the polysynthetically twinned crystal being of unequal thickness.

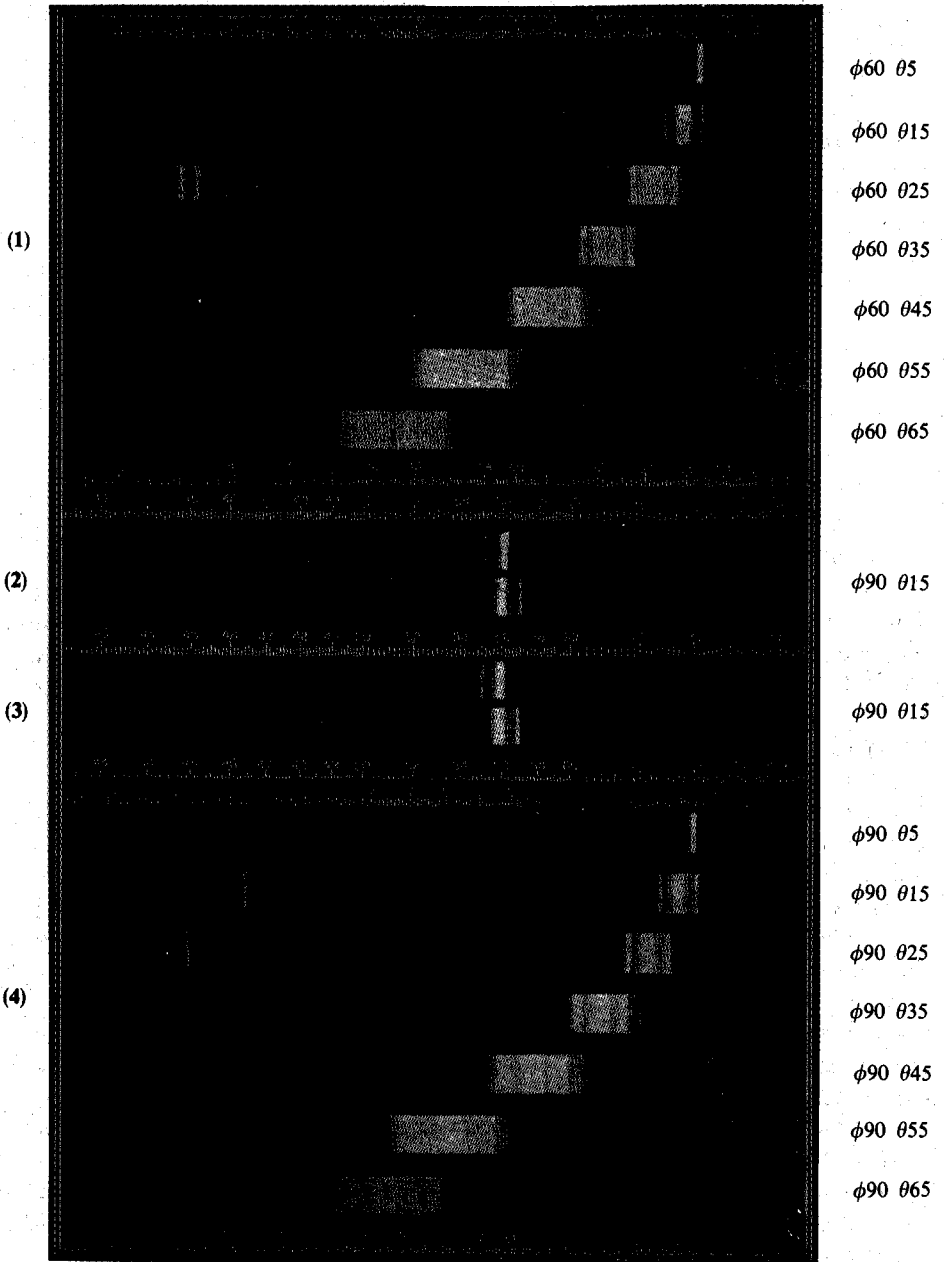
References

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Figures 1-4

Plate I



Figures 1-4

Plate II