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On the iridescence of potassium chlorate crystals—Part I. Its spectral characters

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1. Introduction

It has long been known that potassium chlorate occasionally crystallises in plate-like forms which display a spectacular iridescence, due to the fact that these crystals are polysynthetic twins and that the light traversing the same is reflected at the composition planes of twinning, thereby giving rise to interference effects. An extensive collection of these iridescent crystals was available to us for investigation, and an opportunity recently arose for making a detailed examination of their optical behaviour. Several surprising and interesting results have emerged from our studies, and it is proposed in the series of papers of which this is the first to describe our findings and discuss their significance.

We may usefully recall here the special features of the iridescence of potassium chlorate which drew the attention of the pioneer workers in the field and led them to the explanation stated above. When the crystals are viewed normally, the coloured reflections are absent; they develop and increase in intensity with increasing obliquity of observation, the colour changing more or less rapidly at the same time. Individual cases differ greatly in respect of the brilliancy and colour of the iridescence which they display and in respect of the sequence of changes noticed with increasing angle of incidence of the light. In all cases, however, the irrespective of such angle of incidence the coloured reflection vanishes completely for particular azimuths of the plane of incidence, disappearing twice in each complete revolution as the crystal tablet is rotated in its own plane. A specially noteworthy feature is that the coloured reflection when examined through a spectroscope appears in many cases as a narrow monochromatic band or else as a number of such bands. These bands shift towards shorter wavelengths in the spectrum and simultaneously broaden out to a notable extent as the angle of incidence is increased. The light transmitted by the crystal exhibits effects complementary to those observed by reflected light.

2. Spectral characters of the iridescence

It appeared to us important to obtain a series of spectrograms with selected crystals exhibiting the character of the reflected and of the transmitted light in varying circumstances of observation, viz., over a wide range of angles of incidence, extending from nearly zero upwards, as also over a range of azimuths of incidence extending from that at which the reflections vanish to that at which they attain maximum intensity. One may expect on theoretical grounds to find an increase in the spectral width of the bands of reflection when the azimuthal angle measured from the former position increases from zero to 90°, the angle of incidence of the light remaining the same. This effect has actually been observed by us. Surprisingly enough, however, other and even more striking changes in the nature of the spectra are noticed when the azimuthal angle is changed without changing the angle of incidence.

The spectrograms reproduced in the plates accompanying this paper were obtained with five crystals selected for the reason that all of them at nearly normal incidence of the light exhibit a monochromatic reflection in the visible region of the spectrum. The source of light used was a metal filament lamp run with a heavy current and the spectrograms were recorded with Hilger glass instruments. The crystals were mounted in Canada balsam between two thin prisms of glass facing opposite ways, thereby eliminating the usual reflection from the external faces. We shall refer to the five crystals as A, B, C, D and E respectively. At nearly normal incidence they exhibit respectively deep red, indigo blue, orange red, greenish yellow and green iridescence.

Crystal A: At nearly normal incidence, this has a reflection maximum in the visible spectrum at about λ 6500 in the red having a total width of 100 A.U. In the ultra-violet it shows a reflection maximum at about λ 3290 having a width of about 20 A.U., thereby making it evident that the band in the red corresponds to a first-order reflection. Figure 1 in plate I shows a series of spectrograms of the light in the visible region reflected by this crystal; the plane of incidence was that of maximum intensity of reflection and the seven successive spectrograms show the effect of increasing the angle of incidence by steps from about 5° to 55°; the exposure times were adjusted suitably so that all the spectra were satisfactorily recorded on the same plate. Figure 2 in plate I reproduces a similar series of spectrograms, the azimuth of incidence being however kept constant and nearly that at which the reflections vanish. Longer exposures had naturally to be given for figure 2 than for figure 1.

Examining these spectra, a striking feature is that the principal reflection maximum is accompanied by an extended trail of subsidiary maxima of relatively feeble intensity. The distribution of intensity of these subsidiary maxima shows a notable asymmetry about the principal maximum. They are both more numerous and more intense on the side of longer wavelengths; on the side of shorter wavelengths, the intensity falls off rapidly to zero.

A comparison of figures 1 and 2 in the plate clearly shows that in both cases, the width of the principal maximum increases with increasing obliquity of incidence. On the other hand, it is clear that such increase is definitely less in figure 2 where the azimuthal angle is small instead of being 90° as in figure 1. To illustrate this further, a series of spectrograms have been recorded keeping the angle of incidence nearly constant at about 55° and varying the azimuthal angle by successive steps from nearly 0° to 90°. This series is reproduced as figure 1 in plate V and exhibits a notable increase of the width of the principal maximum in the series. On the other hand, the subsidiary maxima do not exhibit any such widening. Likewise, in the two series of spectrograms taken with increasing obliquity and at a constant azimuth there is no obvious increase in the width of the subsidiary maxima. The increasing dispersion of the instrument in the region of shorter wavelengths results, however, in a corresponding progressive alteration in their apparent width.

3. Splitting of the reflection maxima

We now turn to the spectrograms reproduced in plates II, III and IV which were recorded with crystals B, C and D respectively on the same general plan as those of crystal A reproduced in plate I. Before referring to the features appearing in these spectra, some particulars should be mentioned concerning these crystals. Crystal B gives at nearly normal incidence a reflection maximum at about λ 4780 and 20 A.U. wide; another reflection maximum appears at about λ 3225 with a spectral width of only 8 A.U., from which it is clear that the band in the visible corresponds to a second-order reflection. Crystal C gives at nearly normal incidence a reflection maximum at λ 6150 about 40 A.U. wide. In the violet region, a second maximum at about λ 4155 with a width of 12 A.U. is observed. These two evidently correspond to the second and third order reflections respectively. Crystal D gives a principal maximum at λ 5350 about 20 A.U. wide. This is probably a first-order reflection.

As in the case of crystal A, two series of spectrograms were recorded with each of the crystals B, C and D; in the first series the azimuthal angle was 90° while in the second series it was nearly zero. In each series the angle of incidence was altered by steps from 5° to 55°. A comparison of figures 1 and 2 in the plates referring to each of these crystals shows a striking difference in the nature of the spectra in the two series. When the azimuthal angle is small, the principal maximum of reflection splits symmetrically into components which drift away from each other and also towards shorter wavelengths with increasing angles of incidence. On the other hand, in the spectra recorded at an azimuthal angle of 90° the principal maximum of intensity does not split but merely widens out and drifts towards shorter wavelengths. Simultaneously, however, an additional component or "ghost" appears on either side of the principal maximum in the spectrum but well removed from it. These ghosts or companions broaden and become more intense with increasing obliquity of incidence and the entire triplet simultaneously drifts towards shorter wavelengths. The widening of the central maximum of the triplet in one series of spectra is of the same order of magnitude as the separation of the two components of the doublet in the second series. While this general description covers the effects observed with three crystals, there are some differences in detail, to which attention may be drawn.

Crystal B: As in the case of crystal A, a trail of subsidiary bands accompanies the principal maximum of reflection. These are most clearly seen in the series of spectra reproduced as figure 1 in plate V. One notices that the bands are very fine and numerous. However, they exhibit periodic variations of intensity which convey the impression that a second set of broad bands are superposed thereon.

In order to exhibit the change-over in the nature of the spectra in passing from the azimuthal angle 0° to 90°, a third series of five spectrograms were recorded in which the obliquity of incidence was kept nearly constant at about 45° and the azimuthal angle altered by steps. These are reproduced as figure 2 of plate V from an inspection of which it will be seen that the two components of the reflection maximum in the doublet series coalesce together so as to form the broad central band in the triplet series, while simultaneously, the outer components of the triplet appear and increase in width and intensity.

Crystal C: As will be seen on a comparison of the figures in plates II and III, the general features of the principal reflection maxima exhibited by crystals B and C are similar; the components for crystal C appear rather closer together than for crystal B. It is of interest to note that the doublets and triplets into which the maxima split are to be observed also in the third order reflection appearing towards the violet end of the spectrum. The subsidiary maxima in the spectra of crystal C are somewhat closer than in the case of crystal A but much farther apart than those of crystal B. Their distribution in intensity is very regular and does not show the peculiar features observed in the last-mentioned case.

Crystal D: The components of the triplet are not single but exhibit much detail. It is noteworthy that the components of the reflection maximum in the doublet spectra likewise exhibit a structure. Indeed at oblique incidences, we actually notice in figure 2 of plate IV that the reflection maximum has split into four broad components instead of two as in the case of crystals B and C. The subsidiary maxima in the spectra of this crystal are sharp and numerous, and do not exhibit the regularity of spacing noticed in the case of the other crystals.

4. Transmission spectra

As is to be expected, the transmission spectra in all cases are complementary to the reflection spectra. When the azimuthal angle is nearly zero the reflections and hence also the extinctions are very weak, and only the strongest of the latter are recorded, if at all, in transmission. More detail is however observable in the transmission spectra corresponding to the azimuths of incidence at which the reflection has a maximum intensity.

Figures 1 and 2 in plate VI and figures 1 and 2 in plate VII are a series of transmission spectra recorded with crystals A, B, C and D respectively at an azimuthal angle of 90°, and at varying obliquities of incidence. It will be seen on a comparison with the figures in plates I to IV that they reproduce only the strongest features in the corresponding reflection spectra. In particular, the triplets of the principal maxima exhibited by crystals B, C and D are also to be seen in transmission.

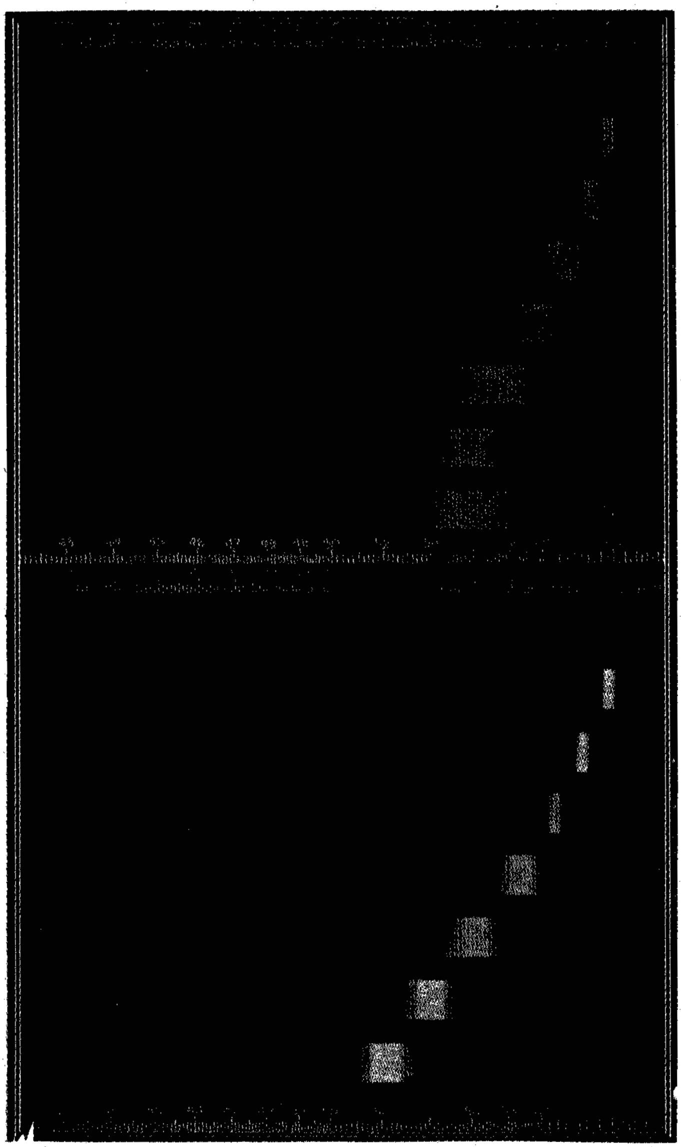
On account of their extreme weakness, the subsidiary maxima are scarcely to be seen in the transmission spectra. Figures 1 and 2 in plate VIII however show for comparison the reflection and transmission spectra of crystal E at varying angles of incidence and at an azimuthal angle of 90°. This crystal shows at nearly normal incidence a maximum of reflection at about λ 5350 and about 150 A.U. wide, and this widens and drifts towards the violet at increasing angles of incidence. The close correspondence in the positions and intensities of the subsidiary maxima of reflection and extinction can be clearly made out from the figures. Figure 3 in plate VIII shows the enormous increase in the intensity of the reflections given by this crystal with increasing azimuthal angle. It will be noticed however, that the positions of the subsidiary maxima remain practically unaltered. Studies made with this particular crystal at very oblique incidences show that both in reflection and extinction, there is a notable widening of the principal band as the azimuthal angle is increased from 0° to 90°.

5. Discussion of the results

Studies described more fully in the second paper of this series have shown that the components of the doublet and the outer components of the triplet recorded with crystals B, C and D are strongly polarised, and related effects have also been observed with crystal A. A detailed discussion of the experimental facts reported in the present paper has therefore to be diferred till we have described and discussed the polarisation effects. The appearance of subsidiary maxima accompanying the strong monochromatic reflections is however intelligible in the light of the general theory of the optical behaviour of stratified media. Reference may be made in this connection to two recent papers in these *Proceedings* by G N Ramachandran dealing with the spectral character of the reflection of light from stratified media and the analogous theory of X-ray reflections in crystals. The spectrograms reproduced in the present paper recall in a striking manner the theoretical curves for the spectral distribution of intensity appearing in the first of the two papers by Ramachandran, quoted above. As has been stressed by him, the spectral width of the principal reflection maximum for a regularly stratified medium is determined by the absolute reflecting power of a single stratification and not by the total number of stratifications present, if the latter be large enough. The experimental findings regarding the effect of varying the azimuth of incidence brought to notice in the present paper fall into line with this indication of the theory.

6. Summary

Spectrograms obtained with five iridescent crystals of potassium chlorate at varying azimuths and obliquities of incidence have been obtained and are reproduced with the paper. Some of the results observed are explicable in terms of the general theory of the optical behaviour of a regularly stratified medium, viz., (a) the appearance of a whole series of subsidiary bands accompanying the principal maxima and distributed asymmetrically about them and (b) the variation of the spectral width of the principal maximum with change of azimuthal angle and obliquity of incidence. Other striking effects are however also observed which are not so explicable, viz., when the azimuthal angle is nearly zero, the principal band splits into a doublet the components of which drift apart progressively and also shift towards shorter wavelengths with increasing obliquity of incidence. When the azimuthal angle is 90° the crystals exhibit the principal maximum as a triplet, the central component of which has a width of the same order of magnitude as the separation of the doublet in the preceding case, while its outer components are much further apart.



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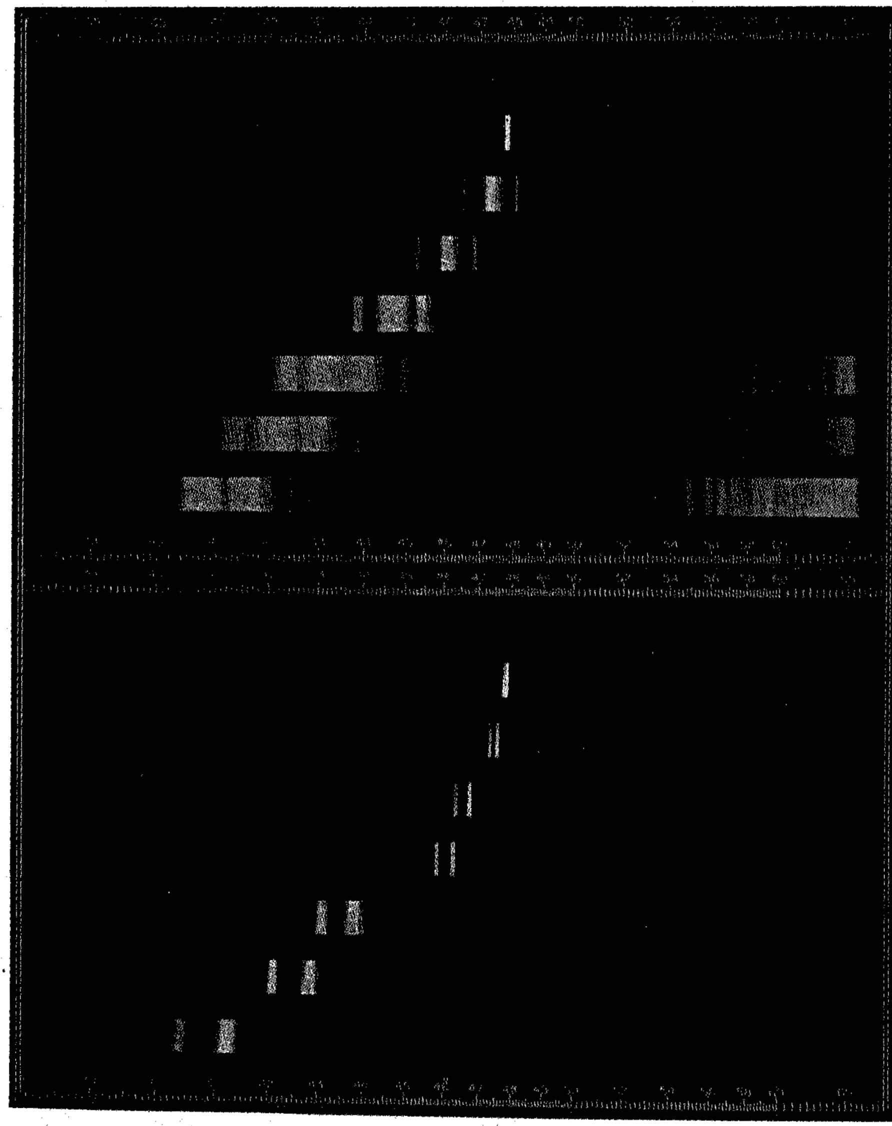
Figures 1 and 2

Plate I



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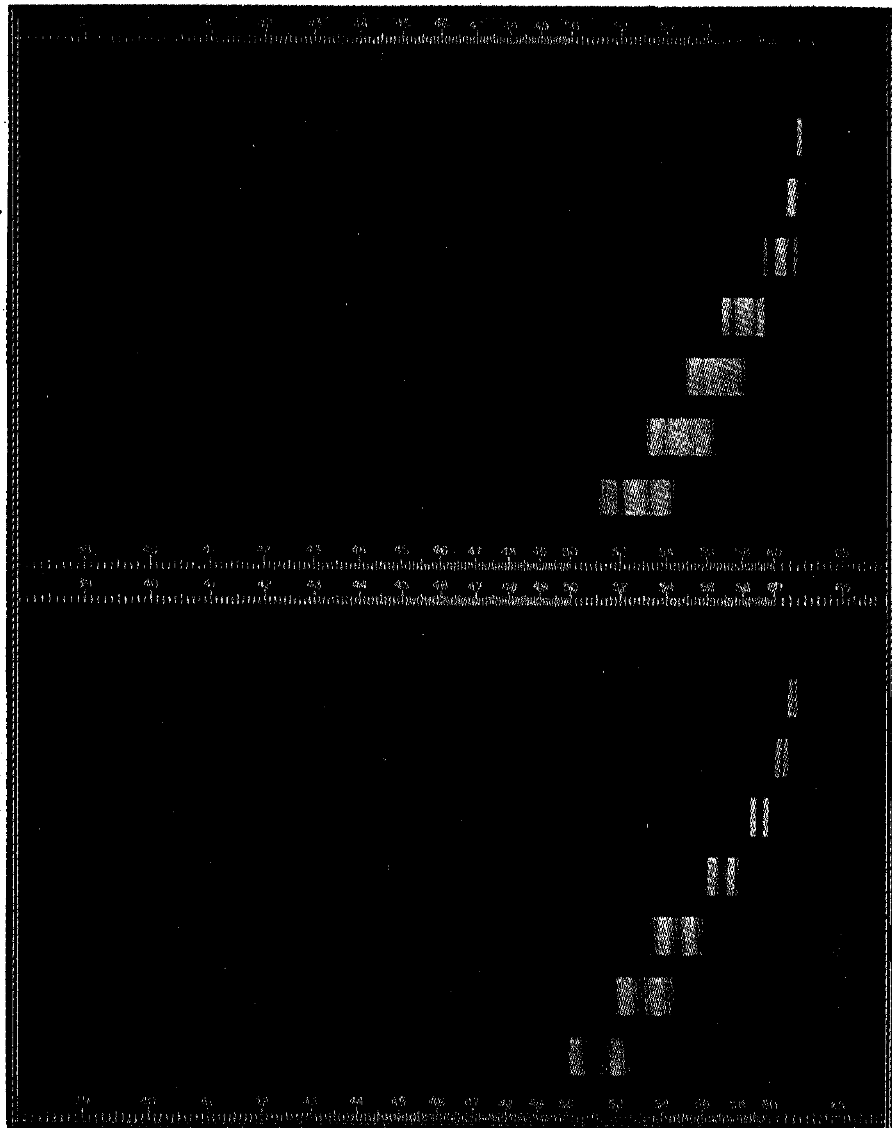
Figures 1 and 2

Plate II



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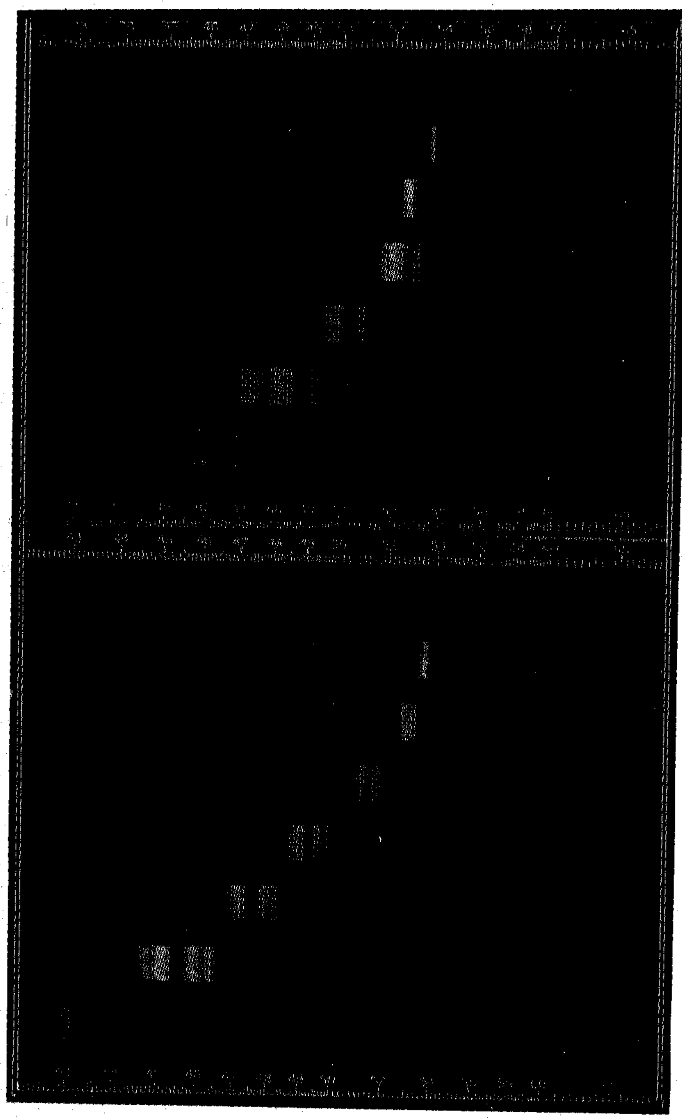
Figures 1 and 2

Plate III



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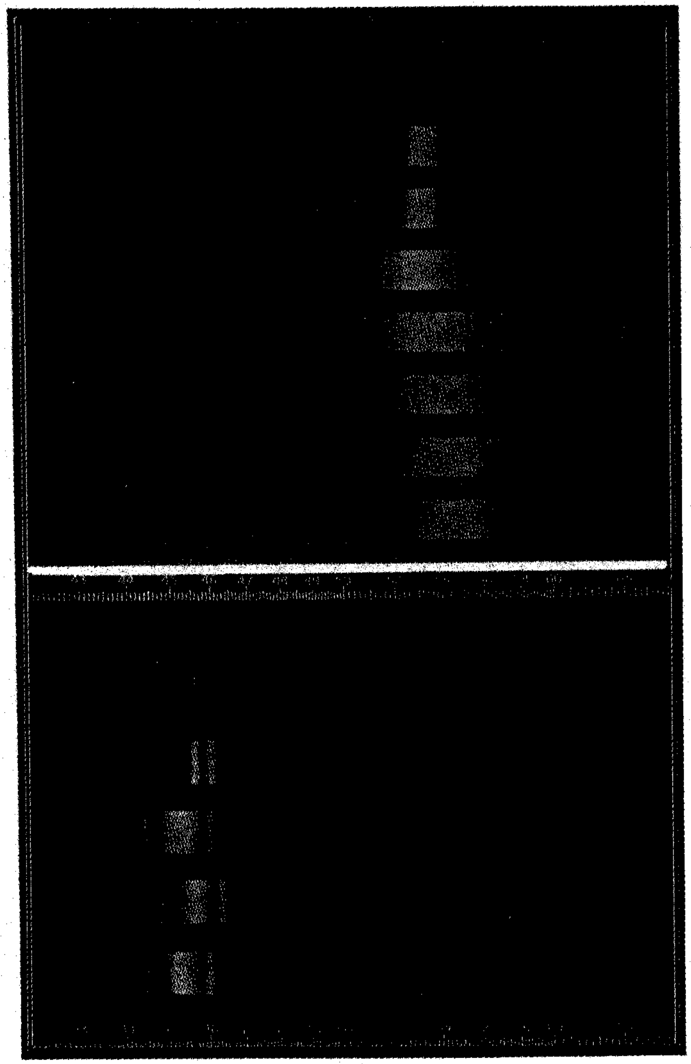
Figures 1 and 2

Plate IV



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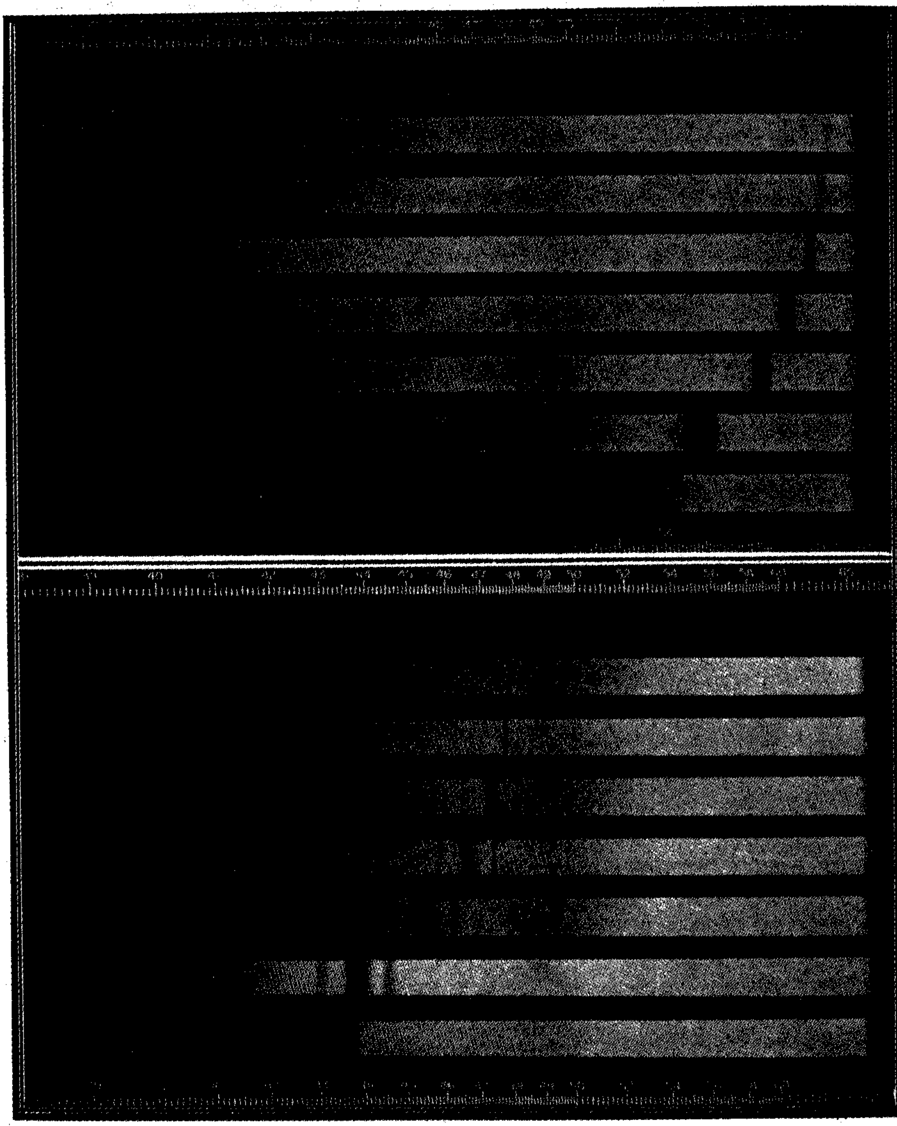
Figures 1 and 2

Plate V



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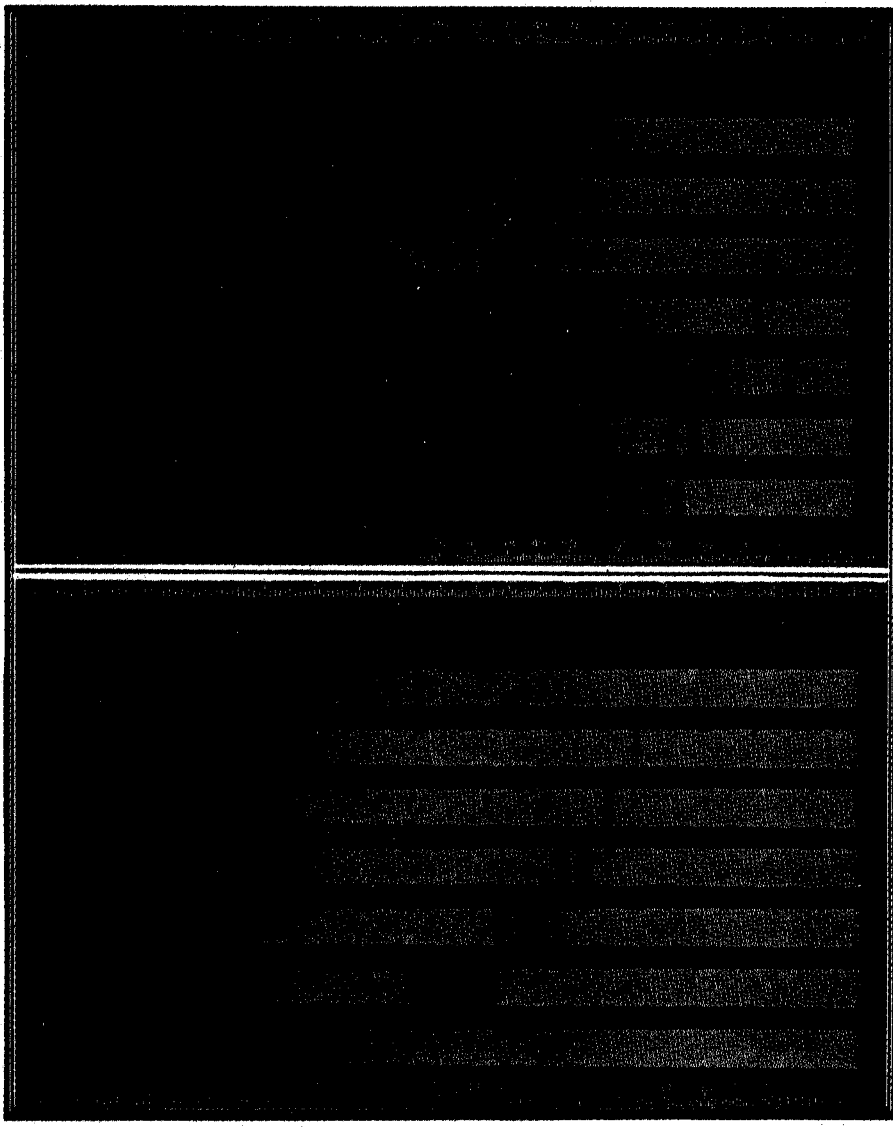
Figures 1 and 2

Plate VI



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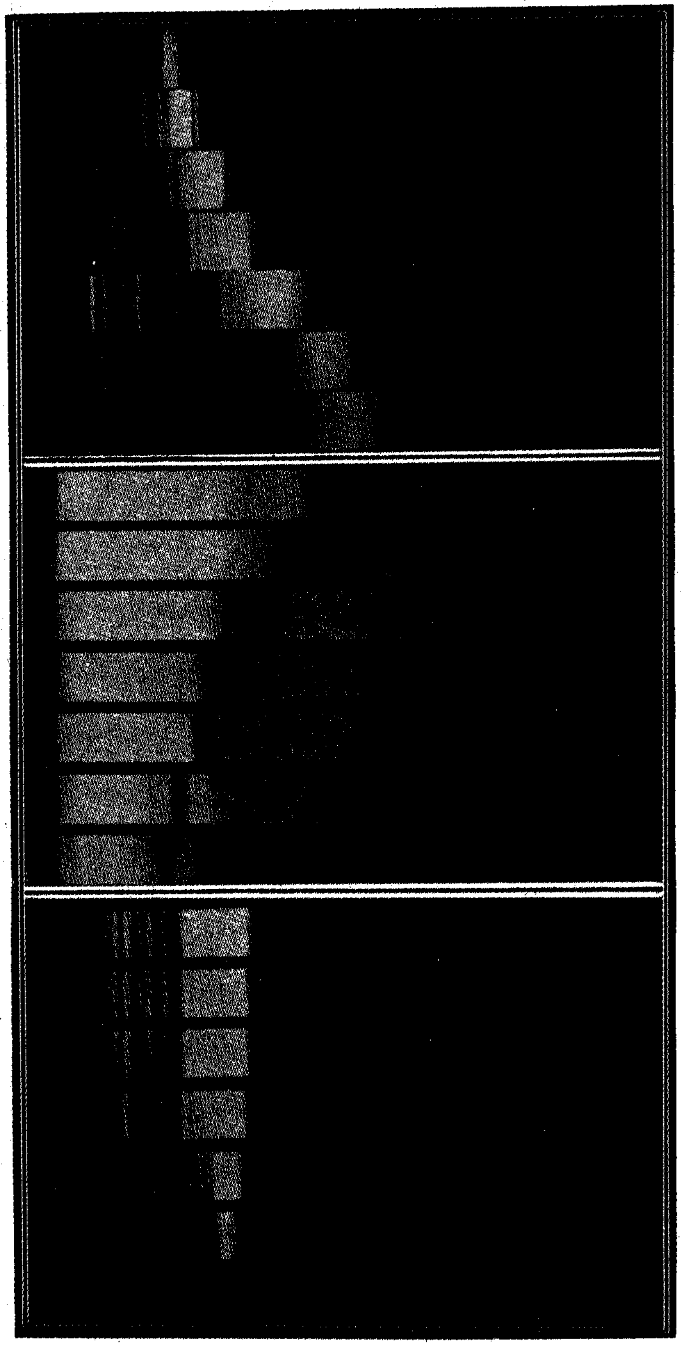
Figures 1 and 2

Plate VII



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Figures 1–3

Plate VIII