

524. *The Intensity of Ultraviolet Light Absorption by Monocrystals. Part I. Measurement of Thickness of Thin Crystals by Interferometry.*

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Two interferometric methods are adapted to measure the thickness of anthracene monocrystals, the results being useful in absorption spectroscopy. The spectral examination of two-beam interference is found to be slightly superior to that of multiple-beam interference. In some instances the use of both methods is advisable.

THE quantitative measurement of light absorption, *e.g.*, by organic monocrystals, has been studied very little, although the results are important in, for example, the theory of electronic states of crystals. In general, a transition observed in a crystal may be intensified or weakened compared with its value in solution in a way that depends on the orientation of the molecules and the polarisation of the transition. Consequently the measurement of crystal extinction values is important in allocating transition polarisations (see Part II, following paper).

Experimentally the chief problem is to measure accurately the thickness of the crystal at the cross-section used for the absorption measurement. Simple methods¹ are insufficiently accurate. For anthracene monocrystals Ehringhaus's² rotatable calcite compensator was found to measure the very small retardations with an accuracy of only 10%. Nor is the determination of oscillator strengths, from measurements of the dispersion of refractive indices of aromatic crystals,³ so simple or so accurate as the two interferometric methods now described.

(a) *Multi-beam Method.*—This depends on the production of Fizeau fringes by a wedge formed from material of refractive index μ . Each fringe is a contour line of equal wedge thickness, d . [For n th order interference of light wavelength λ , the relation $n\lambda = 2\mu d \cos \phi$ holds (where ϕ is the angle of incidence on the wedge).] Multi-reflections, obtained by metallising the wedge surface, increase the fringe definition, but successful results depend⁴ on observing the experimental conditions implied in the theory, *viz.*: (i) small separation of reflecting surfaces; (ii) surfaces of high reflection and small absorption; (iii) monochromatic light; (iv) incident beam parallel, and normal to the surface, to avoid polarisation effects; (v) suitable wedge angle, which is a compromise between that necessary to keep the reflecting surfaces close together and that necessary to observe enough fringes in the field of view.

Since we wished to observe on the one crystal both thickness and the absorption spectrum, making it impossible to transfer a crystal from one mounting to another, conditions for the best measurement of thickness could not be completely satisfied. Thus the reflecting surfaces used were not of silver with 98% reflectivity, because it has an absorption band system of its own at about 3100 Å, but of aluminium with 30–40%. The alternative of mounting the crystal on a clear silica disc which could then be placed between two metallised surfaces for the thickness measurement was tried but found less satisfactory than mounting directly on the aluminised silica disc. The use of an additional disc between the reflecting surfaces so increased

¹ Hartshorne and Stuart, "Crystals and the Polarising Microscope," 2nd edn., Arnold, London, 1950, p. 246.

² Ehringhaus, *Z. Krist.*, 1939, **102**, A, 85.

³ Rodnikova and Eichis, *Zhurn. eksp. teoret. Fiz.*, 1950, **20**, 69.

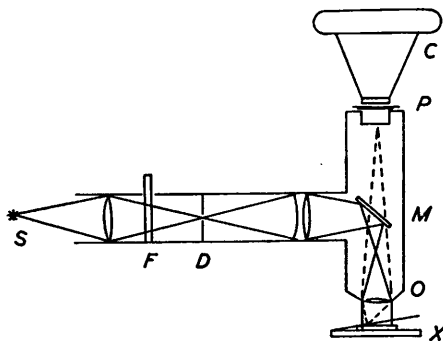
⁴ Tolansky, "Multiple Beam Interferometry," Oxford Univ. Press, London, 1948, p. 143.

the separation that the fringes were much harder to observe [cf. condition (i)]. It was more difficult to mount anthracene plates directly on aluminium than on silica since there was a considerable attraction between the two in the latter case, whereas in the former there was a repulsion when the film had aged. The mounted crystal was then placed on a screw device⁵ which enabled the wedge angle to be varied easily and the fringes made perpendicular to a crystal edge.

A diagram of the apparatus is shown in Fig. 1.

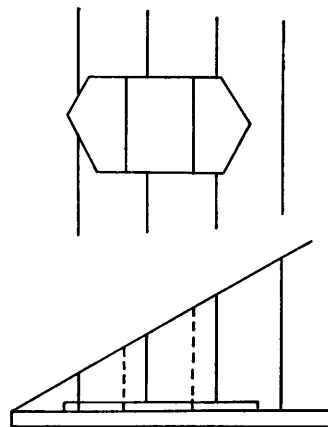
A polariser was necessary since the optical thickness depended upon the polarisation direction of the light. The 45° reflecting disc of thick glass also acted as a polariser and consequently measurements were always made with the more strongly reflected component. If a thin reflector was used, an additional unwanted set of fringes appeared. Nearly monochromatic light was obtained from a sodium lamp or a mercury-vapour lamp with filters. Focusing was effected by a movement of the stage rather than of the tube, so that the side-arm attachment could be fixed permanently. The fringe system could be photographed. A further modification of the original microscope was the fitting of a substage condenser,

FIG. 1. Apparatus for the determination of crystal thickness by multiple-beam interferometry.



S, source; F, filter; D, pinhole; M, mirror; O, objective; X, interference system; P, polariser; C, camera.

FIG. 2. The displacement of interference fringes by a crystal (schematic).



Upper: As seen in the field of view.
Lower: From the side; the crystal is shown between two plates and the fringe positions in the crystal are denoted by broken lines.

polariser, and mirror to give possible illumination by transmission as well as reflection. As a result the extinction position in polarised light could be used to align the crystal in a known way.

Observations were made at a crystal edge and two sets of fringes were compared, due to light which in one case had passed through the crystal and in the other had not (see Fig. 2). The displacement of the one set relative to the other is expressed in units of fringe separation but only the fractional part, f , of the total, $n + f$ (n integral), was observable. Crystals with tapering edges, which would have enabled the total displacement to be observed, were of non-uniform thickness and so unsuitable for the spectral measurements. The fringe displacement ($n + f$) represents a change in optical path by an amount $2d(\mu_c - \mu)$ [d is the physical thickness of the crystal, μ_c the appropriate refractive index of the crystal, μ the refractive index of the surrounding medium]. Since each unit of fringe displacement represents a change in optical path length by λ , then $d = (n + f)\lambda/[2(\mu_c - \mu)]$. A single observation not being sufficient to determine d , observations were made at a number of different wavelengths, *viz.*, 5890–5896 (Na); 5770–5790, 5461, and 4360 Å (Hg). The value of ($n + f$) depended on λ because of the variation in μ_c and μ . From the group of f values so obtained for the various values of λ , d was determined graphically. For a given λ , μ_c , and μ , a plot of d against ($n + f$) is linear, so for a given crystal and for given optical directions within it a chart may be drawn similar to that shown in Fig. 3 for the a and b crystal directions in sublimed anthracene flakes. Inspection of the chart reveals which value of d best correlates with the observed group of f values. Fig. 3 applies to anthracene

⁵ Heavens, *J. Sci. Instr.*, 1950, **27**, 172.

when mounted directly on aluminium and surrounded by air. Difficulties met included : (i) the fact that sometimes for a particular crystal the wavelength used was such that reflection from the upper and the lower crystal surface gave rise to destructive interference, which obscured the dark fringes in the crystal; (ii) because of the fact that the mercury doublet, 5770 and 5790 Å, was not separable by the filter used the definition of the fringes varied with the order of the fringe and so with the crystal thickness; (iii) the sense of the fringe displacement, right or left, was not immediately obvious. Whether an observation was either of f or of $(1 - f)$ was resolved by one or other of the following methods : (a) By applying a gentle pressure to the upper surface of the interference wedge, directly above the crystal, the fringes could be made to move in a direction opposite to that of the original displacement due to the crystal; (b) an increase in the wedge angle caused the fringes to move towards the apex of the wedge. Since the optical path between the reflecting surfaces was increased by the presence of the crystal, the fringes were always displaced by the crystal in the same way; (c) replacement of the point source by an extended source⁶ produced a broadening of the fringes on the side of increasing thickness; (iv) the error in any one observation of f was often 0.1 of a fringe. Consequently, there were sometimes several values of $(n + f)$, and thus of d , which were consistent with the one set of observations of f . In such cases a comparison was made with the results from other

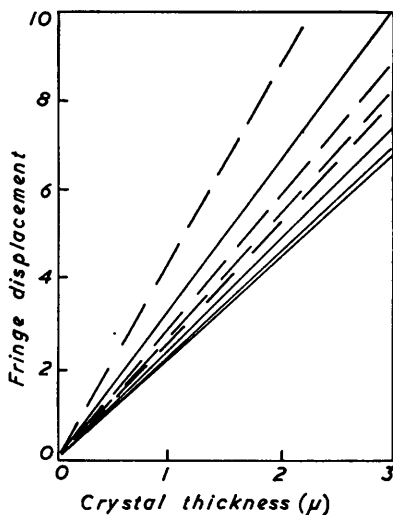


FIG. 3. *Fringe displacement in anthracene.*
Light polarised : broken lines, parallel to b ;
full lines, perpendicular to b .

methods, or else the air inside the wedge was replaced with water and a second group of f values obtained, which with the first indicated an unambiguous value for d . The results on some anthracene crystals which were measured several times with both water and air media are included in Table 2. The error in the observation of f was independent of the value of n and therefore the percentage error in measuring d was greater the thinner the crystal. For crystals 0.3μ thick, which were suitable for spectroscopic work, the accuracy was $\pm 0.015 \mu$. The accuracy is therefore comparable to that obtained in the spectroscopic measurement of absorption intensity.

(b) *Two-beam Method.*—The measurement of crystal thickness by studying the variation in two-beam interference with wavelength is a refinement of the visual observation of interference colours. The interference arises from the light's being reflected from both the front and the rear surface of the crystal. In air, there is a change of phase of π , corresponding to $\lambda/2$, upon reflection from the front surface across which the refractive index increases, but not upon reflection from the rear surface. A crystal of anthracene which lay across an aluminium-silica boundary showed two colours : the area covering silica retained the colour observed at normal incidence in air, whilst the area covering the aluminium changed to the complementary colour. Such experiments established the existence of a phase change at an anthracene-aluminium interface, a fact which was hard to predict because of the variation of the refractive index of aluminium films with thickness.⁷ For a wavelength at which the two beams interfere

⁶ Brossel, *Nature*, 1946, 157, 623.

⁷ International Critical Tables, McGraw-Hill, 1929, 5, p. 252.

destructively upon reflection and at which the transmitted light is a maximum, the optical thickness, t , of the crystal is given by

$$t = n\lambda/2, \text{ where } n = 0,1,2 \dots \dots \dots (1)$$

It is assumed that the crystal is mounted on silica or other material for which $\mu < \mu_c$. For a wavelength at which the transmitted light is a minimum,

$$t = (2n + 1)\lambda/4; n = 0,1,2 \dots \dots \dots (2)$$

for a mounting on silica. When the crystal is on aluminium equation (1) applies to a minimum and equation (2) to a maximum in the transmitted light. The spectrum of such a crystal contains alternate light and dark bands, "apparent absorption" bands, but these are unimportant where true absorption is strong.

A Beckman DU spectrophotometer was used to determine the wavelengths of maximum and minimum light transmission up to about 13,000 Å. Typical curves, for anthracene on silica and

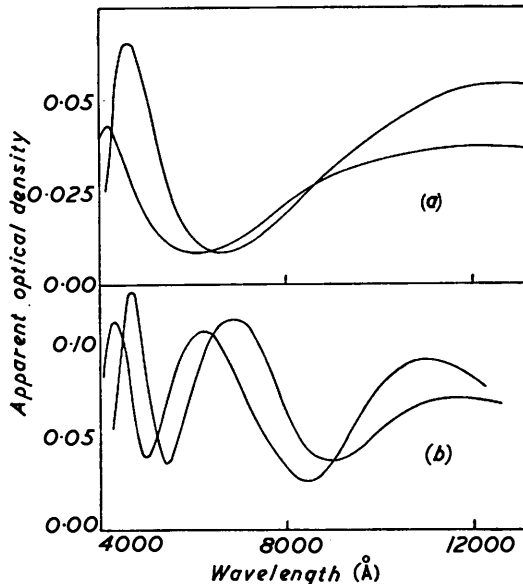


FIG. 4. Two-beam interference bands.
(a) For thin anthracene crystal on silica,
(b) for thicker anthracene crystal on alumina on silica.

(for a somewhat thicker crystal) on aluminium are shown in Fig. 4. Curve (a) is characteristic of low-order interference.

The refractive index of anthracene crystals varies with the wavelength in a known way.^{8,9} Consequently the physical thickness of the crystal can be calculated from the formula $d = k\lambda/\mu_c$ where $k = n/2$ in equation (1) and $k = (2n + 1)/4$ in equation (2). The value of k corre-

TABLE I. Values of λ , λ/μ_c , k , and d , for a and b directions in an anthracene crystal on aluminium.

Transmission	k	a direction			b direction		
		λ^*	λ/μ_c	d^*	λ^*	λ/μ_c	d^*
Minimum †	0.50	1.11	0.695	0.348	1.16	0.682	0.341
Maximum	0.75	0.844	0.510	0.382	0.900	0.512	0.383
Minimum	1.00	0.612	0.370	0.370	0.684	0.383	0.383
Maximum	1.25	0.505	0.299	0.374	0.545	0.300	0.375
Minimum	1.50	0.430	0.246	0.370	0.465	0.245	0.368

Mean $d = 0.369 \pm 0.009$.

* In microns.

† Corresponding to a maximum in optical density.

sponding to the experimentally determined λ/μ_c can easily be found by inspection. By applying this procedure to the thicker crystal of the two in Fig. 4, d was found to be $0.369 \pm 0.009 \mu$ (see Table I). It is not easy to explain the variations in the value of d in Table I unless the

⁸ Obreimov, Prikhotjko, and Rodnikova, *Zhur. eksp. teoret. Fiz.*, 1948, 18, 409.

⁹ Eichis, *ibid.*, 1950, 20, 471.

TABLE 2. *Crystal thickness (in microns) measured by multibeam and two-beam interferometry.*

Crystal	Multibeam		Two-beam
	In air	In water	
1	0.345 ± 0.015	0.355 ± 0.015	0.369 ± 0.009
2	0.350 ± 0.015	—	0.367 ± 0.006
3	0.185 ± 0.015	—	0.192 ± 0.003
4	0.485 ± 0.015	0.510 ± 0.015	0.467 ± 0.007
5	0.460 ± 0.015	—	0.458 ± 0.004
6	0.195 ± 0.015	—	0.177 ± 0.005
7	0.182 ± 0.015	—	0.190 ± 0.010

refractive indices themselves involve a significant error. In particular, the value of μ at 1.11 microns appears to be rather in error. The formula $3\sum r/(N^{3/2})$ was used for the error (r , the modulus of the deviation of an individual value from the mean; N , the number of values of d). For the crystal discussed in Table 1 (No. 1 in Table 2) the error was over 2%. This was higher than that usually found, as may be seen from Table 2.

Experimental errors arise from two causes when the crystal is thin. The few maxima and minima observable in the visible region are broad, since the interference is of low order. The wavelengths of maxima and minima are then measurable with less precision, and the number of turning points is also low.

A comparison of the various methods used shows also that the multibeam method using air gives results consistent with the same method using water as the medium between the plates. Both multibeam methods agreed with the two-beam method to within the errors calculated for each. Of the two, the results indicate that the two-beam method has greater accuracy under the conditions used and since, also, it does not require a mounting on aluminium, it is the more suitable in applications to spectroscopy.

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