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The Concentration of the Solution Round a Growing Crystal

By S. P. F. Humphreys-Owen

Birkbeck College (University of London), Malet Street, London W.C. 1, *England*

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Reference is made to a paper by Goldsztaub & Kern, who, employing a new experimental technique, were unable to confirm the previously reported observation that the concentration at, or very near to, a growing crystal face is not uniform. It is pointed out that there has been an overestimate of the sensitivity of this new method, and that the negative result may thus be explained.

A crystal growing in solution modifies the concentration in its neighbourhood. If the crystal and surrounding solution is confined to a thin film between glass plates, the modification of concentration is revealed by a modification of the optical path through the film, and may be studied by a suitable optical technique. Berg (1938), Bunn (1949), Humphreys-Owen (1949), and Krueger & Miller (1953) employed multiple-beam interference fringes and found, amongst other things, that the concentration at, or very near to, a growing crystal face was not uniform as expected, but had a minimum at the face centre.

On the other hand, Goldsztaub & Kern (1953) employed a different optical technique and were unable to confirm the above-mentioned effect. They suggest that the sensitivity of the previous methods was insufficient, particularly in regard to the sharpness of the fringes.

Now this is not so. Although fringe sharpness in the work before 1953 was admittedly not as good as can now be obtained, it was quite sufficient to bring out the main features, and indeed I was able, for example, to set up empirical equations of some precision (Humphreys-Owen, 1949). But, in addition to this, there are the published photographs by Krueger & Miller (1953, p. 2021, Fig. 5) which leave no doubt as to the existence of the effect under discussion, whatever may be its interpretation.

In view of this, it is worth while to seek an explanation for the negative result obtained by Goldsztaub & Kern. In their method two images of the solution film, laterally displaced relative to each other, are made to interfere. White light is employed and the result is that one point in the focal plane of a microscope focused on the film is a coloured combined image of two points in the solution film.

Let these points be represented by ϱ_1 and ϱ_1', respectively, and let the refractive index of the solution at these two points be n_1 and n_1' respectively. The geometrical path through the film is constant, t, say, and the respective optical paths are tn_1 and tn_1'.

The tint of the combined image at one point in the focal plane of the microscope is determined by the path difference $t(n_1-n_1')$. Similarly, another point in the focal plane will be the combined image of two other points ϱ_2 and ϱ_2' in the solution film, and will have a tint determined by the path difference $t(n_2-n_2')$.

The difference of tint between the two points in the focal plane is a second-order effect determined by the difference of path difference

$$\Delta = t\{(n_1-n_2)-(n_1'-n_2')\} . \tag{1}$$

It is claimed for this method that points of identical tint in the focal plane represent points of identical n in the solution film, so that curves through them are curves of equal concentration in the solution film. It can be seen from (1) that this is true if the lateral displacement of the two images is great enough for one pair of points ϱ_1' and ϱ_2' to be so far from the crystal that $n_1'-n_2' = 0$.

The authors have of course understood this, but they have underestimated the lateral displacement necessary. I have elsewhere pointed out (Humphreys-Owen, 1949, p. 223) that the concentration far from the crystal under these quasi-two-dimensional conditions is not uniform until a distance from the crystal centre is reached of about three times its half-side.

Inspection of the photograph (Goldsztaub & Kern, 1953, Fig. 4) shows a displacement, in the direction of the crystal diagonal, of 0·0066 cm. Consider the task of detecting the difference of n between corner and centre of a crystal face, using this displacement. The quoted supersaturation is 6 g./100 g. solution. Now a crystal whose n-contours are drawn in my paper (Humphreys-Owen, 1949, p. 232, Fig. 11(*b*)) was grown in just this supersaturation. The contours are spaced 0·00020 apart, and the scale is 1 cm. on the page = 0·0091 cm. in the solution film. A count of about 7 contour divisions from centre to corner of the fast-growing face determines n_1-n_2, say. The image displacement of Goldsztaub & Kern corresponds to 0·73 cm. on the page, so that a count of contours cutting a line drawn parallel to the line of the face, and displaced by this amount in a diagonal direction, gives an estimate of $n_1'-n_2'$. In this particular example Δ in (1) would be nearly zero for one side of the face, and fairly large on the other side. In general, however, one can see that the displaced line will be in a region of varying n, and that the method has not the sensitivity claimed for it. The sensitivity would be still further reduced if, as often happens, a face is growing at less than the maximum rate permitted by diffusion, and the contours are less crowded.

It is suggested that, in view of these comments, an explanation has been found for Goldsztaub & Kern's negative result.

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The Space Group of Anthraquinone

By B. V. R. Murty

Physics Department, University of Allahabad, India

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The weak forbidden reflexions which were observed by Sen in the zero-layer [010] Weissenberg photograph of anthraquinone and which prevented him deciding on the space group are shown to be due to Renninger reflexions. By applying the statistical tests of Wilson and Howells *et al.* to the ($hk0$) and ($0kl$) projections, the presence of a centre of symmetry is also proved. The space group of anthraquinone is therefore unequivocally established as $P2_1/a$.

Introduction

The crystal structure of anthraquinone, $C_{14}H_8O_2$, was determined by Sen (1945) by two-dimensional Fourier synthesis. The pseudo-orthorhombic ($hk0$) (monoclinic ($h0l$)) projection was well resolved. On applying Booth's (1945) accuracy test, the value for R_1 for the projection is 0·21, which is a comparatively large figure. Moreover, all the possible reflexions in that projection with Cu $K\alpha$ were not recorded. It was, therefore, thought worth while to undertake a refinement of the structure by a three-dimensional Fourier synthesis. Sen (1940) assigned to the crystal the space group $P2_1/a$, but in his later work (Sen, 1948) mentioned the observation of a few weak forbidden reflexions ($h0l$ with h odd) on a strong Weissenberg photograph, and this led him to ascribe $P2_1$ as the correct space group. In the present investigation a critical re-examination of the space group was therefore undertaken.

Forbidden reflexions

An over-exposed normal-beam zero-layer-line Weissenberg photograph about [010] was taken, using unfiltered Cu radiation, in order to record the forbidden reflexions observed by Sen. In this photograph a few more reflexions of the same type appeared. All these spots were sharper than the normal reflexions, and, moreover, even the strongest of them was not associated with the usual reflexion due to Cu $K\beta$ whereas every equally intense normal $K\alpha$ reflexion had its $K\beta$ reflexion. These reflexions were, therefore, suspected of being due to double reflexions from two strong reflecting planes, as suggested by Renninger (1937). By construction in the reciprocal lattice these reflexions were found to be due to double reflexions, as shown in Table 1. In all cases but the last one the contribution is observed to be from more than one pair, and estimates of intensity agree with the sum of the intensities expected from the various pairs that produce any particular reflexion.

Table 1

Observed forbidden reflexion	Pairs of planes giving rise to the corresponding forbidden reflexion
(101)	$(11\bar{3}, 0\bar{1}4)$, $(211, \bar{1}\bar{1}0)$, $(52\bar{4}, \bar{4}\bar{2}5)$
(102)	$(212, \bar{1}\bar{1}0)$, $(11\bar{1}, 0\bar{1}3)$, $(413, \bar{3}\bar{1}\bar{1})$
$(\bar{1}02)$	$(321, \bar{4}\bar{2}1)$, $(013, \bar{1}\bar{1}\bar{1})$
(302)	$(512, \bar{2}\bar{1}0)$, $(211, 1\bar{1}1)$
$(\bar{5}02)$	$(\bar{2}11, \bar{3}\bar{1}1)$, $(210, \bar{7}\bar{1}2)$
(103)	$(112, 0\bar{1}1)$, $(61\bar{4}, \bar{5}\bar{1}7)$
$(\bar{3}03)$	$(110, \bar{4}\bar{1}3)$

Statistical tests for centrosymmetry

The presence of the centre of symmetry required by this space group was confirmed by the statistical methods of Wilson (1949) and Howells, Phillips & Rogers (1950). Normal-beam Weissenberg photographs about the monoclinic [100] and [001] axes were taken with unfiltered Cu radiation. Integrated intensities of the spots were measured with a Moll recording microphotometer and were corrected for the angle factor only. Relative values of the structure factors were