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Bragg Reflexion Curve from a Perfect Crystal

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It is pointed out that the Ewald and Darwin theories, although they follow very different mathematical methods, lead exactly to the same results when appropriate physical assumptions are made.

It seems not to be generally known that for a symmetrical Bragg reflexion given by a perfect non-absorbing crystal different reflexion curves were given by Darwin (1914*a*, *b*) and by Ewald (1918, 1925) outside the region of total reflexion. A useful table comparing the results of the two theories is given by Zachariasen (1945, p. 142) and is reproduced in Table 1.

Table 1

	Ewald	Darwin
Reflecting power		
$R \begin{cases} \lvert y \rvert \leqslant 1 \\ \lvert y \rvert \geqslant 1 \end{cases}$	1 $1-\sqrt{(y^2-1)}/\lvert y \rvert$	1 $\{\lvert y \rvert-\sqrt{(y^2-1)}\}^2$
Integrated reflexion		
$I=\int_{-\infty}^{+\infty} R\,dy$	π	$\frac{8}{3}$
Half-width in y-units		
w_y	$\frac{2}{3}\sqrt{3}=1\cdot155$	$\frac{3}{4}\sqrt{2}=1\cdot061$

In this, combining formulae (3·141) of Zachariasen (1945) and (6·49, 6·51) of Compton & Allison (1935), we have

$$y=\frac{(\theta-\theta_B)\sin 2\theta_B}{|\psi_H|}-\frac{\psi_0}{\psi_H} \quad \text{for Ewald's theory,} \quad (1)$$

and

$$y=\frac{(\theta-\theta_B)\sin 2\theta_B}{2\Delta}-\frac{\delta}{\Delta} \quad \text{for Darwin's theory.} \quad (2)$$

It is readily seen that the two expressions are equal, for ψ_0 and ψ_H are the Fourier coefficients in the expansion of the dielectric density $(\epsilon-1)$ and $\delta/\Delta=\psi_0/\psi_H$, $2\Delta=\psi_H$.

It is interesting to examine the origin of the difference between the two formulae. It cannot arise from the fundamental assumptions which are the same in both theories, viz. that account is taken of the multiple reflexions between the two directions of incidence and of reflexion. It is actually due to the difference in the assumptions regarding the wave reflected back internally from the back surface of the crystal plate (the X-rays being incident on the plate from the front). Darwin assumes in effect that the plate is of such thickness t that $e^{-2\mu t} \ll 1$ (μ being the linear absorption coefficient), which ensures that no ray of appreciable intensity will emerge from the front surface of the plate after having traversed it in the two directions even for angles for which there is no primary extinction. This contradicts the assumption made otherwise of a non-absorbing crystal, but may be taken to be a reasonable approximation for the region where the much more effective primary extinction ceases to make the calculation of the reflected intensity a fully defined problem. Ewald's formula is obtained without introducing absorption, by dropping the assumption that the crystal plate can be assigned a definite thickness to the accuracy of within an X-ray wave-length. If the plate were truly plane-parallel, high-order interferences between the rays from the front and the back would arise, as from a Lummer-Gehrcke plate. Ewald's solution is obtained by integrating over varying thickness of the plate, while assuming that at any time the plate is perfectly plane-parallel. This, again, is an artificial idealization.

The precise significance of the difference between the two formulae is obtained from the following considerations where both can be derived as two limiting cases of a finite absorbing crystal, according to which of two variables is first made to reach the limit, the number of planes in the crystal to infinity or the absorption coefficient to zero. Starting from Darwin's difference equations, it is possible to solve them for a crystal consisting of a finite number (n) of reflecting planes (Ramachandran, 1942, 1944). If, in this formula, one puts $n \to \infty$, then one obtains the formula given by Prins (1930), in which, putting the absorption coefficient μ zero, one arrives at Darwin's formula as given above. It is obvious that the first limit is inapplicable when $\mu=0$, so that one has implicitly brought in Darwin's assumption in this derivation also. On the other hand, if one first puts the absorption coefficient zero in the formula of a finite crystal and then proceeds to the limit $n \to \infty$, the intensity tends to no limit at all outside the region of total reflexion, but fluctuates owing to high-order interferences. One can, however, arrive at Ewald's formula without the artificial assumption of varying thickness by the following method. If one examines the solution for a fairly thick finite crystal (Ramachandran, 1942), one finds that there is a primary maximum of angular width nearly equal to that for infinite thickness, together with a series of subsidiary maxima on either side. As the thickness is increased, these subsidiary maxima come closer and closer, until in the limiting case one would not observe them at all (it would require an infinite resolving power for this), but only a uniform intensity corresponding to an average over a cycle. Performing this average, one obtains for the intensity an expression $1-|\tanh\alpha|$, where $\cosh\alpha=y$ of equation (2) (Ramachandran, 1944), which is identical with that given in Table 1 under Ewald. Incidentally, it may be noted that the dynamical theory also gives Prins's formula for an absorbing crystal (Kohler, 1933) from which Darwin's formula can be derived by the process given above. It is thus gratifying that the two theories, with their entirely different mathematical techniques, lead to identical results when the appropriate physical assumptions are put in.

It would be clear from the above that the problem of the Bragg reflexion by a perfect non-absorbing, or not sufficiently absorbing, crystal plate requires a more detailed specification of the conditions at the back of the plate. Ewald & Schmid (1936) have shown that, given any such specification, the exact intensity curve can be obtained from Ewald's solution by simple considerations of optical path without rediscussing the dynamics of field propagation. This can also be done by the Darwin method, using the mathematical procedure given by Ramachandran (1942, 1944).

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On the Patterson Transforms of Fibre Diagrams

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A method is given for the calculation of a two-dimensional Patterson transform from the intensity data of a fibre diagram. This vector map is a section parallel to the fibre axis through the cylindrically symmetrical three-dimensional Patterson transform of the fibre.

1. It has become a fairly general practice to begin the theoretical part of the X-ray analysis of single crystals by computing the Patterson diagram or vector map. This is the Fourier transform of the intensity data, and it offers a convenient synopsis of what can be derived about the crystal structure without introducing any assumptions.

From powder or 'amorphous' diagrams statistics of absolute values of atomic distances can be obtained from a similar transform, as Zernike & Prins (1927) have pointed out. (Since orientation is random in crystal powder or amorphous material, it is evident that no information whatever can be derived from these diagrams about the direction of the interatomic distances.) Warren and his school have used this method with considerable success in their investigations of glass, rubber, etc. The equivalent method of tackling the typical *fibre* diagrams, however, seems never to have been developed, and it was, therefore, considered worth while to fill this gap in the theory because the fibre texture is, in most macromolecular substances, the highest degree of orientation attained up to now.

2. In the following we confine ourselves to the ideal fibre texture, defined by (*a*) strict periodicity in the direction of the fibre axis, and (*b*) completely random orientation of azimuth round this direction. No assumptions need be made as to a more or less regular arrangement in directions other than the fibre axis.