Acta Cryst. (1948). **1**, 49

Crystalline Texture and the Determination of Structure Amplitudes

BY W. A. WOOSTER AND G. L. MACDONALD
Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England

(*Received* 23 *September* 1947)

Absolute measurements of the integrated reflexion for selected planes in calcite, quartz, gypsum, fluorspar and mica have been made using both molybdenum and copper characteristic radiations. An experimental method is described whereby the structure amplitude can be determined in spite of the great variations in the integrated reflexion associated with the different degrees of imperfection found in crystals of the same species. It is shown that it is necessary to use more than one wavelength of X-rays in assessing the degree of imperfection of a given specimen from the value of the integrated reflexion.

Introduction

It was discovered in the earliest investigations on the reflexion of X-rays from crystals that the intensity of reflexion depended largely on the perfection of the crystal. In general, the more perfect the crystal the less was the measured intensity of reflexion. Account was taken of this in developing theories (Darwin, 1922) which connected the observed intensities of reflexion with crystal structure. Two extreme states of perfection were recognized, namely, the 'perfect' and the 'ideally imperfect'. The 'perfect crystal' is a conception which corresponds to certain carefully prepared specimens of real crystals, and the 'ideally imperfect crystal' as conceived in the theories is probably also a fairly close representation of some actual crystals. However, crystals contain visible imperfections of many kinds and not all are represented by the theoretically 'ideally imperfect crystal'. Some may be likened to a brick wall in which the bricks are perfect but their relative arrangement is somewhat irregular. Other crystals may be compared with the leaves of a crumpled book in which the arrangement of atoms within any one layer is nearly perfect, but between the layers the fitting together of the atomic arrangement is less perfect. Such a type of crystal texture is probably found in flaky materials such as gypsum or mica. Yet another type of imperfect crystal may be compared with a bundle of metal wires. The arrangement is relatively perfect along a narrow column, but regularity is lost in going from one column to a neighbouring one. Such materials as tremolite, which may be actually fibrous, probably possess crystal textures of this kind. It is not very probable that theories can be developed to cover all types of crystal imperfection, and for this reason the following attempt of a purely experimental character has been made to acquire information about crystal texture and also to see how the measurements may be used in crystal structure determinations.


(*a*) (*b*) (*c*)

Fig. 1. (*a*) Recording of ionization current. $\lambda = 0{\cdot}71$ A. (crystal-reflected Mo $K\alpha$ radiation). Cornish quartz $(10\bar{1}1)$. (*b*) Recording of ionization current produced by direct X-ray beam after passing through 2·76 mm. aluminium. (*c*) Same as (*b*) except that the thickness was 2·07 mm.

Experimental method

All the following measurements were made using the automatic ionization spectrometer described by Wooster & Martin (1936). The record (*a*) shown in Fig. 1 gives the ionization current as ordinate and the angle of rotation of the crystal as abscissa. The ordinates giving the deflexion of the galvanometer were calibrated in terms of the strength of the direct beam by passing the direct beam through a known thickness of aluminium and then into the ionization chamber. The records (*b*) and (*c*) show the deflexion due to the direct beam after passing through two different thicknesses of aluminium. In order to ensure that the reduction factor due to the aluminium is that calculated from the known linear absorption coefficient for the characteristic radiation and the thickness, it is necessary to use radiation reflected from a crystal for which there is no second-order reflexion, and to use a voltage on the X-ray tube insufficient to excite a wave-length one-third of the characteristic wave-length. A cleavage plate of fluorspar was used as the monochromator because it satisfies the above requirement.

The integrated reflexion is derived from the photographic record in the following manner. The intensity of the direct beam I, is given in arbitrary units in terms of the deflexion, f, of the galvanometer and the thickness, t, of the aluminium through which the beam passed before reaching the chamber. The absorption coefficient of the aluminium is taken as μ and we may therefore write:

$$I = f/e^{-\mu t}.$$

The area, A, under the sweep curve was measured with a Coradi planimeter and the angle of displacement of 1 cm. along the record, k, was determined. The integrated reflexion, ρ, is related to A and I in the manner shown in Fig. 2. If I is plotted on the same scale as the ionization current produced by reflexion from the crystal, then the shaded area having sides I and ρ is equal to the shaded area A. Since ρ is expressed in angular measure $I\rho/k = A$ or $\rho = kA/I = (kA/f)\, e^{-\mu t}$.

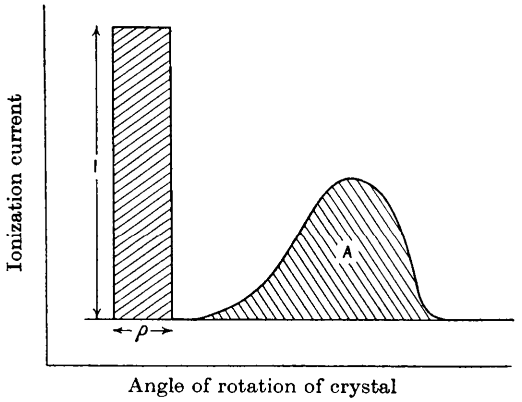

Fig. 2. Diagram showing the method of computing ρ from the equality of the areas of the sweep curve A and the rectangle of sides given by the intensity of the incident X-rays, I and ρ.

The values of ρ were determined for a number of crystals using two wave-lengths, namely, Mo $K\alpha$ ($\lambda = 0{\cdot}71$ A.) and Cu $K\alpha$ ($\lambda = 1{\cdot}54$ A.). Philips Metalix tubes, operated at 35 kV. for Mo $K\alpha$ and 24 kV. for Cu $K\alpha$, were used on a set provided with constant voltage from a local alternator driven by an induction motor. After each recording of the intensity of the beam reflected from the crystal the goniometer head supporting the crystal was removed and the intensity of the direct beam was at once recorded. This procedure was repeated six times for each measurement of ρ in order to minimize the error, which varied somewhat with the perfection of the crystal. On an average the experimental error was about $\pm 5\,\%$.

The crystals used were of calcite, $CaCO_3$; quartz, SiO_2; gypsum, $CaSO_4 . 2H_2O$; fluorspar, CaF_2; and mica, $KAl_2(AlSi_3)O_{10}(OH)_2$. Only one reflecting plane of each crystal was studied. These minerals occur naturally with varying degrees of perfection and use was made of this fact in selecting the specimens. A further control of the perfection can be achieved by grinding or treating the surfaces in various ways. The object pursued in this work was to determine ρ for crystals of the same kind but of various degrees of perfection.

Theoretical variation of ρ with λ and with degree of perfection

The two formulae given by Darwin (1914, 1922) for the value of ρ, when reflexion occurs from an extended crystal face, are as follows:

for the perfect crystal

$$\rho = \frac{4}{3\pi} \frac{Ne^2}{mc^2} \lambda^2 \frac{1 + |\cos 2\theta|}{\sin 2\theta} F_{hkl}, \tag{1}$$

and for the ideally imperfect crystal

$$\rho = \frac{N^2 e^4 \lambda^3}{4\mu m^2 c^4} \frac{1 + \cos^2 2\theta}{\sin 2\theta} F^2_{hkl}, \tag{2}$$

where N = number of unit cells per cm.^{3},
e = electronic charge,
μ = linear absorption coefficient,
m = electronic mass,
c = velocity of light,
θ = Bragg angle of reflexion,
F_{hkl} = structure amplitude of the reflexion.

An approximate correction to the formula for the perfect crystal has been given by Zachariasen (1945, p. 143) and this adds to the expression (1) a factor $(1 - 2\,|g|)$, where $g = \frac{\mu}{2\lambda N F_{hkl}} \frac{mc^2}{e^2}$. This correction is included in the theoretical curves of Figs. 3–7. For all the crystals investigated the expressions (1) and (2) can be completely evaluated and this has been done for wave-lengths 0·56, 0·71, 1·54 and 2·29 A. The results are plotted in Figs. 3–7 as full lines. In these figures the ordinates represent log ρ and the abscissae log λ, the choice of a logarithmic presentation being made for two reasons. In the first place the theoretical value of ρ for any one substance may vary by a factor of 50; and, secondly, the log ρ : log λ theoretical curves are almost straight lines. The upward slope of the curves on Fig. 6 at the right-hand side is due to the small spacing of d_{400} for fluorspar and to the increase of the Lorentz factor beyond $\theta = 45°$.

No correction has been added for polarization by the monochromatizing crystal because, for the small angle of reflexion used, this effect would be small (Compton & Allison, 1935).

Experimental results

The values of the integrated reflexion, ρ, shown in the tables below were obtained with Mo $K\alpha$ and Cu $K\alpha$ radiations.

Calcite, $CaCO_3$. For reflexions 211 (for $a=6{\cdot}36$ A., $\alpha=46° 7'$ (Bragg, 1914)) from the cleavage plane:

Reference letter	ρ For Mo Kα =0·71 A. × 10⁻⁶ rad.	ρ For Cu Kα =1·54 A. × 10⁻⁶ rad.	Treatment
a	49	62	Natural cleavage taken from a mineral collection
b	127	94	Same crystal ground on coarse sand-paper
c	66	74	Natural cleavage; the other side of crystal (*a*)
d	120	76	Same crystal as (*c*) ground with fine carborundum and water
e	133	78	Same crystal as (*d*) ground with coarse carborundum and water
f	385	133	Milky crystal ground on coarse sand-paper

The above results are plotted in Fig. 3.

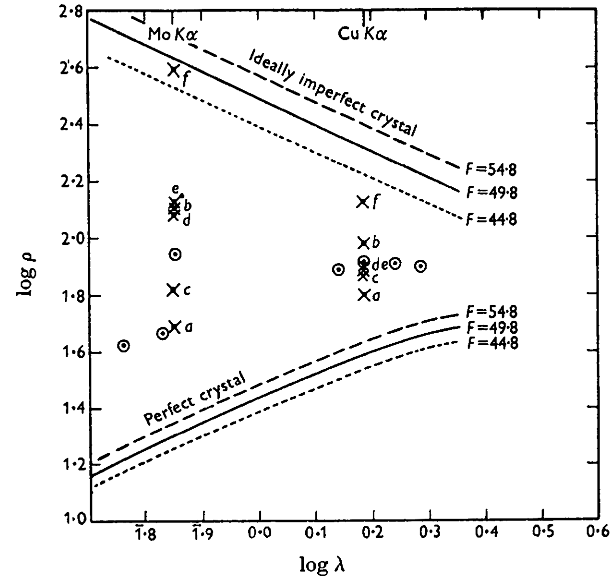

Fig. 3. The lines on the graph show for calcite (211 reflexion) the theoretical variation of log ρ with log λ for the ideally imperfect crystal and the perfect crystal respectively. The crosses denote results given in the text; circles are other results given in the literature.

Quartz, SiO_2. For reflexions $10\bar{1}1$ (for $a=4{\cdot}903$, $c=5{\cdot}393$ A. (Wei, 1935)) from the natural rhombohedron, *r*:

Reference letter	ρ For Mo Kα × 10⁻⁶ rad.	ρ For Cu Kα × 10⁻⁶ rad.	Treatment
a	174	203	Natural rhombohedron face
b	237	216	Same as (*a*) after grinding on medium grade carborundum and water
c	495	239	Synthetic surface grown on to natural crystal from aqueous solution by the method of Wooster & Wooster (1946)

The above results are plotted in Fig. 4.

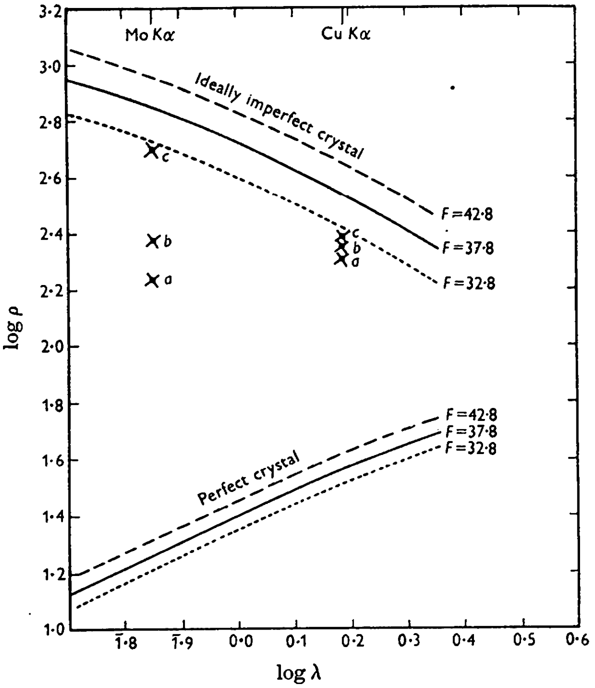

Fig. 4. log ρ: log λ graph for quartz ($10\bar{1}1$ reflexion).

Gypsum, $CaSO_4.2H_2O$. For reflexions 020 (for $a=10{\cdot}47$, $b=15{\cdot}15$, $c=6{\cdot}51$ A., $\beta=151° 33'$ (Wooster, 1936)) from clear cleavage flakes from a large natural crystal:

Reference letter	ρ For Mo Kα × 10⁻⁶ rad.	ρ For Cu Kα × 10⁻⁶ rad.	Treatment
a	41	35	Freshly cleaved face
b	157	66	Same plate as (*a*) after grinding with medium grade carborundum and water and using only a small pressure during grinding

The above results are plotted in Fig. 5.

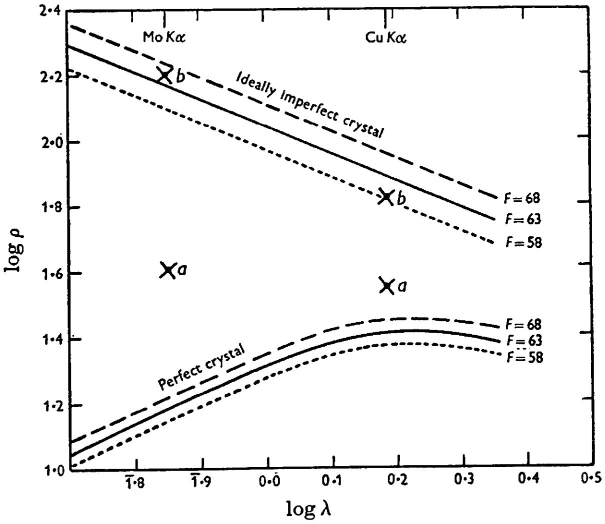

Fig. 5. log ρ: log λ graph for gypsum (020 reflexion).

Fluorspar, CaF_2. For reflexions 400 (for $a = 5{\cdot}45$ A. (Bragg, 1914)) from natural cubes:

Reference letter	ρ		Treatment
	For Mo $K\alpha$ $\times 10^{-6}$ rad.	For Cu $K\alpha$ $\times 10^{-6}$ rad.	
a	41	22	Bright natural cube face
b	112	33	A visually imperfect crystal ground with medium grade carborundum and water

The above results are plotted in Fig. 6.

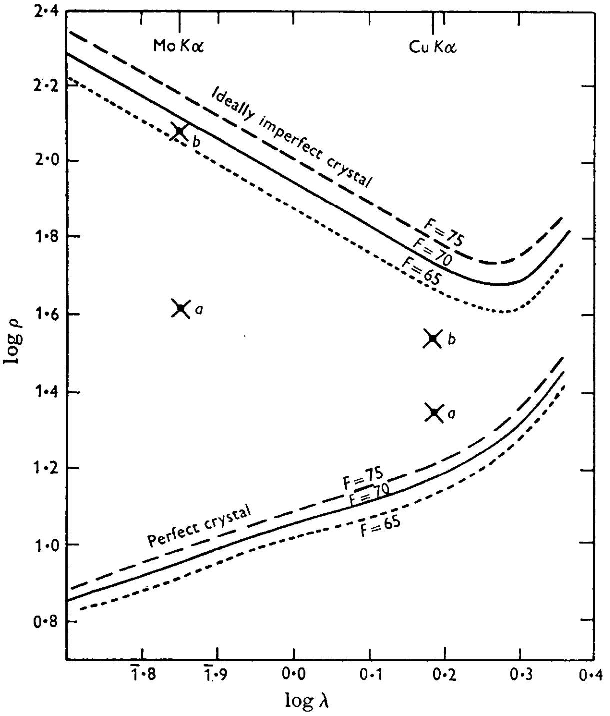

Fig. 6. log ρ : log λ graph for fluorspar (400 reflexion).

Muscovite mica, $KAl_2(AlSi_3)O_{10}(OH)_2$. For reflexions 006 (for $a = 5{\cdot}18$, $b = 9{\cdot}02$, $c = 20{\cdot}04$ A., $\beta = 95°\ 30'$ (Jackson & West, 1930, 1933)) from fresh cleavage flakes:

Reference letter	ρ		Treatment
	For Mo $K\alpha$ $\times 10^{-6}$ rad.	For Cu $K\alpha$ $\times 10^{-6}$ rad.	
a	87	28	Fresh cleavage surface
b	113	68	Same surface after rubbing with dry sand-paper

Phlogopite mica, $KMg_3(AlSi_3)O_{10}(OH)_2$. For reflexions 006 (for practically the same cell as for muscovite mica) from fresh cleavage flakes:

Reference letter	ρ		Treatment
	For Mo $K\alpha$ $\times 10^{-6}$ rad.	For Cu $K\alpha$ $\times 10^{-6}$ rad.	
c	130	62	Fresh cleavage face
d	142	75	Same face after rubbing with dry sand-paper

These results are plotted in Fig. 7.

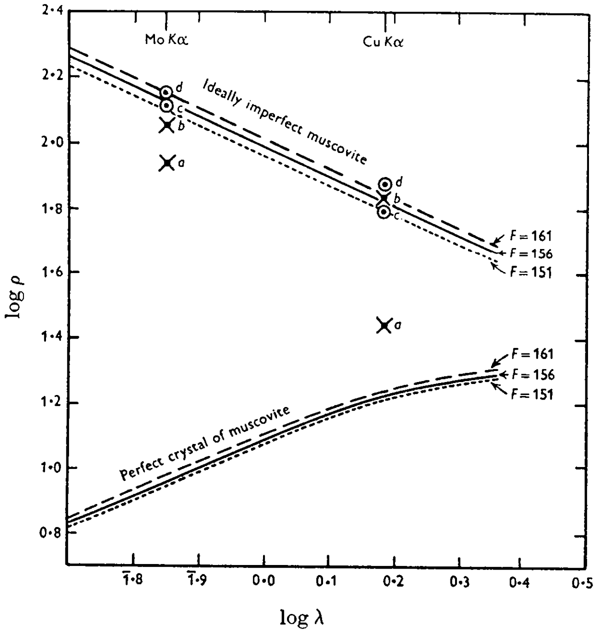

Fig. 7. log ρ : log λ graph for mica (006 reflexion); crosses denote results for muscovite, circles denote results for phlogopite.

Discussion of the experimental results

The study of the variation of the intensity of reflexion of X-rays from calcite with the wave-length of the radiation was carried out some years ago by several authors (Compton, 1917; Davis & Stempel, 1921; Wagner & Kulenkampff, 1922). The purpose of their investigations was to test the validity of the theory of the intensity of X-ray reflexion from a perfect crystal. The results obtained by these authors are included in Fig. 3 and it will be seen that the points corresponding to their measurements lie in the area bounded by the full lines. These early investigations were not primarily concerned with the texture of crystals nor with the measurement of structure amplitudes. Later investigators (Bragg, Darwin & James, 1926; James & Firth, 1927) studied the effects of extinction more carefully and were thereby able to determine more accurately the structure amplitudes from which the crystal structures could be derived. Lonsdale (1947), in a recent paper, has discussed the whole problem of primary and secondary extinction and shown their relative importance in certain crystals. However, in spite of all the careful attention that has been given to the subject of crystalline texture, there is still no adequate classification of texture-types nor any method of stating or measuring quantitatively the features which define a given crystal texture. The present observations can claim only to show that the absolute measurement of the integrated reflexion for more than one wave-length gives some indication of (*a*) the extent to which the texture departs from that of a perfect crystal, and (*b*) the variation of this texture with depth below the surface.

We shall consider first the observations on calcite.

Compton & Allison (1935) showed that the Darwin theory of reflexion from a perfect crystal was reasonably accurate, and hence we may conclude that the natural cleavage faces examined in experiments (*a*) and (*c*) of the table of results for calcite were not perfect. The more general dynamical theory of X-ray reflexion (Ewald, 1918) gives results which do not differ from those of Darwin's theory except when multiple reflexion occurs. It is comparatively easy to increase the integrated reflexion by grinding the surface, though the difference between grinding on sand-paper and grinding on glass with carborundum powder and water is striking. Whereas with Mo $K\alpha$ radiation both methods of grinding increase the integrated reflexion, with Cu $K\alpha$ radiation the sand-paper produces a significant increase in integrated reflexion whereas carborundum does not. (This last fact was pointed out to us by Mr J. N. Kellar of this Laboratory.) The measurement denoted (*c*) was carried out on the back surface of a crystal which had been ground on the front surface. The pressure exerted by the fingers during the grinding would have reduced the perfection of the natural cleavage to some extent. This may account for the difference between the ρ-values for (*c*) and (*a*). A further important result is that neither coarse nor fine grinding was able to increase the degree of imperfection up to that of the ideally imperfect crystal. By choosing a milky crystal, of a kind which could be seen to be imperfect, it was possible to obtain a value of the integrated reflexion which for Mo $K\alpha$ radiation was close to the theoretical value. Using Cu $K\alpha$ radiation even this crystal appeared less imperfect that it did with Mo $K\alpha$ radiation.

In Figs. 3–7 there are, in addition to the full lines, dotted and dashed lines, which give respectively the theoretical curves for an F_{hkl}-value 5 units lower and 5 units higher than that used in deriving the full lines. If we assume that the theoretical lines for the imperfect and the perfect crystal represent the extremes that are possible for actual crystals, then we can judge what should be taken as the F_{hkl}-value. In Fig. 3 a decrease in F_{hkl} from 49·8, which is the value calculated on the basis of the accepted crystal structure, to 44·8 would bring one experimental point outside the permitted range. An increase of F_{hkl} to 54·8 would not bring any points outside the permitted range and so the discrimination in Fig. 3 is not high. In Fig. 4 the points are all too far removed from the lines for the perfect crystal to define the true value of F_{hkl}. In Figs. 5, 6 and 7, however, the discrimination is good along the curve for the ideally imperfect crystal, and the experimental results require the F_{hkl}-values to be the same as the accepted values within ±5 units. In Fig. 7 the theoretical curves have been drawn for muscovite mica. The corresponding curves for phlogopite mica would probably not differ by more than corresponds to a few units in the value of F. It is, however, difficult, without knowledge of the composition and of the particular atomic sites which are occupied by the magnesium atoms, to determine the precise position of the phlogopite mica curves on the graph.

Provided a suitable distribution of the ρ-values over the $\log \rho : \log \lambda$ graph can be obtained, it appears that this method enables the true F_{hkl}-value to be fixed in spite of the great influence of the degree of imperfection on the integrated reflexion.

Returning to the consideration of the imperfection of the crystals quartz, gypsum, fluorspar and mica, we see that quartz, unlike the other three, appears to be more imperfect in copper radiation than in molybdenum radiation. A fresh cleavage of gypsum behaves like a nearly perfect crystal in copper radiation and a ground surface behaves like an ideally imperfect crystal in molybdenum radiation. An optically flat cube face of a transparent fluorspar crystal behaved in copper radiation like a nearly perfect crystal, but in molybdenum radiation it appeared imperfect. A fresh cleavage of muscovite mica appeared less imperfect in copper radiation than in molybdenum, but phlogopite mica, which was chosen because of its mosaic appearance, behaved as an ideally imperfect crystal under all circumstances.

From these results it may be seen that the apparent degree of imperfection shown by crystals is sometimes very different according to the wave-length of the X-rays used. A deeper interpretation of this fact must await a fuller study of the variation of the imperfection with depth below the surface of the crystal.

Summary

An ionization spectrometer is used to measure the absolute integrated reflexion, ρ, from one strongly reflecting plane in each of the crystals calcite, quartz, gypsum, fluorspar and mica. The specimens were chosen to represent as wide a variation in imperfection as possible. The observed values of the integrated reflexions were compared with values calculated on the formulae for perfect and ideally imperfect crystals given by Darwin. In Figs. 3–7 the calculated values of $\log \rho$ are plotted against $\log \lambda$ for both types of crystal. In Cu $K\alpha$ radiation the best obtainable specimens of gypsum, muscovite and fluorspar gave reflexions which corresponded approximately with those for the perfect crystal, though in Mo $K\alpha$ radiation the same specimen gave values intermediate between those for the perfect and the ideally imperfect formulae. For the five types of crystal all the specimens which were selected because of some visible imperfection, or were scratched or ground to make them imperfect, gave values of ρ close to the calculated value for ideally imperfect crystals. These observations suggest that by using a wide variation of wave-length and as great a variation as possible in imperfection it is possible in some crystals to determine experimentally a value of the structure amplitude without assuming any value for the extinction. There is a marked difference between the

quartz and the softer materials gypsum, fluorspar and mica in that quartz appeared equally imperfect in both radiations whereas the other crystals when freshly cleaved appeared much more nearly perfect in the longer wave-length X-rays. This may be a consequence of a variation of perfection with depth or of the greater perfection along a surface than at right-angles to it in the crystals with a good cleavage.

One of us (W.A.W.) is pleased to acknowledge the help afforded by the D.S.I.R. in providing a grant which made possible this work. We also gratefully acknowledge the provision of mineral specimens by the Department of Mineralogy and Petrology, Cambridge.

References

Bragg, W. L. (1914). *Proc. Roy. Soc.* A, **89**, 246, 468.
Bragg, W. L., Darwin, C. G. & James, R. W. (1926). *Phil. Mag.* **1**, 897.
Compton, A. H. (1917). *Phys. Rev.* **10**, 95.
Compton, A. H. & Allison, S. K. (1935). *X-rays in Theory and Experiment.* London: Macmillan.
Darwin, C. G. (1914). *Phil. Mag.* **27**, 675.
Darwin, C. G. (1922). *Phil. Mag.* **43**, 800.
Davis, B. & Stempel, W. M. (1921). *Phys. Rev.* **17**, 608.
Ewald, P. P. (1918). *Ann. Phys., Lpz.*, **54**, 519.
Jackson, W. W. & West, J. (1930). *Z. Krystallogr.* **76**, 211.
Jackson, W. W. & West, J. (1933). *Z. Krystallogr.* **85**, 160.
James, R. W. & Firth, E. M. (1927). *Proc. Roy. Soc.* A, **117**, 62.
Lonsdale, K. (1947). *Miner. Mag.* **28**, 14.
Wagner, E. & Kulenkampff, H. (1922). *Ann. Phys., Lpz.*, **68**, 369.
Wei, P. (1935). *Z. Krystallogr.* **92**, 355.
Wooster, N. & Wooster, W. A. (1946). *Nature, Lond.*, **157**, 297.
Wooster, W. A. (1936). *Z. Krystallogr.* **94**, 375.
Wooster, W. A. & Martin, A. J. P. (1936). *Proc. Roy. Soc.* A, **155**, 150.
Zachariasen, W. H. (1945). *Theory of X-ray Diffraction in Crystals.* New York: Wiley.

Acta Cryst. (1948). **1**, 54

A Critical Examination of the Beevers-Lipson Method of Fourier Series Summation

By W. Cochran

Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England

(*Received* 8 *November* 1947)

The error introduced into a multidimensional Fourier synthesis by approximations made in the course of computation is compared with that due to random errors in the amplitudes of the Fourier components. It is shown that the Beevers-Lipson method of Fourier summation, normally employed in crystallographic work, is an entirely adequate method of calculating the electron density unless the structure amplitudes have been measured to an accuracy such that their standard deviation is less than 2, in the customary units.

Introduction

As a result of improvements in the experimental techniques of X-ray crystallography it has become possible to determine not only the gross structure of molecules but also to measure the electron distribution in regions distant from the atomic centres and hence to investigate directly the bonding between atoms. The practicability of this procedure has been demonstrated by Brill, Grimm, Hermann & Peters (1939). Electron density maps obtained in this way are inaccurate for three reasons:

(*a*) The coefficients of the Fourier series in terms of which the electron distribution is expressed are subject to, at best, random error of measurement. This is of course the fundamental source of error.

(*b*) The Fourier series is necessarily terminated at finite limits. This difficulty has been discussed fully elsewhere (Bragg & West, 1930; van Reijen, 1942); it is sufficient for our purpose to note that it can be surmounted.

(*c*) Approximations are generally made in computing the Fourier synthesis. It has been shown (Booth, 1946*a*) that in practice the Beevers-Lipson method leads to insignificant errors in the *atomic co-ordinates*. In view of the many projects under consideration which would increase the accuracy and/or reduce the labour of computing multi-dimensional Fourier syntheses it would be interesting to know to what extent this result holds for the *electron density*.