Acta Cryst. (1969). A25, 1 A1·1

Welcome to Participants

By the President of the Union Professor N. V. Belov

It is my privilege to greet you, to welcome participants in this meeting in the name of the International Union of Crystallography and to permit myself some introductory remarks. We live in the age of computers. They have not been built for us but we are allowed to use them within satisfactory limits. Notwithstanding that they are very expensive, none of us or our students wish now to compute even the most elementary of our problems with slide rules and Beevers–Lipson strips. We are all impressed by such miracles as reliability coefficients, sometimes less than 4%, but not everyone, even those interested, understands that this does not reflect the reliability of the structures themselves but only the measure of convergence of the tests of calculated and experimental intensities. The computer can give us of the order of nine significant figures whereas the experimental intensities are much less precise. Sometimes, for special reasons, they are far from correct. This means that a structure with a small R may on occasions be a wrong one – which is a pity not only for the scientist concerned, but for science as a whole. Although the production of the best program for use on a computer may sometimes be beyond the means of the individual X-ray crystallographer, care in the production of experimental results is his responsibility alone. To point this lesson is the aim of our meeting; it will be achieved not only by discussion here, but also by the distribution of the proceedings in a future issue of *Acta Crystallographica*.

It is my agreeable task to introduce Sir Lawrence, but I cannot refrain from some introductory words about the creator of Crystal Chemistry. His role is well known to everyone. I remember my own impressions of the first Russian lecture on Bragg's early results which was given by my beloved Professor Joffe during September of 1914. But, for me, the importance of Bragg's achievement is the creation of the crystallography of silicates, which has turned out to be the only true chemistry of silicates, the basis of mineralogy and petrology, indeed the basis of all geological sciences and also of the synthetic chemistry of ceramics, cement and so on. It is a pleasure to work along the lines of the crystal chemistry of silicates in such studies as that of the magmatic history of the earth's crust.

The critical point in laying the foundations of the crystal chemistry of silicates was the establishment of the structure of pyroxenes, especially of diopside, made by Sir Lawrence with his young pupil Professor Warren. The crucial point in this structure was the precise measurement of intensities. The structure was solved and the atomic parameters were determined by the aid of the Fourier method, this being its first application to the structure of pyroxenes.

And so, it is particularly appropriate that our first speaker will be Sir Lawrence.

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The Early History of Intensity Measurements

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There could be no more important subject than intensity measurements for a conference dealing with our methods and techniques. It is a curious feature of X-ray analysis that there are two points in the course of the investigation when it comes, as it were, to a focus. The first is the finale of the experimental measurements which are summed up in a list of values of $F(hkl)$. All the experimental effort and cunning has gone to making these values as accurate and extensive as possible, and they represent the raw material on which the whole analysis is based. The second is of course the list of atomic coordinates, in which again a set of numbers constitutes a full account of all that the investigator has succeeded in establishing. They sum up the outcome of the research; the answer to what he has been seeking is embodied in the 'model'. The tangle of optics simplifies itself in these two principal planes, related by each being the transform of the other.

When I received the very kind invitation to give an opening talk, I proposed to Arndt that I might give some account of intensity measurements in early days. They formed the basis of the very first determinations of structure, though in so primitive a form. The curious might be interested in consulting the analysis of iron pyrites, of which I gave an account on page 60 of *The Crystalline State* (Bragg, 1939). The positions of the sulphur atoms, which are on trigonal axes, were defined by one parameter. Our guides at that time were (*a*) atoms scattered an amplitude proportional to their atomic weight (this was before Moseley's atomic numbers) and (*b*) the normal run of spectra from simple planes had intensities in the ratio 100:20:7:3:1. It is surprising how accurately an atomic position could be fixed with these primitive rules; a later sophisticated determination of the atomic position of S in FeS_2 showed that the original one was in error by about 0·1 Å.

The first accurate intensity measurements were made by W.H. Bragg in 1914, and his methods have been a model for all subsequent techniques. He was testing Debye's theory of the thermal effect. In order to get reliable measurements from a mosaic crystal he integrated the reflexion as the crystal rotated through its range of reflexion, either by summing up the area under the plot of reflexion over the range, or by rotating the crystal with a steady angular velocity and recording the total ionization in the chamber. The results are shown in Fig. 4 of the following paper (Bragg, 1914) and record the very important point that the intensities of the NaCl orders with even indices from any face fall on the same curve. The closeness with which the points fit the curve reflects an accuracy which would be regarded as creditable in modern analyses, and is remarkable considering the apparatus then available. X-ray tubes were most temperamental. My father's favourite for use with the spectrometer had a palladium anticathode. It got hard with use, and one had to let a little gas in by warming a kind of metal appendix on the tube. The hammer-break on the spark coil was a fiendish affair to regulate, and was later replaced by a mercury break. The ionization was measured with a Wilson tilted gold-leaf electrometer. I well remember the fiddly job of cutting strips of gold leaf and fixing them to the plate with a bit of lick. The regular sweep of the crystal through the rotating angle was achieved by having a capstan with spokes which moved the crystal, and pulling the spokes with ones finger in time to the beat of a metronome. It worked! Later, when at Manchester my school of research went in for accurate intensity measurements in a big way, we replaced the Wilson electrometer by a string electrometer, and we measured the charge collected in the chamber of the spectrometer by using a potential divider, with which an opposite charge was induced which brought the string back to zero, but otherwise the method was the same. Various devices for intensity measurement have been tried, but as far as I know the 'sweep' of the crystal through the reflecting range has always proved to be the most reliable.

The landmark on the theoretical side was, of course, the two remarkable papers by Darwin (1914) in which he covered practically the whole ground of the theory of X-ray reflexion, and which have been the basis for all accurate work for half a century. He showed that an absolutely perfect crystal gives specular reflexion over a few seconds of arc, that the integrated reflexion based on this assumption is much smaller than that actually observed, and that the reason for the discrepancy must lie in the imperfection of the crystal. He then calculated the formula for the 'ideally imperfect' mosaic crystal, and this is the formula we all use.

In this calculation, it is supposed that each mosaic element, consisting of a block of perfect crystal, is so small that it only reflects a fraction of the X-rays passing through it. Its contribution to the integrated reflexion is then proportional to its volume, because the greater intensity at the centre of the range when there are many planes is partly balanced by the smaller extent of the range. This leads to the two standard formulae

$$E\omega/I_0 = QV$$

for a small element of volume V bathed in radiation I_0 per unit area and

$$E\omega/I = Q/2\mu$$

for a beam of intensity I falling on the face of a crystal with an absorption coefficient μ. Q is the expression which must be burnt on every X-ray analyst's brain:

$$Q = \left(\frac{Ne^2F(hkl)}{mc^2}\right)^2 \cdot \lambda^3 \cdot \frac{1}{\sin 2\theta} \cdot \frac{1+\cos^2 2\theta}{2}.$$

Ewald, who had arrived at essentially the same formula by a more rigorous mathematical treatment, arranged a conference in Germany soon after the war to discuss X-ray diffraction. James and I took Darwin with us as the English champion, but I well remember that alas he had not troubled to refresh his memory about his mathematics, and at the conference he was unable to deduce his own equations! James and I filled the gap as best we could.

My school at Manchester, in the 1920's, was responsible for showing the far greater power of X-ray analysis when absolute measurements of X-ray intensity were used, 'absolute' implying comparing the reflected with the incident beam. This yielded absolute values of $F(hkl)$ in terms of scattering by a single electron. With James and Bosanquet, I made an intensive examination of reflexion by rocksalt (Bragg, James & Bosanquet, 1921) to check the Darwin formula (this was not the first test; Compton (1917) had shown it gave figures of the right order).

The accuracy attained was sufficiently high for Hartree, James & Waller (1928) to verify the existence of zero-point energy. We tackled crystals with 20 and 30 parameters, which had seemed wildly impossible only a few years earlier. Our methods were summed up in a paper I wrote with West *A Technique for the X-ray Examination of Crystal Structures with Many Parameters* (Bragg & West, 1928). 'Many parameters' has a quaint sound now!

The ionization chamber, however, had to yield to the photographic plate as more complex crystals were tackled, because the number of reflexions to be measured became so large. Accuracy centred on the photometer, or on the uncanny ability of some researchers to get good quantitative measurements by eye estimation with a series of superimposed films. And now, since automation has removed the tedium of ionization measurements on numerous orders, the wheel has turned full circle again and the latest diffractometers are employing just the same principle as we did in 1914 when we turned the spokes on a capstan to the beat of a metronome.

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The Intensity of Reflexion of X-Rays by Crystals

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When a pencil of homogeneous X-rays is incident upon a crystal face it is reflected when, and only when, the angle θ between the pencil and the face satisfies the equation

$$n\lambda = 2d\sin\theta\,,\text{[*]}$$

where λ is the wave-length of the rays, n is an integer, and d is the distance between any plane and the nearest which is similar and similarly placed. In the simplest kind of arrangement, all the planes are similar and equally spaced, and d is then the distance between two neighbouring planes.

If λ and d are given, if, that is to say, a certain X-ray pencil falls on a certain crystal face, several values of θ may be found to satisfy the equation, corresponding to consecutive values of the integer. The reflexions occurring at the angles

$$\sin^{-1}\frac{\lambda}{2d}\,,\ \sin^{-1}\frac{2\lambda}{2d}\,,\ \sin^{-1}\frac{3\lambda}{2d}\,,\ \ldots$$

may be called the reflexions or spectra of the first, second, third order, and so on.

When the planes are equal and equally spaced the intensities of the reflexions decrease rapidly and continuously as n increases; reflexions of an order higher than the fifth or perhaps the sixth have not been observed.

When the arrangement of planes is more complicated this regular diminution in intensity may be greatly modified. Complication may arise in either or both of two ways. The planes may be unequally spaced, or they may be dissimilar. An example of the former effect is to be found in the reflexion from the cleavage face (111) of the diamond. In this case the planes are arranged at distances apart which are alternately as 1 to 3.[*] In consequence the second order reflexion disappears entirely (*loc. cit.*). The intensity of the third and fifth are normal in comparison with the first, but the fourth is twice as strong as it should be.

An example of the effect of want of similarity in the planes may be illustrated by reference to the (111) planes of rocksalt[†]. In this case the spacing is uniform but the planes contain alternately sodium atoms only and chlorine atoms only. The result of this unequal loading is that the reflexions of even order are strongly enhanced in comparison with those of odd order: we are taking d to be the distance from one chlorine plane to the next, in accordance with the definition given above, and the glancing angle of the first order to be $\sin^{-1}\lambda/2d$.

When both spacings and loadings are irregular the relative intensities are more complicated still; as for example in the case of reflexion by the (100) or (111) planes of iron pyrites.[‡]

Since the relative intensities depend so directly upon the spacings and loadings of the planes, and since the manner of dependence can be easily explained, it follows that experimental determinations of the intensities may be used to draw conclusions as to the structure

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[*] W. L. Bragg, *Proc. Camb. Phil. Soc.* **17**, 43.

[*] W. H. Bragg & W. L. Bragg, *Proc. Roy. Soc.* **89**, 277.

[†] W. L. Bragg, *Proc. Roy. Soc.* **89**, 274.

[‡] W. L. Bragg, *Proc. Roy. Soc.* **89**, 476.