Weissenberg's Influence on Crystallography

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In order to understand Weissenberg's contribution to X-ray crystallography it is necessary to appreciate the background to the subject when he entered it around 1922. The discovery of the diffraction of X-rays by crystals had taken place about ten years earlier. Laue, during a discussion with a young research student, Ewald, had learned of the periodic nature of crystals and had conceived the idea of using a crystal as a diffraction grating for X-rays; Friedrich and Knipping agreed to carry out the experiment and, using a crystal of copper sulphate pentahydrate, exposed a photographic plate to catch any possible diffracted beams. Around the centre blackening caused by the direct beam they found a pattern of spots and thus established the effect that they were looking for[1]. X-rays were waves and must have a wavelength of around atomic dimensions; they could therefore be used to explore the structure of matter on an atomic scale. This historic experiment opened up a new era in physics.

But the exploitation of the discovery was not easy. The three-dimensional theory of diffraction, to a mind of the stature of Laue's, presented no problem, but the application of this theory to the understanding of first X-ray diffraction photographs was much more difficult. A simpler theory was needed, and that of W. L. Bragg, who regarded each spot on the photographs as a 'reflexion' from a set of lattice planes[2], provided the breakthrough; on the basis of this idea he and his father, W. H. Bragg, built an ionisation spectrometer which they used to examine the nature of X-ray spectra and then to work out the first crystal structures.

With this instrument W. H. Bragg found that the spectrum of radiation from an X-ray tube contained a continuous (white) component upon which was superimposed some characteristic lines; he identified these with the K radiation that had been discovered some years earlier by Barkia from absorption measurements. It seems odd to us now that Laue had had to postulate more and more wavelengths to explain the first X-ray photographs, but had not apparently extended his ideas to an infinite range. X-ray diffraction started with photographic methods and continued in this way for many years in spite of the Braggs' demonstration of the power of their ionisation spectrometer. This instrument was very awkward to use; I used one of the early instruments in the 1930's and found that it required a great deal of patience and manipulative skill. Moreover, unless considerable checking was made, it could give erroneous results. Photographic methods were much easier; no control of the X-ray intensity was required and all the information was presented on a single film - all nicely arranged and completely trustworthy. Of course, the ionisation spectrometer gave quantitative results, whereas photographic methods could not easily do so, but this seemed a minor difficulty in the early days when to work out a structure at all was triumph and accuracy was of secondary importance. It was indeed surprising how accurately atoms could be placed merely by classifying spots as weak, medium or strong.

The Laue method, as it was called, involved merely placing a stationary crystal in the path of a narrow beam of X-rays, defined by a long metal tube called a collimator, and putting a flat photographic film in a position where it intercepted the transmitted beam and any diffracted beams that were produced. If the crystal were so adjusted that the beam passed along an axis of symmetry, the photograph showed the same symmetry; Laue photographs of highly symmetrical crystals are the most beautiful types of X-ray photographs, as can be seen from Fig. 1(a).

But the analysis of these photographs was difficult. It is necessary to assign to each spot the indices *(*h,k*,l)* of the lattice planes which produce it. This was not too troublesome; a device known as a gnomonic ruler was used and presented a diagram from which the indices could, with some practice, be read off. The real problem lay in the fact that in general the spots are not single but are produced by several superimposed reflexions.

This result can easily be seen from Bragg's theory. Lattice planes of spacing *d* reflect X-rays of wavelength λ according to the equation

nλ=2d sineθ

where θ is the angle - the Bragg angle - of grazing incidence and of reflexion, and n is a number representing the order of diffraction. Thus, if lattice planes of spacing *d* reflect rays of wavelength λ at a Bragg angle θ, they will also reflect rays of wavelength λ/2 at the same angle in the second order (n=2) and of wavelength λ/3 in the third order (n=3) and so on. As long as the X-ray spectrum contains these wavelengths, so the spots on the Laue photographs represent multiple reflexions.

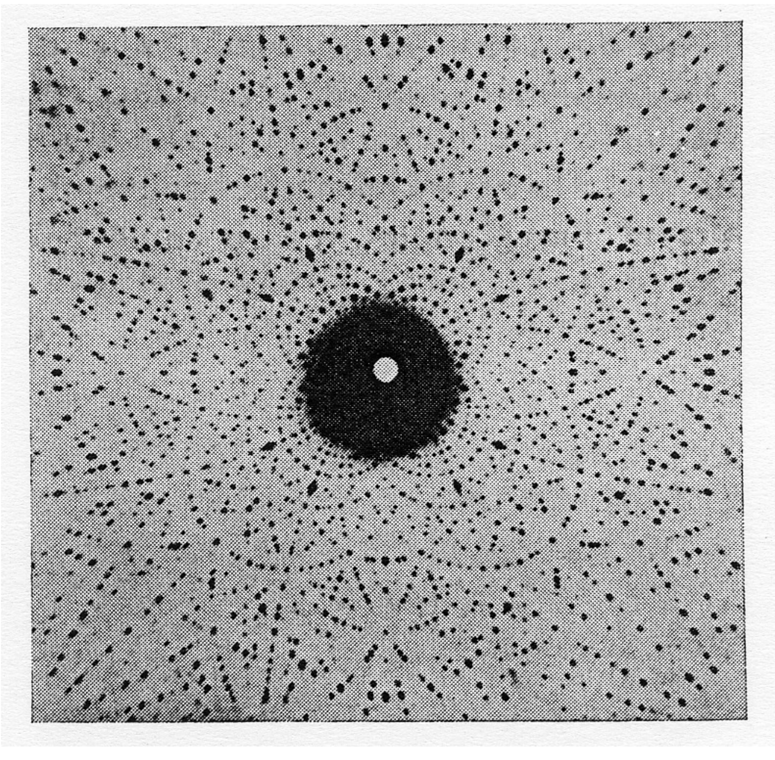

Fig. 1. (a) Laue photograph of a complex silicate (Courtesy of Dr. P. Gay).

This was a grave defect. The separate intensities were required for structure determination and considerable ingenuity was exercised to try to separate out the components of each spot. Wyckoff[3] was largely responsible for developing effective methods; he took photographs with different voltages applied to the X-ray tube. Lower voltages reduced the range of wavelengths in the X-ray spectra, and he was able to note when abrupt changes of intensities occurred, indicating that a high order had ceased to be produced. But this was a complicated procedure - more complicated and less clear in its results than the ionisation spectrometer - and it was obvious that something simpler was required.

In addition, there was another disavantage associated with the Laue method. Even if the intensities of the separate spots could be derived, they could not easily be related to each other. There is a large variation of intensity in the continuous spectrum from an X-ray tube and in order to obtain relative intensities of the X-ray reflexions it was necessary to know both the form of this variation and the wavelengths of all the spots to be measured. This complication also held up advances.

The breakthrough needed was introduced by Niggli in 1919. It was a beautiful idea which now seems so obvious that we take it for granted. He rotated his crystal so that various lattice planes passed through reflecting positions; each set produced a streak on the photograph as the continuous radiation was reflected at varying θ, but on this streak there were intense spots caused by the Kα and Kβ radiations. With these fixed wavelengths, different orders would occur with different Bragg angles and so could be easily recognized. The Kβ radiation could be eliminated with a filter, and the Kα spots were so strong that the continuous streaks could be almost ignored (Fig. 1 (b)). It looked then as though a completely satisfactory solution had emerged.

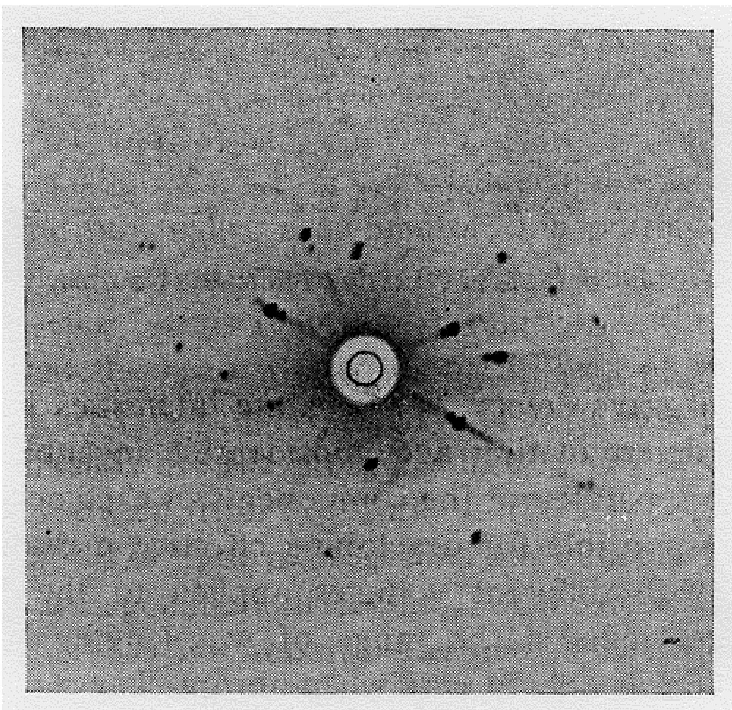

Fig. 1. (b) Part of a photograph from an oscillating crystal, showing continuous-radiation streaks with a and 13 spots superimposed.

But, although it was a great step forward, it was not the end. Rotation photographs, as they were called, were not easy to interpret and they did not always give unambiguous results. If two sets of lattice planes had closely similar or equal spacings they would give reflexions which had the same Bragg angles, and, according to the orientation of the crystal, the resultant spots could be superimposed.

The photographs had their simplest form, which made them most easily amenable to routine interpretation, if the crystal were rotated about an axis parallel to one edge of the unit cell; then, if the crystal were surrounded by a cylindrical film, the spots lay on straight lines called layer lines. These prominent features (see Fig. 1 (c)) greatly simplified the interpretation of the photographs, but they also increased the likelihood of coincident spots. Further developments were required.

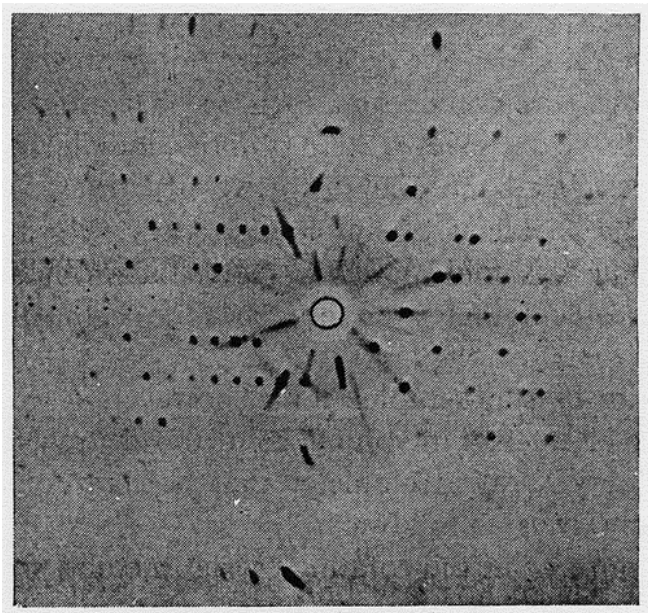

Fig. 1. (c) An oscillation photograph showing straight layer lines from a crystal oscillating about a vertical axis.

The next step was to limit the angular range of the crystal97to oscillate it through a small angle rather than to rotate it completely. Now the chance of coincident spots was greatly reduced, but on the other hand several photographs were needed to cover the range of possible reflexions. Moreover, there had to be some overlapping so that some spots would be common to two photographs, acting as standards for comparison of intensities. In spite of this disadvantage, the oscillation method remained standard for a long period; its dominance was established by a long and detailed paper, published by Bernal in 1926[4], which fully systematized the process of interpretation. An example of an oscillation photograph is shown in Fig. 1 (c).

This preamble sets out the state of the subject when, in 1922, Weissenberg joined the famous school at Berlin-Dahlem where people such as Mark, Polanyi and Schiebold were attempting to exploit the new discovery of X-ray diffraction. Then every crystal-structure determination was a personal triumph since there were no standard ways of deriving a result, as there are today. One tried various possibilities of atomic arrangements, most of them wrong of course. It was an exciting moment when one of them turned out to give a diffraction pattern in reasonable agreement with that observed.

Weissenberg was set to work on some simple compounds such as urea and tin tetraiodide. His results were not in themselves of great importance, but one could even then see his mind stretching to greater heights - to the investigation of more complicated molecules, such as triphenylmethane and distorted structures such as rolled metal foils. The problems of simple structures were not enough to hold him, and he was bold enough to tackle the problem of hydrated cellulose, a problem that even now has no completely accepted solution.

His claim to crystallographic fame, however, rests in the paper that he published in 1924 in volume 23 of the Zeitschrift für Physik, describing a new X-ray goniometer that he had constructed. His line of reasoning was as follows.

As we have seen, in the rotating-crystal method we deliberately arrange for the spots to fall upon lines on the films and therefore we cannot distinguish between spots that have the same Bragg angles although they may be produced from planes in the crystal with quite different orientations. If we had some way of knowing the orientation of the crystal when it was producing a particular spot, then the ambiguity would be removed, and it would be possible to assign indices to the spots unequivocally. He showed that this could be done by moving the film parallel to its axis in such a way that its motion was coordinated with the orientation of the crystal; then spots produced at different orientations would fall on quite different parts of the film. His diagram illustrating this idea is shown in Fig. 2. He realized that the presence of several layer lines would upset the simple interpretation of the resulting photograph and he therefore suggested the interposition of a screen - a layer-line screen - which would pass the spots of one layer line only. Different layer lines would need separate photographs. An example of a zero-layer-line Weissenberg photograph is shown in Fig.1.d.

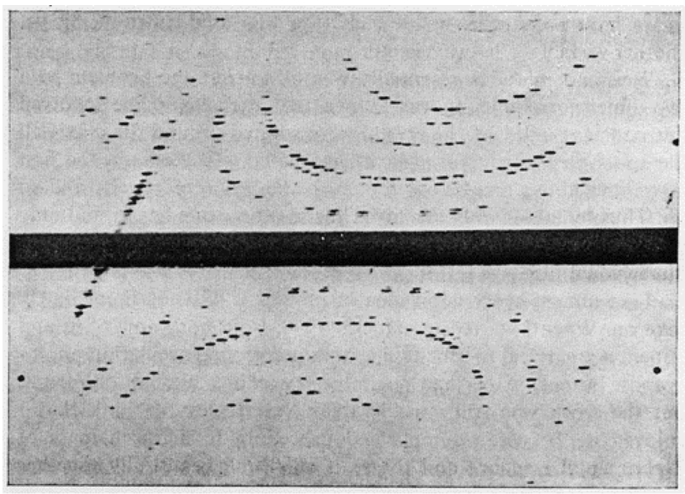

Fig. 1. (d) A zero-layer-line Weissenberg photograph (After Henry, Lipson Lipson and Wooster).

Weissenberg made an instrument incorporating this idea. It was an excellent piece of work and was still in use in the 1950's. Polanyi said of him that 'he had manipulative skill bordering on genius[5]' and those who know Polanyi will know that he would not use such words lightly.

It is possible to look upon Weissenberg's ideas in modern terms, in which the idea of lattice planes plays less part and the general theory of three-dimensional diffraction plays more. A crystal is a three-dimensional diffraction grating and therefore each order of diffraction is specified by three integers - h, k, l - in place of the one integer that is needed for a one-dimensional grating. The diffraction pattern of a crystal is completely described by allotting the value of the intensity of the diffracted wave to each possible combination of values of h, k and l, which may of course be positive, negative or zero. The intensities can be derived from the blackness of the spots on the photographs. But clearly it is impossible to derive the *three* integers h, k and l from the information obtained on a two-dimensional film. This is the basic problem of interpreting X-ray diffraction photographs taken with characteristic radiation. (It was even worse, as we have seen, when white radiation was used, introducing yet another variable - the wavelength.)

Weissenberg's idea essentially was to convert the problem to a two-dimensional one. It was known that each layer line involved one constant index; if the crystal were rotated around the c axis all the spots on the equatorial layer line had 1=0, those on the first layer lines above and below had 1 1 and -1 respectively, and so on. Thus by taking only one layer line at a time one has to find only two indices, and this can be done from the coordinates on a two-dimensional film.

Like almost every good idea in physics it did not immediately take on. When I started research in 1930, I did not know of it, and I spent a great deal of time taking and interpreting oscillation photographs. Bernal's paper had made the procedures almost fool-proof, but the work was still considerable. Nevertheless, I think that I enjoyed it. To use a complicated procedure to derive a mass of experimental evidence and to see it all fitting beautifully together gave me - and still gives me - a great deal of satisfaction. But, even so, one does not want to continue in this way for ever, and by the middle 1930's the work of indexing photographs was beginning to pall.

The Weissenberg idea was becoming known but its adoption was slow; Weissenberg goniometers were not yet commercially made and, even if they had been, few laboratories would have had enough money to buy them. Constructions had not been standardized. Should the axis be vertical as in the generally used Unicam oscillation goniometer or horizontal to make the translational motion easier to effect? (The latter has now won.) Buerger pointed-out the advantage, for layer lines other than equatorial, of having the incident beam inclined at a specific angle to the axis of rotation - the equiinclination method. (This is now standard practice.) Papers were written on the interpretation of Weissenberg photographs and on some of their specific properties. After the War, the Weissenberg method had established itself as a basic technique in X-ray crystallographic procedures.

The Weissenberg photograph is extremely easy to interpret. Generally, the axes - the lines containing spots such as h00 and 0k0 - are readily recognised, and from standard charts (or even sometimes without them) the indices of all the other spots can be read off. Information that might take weeks to acquire by the oscillation method could take only minutes with the Weissenberg method, and it would be more certain. Moreover, there was an extra bonus; the background that exists on all the photographs (see Fig. 1.c) is much weaker than on oscillation photographs, since the radiation that passes through the layer-line screen is spread out over the whole film. Thus the intensities of the spots can be measured more accurately and weaker spots can be detected. Weissenberg's goniometer had everything to commend it.

There is no doubt that the idea was fundamental and that it heralded a new era in X-ray diffraction. But it was not to be the end. There was, in some quarters, dissatisfaction that the Weissenberg photograph resembled so poorly what it was intended to portray - the diffraction pattern of the crystal lattice. This is what is called the reciprocal lattice, a concept introduced by Ewald[6] in 1921. Several people realised that it is possible to photograph sections of the reciprocal lattice by giving the crystal a more unusual motion than mere oscillation, and by using a flat plate with a correspondingly complicated motion. The most popular of such devices is the precession camera of Buerger[7], and an example of such a photograph, used in protein research, is shown in Fig.1.e. This method is invaluable for studying crystals with large unit cells.

From this point of view, then, it might appear that Weissenberg's idea has now served its purpose, to be superseded by still newer ideas. Even if this statement had been true, Weissenberg's claim to crystallographic fame would still have been valid; but in fact his method has *not* been superseded and it is still the most generally used method in ordinary crystal-structure investigations.

The reason is its great range, resulting from its use of a cylindrical film surrounding the crystal. This allows reflexions at high angles - even up to Bragg angles of about 85 ° - to be recorded. All the direct reciprocal-lattice methods require flat plates and cannot record reflexions with Bragg angles more than about 30°. For some investigations this range is adequate, but if smaller spacings are required a radiation with shorter wavelength must be used. Thus MoKγ radiation (λ=07Å) is often used instead of CuKγ (λ=1 5Å). MoKy radiation does not however give as good results; the spots are too close and exposures are much longer because the shorter wavelengths are not greatly absorbed by the photographic emulsion.

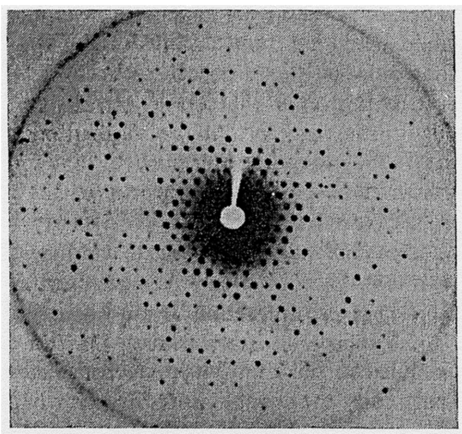

Fig. 1. (e) Precession photograph of protein crystal (Courtesy of Dr. M. F. Perutz).

It might also be thought that automatic diffractometers will make the Weissenberg method obsolete. This is unlikely; photographic methods give an overall view of a crystallographic problem that will probably always be necessary. Only when the unit cell and space group have been properly identified can the diffractometer be brought into play.

It is my guess therefore that the name of Weissenberg will live in crystallography as long as there are crystal structures to be solved.

Of course, as readers of this book are well aware, Weissenberg92s interest in crystal-structure determination did not persist. His earlier investigations of molecular structure turned into an interest in anomalous viscosity. In 1946 he was awarded the Duddell Medal and Prize of the Physical Society of London for his invention of the Weissenberg goniometer; at the meeting in the Science Museum on 10th January 1947, at which he received the award, he characteristically gave a lecture on anomalous viscosity!

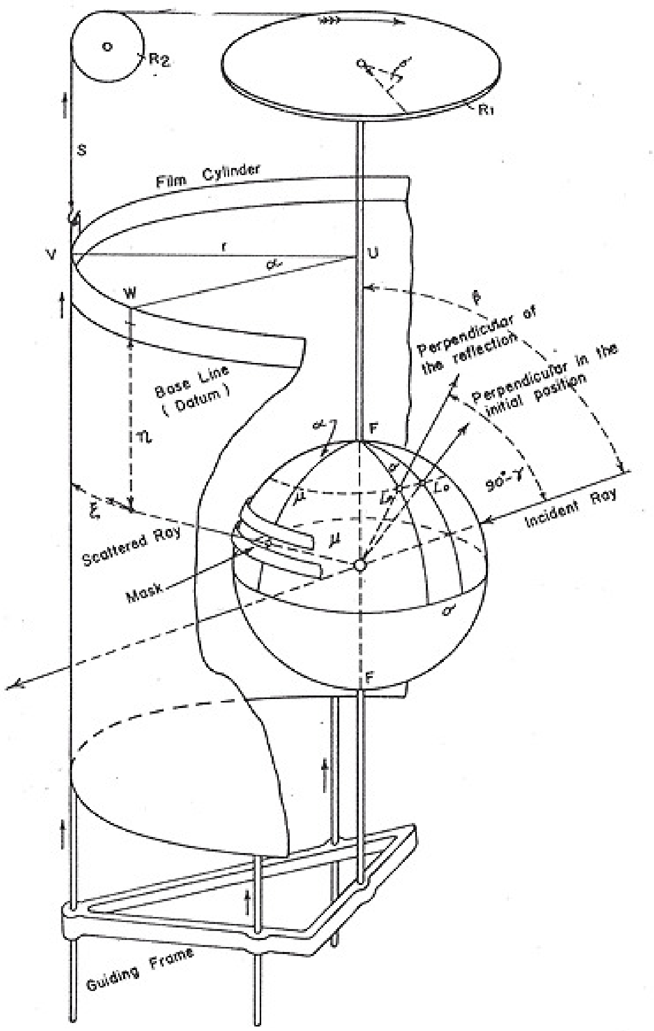

Fig. 2. Weissenberg’s original diagram illustrating the principle of his new goniometer.

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