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Structure Analysis of Single Crystals by Electron Diffraction. I. Techniques

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The possibility of using single-crystal electron diffraction patterns from very small crystals for structure analysis by Fourier methods is discussed. It is pointed out that the crystals used must be no more than a few hundred Ångström units thick in order to avoid modification of the intensities of the reflexions by dynamic interaction or secondary diffraction. The principal experimental difficulties are the manipulation of the specimen and the measurement of the intensities. A new method of intensity measurement, involving the photographic recording of spots spread out by periodic potentials applied to a set of deflecting plates, is described and illustrated. The interpretation of Fourier projections of the potential distribution in a crystal is considered.

1. Introduction

For a number of years it has been known that, in principle, the intensities of reflexions in electron-diffraction patterns may be used, in the same way as X-ray diffraction intensities, for structure analysis by Fourier methods. A Fourier analysis based on electron-diffraction data would give the distribution of potential in a crystal rather than the electron-density distribution. The Fourier development of the periodic potential used by Bethe (1928) and others is

$$\frac{8\pi^2 me}{h^2} V(x, y, z) = \sum_h \sum_k \sum_l v_{hkl} \exp\left[-2\pi i(hx+ky+lz)\right] .$$

Removing the constant terms, we may write

$$V(x, y, z) = \sum_h \sum_k \sum_l E_{hkl} \exp\left[-2\pi i(hx+ky+lz)\right] , \quad (1)$$

where E_{hkl} is the structure factor for electrons, analogous to F_{hkl}. The atomic scattering factor for electrons is related to that for X-rays, f, by the equation

$$\varepsilon(\theta) = (Z-f(\theta))\lambda^2/\sin^2\theta , \quad (2)$$

where Z is the atomic number, λ is the effective wavelength of the electron beam and θ is the Bragg angle.

The practical realization of electron-diffraction structure analysis should allow important progress in some structural problems, where the capabilities of the X-ray method are limited. Since the early days of electron diffraction, many compounds and structural modifications which have not been detected by X-ray methods have been shown to exist in thin surface layers. As an example we may mention the gold–oxygen compounds formed on gold foil heated in air (Moodie, 1953). The structure of such compounds can be investigated only by electron-diffraction methods. Again, electron-diffraction single-crystal patterns have been obtained from very small crystals which give only diffuse ring patterns with X-rays. Examples include crystals of clay minerals and of γ-alumina (Cowley, 1953).

However, very little attempt has been made to apply the techniques of structure analysis to electron-diffraction data. The only published work in which Fourier methods have been used is that of Pinsker and his co-workers. In recent years this group has published the results of structure analyses of a number of compounds, including the mono-hydrates of several halides (Vainshtein & Pinsker, 1949, 1950*a*; Vainshtein, 1949) and paraffin wax (Vainshtein & Pinsker, 1950*b*). In each case their work has been based on the intensities of diffraction patterns from polycrystalline material with the crystallites either highly oriented or at random. For structure analysis these methods have the same limitations as the powder patterns and rotation patterns of X-ray work. In addition it is necessary that the amount of orientation present should be known exactly. In practice this limits the use of patterns from polycrystalline material to cases where there is known to be either complete randomness or near-perfect alignment of one crystal axis and randomness in the rotation about this axis.

Thus, although these methods may be useful in many cases, particularly with layer-lattice crystals, they are limited by difficulties of specimen preparation and of the interpretation of patterns. It will be demonstrated that both difficulties may be overcome by suitable development of single-crystal techniques.

In the past it has been generally accepted that the intensities of the spots in single-crystal electron-diffraction patterns bear little relation to the structure factors of the reflexions, and so are of little use in structure analysis. If, however, a precision electron-optical system (Cowley & Rees, 1953) is used to obtain a beam of only a few microns diameter at the specimen level, instead of about $\frac{1}{2}$ mm. as in common practice, it is possible to find crystals of many substances, not only of layer lattices, which are thin enough (< about

500 Å) to avoid much limitation of the spots to circular Laue zones and yet sufficiently extensive to intercept an appreciable part of the incident beam. The spot intensities are then directly related to the structure factors.

Except in very rare cases, reflexion patterns from single crystals are of no use in structure analysis. Whether the surface is very smooth or rough, the path length of the electrons in the crystal varies from zero to the maximum depth of penetration of the electrons, of the order of several thousand Ångström units. Hence the principal contribution to the pattern comes from relatively thick crystal regions.

2. Intensities of single-crystal reflexions

The relationship between the intensity of a reflexion and the structure factor, E_{hkl}, for electrons is analogous to that between the intensity and structure factor, F_{hkl}, for X-rays. The simple kinematic theory predicts an intensity, I, proportional to E^2. According to the dynamic theory (Bethe, 1928; MacGillavry, 1940), the intensity is proportional to E for thick crystals but becomes proportional to E^2 for very thin crystals. The limiting thickness, beyond which the kinematic approximation ceases to be good, is, in practice, difficult to determine. Blackman (1939) has calculated this limiting thickness for several metals, using the dynamic theory of Bethe. He obtained values ranging from 12 Å for gold to 46 Å for aluminium, for 37·5 kV. electrons. However, this theory is based on the assumption of a strictly periodic potential distribution which can be represented by a Fourier series. In practice the periodicity is impaired by the rise of the potential at crystal boundaries and by various imperfections such as stacking faults, dislocations and so on. These factors probably have the effect of increasing the limiting thickness several-fold.

A number of attempts have been made to test the theoretical predictions by measuring relative intensities, usually of the rings given by thin films of metals. The results have been inconclusive. Some authors found the kinematic relation to fail for crystals less than 100 Å thick. Others found it to hold for crystals several hundred Ångström units thick. On the basis of careful measurements of patterns from polycrystalline metals and his experience in structure analysis, Pinsker (1949) has concluded that the limiting thickness is of the order of 500 Å or greater under normal experimental conditions. Further work, especially on crystals whose thickness is known accurately from interferometric, electron-microscope, or electron-diffraction fine-structure work, is necessary before this question can be resolved satisfactorily. Until more accurate data are available, it may be assumed that the kinematic theory gives a good approximation for most crystals for thicknesses of several hundred Ångström units.

For thick crystals the dynamic theory predicts a further modification of intensities caused by 'dynamic interaction' or interaction of the diffracted beams with the lattice and with each other. Heidenreich (1950) has shown that even a forbidden reflexion, such as the (222) of a diamond-type structure, may attain considerable intensity in this way. The general effect on a spot pattern is to decrease the intensity of strong reflexions and to increase the intensity of weak reflexions so that the intensity distribution becomes more even. Secondary scattering produces the same effects in mosaic crystals built up by the superposition of several thin crystal regions which scatter independently. Most of the published single-crystal patterns show the effects of one or both of these processes to a marked degree and so are of little use for structure analysis. Cowley, Rees & Spink (1951*a*) have shown how the intensities of a spot pattern may be corrected for a small amount of secondary scattering. They used a pattern from a hydrocarbon, showing fairly marked secondary scattering, to demonstrate the correction of intensities for use in structure analysis. However, it is better to avoid such corrections by refining the experimental techniques to obtain patterns from crystals so thin that the effects of dynamic interaction and secondary diffraction are negligibly small.

Dynamic interaction, and probably secondary scattering also, becomes important for a crystal thickness approximately equal to that for which the kinematic intensity relation fails. The dynamic theory indicates that, for this thickness, the intensity of the strongest diffracted beam becomes an appreciable fraction of the primary beam intensity. Experimental observations indicate that, at about this thickness also, the diffuse background due to inelastically scattered electrons becomes appreciable. Hence we may take as a working assumption, that a single-crystal pattern is suitable for use in structure analysis if the background is clear, all spots are weak compared with the primary beam, and there is no indication of the secondary diffraction or dynamic interaction effects.

3. Geometry of the reciprocal lattice

For most structure-analysis work it is desirable to record the intensities of as many as possible of the reflexions corresponding to reciprocal-lattice points lying in one of the principal planes of the reciprocal lattice. For this purpose it is possible to devise a number of rotating-crystal and moving-film arrangements analogous to those used in X-ray work. However, most crystals small enough for electron-diffraction structure analysis give extensive spot patterns when held stationary in a suitable orientation with respect to the beam. This is possible because of the large radius of the Ewald sphere, corresponding to the short wavelength of the electrons normally used (about 0·05 Å); as a first approximation the Ewald sphere may be considered as a plane and the diffraction pattern is then a symmetry-true projection of a section of reciprocal-lattice space. Since the radius of the Ewald sphere is, in fact, finite, the occurrence of an extensive spot-pattern indicates that the scattering regions around reciprocal-lattice points must be considerably extended in at least one direction.

There are three principal factors contributing to the extension of the scattering regions in the direction of the beam:

(1) *Shape transform.*—This is always a contributing factor. Since crystals used for structure analysis have thicknesses of only a few hundred Ångström units, the extension of the scattering region due to the limitation of the lattice in the direction of the beam is considerable. For crystals of uniform thickness the scattering power varies according to the function $(\sin^2 x)/x^2$ (Cowley, Rees & Spink, 1951*b*). Usually the thickness will vary, and the decrease in scattering power with distance from the reciprocal-lattice point will be monotonic and may be approximated by a function such as $\exp(-b^2x^2)$.

(2) *Disorder.*—Faults in the stacking of layers of atoms, very common in small crystals of layer-lattice structures, give rise to continuous lines of scattering power, with more or less regular intensity variations, running through some or all of the reciprocal-lattice points.

(3) *Distortion and mosaic disorientation.*—If a thin lamellar crystal is bent, or is divided into a number of mosaic blocks with varying tilt about an axis normal to the beam, each reciprocal-lattice maximum will, in effect, be spread out over an arc with centre at the reciprocal-lattice origin. The intensities of the diffraction spots will then depend on the relative areas of the crystal inclined at various angles to the beam. The elongation of the individual scattering regions, due to the factors (1) and (2) above, will tend to make the distribution of the scattering power along the arc more even. If it is sufficiently even, a stationary-crystal pattern will be equivalent to a rotation pattern and the measured intensities of the spots will be integrated intensities. If, however, there is evidence that most of the crystal contains only a few orientations, so that the distribution of the scattering power along the arcs is uneven, the stationary-crystal patterns cannot be used for structure analysis.

If the effect of (3) is small, and only (1) and (2) are important, the observed intensity of a diffraction spot may be written

$$I_{hkl} = g(\xi, \eta) . I^0_{hkl} ,$$

where I^0_{hkl} is the integrated intensity of the reflexion and ξ and η are co-ordinates referred to axes in a principal plane of the reciprocal lattice, perpendicular, or nearly perpendicular, to the incident beam. The maxima of scattering power around the reciprocal-lattice points are considered to be extended in the perpendicular ζ-direction. The function $g(\xi, \eta)$ will be centrosymmetric only if the beam is perpendicular to the reciprocal-lattice plane concerned.

If a Fourier summation is made using the observed intensities, the resulting Patterson projection is given, by a well-known theorem of Fourier integrals (Titchmarsh, 1937), as

$$P(X, Y) = \iint G(x, y) . P^0(X-x, Y-y)dxdy , \quad (3)$$

where $P^0(x, y)$ is the Patterson projection corresponding to the integrated intensities, and $G(x, y)$ is the Fourier transform of $g(\xi, \eta)$. Thus the Patterson projection obtained will be the 'true' Patterson projection modified according to equation (3). The modification will usually take the form of a broadening or distortion of the peaks. There will be a similar though less pronounced modification of the peaks of the Fourier projection.

For example, if the variation of the scattering power around a reciprocal-lattice point is represented by $\exp(-b^2\zeta^2)$ and the electron beam is perpendicular to the reciprocal-lattice plane, the Ewald sphere may be approximated by $\zeta = (\xi^2+\eta^2)\lambda^2/2$ so that

$$g(\xi, \eta) = \exp[-c^4(\xi^2+\eta^2)^2] ,$$

where c is a constant.

Then the electron structure factor is

$$E_{hkl} = E^0_{hkl} . \exp[-c^2(\xi^2+\eta^2)]$$

and the Fourier projection, apart from a constant term, is given by

$$V(x, y) = \iint \exp[-(X^2+Y^2)/4c^2] . V^0(x-X, y-Y)dXdY.$$

Hence the only effect on the Fourier projection is a broadening of each peak by an amount depending on the value of c. If the crystal is very thin, b is small and c is small, the spot pattern is extensive, and the peaks in the Fourier projection are sharp.

If the electron beam is not quite perpendicular to the reciprocal-lattice plane the situation is more complicated. The function $g(\xi, \eta)$ does not have the symmetry of the above example. In general, the effect will be to distort the peaks in the Patterson and Fourier projections by broadening them more in some directions than in others. Partial compensation for the effects of a slight tilt may be effected by taking the average of I_{hkl} and $I_{\bar{h}\bar{k}\bar{l}}$, and assuming a centre of symmetry.

It is evident that an increase in the accelerating voltage of the electrons, and so a decrease in their wavelength, will improve spot patterns from stationary crystals for purposes of structure analysis. For higher voltages the Ewald sphere will approximate more closely to a plane, the spot pattern will be more extensive, and the resolution in the Fourier projection will be increased. In addition, an increase in the accelerating voltage will increase the crystal thickness for which the kinematic approximation is valid and reduce the diffuse background of inelastically scattered electrons for a given specimen. Hence it is important to use as high a voltage as possible.

4. Specimen preparation and manipulation

A minimum value for the diameter of a crystal which can be used for structure work is set by the condition that the total electron flux through the crystal must be sufficient to allow the intensities of the diffraction spots to be measured, while the maximum flux density (flux per unit area) must be less than that for which disruption of the structure by electron bombardment is appreciable. From experimental observations it seems probable that the minimum diameter of crystals of most organic compounds is of the order of a few μ under present experimental conditions.

The electron flux density may be increased up to the maximum usable value and the beam diameter decreased at the specimen by using strong electron lenses to form a highly demagnified image of the electron source. If a sufficiently fine beam is used, the resulting divergence of the beam need not be so great as to affect the conditions of diffraction. The resolution in the diffraction pattern suffers accordingly, but high resolution is not necessary when only the intensities of well-separated spots are required.

Substances with layer-lattice structures readily form suitable plate-like crystals. Other substances may be induced to grow in crystals of suitable shape by a number of methods, including deposition of the material on a flat surface by vacuum evaporation, electrolytically or from solution, and the formation of the specimen by chemical reaction of a gas or liquid with a thin film or flat surface. The use of supporting films, such as the films of collodion, Formvar or silicon monoxide used in electron microscopy, should be avoided if possible, since such films usually add a diffuse background to the pattern and so make accurate intensity measurements more difficult.

The requirements of structure-analysis work in the way of specimen manipulation are rather exacting. Ideally it should be possible to translate any crystal in the specimen into the beam and then rotate the crystal about axes passing through its centre until it is correctly oriented. The rotations should be completely independent of the translations and accurate to within a few minutes of arc. No published design for a specimen manipulator seems to meet these requirements. Until a manipulator with the necessary precision movements is evolved, conventional specimen holders must usually be used in a rather tedious hunt among a large number of crystals for one suitably oriented and with suitable dimensions.

5. The measurement of intensities

The techniques available for the measurement of electron-diffraction spot intensities are limited, and further development is desirable. The visual estimation of intensities may be sufficiently accurate for some problems, and seems to be the only possible method in cases where the single spot pattern is superimposed on a confused background of rings, arcs and spots.

The use of a Faraday cylinder (Thomson & Cochrane, 1939) or Geiger counter (Lennander, 1952) to measure spot intensities one at a time would be too slow in view of the contamination and decomposition of the specimen caused by electron bombardment which usually occurs. High speed electronic measuring devices may be conceived but have not been developed.

The microphotometer has been used successfully to measure the intensities of photographically recorded rings, and sometimes arcs, but cannot be used directly on single-crystal spot patterns. Unfocused spots are usually irregular in shape. In focused patterns, if the plate is given enough exposure to make the weaker spots visible, the centres of most spots are blackened beyond the linear region of the plate characteristic. For such a pattern, approximate intensity estimates may be made on the assumption that the diffuse scattering immediately surrounding a spot decreases in the same way for each spot, so that the apparent diameter of a well-exposed spot may be used as a measure of its intensity. The relation of spot diameter to intensity may be determined by making a series of exposures with different exposure times. This method was used by Cowley, Rees & Spink (1951*a*) to estimate the spot intensities in a paraffin pattern, and appeared to give reasonable accuracy.

A new photographic method, applicable to either sharp or irregular, unfocused spots, has now been developed. Two pairs of deflecting plates, taken from a cathode-ray oscillograph tube, have been mounted beneath the specimen in the electron-diffraction camera (Cowley & Rees, 1953). To each pair of plates is applied a periodic potential with a linear 'saw-tooth' waveform. The two oscillations are not synchronized, so that each diffracted beam is scanned rapidly over a small rectangular area, and each diffraction spot is replaced by a uniformly blackened rectangle. Provided that the dimensions of the rectangle are greater than twice the diameter of the diffraction spot, the blackening at the centre of the rectangle depends on the integrated intensity of the diffracted beam, since each part of the diffracted beam spends the same period of time there. In recording diffraction patterns in this way, the intensity of the diffuse background is increased relative to the maximum intensity of the spots. Since, however, crystals suitable for structure analysis give very little diffuse scattering, this effect is not usually important. Fig. 1 shows a portion of a diffraction pattern from a form of lead hydroxide, without and with the deflecting voltages applied. If the aperture or slit of a microphotometer traverses a row of spots in a pattern such as that of Fig. 1(*b*), the microphotometer trace will show a series of flat-topped peaks, such as those in Fig. 2. The heights of these

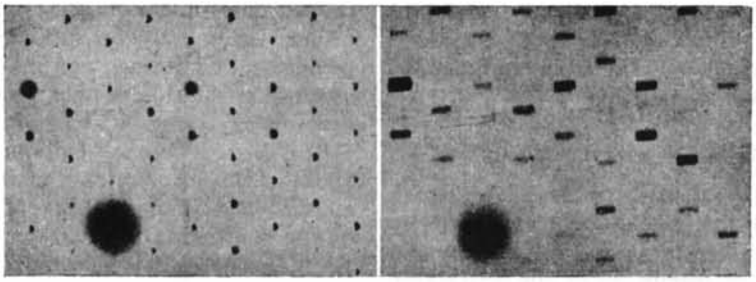

Fig. 1. (*a*) Portion of a diffraction pattern from a crystal of a form of lead hydroxide. (*b*) The same pattern as in (*a*) recorded with two unsynchronized linear deflecting voltages applied.

peaks then correspond to the integrated intensities of the reflexions.

The relation between the peak heights and the relative intensities of the reflexions is also determined by use of the deflector plates. The linear saw-tooth wave on one pair of plates is replaced by a non-linear, approximately exponential, periodic potential variation. When this wave is synchronized with a linear wave on the other pair of plates, the linear scan acts as a 'timebase' to display the form of the non-linear wave. When the two waves are not synchronized, the electron beam is scanned over a rectangular area, and the blackening of the plate increases from one end of the rectangle to the other. The trace given when the microphotometer slit moves along the rectangle may be used to calibrate microphotometer deflexion against intensity, since the intensity at a given point of the rectangle is proportional to the slope of the display curve at the corresponding point. The range of calibration may be extended, if necessary, by making several different-length exposures with the non-linear and linear scans unsynchronized. A typical display curve and non-linearly blackened rectangle are shown in Fig. 3.

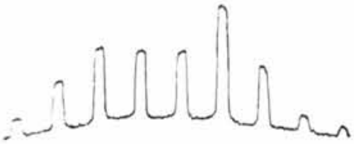

Fig. 2. Microphotometer trace from a line of spots in the pattern of Fig. 1(*b*).

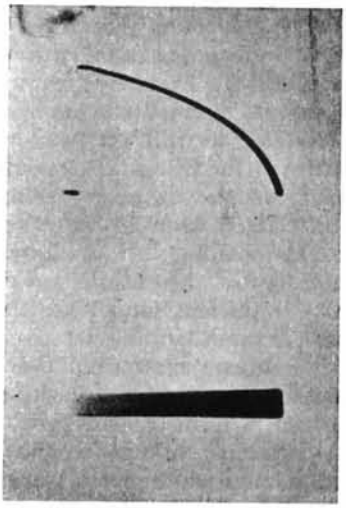

Fig. 3. Calibration curve and rectangle produced by a non-linear and a linear deflecting voltage, synchronized and unsynchronized respectively.

6. Interpretation of potential maps

The relation between relative heights of peaks in Fourier-projection maps and the atomic numbers of the corresponding atoms is difficult to determine with any accuracy. On the basis of the atomic scattering factor curves obtained from equation (2), it is evident that the peak heights for neutral atoms should increase fairly regularly with the atomic number.

Ionization of atoms will have a marked effect on the relative peak heights. The atomic scattering factor for X-rays, f, varies with the state of ionization. Since, from equation (2), the scattering factor for electrons, ε, depends on $(Z-f)$ the percentage change in ε may be much greater, especially for small values of $(\sin\theta)/\lambda$ where f is nearly equal to Z. For a positive ion, f is smaller than for a neutral atom, so that ε is greater and the height of the peak in the potential map is greater. For a negative ion f is larger, ε is smaller and the peak height is less. Since f is greater than Z for negative ions at small values of $(\sin\theta)/\lambda$, ε may become negative if the formula (2) remains valid at small angles. However, there is as yet no evidence that negative values of ε occur in practice. In Fig. 4 the change of ε with ionization is shown by plotting the values of $\varepsilon_{\text{ion}}/\varepsilon_{\text{atom}}$, for oxygen, aluminium and hydrogen, against $(\sin\theta)/\lambda$. The relative change in scattering factor due to ionization becomes less marked as the atomic number increases; it is most pronounced for hydrogen. The scattering power of a neutral hydrogen atom, relative to that of other atoms, is greater for electrons than for X-rays. For ionized hydrogen the difference is even more marked. Hence it should be much easier to determine the positions of hydrogen ions, such as those in hydrogen bonds, when electron-diffraction data rather than X-ray data are used for structure analysis. The atomic scattering factors for ions derived from equation (2) apply to isolated ions only. It is not to be expected that the scattering factors of ions in a crystal lattice will be the same at small angles.

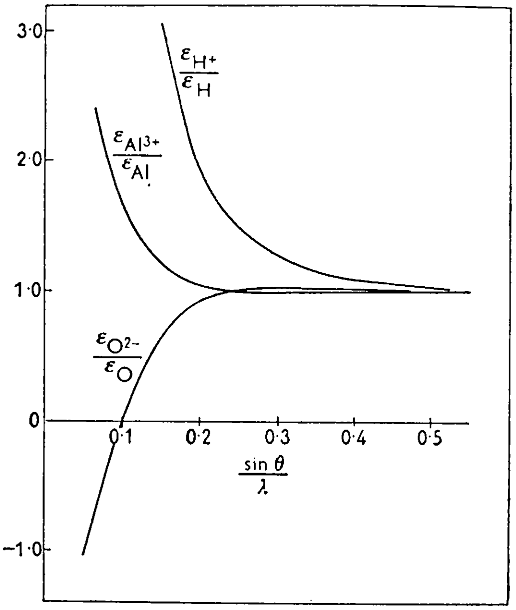

Fig. 4. The ratio of the atomic scattering factors of an ion and a neutral atom plotted against $(\sin\theta)/\lambda$ for oxygen, aluminium and hydrogen.

Potential distributions determined by Fourier methods are normally plotted with an arbitrary potential scale. The methods used to put the electron-density maps obtained from X-ray diffraction on an absolute scale cannot be used in the electron-diffraction case. With X-rays the limiting value of the ratio of observed and calculated structure factors for small values of $(\sin\theta)/\lambda$ may be used to adjust the electron-density scale. For electrons, the uncertainty of the atomic scattering factors due to the unknown ionization states of the atoms makes this ratio indefinite for small values of $(\sin\theta)/\lambda$. The determination of absolute scattering cross-sections, requiring a knowledge of the exact morphology of the scattering crystal and the ratio of the intensities of primary and diffracted beams, is beyond the capabilities of present experimental technique. In special cases, however, the problem could be greatly simplified by using values for a few of the Fourier coefficients determined in an absolute way from linear measurements of details of diffraction patterns. If a substance can be crystallized in the form of small crystals with regular habit, it is possible to take advantage of the fact that the inner potential has two effective values, $E_{000} \pm E_{hkl}$ (usually written $V_0 \pm V_{hkl}$), for each reflexion. Measurement of the distances between features of the fine structure of diffraction spots, revealed under high-resolution conditions, can be used to deduce the values of E_{000} and E_{hkl} for a few reflexions (Sturkey, 1948; Goodman & Rees, 1953). Alternatively, if the substance can be obtained in the form of a near-perfect parallel-sided slab of thickness less than about 1000 Å, the values of a few of the coefficients, E_{hkl}, can be determined from measurements of the spacings of the sets of parallel bands which occur in convergent-beam diffraction patterns (MacGillavry, 1940). The values of E_{hkl} obtained by either of these methods may be used to place all the intensity measurements, and so the potential distribution, on an absolute basis.

In conclusion I wish to acknowledge my indebtedness to A. F. Moodie and P. Goodman for experimental assistance and stimulating discussion.

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