CHAPTER I

DETERMINATION OF STRUCTURE AMPLITUDES

I. INTRODUCTION

The use of X-ray methods in the analysis of the structure of matter, which began with von Laue's discovery of the diffraction of X-rays by crystals forty years ago, has now become a vast field of research. Thousands of crystals have been investigated, and although techniques have been evolved whereby structures of reasonable complexity can be determined completely, no straightforward method, based purely on X-ray data is as yet available. Even for the simpler structures, a knowledge of the chemical structure of the compound and such other information are very useful, and for more complex structures, one cannot proceed much without the aid of such auxiliary data.

In future it may be possible to determine the structure of every crystal unequivocally by X-ray methods alone without having recourse to other data of any kind, but at present there are some difficulties standing in the way of this ultimate goal of the X-ray structure analyst. The interpretation of the observed intensities of reflections in terms of the arrangement of atoms in the unit cell is neither unambiguous nor straightforward. At some time or other trial and error methods based on stereochemical data or physical properties will be needed. X-ray methods, as they stand now, only very rarely lead to complete structure determination, but has
always to be used in conjunction with other measurable properties of the crystal. Only when an approximate structure has been found can we calculate the final picture of the unit cell contents in all its finer details from experimental X-ray diffraction data alone. With the accumulation of data regarding the fundamental structure types it may be possible to tackle structures of ever increasing complexity.

If the unit cell of the crystal to be analysed contains only a few atoms, then it may often be possible to determine directly the atomic positions from the analytical results of space group theory alone; but in most cases this is not possible. For the complete analysis of complicated structures which contain large groups of atoms none of which coincide with any of the symmetry elements of the crystal, the X-ray method can be applied at its full power only when both the positions and intensities of every one of the diffracted beams are used in building up the picture of the arrangement of scattering material in the unit cell. In such cases the crystal structure investigation ordinarily proceeds in two distinct steps. The first is the determination of the geometry of the repeating pattern and this is attained through a knowledge of the crystal class, the unit cell dimensions, the lattice type and the space group of the crystal. This stage of structure analysis is only a matter of pure geometry and the requisite data can, in general, be obtained for any single crystal. The second stage depends on the interpretation of the complete X-ray diffraction data and aims at obtaining from them the arrangements of the atoms in the unit cell. No universal method of solving this
problem is yet available, although various techniques have been
developed for obtaining as complete data as possible.

It is possible to picture an ideal crystal in two ways. In
the atomic representation, the unit cell, the repetition of which
in three dimensions forms the crystal, may be filled with atoms,
each in its proper place, the determination of which is our aim.
Since it is the electrons that diffract X-rays a more complete
description could be given in terms of the electron density distribu-
tion $\rho$ in the unit cell as a continuous function of the co-
ordinates. In this representation, which might be called the
continuous representation, there will be density peaks in the
neighbourhood of the centers of atoms, only the valency electrons
and free electrons in metals being found in between. A detailed
knowledge of the electron density distribution not only helps us
to locate the atomic positions but also enables us to understand
the nature of the binding between the atoms.

In any case, the function $\rho(x, y, z)$, just as any other position
function of the crystal is characterised by three fold periodicity
and hence could be represented by Fourier series. This idea,
which was first suggested by W. L. Bragg in 1915, was extended and
given a three dimensional form by Duane and applied to practical
cases by Havinghurst and Compton in 1928. The periodic distribution
of scattering matter density could be analysed by Fourier methods
into a series of harmonic terms so that we could write

$$\rho(x, y, z) = \sum_{k} \sum_{l} A_{kl} \cos \left[ 2\pi \left( \frac{k_x x}{a} + \frac{k_y y}{b} + \frac{k_z z}{c} \right) - \alpha_{kl} \right] \ldots (1.3)$$

where $k, l$ are integers. If one works with an X-rays of wavelength
far away from the absorption edges of the atoms then the scattering is not accompanied by any change of phase, and then it can be shown that each X-ray reflection corresponds to one of the component sinusoidal density distributions in the crystal and that

$$A_{hkl} = \frac{|F_{hkl}|}{\sqrt{V}}.$$  \hspace{1cm} (1.2)

Here $|F_{hkl}|$ is the modulus of the so-called "structure amplitude" of the plane $(hkl)$ which is related to the intensity of the corresponding reflection, $V$ is the volume of the unit cell and $\alpha_{hkl}$ is the phase angle of the reflection. In equation (1.1) the summation has to be extended over all integral values of $h, k, l$ from $-\infty$ to $+\infty$. The physical nature of $\rho(x,y)$ assures that the Fourier expansion is always valid and that the series is convergent.

Thus the problem of electrons density distribution, and hence the atomic arrangement, can be reduced (in this Fourier approach) to the determination of the three quantities $V, |F_{hkl}|$ and $\alpha_{hkl}$ in equation (1.1). While $|F_{hkl}|$ can be directly obtained from the measured intensities of the various reflections, the determination of $\alpha_{hkl}$ is not so straightforward.

We shall consider in some detail the collection of these three quantities as well as the method of building up the picture of the atomic configuration from them.

In the first chapter, we shall consider the collection of the experimental data, which give in general the geometry of the unit cell and which are needed for obtaining the structure amplitudes for a complete analysis.
I. 2 THE GEOMETRY AND SYMMETRY OF THE UNIT CELL

From Laue photographs, only the point group symmetry of the crystal with the addition of a center of inversion is obtained. Powder photographs give the magnitudes and ratios of the spacings of a number of planes, the exact indices of these planes not being given directly. Hence by this method the unit cell arrangement cannot be directly determined, but we can use the indirect method of postulating the arrangement that gives the spacings of observed magnitudes. These trial arrangements are possible only for the more symmetrical cases like the cubic, the tetragonal and the hexagonal where the number of variables defining the unit cell is not more than two. For lower symmetry crystals with larger number of variables single crystal photographs are necessary. Rotation or oscillation photographs along the three crystallographic axes immediately give the three unit cell dimensions. The other unit cell constants, viz., the cell angles \( \alpha, \beta, \gamma \), could be obtained by the morphological studies using the optical goniometer or by the purely X-ray methods described by Buerger (1942) using Weissenberg photographs.

In order to determine the space group of the crystal it is necessary to assign indices unequivocally to all the reflections. The interpretation of the rotation photographs have been to a large extent simplified by the treatment of Bernal (1926) based on Ewald's concept of the reciprocal lattice. Each reflection is associated with a point of the reciprocal lattice of the crystal. Since a reciprocal lattice could be identified by three coordinates, it is necessary that for unambiguous indexing of the diffracted
beams each beam should be associated with three co-ordinates.

The photographic film, on which the diffracted beams are usually recorded, having only two dimensions it is not in general possible to assign indices unequivocally if they are all recorded on a single film. From this point of view the rotating and oscillating crystal methods are unsatisfactory in that they represent attempts to record the whole or part of the three dimensional reciprocal lattice on a two dimensional film. As Buerger points out, these attempts correspond respectively to attempts at solution of three unknowns from two equations; and with two equations and a pair of inequalities. Of course, the solution is indeterminate in both cases and in general such indexing methods will fail.

By dividing the three dimensional lattice into individual layers of points which are two dimensional and then recording the various layers one at a time on a two dimensional film the indeterminacy in indexing could be got over. This is equivalent to pre-determination of one of the indices \( h, k, l \) of each reflection by preselection. This preselection is done by using layer line screens in the moving film cameras so that the reciprocal lattice points on a single layer are spread out on to the two dimensional film. Here there is exact one to one correspondence between the position where the diffracted beam is recorded and the corresponding reciprocal lattice point so that the moving film photograph may actually be regarded as a projection of the reciprocal lattice level that is being recorded. The projection may be distorted or undistorted depending on the actual moving film mechanism; but in principle there is no difficulty in obtaining the transformation equations connecting
the reciprocal lattice co-ordinates with the film co-ordinates; equations for which unique solutions always exist, and hence uncertainty in indexing never arises in these cases.

Since the symmetry operations involving lattice centerings and translations cause extinctions in certain classes of reflections, a list of X-ray extinctions of a given crystal is these - with certain exceptions - characteristic of the symmetry of the repeating pattern of the crystal, i.e., of the space group of the crystal. Additional lattice translations change the identity period of every plane, glide planes affect only the spacings of planes normal to the glide plane and screw axes affect the identity, period of planes normal to the screw axes. Hence, the extinct class uniquely characterises the symmetry element causing it. But, some time it may happen that the extinction in the more general class of spectra automatically implies extinctions in less general classes and to this extent the latter are unobserved. Thus, the space groups $I_{212}$ and $I_{21}$, are indistinguishable by X-ray methods alone.

In some cases the morphological features might give some clue regarding the crystal class. But, since the symmetry given by the crystal planes may be higher or lower than the actual one depending on the conditions of growth of the crystal, these must be used with caution. Pyro or piezo-electric properties can be used to show absence of center of inversion. If all these do not decide the space group then it might be necessary to try out all possible space groups and adopt the best one based on physical or stereochemical reasoning. However, in spite of certain ambiguities like this it is always possible to determine the geometry and the symmetry of the
repeating pattern of the unit cell provided we can obtain single
crystals of the substance.

1.3 MEASUREMENT OF INTENSITIES OF DIFFRACTED BEAMS

The second stage of structure analysis is essentially based
on the intensities of the various Bragg reflections. Method of
indexing the reflections having already been indicated, we shall
consider the methods of estimating the intensities.

It is well known that crystals have a texture i.e., they may
be ideally perfect, mosaic or in between. Consequently, it is not
the peak value of the reflection that is of importance but another
quantity termed the 'Integrat ed reflection' which is related to
the area under the reflection curve when the crystal is rocked
about the reflection position. This integrated intensity is
related to the structure amplitude $|F_{hk|}$ of the plane under
consideration. However, the exact relationship depends upon the
crystal texture. As early as 1914, barely two years after the
discovery of the diffraction of X-rays by crystals, Darwin showed
that the integrated intensity is proportional to $|F|^2$ for the
mosaic crystal, while it is proportional to $|F|$ for a non-absorbing
perfect crystal. Later studies (Reiniger, 1937; Hirsch and Rama-
chandran, 1950) show that for an absorbing perfect crystal it is in
between. Consequently, for structure analysis, it is best to make
a crystal mosaic if possible. Where it cannot be done, corrections
must be made for extinction effects. However, these effects are
not serious for the weaker reflections. In addition to crystal
texture there are various other factors which affect the integrated
intensities of the reflections. After making the necessary corrections to the observed intensities we could finally obtain the structure amplitudes of the various planes.

The method first used by W.H. and W.L. Bragg (1913) for the measurement of intensities of X-ray reflections made use of the fact that X-rays ionize gases, and that the resulting conductivity is a measure of the intensity of the X-ray beam. By suitable movements of the crystal and the ionization chamber it is possible to measure the diffracted beams at all angles, for one zone reflections at a time. The curve of ionization current against angle of reflection gives peaks, the area under the peaks giving the integrated intensities. Since the intensities of the diffracted beams could easily be put on an absolute scale by comparison with the intensity of the primary beam, this is a very direct way of measuring, the absolute integrated intensities.

The convenience of photographic methods has, however, led to their development and wide popularity with crystal structure analysts. Methods of accurately recording and measuring intensities of reflections from very small crystals bathed in X-ray beam and corrections for extinction etc were necessary in the beginning to get accurate absolute values for the intensities. But this accuracy is neither possible nor necessary in extended surveys required for structure analysis of crystals. The intensities of several hundreds of reflections are necessary in structures of moderate complexity so that rapid methods of recording and measuring integrated intensities are of great importance. The use of double crystal
spectrometer (Wooster & Martin, 1940) enabled one to put the intensities on an absolute scale by recording the reflections from the unknown crystal and a standard crystal side by side on the same film. The use of moving film method is a great advantage in such work by reducing the background intensity around the diffraction spots, thus making the intensity measurements more reliable.

The actual photometry of the X-ray photograph depends on the type of photograph to be studied. Different types of instruments like the photoelectric photometer of Jay (1941) for powder photographs, the Robertson and Dawton's (1941) photometer for single crystal photographs, the X-ray photometer of Astbury (1927, 1929), the positive print method of Dawton (1933), etc., have been used at various times, each method having its own advantages and disadvantages. The simpler method of estimation of intensities by visual comparison with standard set of intensity marks of the same shape and size as the diffraction spots is very widely used now. Even though this method is not very accurate, with some training it is possible to estimate the intensities rapidly with an accuracy of 15-20%; an accuracy which is enough for all except the most accurate determinations.

Whatever the method used for estimating the intensities, the range of intensities of diffracted beams is far too large to be recorded on a single film; an exposure large enough to record the weak reflections with any measurable density would leave the stronger reflections so opaque that no type of
photographic photometry would be possible to estimate its intensity with any degree of accuracy. The multiple-film method of Robertson (1943) enables a much larger range of intensities to be recorded. Here, a suitable set of films are obtained from a single X-ray exposure by placing several films one behind the other in the camera, if necessary with metal foils of suitable thickness in between the films, so that the X-ray intensity from film to film varies by a constant ratio. By using three films it is thus possible to record intensity ratios of 1000 : 1 if the successive photographs are related by an exposure ratio of about 2½ : 1.

Where very accurate intensity estimates are needed, Geiger-counter measurements (Lonsdale, 1943) are most reliable. In addition to its accuracy – the results usually being accurate to within 5% – the counter method has the additional advantage of its extreme sensitivity, it being possible to record the passage of a single X-ray photon whereas about a hundred photons are necessary to make appreciable impression on the photographic film. Geiger-counter is also capable of recording a larger range of intensities than is possible with a single photographic film. After a critical discussion of the three methods of recording X-ray intensities, Wooster, Ramachandran and Lang (1943) come to the conclusion that for long exposures the photographic method is as sensitive as the counter spectrometer used for a few minutes and is more sensitive than the ionization spectrometer. They also claim that the counter method of obtaining the integrated intensities is much more rapid than the use of most optical photometers. The Geiger-counter method,
however, has the disadvantage that the electronic accessories of the counter and the necessary stabilization devices for the X-ray tube output make this method rather more elaborate than the photographic method and hence the additional complexity is justifiable only when extremely accurate estimates of intensities are absolutely essential.

I.4 EVALUATION OF STRUCTURE AMPHITUDES FROM INTENSITIES

Before we could use the intensity data for the calculation of the atomic configuration in the unit cell we have to consider in some detail the relationship between the integrated intensity of reflection and the corresponding structure amplitude of a plane. As mentioned earlier, Darwin had given the relationship for the limiting cases of ideally mosaic crystals and perfect nonabsorbing crystals. In practice, however, most crystals are found to belong to neither of the ideal types treated by Darwin even though in most cases they are nearer to the mosaic crystal type. In early days the crystals were used in their natural state and corrections for mosaicity in the form of primary and secondary extinguitions were applied. It is preferable to make the crystal as mosaic as possible before carrying out the diffraction experiments and use the ideal mosaic crystal formulae in evaluating the structure amplitudes from the intensities. In the case of very small ideally mosaic crystals bathed in an X-ray beam the integrated intensity

\[ I'_{hkl} \text{ of plane } (hkl) \text{ is given by} \]

\[ c \cdot I'_{hkl} = A \cdot T \cdot L \cdot P \cdot |F_{hkl}|^2 \ldots \ldots \ldots (1.3) \]

Here

\[ C = \text{ Scale factor} \]
A = Absorption factor  
T = Temperature factor  
L = Lorentz factor  
P = Polarization factor

are some of the important corrections terms that have to be taken into account. We may call the integrated intensity, corrected for these factors, as the correct intensity \( I_{\text{corr}} \). Obviously

\[ c \cdot I_{\text{corr}} = c \left[ A^{-1} \cdot T \cdot L \cdot P \right] I'_{\text{corr}} = |F_{\text{corr}}|^2 \quad (1.4) \]

It may be mentioned that the factors A, T, L and P depend on the particular reflection and are in general different from reflection to reflection. Hence it is difficult to compare the structure amplitudes of various planes until allowance is made for these factors. We shall briefly consider these factors one by one.

The absorption of X-rays in the crystal causes the intensities of reflections at smaller Bragg angles to be reduced much more than those for the back-reflections. In the case of cylindrical Debye-Scherrer specimens of known diameter and linear absorption, corrections have been calculated (Bralley, 1935). These values could also be used for cylindrically shaped single crystals. For single crystals of arbitrary cross-sections it is possible to calculate the corrections graphically (Albrecht, 1939; Henderson, 1937; Howells, 1950; Evans, 1962) in the case of each reflection and for each crystal, but the calculations are laborious and hence it is much better to reduce the single crystal to a circular cross-section if possible. Of course, the best plan would be to keep the absorption corrections as low as possible by using small enough
crystals - so that, say, \( \mu = 1 \), but in practical cases with inorganic crystals of large values of linear absorption coefficient (\( \mu \)) the corresponding crystal size (\( t \)) becomes too small and introduces experimental difficulties. With ordinary organic crystals this trouble very rarely arises and the correction can be neglected in most cases without causing much error.

The temperature factor arises from the fact that at ordinary temperatures the atoms in the crystal are not at rest but are in vibration. A detailed calculation of these effects requires a knowledge of the vibration spectrum of the crystal. The usual method that is used is to assume a continuous distribution of frequencies and then integrate over the whole spectrum. However, it is not absolutely necessary to make any explicit assumptions regarding the nature of the vibration spectrum of the crystal to make allowance for these effects. In the case of a cubic crystal, if we assume that the atom \( \gamma \) has a mean square displacement \( \bar{\omega}_\gamma^2 \) from its equilibrium position, then its scattering factor \( f_\gamma^T \) at temperature \( T \) can be shown to be related to its value \( f_\gamma^0 \) at temperature zero by the relation of the form

\[
f_\gamma^T = f_\gamma^0 \exp \left[ -B_\gamma (\sin \theta / \lambda)^2 \right] \tag{15}
\]

where, \( B_\gamma = 8\pi \bar{\omega}_\gamma^2 \).

Hence we see that due to the thermal vibrations the atomic scattering factor is effectively reduced and that this reduction is much more prominent for large angle reflections. In this respect the temperature effect is opposite to the absorption effect where the intensities of small angle reflections are reduced more. The thermal effect, of course, increases with temperature.
Actually one must use a different temperature factor $B_\gamma$ for each crystallographically nonequivalent atom in the unit cell, but in effect one may use a mean temperature factor $B$ for all the atoms and thus write

$$\left( F_{hkl} \right)_T = \left( F_{hkl} \right)_0 \exp \left[ -B \left( \frac{s^2}{2} \right) \right].$$

(1.6)

where $B = 8\pi \bar{\omega}^2$, $\bar{\omega}^2$ being the mean square amplitude of the atoms. This is not strictly true, but it is a close enough approximation for many crystals. However, there are many cases in which the vibrations are markedly anisotropic as when the molecule has planar or needle shaped groups. Then it comes to crystals of symmetry lower than the cubic, the theory itself has not been properly developed; some authors prefer to use different $B$ value for different zones, but it is impossible to give general rules which hold universally. Incidentally, it is necessary to include the zero point energy in calculating $\bar{\omega}^2$ theoretically. James and Brindley (1928) showed that on extrapolating to absolute zero, the structure amplitudes did not give values calculated from atomic scattering factors, but differed by a factor corresponding to the zero point energy $\frac{1}{2} \hbar \nu$ per atom (i.e., $\frac{1}{2} \hbar \nu$ per degree of freedom of the atom).

In the general case it is not possible to calculate $B$ accurately, but this knowledge is not absolutely essential for the structure determination by Fourier methods. In uncertainty in $B$ value usually does not lead to much doubt in the interpretation of the diffraction results since an inaccuracy in $B$ means only that the intensities of reflections fall away with greater or lesser rapidity with increasing angle than was expected. In fact, it may
be an advantage to have data at a finite temperature and actually
in certain cases artificial temperature factors (Wooster, 1935) are
applied. However, if the experimental values are to be compared
with the values of the structure amplitudes calculated from the
final atomic positions, then the theoretical values have to be
multiplied by the temperature factor as otherwise large discrepancies
will appear for large angle reflections. The experimental deter-
mination of the temperature factor could be done using the statisti-
cal method of Wilson (1942) for the determination of scale factor or by
the steepest descent method of Booth (1949). These will be discussed
later as occasion arises.

The polarization factor \( P \) depends on the fact that the
incident X-ray beam usually used in diffraction experiments is
unpolarized and the intensity of the scattered beam depends on
the direction of polarization of the incident beam with respect to
the plane of incidence. The effect due to polarization is different
for perfect and mosaic crystals (Ramaseshan and Ramachandran, 1952)
but in each case, this can be applied from knowledge of the
scattering angle for the given reflection. This correction,
generally \( \frac{1 + \cos^2 \theta}{2} \) being dependent only on the Bragg angle is
independent of the method of recording the reflection. The Lorentz
factor arises due to the fact that during recording, the various
reflecting planes pass through their reflecting positions at
different velocities and thus the duration for which they reflect
is different for the various planes. The integrated intensity of
the reflection is directly proportional to this time opportunity
of reflection and depends on the method of recording the diffraction
pattern. These factors \((L\) and \(P\)\) are considered in more detail in Chapter III where these corrections are calculated for the anti-equilibrium Weissenseberg method of recording.

In addition to the above, various other corrections like the correction for the effect of spot size, obliquity, etc., have also been considered (Kaaan and Cola, 1949) and are necessary when very accurate values are to be obtained by photographic methods.

After applying these corrections to the observed integrated intensities \(\bar{I}'\), we get a set of values \(\bar{I}_{4k4}\) (1.4) for each reflection, these being proportional to the corresponding \(|F_{4k4}|^2\) in the case of a mosaic crystal. The constant of proportionality 'c', which is the same for every reflection obtained from a single photograph, is termed the 'scale factor'. It being possible to obt in an explicit expression for 'c' in terms of \(\ell, m, \kappa\) etc. in addition to the intensity of the incident beam we could determine this constant experimentally. Even though for structure determinations based on Fourier methods it is not essential to have \(|F_{4k4}|\) value on an absolute scale, the knowledge of the absolute values is of much use in many cases, such as obtaining the true values of the electron density by Fourier methods, for trial and error methods, for parameter refinement by minimization methods etc. Since actual experimental determination of the absolute integrated intensities is rather laborious other methods have been suggested for obtaining the scale factor. One such method is due to Wilson (1942) and another due to the present author (1952) details of which are given in Chapter IV.

Thus, from the experimentally observed intensities of the
diffracted beams we obtain a set of numbers as the structure amplitudes for the various planes. These values are the moduli of the structure amplitudes which are in general complex. These $|F_{hkl}|$ values form the experimental data from which we build up the correct arrangement of scattering material inside the unit cell which is the aim of the X-ray crystal structure analyst.