Structure Analysis by Electron Diffraction

BY

B. K. VAINSHTEIN

TRANSLATED AND EDITED BY

E. FEIGL

AND

J. A. SPINK

Commonwealth Scientific and Industrial
Research Organization, Melbourne

PERGAMON PRESS LTD.
Headington Hill Hall, Oxford
4 and 5 Fitzroy Square, London, W. 1

PERGAMON PRESS (SCOTLAND) LTD.
223 Teviot Place, Edinburgh, 1

PERGAMON PRESS INC.
122 East 55th Street, New York 22, N.Y.

GAUTHIER-VILLARS ED.
55 Quai des Grands-Augustins, Paris 6

PERGAMON PRESS G.m.b.H.
Kaiserstrasse 75, Frankfurt am Main

Distributed in the Western Hemisphere by
THE MACMILLAN COMPANY · NEW YORK
pursuant to a special arrangement with
Pergamon Press Limited

Library of Congress Catalog Card Number 63-10019

This translation has been made from the book by
B. K. Vainshtein Структурная Электронография
(Strukturnaya Elektronografiya)

Made in Great Britain

Translator's Foreword

THE publication in 1949 of the first Fourier map based on electron diffraction data marked an important step forward in the practical application of electron diffraction to crystal structure analysis. Professor B.K. Vainshtein has been a leading figure in the considerable advances that have been made in the ensuing twelve years and it is appropriate that his recent book on the subject should appear in an English language edition.

I should like to thank Professor Vainshtein who has painstakingly checked our English translation. Thanks are also due to Dr. J.M. Cowley who has carefully checked the scientific accuracy of our translation, and to Mrs A. Daunt and Mrs J. Spink for assistance in the peparation of the manuscript.

In conclusion I wish to pay a tribute to my late colleague and co-translator, Dr. Ernst Feigl, whose sudden and untimely death prevented him from seeing this book in published form. Because of his exceptional ability as a translator and his constant striving for perfection in all he did, Ernst Feigl contributed much to international understanding among scientists and his passing is a great loss to the ever-widening field of scientific translation.

J. A. SPINK

Division of Tribophysics
Commonwealth Scientific and Industrial
Research Organization, Melbourne

Preface to the English Edition

ALTHOUGH a relatively short period of time has elapsed since the appearance in 1956 of the original Russian edition of *Structure Analysis by Electron Diffraction*, considerable advances have been made in the theory and practice of studying the atomic structure of crystalline substances with the aid of electron diffraction.

These advances were made in laboratories situated in many parts of the world, not only in the Soviet Union, where structure analysis by electron diffraction was first developed, but also in other countries, especially Australia, Japan, Great Britain and the United States of America.

Although this English edition corresponds generally to the Russian edition it is, to some extent, supplemented by new material. The English edition contains results obtained during the last five years, which have demonstrated the feasibility of using both kinematic and dynamic scattering of electrons in structure analysis. Chapter III contains new data on atomic scattering, Chapter V describes the results of recent structure investigations of basic salts, metal nitrides and carbides, semiconducting alloys and clay minerals as well as new results obtained in determinations of the positions of hydrogen atoms in crystals.

Structure analysis by electron diffraction must be regarded as an independent method of determining the atomic structure of matter and, as such is finding an ever-widening field of application. The author hopes that the publication of this book in the English language will contribute to the further development of research in this field.

B. K. VAINSHTEIN

Preface

ALONGSIDE the classical method of X-ray diffraction, electron and neutron diffraction methods are becoming increasingly important in the analysis of the atomic structure of crystals. Electron diffraction methods can be applied to the solution of general problems of structure analysis and to special problems which are either difficult or impossible to solve by X-ray or neutron diffraction methods.

The many electron diffraction studies of the atomic structure of crystals recently carried out in the Soviet Union and abroad have led to significant advances in certain fields of crystallography, crystal chemistry, mineralogy, metallurgy and other disciplines. Electron diffraction methods are being used more widely in the investigation of atomic structures of a wide variety of technological materials, in the elucidation of the mechanisms of processes occurring in them, and in the determination of their physical properties.

The present state of the theory and method of structure analysis by electron diffraction allows one to make a systematic presentation of the subject without touching upon the other applications of electron diffraction. This constitutes the purpose of the present book. The characteristics and possibilities of electron diffraction are considered first and compared to other diffraction methods of investigation, and general concepts are formulated concerning the connection between the structure of the scattering object and the diffraction pattern. Later, in conjunction with the main stages of structure analysis, the following topics are developed: the geometrical theory of electron diffraction patterns and the subsequent determination of the unit cell; the theory of intensities; the main properties of the Fourier series, constituting the basis of structure analysis, and their application to electron diffraction studies. The method is illustrated by examples of the determination of structure in inorganic and organic crystals.

Many of the general premises of the structure analysis of crystals (e.g. the theory of symmetry, the construction of Fourier series, etc.) are considered in detail in the textbooks on X-ray diffraction analysis. These topics have therefore been regarded only from the point of view of their specific application to electron diffraction. The derivations of the formulas are not detailed but references to sources containing such details are provided.

The author is grateful to the editor of the book, Professor Z. G. Pinsker, and to B. B. Zvyagin for valuable comments on the manuscript.

Each chapter has independently numbered literature references (square brackets) and equations (round brackets). For cross-reference purposes, the chapter numbers are designated by a Roman numeral, e.g. reference [IV.8], equations (I.29). Where reference is made to material within the same chapter, the Roman numeral is omitted and the number is placed superior.

Contents

CHAPTER I

Diffraction Methods in Structure Analysis

PRESENT-DAY studies of the atomic structure of substances, determinations of the distribution of atoms within crystals and molecules, investigations of the structure of liquids, gases, and even atoms themselves are based on diffraction methods. The structure of the material being studied is not obtained directly in a magnified form, as though viewed under a super-powerful microscope with a magnification of the order of 10^8, but is obtained from calculations in which the diffraction patterns are used as experimental material.

In general, the type of radiation directed at the specimen is immaterial, provided it is of suitable wavelength. The detection of atoms requires a wavelength of about 1 Å or less.

The discovery in 1912 of the diffraction of X-rays in crystals proved, on the one hand, the wave-like nature of the rays and, on the other hand, the periodic lattice structure of crystals – a hypothesis based on a vast amount of experimental data of classical crystallography, but until then lacking decisive proof. The crystal structures of elements and of several thousands of the most important inorganic and organic compounds were then established by X-ray analysis. The development of crystallography, and especially of crystal chemistry, thus received a new impetus from the new wealth of data on crystal structure, the co-ordination of atoms in crystals, and the magnitudes of interatomic distances.

It should be noted that the successful development of structure analysis was made considerably easier by the existence of an already complete theory of all possible forms of particle distribution within the space lattice of crystals – the theory of space-group symmetry developed by the great Russian crystallographer E. S. Fedorov.

Electron diffraction was discovered in 1927. This remarkable phenomenon provided the experimental basis for the development of quantum mechanics, showing that not only electrons but all microparticles possess wave-like properties. Indeed, a little later, positive results were obtained from experiments set up to demonstrate the diffraction of molecules, protons, and neutrons by crystals. Electron and, later, neutron diffraction methods thus found practical application in the investigation of solids.

Although all three methods of structure analysis – X-ray, electron and neutron diffraction – have much in common, they each possess specific features which determine the possibilities and fields of their application.

1. Electron, X-ray and Neutron Diffraction[1-15]

The similarity between electron, X-ray and neutron diffraction lies in the fact that any one of these three methods may be used to solve the main problems of structure analysis, viz. the determination of the coordinates of the centres of gravity of the atoms within a molecule or a crystal. This geometric nature of the problem permits the geometric theory of diffraction, originally developed for X-ray work, to be used in electron and neutron diffraction studies.

The dissimilarities of the three methods are due to the differences of the interaction between the given radiation and the specimen. These differences lead, on the one hand, to limitations due to experimental techniques, and on the other hand, to differences in the physical meaning of the final results, especially if the problem goes beyond the determination of atomic coordinates.

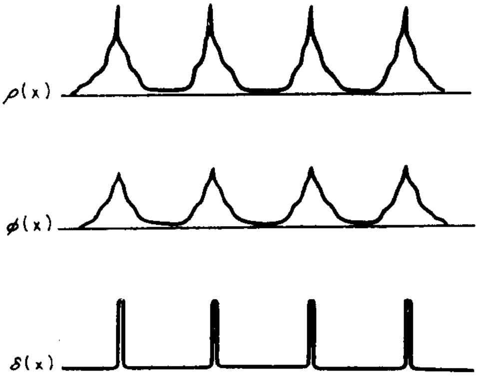

FIG. 1. One-dimensional representation of the distribution of electron density $\varrho(x)$, electrostatic potential $\varphi(x)$ and nuclear scattering function $\delta(x)$ in a crystal with atoms at rest.

X-rays—electromagnetic waves—are scattered by the electron shells of the atoms, atomic nuclei with their positive charges being "invisible" to such radiation. Fourier treatment of experimental X-ray data gives a picture of the distribution of electron density within the crystal, the peaks corresponding to the atoms.

Electrons are scattered by the electrostatic potential due to the atomic nuclei and their electron clouds. The distribution of electrostatic potential about an atom corresponds approximately to that of its electron density, but falls off less steeply as one goes away from the centre of the atom. The construction of a Fourier synthesis from electron diffraction data provides a picture of the potential distribution in the lattice, the maxima again corresponding to the atoms (nuclei).

Scattering of neutrons is due to the action of the delta-function potential of nuclear forces. A comparative picture of the distribution of scattering matter in a lattice of atoms at rest for the three types of radiation is given in Fig. 1.

The diffraction is influenced considerably by thermal motion, since it reflects the mean positions of the atoms in time and crystal volume (in all unit cells). Thermal fluctuations lead to a spreading of the peaks in the ideal pattern (Fig. 1) for fixed atoms. As a result of this, the construction of a Fourier synthesis gives a smudged picture in which many extremely important details are lost (e.g. the layer structure of the electron shells of atoms). However, thermal motion does aid the convergence of Fourier series used in the analysis of crystal structure.

In structure analysis, the problem of distinguishing various types of atoms within the lattice is of primary importance. The scattering of X-rays by atoms is approximately proportional to the atomic number Z. The resolving of light atoms in the presence of heavy ones presents difficulties when the difference in atomic numbers is large, and requires high experimental precision. Scattering of electrons is less dependent on atomic number, and light atoms are therefore more easily resolved.

It is difficult to distinguish atoms with nearly the same Z in a given crystal by either X-ray or electron diffraction. It can be achieved however by neutron diffraction, since scattering of neutrons does not depend directly on atomic number. Neutron diffraction may be used for studies of isotopic and spin differences between atoms in a lattice, these differences being "invisible" to X-rays and electrons. At the same time, quite dissimilar atoms (possessing approximately equal amplitudes of scattering) may prove to be indistinguishable by neutron diffraction methods.

The above general considerations are not the only ones governing the choice of one or other diffraction method for the solution of a given problem. Important requirements may arise from the nature of the experiment, and the following factors need to be taken into account:

(1) availability of sufficiently powerful radiation sources;
(2) convenience and simplicity of apparatus;
(3) possibility of obtaining samples giving the necessary diffraction pattern in a form specific for a given method;
(4) convenience and speed of recording the diffraction pattern.

One of the most important factors determining the nature of the experiment is the interaction of radiation with the substance. The *coherent* scattering within the specimen is used in studies of atomic structure, i.e. scattering that occurs without energy exchange between the incident radiation and the specimen, and without changes in the wavelength of this radiation. The ratio of the intensity of the coherently scattered radiation to that of the incident radiation, determined by the absolute magnitude of the atomic amplitude of scattering, characterizes the extent of the interaction between the radiation and the substance. In evaluating the order of such magnitudes in X-ray, electron or neutron diffraction it is permissible to disregard their dependence on the type of atom (i.e. atomic number Z) and on the angle of scattering. The average absolute magnitude of the atomic amplitude of scattering of X-rays is approximately 10^{-11} cm, that of electrons is about 10^{-8} cm (this is treated in detail below), and that of neutrons is about 10^{-12} cm. Since the intensities are proportional to the squares of the amplitudes, and the atomic amplitudes show the ratio $f_x : f_{\text{elec}} : f_{\text{neut}} \approx 1 : 10^3 : 10^{-1}$, the ratio of the corresponding intensities will be $1 : 10^6 : 10^{-2}$.

The figures given above refer to the scattering by a single atom, the intensity of scattering by crystals consisting of a large number of atoms being proportional to this number.

In order to obtain approximately the same measurable intensity of scattering, the size of specimens must be varied according to the type of radiation being used. The linear dimensions of the specimen must be about 1 mm for X-rays, about 10^{-5} to 10^{-4} mm for electrons, and several millimetres for neutrons. The thickness of the specimen is limited by the increase of effects due to incoherent scattering, secondary scattering of already-diffracted beams, and absorption.

Scattering in air has almost no effect on the intensity of X-ray and neutron beams. Electron diffraction experiments, however, must be carried out in high vacuum, since electron beams are immediately dispersed and absorbed in air.

The above ratios of intensities are used for determining the necessary exposures when X-rays and electrons are recorded photographically. Exposures for X-rays are of several hours duration (with powerful sources and highly sensitive photographic materials), while those for electrons last seconds. Neutrons are recorded, in practice, only with the aid of counters. Thus electron diffraction is the most rapid method.

Electron diffraction apparatus is rather more complicated than that for X-ray diffraction. Neutron diffraction has become possible only with the development of powerful sources of neutrons, i.e. nuclear reactors (piles). Equipment for both electron and X-ray diffraction is being continually improved.

The availability of specimens giving a diffraction pattern suitable for the investigation of atomic structure is of paramount importance for the use of one or other of the above methods. Complete structure analysis of rather complex crystals (and more and more substances of increasing complexity are being investigated) requires the recording of several hundred and sometimes more than a thousand reflections characterizing a given structure, i.e. the complete diffraction field must be obtained. Separation of reflections is necessary for measurement of the intensity of individual reflections. For this purpose X-ray diffraction methods are the most convenient. Moving-film methods, which require a single crystal of 1–0·1 mm, can give a complete set of separated reflections. This has assured, and will continue to assure, a leading place to X-ray diffraction in the structure analysis of crystals.

Specimens in the form of extremely thin films, as used in electron diffraction work, give diffraction patterns which can, in most cases, also be used for structure investigations. This is treated in greater detail in the next section.

Specimens for neutron diffraction studies must be of approximately the same dimensions as for X-ray diffraction work. Neutron diffraction is not recommended for the investigation of unknown complex structures because of the lengthy procedure of recording diffraction patterns with counters. The method is, however, irreplaceable for the solution of special problems connected with isotopic substitution, magnetic effects, etc.

Problems of the structural investigation of any material may, at present, be solved precisely and completely by the appropriate use of one or more of the three methods.

2. Uses of Electron Diffraction. Structure Analysis by Electron Diffraction[1-6]

Electron diffraction was discovered in 1927 by Davisson and Germer who were investigating the reflection of slow electrons (accelerated by a potential of several hundred volts) from a plane face of a nickel single crystal. The first experiments with fast electrons (accelerated by a potential of several tens of kilovolts) were carried out by G.P.Thomson, who obtained photographic records of electron diffraction patterns from polycrystalline films of gold and other metals.

Investigations in the field of fast electron diffraction have been developing along the following main lines during the past twenty-five years:

1. the experimental and theoretical study of the phenomenon itself—investigations of atomic scattering, of dynamic and kinematic scattering, of electron refraction, etc.;
2. electron diffraction studies of molecules—investigation of the structure of molecules in vapours and gases;
3. electron diffraction studies of surface layers—studies of oxide and other films on the surfaces of solids, studies of the state of surfaces (polishing) etc. Work of this type is often based on the "diagnosis" of the presence of a particular crystalline structure on the surface being studied, and for this purpose the results obtained are considered in conjunction with X-ray diffraction data;
4. submicroscopic crystallography—studies on the mutual orientation during contact between different phases, the formation of transition structures, the shape of microcrystals, etc.;
5. structure analysis by electron diffraction—complete determination of the atomic structure of crystals, either as a completely new structure analysis or as a complement to X-ray diffraction data (e.g. determination of the distribution of hydrogen atoms).

Soviet scientists have made important contributions to all fields of electron diffraction.[1,2,4,6] It is sufficient to mention the initial investigations on the diffraction of electrons by a polycrystalline specimen carried out by P.S.Tartakovskii, the invention by A.A.Lebedev of the basic design of the present-day electron diffraction camera incorporating a magnetic lens, the theoretical and experimental work of V. E. Lashkarev, the structural investigations of Z. G. Pinsker and the work of P. D. Dankov and N. A. Shishakov on oxide layers.

The work of Soviet scientists is characterized by the use of electron diffraction methods for solving vital problems in the allied fields of crystallography, chemistry, physical chemistry, and metallurgy, with the emphasis on the solution of the principal problem – the widening of our knowledge of the atomic structure of matter. Advances in crystallography due to Academicians A. V. Shubnikov and N. V. Belov have played a large part in the development of structure analysis by electron diffraction in the Soviet Union.

In 1937–1938 Z. G. Pinsker began developing methods for complete and independent structure analysis by electron diffraction. There is no doubt now that electron diffraction may be used for the complete analysis of crystals whose structure is unknown. This application acquires special significance since among the crystal structures studied by X-ray diffraction methods there are certain unsolved problems, due to the specificity of the X-ray method, which lend themselves particularly well to investigation by electron diffraction. Many natural and synthetic products occurring only in a highly dispersed state are a suitable subject for electron diffraction investigation but not for X-ray studies. Clay minerals are a good example of this type of substance. This also applies to many other organic and inorganic compounds which cannot be obtained in a crystalline form suitable for complete X-ray diffraction analysis. Another important aspect of the use of electron diffraction methods in structure analysis is the investigation of crystals containing light atoms (including hydrogen) as well as heavy atoms. Certain oxides and crystalline hydrates, which are unstable under ordinary conditions but stable in a high vacuum, may also be satisfactorily studied by electron diffraction.

The following points can be regarded as special features of the electron diffraction method: the extremely small amounts of material required for study (as little as 1/100,000 g), the comparative rapidity and simplicity of preparation of specimens, the possibility of observing the diffraction pattern on a fluorescent screen before it is photographed, and the short exposure time.

However, technical difficulties in electron diffraction studies may occasionally arise as a result of the impossibility of obtaining specimens giving electron diffraction patterns of a quality adequate for complete structure analysis. The size of the crystallites comprising the specimen is of primary importance, crystallites with linear dimensions of the order of 10^{-6}–10^{-5} cm being most convenient. Larger crystal sizes are associated with deviations from the kinematic theory of scattering (considered in detail in Chapter III, § 6), and introduce uncertainty as to the correct formula for the conversion of the observed intensities to structure factors. It is possible to use specimens with crystal sizes of the order of 10^{-5} cm, where the intensity of scattering is governed by the dynamical theory (see Chapter III, § 8). Two-dimensional diffraction effects which arise with crystals of linear dimensions smaller than 10^{-6} cm, generally lead to an incorrect relationship between the intensities.

Another, no less important, requirement is a definite secondary structure of the specimen. It is essential to obtain on the specimen support either mosaic single crystal films, or textures. In some cases polycrystalline films can be used. Quite frequently, however, specimens produce a wide variety of intermediate diffraction patterns, when for instance various types of aggregates, imperfect textures, or polycrystalline deposits consisting of "large" crystals, are formed on the specimen support and give ring patterns which are broken up into discrete spots. Such patterns may sometimes be used in electron diffraction investigations, but are generally unsuitable for the evaluation of intensities—an important stage in structure analysis.

In structural investigations transmission recording is almost always used. In some cases, however, important data may be obtained by recording the reflections from the surface of massive specimens (reflection method).

In most cases it is possible to obtain a specimen in a form suitable for analysis by selecting the conditions of preparation. However, it is impossible to guarantee beforehand that any given substance can be investigated by the electron diffraction method. The diversity of the types of electron diffraction patterns calls for a creative rather than a mechanical approach by the investigator. Whereas in X-ray diffraction work it is possible to select and work out beforehand a particular method of photographing (e.g. the method of photographing the reciprocal lattice) for a given specimen, in electron diffraction the operator must be conversant with all methods of recording and interpreting the patterns. The method selected must be correlated with the type of photographs obtainable from a given specimen.

The determination of the symmetry and the unit cell of a crystal is the next step in structure analysis. This is carried out unambiguously on the basis of a purely geometrical theory. The geometrical theory for electron diffraction is much simpler than that for X-ray diffraction because of the shortness of the electron wavelength.

Methods of structure analysis developed earlier for X-ray diffraction are then used, in a modified form, in the determination of the coordinates of the atoms within the unit cell from the measured intensities. The most important of these methods involves the use of Fourier series. In electron diffraction this method gives a picture of the lattice potential, the maxima of which correspond to the nuclei of the atoms. The positions of atoms in simple structures may sometimes be found by trial-and-error methods.

The final stage of the investigation is the determination of the degree of accuracy of the results obtained.

3. Fundamental Concepts of the Theory of Scattering and of the Structure Analysis of Crystals

The corpuscular nature of electrons as well as of neutrons is quite apparent in certain processes. However, the wave-like nature of microparticles is clearly shown in scattering by crystals or by other objects, and this forms the basis for an understanding and explanation of these phenomena. In view of the undulatory character of the particles, the theory of scattering is, in principle, independent of the type of radiation used and is equally true for X-rays, electrons and neutrons. The specificity of the interaction of each radiation with matter can be determined at any given stage by the introduction of characteristic wavelengths and atomic amplitudes.

The fundamental concepts of the theory of scattering and of structure analysis of crystals will be presented in this section with the aid of Fourier series and integrals. These concepts will be used later (Chapters II–IV) for the detailed treatment of problems of structure analysis by electron diffraction.

The methods of calculation in the structure analysis of crystals are based mainly on the kinematic theory of diffraction.

On reaching an object and interacting with it, the primary wave is scattered and secondary waves are set up. The intensity of scattering in various directions may be calculated by taking into account the structure of the object and the phase relationships between the secondary waves which, by interference with one another, are reinforced in some directions and weakened in others. The interaction of waves is here exactly the same as in the diffraction of light (e.g. from optical diffraction gratings), except that optical effects arise from two-dimensional objects, whereas a crystal is a three-dimensional object and secondary waves arise throughout its volume.

The basic assumption of the kinematic theory of scattering may be formulated as follows: since the absolute magnitude of the atomic amplitudes of scattering of electrons, X-rays, and neutrons is very small, the intensities of the scattered beams will, in the presence of a limited number of scattering centres (atoms), be small compared with the intensity of the primary beam. Thus it is possible to ignore the loss of energy of the primary beam in the course of its "expenditure" in the formation of coherently scattered radiation, and also to ignore the coherent scattering of secondary beams which, acting in their turn as primary beams give rise to new diffracted beams, and so on. As the volume of coherent scattering increases, i.e. the number of scattering centres increases, the intensities of secondary beams will increase, and the description of the processes taking place must be based on the dynamical theory of scattering. In this theory, energy interrelationships are taken into account and, generally speaking, all beams are taken as qualitatively equivalent to the primary beam and to one another.

Theoretical calculations and experimental data show that, in electron diffraction, scattering is still of a kinematic nature if the linear dimensions of the crystals are of the order of 10^{-6} to 10^{-5} cm (this is treated in greater detail in Chapter III). For X-rays this limit is higher, being approximately 10^{-1} to 10^{-3} cm. Dynamic effects arise when the dimensions of individual ideal microcrystals or of blocks of mosaic crystals are larger than the above magnitudes.

Amplitude of Scattering. Reciprocal Space

For a kinematic approach, the problem of scattering may be solved as follows. A plane monochromatic wave incident upon the specimen gives rise to an elementary secondary wave in each element of its volume. The amplitude of this scattered wave will, naturally, be proportional to the scattering power of the given element of volume. As has been stated previously and as will be shown more explicitly in Chapter III, scattering of electrons is brought about by the potential $\varphi(\mathbf{r})$, where $\mathbf{r}$ is the vector in the scattering volume. For X-rays, the electron density $\varrho(\mathbf{r})$ is the scattering material while for neutrons it is the "nuclear density" $\delta(\mathbf{r})$. Let $\varphi(\mathbf{r})$ represent scattering material generally, bearing in mind that for electrons $\varphi(\mathbf{r})$ denotes the potential and that for X-rays and neutrons $\varrho(\mathbf{r})$ or $\delta(\mathbf{r})$ are substituted.

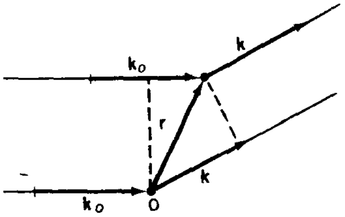

FIG. 2. The origin of a phase difference between waves scattered in the direction **k** from points with $\mathbf{r} = 0$ and $\mathbf{r}$.

Thus the scattering power of an element of volume dv_r is proportional to $\varphi(\mathbf{r})\, dv_r$. The incident wave $\exp(i\mathbf{k}_0 \cdot \mathbf{r})$ with a wave vector $|\mathbf{k}_0| = 2\pi/\lambda$ reaches different points $\mathbf{r}$ of the volume in different phases and consequently the secondary waves $\exp(i\mathbf{k} \cdot \mathbf{r})$ arising from these points also have different phases. The overall phase shift in the secondary wave depends also on the direction of its wave vector $\mathbf{k}$ and equals $(\mathbf{k} - \mathbf{k}_0) \cdot \mathbf{r}$. In the primary wave (Fig. 2) the phase shift is equal to the projection of the vector $\mathbf{r}$ on the direction $\mathbf{k}_0$, i.e. to $-\mathbf{k}_0 \cdot \mathbf{r}$, and in the scattered wave it is equal to the projection $\mathbf{r}$ on the direction $\mathbf{k}$, i.e. to $\mathbf{k} \cdot \mathbf{r}$. To obtain the amplitude of scattering from the whole volume through which $\varphi(\mathbf{r})$ is distributed, the elementary waves $\exp\{i(\mathbf{k} - \mathbf{k}_0) \cdot \mathbf{r}\}\, dv_r$ arising from all its elements with an amplitude proportional to $\varphi(\mathbf{r})$ must be summed (integrated). Taking $\mathbf{k} - \mathbf{k}_0 = \mathbf{s}$ and intergrating over the whole volume of the specimen we find that the amplitude of scattering, f, is equal to:

$$f(\mathbf{s}) = K\int\varphi(\mathbf{r})\exp(i\mathbf{s}\cdot\mathbf{r})\,\mathrm{d}v_{\mathbf{r}}, \tag{1}$$

f being a function of the vector **s**. The proportionality factor K depends on the nature of the radiation. For instance, in electron scattering where the potential is the scattering material, we have $K = 2\pi me/h^2$; in X-ray scattering, where electron density is the scattering material, we have $K = e^2p/mc^2$ (p being the polarization factor). In the following, the constant K will be omitted for the sake of simplicity.

Equation (1) is generally applicable since, on substitution of the distribution $\varphi(\mathbf{r})$ of any object (atom, molecule, crystal), the equation may be used for the calculation of the amplitude of scattering for any **s**, i.e. for any $\mathbf{k} = \mathbf{s} + \mathbf{k}_0$. An important feature of equation (1) is that in its mathematical form it represents a Fourier integral. Thus all the fundamental premises of the theory of scattering and of structure analysis may be obtained from the theory of Fourier integrals and from Fourier series.

Vector **s** in equation (1) has a dimension which is the inverse of that of vector **r** used for measuring distances within the specimen, i.e. $[L^{-1}]$. The values of the amplitude $f(\mathbf{s})$ may be regarded as the distribution of the magnitude f in the space of vector **s**—the so-called reciprocal space—in exactly the same way as the magnitude $\varphi(\mathbf{r})$ is regarded in the real space of the specimen. The concept of reciprocal space and its vector **s** plays an important role in the theory of diffraction.

For a given position of the specimen, i.e. when $\mathbf{k}_0$ is fixed relative to it, the end of vector **s** can only lie along the sphere 1 (Fig. 3a) described by the vector **k**. This sphere is called the Ewald sphere or the sphere of reflection since, in diffraction from crystals, its position determines the formation of discrete reflections, as is shown below. At the point on an X-ray or electron diffraction pattern to which the vector **k** is directed, one generally finds an intensity $J(\mathbf{k})$ corresponding to the square of the amplitudes $f(\mathbf{s})$ cut out from reciprocal space by the sphere of reflection. Figures 3a and b show how the mathematical concepts of reciprocal space and the sphere of reflection are realized in the corresponding diffraction pattern. By changing the direction of the vector $\mathbf{k}_0$ (by a change in the direction of the incident beam or rotation of the specimen), i.e. by moving its origin along the sphere A (Fig. 3a), sphere 1 can be made to pass through any point within sphere 2, the so-called limiting sphere. The angle of scattering 2θ between vectors **k** and $\mathbf{k}_0$ is determined by the expression:

$$|\mathbf{s}| = |\mathbf{k} - \mathbf{k}_0| = (4\pi\sin\theta)/\lambda,$$

since $$|\mathbf{k}| = |\mathbf{k}_0| = 2\pi/\lambda,$$

where λ is the wavelength.

A series of $f(\mathbf{s})$ values may be obtained experimentally by rotating the specimen relative to the primary beam. This operation corresponds to the intersection of various regions of reciprocal space by the sphere of reflection.