THE DIFFRACTION OF ELECTRONS
BY
AMORPHOUS FILMS
AND
THE DIFFRACTION OF ELECTRONS
OF MEDIUM ENERGY.

BY

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EXPERIMENTAL.

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GENERAL INTRODUCTION.

The wave nature of a type of radiation is characterised by some regular periodic variation of the intensity at a point with respect to time. If the rate of this variation is too great to be observed directly, the wave nature of the radiation can be established by superimposing separate systems of waves, the phase difference of which varies for different directions. The amplitudes of the separate wave trains will then reinforce in some directions, and oppose in others; thus causing regular variations of the intensity of the scattered radiation for different directions.

Such interfering trains of waves may be obtained by allowing a single beam of radiation to fall on a slit, or on a regular array of scattering centres in the form of a diffraction grating.

In order to obtain the necessary phase difference the width of the slit, or the unit distance of the grating, must be greater than half the wave-length of the incident radiation; but it must also not be too great compared with the wave-length as the variations of intensity with angle will then be too rapid for interference effects to be observed.

Thus in the case of electromagnetic radiation, the wave nature of short wireless waves can be shown by means of a series of metal rods, with visible light, very thin slits or mechanically ruled gratings are necessary, whilst with X-rays and gamma rays, the regular array of atoms in crystals must be used in order to obtain such interference effects.

When the beams considered are sufficiently wide for diffraction phenomena to be neglected, the behaviour of wave radiation is closely analagous to that obtained with radiation of a corpuscular nature.

This similarity can be seen by a comparison of Fermat's principle in geometrical optics with the laws of motion of a particle as given by the principle of least action. Fermat's principle states that , for a ray travelling from a point P to a point Q, the path followed will be such that the time of transit will have a stationary value.

This can be expressed by

$$\delta \int_P^Q \frac{ds}{u} = 0$$

where ds is an element of path and u is the velocity of the light ray in the region of the element.

Similarily the Principle of Least Action gives as the condition for the path of a single particle travelling in a conservative field between two points

$$\delta \int_P^Q mu \; ds = 0$$

where m is the mass, and u the velocity of the particle.

This close analogy between geometrical optics and particle mechanics was first pointed out by Hamilton, but no attempts were then made to see whether under certain conditions, laws similar to those of physical optics might apply to the motion of particles.

At the beginning of the present century difficulties with regard to the energy distributed of black-body radiation, led Planck to postulate a quantised nature for electromagnetic waves. A similar assumption was shown by Einstein to explain the photo-electric effect~~s~~, the energy of a light quantum being taken as hv, where h is Planck's constant and ν is the frequency of the radiation. The corpuscular nature of electromagnetic radiation was however most conclusively shown in the Compton effect, where X-rays were shown to behave as particles in their interaction with electrons.

This corpuscular aspect of wave radiation led de Broglie to investigate the possibility of wave properties being associated with particles. De Broglie assumed the Einstein relation between energy and frequency to be fundamental, so that the space surrounding a particle of energy E would be pulsating with a frequency ν where $E = h\nu$.

The value of the wavelength, λ ,for a particle of mass m and velocity V is then given by

$$\lambda = \frac{h}{mv}$$

where v is small compared with the velocity of light.

Where v is large the relativity correction must be taken into account and

$$\lambda = \frac{h\sqrt{1-\frac{v^2}{c^2}}}{mv}$$

Substituting the value of h (6.5×10^{-27} erg sec.) in the equation, it can be seen that for macroscopic particles the wavelength will become far too small for observable diffraction effects to occur.

In the case of electrons, however, if their energy is equivalent to their having been accelerated from rest by a potential difference of P volts, the wavelength associated with them will be given by

$$\lambda = \sqrt{\frac{150}{P}}\ A$$

(Neglecting the relativity correction).
Thus if P be of the order of several hundred volts, this wavelength will be equal to that of fairly hard X-rays; therefore if de Broglie's theory is true, diffraction effects might be expected to occur when electrons of these or higher energies interact with crystals.

This was first suggested by Elsasser[2] in 1925 and experiments confirming this were carried out by Davisson and Germer in America[3], and independently by Thomson and Reid[4] in Great Britain in 1927.

Davisson and Germer used a homogeneous beam of slow electrons (65 - 600 volts) falling normally on a nickel single crystal; the intensity of the scattered beams being measured by means of a Faraday cylinder and a sensitive galvanometer. The results obtained showed that electrons had a wave nature, and using the values of the lattice constants of nickel as given by X-ray measurements, the value of the wavelength was found to be in rough agreement with that obtained from the de Broglie relation. The discrepancies which were found to occur have since been shown to be largely due to the inner potential of the crystal causing the emergent electron beams to be refracted.

In the work of Thomson and Reid a beam of fast electrons (up to 40KV) was passed through a film of celluloid, the transmitted electrons falling on a photographic plate. Circular diffraction haloes were obtained, and it was shown that the relation between the wavelength λ and the accelerating voltage of the electrons (P) was of the form given by de Broglie

i.e. $$\lambda \propto \sqrt{\frac{1}{P}}$$

Since however the structure of celluloid was unknown, the absolute value of the wavelength could not be checked.

The work of Thomson[5] with metal films, and subsequent work by others has since shown the de Broglie relation to be true within the limits of experimental error.

The most accurate verification was carried out by von Friesen[6] in 1935, who used the de Broglie relation to determine the value of the charge on the electron (e). Von Friesen used the values of the lattice constants of galena as given by X-ray measurements. These, however, depend on the value of Avogadro's number N, and hence upon e, so that the value obtained in this way did not give the charge on the electron explicitly.

Assuming the correctness of the X-ray value for the lattice constant, however, the de Broglie relation was shown to give the value of e within 0.1% of the value obtained by other methods.

The phenomena of the diffraction of electrons by crystals has since its discovery become of importance quite apart from the verification of the de Broglie relation by its application to problems of the atomic structure of thin films and of surface layers. Electrons of energies of between 30 and 60 KV. have been generally used, the patterns obtained being recorded photographically. With thin films the electron beam is allowed to pass through the specimen, whilst in the examination of surfaces the beam falls on the surface at grazing incidence, the pattern obtained being in the nature of a reflection from the surface.

The advantage of the use of electron diffraction in these problems, as compared with the use of X-rays, lies in the very much lower penetration of the electron beam and the far greater extent to which electrons are elastically scattered by matter. This low penetration of electrons results in diffraction effects being entirely due to the surface layers, whereas with X-rays any effects obtained from the surface will be almost completely masked by diffraction from the interior of the specimen.

A wide range of structure problems in connection with surfaces and thin films have been studied by this method.

The only serious limitations of the application of the method compared with that of X-ray crystallography lie in that the specimens must be examined in conditions of very high vacuum, which may result in some change in the surface conditions, and which also excludes the use of substances which have fairly high vapour presuures. In the case of some insulators, difficulty is often experienced due to the specimen becoming negatively charged thus causing complete distrortion in the path of the electron beam. This difficulty is mainly encountered in the reflection method, and is due to the uneveness of the surface; an increase in the angle of incidence of the electron beam will in many cases overcome this difficulty. Apart from these limitations precautions to prevent contamination common to all surface phenomena investigations must be taken.

Another type of investigation to which the diffraction of electrons may be applied is the examination of the atomic structure of substances in the gaseous and vapour states. The method depends on the theory originally developed by Debye[7] for the determination of the atomic arrangement of gas molecules from observations of the scattering of X-rays from polyatomic gases. The greater extent to which electrons are scattered by gases makes them eminently suitable for these investigations. The method has been successfully applied by Mark and Wierl[8] and more recently by several American workers.

In the present work two separate aspects of the diffraction of electrons are considered. The first of these is the application of the method to the determination of the structure and orientation of amorphous and microcrystalline films, where the minuteness of the diffracting units causes the normally sharp interference patterns observed with crystals to become diffuse.

The second part of the thesis deals with the behaviour of electrons of less than ten thousand volts energy when diffracted. The construction and use of a diffraction camera for these voltages is described and the results obtained are compared with those found at higher voltages, both for reflection from crystalline surfaces and for transmission through thin films.

PART 1.

THE DIFFRACTION OF ELECTRONS BY AMORPHOUS FILMS.

THE AMORPHOUS STATE.

As a result of the application of the method of X-ray diffraction to the determination of the atomic structure of matter, the term crystalline has been extended to apply to all substances which consist of regular three-dimensional atomic lattices, instead of only to substances with external geometrical symmetry.

In all forms of matter some degree of atomic arrangement must exist; for even in the case of a monatomic gas, the impossibility of interpenetration of the atom will prevent the distribution from assuming a completely random character. With polyatomic gases, there will be added the constant interatomic distances within the separate molecules as a result of the chemical bonds. With solids and liquids, the much closer packing of the molecules will cause an upper limit to be placed on the probable distance between the centres of neighbouring atoms in addition to the lower limit imposed by their finite cross sections. There will also be Van der Waals' attractive forces between the molecules which will contribute to the regularity of the arrangement by limiting the thermal motion of the constituent molecules.

The term amorphous, as used in the X ray sense, does not thus imply the complete lack of atomic arrangement but rather the absence of three-dimensional arrays which are sufficient in extent to produce sharp diffraction maxima.

The X ray patterns obtained with gases, liquids and amorphous solids, are generally found to be in the nature of one or more haloes corresponding to broad maxima in the intensity of the scattered radiation. In the case of diffraction by gases, the variations in the intensity can be completely interpreted, in terms of scattering due to individual atoms, and interference between waves scattered from atoms within the same molecule.

With liquids and amorphous solids, however, interference between waves scattered by atoms in different molecules will also occur, and no simple theoretical relation between the structure of the substance and the intensity of the scattered radiation has been derived.

The fact that liquids and amorphous solids give rise to halo diffraction patterns, was first shown by Debye and Scherrer[9]. They attempted to interpret these patterns in the same way as those due to polyatomic gases and ignored the additional intermolecular diffraction effects.

Keesom and De Smedt[10] showed, however, that monatomic amorphous substances, such as liquid argon, still give rise to diffraction haloes, and concluded from this that the diffraction effects were more likely to be due to intermolecular, rather than interatomic interference. They consequently treated the problem as diffraction by pairs of molecules, using the expression derived by Ehrenfest[11] for diffraction by electron pairs.

The unsatisfactory agreement that these simple treatments gave with experimental results, led Raman and Ramanathan[11] to try extending the theory of the diffraction of light by liquids to the case of X rays. They regarded the liquid as continuous with local flucuations which could be allowed for thermodynamically in the manner used by Einstein[12] and Smoluchowski[13] for the case of light. This treatment was found to be satisfactory for small scattering angles, but for larger angles the short wavelength of the X rays made it necessary to take the molecular discontinuities of the liquid into account. To do this Raman and Ramanathan applied the Bragg Law to the mean distance between neighbouring molecules. The value of this mean distance was found from the position of the principal diffraction halo by applying the Bragg Law.

The theory was tested against Hewlett's[14] experimental results for diffraction by liquid benzene, and fairly good agreement was obtained. The consideration of the problem as that of diffraction by a single, mean, intermolecular distance appears to be an over-simplification, and, as this distance was obtained from the principal maximum of the diffraction pattern, the treatment for large scattering angles must be regarded as little more than as an empirical extension of the diffraction of light by liquids to the case of X rays.

In a later paper, Raman[15] attempted to obtain the value for the mean distance between molecules by thermodynamic considerations. The expression he obtained involved a constant k, which according to the theory should be the same for all liquids but which actually involves the "packing factor" of the molecules, and may be expected to vary with different liquids.

Two later mathematical treatments of the problem are due to Zernicke and Prins[16] and Debye and Menke[17] the latter of which has subsequently been extended by Menke.[18] Both these theories employ the idea of a distribution function for the arrangement of the atoms in the liquid; but whilst Prins derives this function theoretically, treating the substance as a regularly packed arrangement of atoms, Debye uses the observed scattering curves to find the nature of the distribution function. Debye further divides the scattering into two parts, which he terms "outer" and "inner" interference. The former is a result of interference between waves scattered from separate molecules, whilst the latter is due to interference from atoms within the molecule itself. Thus the function is expressed as the sum of two terms, one of which represents the scattering which would occur, if the molecules were widely separated as they are in the gaseous state, and the other allows for interferences for atoms not in the same molecule. This second function is similar to that which would apply if the amorphous substance were monatomic. Menke[18], in considering the diffraction of X rays by liquid carbon tetrachloride, uses this theory, and employs the scattering curve observed for liquid mercury to obtain the second part of the expression. The agreement he obtained in this case with the experimental results was fairly good, but it would appear that a better knowledge of the forces which influence the packing in liquids and amorphous solids is necessary before these theories, which involve the determination of a distribution function, can be applied with any degree of exactness. Stewart[19] has considered the nature of this arrangement in a qualitative manner, and suggests that the forces which tend to cause crystallinity will still exist in a liquid state. They will, however, be counteracted by the thermal motion of the molecules. He therefore concludes that the existence of small crystalline groupings is probable; although the members of each group will be constantly changing as a result of thermal agitation. Stewart and Morrow[20] have termed this phenomenon "cybotaxis" and the corresponding state "cybotactic state".

The possibility of such groups occurring had been considered both by Prins and by Debye in deriving their distribution function, and the similarity between the patterns observed for some substances in the liquid and crystalline states seem to support the truth of this assumption.

In considering diffraction by solids, the occurrence of haloes may be attributed either to a truly random distribution of the molecules, or to the existence of crystals of such small dimensions that the poor resolution of the minute gratings would cause a broadening of the diffraction maxima.

Scherrer[21] and Von Laue[22] have derived expressions

For the breadth of diffraction rings produced by such microcrystals. Randall, Rooksby and Cooper[23] have applied this theory to several types of glass which also exist in a crystalline form. They derived scattering curves on the assumption that the structure was the same in the vitreous and crystalline states, but that the minute crystal size in the vitreous state resulted in the broad diffraction maxima. Although this treatment gave fair agreement with the observed scattering curves, Warren has shown that in the case of vitreous silica much closer agreement could be obtained by regarding the substance as amorphous and applying a modified form of the Prins formula. Warren assumed a tetrahedral packing for the silica; eahc silicon atom being at the centre of a tetrahedron with an oxygen atom at each of the four corners. Each oxygen atom is thus shared by two tetrahedral groups, the whole arrangement being in the form of a random network; the SiO_4 groups being the largest fixed elements. The very good agreement that this method has given with the experimental results in the two cases where it has been applied, namely, vitreous silica and vitreous germanium oxide, appears to indicate that the vitreous state can be more accurately described as amorphous than as microcrystalline.

Diffraction by Long-Chain Polymers.

The extent of the atomic arrangement within the individual molecules of most inorganic chemical substances is insufficient to produce sharp diffraction maxima. Some polymerised organic compounds, however, are found to be of extremely high molecular weight, and Staudinger[25] has on chemical grounds assigned a long-chain formation to the molecules of these substances; each molecule consisting of a large number of similar repeating units.

If the chains are straight, each will act as a line diffraction grating, and if the molecules are orientated in one direction, sharp intensity maxima corresponding to the various diffraction orders would be expected to be found. The sharpness of these maxima will depend on the degree of orientation of the molecules as well as on the length of the individual chains.

The diffraction patterns of some natural fibres and some stretched elastic substances show such interference maxima. In addition to these, however, spots of varying degrees of diffuseness are also often found in other directions, which show the regularity in the structure to be three-dimensional. It would thus appear that the molecules in addition to being arranged in parallel chains also fit each other laterally and these lateral arrangements are sufficient in extent to produce diffraction maxima of the observed degree of sharpness.

It is rather in doubt whether when very sharp maxima occur in these "fibre patterns", a truly crystalline character may be assigned to the substance.

Katz[26] has shown that in the case of stretched natural rubber, a definite discontinuity in optical and other physical properties, accompanies the appearance of what he terms "crystalline" interferences, i.e. interferences in directions other than that of stretching. He takes this as an indication of a definite physical change having occurred as a result of stretching and claims that rubber stretched beyond this critical limit should be regarded as crystalline in nature.

The question would appear to be partly one of definition, but the fact that the interferences observed are rarely as sharp as those found with true crystals, and that the crystal size is fixed by the chain length of the constituent molecules, would seem to indicate that the arrangement although it is three-dimensional should be distinguished from that existing in crystals the size of which does not depend on their molecular structure in this way.

The diffraction patterns obtained from these long-chain polymerised compounds when the molecules are isotropically arranged, consist of haloes similar to those found with liquids and with other types of amorphous solids. The difficulty of interpretation of these patterns is generally increased by the absence of information as to the manner in which the macro-molecules are likely to be packed.

The positions of the sharp interferences obtained on stretching are often found to lie just inside the positions of the diffraction haloes found in the unstretched state. Megson and Wood[27] have also recently shown that the polymeristaion of a crystalline phenolic alcohol (2-hydroxymethyl-4-methylphenol) gives a halo diffraction pattern with the position of the haloes corresponding to that of the most intense rings in the original polycrystalline ring pattern. It would thus appear that the application of the Bragg law to the positions of haloes observed in amorphous substances may give approximate values for the interatomic spacings. It should however be noticed that when the maxima of the intensity curve are broad, as they are in these halo patterns, the superposition of several maxima corresponding to different spacing will give rise to a resultant intensity curve, the positions of the maxima of which have no direct significance. The molecules will also generally be orientated in all directions, so that the mean value for the effective spacing will be smaller than that for molecules perpendicular to the direction of the beam. In order to partly overcome this latter difficulty, Katz[28] has suggested that the Debye-Ehrenfest formula for a randomly orientated single spacing should be used in preference to the Bragg law.

Application of Electron Diffraction.

The ease with which thin films of celluloid and cellulose derivatives may be prepared, led several workers to apply the method of electron diffraction soon after its discovery to a study of these films.

They found patterns similar to those obtained by X-ray methods, namely, several diffuse haloes, but superimposed on these sharp crystalline patterns were often found to occur either in the form of sharp rings or of spots similar to those found with cross gratings. This apparent crystallisation was observed by Dauvillier[29], Kirchner[30], Taylor-Jones[31] and Trillat[32] and it was assumed that the substances although amorphous in bulk crystallised more readily when in the form of thin films. The fact that these films gave sharp patterns more often when they had been left standing was taken as further evidence of a slow structural change within the films.

Difficulty was experienced, however, in obtaining these sharp patterns consistently and the patterns when obtained did not appear to correspond to the structure of the compound as found by X-rays. Mark, Motz and Trillat[33] and Natta ~~Nutter~~[34] have shown that these patterns, which were found to be similar for a large number of compounds, were actually due to contamination of the specimens by very thin layers of long-chain paraffins with the molecules orientated perpendicular to the film surface. This contamination could be removed by careful washing of the specimen with grease-free ether, and could also be volatilised by allowing an intense electron beam to fall on the specimen for several minutes; the crystalline pattern would then disappear leaving a halo pattern due to the film which remained intact.

Thomson[35] has shown that similar "grease" patterns occurred as a result of contamination of metal films, the long-chain paraffins being also, in this case, orientated perpendicular to the surface.

The source of the contamination has not yet been definitely established and does not appear to depend on the type of vacuum grease or cement used in the diffraction camera. It would appear that the contamination takes place during the preparation of the specimen and the reason why it is nearly always in the form of a long-chain hydrocarbon has been explained as a result of the ease with which these compounds spread on cellulosic surfaces.

As a result of the difficulty found by X-ray workers in the interpretation of patterns obtained from amorphous substances, very little attention has been paid to the study of amorphous films or those of a fibrous nature by the method of electron diffraction.

Rubber films have, however, been examined, both in the stretched and unstretched condition, by Bresler, Strauff and Zelmanoff[36], Natta and Bruni[37], Trillat and Motz[38], and Krylow[39]. Some earlier work of Natta[40] also deals with several other amorphous polymers, but the sharp patterns observed would appear to be due to contamination by grease. Natta and Baccaredda[41] have more recently obtained patterns from cellulose deposited from a cupro-ammoniacal solution, which appear to show sharper rings than those observed in the normal halo pattern, and which they find to be in good agreement with the X-ray results.

The application of electron diffraction to the determination of the structure of amorphous and fibrous substances must be regarded as complementary to the X-ray investigation, the method, however, has advantages in certain respects as compared to that of X-rays. From the experimental point of view the greate~~st~~r scattering found with electrons and the great sensitivity of photographic plates to fast electron beams, makes the recording of the weak patterns observed with amorphous diffraction much more rapid, and also extremely small quantities of substance may be used. From the theoretical aspect, investigations with films of polymers, the thickness of which is less than the chain length of the molecules should give information as to their orientation. In experiments on stretched rubber, Katz[42] has found in X-ray investigations ~~on~~ that thin films give rise to sharper fibre patterns than the thicker ones which generally have to be used in X-ray work, and the application of electron diffraction to problems of this nature should ~~be~~ prove advantageous.

THEORETICAL.

The work of Debye[7] and Ehrenfest[11] on the scattering of X rays by randomly orientated electron groups, has been the basis for most of the subsequent mathematical treatment of diffraction by amorphous substances.

Debye extended the theory to the diffraction of X rays by gas molecules, and in a later paper[17a] considered diffraction by liquids and amorphous solids. The treatment which follows is based on Debye's theory; the case in which the orientation of the molecules is restricted is then considered.

Diffraction by a system of atoms.

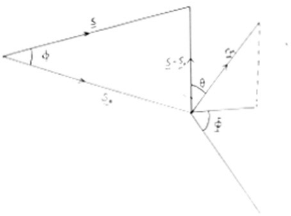
In Fig.1 SO is the direction of a beam of monochromatic radiation of wavelength λ, incident on a system of atoms situated at points P,Q, etc. The radiation may consist either of X rays or of a homogeneous beam of fast electrons, the value of λ is then given by the de Broglie relation.

The radiation will be scattered by the atoms and OS' is the direction of scattering considered; OS' makes an acute angle ϕ with ~~in~~ the direction SO. Unit vectors along SO and OS' are denoted by $\underline{S_0}$ and $\underline{S}$, and the vectors $\underline{OP}$, $\underline{OQ}$, etc. are denoted by $\underline{r_P}$, $\underline{r_Q}$, etc.

The path difference between a wave scattered at O in the direction OS' and the wave scattered at P in a parallel direction, is then given by the scalar product $\underline{r_P} \cdot (\underline{S_0} - \underline{S})$

If the phase at O is taken to be zero, the complex expression for the resultant amplitude of the radiation scattered by

Fig. 1(a).



$\underline{s}$
ϕ
$\underline{s}-\underline{s}_0$
$\underline{s}_0$
θ
$\underline{r}_n$
Φ

Fig. 1(b).

the system of atoms is given at a large distance R by

$$\frac{1}{R} \sum_{p} E_p \, e^{i \frac{2\pi}{\lambda} \underline{r_p} \cdot (\underline{S} - \underline{S_0})} \qquad (1)$$

where E is the atomic scattering factor in the direction of scattering considered and depends on the type of atom and on the nature of the incident radiation.

The intensity I' of the scattered radiation is equal to the square of the modulus of the expression for the amplitude. This is obtained by multiplying (1) by its complex conjugate, so that

$$I' = \frac{1}{R} \sum_{p} E_p \, e^{i \frac{2\pi}{\lambda} \underline{r_p} \cdot (\underline{S} - \underline{S_0})} \times \frac{1}{R} \sum E_p \, e^{-i \frac{2\pi}{\lambda} \underline{r_p} \cdot (\underline{S} - \underline{S_0})}$$

which can be written as a double summation

$$I' = \frac{1}{R^2} \sum_{p} \sum_{q} E_p E_q \, e^{i \frac{2\pi}{\lambda} (\underline{r_p} - \underline{r_q}) \cdot (\underline{S} - \underline{S_0})} \qquad (2)$$

This is a quite general expression for the value of the intensity of the radiation which is coherently scattered by any system of atoms. The expression involves only the differences between the position vectors of the separate atoms and is therefore independent of the choice of origin.

To find the value of the intensity for any known distribution of atoms expression (2) must be integrated for all values and orientations of the interatomic spacings.

Diffraction by gases.

The simplest case is that of a gas where interference between waves scattered by the separate molecules may be neglected.

Expression (2) may then be used for the intemsity due to each individual molecule; the value of the total intensity is obtained by integrating for all orientations of the molecules.

If θ is the angle between a vector of the type $(r_P - r_Q)$ which can be denoted by r_{PQ}, and the vector $(S - S_0)$, the scalar product $r_{PQ} \cdot (S - S_0)$ is equal to

$$r_{PQ} \times 2 \sin\frac{\Phi}{2} \lambda \cos\theta \qquad (3)$$

In order to integrate expression (2) for all orientations, P and Q are taken as a typical atom pair in the double summation. The direction of $(S - S_0)$ is taken as axis and θ and Φ as the polar co-ordinates ~~with~~ for the direction PQ (see Fig.1b).

The number of molecules for which the co-ordinates of PQ lie between θ and $\theta + d\theta$, and Φ and $\Phi + d\Phi$, is given by $N/4\pi \sin\theta \; d\theta \; d\Phi$ where N is the total number of molecules.

Taking the real part of the expression for the intensity as given by (2) and substituting for the value of $[(r_P - r_Q) \cdot (S - S_0)]$ from (3) the total intensity I is given by

$$I = \frac{N}{4\pi R^2} \int_0^{\pi}\int_0^{2\pi} \sum_P \sum_Q E_P E_Q \cos\left(\frac{4\pi r_{PQ} \sin\frac{\Phi}{2}}{\lambda} \cos\theta\right) \sin\theta \, d\theta \, d\Phi \qquad (4)$$

The integration with respect to Φ multiplies the expression by the constant 2π, and the integration with respect to θ gives

$$I \propto \left[\sum_P \sum_Q E_P E_Q \sin x_{PQ} \cos\theta / x_{PQ} \right]_{\theta=0}^{\theta=\pi}$$

$$= E_P E_Q \sin x_{PQ} / x_{PQ} \qquad (5)$$

where $x = 4\pi r_{PQ} \sin\frac{\Phi}{2} / \lambda$

This expression gives the intensity of the scattered radiation as the sum of a series of terms corresponding to the scattering for the individual atoms (i.e. when P = Q), together with terms corresponding to each of the interatomic distances within the molecule.

The simplest case is that of a diatomic gas, each molecule consisting of two similar atoms distance d apart, then

$$I \propto E_1^2\left(1 + \frac{\sin\left(\frac{4\pi d}{\lambda}\sin\frac{\phi}{2}\right)}{\frac{4\pi d}{\lambda}\sin\frac{\phi}{2}}\right) \qquad (6)$$

where E_1 is the scattering factor for each of the atoms.

In the case of X rays allowance should be made for the fact that the incident beam is unpolarised; the effect of the correction is negligible however for small angles of scattering. In the case of the diffraction of fast electrons the angles of scattering considered are even smaller as a result of the shorter wavelength, and there is in any case no experimental evidence to show the existence of polarisation although Darwin[43] and Mott[44] have shown on theoretical grounds that the effect should occur.

Debye's theory for liquids and amorphous solids.

In deriving the theory for the diffraction of X rays by liquids and amorphous solids, Debye[17a] treats the molecules as separate scattering units; the contribution to the ~~in~~ intensity of a molecule pair being given by

$$E_1^2 \exp\left(i\, k\, \underline{r}\cdot\underline{s}\right)$$

where E is the scattering factor for each individual molecule

$K = 2\pi/\lambda$, $\underline{r}$ is the vector joining two molecules and $\mathbf{s}$ is $(\underline{S} - \underline{S}_0)$. The expression is integrated for all orientations, and for values of r from the nearest distance of approach of the molecules to infinity.

The final expression obtained for the intensity I is

$$I = NE^2/R^2 \left[1 - \Omega/V \, \phi(k,s,a) \right] \quad \ldots\ldots\ldots\ldots\ldots \quad (7)$$

where Ω is the effective volume of the molecule,

V is the volume they occupy,

a the molecular diameter where the molecules are considered spherical

$s = 2 \sin \phi/2$

and $\phi(k,s,a)$ is a function depending onthe manner in which the molecules are arranged and for the case of randomly orientated spheres

$$\phi(x) = \frac{3}{x^3} (\sin x - \cos x)$$

E^2 is the value of the intensity due to the "inner" diffraction and is given by expression (5) for the substance in the gaseous state.

If the substance is monatomic E will be the atomic scattering factor. Debye considers in detail the case of a diatomic substance and shows that the second term involving Ω is unimportant beyond the first maximum so that the scattering curve then approximates to that found for a gas.

The effect of thermal motion has been shown by James to be negligible in the case of gases. For liquids and amorphous solids, however, a broadening of the diffraction haloes is found to occur but no exact theory has been derived to allow for the effect.

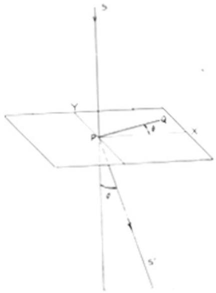


Fig.2.

Diffraction by molecules orientated in a plane.

The expression for the intensity contribution of each molecule when the molecules are orientted parallel to a plane is given as before by expression (2). In order to integrate for all orientations in the plane the scalar product $\underline{r}_{pq}(\underline{S} - \underline{S}_0)$ must be evaluated in terms of the angle $\underline{r}_{pq}$ makes with some fixed direction in the plane.

The case where the incident beam is normal to the plane of orientation of the molecules is first considered. In Fig.2 SP is a direction of the incident beam, and PS' the direction of scattering considered, makes an angle ϕ with SP. PX is the intersection of the plane SPS' with the plane of orientation of the molecules; PY is the line perpendicular to both PS and PX. PQ makes an angle θ with PX.

Taking PX, PY, and PS, as axes, the direction cosines of PQ are $\cos\theta$, $\sin\theta$, and 0, and those for the direction of $S - S_0$ are $\cos\frac{\phi}{2}$, 0 and $\sin\frac{\phi}{2}$, the cosine of the angle between $\underline{r}_{pq}$ and $\underline{S} - \underline{S}_0$ is thus given by $\cos\theta\cos\frac{\phi}{2}$ so that

$$r_{pq}\cdot(S - S_0) = r_{pq}\, 2\sin\frac{\phi}{2}\cos\frac{\phi}{2}\cos\theta$$
$$= r_{pq}\sin\phi\cos\theta$$

The real value of the expression for the intensity due to each molecule then becomes

$$\sum_p\sum_q E_p E_q \cos\left(\frac{2\pi}{\lambda} r_{pq}\sin\phi\cos\theta\right)$$

This must be integrated for all values of θ ; the number of molecules between θ and $\theta + d\theta$ being proportional to $d\theta$

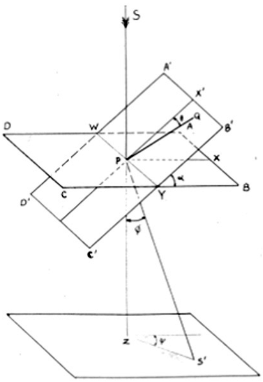


Fig.3.

so that the expression for the total intensity I is given by

$$I \propto \int_0^{\pi} \sum_P \sum_Q E_P E_Q \cos(x' \cos\theta)\, d\theta$$

where $x' = (2\pi r_{PQ} \sin\phi)/\lambda$

therefore $I \propto \sum_P \sum_Q E_P E_Q J_0(x')$ (8)

where $J_0(x)$ denotes a Bessel function of zero order.

Plane inclined to direction of incident beam.

When the incident beam does not fall normally onto the plane of orientation of the molecules, the intensity will not be radially symmetrical. In deriving expressions for the scalar product $\underline{r}_{PQ} \cdot (\underline{S} - \underline{S}_0)$ in terms of the angle of inclination of the ~~film~~ plane to the incident beam and the orientation of PQ in the plane, considerable simplification is achieved if the scattering angle ϕ is taken to be small so that $\cos\phi \doteqdot 1$ and $\sin\phi \doteqdot \phi$.

In the diffraction of fast electrons by thin amorphous films, to which the theory is applied, the approximation will be valid as the angle of scattering considered are never more than a few degrees.

In Fig.3 A'B'C'D' represents the plane in which the molecules are orientated, SP is the direction of the beam incident on P, and PS' is the direction of the beam scattered at an angle ϕ. WY is the line of intersection of A'B'C'D' with a plane ABCD, which is normal to SP, the two planes making an angle α with each other. The plane through P normal to WY cuts AB in X, A'B' in X' and makes an angle ψ with a plane SPS'. SP is produced to Z.

To evaluate $\underline{r}_{PQ}(\underline{S} - \underline{S}_0)$ PX, PY and PZ are taken as axes ;

The scalar products $r_{\rho Q}.S$ and $r_{\rho Q}\cdot S_0$ are then considered separately. The direction cosines of $r_{\rho Q}$ with respect to the axes chosen are

$\cos\theta\cos\alpha$, $\sin\theta$, and $\cos\theta\sin\alpha$,

Those of S_0 are 0,0, and 1 and those of S are $\sin\phi\,\chi$ $\cos\psi$, $\sin\phi\sin\psi$, and $\cos\phi$. Taking $\cos\phi = 1$ and $\sin\phi = \phi$, $r_{\rho Q}(S - S_0) = r_{\rho Q}\phi\,[\cos\alpha\cos\psi\cos\theta + \sin\psi \sin\theta] = r_{\rho Q}\phi[A\cos\theta + B\sin\theta]$

where $A = \cos\alpha\cos\psi$ and $B = \sin\psi$

$r_{\rho Q}\cdot(S - S_0) = r_{\rho Q}\phi\, C\cos(\theta + \epsilon)$

where $C^2 = A^2 + B^2$

and $\tan\epsilon = B/A$.

The intergration for all molecules in the plane with respect to θ gives an expression similar to (6): the total intensity I is given by

$$I \propto \int_0^{2\pi} \sum_\rho \sum_Q E_\rho E_Q \cos(x'' \cos(\theta+\epsilon))\, d\theta$$

where $x''_{\rho Q} = 2\pi/\lambda \; r_{\rho Q}\; \phi\; C$.

Integrating this gives

$$I \propto \sum_\rho \sum_Q E_\rho E_Q J_0(x''_{\rho Q}) \qquad (10)$$

In the direction of scattering for which $\psi = 0$, $A = 0$ and $B = 1$ so that $C = 1$. Therefore $x''_{\rho Q} = 2\pi/\lambda\,\phi\, r_{\rho Q} = x'_{\rho Q}$ of equation (6); the scattered radiation in this direction is thus independent of α the inclination of the plane to the beam.

The intensity is a function of the azimuthal angle ψ as well as of ϕ, so that the curves of constant intensity will not be circles as they are when the plane

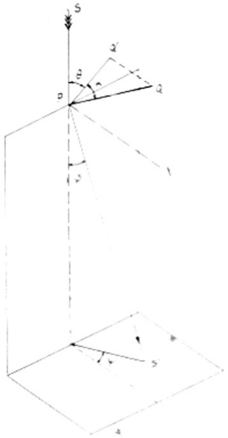


Fig.4

is normal to the incident beam. To find the nature of these curves the variations of the atomic scattering factors with angle must be taken into account. The positions of the maxima will not be appreciably affected however by the atomic scattering factors, and the haloes obtained from a single spacing will therefore lie on curves for which x''_{PQ} is constant.

$$x''_{PQ} = 2\pi/\lambda \; r_{PQ} \; C$$

But $\phi^2 C^2 = (A^2 + B^2) = (\cos^2\alpha\cos^2\psi + \sin^2\psi)$

Putting $\phi\cos\psi = x$ and $\phi\sin\psi = y$

$$x^2\cos\alpha + y^2 = \text{constant.}$$

so that for small values of ϕ the haloes will be in the form of ellipses of axis ratio $\cos\alpha$.

Molecules making fixed angle with plane.

The case in which the spacings make a fixed angle with a plane, the plane being placed parallel to the direction of the incident beam, is now considered. Only the contribution of a single spacing PQ is derived, the expression may be extended to cover any number of spacings by forming a double summation.

As in the other cases it is first necessary to obtain the value of $\underline{r}_{PQ}\cdot(\underline{S} - \underline{S}_0)$ in terms of the angles PQ makes with certain fixed directions.

In Fig.4, SP and PS' are the directions of the incident and scattered radiation, PX is perpendicular to the plane with which PQ makes a constant angle , PY is in this plane and perpendicular to PS and PX. The projection of PQ on the plane makes an angle θ with PS and the plane SPS' makes an angle ψ with the SPX plane. The direction cosines of $r_{\rho Q}$ with respect to PX, PY and PS are

$$\sin\alpha \ , \cos\alpha \ \sin\theta \ \text{ and } \cos\alpha\cos\theta \, .$$

Those of S are

$$\sin\phi\cos\psi \, , \sin\phi\sin\psi \ \text{ and } \cos\phi \, .$$

Those of S_0 are

$$0 \, , 0 \ \text{ and } 1.$$

Taking $\sin\phi = \phi$ and $\cos\phi = 1$

$$r_{\rho Q}\cdot(S - S_0) = r_{\rho Q}\,\phi[\sin\alpha\cos\psi + \sin\psi\cos\alpha\sin\theta]$$
$$= r_{\rho Q}\,\phi\,(A + B\sin\theta)$$

where $A = \sin\alpha\cos\psi$

and $B = \cos\alpha\sin\psi$

The intensity I' due to a single spacing is therefore given by

$$I' = E_\rho E_Q \cos 2\pi/_\lambda \, [A + B\sin\theta]$$

This must be integrated for all values of θ ; taking as limits $-\pi$ to $+\pi$, the total intensity I is given by

$$I \propto \int_{-\pi}^{+\pi} E_\rho E_Q \cos[R\sin\theta + S]\,d\theta$$

where $R = \overset{2\pi r_{\rho Q}}{\cancel{2\pi}}/_\lambda \times (\phi \overset{B}{\cancel{A}})$ $\qquad S = \overset{2\pi r_{\rho Q}}{\cancel{2\pi}}/_\lambda \times (\phi \overset{A}{\cancel{B}})$

$$\therefore I \propto \int_{-\pi}^{+\pi} E_\rho E_Q \cos(R\sin\theta)\cos S\,d\theta$$
$$+ \int_{-\pi}^{+\pi} E_\rho E_Q \sin(R\sin\theta)\sin S\,d\theta$$

The second integral is equal to zero, as the separate integrals from $-\pi$ to 0 and from 0 to $+\pi$ are of equal magnitude but of opposite sign. The expression for the total intensity thus becomes

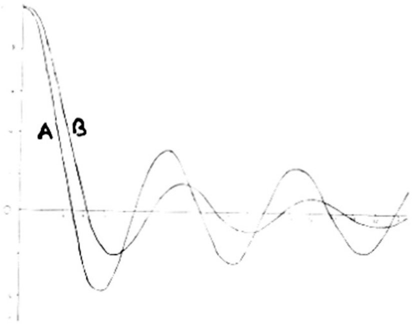


Fig.5.

Curve ~~A~~ B. $y = \sin x/x$.

Curve ~~B~~ A. $y = J_0(x)$.

$$I \alpha E_p E_Q J_0 (R) \quad \cos S$$

On a plane normal to the incident beam, at distance L from the scattering points, the co-ordinates X and Y of a point corresponding to scattering angles ϕ and ψ is given by $L \phi \cos \psi$ and $L \phi \sin \psi$, where ϕ is taken to be small.

The intensity due to two similar atoms is therefore proportional to

where $K = \frac{2\pi}{\lambda}$

$$E^2 (1 + J(K r_q X \cos\alpha / L) \quad \cos(Y K r_{pq} \sin\alpha / L) \qquad (12)$$

so that the intensity distribution along the Y direction is proportional to

$$E^2 (1 + J (K r_{pq} X \cos \alpha / L)$$

and along the X direction to

$$E^2 (1 + \cos (K r_{pq} Y \sin \alpha / L))$$

For a series of spacings the total intensity will be given by

$$E_p E_Q J_0 (R) \quad \cos S \qquad (13)$$

Note on Bessel functions.

A Bessel function may be defined as a particular solution of the differential equation

$$\frac{d^2 y}{dx^2} + \frac{1}{x} \frac{dy}{dx} + \left(1 - \frac{n^2}{x^2}\right) y = 0$$

which is regular at the origin. The order of the function is given by n, and the function is denoted by $J_n (x)$.

The definite integral $\int_0^{2\pi} \cos (x \cos \theta)\, d\theta$, is found on substituting, to satisfy the equation for n = 0, and as it is regular at the origin, it is proportional to $J_0 (x)$ the Bessel function of zero order.

$J_0 (x)$ may be expressed as the infinite series

$$J_0(x) = 1 - \frac{x^2}{2^2 1!^2} + \frac{x^4}{2^4 2!^2} - \frac{x^6}{2^6 3!^2} +$$

For fairly large values of x, $J_0(x)$ asymptotically approaches $\frac{\sin(x+\frac{\pi}{4})}{\sqrt{\frac{\pi x}{2}}}$ and this approximation is quite close for values of x beyond the first maximum of the function.

Fig.4 shows the curve of sin x / x and $J_0(x)$ plotted against x; the values of $J_0(x)$ were obtained from the British Association Tables VI, Part I.

It can be seen that $J_0(x)$ is damped more slowly than sin x/x and that the curves are separated by a phase difference of $\pi/4$ as would be expected from the approximate expression for $J_0(x)$. The slower damping of $J_0(x)$ indicates that the higher orders of diffraction will be more pronounced when the distribution is confined to a plane, than when it is random in three dimensions.

The value of x in the two cases is not quite identical, since in the Debye expression (5) x_{pq} is given by $\left(4\pi r_{pq} \sin\frac{\phi}{2}\right)/\lambda$ and in expression (7) for orientation in a plane x'_{pq} is given by $\left(2\pi r_{pq} \sin\phi\right)/\lambda$; for small values of ϕ however, the difference is of the second order.

<u>Atomic Scattering Factors</u>.

The scattering of X rays by atoms is caused largely by the outer orbital electrons, whilst electrons are scattered principally by the nucleus.

The expression for the amplitude A_X of X rays scattered through an angle θ by a single atom a distance R away is given by

$$A_x = \frac{1}{R} \frac{e^2}{m^2 c^2} f(\theta)$$

and the amplitude A_E in the case of electrons of velocity v is given by

$$A_E = \frac{1}{R} \frac{e^2 m \left(Z - f(\theta)\right)}{\left(\frac{\sin\theta}{\lambda}\right)^2}$$

$$= \frac{1}{R} \frac{e^2 m \left(Z - f(\theta)\right)}{2h^2 \left(\frac{\sin\theta}{\lambda}\right)^2}$$

from the De Broglie relation.

where Z is the atomic number and f (θ) is in both cases equal to the ratio of the amplitude of X rays scattered by a single atom to that scattered by an electron.

The expression for f(θ) is

$$\int_0^\infty U(r) \frac{\sin\left(\frac{4\pi r \sin\theta}{\lambda}\right)}{\frac{4\pi r \sin\theta}{\lambda}} dr$$

where $U(r)$ is the probability of an electron being at a radial distance between r and r + dr from the centre of the atom. It can be seen that this expression is the integral of an expression similar to (1) for the resultant amplitude due to scattering by a series of points. The centre of the atom is taken as origin and the integration is for all values of r.

When θ is very small

$f(\theta) = \int_0^\infty U(r)\, d(r)$ = Z the total number of electrons.

For scattering ~~by~~ of electrons at small angles $Z - f(\theta)$ tends to zero, $\sin^2(\theta)$ tends to zero too however and the ratio is found to approach a constsnt value.

$f(\theta)$ has been calculated[46] from statistical considerations of the electron distribution by the method of Thomas and Fermi; for light atoms the distribution can be more accurately determined by the Hartree method of self consistent fields.

Evaluating the constants, the expressions for the amplitudes are in the two cases given by

$$A_x = 1/R\ 2.82 \times 10^{-13} f(\theta)$$

and $$A_\epsilon = 1/R\ 2.38 \times 10^{-10} \left(Z - f(\theta)\right) / (\sin\theta/\lambda)^2$$

where λ is in cms.

The atomic scattering factors E E etc. used in a previous work will be given by $A_x R$ and $A_\epsilon R$ in the above expressions.

Structure Factor.

If radiation of wavelength λ falls on a regular three dimensional grating and unit distances along the three grating directions which are taken as axes, are a, b, and c, the conditions for a diffracted beam are

$$\underline{a} \cdot (\underline{S} - \underline{S}_0) = a(\cos\alpha_1 - \cos\alpha_2) = h\lambda$$

$$\underline{b} \cdot (\underline{S} - \underline{S}_0) = b(\cos\beta_1 - \cos\beta_2) = k\lambda$$

$$\underline{c} \cdot (\underline{S} - \underline{S}_0) = c(\cos\gamma_1 - \cos\gamma_1) = l\lambda$$

where α_1, β_1, and γ_1 are the angles the incident beam makes with the axes and α_2, β_2, and γ_2 are the angles for the diffracted beam; h, k, and l must be integers and are known as the Laue numbers of the diffraction.

If the unit cell in the grating contains more than one atom the intensity of the diffracted radiation will depend on the arrangement of the atoms in the unit cell as well as on the individual atomic scattering factor.

The amplitude of the wave scattered by a series of points P,Q, etc., when the atom P has co-ordinates x , y , and z , with respect to the axes, will be given by expression (1) i.e.

$$\sum_{p} E_p \, e^{i \frac{2\pi}{\lambda} \underline{r_p} \cdot (\underline{s} - \underline{s_0})}$$

It can be seen that

$$\underline{r_p} \cdot (\underline{s} - \underline{s_0}) = \frac{h}{a} x_p + \frac{k}{b} y_p + \frac{l}{c} z_p$$

so that the intensity which is the square of the modulus ofthe expression for the amplitude will be given by

$$\sum E_p \cos 2\pi \left(\frac{h x_p}{a} + \frac{k y_p}{b} + \frac{l z_p}{c} \right)^2$$

$$+ \sum E_p \sin 2\pi \left(\frac{h x_p}{a} + \frac{k y_p}{b} + \frac{l z_p}{c} \right)^2$$

Breadth of Diffraction Rings.

The breadth of the rings obtained from polycrystalline specimens where the size of the individual crystals is very small has been evaluated by Scherrer[21]. The formula he derives is

$$B = \frac{k\lambda}{D \cos\theta} + b$$

where B is the angular breadth between the points where the intensity falls to half its maximum value, θ is the Bragg angle which is half the angle of scattering; d is the mean length of the edges and b is a constant depending on the breadth of the original beam, k is a constant which Scherrer evaluates to be 0.94. This formula holds for crystals which are similar in size and shape and belong to the cubic system. Brill[47] has derived an identical expression for the diffraction of electrons by microcrystals.

Von Laue has extended the theory to other crystal systems but as in Scherrer's theory the crystals are assumed to be completely non-absorbent and also to be parallelepipeds of similar shape and size. In addition to the theoretical difficulties it is experimentally necessary to have a completely monochromatic beam of parallel radiation and to ensure this, it is best in practice to first determine the width of ring for large crystals of the substance.

The resolution as observed on a plate placed perpendicular to the incident beam at distance L away, is measured by $\delta R/R$, where R is the radius of the ring and δR is its width.

$$R = L \tan 2\theta$$

$$\delta R = L \sec^2 2\theta$$

is the angular breadth B, and substituting from Scherrer's relation ( ) neglecting b,

$$\delta R = L \sec^2 2\theta \frac{K\lambda}{D \cos\theta}$$

$$\therefore \quad \frac{\delta R}{R} = \frac{K\lambda}{D} \frac{1}{\cos 2\theta \, \sin 2\theta \, \cos\theta}$$

$$\therefore \quad \frac{\delta R}{R} = \frac{K\lambda}{D} \frac{1}{2\sin\theta\,(1-\sin^2\theta)(1-2\sin^2\theta)}$$

From the Bragg relation the ring for a spacing b is given by

$$\lambda = 2d\sin\theta$$

$$\therefore \quad \frac{\delta R}{R} = \frac{kd}{D} \frac{1}{1-\left(\frac{\lambda}{2d}\right)^2} \times \frac{1}{1-2\left(\frac{\lambda}{2d}\right)^2}$$

The expression shows that for values of d which are large compared with λ , the resolution will not be appreciably affected by the value of λ , for small spacings however better resolution should be obtained with decreasing and hence theelectron diffraction patterns should be sharper than those found with X rays.

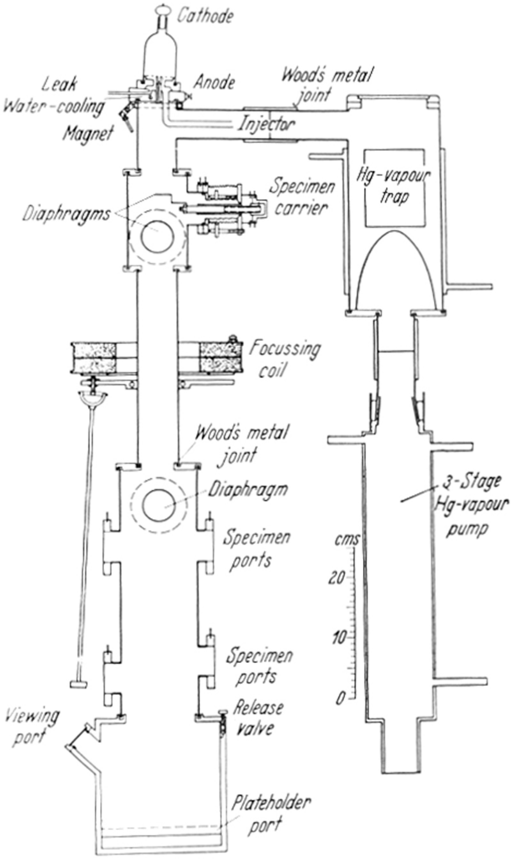


Fig.6. Finch Electron Diffraction Camera.

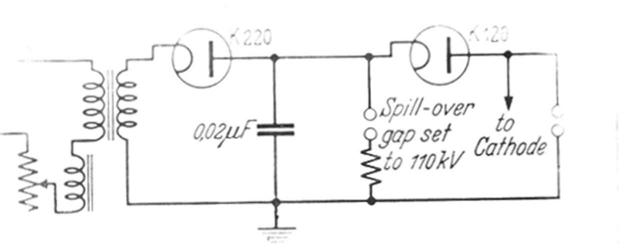


Fig.7. High Tension Supply.

EXPERIMENTAL.

Diffraction Camera.

The electron diffraction camera (Fig.6) used in conjunction with the high tension supply (Fig.7) were both of the type described by Finch and Quarrell[48]. A specimen carrier was fitted with a circular scale which enabled the angle the plane of the specimen made with the direction of the incident beam to be measured.

The accelerating voltages employed were between 45kV. and 60kV., and the patterns were recorded on Ilford Special Rapid quarter plates (H and D 270). The exposures given varied from a few seconds in the case of the intense crystalline patterns to about two minutes for the much fainter halo patterns.

Preparation of Specimens.

Thin films of amorphous organic substances were prepared by allowing a drop of a dilute solution of the substance to spread on a water surface. The solvent evaporated, leaving a thin film of the substance floating on the surface of the water, and a portion of this was removed on a piece of close-mesh nickel gauze.

The water was contained in a tank of the type described by Langmuir and Blodgett[49]. The use of this tank enabled the water surface to be cleaned by sweeping it several times with flat chromium plated metal rods; these rested on the sides of the tank and could slide along just in contact with the surface of the water.

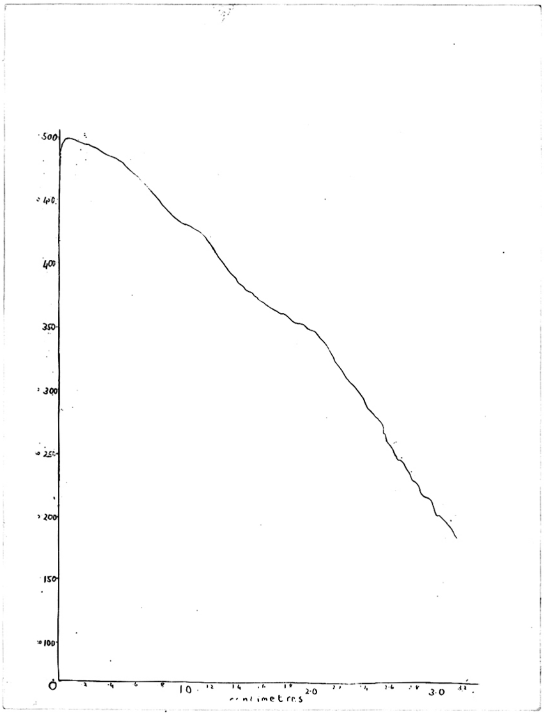


Fig.8. Microphotometer record of Polystyrene pattern.

To avoid contamination of the specimens, solvents of a high degree of purity were employed, and wherever possible separate specimens were prepared from solutions of the substance in different solvents. This was done to ensure that the nature of the solvent used did not in any way affect the structure of the films.

Where it was required to stretch the specimens, this was done in the tank. Two chromium plated bars were allowed to rest on the tank in contact with the floating film; the film adhered to the ba~~th~~rs, which were then separated to stretch the film to the desired extent. A portion of the film was removed on nickel gauze to which it adhered, remaining in the stretched state.

Measurement of Plates.

Fig.8 shows the graph of the microphotometer reading obtained from a photographically recorded collodion pattern. It can be seen that there are no pronounced maxima in the intensity; the positions of the haloes appearing as changes in the gradient of the curve. For similar patterns obtained from gases, Pauling and Brockway[50] have shown that the visual observations of the positions of the haloes are in good agreement with the positions found fromthe intensity curves, and the eye would thus appear to automatically discount the gradual falling off in intensity away from the centre of the pattern.

The plates were examined by placing them on a ground glass screen, this was illuminated by an electric lamp the intensity of which could be varied by means of a rheostat. The diameters of the haloes were measured with dividers.

Reproduction of Diffraction Patterns.

As a result of the low degree of contrast in the halo patterns, and the large drop in the intensity away from the central spot, shading was found to be necessary in obtaining prints.

Printing paper which gives low contrast was found most satisfactory, and the shading was done either by hand, or using a slit-shaped source of light mounted on a rotating gramophone table, as described by Trendelenburg[51].

Fig.9. Unstretched Dimethyl Butadiene Film.

TRANSMISSION PATTERNS.

Dimethyl Butadiene.

Thin films of dimethyl butadiene thermal polymer were prepared from dilute solutions of the substance in benzene. In making up the solutions, the outside layers of the solid were first dissolved away as they contained oxidation products formed by exposure to the air.

The films gave three main diffraction haloes. On applying the Bragg Law to the mean diameters of these, they were found to correspond to first order diffractions by spacings of 5.12 A., 2.25 A., and 1.20 A.

Patterns were taken with the plane of the film making angles down to 15° with the direction of the incident beam but were not found to differ from those taken with the film normal to the beam.

Specimens were also prepared of films stretched to various extents; the extension for the whole film could be measured accurately, but owing to the lack of uniformity in the thickness, the degree of stretching would be expected to vary for different parts of the film, and be greatest for those parts which were sufficiently thin to give clear electron diffraction patterns.

The patterns obtained from the stretched films showed four pairs of lines perpendicular to the direction of stretching (marked A_2, A_3, A_4 and A in Fig.9). The most intense pair A_2 corresponded to a

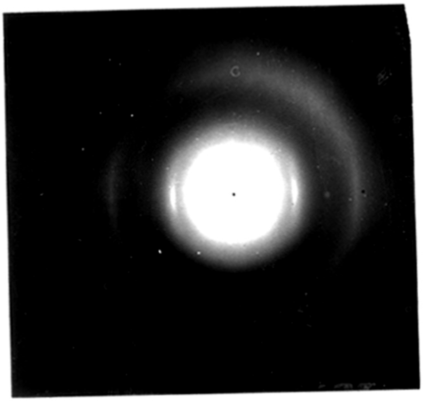


Fig.10. Stretched Dimethyl
Butadiene Film.

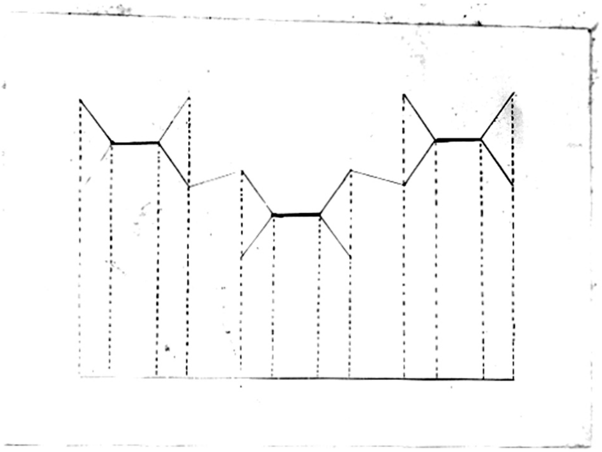


Fig.11. Cis form of Dimethyl Butadiene Chain.

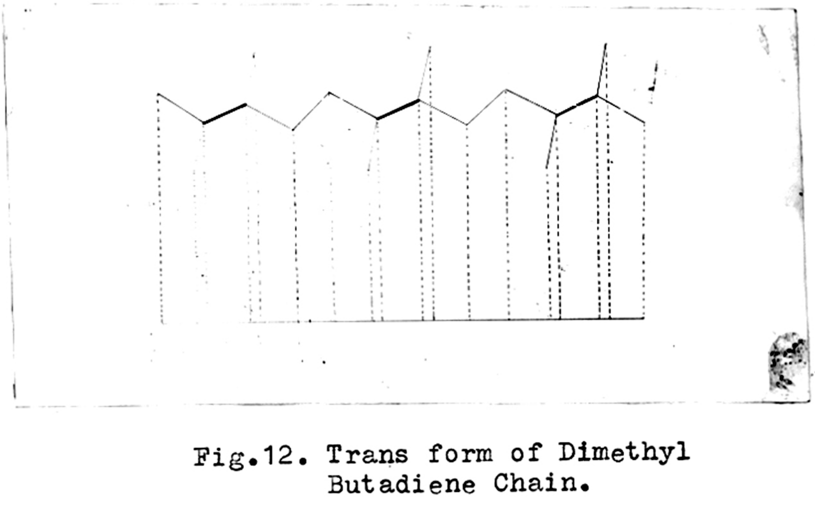


Fig.12. Trans form of Dimethyl Butadiene Chain.

Bragg spacing of 2.42 A. and were situated inside the second halo. The lines A_4 just inside the outer halo were next in intensity, and corresponded to a spacing of 1.21 A. The other two pairs A_3 and A_4 were much less intense and corresponeded to spacings of 1.61 A. and 0.80 A.

The films which had been most highly stretched (to above about three times their original length) also showed spots on the inner halo (marked B in the diagram) perpendicular to the direction of stretching and four faint, diffuse arcs (marked C).

The spots were found to correspond to a spacing of 5.3 A., whilst the arcs corresponded to a spacing of 3.2 A.

When the film was inclined, so that the direction of stretching remained perpendicular to the direction of the incident beam, no change was observed in the pattern. Inclination of the film which changed the angle between the direction of stretching and the incident beam resulted in the lines becoming more and more diffuse, and at an angle of inclination of 45° in this direction, the pattern consisted of haloes similar to those observed with unstretched films except in the case of the most highly stretched specimens, where the B spots could still be seen, together with two arcs, corresponding to the four C arcs, which were in line with the spots.

The positions of the lines A_2, A_3, A_4 and A can be seen to correspond to the second, third, fourth and sixth orders respectively, for diffraction by a grating of unit distance 4.8 A.

Figs.11 and 12 represent the cis and trans forms of chains of dimethyl butadiene. If the spacings for the single and double bonds between carbon atoms are taken to be 1.52 A and 1.31 A., and the angles between the bonds are taken to be tetrahedral, the unit grating distance along the chain, corresponds in the two cases to 4.62 A. and 4.97 A. (In the cis form the true identity period is 9.24 A. consisting of two identical parts of 4.62 A. displaced parallel to each other).

Since inclining the film about the direction of stretching does not affect the pattern, and the lines disappear when the film is inclined about the direction normal to this, the chains would appear to be aligned symmetrically and to be randomly orientated about the direction of their axes.

Diffraction by a system of spacings which make a constant angle with the normal to the incident beam has already been considered. For small values of the angle of scattering ϕ, the resultant intensity is proportional to

$$E_r \; E_q \; J_0 \, (K \, r_{pq} \sin \psi \cos \alpha) \cos (K \, r_{pq} \sin \phi \cos \psi)$$

from equation (12).

Along the direction of the normal, $\psi = 0$, so that the expression becomes

$$E_P E_Q \cos (K r_{PQ} \sin\alpha),$$

the intensity distribution in this direction is therefore the same as that for a spacing of $r_{PQ} \sin\alpha$ along the direction of the normal.

This may be seen more directly by considering the expression for the path difference $\underline{r}_{PQ} (\underline{S} - \underline{S}_0)$ for a spacing in any orientation. If the projection of the spacing on the plane containing the incident beam makes an angle with the direction of the beam, it can be seen from equation (11) that

$$r_{PQ} \ (\underline{S} - \underline{S}_0) = r_{PQ} \phi (\sin\alpha \cos\psi + \sin\psi \cos\alpha \sin\theta)$$

ϕ the angle of scattering being small.

Along the direction of the normal to the plane, $\psi = 0$, so that

$$\underline{r} \quad (\underline{S} - \underline{S}_0) = r_{PQ} \phi \sin\alpha$$

which is independent of θ and is the same as the path difference for a spacing of $r_{PQ} \sin\alpha$ along the direction of the normal.

In considering the effect of the structure of the grating unit on the intensity distribution, the effect along the normal is the same as for atoms situated at points corresponding to the projections of the positions of the atoms along this direction.

Figs. 11 and 12 show the positions of the projections along the direction of the chain. In the cis form the projected grating unit consists of two atoms at 0, one at 0.89 A., one at 2.22 A., and two at 3.12 A. In the trans form the projections are at 0.97 A., 1.29 A., 2.49 A., 2.81 A., and 3.78 A.

The expression for the structure factor (14) giving the intensity I due to a single grating unit, becomes for the direction along the normal

$$I = \left[\ E \cos\left(2\pi \frac{hx}{a}\right)\right]^2 + \left[\ E \sin\left(2\pi \frac{hx}{a}\right)\right]^2$$

where h = 1, 2, 3, etc. for the corresponding orders of diffraction. E is the structure amplitude for carbon, and x is the distance of the projection of the atom along the grating unit, which is of total length a.

The relative values of the intensities for the different orders in the two cases are given by

Table

Order	1	2	3	4	5	6
cis form	1.0	2.25	0.80	1.55	0.30	1.375
trans form	1.0	0.51	0.51	1.54	0.20	0.04

It can be seen that the values for the cis form give fair correspondence with the observed intensities. The fact that the first order was not observed in the pattern may be due to its proximity to the central spot, where the contrast is poor and to the fact that the inner halo which is fairly intense, falls very near to the position where it would be expected to appear.

The assumption that the angles between the carbon bonds are tetrahedral, must be regarded as an approximation, since from the Thorpe-Ingold effect the angles would be expected to increase as a result of repulsion between the terminal groups. The effect of this would be to increase the length of the grating unit, which would account for the difference between the calculated and observed values for this direction.

The structure factor would also be affected by the scattering due to the hydrogen atom, the effect of which has been neglected in comparison with that due to the heavier carbon atoms.

The appearance of spots and diffuse arcs in the most highly stretched specimens shows that the substance is then approximating to a pseudo crystalline state. In view of the extreme thinness of the film, the cross section of the single crystals would have to be very small, and from the fact that rotation of the film about the axis of stretching does not affect the spots, they must be orientated randomly about this direction.

The B spots appear to correspond to constant distances between the parallel chains of 5.3 A., whilst the diffuse arcs show that the chains are aligned approximately in step, so that parallel grating rows occur in directions making constant angles with that of the chains.

Krylow[39] was unable to observe such crystalline interferences in the electron diffraction patterns from dimethyl butadiene films; in the X ray work Katz has observed the effect but Hock only found it to occur when the specimens were cooled as well as stretched. The ease with which the substance crystallises would thus appear to vary for different specimens, and Katz has found that the ease of crystallisation on stretching of synthetic rubber is generally accompanied by good rubber-like qualities.

The application of the Bragg Law to the mean diameters of the haloes would be expected to give too small values for the spacings, since the spacings are not normal to the beam but are orientated randomly in all directions.

The Debye Ehrenfest formula for the intensity I due to a randomly orientated single spacing d is given by

$$I \propto 1 + \frac{\sin x}{x}$$

where $x = \frac{4\pi d \sin\theta}{\lambda}$ (and θ is half the scattering angle)

The Bragg Law gives for the positions of the n^{th} maximum

$$2\, d \sin\theta = n\lambda$$

If d and d are the values of the spacings calculated by the Debye Law and the Bragg Law

$$\frac{d_D}{d_B} = \frac{x_n}{2n\pi}$$

where x_n is the value of x at the n^{th} maximum of the Debye intensity curve.

To find the value of x I is differentiated with respect to x, this gives

$$\frac{dI}{dx} \propto \frac{\cos x}{x} - \frac{\sin x}{x^2}$$

For stationary values this equals zero, so that tan x = x. For the first six maxima

$x_1 = 7.725$ $x_2 = 14.066$ $x_3 = 20.371$

$x_4 = 26.666$ $x = 32.956$ $x = 39.244$

The corresponding ratios are thus given by

1.229 1.119 1.087

1.061 1.049 1.041

These are therefore the factors by which the spacings calculated from the Bragg Law must be multiplied to give the values as found from the Debye Ehrenfest formula, and it can be seen that the correction becomes smaller for higher orders of diffraction.

On applying the corrections to the Bragg spacings obtained from the mean diameters of the second and third haloes found with unstretched dimethyl butadiene polymer, it being assumed that they correspond to second and fourth orders of diffraction, the spacing is found in both cases to become 4.9 A., which is in fair agreement with the value found from the stretched films.

If the order of diffraction can be assigned to a halo the application of the Debye formula will thus

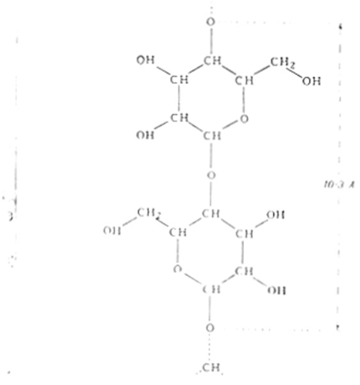


Fig.13. Cellulose Chain

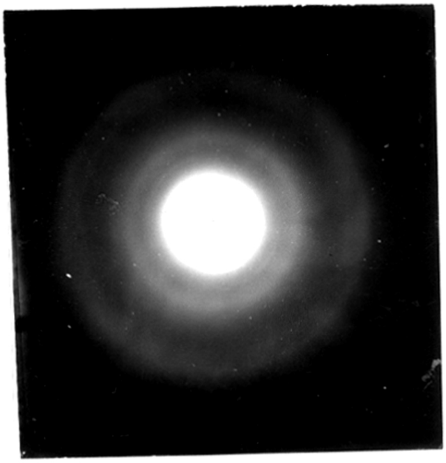


Fig.14. Collodion Pattern. (50 KV)

give a better approximation for the value of the spacing than the Bragg Law.

If, however, only a halo pattern can be obtained, the spacings corresponding to the identity period along the chain cannot be distinguished from the spacings corresponding to the distances between spearate chains.

Cellulose.

Films of acetone collodion were prepared from dilute solutions in acetone and also in amyl acetate.

Three main haloes were observed and in some patterns these could be resolved into seven separate maxima which correspondded to Bragg spacings of 4.75 A., 3.25 A., 2.41 A., 1.9 A., 1.65 A., 1.2 A. and 1.05 A..
Some patterns showed a slight arcing of the first, third and fifth maxima, which would seem to show that strains had been set up in the small portions of the film examined which resulted in the chains becoming aligned.

Fig.13 shows the structure of the cellulose chain as found from chemical evidence. The cellulose chain is assumed to consist of glucose residues formed by the removal of a water molecule from the glucose molecule. $C_6 H_{12} O_6$

The identity period along the chain corresponds to 10.3 A., consisting of two glucose residues. Taking the first, third and fifth maxima to correspond to the second, fourth and sixth orders of diffraction they will correspond to spacings of 10.5 A., 10.2 A., and 10.3 A., the spacings being calculated from the Debye Ehrenfest formula.

The absence of the odd orders of diffraction would be expected from the fact that the grating unit when projected along the direction of the chain, is found to consist of two identical parts.

The other three maxima which did not show arcing and were more diffuse, would appear to correspond to diffraction by the distances between separate chains.

The X ray results on cellulose fibres agree with an identity period of 10.3 A. along the chains but also show crystalline interferences in other directions; Mark and Meyer give as the most probable structure of the unit cell, which is monoclinic;

a = 8.3 A., b = 10.3 A., c = 7.9 A., $\beta = 84°$

Natta and Baccaredda , to whose work reference has already been made, claim to have obtained ring patterns which confirm this structure. The patterns obtained from cellulose and cellulose compounds by other electron diffraction workers have however failed to show any evidence of crystalline structure.

<u>Polystyrene</u>.

Thin films of polymerised ~~syt~~ styrene were prepared from dilute solutions of polystyrene and polymethylstyrene in benzene, chloroform, acetone and amyl acetate.

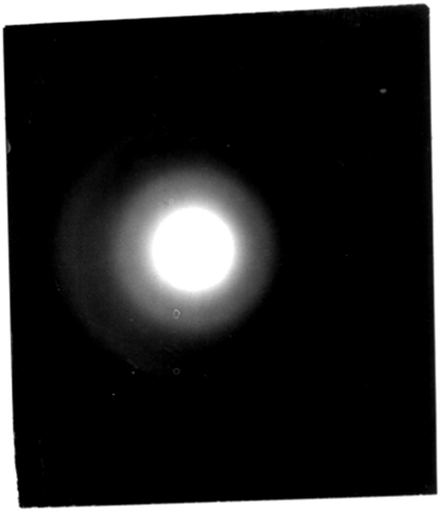
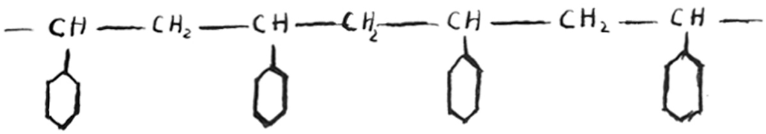


Fig.15 Polystyrene (52 KV.).

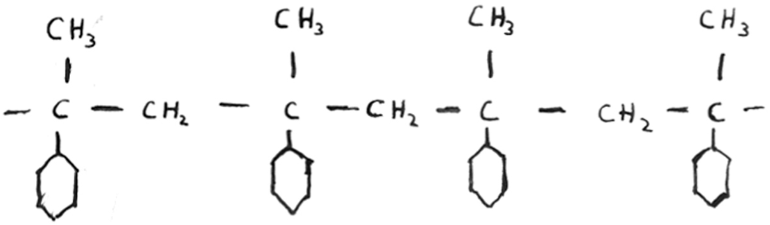
The patterns obtained showed five separate haloes on applying the Bragg formula to the mean diameters of these, they were found to correspond to spacings of

10.0 A., 5.0 A., 3.7 A., 2.15 A. and 1.15 A.

The structure of polystyrene is given on chemical evidence as



and the structure of polymethylstyrene is given by



The unit distance along the chain is therefore 2.50 A. in both cases; the angle between the carbon bonds being taken as tetrahedral.

On applying the Debye Ehrenfest formula to the two outer haloes on the assumption that they are first and second orders of diffraction; the spacings become 2.64 A. and 2.57 A., and would thus appear to correspond to the identity period along the chain. The effect of the benzene groups would be expected to result in an increase in the angle between the carbon bonds obtained and would account for the high values

The 10 A. spacing has been observed by Katz and has been attributed by him to the distances between the chains; the 5 A. spacing would then appear to correspond to the second order diffraction of this. The remaining halo, corresponding to 3.7 A., was faint and very diffuse.

Specimens were prepared from a large number of polymers of styrene of different molecular weights, varying from the trimer to high polymers containing several hundred units. The patterns obtained were found to be the same for all the specimens and were also found to be unaffected by the addition of methyl groups to the chains.

R.Signer has suggested that polystyrene molecules tend to have a linear formation in solution, so that in the thin films formed by evaporation, the molecules should become orientated parallel to the plane of the film.

It has been shown that inclination of the film when the spacings are orientated in a plane will result in the haloes becoming elliptical in shape. Thin films of polystyrene showed no such change in the pattern when they films were inclined, and it must therefore be assumed that the chains are orientated quite randomly in the film.

The patterns showed very little background which would result from inelastic scattering of the electrons, and the film was therefore unlikely to be more than about

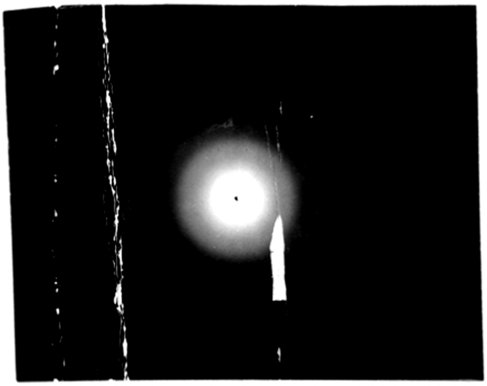


Fig.16. Sulphur. (52 KV)

two hundred angstroms in thickness. The lengths of the chains of the higher polymers were each greater than this and the chains could therefore not be rigid in the films.

The fact that the patterns obtained with films of very low polymers were identical with those from the higher polymers would also seem to show that not more than a few units of the chain were in line in the film.

Sulphur.

Thin films of sulphur were prepared by evaporation from a drop of a solution of rhombic sulphur in benzene which was allowed to spread on a water surface.

Some difficulty was experienced in obtaining diffraction patterns from films, because of the charging-up of the specimens, this did not occur in the thinner parts of the specimens, and the patterns generally showed spots corresponding to ~~ai~~ a single crystal structure, but sometimes haloes showing an amorphous arrangement were observed.

The Bragg spacings corresponding to the mean diameters of the haloes were

3.16 A., 2.10 A., and 1.25 A.

The first halo was intense and had a sharp outer edge, the second was intense but diffuse, and the outer one was weak and diffuse.

Warren and Burwell have shown by X ray analysis that rhombic sulphur consists of 8 atom rings which are puckered in form; the ring consisting of two plane square formations. The squares are 1.3 A. apart and are turned through 45° relative to each other; the distance between the adjacent sulphur atoms is 2.15 A.; the sides of the square correspond to 3.4 A.; and the angle between the sulphur bonds is 105°. This value for the angle is rather smaller than that between equally spaced octahedral bonds; the obtuse angle in this case being 109°28', i.e. the same as the tetrahedral angle between the bonds of a carbon atom.

The three halo spacings would thus appear to correspond to the side of the squares, to the distance between the adjacent sulphur atoms, and to the separation between the squares in an atomic ring.

Warren finds that the nearest distance of approach between the rings corresponds to 3.3 A. which would account for the sharp outer edge of the halo corresponding to this spacing.

Clay.

Transmission specimens of clay were prepared from a suspension in water of clay particles, which had remained deflocculated after treatment in a centrifuge.

A drop of the suspension was allowed to spread on a collodion film on nickel gauze, and was then placed in a dessicator for several hours. The patterns consisted of a series of rings when the beam was normal to the film; the finite width of the rings showing the crystal size to be small.

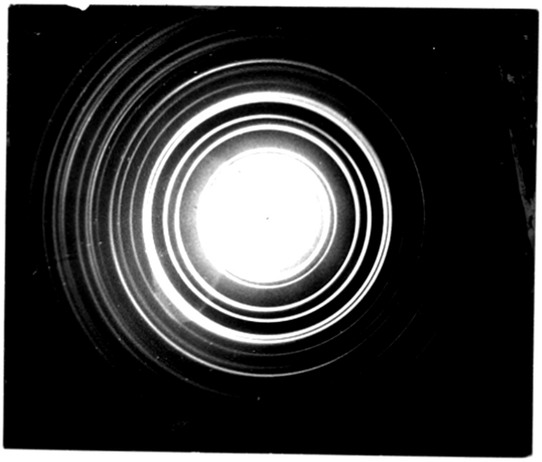


Fig.17. Clay film.

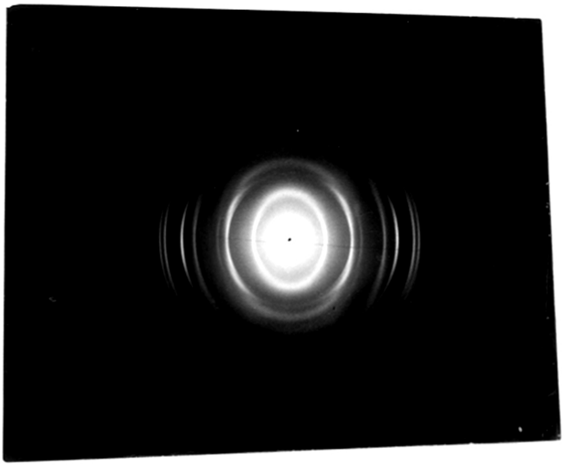


Fig.18. Clay film turned
through 45°.

On inclining the film the rings became elliptical in shape with the minor axes of the ellipses parallel to the axis about which the film was being inclined; the lengths of these minor axes were the same as the diameters of the circular rings. With increasing inclination the ellipses increased in eccentricity and also became more and more diffuse except along the direction of inclination.

The patterns show the specimen to consist of very thin flat crystals orientated parallel to the plane of the film; the diffractions corresponding to the two dimensional cross grating patterns found in optics; the cross gratings being orientated randomly in the plane.

The fact that the ellipses break up for large inclinations shows that the small grating rows in the direction normal to the film are sufficient in extent to decrease the intensity of the scattered radiation in some directions.

REFLECTION PATTERNS.

Diffraction patterns obtained by reflection from thin films of long chain hydrocarbons on metallic discs show a series of lines parallel to the plane of the film which are approximately equally spaced. These "layer" lines correspond to various orders of diffraction by one-dimensional molecular gratings perpendicular to the plane of the film; the sepearation of the lines corresponding to the identity period along the molecular chains.

If in the direction of scattering considered, A is the resultant amplitude due to a single grating unit, and p is the path difference between waves scattered by corresponding points in adjacent units, the modulus of the amplitude due to a grating of n units isgiven by

$$A \quad \frac{\sin \frac{np}{2}}{\sin \frac{p}{2}}$$

the intensity is therefore

$$A^2 \quad \frac{\sin^2 \frac{np}{2}}{\sin^2 \frac{p}{2}}$$

The value of the path difference p is given by the scalar product $\underline{r}.(\underline{S} - \underline{S}_0)$ where r is the length of the grating unit. If the angle of scattering ϕ is small, and ψ is the angle, the plane of the incident and scattered beams makes with the axis of the grating, then from equation (11)

$$r.(S - S_0) = r\phi\cos\psi$$

Let X and Y be the co-ordinates of a point on a photographic plate distance L from the scattering specimen;

the X axis being taken parallel to the film, i.e. normal to the direction of the gratings; then, for small values of

$$X = L\phi \sin\psi \quad \text{and}$$
$$Y = L\phi \cos\psi \; ,$$

so that $p = rY/L$ and the intensity I is therefore given by

$$I = A^2 \frac{\sin^2 \frac{n\pi r Y}{L\lambda}}{\sin^2 \frac{\pi r Y}{L\lambda}}$$

Maxima, which will become sharper with increasing values of N, will thus occur along equidistantly spaced lines parallel to the shadow of the film, and there positions will correspond to integral values of rY/L .

The factor **A** which acts as a structure factor is equal to the intensity of the radiation scattered by a single grating unit. For the zig-zag hydrocarbon chain the unit may be taken to consist of one carbon atom at one end and another half way along; the line joining them making an angle α with the plane of the film.

If the chains are orientated at random about their axes the mean value of **A** will be given by equation (12) so that

$$A^2 \propto E^2 \left[1 + J_0\left(\frac{KXd\cos\alpha}{L}\right) \cos\left(\frac{KYd\sin\alpha}{L}\right) \right.$$

where d is the distance between adjacent atoms inthe chain i.e. 2d[redacted] $\overset{\sin}{}\alpha$ = r, and **E** is the atomic scattering factor for carbon.

Substituting for A the intensity I is given by

$$I \propto \frac{\sin^2 \frac{n\pi r Y}{L\lambda}}{\sin^2 \frac{\pi r Y}{L\lambda}} \left[1 + J_0\left(\frac{\pi r X \cot\alpha}{L\lambda}\right) \cos \frac{\pi r Y}{L\lambda} \right]$$

Along the layer lines rY/L is integral so that

$$I \propto 1 \pm J_0\left(\frac{\pi r X \cot\alpha}{L\lambda}\right)$$

the positive and negative sides corresponding to even and odd orders respectively.

Along the normal to the incident beam X = 0, so that the odd orders disappear along this line and become visible on either side reaching a maximum value when

$$\frac{\pi r X \cot\alpha}{L\lambda} = \pm 3.832$$ (the first minimum of $J_0(x)$

The even orders have their maxima along the normal, the intensity dropping to a minimum at the minima of J (x).

The problem of diffraction by randomly orientated hydrocarbon chains with their axes in a fixed direction has been considered by Murison[56], no approximation was made, however, for the small angle of scattering which resulted in a much more complicated expression being derived, this was given in terms of an infinite series.

Germer and Storks[57] have recently given an expression for scattering by a monomolecular layer of stearic acid, the orientation of the molecules being the same as the one considered here. The expression is equivalent to the one derived above, the actual evaluation was not, however,

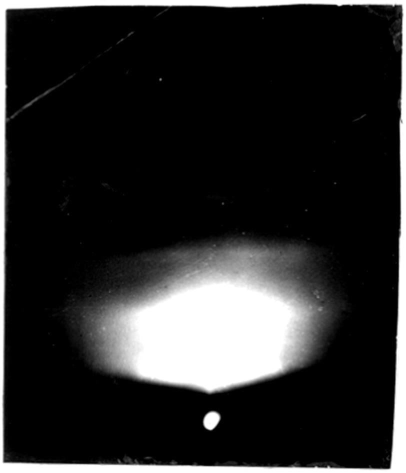


Fig. 19. Reflection pattern from Beeswax.

Fig.20. Reflection pattern from Paraffin Wax.

included.

Long-chain hydrocarbons.

The specimens of hydrocarbons were prepared by evaporation of a film of a dilute solution of the substance which had been spread on a stainless steel or highly polished disc. Rubbing the films with tissue paper was found to result in higher orientation of the chains.

The patterns obtained from impure hydrocarbons, such as beeswax, showed a series of layer lines, the intensity distribution of which corresponded to the theory.

Films of paraffin wax also showed broad spots on the layer lines corresponding to spacings between the chains which were arranged in the form of single crystals orientated normal to the film.

The layer lines are found to be unequally spaced; this may be interpreted in terms of the refractive index effect caused by the inner potential of the film.

If the accelerating potential of the electrons is taken as E and the potential in the film is V, the refractive index is given by the ratio of the velocities of the electron inside and outside the film and is therefore $= \sqrt{1 + V/E}$, the relativity correction being neglected.

The effect of refraction will be to bring the layer lines nearer to the central spot, the change being greatest for the lower orders of diffraction where the angle of scattering is small.

In addition to the bending of the beam the wavelength

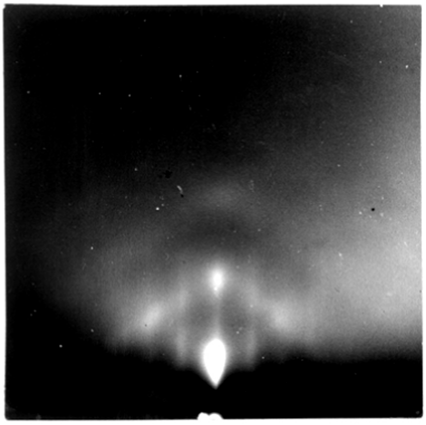


Fig.21. Reflection pattern
from Stearic Acid.

associated with the electrons will be slightly changed, but the effect of this will not be observable for high speed electrons as the change in wavelength is of the order of one in five thousand.

Murison has determined the value of the inner potential for various hydrocarbons and found it varied for different substances between about three and six volts.

Stearic acid.

Reflection ~~patterns~~ specimens of stearic acid were prepared by allowing a film of dilute solution of the substance in benzene to evaporate on a polished stainless steel disc.

The patterns showed two symmetrically arranged sets of layer lines which were equally inclined about the direction of the normal to the film through the incident beam. Diffuse spots could be seen on the lines corresponding to the spacings between separate chains.

These layer line patterns would appear to correspond to a randomly arranged system of chain molecules, the axes of which make a constant angle with the plane of the film.

Diffraction by spacings making a constant angle with the plane have already been considered, but the problem is in this case complicated by two factors. Firstly the diffraction is caused by a one-dimensional grating of spacings instead of by a single spacing, and, secondly, each grating unit consists of two carbon atoms; the line joining them making a constant angle with the axis of the chain.

For diffraction by a grating of several units the arrangement in an individual unit will affect the relative intensities of the maxima; the positions of the maxima will not, however, be changed appreciably, so that in determining these positions each grating unit may be regarded as corresponding to a single scattering centre.

For stearic acid $CH_3(CH_2)_{16}$ COOH there will be a chain of eighteen carbon atoms and hence there will be eight complete units. Equation (13) gives the intensity distribution for a system of spacings making fixed angles with the plane. In this case the summation will contain eight terms corresponding to a single spacing, seven corresponding to twice the spacing, and so on.

The intensity along the X axis, i.e. normal to the film, will therefore be proportional to

$$8 \cos S + 7 \cos 2S + \ldots\ldots\ldots\ldots + \cos 8S$$

where $S = \frac{2\pi d \sin\alpha\, Y}{L\lambda}$

d being the unit grating distance.

Where $\frac{dY \sin\alpha}{L\lambda}$ is integral,

sharp maxima will appear; the intensity distribution being similar to that due to a grating of identity period $d \sin\alpha$ along the normal.

Along the Y axis, i.e. in a direction parallel to the plane of the film passing through the intercept~~s~~ of the incident beam on the plane, Y = 0, and the intensity is given by

$8\,J(R) + 7\,J(2R) + 6\,J(3R)\,\ldots\ldots\ldots\ldots\ldots J(8R)$

where $R = \dfrac{2\pi d\cos\alpha X}{L\lambda}$

The maxima of the Bessel function are not, however, exact multiples of any fixed value of R; the first four maxima of $J_0(x)$ corresponding to

$$x = 7.016,\quad 13.323,\quad 19.616,\quad 25.903.$$

If as a first approximation we consider only the effect of the single spacings, the first maximum occurs when

$$\frac{2\pi d\cos\alpha X}{L\lambda} = 7\cdot016 \quad \text{i.e.} \quad X = \frac{7\cdot016}{2\pi}\;\frac{L\lambda}{d\cos\alpha}$$

the second when X equals $\dfrac{13\cdot323}{2\pi}\;\dfrac{L\lambda}{d\cos\alpha}$, and so on. The higher maxima thus correspond approximately to those found with a spacing of d cos parallel to the film.

The angle the layer lines make with the shadow edge of the film is therefore approximately given by cot which is complementary to the angle the stearic acid chains make with the film; for the lower order layer lines this angle will, however, be smaller.

The patterns of stearic acid showed this angle to be approximately 50°; the spacings along the chain being 2.5 A. The odd orders were more pronounced as would be expected from the symmetrical nature of the unit in the zig-zag hydrocarbon chain.

The effect of the two oxygen atoms in the COOH groups has not been taken into account; the positions of the layer lines will not, however, be appreciably affected by the scattering due to these.

The refractive index effect will result in a change in the positions of the maxima along a direction normal to the film, but it will not change their positions in the direction parallel to the film; the inclination of the layer lines to the film will thus be decreased.

CONCLUSION.

Between the regularly periodic, three dimensional, arrangement of atoms in an undistorted single crystal, and a completely amorphous condition in which the atomic distribution is random and isotropic, a variety of different intermediate states are found to exist.

Thus in the case of stretched rubber-like compounds, the molecular chains are aligned in the direction of stretching, but appear to be randomly arranged with respect to each other. The reflection patterns from films of long chain hydrocarbons show a similar one dimensional arrangement whilst the cross grating patterns from clay show the arrangement in two directions to be of considerable extent, but a degree of arrangement normal to the plane of the cross grating to be much smaller.

These atomic arrangements, in what may be termed one dimensional and two dimensional crystals, can be most easily observed with thin films, and the method of electron diffraction is thus particularly suited to their investigation.

The mathematical treatment of diffraction by arrangements of this kind falls between the comparatively complete theory of diffraction by crystalline bodies, and the much more fragmentary work on diffraction by substances in the amorphous state.

The theory of diffraction by spacings arranged randomly in a plane has been considered here, and it has been shown that the Bessel Function of zero order is involved in this case similarly to the way in which the function sin x/x occurs the Debye treatment for diffraction by gases. Only the effect of the spacings within the molecule have been considered, as the effect of interference between waves scattered from different molecules involv~~ing~~es a knowledge of the molecular packing.

Diffraction by systems of spacings making constant angles with a plane, such as that found with saturated fatty acid films, is of interest as an example of diffraction which is intermediate between orientation of the spacings in the one direction and a random orientation in a plane. It has been shown that in the direction normal to the plane, the intensity distribution is similar to that found from spacings arranged along this direction, whilst in a direction parallel to the plane the distribution is given as a sum of Bessel functions corresponding to spacings orientated randomly in the plane. Between these two directions the distribution is given by the product of a regularly periodic, trigonometric function and a Bessel function, and the actual evaluation of the distribution would appear to involve considerable computation.

Inclination of the films of long chain organic compounds to the direction of the electron beam produced no apparent change in the diffraction patterns. This was found with the substances already mentioned, namely, dimethyl butadiene, collodion, polystyrene and polymethyl styrene, as well as with gliadin, unstretched rubber, and a highly polymerised methacrylic ester, films of which were examined. This random distribution of the spacings in these films shows that the chains are flexible, which is in agreement with the chemical evidence as to their structure.

The work of Langmuir, Adam and others on the orientation and spreading of thin surface layers of long chain compounds has shown the importance of the nature of the terminal groups on the orientation of the molecules in the films. The electron diffraction investigation of monomolecular films produced by the Langmuir-Blodgett technique to provide information as to the actual orientations of the molecules and should show the effect of diffraction by various different types of two dimensional arrangements.

PART 2.

THE DIFFRACTION OF ELECTRONS OF MEDIUM ENERGY.

INTRODUCTION.

Investigations by the method of electron diffraction have been carried out almost entirely with the use of accelerating voltages which fall into one of two ranges. By far the greater amount of work has been done with electrons accelerated between 30 and 60 kV., the patterns being recorded photographically. The other investigations have been with electrons accelerated up to a few hundred volts; the intensities of the scattered radiation being measured electrically.

Very little information has been derived from the investigations with slow electrons because of the difficulty of interpretation of the observed phenomena. As the inner potential of the solids examined, are here comparable with the accelerating voltage, the refractive index effect is large, and also the local ~~varaia-~~ variation in potential become important. In addition to this the large scattering by the adsorbed gas layer complicates the diffraction patterns.

The only work that appears to have been done using accelerating voltages between these two ranges has been by Ponte[58], Tillman[59], Loria and Klinger[60], and very recently by Trillat[61].

Ponte examined metallic oxide transmission specimens in the range of about 7,000 to 17,000 volts. Tillman in determining the inner potential of single crystals used voltages of about 4,500. Loria and Klinger examined oxide specimens down to 5,000 volts, and Trillat has described a camera using external photography, in which he has taken patterns down to 3,500 volts.

There are three main difficulties in the technique at voltages below 10,000 as compared with that at higher voltages. Firstly, to obtain transmission patterns extremely thin films must be employed, and with reflection patterns a very slight contamination of the specimen is sufficient to prevent the patterns being observed.

Secondly, to obtain sharp patterns the vacuum must be very high, as the effect of scattering by gas molecules is much greater than it is at higher voltages.

Finally, the recording of the photographs is much more difficult as the sensitivity and contrast of photographic plates is much lower at these voltages.

The purpose of the following investigations was to compare the patterns obtained at these low voltages with those found from the same specimens at higher voltages (50kV.).

The comparison patterns at hg the higher voltages were taken with a diffraction camera of the Finch type as used in the first part of the work for the investigation of diffraction by amorphous films.

THEORETICAL.

The use of lower accelerating voltages will result in the following changes in the behaviour of the electron beam from the point of view of diffraction.

(1). The wavelength will increase.

(2). The electrons will be scattered more easily and the penetration of the beam will consequently be lower.

(3). On entering a field of different potential greater refraction will occur.

(1) The de Broglie relation gives for the wavelength associated with a beam of electrons of velocity v

$$\lambda = \frac{h\sqrt{1-\frac{v^2}{c^2}}}{mv}$$

m being the rest mass of an electron.

If P is the accelerating voltage,

$$\frac{eP}{300} = \frac{m_0 c^2}{\sqrt{1-\frac{v^2}{c^2}}} - m_0 c^2$$

eliminating v from these two equations and approximating we have

$$\lambda = \frac{h\sqrt{\frac{150}{ePm}}}{\sqrt{1+\frac{eP}{600mc^2}}} \simeq \frac{h\sqrt{\frac{150}{ePm}}}{1+\frac{eP}{1200mc^2}}$$

The wavelength is thus approximately inversely proportional to the square root of the accelerating voltage. The relativity correction is small as $eP/1200\ mc^2 = 4.9 \times 10$ P. and at 10 kV.

$$\lambda = .122 \text{ A.}$$

The Bragg law gives $2d \sin\theta = n\lambda$ and at high voltages the angle of scattering considered, i.e. 2θ, is generally small, so that the ratio of the radius of the ring to the camera length may be used for $2 \sin\theta$. Approximation is no longer valid and tables must be used to find the values of $\sin\theta$.

(2). The penetration of the electron beam is limited by inelastic scattering of the electrons, and this is found to increase approximately as the inverse of the energy, the penetration would thus be expected to be inversely proportional to the accelerating voltage.

The change in the atomic scattering factor depends only on the ratio $\sin\theta/\lambda$, so that the relative intensity of the diffractions will not be affected by the voltage of the electrons.

(3). The refractive index of a medium of inner potential V is given by $\sqrt{1 + V/P}$ and the actual value of the refractive index will therefore be greater for lower accelerating voltages. The raltive change in the position of the diffracted beam is however of a second order, since from the Bragg law it can be seen that the scattering angle will increase with the wavelength, i.e. as the square root of the accelerating voltage.

EXPERIMENTAL.

The Diffraction Camera.

The arrangement of the diffraction camera is shown in Fig.22.

The source of electrons was a heated tungsten fialament in the form of a V which was spot welded on to two nickel wires passing through a twin bore silica tube. The tube was held in position by Apeizon wax W and could be easily removed when the filament required replacing. The filament was heated from the secondary of a transformer which gave an alternating current of up to 3 amperes at 4 volts; the insulation between the primary and secondary of the trnasformer being sufficient to withstand the accelerating voltages employed.

The anode was a copper tube fitted with two axial diaphragm holes, and a small movable magnet was employed to obtain the maximum intensity of the beam in the camera. Water cooling of the anode was found to be unnecessary, the anode being mounted in a thick brass plate.

A short hard glass tube was fitted round the fialment and anode; which resulted in the beam being electrostatically focussed down the axis of the tube.

The axis of the whole assembly was slightly inclined to the axis of the camera, this prevented the light from the hot filament, as well as X rays and heavy negative ions, from reaching the photographic plate,

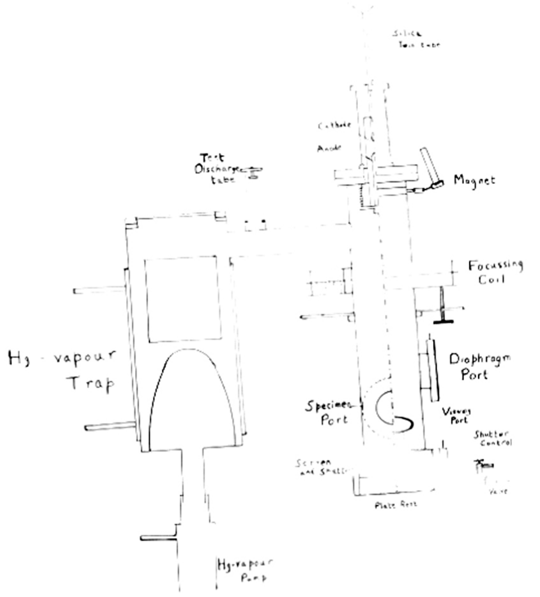


Fig.22. Low Voltage Electron Diffraction Camera.

whilst the electron beam could be brought to the centre of the fluorescent screen using the small magnet or the focussing coil lower down.

As an alternative source of electrons, a cathode ray tube assembly supplied by Messrs Ferranti Ltd. was employed. This was fitted with an oxide coated filament and had to be activated originally by means of an eddy current heater, and reactivated if exposed to the air. It was therefore necessary to keep the tube containing the assembly continually in an evacuated state; this was done by means of a ground glass tap which isolated the tube from the rest of the camera. A subsidiary focussing coil was used to pass the broad electron beam through the tap; a fine diaphragm limiting the beam before it entered the camera.

The assmebly was fitted with a grid and by making this at a negative potential relative to the filament a partial focussing of the beam could be attained, also the use of an oxide coated filament enabled a more intense beam to be obtained.

The method was however eventually abandoned in favour of the use of a plain tungsten filament which was found to be much simpler in operation.

A hot cathode was chosen in preference to a cold gas discharge, because at the voltages used, the pressure in the discharge tube would have to be comparatively high to obtain a sufficiently intense beam, and this would

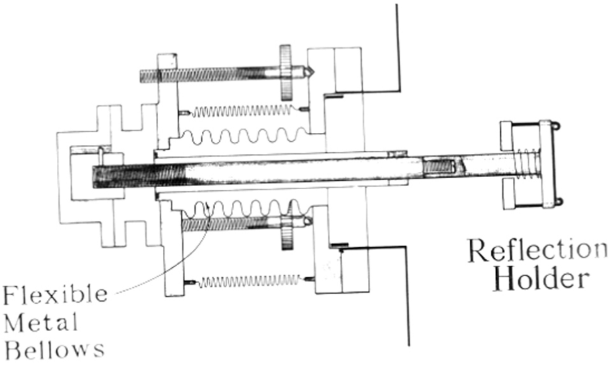


Fig.23. Specimen Carrier.

High Tension Supply.

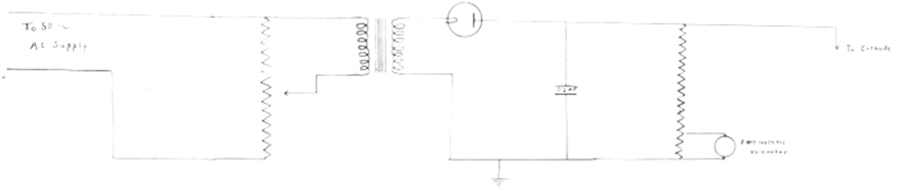


Fig.24. High Tension Circuit.

necessitate separate evacuation of the discharge tube and the rest of the ~~camrea~~ camera, and also the use of a very fine connecting diaphragm between the two.

The rest of the apparatus was a modified form of the Finch diffraction camera; the number of ground joints was kept at a minimum in ~~the~~ view of the high vacuum required. Ground metal joints were used with Apeizon or other vacuum grease of low vapour pressure.

Fig.23 shows the specimen carrier fitted with a reflection holder; for transmission specimens a clip holder was employed.

The use of this type of specimen carrier enabled the following adjustments to be made.

(1). By adjusting the three screws, the plane of the specimen could be varied over a small range in any direction, and the specimen could be moved across the electron beam.

(2). By turning both control heads the specimen could be rotated in an azimuthal plane.

(3). By turning the control heads relative to each other the specimen could be moved in a direction normal to the electron beam.

The camera length was 9 cms. when the shaft of the specimen carrier was normal to the beam. The beam was collimated by the double diaphragm in the anode, and the focussing coil further decreased the cross section of the beam.

The specimens were examined by tilting the focussing coil; this brought the beam to any desired part of the specimen. The focussing coil was connected to a battery of accumulators, which were "trickle-charged" from the mains supply; the direct use of the mains was found to produce changes in the position of the focussed spot, resulting from fluctuations in the voltage.

A fine diaphragm was mounted on a second specimen carrier and this could be brought directly over the portion of the specimen which was being examined. The effect of this diaphragm was give a finer electron beam and decrease the background scattering, also, as it was used in conjunction with a focussing coil, a more homogeneous beam of electrons was obtained. The diaphragm was put into position before a photographic recording of a pattern was obtained.

The patterns were observed on a zinc sulphide fluorescent screen; this was mounted on a shutter which could be raised to expose the photographic plate to the electron beam. The photographic plates were 6 x 9 cms. and were slipped into the plate section which was then closed by means of a ground rectangular metal plate.

The evacuation of the camera was continuous and was carried out by means of a mercury vapour diffusion pump backed by a rotary oil pump. Air was allowed into the camera by a specially provided tap.

A small test discharge tube was fitted between the diffusion pump and the camera, this was connected to a small induction coil. Only when no discharge could be seen in this tube were the high tension and the heating current of the filament switched on. The tube was also useful in testing the location of leaks in the apparatus; the colour of the discharge being changed from red to blue when cotton wool soaked in ether was brought into contact with the leaking joint.

The camera was earthed at several points; no separate earthing being provided for the anode.

High Tension Supply.

The high tension circuit is shown in Fig.24. The current in the primary was supplied by a potentiometer arrangement, which enabled the voltage across it to be varied continuously from zero to the full mains voltage; the maximum A.C. voltage across the secondary was about 10kV.

The rectification was carried out by a diode rectifying valve; the filament of which was heated from a separate transformer; the valve gave an emission up to 20 milliamperes.

The voltage was smoothed by oil condensers of one microfarad capacity each, five of these were joined in series; all having been tested for 2,500 volts insulation.

The condenser smoothing made the constant potential across the condensers equal to a peak voltage of the alternating supply from the secondary of the

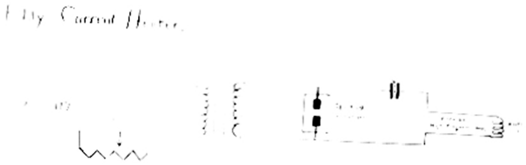


Fig.25. Eddy Current Heater Circuit.

transformer, i.e. the voltage was increased by the factor $\sqrt{2}$.

The resultant capacity of the condensers was 0.2 microfarad and this should have kept the voltage variation at 1% where the current was One milliampere, the voltage 10,000, and the frequency 50 per second. The effect of the focussing coil and diaphragm system would result in the variation in the beam incident on the specimen being lower than this, also, from the de Broglie relation, it can be seen that the variation in the wavelength will be half that in the voltage.

The voltage was measured by means of an electrostatic voltmeter, which could read up to 2,500 volts. Twenty 5-megohm resistances were connected in series across the high tension, and one terminal of the electrostatic voltmeter was connected to earth, the other could be connected to various tappings along the resistance to give the desired ratio between the voltage and the readings on the instrument. The voltmeter could be read to an accuracy of about ± 25 volts, so that when the ratio was adjusted to give a full scale deflection the voltage could be measured to about 1%.

Eddy Current Heater.

The circuit of the eddy current heater used with the oxide coated filaments is shown in Fig.25.

A transformer which gave up to about 100 milliamperes at 10,000 volts was connected across an adjustable spark gap; this consisted of two cylindrical copper pole

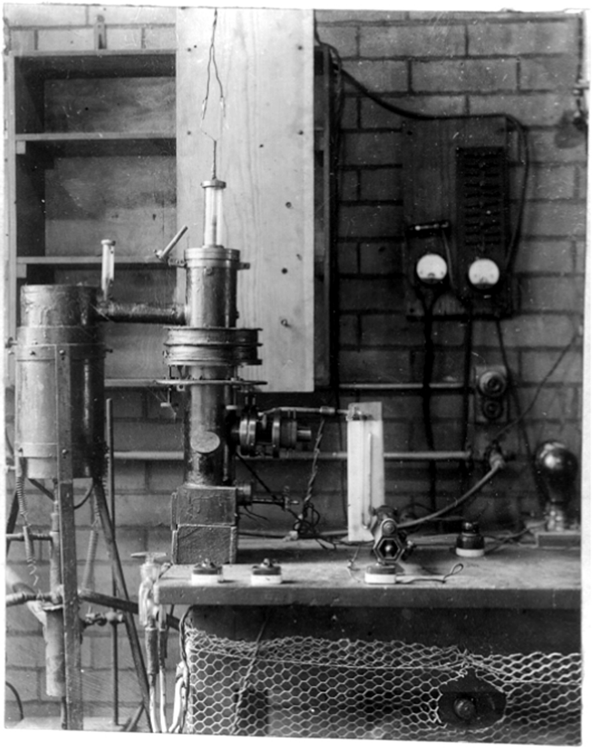


Fig.26. Photograph of Apparatus.

pieces mounted in an hermetically sealed box. Coal gas was passed through the box by means of two tubes; the effect of this being to quench the spark more rapidly and to cool the pole pieces. Across the spark gap were connected a 0.2 microfarad air condenser in series with the heating coil; this consisted of about six turns of 1/4 inch copper tube. Flexible high frequency leads were used with the heating coil, and the other connections in the circuit were made with thick copper strips.

To degas the cathode ray tube assembly the heating coil was fitted over it; the metallic parts were then brought to a bright red heat, flash discharges occurring in the tube as the adorbed gas was given off. When no further flashes occurred the filament current was switched on and the filament was activated by bringing it to a red heat.

Photographic Recording.

One of the chief difficulties of the technique of electron diffraction at voltages below 10 kV. is the photographic recording of the patterns.

Three separate effects would appear to be involved; firstly, the lower energies of the electrons prevent them from penetrating the gelatine in the emulsion, this difficulty being similar to that found with the photographic recording of ultraviolet light of short wavelength; secondly, the lower sensitivity of the photographic grains themselves to the electrons of lower energy, and, finally, the X rays caused by the impact of the electrons on the photographic plate caused fogging with resultant decrease in the contrast.

One method of overcoming these difficulties in recording the patterns, is to accelerate the electrons after they have been diffracted to much higher voltages; this method has been used by Ehrenberg for very slow electrons. A complicated system of grids must however be used to prevent distortion of the patterns, and either the specimen must be kept at a large negative potential or the plate carrier must be at a large positive potential.

Trillat has used a method of external photography of the fluorescent screen which has the advantage of allowing a number of ~~aptt~~ patterns to be taken without releasing the vacuum in the camera; a certain loss in the detail of the pattern would however be expected to occur in this method as compared with direct photography. The method should prove useful at voltages below 3,000 where photographic plates are extremely insensitive, although intense fluoresence still occurs on the screen.

Photographic plates can be sensitised to low voltage electrons in one of two ways. Either an emulsion containing very little gelatine may be used or the plates may be coated with a thin film of some fluorescent material.

Both these methods were tried in the recording of the diffraction patterns. Specially prepared "Q" plates containing very little gelatine in the emulsion were found to be fairly sensitive to electrons of energies down to about 4,000 volts; the removal of the gelatine from ordinary plates with dilute sulphuric acid was also found to increase the sensitivity.

Plates coated with thin films of salicylic acid and low vapour pressure oils were also employed. Salicylic acid was tried as it is found to be very effective as a fluorescent film in ultra-violet photography; it did not, however, appear to increase the sensitivity of the plates to electrons.

Oil coated plates were found to be more sensitive, but care was necessary in the coating of the plates to produce a uniform effect.

The low penetration of the electron beam in the emulsion limits the maximum blackening which can occur as a direct result of the impact of the electrons; (fluorescence set up in the gelatine by the electron beam will cause secondary blackeneing throughout the thickness of the photographic emulsion).

A number of different types of photographic plates were tried; their sensitivity to the electron beam did not appear to be directly connected with the sensitivity to light; Process and Lantern plates being found to be most sensitive.

Ilford Special Lantern plates were found also to give a high degree of contrast and were eventually used for recording patterns down to about 4,000 volts.

The exposures necessary increased rapidly with decreasing voltage; ranging from afew seconds up to about four minutes.

Preparation of Transmission Specimens.

Extremely thin transmission specimens were necessary at the voltages employed because of the lower penetration of the electron beam.

Cochrane has shown that at 30 KV., gold films more than 500 A. in thickness do not give ~~do not gi~~ve diffraction patterns, as the effective penetration would be expected to be about a third of this at 10 KV. Gold specimens would certainly have to be less than 200 A. for diffraction patterns to be observed. Where the atoms have lower scattering powers, thicker films may be employed, and mica is found to give transmission patterns consisting of spots up to thicknesses of about 2,000 A.

Most substances in the form of thin uniform films will collapse very easily, and specimens in which large variations occur in the thickness are found to be most satsifactory; the patterns being obtained by passing the beam through"holes" in the film.

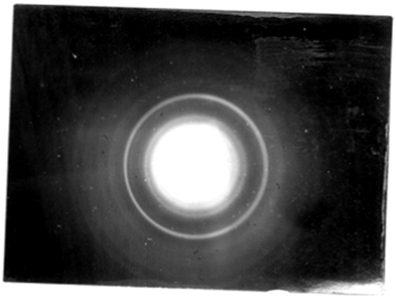


Fig.27. Aluminium Oxide (5 KV.).

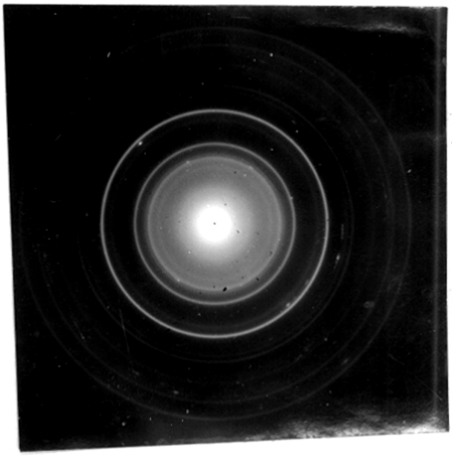


Fig.28. Aluminium Oxide (50 KV.).

TRANSMISSION PATTERNS.

Metallic Oxides.

Polycrystalline specimens of metallic oxides which give clear patterns with low voltage electrons are easily prepared, and Ponte[58] and Loria and Klinger[59] verified the de Broglie relation in this region using specimens of the oxides of zinc, cadmium and magnesium.

Figs. 27 and 28 show the patterns obtained by transmission from aluminium oxide at 5,000 volts and 50,000 volts respectively; there is no change in the pattern except, that as a result of the larger angles of scattering, the outer rings are relatively further out at the lower voltage.

The specimens were prepared by dipping a loop of nickel wire in molten aluminium; a thin film of aluminium and aluminium oxide which floated on the surface adhering to the loop. The film contracted on cooling, forming several thin transparent "cracks" which were found to give good transmission patterns. Specimens of zinc oxide and tin oxide were similarly prepared.

These oxide specimens showed patterns on the fluorescent screen with accelerating voltages down to 2,500 volts; patterns could not, however, be recorded with the photographic plates employed much below 4,000 volts.

For preparing other polycrystalline specimens thin films of collodion could be used as a support. The background scattering ~~could~~ due to the collodion was more intense, however, than it is at higher voltages.

Ammonium chloride evaporated on to a collodion film gave a set of rings visible down to about 6,000 volts; no pattern was obtained, however, from a colloidal suspension of graphite spread on a collodion film. The graphite specimen gave a bright ring pattern at higher voltages, and it would thus appear that the size of the individual crystals was too great for a pattern to be obtained.

Metallic Specimens.

Several workers[63] have found that metallic films do not give clear patterns by transmission with electrons of energies less than about 12,000 volts. The work by Rupp for transmission at a few hundred volts has since appeared to be in doubt .

Gold films thinned down by floating gold leaf on dilute solutions potassium cyanide, yielded only a faint ring pattern with a very heavy background at 10,000 volts. A specimen of silver was prepared, however, which gave patterns down to about 4,500 volts.

It has been shown that if silver is evaporated in vacuo on to the cleavage face of heated rocksalt, the silver film consists of a large number

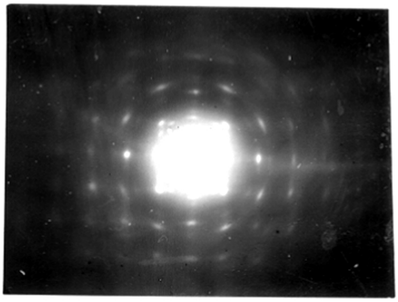


Fig. 29. Silver transmission
pattern (7 KV.).

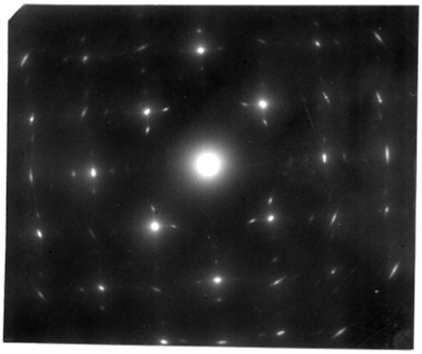


Fig.30. Silver transmission
pattern. (47 KV.)
Camera length

of crystals orientated with their axes parallel to that of the rocksalt substrate; the film being approximately in the form of a silver single crystal.

A specimen of this type was prepared using an electrically heated silver wire as filament; the rocksalt was dissolved away and the film collected on a piece of nickel gauze. The patterns at 7,000 volts and 50,000 volts are shown in Figs. 29 and 30 respectively.

The orientation of the separate crystals in the film in a fixed direction result in the pattern being much more intense than the rings obtained from unorientated polycrystalline films, and this would account for the low voltages at which the pattern could still be observed.

Single crystals.

When electrons are diffracted by very thin single crystals a cross-grating pattern similar to that obtained with two-dimensional lattices are observed. The reason for this is that the lattice rows parallel to the direction of the beam are short and do not influence the intensity of t he scattered radiation over the small angles considered. With thicker crystals the effect of these gratings becomes appreciable and thr spots become intenser along circular bands round the centre of the pattern; the spots between these bands

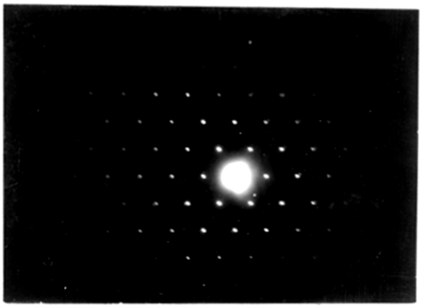


Fig.31. Molybdenite (18 KV.)

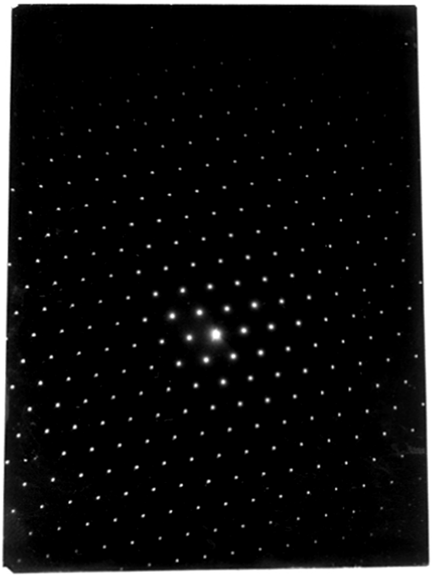


Fig.32. Molybdenite (50 KV.)
Camrea length 22 cms.

becoming lower in intensity.

Specimens of molybdenite were prepared by cleavage of flakes of the substance. When examined with high speed electrons some parts of the specimens showed cross grating patterns; the intensity of the spots falling off uniformly, whilst in other parts circular zones of intense spots were observed. The examination of the specimens with slow electrons yielded only cross grating patterns, showing the penetration of the electron beam at these voltages to be too low to pass through films ~~of~~ in which the third condition was operative.

Thin films of mica which gave brilliant cross grating patterns with high speed electrons did not show any patterns at all at 10 KV. The evenness with which sheets of mica cleave would probably account for this, as ~~their~~ there would be no flaws in the films, and any films thin enough to give patterns over a considerable area would be too fragile to be conveniently manipulated.

Crystals of anthracene which were prepared by evaporation of the substance on to a nickel gauze were also examined. As anthracene evaporates under vacuo, these crystals would become progressively thinner in the camera. A few spots were visible in the patterns obtained at 10,000 volts but the patterns were in no way comparable in intensity with those obtained with the higher speed electrons. The charging up of the specimens was also found to be more troublesome than with the higher voltages.

REFLECTION PATTERNS.

In obtaining electron diffraction patterns by reflection very small angles of incidence are used, and the penetration of the beam into the specimen for which inelastic scattering does not occur, is consequently much smaller than for transmission.

Finch and Wiman have shown that with fast electrons a monomolecular layer of the long chain paraffin $C_{32}H_{66}$ on a single crystal is sufficient to completely obliterate the pattern of the crystal substrate, only a series of layer lines due to the paraffin being observed. The paraffin chains are orientated normally to the surface, and the penetration can therefore not be greater than 43 A., which is the length of the chains. The scattering is here caused by carbon, which has a comparatively low scattering power and for a medium consisting of heavier atoms the penetration at these voltages will be even less. The actual penetration of the beams for which inelastic scattering occurs is much higher, and a heavy background is therefore generally found in reflection patterns.

With electrons of energies below 10 KV. the penetration should be proportionally lower and the diffraction observed would thus be expected to be caused by at most the first three or four atomic layers of the crystal surface, so that the Laue condition in this direction should be very considerably relaxed.

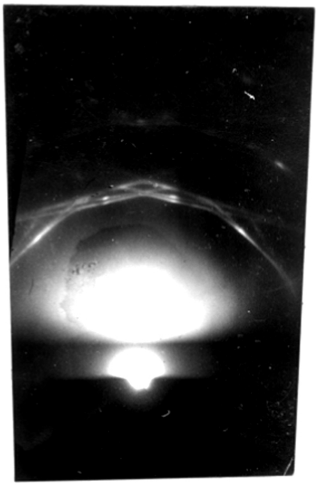


Fig 33 DIAMOND REFLECTION (9500 volts)
(111 FACE

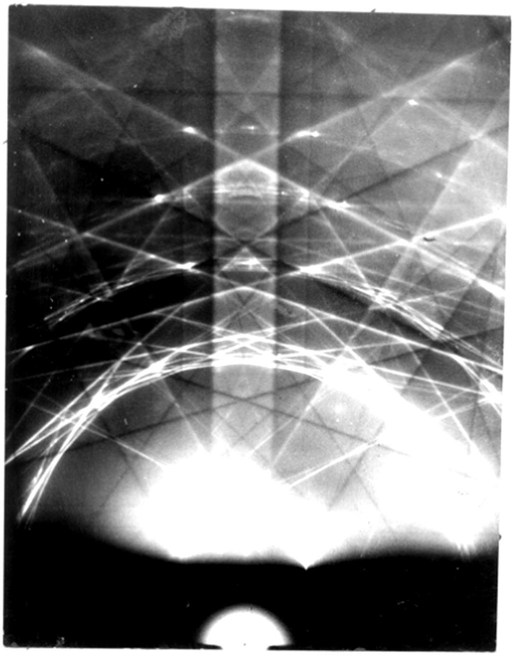


Fig 34. DIAMOND REFLECTION (50 KV)
(111 FACE)

Fig 35 DIAMOND REFLECTION (8 KV)
(111 FACE)

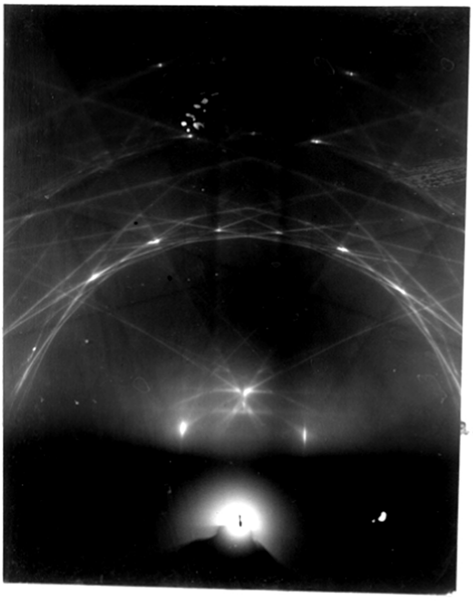


Fig 36 DIAMOND REFLECTION (50 KV)
(111 FACE)

If there are small projections on the surface of the crystal diffraction will occur by transmission of the beam through these projections and the effective penetration in the direction normal normal to the surface will be much higher.

Polished faces of diamond, corundum and quartz, and cleavage faces of crystals of rocksalt, zinc blende, galena and mica were examined. In all cases bright Kikuchi lines were observed down to about 4,000 volts but very few spots were found to occur together, these flashing in and out as the crystal was rotated. With lowering voltage the Kikuchi lines appeared to decrease in intensity, and more spots were observed to occur together.

The disappearance of the Kikuchi lines with lowering voltages would be expected as a result of the much lower penetration, which would also cause the practically complete relaxation of the diffraction condition in the direction normal to the specimen and hence a larger number of spots.

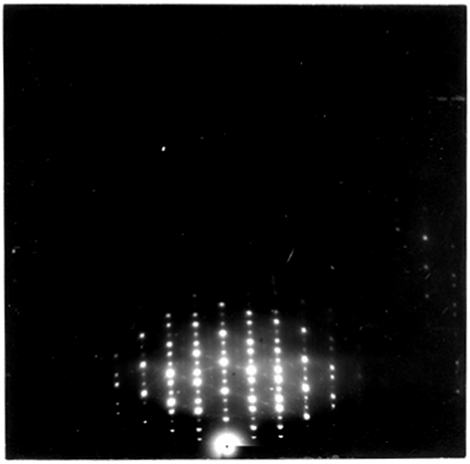
Freshly cleaved crystals were found to give much brighter patterns than those which had been exposed for some time, and eventually the specimens were found to give no patterns at all. Very careful cleaning of the cleavage face with grease-free solvants seemed to only partly restore the brilliancy of the patterns. With the polished specimens frequent cleaning was also found to be necessary, and slight abrasion of the surface was found to increase the brightness of the patterns.

This "contamination" did not appear to decrease the intensity of the patterns for high speed electrons and would thus appear to be due to a layer not more than a few angstroms thick. The difficulty found in removing it with the aid of solvents would seem to show that it was in some way absorbed by the crystalline surface and in view of its probable thickness would appear to be in the form of a monolayer.

A very fine beam was necessary with the reflection specimens for sharp patterns to be obtained, since, at the small angles of incidence employed, the area over which the beam makes contact with the specimen is large so that a considerable variation in the effective camera length would occur. A fine hole in the diaphragm just above the specimen was therefore used.

A polycrystalline iron oxide specimen which gave a brilliant ring pattern by reflection with high speed electrons ~~was~~ did not give any pattern at all with the lower voltages. Patterns of semicircles obtained by reflection from polycrystalline ~~specimens~~ surfaces were due to transmission of the electron beam through the crystals on the surface and the absence of the pattern would appear to indicate that the size of the individual crystals was too great for the beam to penetrate.

Nickel oxide on Corundum 8000 volts



Nickel oxide on corundum (50 KV)

Nickel oxide evaporated on to a polished face of corundum is found to give a brilliant reflection pattern consisting of a set of spots formed by the orientation of the nickel oxide crystals on the surface in two separate symmetrical orientations are found to occur; the main pattern approximating to that found from two single crystals. With high speed electrons secondary spots due to the double diffraction are found to occur, the diffracted beams acting as primaries for the lattice. Specimens showing this phenomenon were examined at lower voltages but only the primary spot pattern was observed. Figs. 37 and 38 show the patterns obtained at 8,000 volts and at 50,000 volts.

The absence of double diffraction is likely to be due to the lower penetration of the beam, but may also be a result of the longer wavelength which would cause the diffracted beams to emerge at a greater angle from the specimen and therefore have a smaller chance of again being elastically scattered.

CONCLUSION.

The investigations have shown that visual electron diffraction patterns can be obtained with electrons of much lower energies than those normally used, for a considerable variety of specimens using both reflection and transmission. The effect of the lower penetration of the beam has been seen to seriously limit the choice of transmission specimens, but all single crystals which gave bright patterns at higher voltages were found to give patterns with the lower speed electrons, and the lower penetration would appear to be a considerable advantage in the study of the surface action, in which single molecular layers are involved.

The increased wavelength would not appear to be of much importance but may prove of use in conjunction with a long camera length for the investigation of diffractions by spacings greater than 10 A., which are often found to occur in organic crystals; since the diffractions due to these fall extremely near to the central spot in observations with fast electrons.

The difficulty of photographing the patterns at low voltages was only partly overcome, and the most satisfactory method of overcoming the difficulty would appear to be the use of some convenient fluorescent coating of the photographic plates.

ACKNOWLEDGEMENTS.

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Electron Diffraction Studies of High Polymers

(carried out in A.P.C. Lab. by A.Charlesby, H.Kolsky, and G.[illegible]

A.Charlesby (Proc Phys.Soc. 1945,57, 496 and 510) made an electron diffraction study of the group of very long chain normal hydrocarbons known as polythene. His aim was to provide further experimental data on which theoretical studies of the intermolecular binding forces in these simple hydroarbons could be based: the advantage of this particular group of polymers was that the extremely great chain length minimised the disturbing effects of the end-groups.

Most of the work was carried out on thin films deposited from hot xylol solution on to a water surface at 5 C.

C.W.Bunn (1939) had previously examined polythene by means of X-ray diffraction and in so far as the results overlapped, the electron-diffraction results were in good agreement with these, both investigators giving an orthorhombic lattice with very similar axial lengths; the actual figures were: Bunn, a 7.40, b 4.93, c 2.534: Charlesby, a 7.426, b 4.934, c 2.532. The electron-diffraction results, however, showed in addition a number of new features which are summarised below.

a) Crystallisation Whereas specimens used for X-ray work contain a large amount of amorphous material the thin films used for the electron-diffraction work are almost entirely crystalline, the patterns showing sharp rings with little or no trace of background haloes.

b) Orientation Films picked up from a water surface indicate a pronounced orientation such that the b crystal axis film but the a axis is inclined to it and ~~the~~ consequently the c axis is inclined away from the normal to the film plane. This tilt is explained as being due to steric hindrance arising from an akwardly shaped end-group $-CH=CH_2$.

c) Deformation. On stretching the films the orientation changes and the long chains tend to lie in the direction of extension.

d) Films deposited on metal surfaces. The molecules are found to be relatively mobile. ~~The~~ They may be oriented mechanically to produce a structure basically similar to that of the stretched films.

e) Effect of temperature. As temperature is raised the a/b axial ratio varies in a similar way to that of the shorter paraffins so that the structure tends towards a pseudo-hexagonal form. Melting, however, sets in before this pseudo-hexagonal form is attained.

Films heated to a little above their melting point(180 C) show"memory" of their previous orientation on recooling, but if heated to 300 C this "memory" disappears.

H.Kolsky (PhD. thesis 1939) carried out a theoretical investigation on the interpretation of the halo patterns obtained from amorphous polymers and applied his results in an examination of the electron-diffraction patterns from dimethyl butadiene, cellulose and polystyrene.

Briefly,he showed that estimates of interatomic spacings from radii of haloes, based on the application of Bragg's law are subject to errors from two major sources (in addition to the uncertainty in the estimation of the intensity maxima) These are firstly that where maxima are broad, as inthese cases,the resulting intensity curve may be a superposition of curves from several spacings which do not differ greatly , and the resulting maximum has no direct meaning, and, secondly, that where the molecules are arranged at random the effective (projected) mean spacing is less than the actual spacing and the spacing estimated directly from application of Bragg's Law will therefore be low. Confirmation of this is seen in the patterns from stretched dimethyl butadiene in which both the fibre diagram from the oriented molecules and the halo pattern from the amorphous material are apparent; the sharp arcs of the former are seen to lie just inside the maxima of the corresponding haloes.

A better approximation to the true spacing is obtained by using a formula due to Debye(which takes into account the distribution function) but in order to apply this it is necessary to know the order of the diffraction considered.

Summarising, it may be said that where an estimate of the orders of diffraction in a halo pattern is available either from a partially oriented specimen or from general chemical knowledge of the structure or from any other source, the halo pattern yields useful information regarding molecular structure, but where such knowledge is not available the information obtainable is somewhat limited. In the three materials examined, the orders of diffraction could be inferred and it was possible to determine the identity periods along the polymer chains. In the case of the dimethyl butadiene which showed some orientation on stretching, a study of the intensity distribution among the layer lines demonstrated that the chains take the <u>cis</u> form relative to the double bonds.

<u>D.G.Fisher</u>(Proc.Phys.Soc. 1948,<u>50</u>,99 and thesis) obtained electron-diffraction patterns from natural rubber, gutta percha, and polychloroprene, all of which showed crystalline ordering on stretching

Thin films of natural rubber yielded electron-diffraction patterns which exhibited, in addition to the Laue arcs, a pattern of diffuse zones. This latter is reminiscent of pattrns obtained by Charlesby, Finch, and Wilman for anthracene and other aromatic compounds; it is explained on the basis of thermal vibrations of the long-chian rubber molecules in the crystalline regions. It arises from molecules in the crystal but is similar to the pattern which would be obtained from independent molecules oriented as in the crystaland is therefore particularly valuable in the elucidation of complex molecules since it gives a direct indication of the configuration of the molecule independent of ots mode of fitting into any particular crystalline lattice. An examination of this pattern in relation to two suggested structures for the rubber .

led to the view that the molecule approximates more closely to a simple form having standard bond lengths and angles and planar units than to the more complex form suggested by Bunn on the basis of X-ray results.

Some subsidiary experiments with stretched rubber films at low temperatures demonstrated an ~~orientat~~ interesting phenomenon Normal hydrocarbons ~~deposited-~~ evaporated onto the stretched rubber surface showed azimuthal orientations closely associated with that of the rubber substrate.

The patterns from gutta percha led to the identification of three separate crystalline forms where only two had previously been observed.

The patterns from polychloroprene showed considerably less crystallisation than natural rubber or gutta percha but indicated an interesting intermediate stage of uni-directional ordering in which it appeared that the long molecules were oriented in the direction of extension and were separated by a fixed distance but were quite free to slide over one another in the direction of their lengths.