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The Diffraction of Waves by Crystals

By KARL K. DARROW

This is an elementary introduction to the phenomena of diffraction of waves by crystals, one of the most striking and important discoveries of the last twenty years of physics. These phenomena have proved that X-rays and electrons are partly of the nature of waves, and have supplied the best available methods of measuring their wave-lengths; while on the other hand, the study of the diffraction-pattern of a crystalline substance makes it possible to determine the arrangement and the interrelations of the atoms with a precision and fullness heretofore unimagined, which has already yielded knowledge of great value in all the fields of science and promises immeasurably more.

THE diffraction of waves by crystals was discovered in 1912, the very year in which the first of the revolutionary new theories of the atom was being thought out by Bohr. But while since then the atomic theory has undergone mutation after mutation—until one can hardly guess any more what is stable and what is unstable, what it is expedient to retain and what should be forgotten— the consequences of that other discovery have steadily and serenely broadened out. Already they have penetrated into more fields of science than the deductions from the new atomic theories. Eventually their effects, not only on physics but on mineralogy and chemistry and engineering practice and even on biology, may well become so great that diffraction by crystals will prove the most valuable instrument for research which the physicists of our time have presented to the world.

The discovery was not an accident, but a rarely perfect example of theoretical foresight. A mathematical physicist, von Laue, was pondering the theory of diffraction by ruled gratings and the other standard instruments of optical research. He was at a university (Munich) where Roentgen was professor and interest in X-rays was intense. There was a controversy then over the question whether these rays are waves or corpuscles. In those days, the antithesis was absolute; people thought that either answer must exclude the other; they did not realize that in ten or fifteen years they would be accepting both. Towards 1912 the weight of evidence seemed to be forcing the wave-theory from the scene. There was however one piece of evidence which could be interpreted in its favor, provided that the wave-length of the rays was of the order 10^{-8} centimeter. It was also known,

though the knowledge was at that date very recent, that the number of atoms in a cubic centimeter of an ordinary crystal is such that the average distance between them must be of that same order. It was also known, as it had been for many years, that the atoms of a crystal must be arranged in a regular order—a pattern, a network, or a lattice; like soldiers on parade, except that the atoms parade in three dimensions instead of two. Laue was aware of all these facts; and one day it occurred to him, taking them all together, that if a beam of X-rays was truly wave-like a crystal would *diffract* it— would split it into a multitude of diverging beams, themselves grouped in a pattern so curious and so symmetrical that if such a pattern were indeed observed it could not be fortuitous, but by itself must prove the assumption.

The experiment was performed by two of Laue's colleagues on "the experimental side," Friedrich and Knipping, with a crystal of zincblende and a beam of X-rays from an ordinary X-ray tube. The multitude of diverging beams made their appearance: the diffraction pattern was exactly as predicted.

From this magnificent point of departure the advance was early and rapid, in two directions. Crystals being able to diffract X-rays, the phenomena could be used as sources of information either about the rays or about the crystals. The former field was dominated the sooner. In the fifteen years since the discovery, the technique of using crystals to analyze X-ray spectra and measure the wave-lengths of X-rays has been carried near to perfection. Nearly all the rays which atoms can emit from their electron-shells, many of those which proceed from their nuclei, have now been measured; and the advantage to atomic theory is immense. It is true that one can no longer say that except for diffraction by crystals we should not know that the X-rays are wave-like or what their wave-lengths are; for now physicists are beginning to map the X-ray spectra with optical ruled gratings. But the crystals were the first to present us with these data, and in most cases, I suppose, they are still the best.

By contrast, the field in the other direction—the exploration of the arrangement of atoms in crystals by means of their diffraction patterns —seems unlimited. Newton's "ocean of undiscovered truth" is not too strong a metaphor. The crystalline state, it transpires, is universal. It is not confined to the lovely glassy specimens of the mineralogical museum, with their smooth facets, sharp edges and pointed pyramids—the jewels of Nature, from which the jewels of art are made by perfecting or perverting the original design. The vivid geometry of such as these is a signal of a regular, a "crystalline" ar-

rangement of the atoms; but where the advertisement is wanting, the inner order may be none the less precise.   Nearly every solid substance owns it; metal, brick, stone and sand, wood, cotton, wool and bone approach in varying degrees to crystalline perfection; so do films of grease and films of liquid, and even in the middle of a liquid mass there are traces of regular arrangement.   The diffraction patterns disclose all this, revealing the fine details of crystalline structure even where the eye sees nothing but a shapeless mass.

Even with the beautiful finely-formed crystals of the minerals in museums, the diffraction-pattern teaches more than the crystallographer could learn without it.   I would not disparage the crystallographers.   Perhaps there are few physicists who realize how far they went before the time of X-rays, and certainly any who thinks that it was Laue's work which showed the world how to tell whether a crystal is cubic has specialized in his science not wisely but too well. Organic chemists also made many inferences about the arrangement of atoms in large organic molecules, which the X-rays are now beginning to verify.   But the X-rays in these few years have carried us clear beyond the farthest reach of inference to which chemist or crystallographer could have aspired.

Another service of diffraction is its disclosure of the ways in which the tiny crystals making up an ordinary piece of metal are distributed, their orientations in particular; these are liable to variations whenever the metal is twisted or extended or rolled or hammered or annealed, and it may some day be possible to explain from them the variations of the mechanical properties of the mass.

Yet another service of diffraction, and a very great one to the physicist, is the information which it gives about the individual group of atoms—sometimes indeed about the individual atom—which is repeated over and over again to form the crystal.   The beams of the diffraction-pattern shooting off in their various directions may be regarded as the beams proceeding in those same directions from any individual group of atoms, tremendously amplified by the cooperation of the other groups which go with it to make up the entire crystalline network.   The amplification-factor can often be estimated; and dividing the observed intensities by it, one obtains an idea of the diffraction-pattern which one group of atoms by itself would form, and from this in turn may infer something about atoms.

Diffraction-patterns are not formed exclusively with X-rays; crystals may build them out of waves of another sort.   Towards 1924 Louis de Broglie suggested that electricity and matter are partially wave-like in nature.   The philosophy of physicists had changed since 1912,

26

and it was no longer necessary to lay down an "either . . . or" alternative. It was conceivable that in spite of all the evidence that a stream of negative electricity through a vacuum consists of particles, yet in some ways it might act as though it consisted of waves. In 1925 Elsasser did remark that such a stream might be diffracted by a crystal; for the wave-lengths which de Broglie had assigned to electrons, moving with such speeds as are customary in technical vacuum tubes, were again of that order of magnitude 10^{-8} cm., which had suggested to Laue that X-rays might be diffracted by crystals. Early in 1927 Davisson and Germer looked for the diffraction-pattern of negative electricity with a crystal of nickel, as Friedrich and Knipping nearly fifteen years before had looked for that of electro-magnetic radiation with a crystal of zincblende. The techniques were very different, and for a time there was confusion due to the refraction of the electron-waves in the crystalline substance; but even at the start they found a pattern very like that which was predicted, and when the influence of refraction was understood, the discrepancies were cleared away. So they proved that negative electricity is partly of the nature of waves, and initiated the spectro-scopy of electrons; and in examining how the diffraction-pattern was affected by films of gas on the surface of the crystal, Davisson and Germer were the first to perform a crystal analysis by electron-waves.

The accepted model for an ideal crystal—accepted now these last two hundred years—is an array of objects or particles much too small to be seen, all exactly alike, all oriented exactly alike, and spread out in three-dimensional space with perfect regularity of arrangement. These particles are marshalled in ranks and files like soldiers on parade, except that the parade is in three dimensions instead of two, as if on every floor of some colossal building a regiment were drawn up. Were the arrangement only in two dimensions, I could find numberless other examples—the pattern of printed wallpaper, a chessboard, the meshes of a handkerchief, the array of jacks on a telephone switch-board, the sections or the townships into which mid-western prairie country is divided, the unvaried multitude of windows on the walls of many a skyscraper. But in three dimensions the only similes which present themselves are a honeycomb, and cannonballs piled in a heap such as are set around old war memorials, and the girders of a steel-frame building as we see them before the walls cover them over. All these pictures fall very far short of suggesting the millions upon millions of particles which are conceived to constitute even the smallest of visible crystals, or their continual trembling in thermal agitation.

The particles are said to be arranged upon a *lattice*. The lattice is

an abstraction, like a coordinate-frame, or the network of meridians and circles of latitude which intersect upon a map. It is usually conceived as a network of three sets of parallel planes, the planes of any set following one another at even intervals of spacing. For convenience of drawing, each plane is sketched as a network of two sets of parallel lines (Fig. 1). The intersections of three planes are the
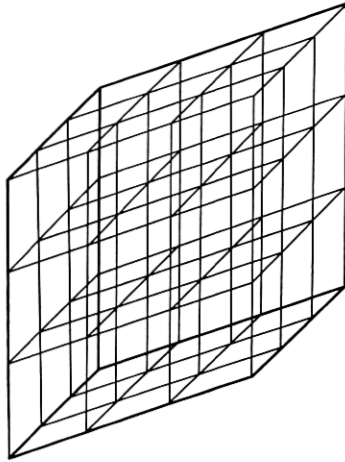

Fig. 1—A space-lattice.   Intersections of three lines are lattice-points.

lattice-points; the intersections of two planes are *axes of the lattice.* Axes of the lattice run in three directions, and along each there is a constant spacing from one lattice-point to the next. The three may be at right angles to one another, and the spacings along all three may be the same, in which case the lattice is *cubic;* but this need not be the case. All these ideas are required to make definite the notion of *regularity of arrangement* which as I have mentioned is the distinction of a crystal. They will probably become clearer in what follows.

Around each lattice-point a particle is placed. I say *around* rather than *at,* for it is desirable to think of the particles as rather bulky, each containing a lattice-point at some definite place within itself, and filling an appreciable part of the space extending from that point to its neighbors. Moreover it is desirable to think of them as quite irregularly-shaped objects, not as spheres, the way they are drawn in Fig. 2. Some crystals do have such properties that the picture of spherical particles is nearly adequate; but usually, if we were to assume that the particle has the full and complete symmetry of the sphere, we should be restricting the model to such an extent that it could not be adapted to the properties of the actual crystals. The observations

of crystallographers on the forms which crystals assume and the ways in which they act on light lead to conclusions about the symmetry of these elementary particles; and it is found that while they usually have some degree of symmetry, they do not have that full degree which the sphere represents. In later sketches, therefore, I have followed Bragg in representing the particles by perfectly unsymmetrical figures, like large commas (Figs. 4 and 5). Only, they should be unsymmetrical in three dimensions instead of only two; the reader may conceive each comma as being rough on one side, smooth on the other.
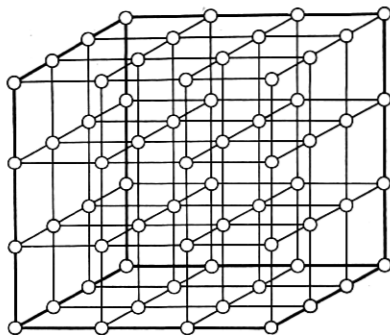

Fig. 2—A cubical space-lattice, with particles of full spherical symmetry indicated at the lattice-points.

The next obvious question is: what is the relation between these particles, and the atoms of the crystal if it is a crystal of some chemical element, or the "molecules" if it is a crystallized chemical compound? One might expect that they would be the same; but one would usually be wrong. When for instance gaseous potassium or argon condense into crystals, it takes four atoms of the argon gas to make up the elementary particle of the argon crystal, while that of the potassium crystal consists of two atoms.[1] With chemical compounds the crystal particle may be the molecule, part of the molecule or a group of several molecules. I will consequently use for it hereafter the colorless name *atom-group*, with occasional variation by the conventional but not very descriptive term *unit cell*.

Now to visualize the diffraction-pattern, let us conceive the crystal set at the centre of a transparent bulb painted inwardly with some fluorescent matter, so that wherever X-rays or electrons fall upon its

[1] Provided that we conceive the lattices as cubic, which is customary. There happens to be in these cases something like what in other fields of physics is called a "degeneracy": one and the same lattice may be viewed either as cubic or (with a different choice of axes) as non-cubic, and with the latter conception the "particle" turns out to be a single atom.

inner surface it will shine. The crystal should be very small in comparison with the bulb, and the incident beam of waves extremely narrow. We suppose that this beam comes in at a window, and follows a diameter of the bulb, and the unscattered part after flowing through the crystal goes out through another window. If the rays are plane-polarized X-rays, the electric vector will remain constantly parallel to some direction at right angles to the beam. If they are unpolarized X-rays, the electric vector will run or swing rapidly around in the plane at right angles to the beam. Thus far it is customary to use in crystal analysis X-rays which either are unpolarized, or have the slight degree of polarization usually imprinted on such rays at their excitation in a discharge-tube or a Coolidge tube.[2] We do not positively know whether electron-waves are polarized, but we cannot alter their degree of polarization whatever it may be, and it seems probable that they are not.

This "imaginary bulb" is very nearly realized in practice, although instead of a fluorescent screen it is customary to use a photographic film on which the imprints of the diffraction beams are permanent spots. The film is usually flat instead of spherical, so that the rings presently to be mentioned are distorted from circles into ellipses. Often an ionization-chamber (for X-rays) or a Faraday chamber (for electrons) is swung around in arcs over a spherical surface centred at the crystal, and the current which it reports is plotted as a function of its position; the curves then display peaks wherever the chamber is so placed as to capture a beam. In what follows I shall use the terms "diffraction beam," "diffraction peak" and "diffraction spot" almost as synonyms.

On the inner coating of the bulb, then, we shall see the diffraction-pattern of the crystal. It will be an assemblage of luminous spots arranged in a symmetrical array recalling the symmetry of the crystal lattice. In making this statement I am anticipating what is presently to be proved, or rather to be deduced from the fact that the atom-groups of the crystal are marshalled on a lattice. Indeed, if the incident waves are monochromatic or nearly so, we shall not see even spots unless by happy accident or by a careful choice of wave-length. Most waves are not diffracted by a three-dimensional crystal lattice. If we could reduce our crystal to a single plane of atom-groups forming a two-dimensional network, there would be a pattern of spots for any wave-length whatever. If we could isolate a single row of atom-groups, there would be rings of light on the coating of the bulb,

[2] Because the electrons which produce the rays in falling onto the target of the tube are all moving along parallel lines when the impinge upon it.

instead of only spots. And if we could remove all but one of the groups, and then in some magical way magnify the luminescence which the waves that this survivor scatters produce at the wall of the bulb, then we should see the wall shining all over with a continuous brightness, sinking to zero perhaps nowhere, perhaps at occasional points.

Reverse the process, starting from the solitary atom-group. The intensity of the scattered waves of which it is the source varies continuously with direction, and the brightness of the wall of the bulb varies correspondingly from point to point. If this brightness is proportional to that intensity, its distribution over the spherical wall is the scattering-pattern or diffraction-pattern of the atom or group of atoms. However it is immeasurably too faint to see.
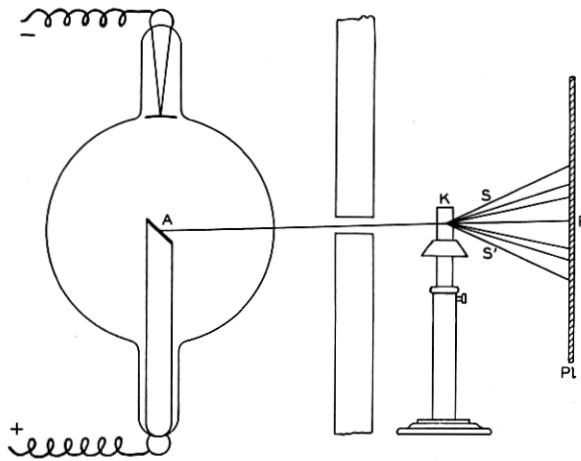

Fig. 3—Illustrating how a beam of waves is split by a crystal (at K) into diffraction beams forming spots on a plane screen (P). (Apparatus of the first experiment on X-rays by Friedrich and Knipping.)

Add now to the solitary group a great number of similar and similarly-oriented groups of atoms, forming altogether a long and evenly spaced row. The luminescence now fades out everywhere except over certain rings upon the wall, but along these rings it is enhanced. The newly-added atom-groups have amplified the waves scattered by the original one along the directions leading to these rings; in compensation they have effaced those scattered in other directions. These are effects of interference.

Add next a great number of such rows of similar and similarly-oriented groups, forming altogether a lattice in a plane. The rings now all fade out except for occasional spots, which however are much

brighter than they were before. Interference between the waves scattered from the various atom-groups has exalted the brightness of certain points on the wall of the bulb, to the detriment of all the rest; it has amplified the diffraction-pattern of the single group in certain directions, and destroyed it in the others. The spots due to the atoms of a single plane have been observed with electron-waves, but never with X-rays (Figure 6).

Add finally a great number of such planes, thus building the three-dimensional crystal. Now except for certain wave-lengths the spots vanish altogether. For those exceptional waves, however, they are intensified into visibility. One group of atoms by itself would have produced a complete diffraction-pattern—at least we suppose that it would—but never one intense enough to be perceived. But when it is joined with an enormous number of its peers in a lattice, they all conspire to enhance not indeed the entire pattern, but the intensities at certain of its points. The physicist, if he varies the direction in which the rays fall upon the crystal or the wave-length of the rays or both, can observe a great number of these intensities which the crystal has so obligingly amplified for him; and out of them he can reconstruct the entire diffraction-pattern of the individual atom, which but for this amplification would have been forever out of his reach.[3]

I must not leave the impression that the diffraction-pattern of the atom-group is amplified equally in all the directions in which the lattice amplifies it at all. Amplification depends on direction. If the observer sees two spots produced by diffraction-beams inclined say at 45° and at 60° to the primary beam, he is not to infer that the ratio of their brightnesses is the ratio of the intensities of the waves scattered at 45° and at 60° by the individual group. A correction-factor must be employed to translate one ratio into the other. Later on we will consider this factor. Meantime, not forgetting it but not yet taking it into account, we will calculate the directions in which amplification occurs.

We start as before from the solitary atom-group. In Fig. 4 this is depicted as a two-dimensional figure, irregular and utterly without symmetry. It ought to be conceived as a three-dimensional, perfectly unsymmetrical mass. This depiction is meant to imply that if a stream of waves strikes the atom-group on any side, the intensity of the waves scattered in any direction—what above I called the diffraction-pattern of the group—is or may be a thoroughly unsym-

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[3] If the atoms or atom-groups of a substance would orient themselves all alike without at the same time spacing themselves at regular intervals, and without being too much crowded together, the entire pattern would be amplified instead of certain spots only.

metrical function of direction. Also it may depend on the side of
the group on which the primary waves impinge, or, in better words,
on the direction whence they come. Of course, in any particular
case, it might turn out to be a symmetrical function of direction, or
it might be the same function whichever the side of the atom which
the primary waves encounter; but we should not rely in advance on
either of these simplicities. I must qualify this statement somewhat:
the crystallographers have their ways of learning more or less (and
sometimes a good deal) about the symmetry of the atom-group, and
thus foretelling certain aspects of its diffraction-pattern. Moreover
in many cases it is possible to make in advance a good estimate of the
absolute intensity of the scattered waves. It will do no harm to
remember these encouraging facts; nevertheless it will be best for us
to keep our ideas fluid by supposing an atom-group of absolute
asymmetry, the scattering-pattern of which is one of the ultimate
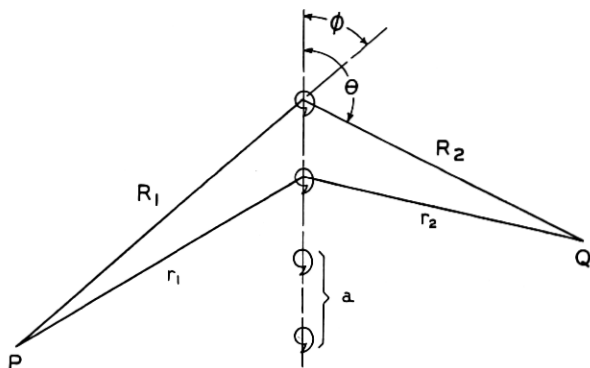objects of the quest.

Fig. 4—Illustrating diffraction by a single file of atom-groups.

I must state with all emphasis that whatever may be foretold or
measured in the scattering-pattern for electromagnetic waves (X-rays)
need not always be valid in the scattering-pattern for electron-waves.

Consider now the amplification which ensues when other atom-
groups are added to the first one, to form with it an evenly-spaced row.

Denote by a the distance between corresponding points in adjacent
groups (Fig. 4). Suppose the primary waves to emanate from a
point P, while the observation of the scattered intensity is made at a
point Q (on the wall of the bulb, to continue the picture). In practice
the distance a is so submicroscopically small, that P and Q are practi-
cally infinitely far away; yet it is easiest to begin by thinking of them
as nearby, and passing to the limit. Designate then by R_1, R_2 the

distances from any atom-group A to P and Q, by r_1 and r_2 the distances to these points from the adjacent group B. We shall not assume that R_1, r_1 are coplanar with R_2, r_2, though owing to the flatness of the page the drawing must make them seem so. Denote by ϕ, θ the angles between the direction of the row of atom-groups and the directions in which the primary and the scattered waves advance, respectively—these latter being the directions from A *away from P* and *towards Q*, respectively.

Under what condition will the waves scattered by the atom-groups A and B reinforce one another best at Q? Best reinforcement will occur, greatest enhancement of the effect of either atom by the presence of the other, when the waves from both arrive at Q in identical phase. This will occur when Q is so located that the path from P to Q *via* A either is equal to the path from P to Q *via* B, or differs from it by an integer number of wave-lengths.[4]

$$(R_1 + R_2) - (r_1 + r_2) = (R_1 - r_1) + (R_2 - r_2) = n\lambda;$$
$$n = 0, \pm 1, \pm 2, \ldots \quad (1)$$

Let P and Q recede to infinity; in the limit:

$$R_1 - r_1 = a \cos \phi, \qquad R_2 - r_2 = -a \cos \theta \quad (2)$$

and the condition for optimum reinforcement at Q is this:

$$a(\cos \theta - \cos \phi) = n\lambda. \quad (3)$$

In all directions for which θ satisfies this equation, there will be maximum amplification of the diffraction-pattern of A (or B) by the presence of B (or A). For every such value of θ, there will be a ring on the wall of the bulb. If the two atom-groups by themselves could make the wall fluoresce brightly enough, we should see annular fringes. They would be broad and hazy, for though the cooperation between the scattered waves is best at the definite angles determined by equation (3), it is also very good over quite a range of nearby angles. Equation (3) would give the locations of the central rings of the broad fuzzy bright fringes. Thus, when visible light is sent through a pair of parallel similar slits in a screen, one sees hazy fringes superposed on the diffraction-pattern which either slit by itself can produce; and the formula analogous to equation (3) locates the central lines of these.

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[4] This statement implies the tacit assumption that there is a constant phase-difference (whether it is zero or not is of no importance) between the primary waves striking an atom-group and the scattered waves leaving it—the very important assumption of *coherence*.

This allusion to parallel slits in a screen will simplify the next steps. It is well known that when to a pair of parallel slits, new ones just like them are added at equal intervals one after the other, the fringes are not displaced. The bright fringes shrink, the dark ones widen, but their central lines remain unshifted. As more and more slits are added, as more and more lines are ruled on a metal surface to constitute a grating, the dark fringes encroach steadily on the bright ones, and it becomes easier to locate the central lines of these latter with precision. As they grow narrower, they brighten, the energy which was lavished over a wide angular range being gathered into a small one as it is progressively increased by the addition of new slits or rulings. So there is a double gain. In the limit, nothing remains but the central lines, and these are brilliant. And in the limit, these lines are still located where the formula derived for only two slits predicted that the maxima of brightness should be found.

Now in the same way, when to a pair of like and likewise-oriented atom-groups additional such groups are added so as to form an evenly spaced row, the annular fringes on the wall of the ensphering bulb are not changed in location but in distinctness. The bright fringes contract into brighter rings, the dark ones broaden into (relatively) dark bands. *The multitude of the atoms sharpens the diffraction-pattern.* In the limit, the bright rings are very sharp and brilliant, and they are still located at exactly the angles predicted by equation (3) derived for two atom-groups only. Remember however that a ring may not be equally bright all around its circuit. It is only an enhancement of the scattering-pattern of the individual atom-group; and this in general will vary from one point to another.

So much for the single row or file of groups of atoms! We must now pass to two dimensions, and predict the diffraction by a plane in which groups are arranged in a network. In the plane, rows of atoms lie side by side at equal spacings. We might start with one of the rows, and estimate how its diffraction-pattern is amplified by the cooperation of a second and then a third and a fourth and eventually an infinite number of added rows laid parallel with it at equal intervals. Owing to this equality of intervals and the new periodicity which it entails, the diffraction-rings of the pattern of the individual rows will be amplified not uniformly, but only at certain points; precisely as owing to the equal intervals between the atom-groups of the single row these amplified the pattern of the individual group not uniformly, but only over certain rings. However we can reach this result in another way, by considering three atom-groups forming a triangle, as formerly we considered two forming a pair.

Start then as heretofore from a solitary atom-group A, and add to it two others B and C (Fig. 5). They must not all three be collinear; as a rule it is best that B and C should be the two groups nearest A.[5] As before P stands for the source of the primary waves, Q for the point (on the wall of our imaginary bulb) where the scattered waves are to be measured. The question is: under what condition do the scattered waves from A and B and C all three reinforce one another best at Q? under what condition do the waves from all three groups arrive at Q in identical phase?
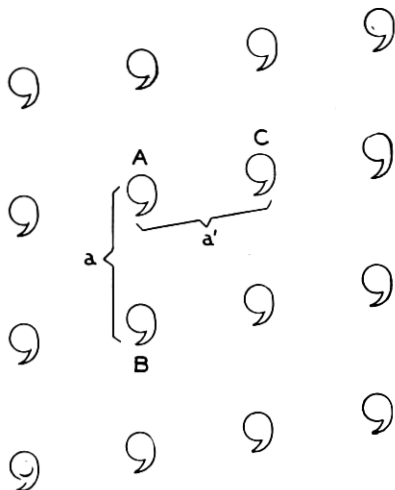
Fig. 5—Illustrating diffraction by a plane of atom-groups in regular array.

Evidently we have only to restate the condition that the waves from A and B arrive in identical phase, and supplement it with one exactly like it for the waves from A and C. We have only to repeat equation (3), and beside it write another like it in which a is replaced by a', the distance from A to C; ϕ by ϕ', the angle between the direction of the primary waves PA and that from A to C; and θ by θ', the angle between the direction of the scattered waves AQ and that from A to C. When the waves from all three atom-groups reinforce one another, both equations prevail:

$$a(\cos \theta - \cos \phi) = n\lambda, \tag{3}$$

$$a'(\cos \theta' - \cos \phi') = n'\lambda. \tag{4}$$

[5] The choice of groups to serve as B and C is purely a question of expediency. The same results are reached whichever two we choose, so long as they are not collinear with A; but the results when reached are in a form which depends upon the choice, and is most convenient when AB and AC are parallel to the crystallographic axes in the plane.

In these equations n and n' stand for integers but they need not stand simultaneously for the *same* integer. In all directions for which θ and θ' satisfy equations (3) and (4), there will be maximum amplification of the diffraction-pattern of any atom-group by its pair of neighbors.

Now equation (3), with various integer values 0, 1, 2, $\cdots$, substituted for n one after the other, described a system of rings on the wall of the bulb—parallel rings like latitude-circles, with the poles at the points where the bulb is intersected by the line drawn through its centre parallel to AB. Likewise equation (4), with various integer values for n', describes a system of rings oblique to the first, having *its* poles at the points where the diameter drawn parallel to AC
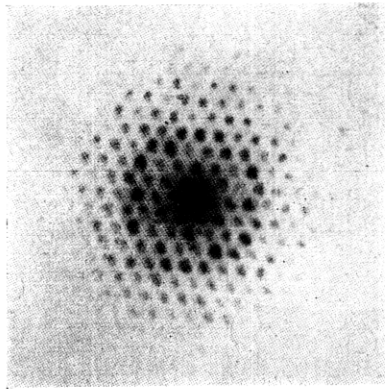

Fig. 6—Diffraction pattern of electron-waves attributed to the array of atom-groups in the superficial plane of a mica crystal. (S. Kikuchi; *Japanese Journal of Physics.*)

through the centre of the bulb reaches the wall. There are intersections between the rings of the two systems, and these intersections are the points—the discrete, the finitely numerous points—where the diffraction-pattern of the atom-group is most greatly amplified. So long as there are but three of the groups, these points are merely the centres of broad, hazy, bright (of course, in practice, utterly invisibly dim) blotches. But when to the three groups we add enormously many others to form the extensive two-dimensional network of which a section is depicted in Fig. 5, interference eats away the edges of these patches and enhances their centres, and in the limit nothing remains of the diffraction-pattern except brilliant dots at the intersections of the rings.

The next and last step follows immediately. The crystal is built

up of planes of atom-groups laid parallel to one another at equal intervals. Suppose the space above and below the plane of Fig. 5 to be thus stratified; select, from the stratum just above or just below that figured on the page, an atom-group close to A, preferably the closest. Call it D; let a'' stand for the distance from A to D, ϕ'' for the angle between the direction in which the primary waves advance and the direction AD, θ'' for the angle between the direction from A towards Q and that from A to D. When the scattered waves from all *four* groups $ABCD$ reinforce one another best at Q, all these three equations are valid simultaneously:

$$a(\cos \theta - \cos \phi) = n\lambda, \tag{3}$$

$$a'(\cos \theta' - \cos \phi') = n'\lambda, \tag{4}$$

$$a''(\cos \theta'' - \cos \phi'') = n''\lambda, \tag{5}$$

n'' standing for a third integer, which may or may not be the same as either of the other two. In all directions for which θ, θ', θ'' conform with equations (3), (4), and (5), there will be maximum amplification of the scattering-pattern of any atom-group by its triad of neighbors.

Now in thus adding a third equation to the previous one and two, we have made the conditions so severe that save in exceptional cases they are quite unfulfillable. Equations (3) and (4) confined the amplification-effects for which we seek to the points of intersection of a few rings belonging to two families, oblique to one another upon the wall of the bulb. Equation (5) supplies a third family of rings oblique to both, having for its poles the points where the diameter parallel to AD reaches the wall of the bulb. Agreement of phase between the waves scattered from A and B and C and D, optimum amplification, can occur only if and where a ring of the third family cuts rings of the first and the second just where these happen to cut one another. And when the set of four atom-groups $ABCD$ is repeated over and over again in an extensive crystal lattice, these points of optimum amplification are the only points where the amplification is great enough to enhance the diffraction-pattern into visibility. Visible luminous spots will appear on the coating of the wall of the bulb, only if three rings one from each family happen to intersect at the same point—*only by coincidence*, in the popular sense of the word.

To bring about such a coincidence, there are four practicable ways.

(I) If the incident beam is monochromatic, or comprises a narrowly limited range of wave-lengths, we can rotate the crystal—presenting it to the beam under varying aspects, and so in effect varying the

direction of incidence (the angles ϕ of the equations). Now and then the desired coincidence occurs.

This is Bragg's method. Instead of the fluorescent screen there is usually a photographic film bent to follow an arc, or an ionization-chamber swinging over an arc, of the surface of the imaginary bulb.

(II) If the incident beam is monochromatic or nearly so, and its wave-length can be varied continuously, we can keep the crystal motionless and the direction of incidence constant, and yet count on the coincidence turning up occasionally (Figs. 13, 15 and 16).
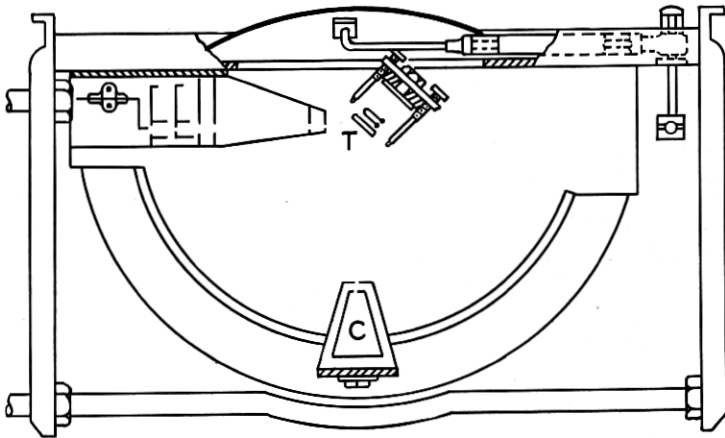

Fig. 7—Illustrating how a crystal (T) is mounted so that it may be oriented in various ways relatively to the oncoming beam of electron-waves (emerging from the electron-gun on the left) while a collector (C) is moved around to catch the diffraction beams. (Davisson and Germer.)

This is the method used with electron-waves by Davisson and Germer, the method whereby it was first shown that free negative electricity possesses some of the qualities of waves. To waves of this kind it is especially adapted, as their wave-lengths can easily be varied by varying the voltage-rise which endows the electrons with their speed. Instead of a fluorescent screen a Faraday chamber is used which swings in an arc over the surface of the imaginary bulb.

(III) If the incident beam is a mixture of wave-lengths covering a very wide range, we can keep the crystal motionless and the direction of incidence constant, and yet count on the coincidence turning up for some of the wave-lengths (Figs. 8, 9, 10, 11 and 12).

This is Laue's method, the first to be applied to the analysis of crystal structure, and the one whereby it was first proved that X-rays are waves—as people said at the time, which was 1912. Nowadays

we say that it was proved that X-rays possess some of the qualities of waves.

To make the spots appear a fluorescent coat or a photographic film is spread on a flat screen, instead of the spherical bulb. The locations on the screen can be deduced from those on the imaginary bulb by simple projection. Different spots are likely to be due to components of different wave-length in the primary beam, which will probably not be equally intense—a thing to be remembered when deducing the diffraction-pattern of the atom-group.
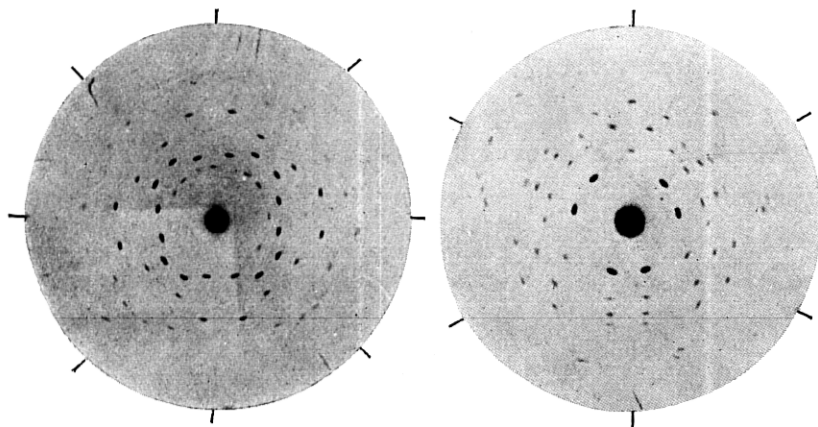
Figs. 8, 9—Diffraction-spots ("Laue patterns") obtained when a beam including waves of many wave-lengths is directed against a fixed single crystal. These are the historic patterns obtained with X-rays and a zincblende crystal by Friedrich and Knipping. The two correspond to different orientations of the crystal relative to the primary beam.

(IV) If the incident beam is monochromatic or nearly so we can present to it not a single stationary crystal but a confused mass of tiny crystals oriented in every way whatever. The desired coincidence will certainly occur for some among the crystals.

This is the "powder method" invented and applied to X-rays by Hull and by Debye and Scherrer, and applied to electron-waves by G. P. Thomson. The term implies that the chaotic mass of little crystals is obtained by pulverizing a large one; but small pieces or thin films of ordinary metals are likely to present quite as complete a chaos. The diffraction-pattern when formed on the wall of the bulb or on a flat screen set normal to the direction of the primary waves, consists not of separate spots but of continuous rings (Figs. 17–20).

Such in outline are the four great methods for the analysis of waves by crystals and of crystals by waves. Each has its own field; each

is beautifully adapted to certain problems as nature or art present them, not so useful or altogether useless for others. So for instance, the first is enormously the best for the spectroscopy of X-rays; the second is the outstanding method for long electron-waves (of the
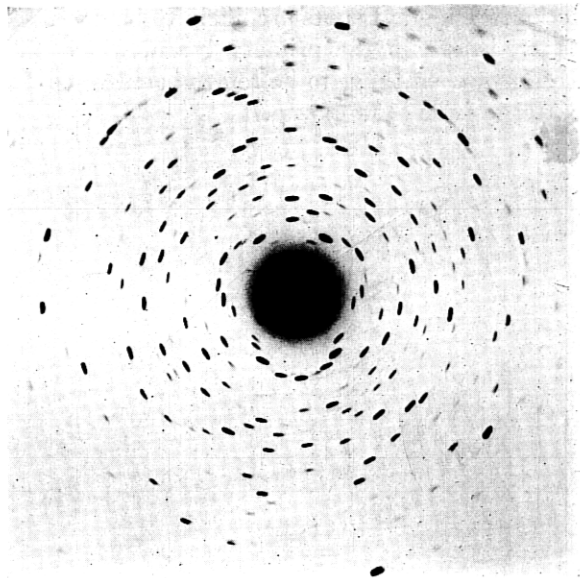

Fig. 10—Laue pattern of a mica crystal. (R. M. Bozorth.)

order of an Angstrom) and thin films of matter; the third is very useful in the analysis of reasonably large crystals formed by intricate chemical compounds, and the fourth is invaluable for substances like the metals of which the crystals are often very small and tangled up together. But the fourth does not carry the investigator so far into the delicate details of crystal structure, as do the third and the first, when large crystals are available; the third and the first are impotent, when large crystals are not to be had; and the second would be exceedingly toilsome with X-rays. The complete crystal-structure laboratory now contains apparatus for the first method, the third, and the fourth. Perhaps it will not be long before the second also is demanded.

Before entering into details I wish to comment on four assumptions which have crept unsignalized into these deductions.

(i) *The assumption of the unlimited perfect crystal.* As I have already said sufficiently, a crystal composed of only a few atom-groups would produce broad hazy spots instead of sharp ones, as a grating with

only half-a-dozen rulings would cast a spectrum of indistinct wide fringes instead of fine sharp "lines." It takes a multitude of atom-groups or rulings to produce the efficient destructive interference which etches out the borders of these blotches and leaves the centres standing up in high relief,—which in technical language makes the resolving-power high. In actual crystals, are there atom-groups enough?
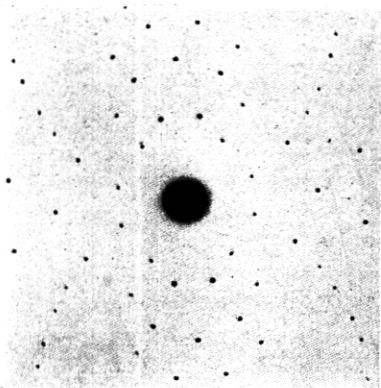

Fig. 11—Laue pattern of an iron crystal, showing that these crystals are built on a cubic lattice, though they are seldom so shaped as to reveal the fact. (G. L. Clark.)

In actual crystals, there are usually plenty. Infinite resolving-power or infinite sharpness of diffraction-pattern would of course imply infinitely many groups arrayed at perfectly regular intervals; but infinity and perfection are not workable ideas in physics. The practical question is, whether the actual defects of the diffraction-pattern from infinite sharpness arise because the crystal lattices are not prolonged enough, or from other causes. Usually they are due to other causes, which are numerous; for instance, appreciable breadth of the primary beam and appreciable size of the crystal. In the rare cases where the fuzziness of the diffraction-spots betokens that the crystal lattice is limited, the fact is often of scientific importance. The size of exceedingly small—submicroscopic—crystals can be determined in this way; the dimensions of colloid particles, and of the crystals in metals, are estimated thus.

(ii) *The assumption of stationary atoms.* This of course is faulty, for the atoms are in thermal agitation. Their oscillations make the spots of the diffraction-pattern somewhat hazy, and alter furthermore their relative intensities. Out of this circumstance the physicists

27

have drawn some profit; they have estimated the amount of the thermal agitation and determined how it alters as the temperature goes down. It decreases, of course; not however in such a way as to imply entire standstill at absolute zero, but quite the contrary.

(iii) *The neglect of absorption*. Since the energy of the scattered waves is drawn from that of the primary beam, this cannot retain its amplitude unaltered as it progresses through a crystal lattice; and calculations based on the assumption that all the atom-groups of a crystal scatter equally cannot be correct, for they do not all have
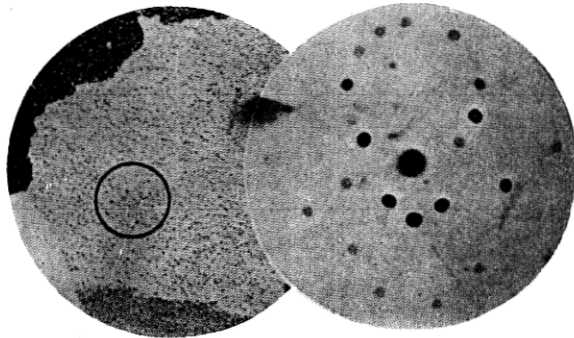

Fig. 12—Laue pattern of an aluminium crystal, introduced to show that if the primary beam does not happen to follow an axis of the crystal lattice there are still diffraction-spots though not so regularly arranged as in the previous cases. The crystal appeared under the microscope as an irregular patch on the metal surface (left-hand figure; the circle shows where the primary beam struck.) (Czochralski.)

incident waves of the same amplitude to scatter. This might well be serious, in a large crystal. It turns out however that large crystals are seldom if ever perfect; instead, they are likely to consist of smaller crystals tilted with respect to one another. The tilts are very small, but they are sufficient to suspend the consequences which should strictly follow from the assumption that absorption may be neglected.

(iv) *The neglect of refraction*. It has been tacitly assumed that there is neither bending of path nor change of wave-length when primary waves enter a crystal lattice or scattered waves emerge. Refraction however entails both of these phenomena; and refraction will in general occur. However with X-rays it is so slight (the refractive index is so nearly unity) that it need seldom be allowed for in crystal analysis, and must indeed be looked for with care and skill if it is to be detected. The like is true for short electron-waves. With the long electron-waves first studied, however, the refraction is considerable; and during the interpretation of the earliest data, there was serious confusion.

We will now work out the details of the diffraction-pattern of a *cubic* lattice. This kind of lattice is much the easiest to treat, and Nature has kindly bestowed it on many of the commonest crystals.
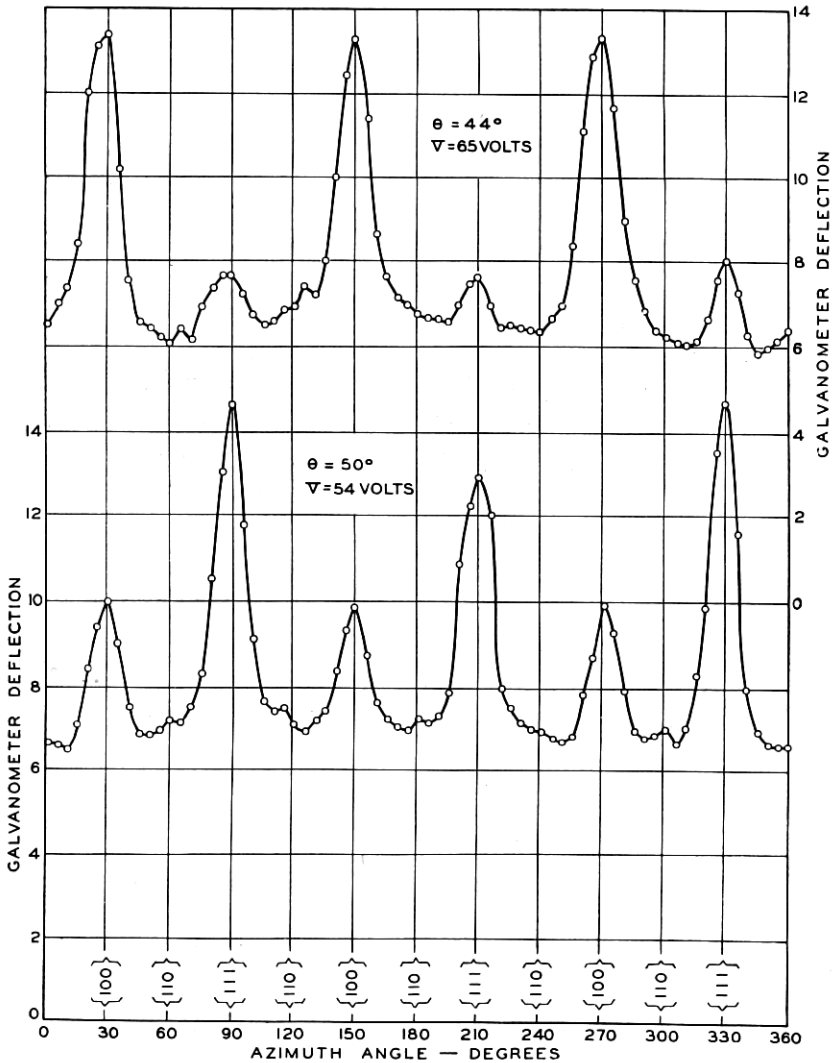

Fig. 13—Diffraction-peaks obtained with a fixed crystal and monochromatic electron waves (the two curves correspond to different wave-lengths chosen because they satisfy the condition for producing diffraction-beams) by moving a collector around so as to capture one beam after another.   (Davisson and Germer.)

In the cubic lattice, the nearest neighbors of any atom-group lie at equal distances from it along three directions at right angles to one another.   Moreover any atom-group in the entire (perfect) lattice

can be reached from the one first chosen by a sequence of three dis-
placements, one along each of the three directions and each an integer
multiple of the minimum distance, or "spacing," or "grating-constant,"
or "edge of the unit cube." In other words, any atom-group can be
brought into coincidence with any other by a sequence of three such
shifts. This way of putting it brings out the point that all the groups
in the lattice are oriented alike.

Denote by a the magnitude of the spacing. Install a system of
rectangular coordinates with its origin at some one atom-group, say A
of our previous picture, and its axes along the three directions stated.
Among the six neighbors of A we pick out three to serve as B, C, D
of our previous picture; say the three groups shifted from A through
the interval a in the *positive* senses of the three axes, so that the
coordinates of the four shall be:

$$A(0, 0, 0); \quad B(a, 0, 0); \quad C(0, a, 0); \quad D = (0, 0, a).$$

The directions of the diffraction-spots are to be deduced from the
general equations (3), (4) and (5), with all the simplifications from
which we benefit thanks to the lattice being cubic. The three spacings
are now all equal; but the greatest advantage is, that the various
cosines which figure in the equations are now direction-cosines, and
we can avail ourselves of the theorems to which direction-cosines
conform. There are two of these which we shall use: the theorems
that the sum of the squares of the direction-cosines of any line is
unity, and that the cosine of the angle between any two lines is the
sum of the three products formed by multiplying together corre-
sponding direction-cosines of the two. Denote by α_1, α_2, α_3 the
direction-cosines of the primary, by β_1, β_2, β_3 those of the diffracted
beam. The first three are the quantities $\cos \phi$, $\cos \phi'$, $\cos \phi''$ of
equations (3), (4) and (5); the second three are $\cos \theta$, $\cos \theta'$, $\cos \theta''$.
To bring the notation fully into harmony with usage I further write
h_1, h_2, h_3 for the integers n, n', n''.

Then by translating equations (3), (4) and (5) into the new notation
and adding two more supplied by the first of the foregoing theorems,
we form a family of five equations:

$$a(\beta_1 - \alpha_1) = h_1\lambda, \tag{6a}$$

$$a(\beta_2 - \alpha_2) = h_2\lambda, \tag{6b}$$

$$a(\beta_3 - \alpha_3) = h_3\lambda, \tag{6c}$$

$$\alpha_1{}^2 + \alpha_2{}^2 + \alpha_3{}^2 = 1, \tag{6d}$$

$$\beta_1{}^2 + \beta_2{}^2 + \beta_3{}^2 = 1. \tag{6e}$$

They involve seven variables: the wave-length, the direction-cosines of the primary or oncoming beam, the direction-cosines of the scattered or outgoing beam.
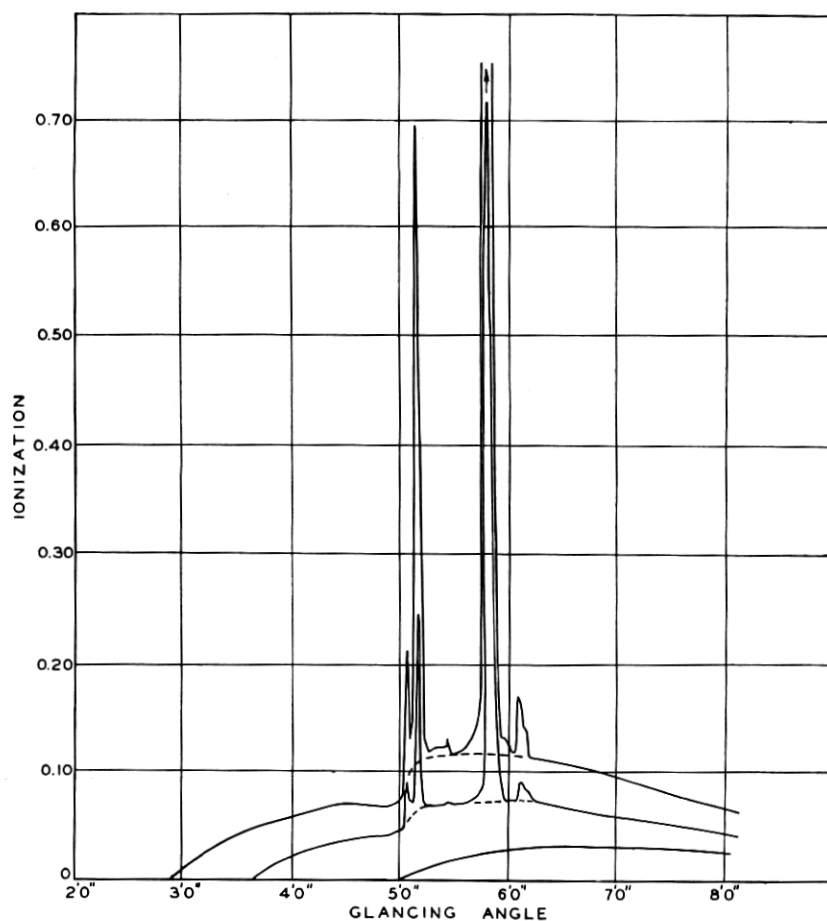

Fig. 14—Diffraction-peaks obtained with X-rays and a revolving crystal. The X-rays contained very intense waves of several different wave-lengths, and the collector was shifted continually so that it would capture a certain strong diffraction-beam produced by each of these in turn. (D. L. Webster.)

Now that we have this family of equations, the features of the four great methods of crystal analysis can be restated in few words. In the methods of Laue and of Davisson (II and III) the crystal and the primary beam are fixed in space, which amounts to prescribing values for α_1, α_2, α_3; then only four equations are left ($6d$ has fallen

out) and they contain four variables (λ, β_1, β_2, β_3) so that diffraction-spots can appear only for special sets of values of these four, to be obtained by solving the equations. In the original method of Laue, a wide range of values of λ is constantly provided, and the screen extends over a wide range of values of β_1, β_2, β_3; consequently the chance of observing spots is good. In the method of Davisson and
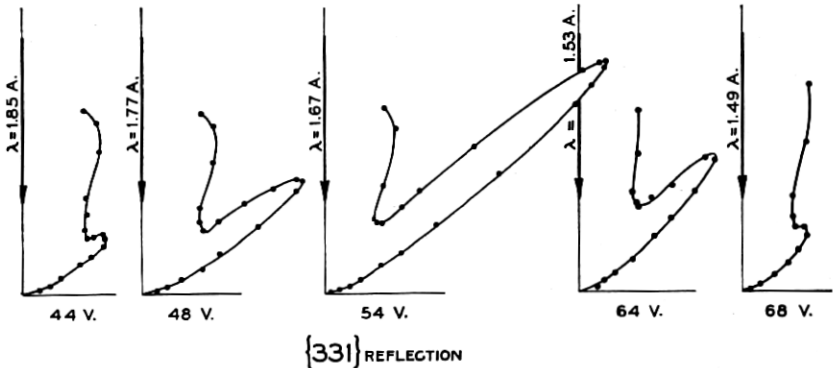

{331} REFLECTION

Fig. 15—Gradual appearance and disappearance of a diffraction beam as the mean wave-length of the primary waves passes through one of the values compatible with equations (6). (Davisson and Germer.)

Germer the different values of λ are realized in succession and a movable Faraday chamber searches out the peaks—a process much more long-drawn-out, but whenever one finds a peak one knows the wavelength to which it is due. With the other two methods the value of λ is prescribed, and consequently two at least of the direction-cosines α must be variable; therefore the crystal with its implanted coordinate-frame must be revolved, or else a multitude of crystals oriented every way must be placed in the path of the incident beam.

In the foregoing passage it seems as if I had taken for granted that the integers h_1, h_2, h_3 have fixed unchangeable values. As a matter of fact they may be any three integers at all. Strictly speaking, there is a different quintet of equations for every conceivable triad of integral values of the "indices" h. One might infer that in Laue's experiment the screen would be found completely covered with spots due to all the different triplets. However it turns out that only the spots for which all the integers are small stand out strongly enough to be seen. Meanings for these integers must now be found; but before finding them I will deduce two more equations out of the quintet.

Squaring and adding the left-hand members of equations (6a, 6b, 6c), doing the same with the right-hand members, equating the sums and

substituting from (6d, 6e), we obtain:

$$2 - 2(\alpha_1\beta_1 + \alpha_2\beta_2 + \alpha_3\beta_3) = \frac{\lambda^2}{a^2}(h_1^2 + h_2^2 + h_2^2). \tag{7}$$

Now by the second of the theorems concerning direction-cosines, the quantity in parentheses on the left is none other than the cosine of the angle between the direction of advance of the primary beam, and the direction of the scattered waves which go to form the spot or
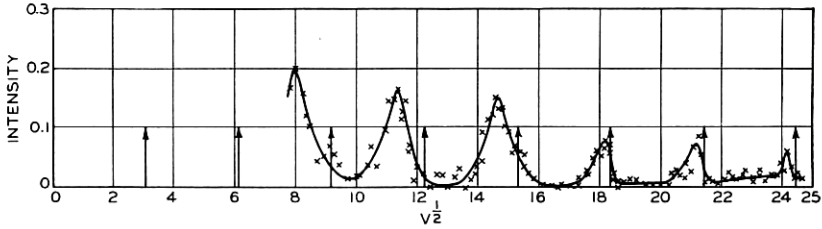

Fig. 16—Diffraction-peaks obtained with a fixed crystal and a fixed collector, *i.e.* with a constant value of the angle of deflection Φ, by varying the wave-length. (Davisson and Germer.)

diffraction-maximum of the indices h_1, h_2, h_3. If we conceive the diffraction-beam as the path of a portion of the energy which came with the primary stream and was deflected out of it, then this is the angle of deflection. Call it Φ. We have:

$$1 - \cos \Phi = \frac{\lambda^2}{2a^2}(h_1^2 + h_2^2 + h_3^2), \tag{8}$$

$$\sin\frac{1}{2}\Phi = \frac{\lambda}{2a}\sqrt{h_1^2 + h_2^2 + h_3^2}. \tag{9}$$

As the reader will observe, there is no allusion here, explicit or implicit, to the orientation of the crystal. This is therefore the appropriate equation for the "powder method," in which crystals turned every way are presented all together to the primary stream, and no one knows the orientation of any particular one—indeed the individuals are often too small to be seen.

Equation (9) describes a cone, having for its origin the mass of assembled crystals, for its axis the direction of the primary beam, for its apical semi-angle the angle Φ. Such a cone intersects any sphere centred at the crystals (our imaginary bulb), or any plane at right angles to the primary wave-stream, in a *ring*. There are in principle as many of these rings as there are triads of integers (h_1, h_2, h_3) except that when two different triads have the same value of the
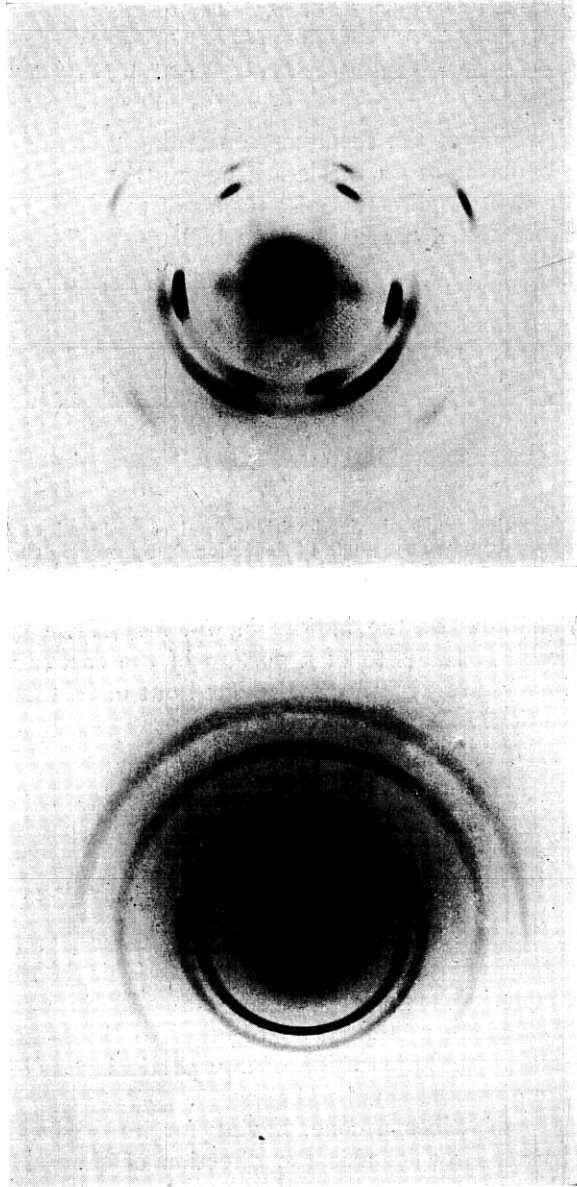
Figs. 17, 18—"Powder method" diffraction-rings obtained with X-rays and masses of small crystals of a nickel-iron alloy built on a cubic lattice. The rings are uniformly dark for one sample because the crystals were oriented quite at random, while for the other there were certain preferred orientations and the rings are "spotted." (R. M. Bozorth.)

sum-of-squares $(h_1^2 + h_2^2 + h_3^2)$, their rings coincide. They appear as dark circles on a photographic film so placed as to coincide with such a sphere or such a plane, exposed and subsequently developed. Each of these circles consists of the diffraction-spots with the appropriate indices cast by the various crystals. If the crystals are few, one sees the individual spots (the ring looks ragged and spotty, like a star-cluster); if they are few and small the spots are hazy; if instead of being turned at random they favor certain orientations, the circles are not evenly dark all the way round. But these are matters for later study.
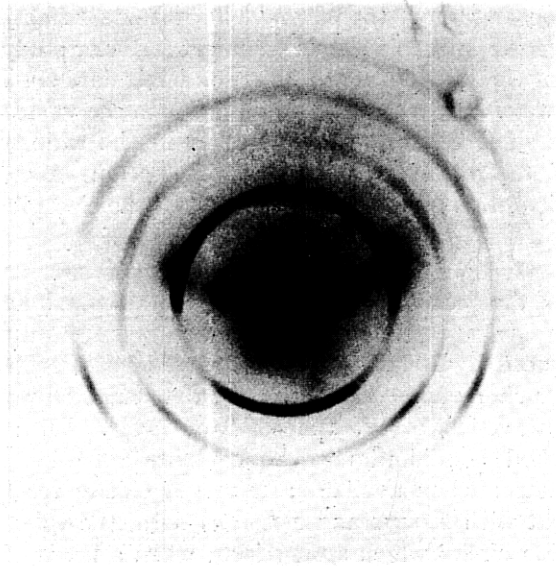

Fig. 19—"Powder method" diffraction-rings obtained with X-rays and a nickel-iron alloy. Like the alloys used in Figs. 17, 18, the crystals of this are built on a cubic lattice but with a differently-shaped atom-group, whence the changed appearance. (R. M. Bozorth.)

If we measure the radii of the first few rings and calculate from them the values of $(1 - cos \Phi)$ for the corresponding cones (a simple matter of geometry) we should find that these stand to one another as $1 : 2 : 3 : 4 \cdots$—provided, that is, that the lattice is cubic and the incident waves are nearly monochromatic. This is verified by experience for X-rays and electron-waves. The first ring consists of spots having the indices (1, 0, 0) or (0, 1, 0) or (0, 0, 1); the indices for the second ring are (1, 1, 0) or (0, 1, 1) or (1, 0, 1), while those for the third are (1, 1, 1). The reader can easily guess the indices

which yield other small integer values for the sum (h_1, h_2, h_3)—but not in every case.   There is no triad of integers of which the squares add up to seven, and there is none for which they add to fifteen. If the radii of the rings are plotted as a function of their ordinal number, there are breaks in the smooth curve beyond the sixth and the thirteenth, as if two were absent from the regular sequence. To express it more graphically than accurately, the seventh and the fifteenth rings are missing.   Other rings also may be wanting, for the atoms in the atom-groups may be so disposed that in certain directions the individual groups scatter no waves whatever;   and even if the lattice were so proportioned that waves in such a direction would be tremendously amplified, there would be nothing to amplify and no diffraction-spot.   But this also is a subject for later study.

   If we measure the radius of any ring and calculate $\sin \frac{1}{2}\Phi$, and then change the wave-length and repeat the process, the values so obtained for the sine should stand to one another in the ratio of the wave-lengths.   If the waves in question are electron-waves, then since their wave-length is inversely as the speed of the electrons, the radius of each ring should vary inversely as the speed of the electrons falling upon the crystals.[6]   This was verified by G. P. Thomson.   Knowing the values of the spacing a of the metal crystals which he had used— these values having been deduced in earlier days from the diffraction-circles produced by X-rays of known wave-length, scattered by the crystals of such metals—Thomson also determined by equation (8) the actual wave-lengths of the electron-waves.   With X-rays the powder-method is seldom used to evaluate wave-lengths, Bragg's being the better when available;   it serves chiefly for the study of lattices.   But with X-rays and electrons both, the splendid array of the diffraction circles which spring forth when a beam of either kind is sent against a mass of tiny crystals is the most easily adducible, the simplest and perhaps the most vivid and striking evidence that there is something wave-like in the nature of either.

   So much for the fundamental equation of the powder method! We will now derive, from equations $(6a \cdots 6e)$, the fundamental equation of the method invented by Bragg.

   We have seen that the diffracted beam forming the spot with

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   [6] More precisely, the radii should vary inversely as the momentum of the electrons. The true formula for the wave-length as function of the electron-speed is probably

$$\lambda = (h/m_0 v) \sqrt{1 - v^2/c^2}$$

instead of $\lambda = h/m_0 v$ (here v stands for the speed and m_0 for the mass-at-zero-speed of the electrons); but as yet the speeds employed have not been great enough nor the measurements exact enough to distinguish between the formulae.

indices (h_1, h_2, h_3) is inclined to the primary beam at a certain angle Φ for which we have found the formulæ (8) and (9). We may conceive that this *deflection* is due to a *reflection* of part of the incident wave-motion from a mirror or mirrors traversing the crystal, so tilted that their plane bisects the angle Φ. The picture would be legitimate even if there were nothing physical corresponding to these "mirrors"; but we shall presently see that they are not imaginary. The normal to their plane makes supplementary angles θ_0 and $\theta = \pi - \theta_0$ with
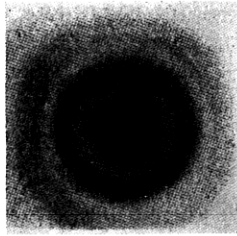

Fig. 20—"Powder method" diffraction-rings obtained with electron-waves and a thin film of gold. (G. P. Thomson, *Proc. Roy. Soc.*)

the primary and the diffracted beams, respectively; and ($\theta_0 - \theta$) is the angle of deflection Φ.[7] Combining these statements, and choosing the positive sense of the normal so that it shall make an acute angle with the diffracted beam, we find:

$$\theta = \tfrac{1}{2}\pi - \tfrac{1}{2}\Phi; \qquad \theta_0 = \tfrac{1}{2}\pi + \tfrac{1}{2}\Phi. \qquad (10)$$

We wish to deduce the direction-cosines of the normal—denote them for the moment by the symbols γ_1, γ_2, γ_3—from the conditions that it makes the angles θ_0 and θ with the rays having the direction-cosines α_1, α_2, α_3 and β_1, β_2, β_3 respectively. These conditions are thus expressed by the aid of equation (9):

$$\alpha_1\gamma_1 + \alpha_2\gamma_2 + a_3\gamma_3 = \cos\theta_0 = -\sin\frac{1}{2}\Phi = -\frac{\lambda}{2a}\sqrt{h_1^2 + h_2^2 + h_3^2}, \quad (11)$$

$$\beta_1\gamma_1 + \beta_2\gamma_2 + \beta_3\gamma_3 = \cos\theta = +\sin\frac{1}{2}\Phi = +\frac{\lambda}{2a}\sqrt{h_1^2 + h_2^2 + h_3^2}, \quad (12)$$

and the reader can easily show by means of equations (6a, 6b, 6c) that they are satisfied when:

$$\gamma_1 = \frac{h_1}{\sqrt{h_1^2 + h_2^2 + h_3^2}}; \quad \gamma_2 = \frac{h_2}{\sqrt{h_1^2 + h_2^2 + h_3^2}}; \quad \gamma_3 = \frac{h_3}{\sqrt{h_1^2 + h_2^2 + h_3^2}}. \quad (13)$$

[7] It is the custom to say that the normal to a mirror makes *equal* angles with the incident and the reflected beams, but this manner of statement implies that the positive senses along the directions of the beams are defined oppositely—one *with*, the other *against* the sense in which the waves are advancing. The convention adopted here is the more logical, and leads to more symmetrical equations.

If therefore a diffraction-spot (h_1, h_2, h_3) can with any reason be attributed to a reflection of part of the incident energy from mirrors traversing the crystal, then these mirrors must be so tilted that their normal is pointed in the direction defined by equation (13).

This equation being attained, we are prepared to discern the physical meanings of the integers h.

One of their meanings is evident. They state the "order" of the diffraction-spot, in the sense in which that word is used in describing the spectra cast by optical gratings. An ordinary ruled grating supplied with light of a single wave-length forms, it may be, six or seven or even more different "lines" on the focal plane of the lens installed in front of it. These correspond to diffraction-spots on the surface of our imaginary bulb. Take any one of these lines, say the nth. The paths of the light from the source *via* consecutive rulings of the grating to this nth line differ by precisely n wave-lengths; the contributions of any two adjacent rulings to the wave-motion at this line differ in phase by n complete cycles. It is named the line, or the image, or the diffraction-maximum *of the nth order*. There may be lines of positive, of negative and of zero order; the line of zero order is commonly called the "direct image" of the source.

Now in the same sense a diffraction-spot with the indices h_1, h_2, h_3, cast by a crystal, is of three orders simultaneously; these indices are its orders with respect to the three principal directions of the crystal lattice. Referring to our quartet of atom-groups $ABCD$: the paths of the waves from the source *via* A and B to the diffraction-spot differ by h_1 wave-lengths, those *via* A and C differ by h_2 and those *via* A and D by h_3 wave-lengths. The (000) spot is in the prolongation of the incident stream, and is called the "direct image."

This is one important meaning of the indices h. Happily there is another which is much more picturesque—happily indeed, for otherwise it is likely that the art of crystal analysis would have developed more slowly than it has, while the art of X-ray spectroscopy might not even have begun for years. It does not always happen, perhaps indeed it rarely happens, that the earliest formulation of a theory is the one best adapted to make it widely understood and useful. Someone other than the founder meditates upon the idea, and tries to re-express it to himself, and hits upon a novel way of stating it— a new aspect to it, possibly, or perhaps nothing more than a new distribution of the emphasis, laying the greatest stress upon some feature which to his forerunner seemed minor. Then suddenly the theory appeals to the world of physicists in general. Experimenters see what can be done with it, how it can easily be tested and how it

can be applied after the tests are passed; and progress for a time is furiously fast. Something much like this befell the theory of the diffraction of waves by crystals. The form in which I have thus far developed it (except while describing the powder method) is the one in which it was clothed by the brilliant inspiration of Laue. However it was W. L. Bragg who made the theory well known and widely used all the world over, by singling out and featuring the fact that *each diffraction-beam is due to its own special set of atom-strata in the crystal, which reflect it as light is reflected by a pile of parallel mirrors.*

The integers *h* are then no other than the indices, by which the crystallographers denote these strata. For, to the student of crystallography, the strata are very real— as much so as the rows of atom-groups, by referring to which I developed the theory of the diffraction-spots in Laue's way. We started with the individual group and went on to the row, and then constructed the plane by laying rows down side by side; but we might have started with planes, and defined the rows of atom-groups as the lines or edges where two planes intersect, and located individual atom-groups at corners where three planes meet. This is the historical way; for the planes are the prominent feature of any well-developed crystal. The smooth flat facets which are the boundaries of every well-formed crystal are parallel to important strata, they are themselves examples of important strata. In studying a crystal otherwise than by diffraction, the first step is to measure the directions (relative, of course) of all the available facets. Before the invention of analysis by diffraction, this was often the last step also; but if the crystals available have grown up really well, it is a very long step. Having taken it, the crystallographer proceeds to visualize the crystal as a region of space which is intersected and partitioned by flocks of planes, long sequences of evenly-spaced planes parallel to the facets; and he locates the atom-groups at their intersections. How then shall we harmonize these inferences of his with the implications of the diffraction pattern?

A good way to unify the two procedures is to explain the notation by which the crystal planes are named. In doing this, I shall often speak of planes "containing atom-groups," meaning in the strict sense planes containing lattice-points around which atom-groups are placed.

Return to the cubic lattice and to the basic set of four atom-groups *ABCD*, so chosen that the lines *AB*, *AC*, *AD* are three edges of the fundamental or "unit" cube. Complete the cube by adding four more atom-groups *EFGH*. We will pick out the planes which contain three or four of these eight groups. They will be the most populous with atom-groups of all the planes traversing the cube or

"cell"; hence the most populous of all the planes traversing the crystal. I have spoken above of the "important" strata of the crystal, meaning those which are likely to be parallel to facets. The word "important" is vague, and it is better that it should remain somewhat vague; but, in a rough way, the more populous a stratum is the more likely it is to be "important" in that sense, and also in the sense that it produces strong diffraction-spots. We will therefore consider chiefly the planes, which cut through the unit cube in such a way as to traverse three or four of the atom-groups. Put the origin of coordinates at A, the x, y, z axes through C, B, D respectively.
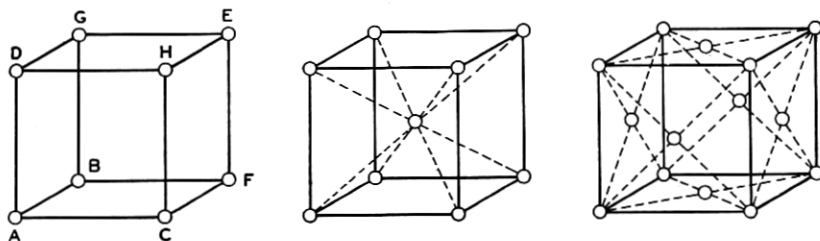

Fig. 21—Illustrating the cubic lattice.

Commence with the plane containing BCD, normal to the direction AE which is one of the principal diagonals of the cube. We wish a symbol for this plane that shall describe its orientation, which is its important feature,—a symbol that shall denote not only the plane BCD, but equally all those which are parallel to it, such as FGH and the parallel planes through A and E and other unit cells. We might use the three direction-cosines of the normal to this family of planes; or we might use the three intercepts of BCD on the three coordinate-axes, multiplied by an arbitrary factor to convert them into convenient integers and show that we are not more concerned with BCD than with any other member of the family; or we might use the reciprocals of these three intercepts, also multiplied by some convenient arbitrary factors. The last choice is the standard one. The three intercepts are a, a, a; their reciprocals are $1/a$, $1/a$, $1/a$; we multiply these by a and obtain $(1, 1, 1)$ as the symbol for not only the plane or stratum BCD, but all the strata parallel to it, including for example any facets that may be formed upon such strata. The reader will easily identify three other families of planes for which the symbols are $(-1, 1, 1)$; $(1, -1, 1)$; and $(1, 1, -1)$. Some substances with cubic lattices form crystals in the shape of octahedra; the surfaces of these are strata with such symbols. Usually the commas are left out of the symbols, and the minus signs printed over the digits.

Now try the plane containing the atom-groups *BCGH*. Its inter-cepts on the *x* and *y* axes are both equal to *a*, but it is parallel to the *z*-axis, a fact which is described by giving its *z*-intercept as infinity. The reciprocals of its intercepts then are $1/a$, $1/a$, 0; we multiply by *a* and obtain (1 1 0) as the symbol for all the strata parallel to the one containing the atom-groups *BCGH*. The reader can easily identify members of the (0 1 0) and (0 0 1) families, and ascertain how many new families of planes he can get by reversing the signs of some or all of the indices. There are six altogether; one sometimes sees facets with these indices, beveling off the edges of natural cube-shaped crystals.

Next consider the plane containing *CFHE*. It is parallel to the *yz*-plane and distant from it by *a*, so that its intercepts are *a*, ∞, ∞, and its symbol is (1 0 0). One sees immediately that (1 0 0) and (0 1 0) and (0 0 1) are the symbols for the three families of planes which comprise these which we have taken for our coordinate-planes. When a substance with a cubic lattice forms crystals which are cubes, their facets belong to these families.

What could a symbol such as (2 1 0) imply? It would stand for a family of planes, one of which would have for its intercepts the values $a/2$, $a/1$, $a/0$ or $\tfrac{1}{2}a$, *a*, ∞. This plane would be parallel to the *z*-axis and would traverse the atom-groups *B* and *G*, and would slant across the cell in such a way as to pass through the wall *ACDH* midway between its vertical edges. Continuing it and the lattice in imagi-nation, one sees that at the far angle of the *next* cell it would traverse another pair of atom-groups, and at the far angle of every second cell thereafter it would do the like. It is therefore a fairly "important" stratum, though not so populous as those of which the indices are zeros and ones exclusively. It might form facets, and would be likely to give a noticeable diffraction-spot. But in general as the indices mount up, the importance of the plane declines.

It is evident that if any set of indices is multiplied by any constant, the new set thus obtained corresponds to the same family of planes. To choose one set definitely for each family, we may agree to adopt the triad of integers having no common divisor. Thus all three of the symbols (963), (642) and (321) refer to the same family of planes; we always choose the last one.

Given these the so-called "Millerian" indices of a family of planes, what are the direction-cosines of their common normal?

Denote the three indices by H_1, H_2, H_3. The question is: what are the direction-cosines $\gamma_1\gamma_2\gamma_3$ of the normal to a plane, of which the intercepts on the coordinate axes are a/H_1, a/H_2, a/H_3? The an-

swer is given by a standard formula: the three direction-cosines are:

$$\gamma_1 = \frac{H_1}{\sqrt{H_1{}^2 + H_2{}^2 + H_3{}^2}};$$

$$\gamma_2 = \frac{H_2}{\sqrt{H_1{}^2 + H_2{}^2 + H_3{}^2}};$$ \hfill (14)

$$\gamma_3 = \frac{H_3}{\sqrt{H_1{}^2 + H_2{}^2 + H_3{}^2}};$$

The common factor a has vanished, as it should.

Compare these expressions with those in equation (13). One sees instantly that the strata (H_1, H_2, H_3) are so oriented that these strata could serve as mirrors to reflect the primary beam towards the diffraction-spot of which the indices are $h_1 = H_1$, $h_2 = H_2$, $h_3 = H_3$; or towards the spots of which the indices are (nH_1, nH_2, nH_3), where n stands for any integer. Or: the diffraction-spot (h_1, h_2, h_3) may be conceived as due to a reflection of part of the wave-motion in the incident stream, by the atom-layers of which the symbol is n_1/C, n_2/C, n_3/C; C standing for the greatest common divisor of h_1 h_2 h_3.

This is part of the principle which Bragg deduced from Laue's theory, but not the whole of it.

I have shown in an earlier article of this series [8] (and the reader can easily work out) that when a beam of plane waves falls successively on two plane parallel surfaces which reflect a part and transmit a part of it, the two reflected beams are in phase with one another and the resultant is maximum, when the following relation prevails between the wave-length λ of the light, the distance d between the mirrors, and the angle θ of incidence and of reflection:

$$n\lambda = 2d \cos \theta, \qquad n = 0, 1, 2, 3 \cdots. \hfill (15)$$

When instead of a pair there is an endless or a very long sequence of mirrors spaced at equal intervals, the result is much the same as when a pair of atoms is supplemented by a very long row. The angles defined by equation (15) are now not merely the angles of maximum reflection; they are the *only* angles where reflection is at all appreciable. If a pile of parallel semi-transparent mirrors is to reflect to any notable extent, their thicknesses and the wave-length and the angle of incidence of the light must be very carefully adjusted according to equation (15) with some integer value for n.

[8] Number 15 (October, 1928), p. 24. The formula there given contains an index of refraction which I here equate to unity, and an additive constant which vanishes if the phase-change at reflection is the same at each of the reflecting surfaces, which is here the case.

Now the principle emphasized by Bragg is this, in full: *any diffraction-spot results from reflection by the strata having the same indices as the spot, at the angle of selective reflection defined by equation (15).*

The proof of this statement depends on the following formula [9] for the distance between adjacent strata of the family having the Millerian indices $H_1H_2H_3$:

$$d = a/\sqrt{H_1^2 + H_2^2 + H_3^2}. \qquad (16)$$

Substituting into equation (12) the value of a given by this formula, we find that:

$$\cos\theta = \frac{\lambda}{2d}\frac{\sqrt{h_1^2 + h_2^2 + h_3^2}}{\sqrt{H_1^2 + H_2^2 + H_3^2}} \qquad (17)$$

and since the quantities H are integers without a common divisor, while the quantities h_1 are integers for which $h_1/H_1 = h_2/H_2 = h_3/H_3$, the ratio of the two radicals must be an integer.

The mirrors which I introduced at a previous page as a way of accounting for the spots do actually exist. They are the strata into which the groups of atoms fall. Each one by itself, however, reflects so little that in effect there is no reflection to speak of, unless and until an entire procession of parallel strata is brought into play. Earlier we located the diffraction-beams as the directions in which the scattered waves from four adjacent atom-groups enhance one another most by constructive interference. Multiplication of atom-groups beyond the first four merely made the beams sharper and more intense. Alternatively we may now locate these beams as the directions in which the reflected waves from two adjacent parallel strata enhance each other most. Multiplication of strata beyond the first two intensifies and sharpens them.

This theorem of Bragg's thus gives a remarkably helpful picture of "the way of a crystal with a beam of waves"; a picture most valuable, when one has a single large crystal of which the surfaces are natural facets. Suppose for instance one has a cubic crystal of rocksalt, one of

[9] Let O and P stand for two planes of the family $(H_1H_2H_3)$, one being drawn through the origin, the other through any other lattice-point. The components of the vector r from the origin to this other lattice point must be integer multiples l_1a, l_2a, l_3a of the spacing a. The projection of this vector on the direction of the normal drawn from the origin to the plane P is equal to $(\gamma_1l_1 + \gamma_2l_2 + \gamma_3l_3)a$; the values of $\gamma_1\gamma_2\gamma_3$ are to be taken from (14). This projection is equal to the distance D between the planes O and P, for which we therefore have:

$$H_1l_1 + H_2l_2 + H_3l_3 = \frac{D}{a}\sqrt{H_1^2 + H_2^2 + H_3^2}.$$

The least value (except for zero) which the quantity on the left can and does assume is unity; whence equation (16).

its faces being parallel to the (100) strata.   If one has a monochromatic beam of X-rays incident on that face and revolves the crystal so that θ varies steadily from zero to 90°, then for the several angles given by equation (15) with various values of n diffraction-beams spring forth. One may set up a photographic plate beside the crystal, and find the imprints of all the beams upon it after the rotation is completed; or alternatively one may revolve an ionization-chamber at double the angular speed of the crystal, so that whenever a beam shoots out the chamber is in the right place to capture it, and then the curve of ionization-current versus angle θ shows a peak for every value of θ corresponding to an integer value of n.   If the incident beam comprises many wave-lengths, one finds their spectrum spread out in the ionization-current curve; three examples are shown in Fig. 14, where each of the sharp tall peaks is due to the first-order diffraction-beam of a monochromatic wave very intensely represented in the primary wave-mixture.   Or one may hold the crystal and the collector still and vary the wave-length, obtaining a peak wherever λ is such that for some integer value of n the equation (15) is satisfied; the curve of Fig. 16 was obtained in this way, using waves of negative electricity.

The process of measuring wave-lengths of X-rays is usually conducted by this method, using a crystal such as rocksalt for which the density is very accurately known.   For if we know the density of the crystal we know how many atoms it contains in a given volume; and if we know in addition how many atoms constitute the atom-group which is repeated over and over again to form the crystal, we can compute by simple division what is the volume of the unit cell, and what therefore is the spacing from one atom-group to the next—the edge of the elementary cube.   If we then set up the crystal so as to get reflections from the 100 face we know that the edge of the cube is the quantity d which figures in the equation (15); and measuring then the values of θ corresponding to several diffraction beams we can identify the corresponding values of n, and so evaluate λ.   Diffraction of X-rays by ruled gratings can now be called upon in confirmation—or in correction, as certain recent data indicate.

The determination of the number of atoms in the atom-group is the delicate point of this computation; and perhaps it is to be accounted a piece of luck that with the first crystals used in the spectroscopy of X-rays the guess was easy and was rightly made.   The routine of determining it is but a part of the general process of learning from the diffraction as much as possible about the atom-group; and this deserves an article to itself, or many.   Two examples of this process however are interesting, useful and very simple.

I remarked near the beginning of the article that while it would be the simplest possible thing to suppose that the particles arranged in a cubic lattice have full spherical symmetry, yet this supposition is as a rule too simple for the facts. In particular it is too restricted to explain the diffraction-pattern of any one of the numerous elements which crystallize on cubic lattices. One might then be forced to assume that the atoms themselves do not have spherical symmetry. But luckily this is unnecessary; for it happens that if with each lattice-point of the cubic lattice we associate a properly-spaced and properly-oriented *group* of spherical atoms—in some elements a pair, in other elements a group of four—the difficulties vanish. The diffraction-patterns are explained, and there is no outstanding conflict with the data assembled by the crystallographers; for both of these arrangements, like that in which each lattice-point is occupied by a single spherical atom, possess full cubic or isometric symmetry in the crystallographic sense of those words.

In the first of these permitted arrangements, the two atoms associated with each lattice-point are so placed and so spaced, that if we label them, say, *A* and *B*, the atoms *A* by themselves form one single cubic array, and the atoms *B* by themselves form another simple cubic array with an atom *B* in the very centre of each cube composed by atoms *A*—and vice versa. This is the "body-centred cubic" arrangement. It is depicted in the middle drawing of Fig. 21. The atom at the centre of the cube may be associated with any one of the eight corner atoms to form a pair; this pair is then repeated over and over again on the cubic lattice to form the crystal. The alkali metals, iron, and several other elements are addicted to this arrangement.

In the second of the arrangements, the four atoms forming a group are so placed and so spaced that if we call them *A*, *B*, *C*, and *D*, the atoms of each letter form a cubic array; and these four cubic arrays are interlocked in such a fashion, that the cubes of any one of these arrays have in the centres of all their faces atoms belonging to the others. Thus in the righthand sketch of Fig. 21 the atom at any corner may be associated with the atoms in the centres of the three faces which meet at that corner, and these four form the atom-group which is repeated over and over again on the cubic lattice to build the crystal. Many of the metallic elements have adopted this "face-centred cubic" arrangement, the noble metals for example, and argon also.

How does one recognize from the diffraction pattern which of these arrangements exists in a cubic lattice? At this point I will not give an exact answer: but the principle is simple. Even as on an earlier page it was shown that for certain directions of diffraction adjacent

28

atom-groups *reinforce* the scattering from one another, so it may be shown that for certain directions the different atoms of a single atom-group *destroy* the scattering from one another.   One has only to write down the condition that the distance from source P to fieldpoint Q *via* one atom of the group differs by an odd-integer multiple of $\frac{1}{2}\lambda$ from the distance *via* the other; or if there are four atoms in the group, that the waves scattered to Q from the four are so balanced in phase that they annul one another.

Now if it should turn out that one or more of the diffraction-spots expected from the cubic lattice fall exactly where the effects of the atoms of each individual group cancel each other out, then those spots will be lacking.   For the spots are due to amplification of the diffraction-pattern of the individual atom-group; but if at the location of a predicted spot this pattern sinks to a vanishing intensity, there is nothing to amplify.   Well! owing to the neat and accurate way in which the spacings between atoms of a group are related to the spacings between the atom-groups, this sort of coincidence occurs for a respectable fraction of the diffraction-spots—or, in the powder method, it occurs for several of the diffraction-rings.   From the missing spots or rings therefore one identifies which style of atom-group prevails in the cubic crystal.   And there is much more yet to be learned; but that will be material for another article.