CONTENTS

PAGE

PREFACE ii

ACKNOWLEDGMENTS iv

CHAPTER I

THE THEORY OF DIFFRACTION OF X-RAYS BY A CRYSTAL 1
Diffraction of x-rays—Standards for the determination of *d* in Bragg's law—The intensity of the diffracted beam.

CHAPTER II

CRYSTAL LATTICES 20
The six systems of crystals—Names of the atomic planes—Densities of crystals.

CHAPTER III

THE CALCULATION OF INTERPLANAR SPACINGS 38
Interplanar spacings in a cubic crystal—The general equation for interplanar spacings.

CHAPTER IV

THE LAUE METHOD OF CRYSTAL ANALYSIS 54
X-ray spectra and their application to crystal analysis—The Laue diffraction pattern—Projection diagrams—The gnomonic projection—The stereographic projection—Identification of Laue spots by means of the gnomonic projection—Interpretation of the Laue pattern.

CHAPTER V

THE BRAGG METHOD OF CRYSTAL ANALYSIS 86
Experimental technique—Interpretation of the diffraction pattern—Structures of typical substances.

CHAPTER VI

THE POWDER METHOD OF CRYSTAL ANALYSIS 111
The powder method—Experimental technique—The diffraction pattern and its interpretation—Graphical methods of interpretation—Structures of typical substances—Precision measurements of crystal parameters.

CHAPTER VII

THE ROTATING-CRYSTAL METHOD 171
Apparatus and technique—Theory of the rotation photograph—Theory of reciprocal lattice—Assignment of indices by the graphical method—Use and interpretation of oscillation photographs—Intensity relations for diffraction spots on rotation photographs.

PAGE

CHAPTER VIII

THE THEORY OF SPACE-GROUPS 211
Symmetry machines—The 32 point-groups—The coordinates of the 32 point-groups—The 230 space-groups.

CHAPTER IX

THE APPLICATION OF THE THEORY OF SPACE-GROUPS 265
Determination of the structure of NaCl by the Laue method—Determination of the structure of calcite by the Laue method—Determination of the structure of tricalcium aluminate by the powder method.

CHAPTER X

STRUCTURE FACTOR 292
Effect of atomic structure on the intensity of the diffracted beams—The probable distributions of electrons in a crystal.

CHAPTER XI

APPLICATIONS OF THE STRUCTURE FACTOR METHOD 323
The structure of diopside—The structure of topaz.

CHAPTER XII

THE MECHANISM OF CRYSTAL GROWTH AND ITS CONSEQUENCES 363
Growth from the vapor—Growth from the melt—Growth from solution—Growth in solids—Secondary crystal structure (π-planes and Π-planes).

CHAPTER XIII

THE PACKING-SHAPES AND PACKING-SIZES OF ATOMS AND IONS 396
The packing-shapes and packing-sizes of atoms from crystal structure data—Other estimates of shapes and sizes of atomic domains—The packing-shapes and packing-sizes of ions from x-ray data—Other estimates of packing-sizes of ions—Packing sizes and shapes of atoms in non-polar combination.

CHAPTER XIV

THE REFRACTION OF LIGHT BY CRYSTALS 439
Basic data for the theoretical calculation of index of refraction of a crystal—Calculation of index of refraction of an isotropic substance—Calculation of index of refraction of a non-isotropic substance—Calculation of index of refraction of calcite and of aragonite—Interionic spacings from optical calculations.

CHAPTER XV

THE CALCULATION OF LATTICE ENERGIES 453
The potential energy of an atom in a crystal—Physical data calculated from lattice potentials—Short-cut methods of calculating lattice potentials.

CHAPTER XVI

THE DIFFRACTION OF X-RAYS BY AMORPHOUS MATERIALS 471
Structure of liquids—Structure of gels and glasses—Structure of gases.

CHAPTER XVII

THE ORIENTATION OF CRYSTALS 501
Determination of the orientation of single crystals—Determination of preferred orientations of polycrystal material—Pole figures.

PAGE

CHAPTER XVIII

SOLID SOLUTIONS 523
Criteria for the existence of solid solutions—Theory of solid solution.

CHAPTER XIX

CHEMICAL INFORMATION TO BE GAINED FROM CRYSTAL-STRUCTURE STUDIES . . 543
Types of chemical combination—Variate atom equipoints—Contribution of crystal structure to organic chemistry—Molecular symmetries.

APPENDIX I

X-RAY TUBES, TRANSFORMERS, AND ACCESSORIES 575
X-ray tubes for crystal analysis—X-ray power units—Operation of units—Technique of assembly and disassembly of the Hadding-type tube—Voltage and current measurements—X-ray protection.

APPENDIX II

SEMILOGARITHMIC CHARTS FOR USE WITH THE POWDER METHOD 596
Charts for the hexagonal system—Charts for the tetragonal system—Charts for the orthorhombic system.

APPENDIX III

TABLES 615
Tables I to XXXII; The 230 space-groups listed according to the crystal systems to which they belong—Tables XXXIII to XXXIX; The kinds of configurations of points which can be obtained from each of the space-groups and the number of each kind which can be obtained—Table XL; The symmetry characteristics of the 32 point-groups—Table XLI; Tables of the 230 space-groups according to the Zurich (Hermann-Maugin) notation.

APPENDIX IV

A GRAPHICAL PROJECTION METHOD OF DETERMINING THE COORDINATES OF CERTAIN POINT-GROUPS 675
Cubic system—Hexagonal system.

INDEX 685

A STUDY OF CRYSTAL STRUCTURE AND ITS APPLICATIONS

CHAPTER I

THE THEORY OF DIFFRACTION OF X-RAYS BY A CRYSTAL

Practically all rigid solids except the glasses and possibly certain ~~waxes are composed of crystals. It is known to every metallurgist that~~ metals and their alloys exist in the form of crystals, and the crystalline state of most chemical compounds is universally accepted. Even cellulose, of which wood and cotton are largely composed, shows real evidence of crystallinity. It is therefore evident that any study of the properties of materials will be very largely a study of the crystalline state of matter. There is the same difference between crystalline and noncrystalline substances that there is between an army and a mob, for a crystal represents an organized array of atoms all arranged in definite rows with regular spacings between rows, while the atoms in a noncrystalline substance have a chaotic, hit-and-miss placing.

It has long been known that the mechanical and chemical properties of crystals depend markedly upon the direction in the crystal in which these properties are measured. It was early taken for granted that this was caused by the various rows of atoms acting as units so that the effect of one atom was added to that of its neighbor in a perfectly systematic way. For a long time this picture was necessarily rather hazy, for no means were at hand to measure the distances between the atoms in the various rows and the distances between rows. These distances are so minute that if an ordinary pinhead were magnified until its diameter became 100 miles, the distance between centers of adjacent atoms would be about one inch. Such measurements can now be made easily to within 1 part in 1,000 by means of the diffraction of x-rays. In other words, x-rays furnish us with a micrometer by which we can measure without difficulty a distance of 10^{-8} cm. with an accuracy of $\frac{1}{10}$ per cent.

A micrometer of this sort differs from an ordinary micrometer not only in the exceedingly small distances which it measures but also in the fact that these distances lie hidden in the body of the crystal itself. As is the case with other micrometers, the measurement of a small

此为试读，需要完整PDF请访问：www.ertongbook.com

distance is accomplished by measuring a relatively large distance (in this case, several centimeters) which is related to the desired distance by some known law. It will therefore be necessary to consider in detail the law of diffraction of x-rays and how this law may be made to relate large, easily measurable distances to the distances between atoms in crystals. In short, we must first study the theory of our micrometer.

Such a study must be combined with other information on the spatial relationships which are possible inside a crystal. This will then enable us to see how the interatomic distances in a crystal may be used to determine the arrangement in space of the atoms of which the crystal is composed. The knowledge, thus gained, of the structure of crystals is the starting point for a rapidly growing body of information which is of considerable theoretical and practical importance. From a knowledge of the structure of crystals it is possible to obtain information as to the sizes and shapes of atoms and ions, and to find valuable hints as to the mechanism of chemical combinations. Evidence is found leading to fundamental ideas in the theory of solid solutions and the inner structure of alloys, so that a more rational explanation may be made of certain metallurgical phenomena. Evidence may also be obtained of the effect of mechanical working on the orientation of crystals in metals, so that we may hope some time in the future to roll and draw metal better than we can today. This short résumé shows that a study of crystal structure is not only of interest to the so-called "pure scientist" working in physics, chemistry, and physical chemistry, but that it gives much promise of practical results to the metallographer and through him to almost every branch of industry.

DIFFRACTION OF X-RAYS

It was stated in the foregoing that the "micrometer" used in measuring interatomic distances is based upon the diffraction of x-rays. When x-rays of a given wave length strike a substance, part of the radiation is scattered so that it appears at every possible angle to the incident beam. If the scattering substance is a crystal, the scattered radiation is much more intense at certain angles than at others, *i.e.*, the x-rays are diffracted through definite angles. These angles depend upon the wave length of the x-rays employed and upon the arrangement and spacing of the atoms in the crystal. The distances measured in determining these angles and the relative intensities of the x-ray beams at these angles form the basis of study in x-ray crystallography.

Bragg's Law.—It is shown in elementary texts on physics that ordinary light can be diffracted from a plane grating. A crystal acts toward x-rays like a family of plane gratings placed one above the other. The introduction of *height* in addition to *width between lines* changes the final form of the diffraction law considerably. It may be shown experimentally that this changes the diffraction law from the form found in texts on physical optics to the form known as Bragg's law:

$$n\lambda = 2d \sin \theta \tag{1}$$

where λ is the wave length of the x-rays and θ is the grazing angle of incidence between the x-ray beam and the diffracting family of atomic planes in the crystal. The experimental fact of the diffraction of x-rays according to Bragg's law may be explained either on the basis of the classical spreading-wave theory[1,2] or on the basis of the quantum theory.[3,4] A consideration of the two types of explanation shows that they give identical results.

Diffraction of a Spreading Wave.—According to the spreading-wave theory, x-rays and ordinary light are both thought of as being trains of electromagnetic waves which tend to spread out in all directions from their source, *i.e.*, they tend to advance on a spherical wave front. The difference between ordinary light and x-rays is, according to this theory, merely a matter of wave length. The distance "from crest to crest" of an x-ray is supposed to be about one ten-thousandth as great as the corresponding distance for visible light.

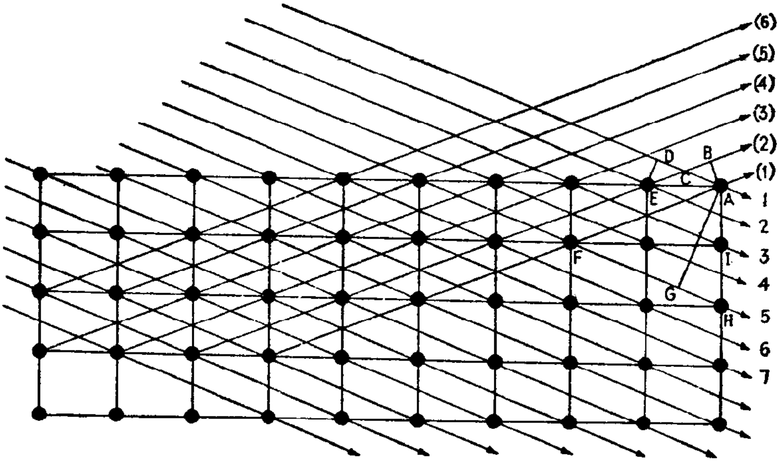


FIG. 1.—Diffraction of a plane wave by a crystal.

Let the network of dots in Fig. 1 represent the atoms of a crystal, and let the crystal receive x-rays from a source sufficiently distant so that the wave fronts may be considered to be planes. Let the arrows 1, 2, 3 . . . represent normals to these wave fronts, and let the arrows (1), (2), (3) . . . represent the corresponding normals for the first order of the diffracted beam. Experimentally, it is found that the grazing angles of incidence and emergence are equal, *i.e.*, that $DAE = BEA$. Let AG be drawn perpendicular to FH. The path of the beam 5 to the point G is equal in length to the path of the beam 1 to the point A. The difference in path length between the beam 1 at A and the beam 5 diffracted from F to A is GH, since FH is equal to FA. GH is equal to AH sin GAH. But the angle GAH is equal to the grazing angle of incidence DAE. Since AH is twice AI, *i.e.*, it is twice the interplanar distance d of the crystal, and since DAE is the grazing angle θ, we know the waves diffracted along (1) from incident beams 1 and 5 will meet in phase if

$$n\lambda = 2d \sin \theta \tag{1}$$

where n is any whole number and λ is the wave length of the x-rays employed. The integer represented by n is called the "order" of diffraction and is the number of wave lengths difference in the two paths. Similar beams such as (2), (3), (4) . . . will be in phase with beam (1); for let ED and AB be perpendicular respectively to 1 and (2). Then, since $BEA = DAE$, we have the two right triangles with an acute angle and hypotenuse of one equal to an acute angle and hypotenuse of the other. Therefore, the path EB equals the path DA, which is the condition for beams (1) and (2) being in phase with each other. In a similar manner it may be shown that (1) and (3), (1) and (4), etc., are all in phase.

It is therefore possible to have a whole wave front of diffracted x-rays emerging from a crystal at an angle equal to the angle of incidence, provided this angle is related to the wave length of the x-rays and the interplanar distance of the crystal in the manner shown by Eq. (1). It may be shown that, if the crystal were infinitely thick and offered no absorption to the x-rays, there could be no first-order diffracted beam at any other angle; for no matter what other angle we choose for diffraction from a given point in the crystal, there will be some other point which can send out a wave in the same direction which will meet the first wave a half wave length out of phase. Experimentally, it is found that it is sufficient if the crystal is about 10^3 molecules thick. If the crystals are too thin, the diffracted beam tends to widen because of incomplete interference at angles other than that which is equal to the angle of incidence.

The diffraction of x-rays by a crystal may be shown analytically as follows. The three-dimensional diffraction grating of a crystal may be regarded as composed of three sets of unidimensional gratings, each one of which consists of a row of atoms parallel to one of the three axes of the crystal. Let the interatomic distances along the three axes be x_1, y_1, and z_1. Let the directions of the incident and diffracted beams be expressed by their direction cosines α_1, β_1, γ_1 and α_2, β_2, γ_2, respectively. Then the conditions for diffraction along these three sets of linear gratings are

$$\begin{aligned} x_1(\alpha_2 - \alpha_1) &= e\lambda \\ y_1(\beta_2 - \beta_1) &= f\lambda \\ z_1(\gamma_2 - \gamma_1) &= g\lambda \end{aligned} \tag{2}$$

where e, f, and g are integers representing the order of the diffracted beam from each of the gratings.* In the simplest case, that of a cubic crystal, $x_1 = y_1 = z_1 = a$, the edge of the unit-cube. Remembering that

$$\alpha_1^2 + \beta_1^2 + \gamma_1^2 = \alpha_2^2 + \beta_2^2 + \gamma_2^2 = 1$$

we have by squaring and adding

$$2 - 2(\alpha_1\alpha_2 + \beta_1\beta_2 + \gamma_1\gamma_2) = \left(\frac{\lambda}{x_1}\right)^2(e^2 + f^2 + g^2)$$

But, since, by a well-known theorem in trigonometry,

$$\alpha_1\alpha_2 + \beta_1\beta_2 + \gamma_1\gamma_2 = \cos\phi$$

where ϕ is the angle between the incident and the diffracted beams, and since

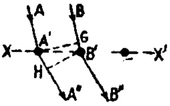
$$2(1 - \cos\phi) = 4\sin^2\frac{\varphi}{2}$$

we have

$$2\sin\frac{\phi}{2} = \frac{\lambda}{x_1}\sqrt{e^2 + f^2 + g^2} \tag{3}$$

We may therefore calculate the angle of deviation ϕ from the wave length λ, the grating space x_1, and the orders of the diffraction patterns of the three sets of linear gratings.

* To arrive at the equation for diffraction by one of these three sets of linear gratings, consider a series of diffraction centers equally spaced along the line XX'. On striking the diffraction center A', the beam A will be diffracted in the direction $A'A''$. In the same way the beam B will be diffracted in the direction $B'B''$. Now, the path AA'' is longer than the path BB''. Diffraction can occur only if the difference in path length is equal to a whole number of wave lengths. To obtain a value for this path difference, drop the perpendiculars $A'G$ and $B'H$. The difference in the path lengths of AA'' and BB'' is given by $(A'H - GB')$. But $A'H$ is $A'B'$ cos $B'A'H$ and GB' is $A'B'$ cos $A'B'G$. Cos $B'A'H$ is, by definition, the direction cosine, α_2. Cos $A'B'G$ is, by definition, the direction cosine, α_1. The distance $A'B'$ is the interatomic distance x_1. We may therefore write as the condition for diffraction along the X-axis



$$x_1(\alpha_2 - \alpha_1) = e\lambda$$

where e is an integer. Similarly for diffraction by the linear gratings along the Y- and Z-axes,

$$\begin{aligned} y_1(\beta_2 - \beta_1) &= f\lambda \\ z_1(\gamma_2 - \gamma_1) &= g\lambda \end{aligned}$$

Equation (3), derived in this way, may be regarded as typical of the viewpoint of Laue at the time of his discovery of x-ray diffraction. It may be expressed in terms of the more useful Bragg viewpoint as follows: A plane of atoms in a crystal is most commonly defined by its "Miller indices,"* which are the reciprocals of the intercepts of the plane upon the X-, Y-, and Z-axes, respectively. For instance, the (100) plane cuts the X-axis at unit distance and is parallel to the other two axes; it is the edge of a cube or of some other symmetrical figure. The (321) plane cuts the X-axis at $\frac{1}{3}$, the Y-axis at $\frac{1}{2}$, and the Z-axis at unity. It is customary to express these reciprocal intercepts in terms of their lowest prime numbers, so that, if the reciprocal intercepts are given as h, k, l, the actual reciprocal intercepts will be nh, nk, and nl, where n is any integer. If, therefore, we choose such a plane of atoms that

$$\begin{aligned} e &= nh \\ f &= nk \\ g &= nl \end{aligned}$$

we may regard the diffracted beam of Eq. (3) to be a diffracted beam of the nth order from the plane $(h\,k\,l)$.† Equation (3) may therefore be written

$$2 \sin \frac{\phi}{2} = \frac{\lambda}{x_1} n \sqrt{h^2 + k^2 + l^2}$$

or

$$n\lambda = 2 \frac{x_1}{\sqrt{h^2 + k^2 + l^2}} \cdot \sin \frac{\phi}{2} \tag{4}$$

It will be shown in Chap. III that $x_1/\sqrt{h^2 + k^2 + l^2}$ is the distance between successive $(h\,k\,l)$ planes. It is the d of Eq. (1).

The grazing angle of incidence (or the angle of diffraction) is $\phi/2$ and is the θ of Eq. (1). It is therefore evident that Eqs. (4) and (1) are identical. If, instead of confining ourselves to the cubic system, we had taken any other crystal system, we should have arrived at a new expression in the denominator of Eq. (4) which would represent

---

* Miller indices are treated at greater length in the next chapter.

† It should be noted that this substitution of nh, nk, and nl for e, f, and g, is only done as a matter of convenience in the study of crystal structure. A tiny crystallite may be so small that it does not contain representatives of many of the atomic planes found in larger crystals of the same substance yet it is theoretically capable of giving a diffraction pattern corresponding to every linear grating in the crystal. The changes to be made in Eq. (4) in such cases will be obvious. In the case of the crystallite, there will be a very rapid falling off in the sharpness and intensity of the diffracted beams with increasing angle of diffraction. For most practical purposes the effect is therefore somewhat the same as we should have had if diffraction had occurred only from individual families of planes which were actually present in the crystal.

the distance d between successive planes for that crystal system. Equation (1) is therefore perfectly general and applies to all types of crystals.

Diffraction of a Quantum.—In the preceding section on Diffraction of a Spreading Wave we have regarded an x-ray as a train of spherical waves of short wave length spreading out from a point source. The picture of an x-ray from the standpoint of the quantum theory may be given sufficiently well for our present purpose by regarding it as a wave train of very small cross-section (possibly of the order of 10^{-25} sq. cm.) proceeding out in a straight line from its source.[5] Any x-ray beam with which we ordinarily deal is supposed to contain an enormous number of these quanta coming out in all directions from the "focal spot" on the anode of an x-ray tube. In many ways, the whole bundle of quanta acts much like a train of spreading spherical waves, but the mechanism by which diffraction must be explained is quite different for quanta from that for spreading spherical waves.

According to the quantum theory, it is a characteristic of a quantum that its energy E determines the frequency of its waves, *i.e.*,

$$E = h\nu = \frac{hc}{\lambda} \tag{5}$$

where ν is the frequency, λ the wave length, c the velocity of light, and h is a proportionality constant known as "Planck's constant." If for any reason a quantum loses a portion of its energy, it must decrease the frequency of its waves until the new frequency multiplied by Planck's constant gives a product equal to the energy still remaining in the quantum. Since the wave has energy and has a definite velocity c it may be said (at least figuratively) to have mass and therefore momentum. It may be shown that the momentum of a quantum is*

$$M = \frac{h\nu}{c} = \frac{h}{\lambda} \tag{6}$$

The ordinary law of conservation of momentum which holds for the impact of material bodies is assumed to hold for the impact of quanta on atoms and electrons. It is further assumed that a quantum can give up momentum to an atom or electron in definite units. Since h has the dimensions of a momentum multiplied by a length,† it is assumed that the quantum unit of momentum is h/l where l is any length which may be shown to have a physical meaning in the diffracting substance.

---

* The kinetic energy of the electrostatic vector of the quantum is $\frac{1}{2}mc^2$. The kinetic energy of the electromagnetic vector of the quantum is also $\frac{1}{2}mc^2$. The total kinetic energy E of the x-ray quantum is therefore, mc^2. Its momentum M, is, by definition, mc. Evidently, then, $M = E/c = h\nu/c$.

† h has the dimensions $\frac{\text{energy}}{\text{frequency}} = ML^2T^{-1}$. Momentum has the dimensions mass × velocity $= MLT^{-1}$.

此为试读，需要完整PDF请访问：www.ertongbook.com

Let a quantum of x-rays fall upon a crystal as shown in Fig. 2, so as to make a grazing angle θ_1. At some point in its path it may hit an electron belonging to one of the atoms of the crystal and be deflected so that it emerges at an angle θ_2. The momentum transferred to the crystal in a direction parallel to the X-axis is

$$\frac{h\nu}{c}(\cos\theta_1 - \cos\theta_2) = n_1\frac{h}{x_1} \tag{7}$$

where the interatomic distance x_1 is the only length in the X-direction which has any physical meaning, and where n_1 is any positive integer including zero. Similarly, the momentum transferred in the Y-direction is

$$\frac{h\nu}{c}(\sin\theta_1 - \sin\theta_2) = n_2\frac{h}{y_1} \tag{8}$$

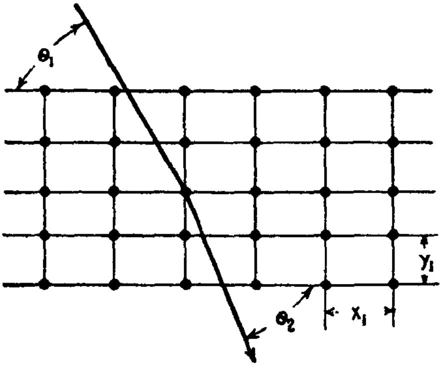


FIG. 2.—Diffraction of a quantum by a crystal.

If n_1 and n_2 are both zero, there is no transfer of momentum and no change in direction, so that the quantum passes on through until it hits an electron in some other atom. If n_1 is zero and n_2 is not zero, then $\cos\theta_1$ equals $\cos\theta_2$ but $\sin\theta_1$ does not equal $\sin\theta_2$. This means that $\sin\theta_1$ must be equal to $-\sin\theta_2$. Equation (8) therefore becomes

$$\frac{2h\nu}{c}\sin\theta_1 = n_2\frac{h}{y_1} \tag{9}$$

or

$$n_2\lambda = 2y_1\sin\theta_1 \tag{10}$$

which is identical with Eq. (1) for diffraction from the X-Z planes. Similarly, if n_2 is zero but n_1 is not zero,

$$n_1\lambda = 2x_1\sin(90^\circ - \theta_1) \tag{11}$$

which represents diffraction from the *Y-Z* planes. Equations (10) and (11) may therefore be written in the form of Eq. (1)

$$n\lambda = 2d \sin \theta \tag{1}$$

If n_1 and n_2 are both integers other than zero, Eqs. (7) and (8) give the same law of diffraction for still other families of planes in the crystal.

Exceptions to the Simple Form of Bragg's Law.—Equation (1) does not correlate all the known facts on the diffraction of x-rays. It is therefore necessary to extend the simple theories on which Eqs. (1), (10), and (11) were founded. It is found experimentally that, for a given crystal, Eq. (1) gives slightly higher values for wave lengths when n is small (1 or 2) than when n is larger. In the same way, if the wave length is assumed to be known, the first few lines in the diffraction pattern appear to be caused by interplanar spacings in the crystal which are slightly larger than those calculated from the second order of these same lines. This effect is explained as being caused by certain electrons in the atom having natural periods of vibration close to that of the incident beam of x-rays, thus giving the effect of a refractive index less than unity.[6]

Davis and v. Nardroff[7] have determined the refractive index of pyrites for four wave lengths and have compared their results with calculations based on the Lorentz dispersion formula

$$1 - \mu = \frac{e^2}{2\pi m}\left(\frac{n_1}{\nu^2 - \nu_1^2} + \frac{n_2}{\nu^2 - \nu_2^2} + \cdots\right)$$

where μ is the index of refraction, ν is the frequency of the incident beam, and $n_1, n_2, \ldots$ are the number of electrons per unit of volume having natural frequencies $\nu_1, \nu_2, \ldots$, and e and m, as usual, represent the charge and mass of an electron. Their calculated and experimental values are compared in Table I.

When the planes of atoms from which the rays are diffracted are parallel to the surface of the crystal (as is the case when a cleavage face is used), the error caused by refraction is very small. For instance, the bending is only about three seconds of arc for the $K\alpha$ rays of Mo from

TABLE I.—INDEX OF REFRACTION OF PYRITES CRYSTAL FOR X-RAYS

λ	$1 - \mu$, experimental	$1 - \mu$, calculated
0.6311Å.	2.82×10^{-6}	2.64×10^{-6}
0.7078	3.33	3.29
1.389	13.2	13.5
1.537	17.6	17.6

a cleavage face of calcite. This bending increases as the angle between the atomic planes and the crystal surface is increased. It is greater the shorter the wave length of x-rays employed. This is illustrated by the data of Table II from Davis and v. Nardroff for pyrites. Additional data on glass, tin, silver, selenium, and zinc have been published by Doan[8]

TABLE II.—EFFECT OF ANGLE AND WAVE LENGTH ON THE ANGLE OF BENDING OF X-RAYS

λ	Angle between crystal surface and atomic planes	Angle of bending of x-rays	$1 - \mu$, experimental	Weighted mean $1 - \mu$
0.7078Å.	0° 0′ 0″	3.6″	4.6×10^{-6}	
	6° 31′ 57.5″	39 ″	3.26×10^{-6}	
	7° 18′ 39″	159 ″	3.37×10^{-6}	3.33×10^{-6}
0.6311Å.	0° 0′ 0″	3 ″	3.87×10^{-6}	
	6° 31′ 57.5″	160 ″	2.82×10^{-6}	2.82×10^{-6}

and by Edwards,[9] and on aluminum by Davis and Slack.[10] For further details see a review of the subject by Bergen Davis in the *Journal of the Franklin Institute.*[11]

Because of the refraction of the rays, Bragg's law must be applied not to the original direction of the incident beam but to the direction of the refracted beam inside the crystal. It is hardly necessary to make this correction in the determination of the configuration of atoms in a crystal, since it affects only the exact size of the unit-crystal. Where the exact size of the unit-crystal is ~~important (see Chap. VI)~~, the experimental technique may be made such as to make the correction unnecessary.

PRIMARY AND SECONDARY STANDARDS FOR THE DETERMINATION OF *d* IN EQ. (1)

Equation (1) gives the relation between the wave length of x-rays and the interplanar spacing for diffraction at a given grazing angle. In order to determine one of these quantities by means of this equation it is necessary to know the other. Using the method of W. H. and W. L. Bragg[12] we may determine the dimensions of the unit-crystal* of NaCl as follows: A study of the diffraction patterns of NaCl and KCl shows that these patterns may be accounted for if these salts crystallize as simple cubes of ions, with the alkali and halogen ions occupying alternate

---

* The *unit-crystal* is the smallest crystal which can show the symmetry characteristics of the crystal. When the symmetry is cubic, the unit-crystal is called the *unit-cube;* when it is rhombohedral it is called the *unit-rhombohedron,* etc. The term "unit-crystal" is also sometimes applied loosely, as here, to represent the smallest portion of the crystal capable of showing the configuration of atoms.

corners of the cubes.* Since this is the simplest structure which accounts for the experimental facts, it will be adopted as the structure of NaCl. Each corner of one of the elementary cubes (unit-cubes) of the crystal contributes $\frac{1}{8}$ atom to the cube. The mass of the unit-cube of NaCl is therefore

$$[\tfrac{4}{8}A_{\mathrm{Na}} + \tfrac{4}{8}A_{\mathrm{Cl}}]m = \tfrac{1}{2}[A_{\mathrm{Na}} + A_{\mathrm{Cl}}]m$$

where A_{Na} = atomic weight of Na = 22.997.
A_{Cl} = atomic weight of Cl = 35.458.
m = mass in grams associated with one unit of atomic weight.

The factor m is most easily found as e/F, where e is the charge on the electron and F is the Faraday constant in electrolysis. Millikan[13] gives e as 4.774×10^{-10} absolute electrostatic unit (abs. e.s.u.) of charge or 1.591×10^{-19} absolute coulomb The maximum error is about 0.1 per cent. Vinal and Bates[14] give F as 96,500 absolute coulombs with a maximum error of 0.01 per cent. The factor m is therefore 1.649×10^{-24} gram (g.).† This makes the mass of the unit-cube of NaCl equal to 4.820×10^{-23} g. If we divide the mass of the unit-cube of NaCl by the density, we obtain the volume of the unit-cube. From this we can calculate at once the length of the edge of the unit-cube.

Many values for the density of NaCl may be found in the literature. These differ among themselves considerably, partly due to impurities in the salt used by some of the workers and partly due to the difficulty of growing large crystal aggregates of NaCl free from voids or to the equally great difficulty of growing large single crystals of NaCl free from strains which, by reason of the dislocation of the atoms, tend to lower the effective density. The density of NaCl is given twice in the "International Critical Tables."[15,16] In Vol. I it is given as $d_4^{20} = 2.163$. In Vol. III it is given as

$$\begin{aligned} d_4^{20} &= 2.1680(1 - 20 \times 11.2 \times 10^{-6} - 400 \times 0.5 \times 10^{-7}) \\ &= 2.1631 \end{aligned}$$

This second value considers the work of the most careful workers up to the end of 1925, and we shall accept it as being the most reliable value obtainable by direct experiment. If we consider it to be in error by as much as 0.004, *i.e.*, 0.2 per cent, it has the largest percentage error of any of the items which enter into our calculations of volume. Even if the error in the value of m happens to affect the final result in the same direction as the error in the value of d, our value for the volume of the unit-cube of NaCl can be in error only by 0.3 per cent. This would give an uncertainty of only 0.1 per cent in our value for the edge of the

---

* See Fig. 7, Chap. V.

† This factor is given by R. T. Birge, *Phys. Rev. Supplement*, Vol. 1, No. 1 (1929) as $1.6489_5 \pm 0.0016 \times 10^{-24}$.

unit-cube. Denoting the length of the edge of the unit-cube by a_0, we would therefore have

$$a_{0_{\mathrm{NaCl}}} = \sqrt[3]{\frac{4.820 \pm 0.005 \times 10^{-23}}{2.163 \pm 0.004}} = 2.814 \pm 0.002 \times 10^{-8}\ \mathrm{cm.}$$

It is, however, hardly possible that the above value of the density can be in error by more than ±0.001, so that we may narrow down our value to

$$a_{0_{\mathrm{NaCl}}} = 2.814 \pm 0.001 \times 10^{-8}\ \mathrm{cm.}$$

This agrees, within the precision of the underlying data, with the value 2.814×10^{-8} cm. used by Duane in his *Bulletin of the National Research Council* (November, 1920).

The density of calcite can be measured with greater accuracy than the density of NaCl since calcite can be obtained in large single crystals which are quite free from strains. For this reason, in the unit-rhombohedron of calcite whose faces are parallel to the cleavage planes, the distance between successive atomic planes which are parallel to the faces* is taken as the primary standard of length in all crystal-analysis work. The true value of the edge of the unit-cube of NaCl is determined from this as a secondary standard.[17,18,19] Optically clear calcite may contain Mn or Mg. Since both $MnCO_3$ and $MgCO_3$ have higher densities than those listed for calcite, it is clear that the lower the value reported in the literature, the more likely it is that the calcite was of high purity. Birge[20] gives as the best experimental value for the density of calcite, $d_{20} = 2.7102 \pm 0.0004$ g. per cubic centimeter. The interaxial angle of the cleavage rhombohedron of calcite is 101° 55′,[21,22] so that the volume of the unit-rhombohedron is $1.09630 \pm 0.00007 \times \left(a_{0_{\mathrm{CaCO_3}}}\right)^3$ where $\left(a_{0_{\mathrm{CaCO_3}}}\right)^3$ is the grating space of calcite. The molecular weight of $CaCO_3$ is[20]

$$\begin{array}{r}
40.075 \pm 0.005 \\
12.003 \pm 0.001 \\
48.000 \pm 0.000 \\
\hline
100.078 \pm 0.006
\end{array}$$

---

* As was pointed out by Wyckoff [*Amer. Jour. Sci.*, **50**, 317 (1920)] this is not the true theoretical unit of structure. It does, however, afford an easy way of visualizing the spacing between successive cleavage planes of calcite, *i.e.*, the crystal analyst's fundamental unit of length. It is, perhaps, only fair to say that crystal analysts practically never actually use calcite as a comparison standard (see Chap. VI) in measurements of interplanar spacings. Either they use NaCl (a_0 = 2.814Å.) or they arbitrarily adopt some measured wave length which they find in the literature or in some book such as Siegbahn's. The discrepancies introduced are usually of only academic interest.

It will be shown in a later chapter that a unit-rhombohedron, which for our present purposes may be considered as the unit of structure of calcite, contains one-half a molecule. Therefore

$$d_{20} = 2.7102 = \frac{\frac{1}{2} \times 100.078 \times 1.64898 \times 10^{-24}}{1.09630 a_0{}^3}$$

so that at 20°C.,

$$a_{0_{\mathrm{CaCO_3}}} = 3.0283 \pm 0.0010 \times 10^{-8} \text{ cm.} \tag{12}$$

This is the primary standard of length used in all crystal-structure work. Diffraction experiments,[17,23] of which those of Siegbahn are probably the most accurate, show that the ratio

$$\frac{\text{Grating space of calcite}}{\text{Grating space of NaCl}} = 1.076417$$

($= \log^{-1} 0.0319806$). This requires us to adopt for the true grating space of NaCl at 20°C. the value

$$a_{0_{\mathrm{NaCl}}} = 2.8135 \pm 0.0010 \times 10^{-8} \text{ cm.}$$

This value again agrees, within the precision of the underlying data, with the value 2.8140×10^{-8} cm. proposed by Duane.[24] Since a large fraction of the published data is given in terms of Duane's value, it has become customary to consider the secondary standard of distance for crystal-structure work as

$$a_{0_{\mathrm{NaCl}}} = 2.8140 \pm 0.0010 \times 10^{-8} \text{ cm.} \tag{13}$$

CdO crystallizes with the same type of structure as NaCl, but the crystals are more perfect and yield unusually sharp maxima in the diffraction pattern. For the same exposure time a much wider range of diffracted beams can be photographed from CdO than from NaCl. CdO has therefore been suggested[25] as a tertiary standard for practical laboratory work.

Both for spectroscopically pure CdO and for the "commercially pure" CdO containing traces of CO_2 and ZnO,

$$a_{0_{\mathrm{CdO}}} = 4.681 \pm 0.002 \times 10^{-8} \text{ cm.} \tag{14}$$

It will be shown in a later chapter that it is sometimes convenient to have a standard of length in terms of the grating space of some element of higher atomic weight. For this reason the edges of the unit-cubes of Cu, W, and Au have been set up as additional tertiary standards,[26,27] with the following values at room temperature (approximately 20°C.):

此为试读，需要完整PDF请访问：www.ertongbook.com