

THE INTENSITY OF REFLECTION OF X-RAYS BY POWDERED CRYSTALS, I. SODIUM CHLORIDE AND SODIUM, LITHIUM AND CALCIUM FLUORIDES.*

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ABSTRACT

Through measurements by the ionization method of the relative intensities of reflection of x-rays by the different planes of *powdered crystals*, the author has obtained data which are free from the errors inherent in the work with large single crystals. Darwin's formula for the intensity of reflection from an ideally imperfect crystal may be applied to these results without correction for primary or secondary extinction. In order to get reflected radiation of sufficient intensity to permit accurate measurement, a focussing method has been used, in which a primary beam of wide divergence strikes the surface of a briquet of the powder under investigation and the reflected beam is focussed sharply at the ionization chamber slit. Measurements were made out to angles slightly larger than $\theta = 45^\circ$. The absolute values of the intensity of reflection were determined by comparison with reflections from powdered sodium chloride, the results of Bragg, James and Bosanquet on the latter crystal, after allowance for secondary extinction, being taken as correct.

Structure factor and atomic scattering curves.—Application of the equation for the intensity of x-ray reflection to the experimental results gives the structure factors for the reflections from the different crystals. These factors, when plotted against $\sin \theta$, fall upon smooth curves from which can be obtained the atomic scattering curves representing the variation of the atomic structure factors with the angle of reflection. For fluorine in all three fluorides, the F curves are almost identical, but for sodium in NaF and NaCl there is a notable difference, indicating that the electron distribution for Na is not the same in the two compounds. The effect of the excess positive or negative charge which tightens or loosens the electron atmosphere of an ion is made evident by comparison of the F curves for ions of different charge but with the same number of electrons. Use of experimental structure factor curves in crystal analysis is discussed.

INTRODUCTION

RECENTLY there has appeared a paper by W. L. Bragg, Darwin and James¹ which gives a comprehensive survey of theoretical and experimental work on the intensity of reflection of x-rays by crystals. Theoretical treatment of the problem gives rise to two different expressions for the intensity of reflection, depending upon certain assumptions as to the nature of the crystal. One of these expressions may be applied to the case of reflection by a perfect crystal; that is, one which

* A preliminary account of a part of this work has been published in Proc. Nat. Acad. Sci. 12, 380 (1926).

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¹ W. L. Bragg, Darwin and James, Phil. Mag., 1, 897 (1926).

is a homogeneous unit, with each atomic plane strictly parallel to every corresponding atomic plane. The other expression applies to the case of an ideally imperfect crystal; that is, one which is composed of a *mosaic* of very small perfect crystal blocks that are only approximately parallel to each other. The most important difference between the two expressions is that the formula for the perfect crystal makes the intensity of reflection proportional to the first power of the structure amplitude, while the formula for the imperfect crystal, on the other hand, makes the intensity proportional to the square of the structure amplitude. Through experimental tests on various crystals, it has been found that most of them are of the imperfect rather than of the perfect type, but their perfection is nevertheless sufficiently high to make it necessary to modify the mosaic formula. The modification takes the form of a correction for *primary extinction* in the crystal, which can be evaluated only indirectly. The nature of extinction and the manner of determining and applying the correction have been fully discussed by these authors, and we shall base the text of this paper on the assumption that the reader is familiar with the status of the problem as presented by them.

The writer has been working on the problem of the intensity of x-ray reflection from a somewhat different angle, which seems to offer a direct means of determining the scattering power—that is, the effect of extinction is mechanically eliminated and the formula for the ideally imperfect crystal applies strictly to the measurements. Preliminary accounts of this work have been published,² giving the conclusions of the author in regard to the nature of crystals and the amount of extinction to be met in measurements on single crystals which are in general agreement with the ideas of Bragg, Darwin and James.

The method used by the author consists of the measurement of the intensity of x-ray reflection from powdered crystals. When the individual crystal particles become as small as 10^{-2} – 10^{-3} cm in size, secondary extinction becomes negligible; it may be dismissed from consideration in measurements by the powder method. Primary extinction, on the other hand, remains effective until the size of the perfect crystal blocks in the powder is as small as 5×10^{-5} cm. The size of the particles of a powder ground mechanically is usually larger than 10^{-5} cm, hence if the powder particles are perfect crystals, primary extinction would still be present. In an investigation of primary extinction which is described in the following paper, the author has measured the reflections from powdered crystals of various particle sizes; these measurements indicate

² Havighurst, Proc. Nat. Acad. Sci. **12**, 375, 380 (1926); Phys. Rev. **27**, 243 (1926).

that primary extinction is absent from a thoroughly ground powder of any of the substances to be considered here, so the perfect crystal blocks must be smaller than the powder particles themselves. We may anticipate this result then, and assume for the purposes of the present paper that extinction, both primary and ordinary, is entirely eliminated in measurements by the powdered crystal method.

Preliminary measurements have been made by Compton and Freeman³ on powdered sodium chloride, and Darwin⁴ has suggested that measurements by the powder method should give valuable information concerning extinction. The chief difficulty in the way of obtaining reliable intensity measurements by the powder method lies in getting enough radiation reflected from the planes reflecting at large angles for accurate measurement with an ionization chamber.

A brief description of the author's method of securing the necessary intensity will be followed by a survey of measurements upon sodium chloride and lithium, sodium and calcium fluorides. From these measurements the structure factor curves for the various classes of planes in the crystals and finally the atomic scattering curves for the atoms composing these crystals, are obtained.

EXPERIMENTAL

In Fig. 1 is shown a diagram of the experimental arrangement. Brentano⁵ has described the focussing method, which is a generalization of the familiar Bragg "focussing condition." For reflection from the face of a briquet of powder, *A*, mounted at the center of an ionization spectrometer, the distances from focal spot to powder, *a*, and from powder to ionization chamber, *b*, determine the ratio $a/b = \sin \alpha / \sin \beta$, where α is the angle between the primary beam and the surface of the briquet, and $\beta = 2\theta - \alpha$. When this condition is fulfilled the reflected radiation is focussed at the ionization chamber slit to a beam of the same width as that of the primary beam issuing from the focal spot. By means of the auxiliary slit *S*₁, the divergence of the primary beam may be regulated so that a reflected beam of the desired intensity is obtained; at small angles of reflection, *S*₁ is rather narrow, but for the measurement of reflections at large angles, *S*₁ is widened until the divergence of the primary beam is

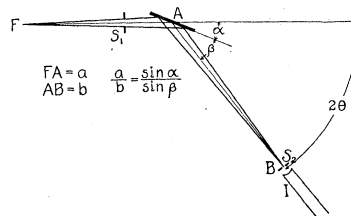


Fig. 1. Diagram illustrating focussing method.

³A. H. Compton and N. L. Freeman, *Nature* **110**, 38 (1922).

⁴Darwin, *Phil. Mag.* **43**, 800 (1922).

⁵Brentano, *Proc. Phys. Soc. London* **37**, 184 (1925).

5 to 6°. Measurements are made over groups of reflections which do not differ too greatly in intensity, the only precaution beyond the fulfillment of the focussing condition being that the surface of the briquet shall intercept the whole of the primary beam in every case. With the apparatus in use by the author, reflections were measured out to angles slightly larger than $\theta = 45^\circ$.

The primary beam from a Mo tube was rendered nearly monochromatic by filtration through enough ZrO_2 to reduce Mo K($\gamma + \beta$) to less than 0.4 percent of Mo K($\alpha_1 + \alpha_2$), while the maximum height of the general radiation curve corresponded to an intensity of about 0.3 percent of the α peak at $\lambda = .710\text{A}$. Only in two or three cases where the β peak from a strongly reflecting set of planes fell in the neighborhood of a very weak α reflection was it necessary to take into consideration the existence of the β peak. The x-ray tube was operated by a high potential storage battery⁶ at 35000 volts and about 25 milliamperes.

Relative intensities could be measured with an error of less than 5 percent except in the case of very weak reflections. The ionization chamber was moved through the width of the slit at each reading and the sum of the ionization currents, after application of a base-line correction, was taken as a measure of the intensity of reflection. Various slit widths were used, including some wide enough to take in the whole reflected beam, with concordant results. The chief source of error lay probably in the base-line correction, since the reflection on the long wave-length side of a peak is always slightly larger than that on the short wave-length side in the case of filtered Mo radiation. However, a standard method of drawing the base-line was adopted, and should be quite satisfactory in the measurement of relative intensities, the only kind of measurements which the author has made. The conceivable sources of systematic error have been investigated. It was found that the pressure used in making the briquet had a tendency to orient the surface layer of crystals if they were larger than 10^{-3} cm in size. Consequently, the original surface of each briquet was shaved off.

As a check on the measurements by surface reflection, and also in the measurements (to be described below) of the relative intensity of reflection by different substances, the method of measuring the intensity of the radiation reflected by and transmitted through a thin plate of powder was used. Because the primary beam must be narrow in this method, only the strongest reflections could be measured, but these

⁶ Armstrong and Stifler, J. Optical Soc. Am. **11**, 509 (1925).

measurements agreed satisfactorily with those made by the surface reflection method.

STRUCTURE-FACTOR DETERMINATIONS FROM POWDER-METHOD MEASUREMENTS

In his discussion of the intensity of x-ray reflection,⁷ A. H. Compton sets forth the theory of reflection by a powder and derives the following formula for the intensity of reflection of x-rays from the surface of a thick briquet of powder:

$$\frac{P_s}{P} = \frac{j l}{16\pi r \mu \sin\theta} \times Q = \frac{j l N^2 F^2 \lambda^3}{64\pi r \mu} \frac{e^4}{m^2 c^4} \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos\theta} \quad (1)$$

P is the power in the primary beam; P_s is the power in the scattered beam which is reflected into an ionization chamber distant r from the powder and having a slit height l which is small compared with $r \sin 2\theta$; j is the number of planes belonging to the crystal form which is reflecting the x-rays; the Q of Bragg, Darwin and James would take the form given above when actually used with experimental data; N is the number of molecules per cc and F^2 contains the Debye temperature factor, $e^{-(b^2 \sin^2 \theta)/\lambda^2}$. It seems best to include the Debye factor in the structure factor F because of the difficulty in making a separate evaluation of it. Both factors depend upon $(\sin \theta)/\lambda$ and the arrangement of the electrons in the unit cell, and the inclusion of the Debye factor in F simply means that the structure factor now depends upon the time means of the positions of the electrons with respect to the stationary points of the crystal lattice, rather than upon their positions with respect to nuclei which, together with their electron atmospheres, are subject to the motions of thermal agitation.

Using the above expression it is possible to calculate the absolute value of F from a measurement of the intensity of reflection. But we are primarily interested in relative F values, and consequently may drop everything out of Eq. (1) which is independent of the angle of reflection. This leaves

$$F^2 \propto \frac{P_s}{j} \frac{\sin^2 \theta \cos\theta}{1 + \cos^2 2\theta} \quad (2)$$

A single absolute F value for each substance will suffice to place on an absolute scale all of the results obtained by the use of expression (2).

⁷ A. H. Compton, X-rays and Electrons, Chap. 5; Van Nostrand and Company (1926). The author wishes to thank Professor Compton for the privilege of using this material in manuscript form.

The author's method of determining absolute values of F depends upon a measurement of F for one or more planes of each substance relative to the F value of the NaCl (220) reflection. From the measurements of Bragg, James and Bosanquet⁸ on single crystals of rock-salt, corrected for secondary extinction, we find $F(220) = 15.75$. There is good reason to believe that this determination is unaffected by primary extinction, since the powder method measurements of relative intensity are in agreement with those of Bragg, James and Bosanquet when the latter are corrected for secondary extinction. Therefore all F determinations in this paper are based upon an absolute value of 15.75 for $F(220)$ of NaCl.

If we measure P_s for the (220) plane of NaCl and then, keeping the intensity of the primary beam constant, replace the briquet of NaCl with a briquet of another substance (X) and measure P_s for some set of planes in this substance, we get from Eq. (1)

$$F_X^2 = \frac{P_{sX}}{P_{sNaCl(220)}} \left(\frac{j N^2 F^2}{\mu} \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right)_{NaCl(220)} \left(\frac{\sin^2 \theta \cos \theta}{1 + \cos^2 2\theta} \frac{\mu}{j N^2} \right)_X \quad (3)$$

By a similar process we get, for the case of reflection through a thin plate of crystal powder which is always kept in such a position that the normal to its surface makes an angle θ with the incident beam,

$$F_X^2 = \frac{P_{sX}}{P_{sNaCl(220)}} \frac{(h \sec \theta e^{-\mu h \sec \theta})_{NaCl(220)}}{(h \sec \theta e^{-\mu h \sec \theta})_X} \left(\frac{j N^2 F^2 (1 + \cos^2 2\theta)}{\sin^2 \theta \cos \theta} \right)_{NaCl(220)} \left(\frac{\sin^2 \theta \cos \theta}{j N^2 (1 + \cos^2 2\theta)} \right)_X \quad (4)$$

h is the thickness of the crystal powder plate and μ is the linear absorption of the powder, the thickness being determined by the weight and surface area of the sample, so that the interstices between the powder particles do not cause error.

In some cases the author used both surface reflection and transmission methods, but the latter proved the more satisfactory. At least one reflection was evaluated for each of the fluorides of lithium, sodium, and calcium, the results being given in Table I.

With the aid of the F values of Table I, we can evaluate the data obtained by the application of expression (2) to the powder method measurements. In Tables IIA and IIB are given the F values for all the reflections which were measured, as well as the atomic F values for the separate atoms composing the crystal planes.

⁸ W. L. Bragg, James and Bosanquet, *Phil. Mag.* **42**, 1 (1921).

TABLE IIB
F values for sodium fluoride and lithium fluoride

Plane	NaF				LiF			
	sin θ	<i>F</i>	<i>F</i> _{Na}	<i>F</i> _F	sin θ	<i>F</i>	<i>F</i> _{Li}	<i>F</i> _F
111	0.133	1.27			0.153	4.61	1.26	5.89
200	.154	14.25	7.76	6.49	.177	6.73	1.25	5.46
220	.217	10.80	6.15	4.65	.250	4.70	1.09	3.63
311	.255	1.38		3.73	.293	1.96	2.91	0.95
222	.266	8.39	4.90	3.49	.306	3.70	2.78	0.92
400	.307	6.59	4.03	2.56	.354	2.64	2.12	0.53
331	.335	1.46		2.13	.386	1.34	1.87	0.53
420	.344	5.51	3.44	2.07	.396	2.31	1.78	0.53
422	.377	4.75	2.99	1.76	.433	1.93	1.47	0.46
511	.399	1.06	2.65	1.59	.460	0.89	1.30	0.41
333								
440	.435	3.46	2.09	1.37	.501	1.37	1.06	0.31
531	.455	0.63		1.23	.524			
600	.461	3.04			.531			
442								
620	.486	2.55			.560	0.96	0.79	0.17
533	.504				.580	0.58		
622	.510	2.38	1.40	0.98	.587	0.87		
711	.550				.632	0.47		
551								
640	.554				.638	0.73		
642	.575	1.86			.662	0.70	0.57	0.13
553	.590	0.39	1.06	0.67	.680	0.41	0.53	0.12
731								
733	.629				.724	0.35		
820	.634	1.41			.730	0.53	0.45	0.08
644								
822	.652	1.33	0.78	0.55				
660								
840	.688	1.22						
842	.705	1.03						
664	.721	0.92						
931	.733	0.00	0.43	0.43				

STRUCTURE-FACTOR CURVES

In Figs. 2-5 the *F* values for the crystal planes are plotted against sin θ . The resulting curves are generally smooth, but show certain definite irregularities which will be discussed later.

Sodium chloride. The curves agree with those of Bragg, James and Bosanquet when the latter are corrected for secondary extinction. The extent of the agreement is shown in Fig. 2, where the author's data are represented by circles, and those of Bragg, James and Bosanquet by crosses.

Lithium fluoride. Since a small amount of heavy impurity in solid solution would cause a considerable change in the scattering power of LiF, the sample was carefully freed from Ca and Mg and several times reprecipitated. The upper curve of Fig. 3 represents planes with all even indices, in which Li and F re-enforce each other; in the lower curve,

for planes with all odd indices, Li interferes with F. Debye and Scherrer⁹ have determined the relative intensities of reflection from the first nine planes of LiF by a photometric study of powder method photographs.

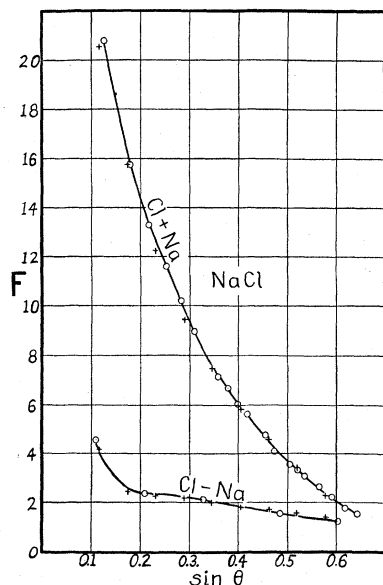


Fig. 2. Structure factor curves for sodium chloride.

Their results fall reasonably well upon the curves of Fig. 3. They interpreted their work as proof that the crystal lattice consists of Li^+ and F^-

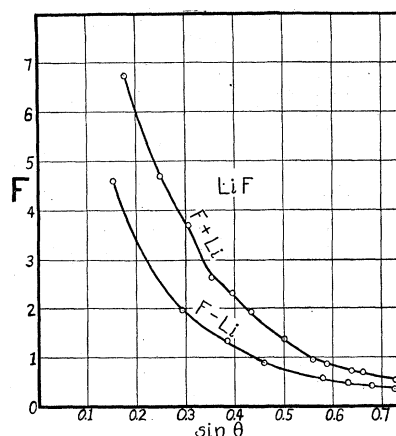


Fig. 3. Structure factor curves for lithium fluoride.

ions, rather than of neutral atoms. We know that the F values should be equal to the number of electrons in the atoms composing the crystal planes at zero angle of reflection. Consequently the $F+Li$ curve should approach the value 12, and the $F-Li$ curve should approach the value 8 if the lattice consists of ions, or 6 if the lattice consists of neutral atoms. The corresponding ratios of $(F+Li)/(F-Li)$ are 1.5 and 2. Debye and Scherrer, by extrapolating the curve representing this ratio to zero angle of reflection, obtained a value of approximately 1.5. While there is abundant evidence from other sources that the lattice of the alkali halides is ionic, the shape of the F curves at small angles is entirely unknown to us and reliance can hardly be placed upon curves extrapolated into this region. The ratio $(F+Li)/(F-Li)$ in Fig. 3 varies between 2 and 1.5, and seems to be approaching the smaller value at small angles.

It is interesting, in connection with recent investigations of the Compton effect in lithium, to observe that the regularly scattered radiation from Li in LiF has not fallen to zero at $\theta=45^\circ$, corresponding to a

⁹ Debye and Scherrer, *Physik. Zeits.* 19, 474 (1918).

scattering angle of 90° . It seems probable then, that there is still some unmodified radiation scattered by atomic lithium at 90° .

Sodium fluoride. Samples from two different sources, each sample containing about 99 percent NaF, were investigated, with results which were in satisfactory agreement. The curve labelled Na-F is of particular interest because it represents the difference in scattering power of the Na^+ and F^- ions, on the assumption that the lattice is ionic. This curve should pass through zero at $\sin \theta = 0$. Since the ions have the same number of electrons, there seems at first no reason for assigning to Na^+ the larger scattering power. But Na^+ , possessing a nuclear charge of $+11$, would bind its electrons more tightly than F^- , with a nuclear charge of $+9$. A system with electrons nearer its center has a larger scattering power through the angular domain covered by the curves of Fig. 4.

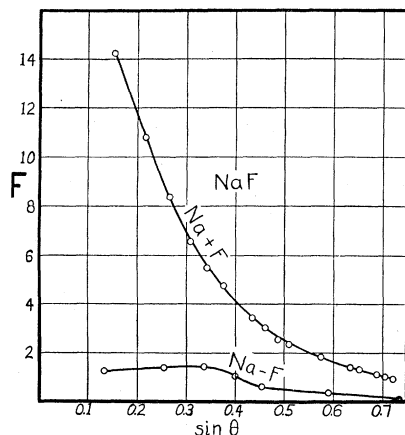


Fig. 4. Structure factor curves for sodium fluoride.

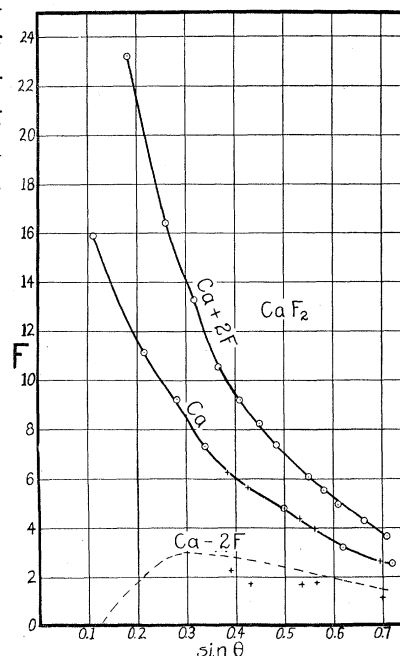


Fig. 5. Structure factor curves for calcium fluoride.

Calcium fluoride. Samples of ground fluorite, and a precipitated product containing less than half of one percent impurity, gave similar results. Fluorite, with a crystal structure different from that of the alkali halides, gives reflections which fall into three classes, as shown in the figure. The Ca-2F reflections are very weak, and occur so close to the Ca reflections that their measurement by the powder method is quite difficult; the points marked + on the two lower curves were obtained by an indirect method as follows: the combined intensity of a Ca reflection and its neighboring Ca-2F reflection was measured, an inter-

polated value from the Ca curve was used for the intensity of the Ca reflection and the amount left over from the total was assigned to the Ca-2F reflection. These values, which are italicized in Table IIA, are therefore only approximate. The broken line curve is that obtained for Ca-2F from the two upper curves. If the Ca^{++} ion, with eighteen electrons, is assumed to be present in the lattice together with two F^- ions, with 10 electrons apiece, the curve representing Ca-2F must drop to zero and rise again as a 2F-Ca curve to a value of 2 when $\sin \theta = 0$. Here we see that Ca^{++} , with an excess positive charge, has drawn its electrons in and consequently scatters x-rays more strongly than the two F^- ions, which possess excess of negative charge.

ATOMIC SCATTERING CURVES

In Figs. 6 and 7 are the atomic scattering curves obtained from the data of Tables IIA and IIB. Of particular interest is a comparison of the curves for the same ion in different compounds. It will be observed

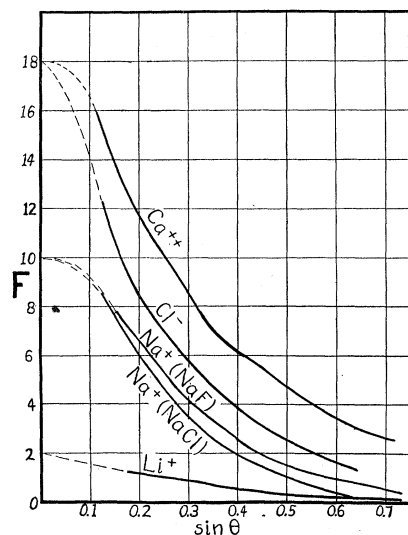


Fig. 6. Atomic scattering (structure factor) curves for various atoms.

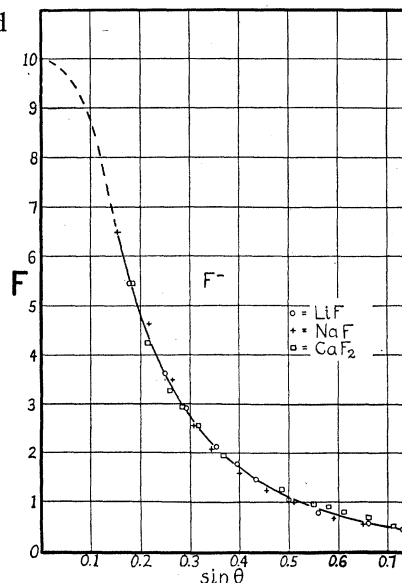


Fig. 7. Atomic scattering (structure factor) curve for fluorine.

that the Na curves from NaF and NaCl are considerably different, probably because of a difference in chemical, thermal, and crystal lattice forces in the two compounds. These forces have in NaF produced a marked tightening of the electron atmosphere of Na. On the other hand, the curves for fluorine from the different compounds are nearly alike. The

conclusion must be that the fluorine ion is in a force field of approximately the same magnitude in all three crystals. The curves for the atoms in fluorite are not in entire agreement with those of James and Randall,¹⁰ because their correction for the extinction operative in their single crystal measurements does not make their results coincide with the author's powder method measurements.

DISCUSSION OF RESULTS

Upon the basis of reliable atomic scattering curves may rest two very important results. In the first place, we may obtain direct evidence concerning the distribution of electrons in atoms. The author has worked out the electron distributions in all of the atoms considered here by means of a Fourier analysis based upon the data of this paper, and a description of this work will be published soon. In the second place, atomic scattering curves are an aid in the analysis of crystal structure. With a knowledge of the scattering curves of the atoms in a crystal, the structure factor for any atomic arrangement may be calculated and a quantitative analysis of the crystal structure can be made, provided the intensities of reflection are measured by the powder method or corrected satisfactorily so that the formula for the mosaic crystal holds strictly.

There is one serious error which may arise in an analysis of crystal structure made by this method. The atomic scattering curves may be appreciably different for the same atom in different chemical compounds, as in the case of Na from NaF and NaCl. In such a case it would be impossible to predict the scattering curve in the crystal under consideration. A discussion of the determination of parameters in crystal structure by the use of atomic scattering curves, as well as a description of another method of determining parameters which does not depend upon atomic scattering curves but involves a Fourier analysis making use of experimental measurements on the intensity of x-ray reflection, has recently been published.¹¹

A study of the ratios of the ordinates of the atomic scattering curves for different values of $\sin \theta$ shows clearly that the assignment of scattering power to atoms in accordance with their total number of electrons is only a crude approximation. A similar variation of scattering power with angle of scattering is predicated by such a procedure. Especially erroneous is this assignment of scattering power in the case of oppositely charged ions (the usual case in crystal analysis) because the excess positive or negative charge produces a tightening or loosening of the elec-

¹⁰ James and Randall, *Phil. Mag.* **1**, 1202 (1926).

¹¹ Havighurst, *J. Am. Chem. Soc.* **48**, 2113 (1926).

tron atmosphere of the original atom which profoundly affects its scattering properties.

The irregularities which are to be observed in the experimental curves may be due not so much to experimental error as to an actual difference of intensity of reflection by a crystal in different directions; that is, the electron distributions of the atoms may not be spherically symmetrical about the nuclei. It is very probable that in many crystals the atoms do not possess spherical symmetry, although the nearest approach to this condition would be expected in atoms belonging to crystals having a high cubic symmetry. At present there are no experimental measurements of sufficient accuracy to decide the question. Irregularities of a more smooth type would be expected from atoms in which there are definite shell-like structures of electrons and the gradual changes of slope due to such irregularities may exist in the experimental curves.

In conclusion the author wishes to express his gratitude to Professor William Duane for his advice and interest in this work.

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