# PHYSICAL REVIEW

# THE INTENSITY OF REFLECTION OF X-RAYS BY POWDERED CRYSTALS. II. THE EFFECT OF CRYSTAL SIZE\*

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#### Abstract

The problem of extinction in its relation to the intensity of reflection of x-rays is studied by a comparison of measurements upon large single crystals with those upon powdered crystals of various particle sizes. The apparatus and method of making the measurements upon powders have been described in the preceding paper. Secondary extinction was not operative in the powder method measurements. Primary extinction is also absent in measurements upon thoroughly ground crystals of substances which, like the alkali halides, naturally form rather imperfect crystals; but a small amount of primary extinction may be produced by heat treatment of the powder. The relative intensities of reflection from the different planes of powdered NaCl, CaF<sub>2</sub> and calcite are compared with similar data from single crystal measurements on these substances. In the case of rock-salt, it is found that the single crystal measurements of Bragg, James and Bosanquet, when corrected for secondary extinction, agree with the powder method results, hence primary extinction was not operative in their experiments. The empirical correction for secondary extinction applied by James and Randall to their single crystal measurements upon CaF<sub>2</sub> is not quite large enough to produce agreement with the powder method data. Although the powder method measurements upon calcite, when compared with single crystal data, show that the latter have been affected by a great deal of extinction, it is not certain that a small amount of primary extinction was not operative even in the powder method measurements, for calcite forms very perfect crystals.

## INTRODUCTION

The importance of obtaining accurate measurements of the intensity of reflection of x-rays from crystals and the difficulty of interpreting the measurements after they have been obtained have been mentioned in the preceding paper and discussed fully in a paper by W. L. Bragg, Darwin and James.<sup>1</sup> In brief, the difficulty is this—there are two formulas for the intensity of x-ray reflection, one for the case of reflection by an absolutely perfect crystal, the other applying to an ideally imperfect crystal; measurements upon single crystals indicate that in some cases neither the conditions of absolute perfection nor those of absolute imperfection are actually satisfied, and consequently one of the formulas

\* A preliminary account of part of this work has been published in Proc. Nat. Acad. Sci. 12, 375 (1926).

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<sup>1</sup> W. L. Bragg, Darwin and James, Phil. Mag. 1, 897 (1926).

must be used (the one for an imperfect crystal) with a correction for the partial perfection of the crystal. Furthermore, there is no satisfactory method for the complete evaluation of this correction.

It is the author's purpose in this paper to prove that at least some crystalline substances when ground to fine powders become ideally imperfect crystals, and the corresponding formula may be applied without correction to measurements of the intensity of x-ray reflection by the powder method.

Darwin's formula<sup>2</sup> for the "integrated reflection,"  $\rho$ , from a large ideally imperfect single crystal (one composed of a mosaic of very small blocks which are only approximately parallel to each other) is

$$p = \frac{N^2 e^4}{m^2 c^4} \frac{F^2 \lambda^3}{2\mu} \frac{1 + \cos^2 2\theta}{\sin 2\theta} = \frac{A^2}{2\mu} \frac{1 + \cos^2 2\theta}{\sin 2\theta} = \frac{Q}{2\mu}$$
(1)

where N is the number of molecules per cc and the Debye temperature factor is included in  $F^2$ . Certain modifications of this formula which must be made before it can be applied to single crystal measurements take the form of corrections for primary and secondary extinction. Secondary extinction takes place only in imperfect crystals and represents a decrease in the intensity of reflection due to shielding of the blocks deep within a crystal by the reflection of the x-rays from the blocks near the surface. Single crystal measurements may be corrected satisfactorily for secondary extinction. It is proportional to the intensity of reflection and causes an effect of the same order of magnitude as that of the ordinary absorption in the crystal; consequently if the crystal is so small that its ordinary absorption for the radiation is negligible (1 or 2 percent), secondary extinction is negligible. The ordinary absorption becomes very small in a crystal as its thickness decreases from  $10^{-2}$  to  $10^{-3}$  cm, and secondary extinction may therefore be neglected in measurements upon crystal powders whose particles are smaller than this lower limit.

#### PRIMARY EXTINCTION

Primary extinction represents the shielding of lower layers by reflection from the parallel upper layers of the same homogeneous fragment, and takes place only in a perfect crystal. If the perfect crystal block has a thickness greater than about  $5 \times 10^{-5}$  cm, primary extinction is appreciable. Its effect is represented by the fractional correction factor in the expression

$$Q' = Q \frac{\tan h \sqrt{(2Qd^2 \cot \theta)/\lambda}}{\sqrt{(2Qd^2 \cot \theta)/\lambda}}$$
(2)

<sup>2</sup> Darwin, Phil. Mag. **43**, 800 (1922).

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Q' is proportional to the measured intensity of reflection and becomes equal to the Q in Eq. (1) when extinction is negligible; d is the thickness of the crystal.

To get some idea of the magnitude of primary extinction, let us evaluate Eq. (2) for rock-salt, using the value of Q' obtained by Bragg, James and Bosanquet<sup>3</sup> for the (200) reflection and corrected for secondary extinction as the Q under the radical. For  $d=5\times10^{-5}$  cm, the correction factor is 0.96, while for  $d=5\times10^{-3}$  cm, the factor is 0.03. Since the value of Q used to obtain these figures is really a Q' value and may have been reduced by primary extinction, it is evident that these are maximum values of the correction factor. If each powder particle of a sample under investigation is a perfect crystal, the intensity of reflection should vary with the size of the particles until they are less than  $5\times10^{-5}$  cm in thickness. Further, the relative intensities from different planes would vary, because the extinction depends upon the intensity of reflection. It will be noticed that primary extinction depends not only upon Q, as does secondary extinction, but also upon cot  $\theta$ .

The evidence gathered by Bragg, Darwin and James indicates that most crystals, when subjected to x-ray investigation, are of the imperfect mosaic rather than of the perfect type, and that primary extinction is not very effective; but the fact that a crystal face must be very thoroughly ground before reliable measurements can be made with it, and that grinding invariably increases the intensity of reflection markedly, may be taken to prove that the grinding process has served to convert the reflecting surface of the crystal into a mosaic. Mechanical strains probably break up the crystal blocks near the surface or produce distortions in them which reduce primary extinction. The much more thorough process of grinding a crystal to a powder would therefore be expected to so distort the powder particles that the size of the particles themselves.

There is reason to believe, from evidence which has been gathering from different sources,<sup>4</sup> that even in a crystal which has been subjected to no mechanical strains there is a notable lack of perfection. The mosaic structure is the usual structure for a crystal, with the size of the perfect crystal blocks and their divergence from the mean orientation depending upon the composition of the crystal and upon the mechanical and thermal

<sup>\*</sup> W. L. Bragg, James and Bosanquet, Phil. Mag. 42, 1 (1921).

<sup>&</sup>lt;sup>4</sup> Mark, Naturwissenschaften 13, 1042 (1925); Becker, Physik. Zeits 26, 919 (1925); Smekal, Physik. Zeits. 26, 707 (1925).

treatment which it has undergone. Estimates of the linear dimensions of the perfect crystal blocks in various substances vary from  $10^{-5}$  to  $10^{-4}$  cm.

#### Experimental

Measurements of the relative intensities of reflection of the Mo Ka doublet by the different planes of crystal powders of various particle sizes have been made, as well as measurements of the relative intensity of reflection of these different samples with respect to a standard sample of NaCl. The experimental procedure has been described in the 200 preceding paper.

Sodium chloride. In order to compare the powder method measurements on NaCl with the data of Bragg, James and Bosanquet on the reflection of Rh K $\alpha$ radiation by single crystalsof rocksalt, it is necessary to make allowance for the difference in wavelength. This is done by express-



Fig. 1. Comparison of powder method and single crystal measurements on sodium chloride.

ing the results in terms of the  $A^2$  of Eq. (1), the relative values of  $A^2$  from various crystal planes being independent of wave-length. From expression (2) of the preceding paper, we get, for the powder method

$$A^2 \propto F^2 \propto \frac{P_s}{j} \frac{\sin^2\theta \cos\theta}{1 + \cos^22\theta}$$
 (3)

In Fig. 1 the relative values of  $A^2$  are plotted against  $(h^2+k^2+l^2)$ , the sum of the squares of the Miller indices multiplied by the order of reflection. Extinction, either primary or secondary, should be detected by a change in relative intensities, as is shown by the difference between the corrected and uncorrected curves of Bragg, James and Bosanquet. Variation in the powder method curves must be due to primary extinction, for the particle size was always too small to permit a noticeable effect from secondary extinction.

The data for Fig. 1 are given in Table I. Sample 3 was a powder which had been ground until the particles were all smaller than  $4 \times 10^{-3}$  cm.

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The  $A^2$  values are seen to fall upon a smooth curve which coincides with that representing the data of Bragg, James and Bosanquet when the latter are corrected for secondary extinction. Some of sample 3 was ground mechanically for several days (sample 5) until the particle size

TABLE I

·						1					
1		Sodium ch	ıloride. Val	ues of	$A^2$ in	ı Eg. (	(1).				
lane	Sing	le crystal	Powdered crystals								
	∴(uncc	orr.) (corr.)	#3	5	6	7	8	8'	9	9'	
11	26	28	26	26						5.2	
00	345	524	539	532	546	447	443	505	491	502	
20	246	312	310	314	319	296	284	323	315	306	
22	203	242	221	214		211			206		
00	142	164	168	170	170	161	163	173	167	166	
20			130	134					130		
22			100	100	100	100	100	100	100	100	
40	66	68	64							1.	
507		57	56								
421											
$\tilde{20}$			45								
22		37	39								
44		40	• • •							+	
42	1	10	21								
ก้ก		14	15 6								
221	1. A.	12.8	11 9								
ร์ก็ไ		12.0	11,7								
	lane 1 10 20 20 20 20 20 20 20 20 20 2	lane         Sing (uncc)           1         26           00         345           20         246           22         203           300         142           20         22           40         66           20         22           44         42           20         22           60         60	$\begin{tabular}{ c c c c c c } \hline Sodium ch \\ \hline lane & Single crystal \\ (uncorr.) (corr.) \\ \hline 1 & 26 & 28 \\ 00 & 345 & 524 \\ 20 & 246 & 312 \\ 22 & 203 & 242 \\ 20 & 142 & 164 \\ 20 & 142 & 164 \\ 20 & & & \\ 22 & & & & \\ 142 & 66 & 68 \\ 00 & 57 \\ 42 & & & & \\ 22 & & & & & \\ 22 & & & & & $	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

was  $1 \times 10^{-4}$  to  $2 \times 10^{-3}$  cm, and gave results identical with those of the original powder. Sample 6, a powder which had passed a 200-mesh sieve and been held back by a 325-mesh sieve, with particle size 4.4 to  $7.4 \times 10^{-3}$ cm, was heated at 760° for 40 hours, then cooled gradually to room temperature. Because of the high vapor pressure at 760° the crystals had grown. After having been reground to their original size, they gave results in agreement with sample 3. Samples 7 and 8 were from the same lot as 6, but were heated at a lower temperature, 700°, for 16 and 46 hours respectively, then cooled slowly to room temperature. The part of the powder which remained between the original limits of size was investigated, care being taken to avoid mechanical strains. The results from these two samples were in close agreement and are plotted in the figure. Evidently sufficient diffusion took place within each powder particle to relieve some of the distortions, and a small amount of primary extinction took place. Analogous results have been obtained by James<sup>5</sup> on heating single crystals of rock-salt. Sample 8, after having been ground for two hours, was reinvestigated (sample 8') and then gave results in agreement with sample 3. Sample 9 was prepared by condensing the vapor of NaCl which had been vaporized from a hot platinum wire. Most of the particles were about 10<sup>-5</sup> cm in diameter, being mere points

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<sup>&</sup>lt;sup>5</sup> James, Phil. Mag. 49, 585 (1925).

when viewed through the oil immersion lens of a microscope, but a few were as large as  $3 \times 10^{-4}$  cm. The measurements show a slight amount of primary extinction, which modified the most intense reflection. Probably crystals formed from the vapor phase are more nearly perfect than those formed from solution, and even though most of the particles were so small that primary extinction in them was negligible, the few larger particles produced an extinction the effect of which was measurable. Although sample 9 was later ground for two hours, there was no change in the intensities of reflection (sample 9'), probably because the particles were so small as to undergo no strains during the grinding.

The results of measurement of the relative intensities of reflection of various samples with respect to the NaCl (220) reflection from NaCl No. 5 are given in Table II. Sample 8 of NaCl here shows no difference from the others, yet in Table I the (200) reflection is found to be reduced 20 percent. A possible explanation seems to be that the measurements of Table II were made three months after the preparation of sample 8 and

The transmission	method was	used and R. is	$P_{sX}(h \sec \theta \exp[-\mu h \sec \theta])_{NaCl(200)}$					
	method was	$P_{s_NaCl}(hs)$	$\frac{1}{P_{s_{NaCl}}(h\sec\theta\exp[-\mu h\sec\theta])_X}$					
Substance	Plane	$R_t$	Substance	Plane	Rt			
NaCl #5,3	200 220	1.75	CaF <sub>2</sub> #2,3	111 220	$2 \cdot 18$ $2 \cdot 44$			
NaCl #8	200 220	1.74 1.01	Calcite #1	211	1.00			
NaCl #9'	200 220	1.65 1.00						

 TABLE II

 Intensity of reflection relative to that from NaCl(200) #5.

  $P_{ex}(bsecdexp[-whsecd])_{xec}(200)$ 

the measurements of Table I, and after the powder had been several times broken up and compressed; during this period the powder particles underwent sufficient strain to cause them to lose whatever perfection they had gained as a result of the original heat treatment. Sample 9' shows a definite decrease of reflected intensity in the (200) reflection of about the same magnitude as the decrease indicated in Table I. This sample, it will be remembered, was unaffected by grinding.

Calcium fluoride. James and Randall<sup>6</sup> have measured the relative intensities of reflection of Mo K $\alpha$  rays from single crystals of fluorite, while MacInnes and Shedlovsky<sup>7</sup> have performed similar experiments with Pd K $\alpha$  rays. Since the measurements of James and Randall were made with the same wave-length as that used by the author, their results will be utilized for comparison.

- <sup>6</sup> James and Randall, Phil. Mag. 1, 1202 (1926).
- <sup>7</sup> MacInnes and Shedlovsky, Phys. Rev. 27, 130 (1926).



calcium fluoride.

Powder method measurements were made upon three different samples of CaF<sub>2</sub>, with results which were in agreement within experi-

mental error. Sample 1 was made by grinding a clear colorless fluorite crystal to 4.4 to  $7.4 \times 10^{-3}$  cm; sample 2 was from the same crystal but was further ground for one day to  $4 \times 10^{-3}$  to  $1 \times 10^{-4}$  cm; sample 3 was a pure precipitated product with particles all smaller than  $4 \times 10^{-3}$  cm. For comparison with the results of James and Randall the powder method values of  $A^2$  are converted into  $\rho$  values by the use of the relation, obtained from Eq. (1) and expression (3)

$$\rho \propto \frac{A^2}{j} \sin\theta \tag{4}$$

The relative values of  $\rho$  obtained Fig. 2. Comparison of powder method in this way were plotted against and single crystal measurements on  $\sin \theta$  in Fig. 2 so as to agree with the results of James and Randall

at large angles of reflection. The data of this figure are contained in Table III. The difference between the two pairs of curves is due to ex-

Calcium fluoride								
Plane	$\sqrt{\rho} \times 10^3$			$\sqrt{\rho} \times 10^3$				
	Single <b>cr</b> ystal (uncorr.)	Powdered crystals		Single crystal (uncorr.)	Powdered crystals			
111	11.18	17.3	642	energy managements	3.32			
220	11.18	19.4	553		$2 \cdot 12$			
311	6 • 63	8.55	731)					
400	8 • 49	11.15	800	2.96	-			
331		6.03	660	2.47	2.49			
422		8.06	555	1.67	1.60			
333	3.56	4.25	840	······	2.18			
440	4.82	5.78	931		1.22			
531	And the second diversion of th	3.33	933	1.18				
620		4.68	862	getting of the same	1.60			
533		2.80	10 42		1.35			
444	diversion of the second second	3.93	755		0.95			
			880	1.43				

TABLE III

tinction which was operative in the single crystal measurements; whether the extinction was all of the secondary type cannot be definitely decided.

James and Randall corrected their results for extinction by assigning to the (111) reflection from CaF<sub>2</sub> an arbitrary F value obtained from the F curve of Ca<sup>++</sup> given by Hartree,<sup>8</sup> and calculating, on the basis of the difference between the assigned and measured values, a correction factor which was proportional to the measured intensity of reflection. The broken-line curves in Fig. 2 represent their corrected results; the curves are seen to fall definitely below those of the powder method for the more intense reflections. The author's F value for the Ca<sup>++</sup> reflection at sin  $\theta = 0.1124$  is 15.9, as against Hartree's value of 15.5, and this difference will account for a part of the discrepancy, but the corrected (220) reflection of James and Randall would still be notably weaker than that observed by the powder method.

Calcite. In spite of the difficulty of obtaining accurate powder method measurements because of the proximity of the different reflected beams from calcite, the measurements of Table IV have been made with sufficient accuracy to show clearly the effect of extinction on the single crystal measurements of W. H. Bragg.<sup>9</sup> Sample 1 was a clear calcite crystal which had been ground for several days to particle size of  $2 \times 10^{-3}$  to  $5 \times 10^{-5}$  cm; sample 2, from the same crystal, was ground for only a

Calcite. Values of $A^2$ in Eq. (1)											
Single crystal			Powdered Crystals								
Plane <sup>–</sup>	$A^2$	Plane	Re	lative int	ensity		$A^2$				
	(uncorr.)		No. 1	No. 2	No. 3	No. 1	No. 2	No. 3			
110	71	110		170			112				
211	395	211	835	841	856	892	898	913			
110	153	110	95	94	117	152	151	188			
220	147	220				182	209	184			
332	263	332	487	562	496	646	745	657			
		321				271	312	276			
		310				100	100	100			
422	100	422	100	100	100	100	100	100			
		432				77	77	77			
220	89	$2\overline{2}0$	31	30	40	75	73	95			
	.,	543				75	73	95			

TABLE IV

short time, to 7.4 to  $4.4 \times 10^{-3}$  cm; sample 3 was prepared by addition of a saturated solution of ammonium carbonate to a saturated solution of calcium chloride. The crystals of sample 3 were in clusters, 1 to  $5 \times 10^{-4}$ cm in diameter, with the individual crystals much smaller. No attempt has been made to interpret the differences between the powder measurements, these differences being of a much smaller order of magnitude than

<sup>9</sup> W. H. Bragg, Phil. Trans. Roy. Soc. A. 215, 253 (1915).

<sup>&</sup>lt;sup>8</sup> Hartree, Phil. Mag. 50, 289 (1925).

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those between the single crystal data and the powder method data. The indices given in Table IV are based upon a unit rhombohedron containing two molecules of CaCO<sub>3</sub> with  $a_0 = 6.362 \ A$  and  $\alpha = 46^{\circ} 6'$ . In the cases where reflections were superposed in the powder method, the total intensity was divided among the components in the ratios suggested by their structure factors as approximated by the ordinary formula used in crystal analysis. The F value for the (211) reflection from sample 1, determined from the data of Table II, is 19.8, while the limiting value for F at  $\sin \theta = 0$  for this class of planes is 34. Perhaps the large decrease in F should be taken to indicate that some ordinary extinction is still effective in the powder method results. A. H. Compton<sup>10</sup> determined F for the (211) reflection of a large calcite crystal, his value without any correction for extinction being about 11.

## Conclusions

The formula for the intensity of x-ray reflection from an ideally imperfect crystal may be applied without modification to measurements by the powder method, provided that the crystals have been ground to less than  $10^{-3}$  cm in thickness. This conclusion may not hold strictly for a few substances like calcite, which form very perfect crystals. Upon the basis of atomic scattering curves obtained from powder method data, reliable determinations of electron distribution may be made. Further, the correction for secondary extinction as determined and applied by Bragg, James and Bosanquet was satisfactory in the case of rock-salt, while primary extinction was not operative in their experiments. Although experimental determinations of secondary extinction have been made for no other crystals and a rigid test cannot therefore be applied, the indications are that the formula for the ideally imperfect crystal may be applied to most single crystal measurements after the latter have been corrected for secondary extinction.

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<sup>10</sup> A. H. Compton, Phys. Rev. 10, 95 (1917).