

PRECISION MEASUREMENTS OF CRYSTALS OF THE
ALKALI HALIDES.

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SYNOPSIS.

Crystal structure and dimensions for all the alkali halides.—The Hull powder method of obtaining x-ray diffraction patterns was used. By comparing each diffraction pattern directly with the pattern of NaCl simultaneously recorded on the other half of the film, the grating space of each crystal powder was measured in terms of the side of the unit cube of NaCl, assumed to be 2.814 Å, with a precision of about 0.1 per cent. The average results for the sides of the unit cubes are as follows:

	Li.	Na.	K.	Rb.	Cs.
Fluorides.....	2.007	2.310	2.664	3.663	3.004
Chlorides.....	2.566	Assumed	3.138	3.267	4.118
Bromides.....	2.745	2.968	3.285	3.418	4.287
Iodides.....	3.537	3.231	3.525	3.655	4.558

The arrangement of the ions is simple cubic except for RbF, CsCl, CsBr and CsI for which it is body-centered cubic. The relative intensities of the lines reflected from various planes and the corresponding computed interplanar distances are tabulated for each halide. It was observed that Cs and I ions are as equal in diffracting power as are the atoms of Mo, Ta and W, which crystallize with the same structure as CsI, and that K and Cl ions also have equal diffracting power.

Crystal densities of all the alkali halides, computed from x-ray data.—The results, accurate to within about 0.3 per cent, are as follows, assuming the density of NaCl to be 2.163:

	Li.	Na.	K.	Rb.	Cs.
Fluorides.....	2.646	2.809	2.534	3.504	4.617
Chlorides.....	2.069	Assumed	1.990	2.859	3.973
Bromides.....	3.463	3.246	2.768	3.415	4.453
Iodides.....	2.494	3.665	3.125	3.557	4.523

For the chlorides and iodides, except LiI, the values agree with those obtained by other methods within 0.2 per cent on the average, whereas for the others the values are higher by 0.5 to 1.5 per cent for the bromides and 1 to 9 per cent for the fluorides.

THE results of the measurements of crystals of the alkali halides have been presented from time to time at the meetings of the American Physical Society. It is the purpose of the present article to record these results in a form suitable for reference. The apparatus used has already been sufficiently described.¹ The method was the well-

¹ Davey, A New X-ray Diffraction Apparatus. Journ. Opt. Soc. Am., V., 479 (1921); General Electric Review 25, 565, (1922)

known Hull powder method. The opacity of the crystals to x-rays was decreased by diluting the crystal powder with flour or cornstarch. By simultaneously recording the x-ray diffraction pattern of NaCl on one half of the film, and the pattern of the crystal under investigation on the other half of the same film, it is possible to determine the dimensions of the second crystal in terms of the dimensions assumed for NaCl. The side of the unit cube of NaCl was taken as 2.814 Å, following Duane.¹

TABLE I.

CsI.

Plane.	Intensity.	Interplanar Distance.			
		(1)	(2)	(3)	(4)
1 1 0.....	100	3.23	3.23	3.21	3.23
1 0 0.....	40	2.28	2.28	2.28	2.28
2 1 1.....	80	1.858	1.862	1.862	1.862
1 1 0 (2).....	25	1.613	1.614	1.612
3 1 0.....	30	1.440	1.443	1.441	1.442
1 1 1.....	6	1.317	1.318	1.316	1.318
3 2 1.....	25	1.217	1.220	1.219	1.218
1 0 0 (2).....	3	1.139	1.140
{ 4 1 1	6	1.074	1.076	1.074	1.076
1 1 0 (3).....					
2 1 0.....	4	1.016	1.018	1.019	1.019
3 3 2.....	4	.970	.971	.970	.972
2 1 1 (2).....	3	.929	.930	.930
{ 4 3 1.....	6	.894	.894	.893
5 1 0					
5 2 1.....	3	.830	.831
1 1 0 (4).....	1
{ 5 3 0	3	.780	.781
4 3 3.....					
{ 1 0 0 (3)	1
2 2 1.....					
{ 6 1 1	2	.738	.740
5 3 2.....					
Side of unit cube.....		4.553	4.560	4.559	4.561

CsI.—Diffraction pattern, body-centered cubic.

Crystal structure, body-centered cube of ions. $d = 4.558 \pm .005$ Å.

Distance of closest approach of Cs and I, — 3.947 Å.

Density { from x-ray data, — 4.523 ± .014.
from literature, — 4.509.

The lines in the diffraction pattern, especially those which are nearest the zero-line, have a shape roughly like that of the cross section of some part of a plano-concave or convex-concave lens, since the source of the pattern is a line instead of a point. The reading of each line was taken at a point corresponding to the center of the "lens." No accuracy is

¹ Duane, Bulletin of the National Research Council, Vol. 1, part 6, No. 6 (1920).

claimed for lines caused by planes having a spacing of more than 2.00 Å. Every line which corresponded to an inter-planar distance of 2.00 Å or less was made to give a value for the side of the unit cube by multiplying the interplanar distance by the appropriate theoretical ratio. The values

TABLE II.

CsBr.

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
100.....	1	4.33
110.....	100	3.03	3.03
111.....	$\frac{3}{2}$	2.42
100 (2).....	10	2.15	2.14
210.....	$\frac{3}{4}$	1.925
211.....	35	1.750	1.750
110.....	7	1.520	1.516
{ 221			
100 (3).....	$\frac{1}{2}$	1.431
310.....	5	1.356	1.355
311.....	$\frac{1}{4}$
111 (2).....	$1\frac{1}{2}$	1.240	1.239
320.....	$\frac{1}{4}$
321.....	$3\frac{1}{2}$	1.148	1.147
100 (4).....	$\frac{3}{4}$	1.073
{ 410			
322.....	$\frac{1}{4}$
411 }.....	$1\frac{1}{2}$	1.011	1.010
110 }.....			
331.....
210 (2).....	$\frac{3}{4}$.957
421.....
332.....	$\frac{3}{4}$.914
211 (2).....	$\frac{3}{4}$.875
{ 430			
111 (5).....
431 }.....			
510 }.....	$1\frac{1}{2}$.841	.840
Side of unit cube.....		4.288	4.287

CsBr.—Diffraction pattern, simple cubic. The strong lines form a body-centered cubic pattern.

Crystal structure, body-centered cube of ions, $d_0 = 4.287 \pm .004$ Å.

Distance of closest approach of $\overset{+}{\text{Cs}}$ and $\overset{-}{\text{Br}}$, 3.713 Å.

Density { from x-ray data, $4.453 \pm .013$.
from literature, 4.433.

so obtained from any one film were clustered about some one value according to the probability law. For a given kind of crystal the most probable value of the side of the unit cube (measured graphically)¹ differed from film to film by not more than 0.1 per cent from the mean

¹ Whipple, Journ. Franklin Inst., 182, 37-205 (1916).

except in the case of LiF, where the variation was less than 0.2 per cent from the mean.

As a check on the results, the densities of the crystals were calculated from the x-ray data and compared with the densities ordinarily found in the literature. Wherever possible the values are those given by Baxter

TABLE III.

CsCl.

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
1 0 0.....	$1\frac{1}{2}$	4.2	4.2
1 1 0.....	10	2.90	2.92
1 1 1.....	1	2.38	2.38
1 0 0 (2).....	$1\frac{1}{2}$	2.05	2.06
2 1 0.....	$1\frac{1}{2}$	1.840	1.848
2 1 1.....	3	1.681	1.681
1 1 0 (2).....	$1\frac{1}{2}$	1.454	1.458
2 2 1			
{ 1 0 0 (3).....	1	1.372	1.373
3 1 0.....	$1\frac{1}{2}$	1.303	1.303
3 1 1.....	$\frac{1}{2}$	1.238	1.241
1 1 1 (2).....	$\frac{1}{2}$
3 2 0.....	$\frac{1}{2}$
3 2 1.....	2	1.102	1.102
1 0 0 (4).....	$\frac{1}{2}$
{ 4 1 0			
3 2 2.....	$\frac{1}{2}$.999	.997
4 1 1			
{ 1 1 0 (3).....	$\frac{3}{4}$.972	.971
3 3 1.....
2 1 0 (2).....	$\frac{1}{2}$.921	.919
4 2 1.....	$\frac{1}{2}$.897
3 3 2.....	$\frac{1}{2}$.877
2 1 1 (2).....	$\frac{1}{4}$
{ 4 3 0			
1 0 0 (5).....	$\frac{1}{2}$
4 3 1			
{ 5 1 0.....	$\frac{1}{2}$.806	.806
Side of unit cube.....		4.116	4.120

CsCl.—Diffraction pattern, simple cubic.

Crystal structure, body-centered cube of ions. $d = 4.118 \pm .004$ A.

Distance of closest approach of $\overset{+}{\text{Cs}}$ and $\bar{\text{Cl}}$, 3.566 A.

Density { from x-ray data, 3.973 \pm .012.
 { from literature, 3.974

and Wallace at 25° C.¹ Other sources are specifically mentioned when used. Since the calculated densities are free from errors in weighing due to voids and to the presence of moisture, they may be expected to

¹ Baxter and Wallace, Journ. Am. Chem. Soc., 38, 260 (1916). These authors give references to the earlier determinations. Further references may be found in Groth's *Chemische Krystallographie*, Vol. I (1906).

be more accurate than most of the currently accepted densities. If the crystal data are accurate to 0.1 per cent, the calculated densities should be correct to 0.3 per cent. In the calculation of the densities, the mass associated with each unit of atomic weight was taken to be 1.649×10^{-24} grams.¹

TABLE IV.

CsF.

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
111.....	10	3.47	3.48
100.....	15	2.99	3.01
110.....	15	2.12	2.13
311.....	8	1.812	1.815
111 (2).....	4	1.735	1.736
100 (2).....	2	1.502	1.501
331.....	3	1.379	1.381
210.....	5	1.342	1.341
211.....	2½	1.227	1.225
{ 511			
111 (3).....	3	1.157	1.158
110 (2).....	½	1.062
531.....	1½	1.016	1.017
{ 100 (3)			
221.....	1	1.001	1.001
310.....	½	.950	.948
533.....	1917
311 (2).....	1905
111 (4).....	½868
{ 711			
551.....	¾839
320.....
321.....	¾803
{ 553			
731.....	¾782
100 (4).....	½751
733.....
{ 410			
322.....	½728
Side of unit cube.....		6.006	6.008

CsF.—Diffraction pattern, face-centered cubic.

Crystal structure, simple cube of ions. $d = 3.004 \pm .003$ A.

Distance of closest approach of $\overset{+}{\text{Cs}}$ and $\overset{-}{\text{F}}$, 3.004 A.

Density { from x-ray data, $4.617 \pm .014$.

{ from literature, 4.38 (H. E. Merwin, quoted by Wyckoff and Posenjak, Jl. of Wash. Acad. Sci., 12, 248, 1922).

In the case of the elements, the intensities of the lines in the diffraction patterns depend upon the effects of temperature, absorption, size of crystals, distribution of electrons, variation of reflecting power with

¹ Davey, Science, Nov. 18, 1921.

TABLE V.

RbI.

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
111.....	1	4.24	4.25
100.....	7	3.69	3.69
110.....	2	2.59	2.55
311.....	$\frac{1}{2}$	2.21	2.20
111 (2).....	1	2.12	2.11
100 (2).....	$\frac{1}{2}$	1.828	1.830
331.....	$\frac{1}{2}$
210.....	1	1.636	1.635
211.....	1	1.493	1.491
511 and 111 (3).....	$\frac{1}{2}$
110 (2).....	$\frac{1}{2}$	1.292
531.....	$\frac{1}{2}$
100 (3) and 221.....	$\frac{1}{2}$	1.218	1.217
310.....	$\frac{1}{2}$	1.156
533.....	$\frac{1}{2}$	1.101
311 (2).....	$\frac{1}{2}$
111 (4).....	$\frac{1}{2}$
711 and 551.....	$\frac{1}{2}$	1.014
320.....	$\frac{1}{2}$.976
Side of unit cube.....		7.310	7.309

RbI.—Diffraction pattern, face-centered cubic.Crystal structure, simple cube of ions. $d = 3.655 \pm .004$ A.Distance of closest approach of Rb^+ and I^- , -3.655 A.Density: from x-ray data, $3.557 \pm .011$; from literature, 3.550.

TABLE VI.

RbBr.

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
100.....	15	3.41	3.45
110.....	10	2.41	2.42
111.....	3	1.970	1.975
100 (2).....	1	1.703	1.706
210.....	3	1.527	1.530
211.....	2	1.396	1.393
110 (2).....	$\frac{1}{2}$	1.211
221 and 100 (3).....	1	1.140
310.....	$\frac{1}{2}$	1.083
311.....	$\frac{1}{2}$	1.030
Side of unit cube.....		3.418	3.417

RbBr.—Diffraction pattern, simple cubic.Crystal structure, simple cube of ions. $d = 3.418 \pm .003$ A.Distance of closest approach of Rb^+ and Br^- , 3.418 A.Density: from x-ray data, $3.415 \pm .010$; from literature, 3.349.

TABLE VII.

RbCl:

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
111.....	2	3.77	3.77
100.....	3	3.25	3.25
110.....	2	2.29	2.30
311.....	$\frac{1}{2}$	1.971	1.970
111 (2).....	1	1.890	1.884
100 (2).....	$\frac{3}{4}$	1.633	1.635
331.....	$\frac{1}{2}$	1.497
210.....	1	1.463	1.462
211.....	$\frac{3}{4}$	1.333	1.333
Side of unit cube.....		6.536	6.534

RbCl.—Diffraction pattern, face-centered cubic.

Crystal structure, simple cube of ions. $d = 3.267 \pm .003$ A.

Distance of closest approach of $\overset{+}{Rb}$ and \bar{Cl} , 3.267 A.

Density $\left\{ \begin{array}{l} \text{from x-ray data, } 2.859 \pm .009. \\ \text{from literature, } 2.798 \text{ (Baxter and Wallace).} \end{array} \right.$

2.806 — 2.827 (Groth, Chemische Krystallographie).

TABLE VIII.

RbF.

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
100.....	10	3.69	3.66
110.....	8	2.61	2.59
111.....	2	2.12	2.11
100 (2).....	1	1.840	1.835
210.....	3	1.639	1.638
211.....	$1\frac{1}{2}$	1.496	1.492
110 (2).....	$\frac{3}{4}$	1.292	1.290
{ 221			
{ 100 (3).....	1	1.219	1.220
310.....	$\frac{3}{4}$	1.159	1.157
311.....	$\frac{1}{2}$	1.105
111 (2).....	$\frac{1}{2}$
320.....	$\frac{1}{2}$
321.....	$\frac{3}{4}$.979	.979
Side of unit cube.....		3.665	3.661

RbF.—Diffraction pattern, simple cubic.

Crystal structure, body-centered cube of ions. $d = 3.663 \pm .004$ A.

Distance of closest approach of $\overset{+}{Rb}$ and \bar{F} , — 3.172 A.

Density $\left\{ \begin{array}{l} \text{from x-ray data, } 3.504 \pm .010. \\ \text{from literature, } 3.202 \text{ (Van Nostrand's Chem. Annual).} \end{array} \right.$

angle, and the number and grouping of the cooperating planes. In the case of compounds, the intensities depend also upon the relative number of electrons in the atoms or ions. For instance, Cs^+ and I^- have the same number of electrons, and act identically, within experimental error. The pattern is that of a body-centered cube. In CsBr , the Br^- has fewer electrons than the Cs^+ . The reflection from Br^- is weaker than that from Cs^+ , so that the diffraction pattern of CsBr is that of a body-centered cube of strong lines, with weaker lines added which change the

TABLE IX.

KI.

Plane.	Intensity.	Interplanar Distance.		
		(1)	(2)	(3)
111.....	2	4.07	4.07	4.07
100.....	8	3.53	3.53	3.53
110.....	6	2.49	2.49	2.49
311.....	2	2.13	2.13	2.13
111 (2).....	3	2.04	2.04	2.04
100 (2).....	$1\frac{1}{2}$	1.763	1.764
331.....	1	1.620	1.620
210.....	4	1.578	1.576	1.577
211.....	3	1.442	1.439	1.440
{ 511.....	$\frac{3}{4}$	1.356	1.355	1.358
111 (3).....				
110 (2).....	$1\frac{1}{2}$	1.247
531.....	$\frac{1}{2}$	1.194
{ 100 (3).....	1	1.172	1.174	1.176
221.....				
310.....	1	1.114	1.114	1.115
533.....	$\frac{1}{2}$
311 (2).....	$\frac{3}{4}$	1.061	1.061
111 (4).....	$\frac{1}{2}$
{ 711.....	$\frac{1}{2}$
511.....				
320.....	$\frac{1}{2}$
321.....	1	.940	.941	.941
Side of unit cube.....		7.050	7.045	7.054

KI.—Diffraction pattern, face-centered cubic.

Crystal structure, simple cube of ions. $d = 3.525 \pm .004$ A.

Distance of closest approach of $\overset{+}{\text{K}}$ and $\overset{-}{\text{I}}$, 3.525 A.

Density { from x-ray data, 3.125 \pm .009.
from literature, 3.123.

pattern into that of a simple cube. In CsCl , since the number of electrons in Cl^- is still less than in Br^- , the interference is still less complete, so that those lines which were faint in the case of CsBr are considerably stronger in the diffraction pattern of CsCl .

The accuracy with which the intensities of lines in a diffraction pattern

can be estimated from a photographic film is low. The rate at which energy is received by the film is so small that the ordinary exposure law no longer holds. Small changes in blackness often represent large changes in incident energy. For this reason no numerical estimate of x-ray intensities has been made, but the blackness of each line on the photographic film is expressed in terms of an arbitrary scale of 100. If a comparison is desired of the relative intensities of the lines in the patterns of two substances, both patterns should be taken on the same film and should have about the same range of exposure. Equality of exposure times for the same exposure-range may be obtained by diluting the more active specimen with flour or cornstarch.

TABLE X.

KBr.

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
111.....	2	3.78	3.80
100.....	10	3.27	3.30
110.....	9	2.32	2.32
311.....	$1\frac{1}{2}$	1.975	1.982
111 (2).....	5	1.895	1.901
100 (2).....	$1\frac{1}{2}$	1.638	1.643
331.....	$\frac{3}{4}$	1.510
210.....	6	1.465	1.470
211.....	3	1.343	1.343
{ 511	$1\frac{1}{2}$
{ 111 (3).....			
{ 110 (2).....	$\frac{3}{4}$	1.162
{ 100 (2)	1	1.096	1.095
{ 221.....			
{ 310.....			
{ 311 (2).....			
321.....	$\frac{1}{2}$.989	.990
321.....	$\frac{1}{2}$879
Side of unit cube.....		6.564	6.576

KBr.—Diffraction pattern, face-centered cubic.Crystal structure, simple cube of ions. $d = 3.285 \pm .003$ A.Distance of closest approach of $\overset{+}{K}$ and $\overset{-}{Br}$, 3.285 A.Density { from x-ray data, $- 2.768 \pm .008$.
from literature, $- 2.749$.

Certain lines were so faint on some of the films that no accurate reading of the inter-planar distance could be made. In such cases an estimate was made of the blackness of the line in terms of the arbitrary scale, as an indication that the line was actually present in the diffraction pattern.

CsI.—This was a sample obtained from the Chemical Laboratory of the University of Illinois. The pattern is of the body-centered cubic

type. The density shows that the arrangement of ions is also body-centered cubic. This is the arrangement to be expected for close-packing of equal numbers of oppositely charged spheres. Table I. shows the data taken from three films. One of these was read twice with a time interval of about three months between readings. Both readings (1 and 2 in the table) are given to show how nearly the readings may be duplicated. Two other films, not shown in the table, were taken in which the NaCl calibration was replaced by the diffraction patterns of Mo and Ta

TABLE XI.

KCl.

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
1 0 0.....	15	3.12	3.13
1 1 0.....	10	2.21	2.21
1 1 1.....	3	1.812	1.814
1 0 0 (2).....	1	1.567	1.575
2 1 0.....	$2\frac{1}{2}$	1.403	1.404
2 1 1.....	$1\frac{1}{2}$	1.281	1.281
1 1 0 (2).....	$\frac{1}{2}$	1.110
{ 2 2 1	1	1.045	1.046
1 0 0 (3).....			
3 1 0.....	$\frac{1}{2}$.991	.992
3 1 1.....	$\frac{1}{2}$.944	.946
1 1 1 (2).....	$\frac{1}{2}$.905
3 2 0.....	$\frac{1}{2}$.869
3 2 1.....	$\frac{1}{2}$.838	.839
Side of unit cube.....		3.136	3.140

KCl.—Diffraction pattern, simple cubic.

Crystal structure, simple cube of ions. $d = 3.138 \pm .003$ A.

Distance of closest approach of $\overset{+}{K}$ and \bar{Cl} , 3.138 A.

Density { from x-ray data, $1.990 \pm .006$.
 from literature, 1.987.

respectively for the purpose of comparing the intensities of the various lines. These films show that the relative intensities of the lines of CsI, Mo and Ta are identical within experimental error. Since the marshalling of ions in CsI is identical with the marshalling of atoms in Mo and Ta, the equality of intensities shows that, within experimental error, Cs^+ and I^- are as equal in diffracting power as the atoms of Mo or of Ta. The value $4.558 \pm .005$ A assigned to the side of the unit cube of CsI

agrees well with the value 4.562 Å reported by Clark and Duane.¹ As far as is known to the writer these values represent the only attempts to date to obtain a precision measurement of the cube of CsI.

TABLE XII.

KF.

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
111.....	$1\frac{1}{2}$	3.11	3.09
100.....	10	2.69	2.67
110.....	8	1.887	1.882
311.....	1	1.609
111 (2).....	2	1.539	1.538
100 (2).....	1	1.333	1.334
331.....	$\frac{3}{4}$	1.222
210.....	$2\frac{1}{2}$	1.192	1.193
211.....	$1\frac{1}{2}$	1.087	1.088
{ 511.....	$\frac{1}{2}$	1.024
{ 111 (3).....			
{ 110 (2).....			
{ 531.....			
{ 100 (3).....	$\frac{1}{2}$.939
{ 211.....	$\frac{1}{2}$.900
{ 310.....	$\frac{1}{2}$.887
{ 533.....	$\frac{3}{4}$.842
{ 311 (2).....	$\frac{1}{2}$.803
{ 111 (4).....	$\frac{3}{4}$
{ 711.....	$\frac{1}{2}$
{ 551.....	$\frac{1}{2}$
{ 320.....	$\frac{1}{2}$
{ 321.....	$\frac{3}{4}$.711
Side of unit cube.....		5.327	5.330

KF.—Diffraction pattern, face-centered cubic.

Crystal structure, simple cube of ions. $d = 2.664 \pm .003$ Å.

Distance of closest approach of $\overset{+}{K}$ and $\overset{-}{F}$, 2.664 Å.

Density $\left\{ \begin{array}{l} \text{from x-ray data, } 2.534 \pm .008. \\ \text{from literature, } 2.35 - 2.48 \text{ (Groth, Chemische Krystallographie).} \\ \quad \quad \quad 2.454 \text{ (Van Nostrand's Chem. Annual).} \end{array} \right.$

CsBr.—This was made by treating the iodide with HBr in the presence of H₂O₂. The CsBr was crystallized out from aqueous solution. Readings are tabulated from two films.

¹ Clark and Duane, Phys. Rev. 20, 85, (1922).

CsCl.—This was made by treating the iodide with HCl in the presence of H_2O_2 . The CsCl was crystallized out from aqueous solution. Readings are tabulated from two films, one of which had more exposure than the other. All the lines of the fainter film match the theoretical simple cubic pattern. The more strongly exposed film shows four additional

TABLE XIII.

NaI.

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
111.....	4	3.74	3.75
100.....	6	3.24	3.24
110.....	5	2.29	2.29
311.....	4	1.953	1.954
111 (2).....	2	1.864	1.870
100 (2).....	$1\frac{1}{2}$	1.615	1.619
331.....	2	1.486	1.485
210.....	3	1.448	1.445
211.....	$2\frac{1}{2}$	1.319	1.319
{ 511.....			
111 (3).....	$1\frac{1}{2}$	1.245	1.244
110 (2).....	1	1.145	1.142
531.....	1	1.096	1.093
{ 100 (3).....			
221.....	1	1.077	1.077
310.....	1	1.022	1.020
533.....	$\frac{1}{2}$.987	.986
311 (2).....	$\frac{3}{4}$.973	.972
111 (4).....	$\frac{1}{2}$
{ 711.....			
551.....	$\frac{1}{2}$.905	.904
320.....	$\frac{1}{2}$.897	.895
321.....	$\frac{1}{2}$.864	.862
{ 731.....			
553.....	$\frac{1}{2}$.841	.840
100 (4).....
733.....
{ 410.....			
322.....	$\frac{1}{2}$.782
{ 110 (3).....			
411.....	$\frac{1}{2}$.761
Side of unit cube.....		6.466	6.460

NaI.—Diffraction pattern, face-centered cubic.

Crystal structure, simple cube of ions. $d = 3.231 \pm .003$ A.

Distance of closest approach of Na^+ and I^- , 3.231 A.

Density { from x-ray data, $3.665 \pm .011$.
from literature, 3.665.

faint lines. As nearly as could be measured, these corresponded to interplanar distances of 2.26, 2.15, 1.94 and 1.89 A. They are probably due to a trace of impurity, as they are also present as faint lines on a badly overexposed film mentioned below under CsF.

CsF.—Attempts to make *CsF* from Cs_2CO_3 according to the directions given in Gmelin-Kraut gave an almost amorphous mass. Prolonged exposure gave only a general fog on the film with a few faint lines, some of which were mentioned above under *CsCl*. The lines showed interplanar spacings of 3.18, 2.60, 2.26, 2.15, 1.94, 1.89, 1.83 and 1.42 Å as nearly as could be determined. The general fog was so great and the lines were so faint that no accuracy can be claimed for the readings. The *CsF* was so hygroscopic that it was difficult to keep it water-free.

TABLE XIV.

NaBr.

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
111.....	$2\frac{1}{2}$	3.45	3.45
100.....	8	2.98	2.98
110.....	10	2.10	2.10
311.....	3	1.791	1.788
111 (2).....	3	1.714	1.711
100 (2).....	1	1.483	1.485
311.....	1	1.363	1.359
210.....	3	1.329	1.325
211.....	2	1.213	1.213
{ 511.....	2	1.144
{ 111 (3).....			
110 (2).....	$\frac{1}{2}$	1.049	1.049
531.....	$\frac{1}{2}$	1.005
{ 100 (3).....	1	.989	.988
{ 221.....			
310.....	1	.938	.938
533.....	$\frac{1}{2}$
311 (2).....	$\frac{1}{2}$
111 (4).....	$\frac{1}{2}$
{ 711.....	$\frac{1}{2}$
{ 551.....			
320.....	$\frac{1}{2}$
321.....	$\frac{1}{2}$.794
Side of unit cube.....		5.939	5.932

NaBr.—Diffraction pattern, face-centered cubic.

Crystal structure, simple cube of ions. $d = 2.968 \pm .003$ Å.

Distance of closest approach of Na and Br, 2.968 Å.

Density { from x-ray data, $3.246 \pm .010$.
from literature, 3.203.

An effort was made to suck up molten *CsF* into a glass specimen tube. The melting point of the *CsF* was above the softening point of the glass, so that it was not possible to fill the tube. A sample of *CsF* obtained from the Geophysical Laboratory through the kindness of Dr. Sosman and Mr. Posenjak gave results tabulated in Table IV. This sample is from the same lot of salt as that used by Posenjak and Wyckoff.¹

¹ Posenjak and Wyckoff, Jour. Wash. Acad. Sci., 12, 248, (1922).

RbI.—This was a sample bought from Merck. The data from two films are tabulated in Table V.

RbBr.—This was made from the iodide in the same manner as CsBr. All the Rb salts and all bromides give considerable fog on the films due

TABLE XV.

NaCl.

Plane.	Intensity.	Theoretical Interplanar Distance ($d_{NaCl} = 5.628$).
111.....	3	3.249
100.....	100	2.814
110.....	90	1.990
311.....	$\frac{3}{4}$	1.697
111 (2).....	15	1.625
100 (2).....	4	1.407
331.....	$\frac{3}{4}$	1.291
210.....	20	1.259
211.....	10	1.149
{ 511.....		
{ 111 (3).....	$\frac{1}{2}$	1.083
{ 110 (2).....	2	.995
{ 531.....	$\frac{1}{2}$.951
{ 100 (3).....		
{ 221.....	$2\frac{1}{2}$.938
{ 310.....	2	.890
{ 533.....	1	.858
{ 311 (2).....	$\frac{3}{4}$.848
{ 111 (4).....	$\frac{1}{4}$.812
{ 711.....		
{ 551.....788
{ 320.....	$\frac{1}{2}$.780
{ 321.....	1	.752
{ 551.....		
{ 731.....733
{ 100 (4).....703
{ 733.....688
{ 410.....		
{ 322.....	1	.602
Side of unit cube.....		5.628

NaCl.—Diffraction pattern, face-centered cubic.

Crystal structure, simple cube of ions. " d " is assumed to be 2.814 A.

Density { on the basis of $d = 2.814$ A, 2.163.

{ from literature 2.161 (Baxter and Wallace).

2.167 - 2.188 (Groth, *Chemische Krystallographie*).

to fluorescent characteristic rays of Rb or Br which are strongly excited by the α lines from Mo. In the case of RbBr this fog is especially bad. The fog limits the number of lines which can be accurately measured on the diffraction pattern.

RbCl.—This was made from rubidium alum in the ordinary way by treating the alum with HCl and BaCl₂, and then removing Ba and Al by means of NH₄OH and (NH₄)₂CO₃. The RbCl was crystallized out from aqueous solution.

TABLE XVI.

NaF.

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
111.....	$\frac{1}{2}$
100.....	15	2.33	2.32
110.....	10	1.636	1.632
311.....	$\frac{1}{2}$
111 (2).....	2	1.335	1.337
100 (2).....	1	1.158	1.155
331.....	$\frac{1}{2}$
210.....	2	1.033	1.034
211.....	1	.943	.944
{ 511			
{ 111 (3).....
{ 110 (2).....	$\frac{1}{2}$.815	.816
{ 531.....
{ 100 (3)			
{ 221.....	$\frac{3}{4}$.769	.768
{ 310.....	$\frac{3}{4}$.730
{ 533.....
{ 311 (2).....	$\frac{1}{2}$.696
Side of unit cube.....		4.620	4.622

NaF.—Diffraction pattern, ordinarily appears to be simple cubic. Prolonged exposure gives additional lines which complete the pattern of a face-centered cube of double the cube size.

Crystal structure, simple cube of ions. $d = 2.310 \pm .002$ A.

Distance of closest approach of Na and F, $\bar{2.310}$ A.

Density { from x-ray data, $2.809 \pm .008$.
 from literature, 2.558 (Groth), 2.766 (Van Nostrand's Chem. Annual).

RbF.—This was made from the chloride in the same manner as CsF. It was, however, nicely crystalline. Results are given in Table VIII. It should be noted that the arrangement of the ions in the crystal differs from that of the other Rb halides. The evidence of the diffraction pattern is, however, so definite that there is no chance of error in the interpretation. It would be interesting to see if RbF would show a simple-cubic structure at higher temperatures.

KI, KBr, KCl, KF.—These were obtained from stock. The original sources are unknown. All four salts crystallize as simple cubes of ions. The value $3.525 \pm .004$ A assigned to the side of the unit cube of KI agrees well with the value 3.532 A reported by Duane and Clark.¹ KI,

TABLE XVII.

LiI.

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
111.....	3	4.10	4.13
100.....	15	3.58	3.58
110.....	10	2.51	2.51
311.....	2	2.13	2.14
111 (2).....	3	2.05	2.04
100 (2).....	$1\frac{1}{2}$	1.771	1.775
331.....	1	1.621	1.625
210.....	2	1.582	1.584
211.....	2	1.442	1.446
{ 511.....	$\frac{3}{4}$	1.362	1.365
{ 111 (3)			
110.....	$\frac{3}{4}$	1.249	1.252
531.....	$\frac{3}{4}$	1.195	1.196
{ 100 (3)			
221.....	1	1.178	1.181
310.....	$\frac{1}{2}$	1.117	1.120
533.....	$\frac{1}{2}$	1.080
311 (2).....	$\frac{1}{2}$	1.064	1.068
111 (4).....	$\frac{1}{2}$	1.020	1.025
{ 711.....	$\frac{1}{2}$987
{ 551.....			
320.....
321.....	$\frac{3}{4}$.944	.945
{ 553.....	$\frac{1}{2}$
{ 731.....			
100 (4).....	$\frac{1}{2}$
733.....	$\frac{1}{2}$
{ 410.....	$\frac{1}{2}$.856
{ 322.....			
Side of unit cube.....		7.066	7.083

LiI.—Diffraction pattern, face-centered cubic.

Crystal structure, simple cube of ions. $d = 3.537 \pm .005$ A.

Distance of closest approach of $\overset{+}{\text{Li}}$ and $\overset{-}{\text{I}}$, — 3.537 A.

Density { from x-ray data, $2.494 \pm .015$.
from literature, 3.485 — 4.061 (Groth, Chemische Krystallographie).

KBr and KF give face-centered cubic patterns because the positive and negative ions do not act as equal diffracting centers. KCl gives a simple cubic pattern—*i.e.*, K^+ and Cl^- act as practically equivalent diffracting

¹Duane and Clark, Phys. Rev. 20, 84, (1922).

centers.¹ KCl is comparatively transparent to the rays employed and gives little fluorescent radiation to fog the film. It gives beautifully clear films with strong lines. One film was therefore given double the normal exposure so as to see whether any faint lines could be detected which would show a slight difference in the diffracting power of K⁺ and Cl⁻. No such lines could be found. It therefore seems safe to assume that the diffracting powers of K⁺ and Cl⁻ are actually equal. Data for the potassium halides are given in Tables IX., X., XI. and XII.

TABLE XVIII.

LiBr.

Plane.	Intensity.	Interplanar Distance.		
		(1)	(2)	(3)
1 1 1.....	5	3.19	3.18	3.16
1 0 0.....	5	2.75	2.74	2.75
1 1 0.....	2	1.939	1.940	1.939
3 1 1.....	5	1.654	1.656	1.657
1 1 1 (2).....	1	1.584	1.586
1 0 0 (2).....	$\frac{3}{4}$	1.373
3 3 1.....	2	1.260	1.261	1.258
2 1 0.....	1	1.228	1.228	1.227
2 1 1.....	1	1.124	1.120	1.119
{ 5 1 1	1	1.057	1.057
1 1 1 (3).....				
1 1 0 (2).....
5 3 1.....	$\frac{3}{4}$.928
{ 1 0 0 (2).....	$\frac{3}{4}$.914
2 2 1.....	$\frac{1}{2}$.868
3 1 0.....				
Side of unit cube.....		5.490	5.491	5.488

LiBr.—Diffraction pattern, face-centered cubic.

Crystal structure, simple cube of ions. $d = 2.745 \pm .003$ A.

Distance of closest approach of Li⁺ and Br⁻, 2.745 A.

Density { from x-ray data, $3.463 \pm .010$.
from literature, 3.464 (Baxter, J. Am. Ch. Soc., 1904).

NaI, NaBr, NaCl, NaF.—These salts were from stock. The original source is unknown. The NaCl used for calibrating was free from K and Mg. NaF ordinarily gives a simple cubic pattern, since the Na⁺ and F⁻ are nearly equal in diffracting power. Prolonged exposure, however, shows that the complete pattern is face-centered-cubic, and the numerical results are tabulated on that basis. Data for the sodium halides are given in Tables XIII., XIV., XV. and XVI.

¹ See also W. H. and W. L. Bragg, "X-rays and Crystal Structure."

LiI.—This was made by treating Li_2CO_3 with HI. The resulting product was then evaporated to dryness in vacuo over H_2SO_4 . Remaining traces of water and some of the free iodine were removed by washing in absolute alcohol. The rest of the free iodine was removed by grinding the crystals of LiI under amyl acetate. The salt was so hygroscopic that it had to be handled entirely under amyl acetate, even when filling the glass specimen tube. The specimen tube therefore contained LiI, flour and amyl acetate. Results are given in Table XVII.

TABLE XIX.

LiCl.

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
111	40	2.96	2.98
100	40	2.55	2.58
110	20	1.814	1.821
311	15	1.549	1.551
111 (2)	3	1.482	1.484
100 (2)	$1\frac{1}{2}$	1.281	1.283
331	2	1.178	1.179
210	3	1.147	1.149
211	2	1.044	1.048
{ 511	2	.985	.988
111 (3)			
110 (2)	$\frac{1}{2}$
531	1	.866	.869
{ 100 (3)	$1\frac{1}{2}$.854	.855
{ 221	1	.810	.812
310			
533	$\frac{1}{2}$
311 (2)	$\frac{1}{2}$
111 (4)	$\frac{1}{2}$
{ 711	$\frac{1}{2}$.718
{ 551	$\frac{1}{2}$
Side of unit cube		5.127	5.137

LiCl.—Diffraction pattern, face-centered cubic.

Crystal structure, simple cube of ions. $d = 2.566 \pm .003$ A.

Distance of closest approach of Li^+ and Cl^- , 2.566 A.

Density { from x-ray data, $2.069 \pm .006$.
from literature, 2.068 – 2.074 (Groth, *Chemische Krystallographie*).

LiBr.—A sample of salt labeled LiBr gave a simple cubic pattern of side 4.008 A. Since this does not check even approximately the published density of LiBr, it was assumed that either the salt was not LiBr or that it was not anhydrous. The salt was therefore fused and then ground with flour under amyl acetate. It was soluble in the amyl acetate. The solution was then concentrated with heat and was sucked up into one end of a specimen tube. It solidified on cooling. The other end of

the tube was filled with NaCl as usual. No diffraction pattern of LiBr was obtained. Results from a second sample of salt are given in Table XVIII. This sample was sent me by Dr. Sosman of the Geophysical Laboratory. It is from the same lot of salt as that used by Posenjak and Wyckoff.¹

LiCl.—This was obtained from Li_2CO_3 by the action of HCl. The salt was crystallized from aqueous solution. Results are given in Table XIX.

LiF.—This was obtained from stock. The origin is unknown. Results are tabulated in Table XX.

TABLE XX.

LiF.

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
111.....	40	2.31	2.29
100.....	60	2.00	2.004
110.....	40	1.422	1.417
311.....	3	1.211	1.209
111 (2).....	3	1.161	1.159
100 (2).....	$1\frac{1}{2}$	1.006	1.000
331.....	1	.920	.919
210.....	$2\frac{1}{2}$.899	.896
211.....	2	.821	.819
{ 511	$\frac{1}{2}$
111 (3).....	
110 (2).....		.710
531.....		.679
{ 110 (3)	1
221.....		.670
310.....		.636
Side of unit cube.....		4.020	4.008

LiF.—Diffraction pattern, face-centered cubic.

Crystal structure, simple cube of ions. $d = 2.007 \pm .004$ A.

Distance of closest approach of Li^+ and F^- , — 2.007 A.

Density { from x-ray data, $2.646 \pm .016$.
 from literature, — 2.295 (Groth, *Chemische Krystallographie*).
 2.601 (Van Nostrand's *Chemical Annual*).

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¹ Posenjak and Wyckoff, *Jour. Wash. Acad. Sci.*, **12**, 248, (1922).