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PRECISION CRYSTAL MEASUREMENTS ON SOME ALKALI AND AMMONIUM HALIDES

BY R. J. HAVIGHURST, E. MACK, JR. AND F. C. BLAKE

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Accurate values for the dimensions of crystal lattices are becoming increasingly important and necessary and the X-ray examination of crystals is probably the best method for obtaining these values. This paper is a report of precision X-ray measurements on some of the alkali and ammonium halides. The ammonium halides have not been subjected to precision measurement, although Bartlett and Langmuir,[1] and Vegard[2] have published values for the cube sides which are in fair agreement. Davey[3] has reported precision measurements upon all of the alkali halides, but it seems desirable to repeat a part of his work with salts of known purity.

Experimental Part

Apparatus.—We have employed the photographic powdered-crystal method. The K-α doublet of molybdenum, with a mean wave length of 0.710 Å. U., was the line recorded on the diffraction patterns. Two cameras were used. The first is similar to that of Wyckoff at the Geophysical Laboratory. Its film radius is 15 cm. and to produce a nearly parallel beam of X-rays, a slit system composed of two gold slits, 15 cm. apart, is provided. With this camera, the lines on the diffraction pattern are very fine. The second camera is similar to the casset used by Davey[4] except that a full semicircle is used, with the zero beam striking the film in the middle. The film radius is 16.5 cm., and the slits are about 3 cm. apart.

With these cameras, we are able to duplicate the arrangements of different observers and to compare their methods. This has been done particularly with reference to the method of mounting the sample. Our experience is that with a proper method of calibration of films, the usual variations in technique are permissible.

Mounting of Sample.—There are two methods generally employed for mounting powdered crystals. In one, the powder is placed in a slender glass tube, and the X-ray beam is wider than the tube. In the other, the powder is mounted on a flat film of some sort with an organic binder, and the X-ray beam is made very narrow. We have studied both methods of mounting, keeping all other conditions the same. There is a marked difference in the type of calibration curve, as shown in Fig. 1. A is typical of the curves obtained with our apparatus when the sample is in a *tube*, and B when the sample is on a *film*. Clearly, to obtain check results from the two methods, careful calibration of the film is essential.

The method of calibration is as follows. As a standard, sodium chloride is mixed[5] with the substance under investigation, thus causing a superposition of the two diffrac-

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[1] Bartlett and Langmuir, THIS JOURNAL, **43**, 84 (1921).

[2] Vegard, *Z. Physik*, **5**, 17 (1921); *Phil. Mag.*, **33**, 395 (1917).

[3] Davey, *Phys. Rev.*, **21**, 143 (1923).

[4] Davey, *J. Opt. Soc. Am.*, **5**, 470 (1921).

[5] This method of mixing the standard directly with the substance was suggested by Dr. Wyckoff.

tion patterns on the film. Assuming a constant radius for the film, we calculate the position of each line due to sodium chloride, then measure its actual position and use the difference between the two values as a correction for that part of the film. We measure the "double displacement" of a line, that is, the distance between corresponding lines on each side of the undeflected beam. It is not safe to mix sodium chloride with any substance with which it is miscible at room temperature. Sodium bromide, for example, exhibits a strong tendency to form a mixed crystal with sodium chloride when the two salts are even gently rubbed together.

That the method of calibration is successful is attested by the fact that we find no difference in our results, whether the sample be mounted in a tube or on a film. We believe that this method, because it makes the centers of diffraction identical, is more reliable than that of placing the standard in one half of the tube, and the substance under investigation in the other half.

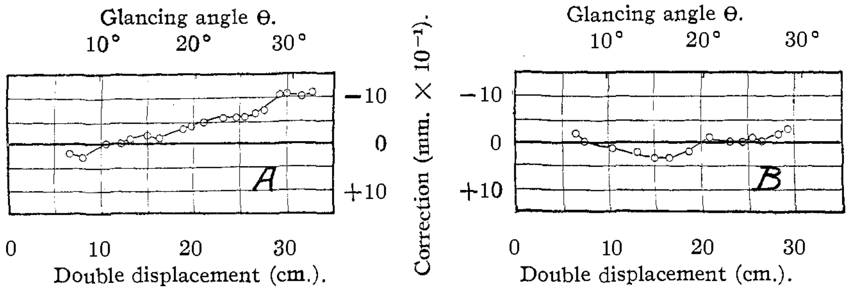

Fig. 1.—Film calibration curves.

Effect of Impurities on Length of Side of Unit Cube.—The effect of *small amounts* of isomorphous impurities on the dimensions of the unit cube has not previously been studied. If there is a marked effect, it will be necessary to take particular precautions in the preparation of samples for precision work. Differences in results might be attributed to differences in purity of the substances used.

Work by Vegard,[2] as well as some work which we are now doing with mixed crystals, indicates that the length of the unit cube of a mixed crystal of two isomorphous salts is very nearly an additive function of the cube sides of the pure components and their respective mole fractions. The alkali halides are not miscible at ordinary temperatures if the difference of their cube sides is more than 5 to 6% of the mean value of the two. When this difference is exceeded, the salts crystallize out of a joint solution almost pure. If the rule of additivity holds for very small mole fractions of one substance in another, 1 or 2% of an isomorphous impurity which is capable of existing in solid solution in the substance under investigation would cause a change in the side of the unit cube of approximately 0.05–0.1%, which is just about the amount of experimental error to which we are subject. Consequently, any ordinary C.P. salt, which contains only a fraction of a per cent. of impurity, even if it were all isomorphous, should give the true value for the side of the unit cube.

We have tested the predictions of the preceding paragraph by preparing some mixed crystals containing 1 to 3% of an isomorphous impurity. In every case, the value of the cube side was very nearly that for the pure salt. The numbers marked "*a*" in Table I indicate these values, and the kind and amount of impurity are noted.

TABLE I

CRYSTAL MEASUREMENTS

Film	NH_4Cl Structure: body centered cubic. Simple cubic for each ion. Diffraction pattern: simple cubic. Side of cube Å.U.	NH_4Br Structure: body centered cubic. Simple cubic for each ion. Diffraction pattern: simple cubic. Side of cube Å.U.	NH_4I Structure: face centered cubic for each ion. Diffraction pattern: face centered cubic. Side of cube Å.U.
1	3.866	4.047	7.244
2	3.865	4.049	7.245
3	3.865	4.047	7.247
4	3.870	4.044	7.245
5	3.867	4.049	7.243
6 1% KCl	3.867[a]	1.5% KBr 4.048[a]	1.5% KI 7.242[a]
7 2% KCl	3.863[a]	...	...
8 2.9% CsCl	3.874[a]	...	...
9 3.3% RbCl	3.867[a]	...	...
Weighted mean	3.866±0.002	4.047±0.002	7.244±0.003

	KCl Structure: face centered cubic for each ion. Diffraction pattern: simple cubic. Side of cube	KBr Structure: face centered cubic for each ion. Diffraction pattern: face centered cubic. Side of cube	KI Structure: face centered cubic for each ion. Diffraction pattern: face centered cubic. Side of cube
1	6.280	6.575	7.055
2	6.281	6.581	7.050
3	...	6.577	7.050
4	...	6.572	...
5	...	6.577	...
Weighted mean	6.280±0.003	6.578±0.003	7.052±0.003

	RbCl Structure: face centered cubic for each ion. Diffraction pattern: face centered cubic. Side of cube	RbBr Structure: face centered cubic for each ion. Diffraction pattern: simple cubic. Side of cube	RbI Structure: face centered cubic for each ion. Diffraction pattern: face centered cubic. Side of cube	CsCl Structure: body centered cubic. Simple cubic for each ion. Diffraction pattern: simple cubic. Side of cube
1	6.573	6.870	7.325	4.109
2	6.572	6.865	7.324	4.109
3	6.565	...	...	4.112
4	...	...	...	4.111
5	...	...	...	KCl 4.107[a]
Weighted mean	6.571±0.004	6.868±0.004	7.325±0.004	4.110±0.002

[a] Sample crystallized with impurity. Not counted in calculation of weighted mean. All percentages are expressed in mole-per cent.

Summary of Crystal Measurements.—Table I gives a survey of the measurements we are reporting. Tables II–IV present the data for the

Table II

Ammonium Chloride

Plane	Intensity	Mean θ	Spacing Å. U.	Side of cube Å. U.	Weight
100	30	5° 15.5′	3.874	3.874	4
110	100	7 27.6	2.734	3.866	5
111	7	9 8.8	2.233	3.867	5
100 (2)	15	10 34.5	1.934	3.868	5
210	12	11 51.4	1.728	3.864	5
211	40	13 0.3	1.5773	3.864	5
110 (2)	10	15 3.2	1.3668	3.866	5
221 100 (3)	12	15 59.2	1.2891	3.868	5
310	15	16 53.2	1.2221	3.865	5
311	3	17 42.9	1.1660	3.869	3
111 (2)	2	18 31.8	1.1169	3.868	5
320	2	19 31.0	1.0715	3.862	4
321	20	20 6.3	1.0328	3.865	5
100 (4)	1	21 34.1	0.9656	3.863	1
410 322	1	22 14.7	.9376	3.865	2
411 110 (3)	6	22 56.4	.9108	3.865	5
331		.. ...	...	...	...
210 (2)	3	24 14.5	.8646	3.866	4
421	2	24 51.4	.8445	3.870	1
332	1	25 32.5	.8234	3.862	3
211 (2)	2	26 44.7	.7887	3.865	2
430 100 (5)	4	27 16.6	.7745	3.873	1
431 510	7	27 54.7	.7584	3.867	2
521	1	30 9.5	.7065	3.869	2

Weighted mean side of cube: 3.8663 Å. U.

Table III

Ammonium Bromide

Plane	Intensity	Mean θ	Spacing Å. U.	Side of cube Å. U.	Weight
100	40	5° 1.8′	4.049	4.049	5
110	100	7 7.2	2.864	4.050	5
111	20	8 44.3	2.337	4.047	4
100 (2)	20	10 6.3	2.023	4.046	2
210	35	11 18.8	1.8097	4.047	5
211	40	12 24.0	1.6531	4.049	5
110 (2)	15	14 20.3	1.4335	4.055	3
221 100 (3)	10	15 16.6	1.3474	4.043	5
310	10	16 6.6	1.2794	4.046	2
311	8	16 57.0	1.2176	4.038	3
111 (2)	5	17 41.7	1.1679	4.045	2

TABLE III (*Concluded*)

Plane	Intensity	Mean θ	Spacing Å. U.	Side of cube Å. U.	Weight
320	5	18° 27.3′	1.1212	4.042	2
321	20	19 9.6	1.0814	4.048	4
410 322	2	21 11.7	0.9818	4.047	1
411 110 (3)	3	21 51.0	.9539	4.049	1
521	2	28 43.1	.7388	4.046	1

Weighted mean side of cube: 4.0470 Å. U.

TABLE IV

AMMONIUM IODIDE

Plane	Intensity	Mean θ	Spacing Å. U.	Side of cube Å. U.	Weight
111	100	4° 52.2′	4.182	7.243	5
100	90	5 37.4	3.623	7.246	5
110	80	7 57.8	2.562	7.248	5
311	50	9 21.1	2.1848	7.246	5
111 (2)	18	9 46.7	2.0903	7.239	5
100 (2)	8	11 18.2	1.8113	7.246	5
331	15	12 20.2	1.6615	7.243	5
210	Double with NaCl 111 (2)		....	...	..
211	20	13 53.7	1.4781	7.243	5
511 111 (3)	8	14 45.5	1.3935	7.243	5
110 (2)	2	16 4.0	1.2826	7.254	3
531	5	16 51.3	1.2243	7.244	5
100 (3) 221	2	17 6.5	1.2067	7.241	5
310	...	.. ..	....	...	..
533	1	18 44.4	1.1058	7.244	3
311 (2)	2	18 59.5	1.0919	7.234	2
111 (4)	...	.. ..	....	...	..
711 551	4	20 30.1	1.0137	7.241	3
320	...	.. ..	....	...	..
321	3	21 31.4	0.9676	7.243	3

Weighted mean side of cube: 7.2438 Å. U.

individual ammonium halides. We have recorded the mean of the values of the glancing angle for each set of planes, for from one to five films. The spacing corresponding to this angle is shown, and the value of the side of the unit cube corresponding to this spacing. To this value is given, as a weight, the number of films upon which the line appeared and was measured. The weighted mean is taken as the correct value for the unit cube side. The individual errors are found to differ from the most probable error in the manner expected from the law of probability. The values for the individual films in Table I are the means of from ten to twentyfive lines for each film. Table V is a review of our results together with a comparison with Davey's values.

TABLE V

UNIT CUBE SIDES FOR AMMONIUM AND ALKALI HALIDES

Substance	This paper Å. U.	Davey[a] Å. U.
NH_4Cl	3.866±0.002	....
NH_4Br	4.047± .002	....
NH_4I	7.244± .003	....
KCl	6.280± .003	6.276±0.006
KBr	6.578± .003	6.570± .006
KI	7.052± .003	7.050± .008
RbCl	6.571± .004	6.535± .006
RbBr	6.868± .004	6.835± .006
RbI	7.325± .004	7.310± .008
CsCl	4.110± .002	4.118± .004

[a] Ref. 3. Davey used a graphical method for computing the most probable value for the unit cube side. Compare Whipple, *J. Franklin Inst.*, **182**, 37, 205 (1916).

Preparation of Samples.—In view of our conclusion that the effect of a limited amount of isomorphous impurity is negligible, it is necessary only to make sure that this limit is not exceeded. Ordinary C.P. potassium and ammonium salts are probably pure enough. In every case, measurements were made upon samples from two or more different sources. To be quite safe, however, we prepared the ammonium halides by adding carefully prepared constant-boiling hydrogen halide to ammonia distilled into conductivity water. The analyses of these preparations are given below. X-ray measurements upon these salts did not differ within the experimental error from those on the regular C.P. substances.

Pure rubidium salts seem particularly difficult to obtain. One reason for this is that the rubidium and potassium halides are miscible in all proportions and cannot be completely separated by recrystallization. A particular sample of rubidium iodide, supposedly C.P., was found on chemical analysis to give too great a weight of both silver iodide and rubidium sulfate. The only isomorphous impurity which could lead to these results, so far as we know, is potassium iodide. Calculation, on the assumption that potassium iodide was the impurity, showed the presence of about 10 mole-per cent. X-ray measurements on this sample gave a value for the side of the unit cube of 7.290 Å. U., much lower than that of the pure salt. The presence of potassium iodide in solid solution would cause a deformation of this sort.

A sample of rubidium chloride, also supposedly C.P., gave too much silver chloride. The length of side of the unit cube was 6.560 Å. U., rather close to that of the pure salt whose analysis appears below. Consequently, the impurity was probably largely an immiscible substance, which would have no effect upon the dimensions of the rubidium chloride crystals. A diffraction pattern from this impure sample, without admixture of sodium chloride, showed the strongest of the sodium chloride lines. Sodium chloride was therefore the impurity, about 15 mole-per cent. being present in the rubidium chloride. These two salts are immiscible at room temperature.

Pure rubidium bromide and rubidium iodide were prepared from the pure rubidium chloride whose analysis appears below, by conversion of the chloride to the sulfate, and treatment of the sulfate with the calculated amount of barium bromide or barium iodide. The chemical analysis of the rubidium bromide is given. It was difficult to add an exactly equivalent amount of barium iodide, because of its hydrolysis. Consequently, the rubidium iodide contained a small amount of rubidium sulfate. The sulfate is not miscible with the iodide, hence its presence should cause no error. The advantage of the above method of preparation lies in the fact that there is no chance for isomorphous impurity provided the rubidium chloride is pure.

It will be observed that our values for the cube sides of the rubidium salts differ considerably from those of Davey. Since he does not give analyses of his samples, it is possible that the discrepancy is due to impurities in them.

The results of the analyses are as follows.

	Calcd.	Found
AMMONIUM CHLORIDE		
AgCl	0.6722 g. .7138	0.6714 g. .7128
AMMONIUM BROMIDE		
AgBr	0.5421 .6557	0.5425 .6562
AMMONIUM IODIDE		
AgI	0.5078 .5529	0.5071 .5519

	Calcd.	Found
CESIUM CHLORIDE		
AgCl	0.3648 g. .4082	0.3656 g. .4087
RUBIDIUM CHLORIDE		
AgCl	0.3585 .4394	0.3586 .4397
RUBIDIUM BROMIDE		
AgBr	0.3667 .4138	0.3669 .4137

Summary

The importance of calibration of films in powder method work is emphasized and a reliable method of calibration is outlined.

The effect of small amounts of isomorphous impurities on the length of the unit cube side has been found to be negligible.

Precision X-ray measurements are tabulated for ammonium chloride, ammonium bromide, ammonium iodide, cesium chloride, rubidium chloride, rubidium bromide, rubidium iodide, potassium chloride, potassium bromide, potassium iodide and the chemical purity of the samples is established within the required limit.

COLUMBUS, OHIO