measurement can never exceed that of the best photometry, that is, about 0.2%. For sensitive and rapid work it takes its place with other volumetric methods.

The phenomena of diffuse reflection and transmission are much more complicated than is here represented, many secondary effects occurring that cannot be neglected The experimental dilution law is an example of the departures which are to be expected. Moreover, the particles are usually distributed in size, and must be studied statistically. But the simple theory represents the general march of the phenomena,[10] and it may serve as a point of departure for experimental investigations.

WASHINGTON, D. C.

THE CRYSTAL STRUCTURES OF POTASSIUM AND AMMONIUM CHLOROSTANNATES.

BY ROSCOE G. DICKINSON.[1]

1. Introduction.

There is a large group of substances of the type R_2MHl_6 where R is potassium, rubidium, cesium, or ammonium; M is one of the platinum metals or tin, antimony, selenium, tellurium or lead; and Hl is one of the halogens, chlorine, bromine or iodine. Although few members of this group have been thoroughly studied crystallographically, many of them are apparently isomorphous[2] and belong to the cubic system. They crystallize chiefly in octahedra, and show a very good octahedral cleavage. There are in addition other salts, such as K_2SiF_6, which have similar cubic modifications.

Since the crystal structures of these salts presumably differ only in detail, the determination of the structures of one or two of them by means of X-rays should furnish the key to the group as a whole.[2a] Potassium chlorostannate (K_2SnCl_6) was chosen for the investigation, since definite

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[10] See, for example, R. C. Tolman and others, THIS JOURNAL, 41, 575 (1919). Tolman's tyndallmeter measures the diffuse reflection of a single sample at right angles to the incident beam. The (fixed) depth is small, so that Equations 11 and 12 apply. The diameter of particles is found to be fairly linear with the concentration over considerable ranges.

[1] National Research Fellow in Chemistry.

[2] Groth, "Chemische Krystallographie," Engelmann, Leipzig, 1906, vol. 1, p. 467.

[2a] Since the submission of this paper for publication the determination of the structure of another crystal of this series has been published by Wyckoff and Posnjak (THIS JOURNAL, 43, 2292 (1921)). Their results are in entire agreement with those described here, and afford an interesting comparison of interatomic distances.

crystallographic information[3] is available, and since sufficiently good crystals can be prepared. Ammonium chlorostannate $((NH_4)_2SnCl_6)$ was also found to give good crystals, and it was studied to confirm the work on the potassium salt.

All of the X-ray data were obtained photographically. Two methods of experimentation were used: (1) characteristic X-rays were reflected from single faces of the crystals, and line spectra obtained; (2) general radiation was passed perpendicularly through slips of crystal cut at a small angle with an important face, and unsymmetrical Laue photographs obtained.

II. Spectral Photographs of Potassium Chlorostannate.

The method used in obtaining the line spectra was similar to that used by Wyckoff,[4] in that the X-rays were allowed to fall simultaneously on the crystal under investigation and on a reference crystal, the two crystals being mounted one above the other on a holder oscillating about an axis in the plane of the crystal faces. The rays reflected from both crystals were registered on a photographic plate placed perpendicularly to the incident beam. The K radiation from a rhodium target was used, and the lines measured were β and α_1, (wave lengths[5] 0.5453 and 0.6121Å., respectively), and for reference, the (100) face of calcite was used ($d = 3.028$Å.). Spectra of more than one order appeared on the photograph; and since a rough comparison of the intensities was useful in the present case, it was attempted to make the intensities reliable by choosing a sufficiently large crystal, using a narrow slit, grinding the face carefully, and oscillating with uniform velocity.

The crystals of potassium chlorostannate were prepared either by the slow evaporation or by slow cooling of a solution of stannic chloride and potassium chloride to which a small amount of hydrochloric acid was added. Two density determinations each gave the value 2.71 g./cc. The values quoted by Groth are 2.687 and 2.700.

The photographs were treated in the following manner. First, the angle of reflection, θ, of each calcite line was calculated, using the equation $n\lambda = 2d \sin \theta$, in which λ and d are known. From these the values of tan 2θ were obtained. Then an arbitrary straight line was fixed on the photograph parallel to the spectral lines. The distance of each spectral line from the arbitrary line was measured. This distance is evidently a linear function of $tan\ 2\theta$. The measured distances for calcite were plotted against the corresponding values of $tan\ 2\theta$ and a straight line was drawn. From this graph the values of $tan\ 2\theta$ for the crystal under investigation were immediately taken. It was thus possible to measure the angles of reflection

[3] Ref. 2, p. 488.

[4] Wyckoff, THIS JOURNAL, 42, 1102 (1920).

[5] Duane, *Nat. Research Council, Bull.* 1, No. 6 (1920).

without a knowledge of either the distance of the plate or the center of the central image.

TABLE I

REFLECTION DATA FOR POTASSIUM CHLOROSTANNATE

Plane	Line	Observed angle of reflection	$\frac{n^3}{m}$	n	d_{100}	Intensity
(110)	β	4°26'	2.01	2	9.98	
	α_1	4 59	2.01	..	9.96	Medium
	β	8 55	....	4	9.95	
	α_1	10 3	....	..	9.92	Strong
(111)	β	2 41	0.242	1	(10.1)	
	α_1	3 2	0.248	..	(10.0)	Strong
	β	5 26	....	2	9.97	
	α_1	6 6	....	..	9.97	Strong
	β	8 10	....	3	9.97	
	α_1	9 13	....	..	9.93	Weak
	β	10 56	....	4	9.96	
	α_1	12 20	....	..	9.93	Medium

Mean 9.96 Å.

Calc. from density 9.99

The angles of reflection obtained in this way are given in the third column of Table I. The order of each spectrum is in the first instance unknown. If the crystal be regarded as built up by the repetition on a simple cubic lattice of a unit structure containing m molecules of K_2SnCl_6 then $\frac{n^3}{m} = \left(\frac{2 \sin \theta}{\lambda \sqrt{h^2 + k^2 + l^2}}\right)^3 \frac{M}{N\rho}$ where M is the molecular weight, ρ the density, and N the Avogadro number,[6] 6.062×10^{23}. For the first spectrum from the (110) face the value of n^3/m is evidently 2, and for that from the (111) face it is $1/4$. Since n is an integer in each case and m is presumably a submultiple of 192, there are evidently either 4 or 32 molecules per unit of structure. On the simpler assumption of 4 molecules, the first spectrum from (110) is of the second order, and the first from (111) is of the first order. The repetition distance d_{100} of the lattice may now be calculated from the formula $d_{100} = \dfrac{n\lambda\sqrt{h^2 + k^2 + l^2}}{2 \sin \theta}$. The values so obtained are given in the sixth column.

III. Application of the Theory of Space Groups.

The theory of space groups will now be applied to the foregoing data, taking the point of view outlined by Wyckoff.[7]

There appears to be no crystallographic evidence that the symmetry of potassium chlorostannate is less than that of the holohedry of the cubic

[6] Millikan, *Proc. Nat. Acad. Sci.*, 3, 314 (1917).

[7] Wyckoff, *Am. J. Sci.*, 1, 127 and 138 (1921).

system. However, there is not much positive evidence of holohedry. As no evidence of dissymmetry was observed in the Laue photographs described below, the atomic arrangement probably has a symmetry isomorphous with that of one of the point-groups[8] T^d, O, or O^h; a consideration of the symmetry alone of the photographs takes us no further than this, since apparently all crystals behave toward X-rays as if they possessed a center of symmetry.

It will be assumed that all of the potassium atoms are equivalent, likewise all of the tin atoms. From a chemical point of view, it might seem reasonable to assume that, among the chlorine atoms, two are not equivalent to the other four. Then since there are either 4 or 32 K_2SnCl_6 groups per unit of structure, a space group is required which gives either 8, 4, 8, and 16, equivalent positions per unit of structure, or 64, 32, 64, and 128 such positions. But, according to the tabular summary given by Niggli,[9] no cubic space group has this property. If the assumption is made that all of the chlorine atoms are equivalent, the proper space group should give either 8, 4, and 24 positions, or 64, 32, and 192 positions. The same table indicates that the space groups O^2, O^3, O^6, O^7, and O_h^4 and O_h^5 are possible with 4 K_2SnCl_6 groups per unit, and O_h^8, with 32 per unit.

The coördinates defining all of these arrangements need not be given. It may be said that those derived from the space groups O^2, O^6, O^7, and O_h^4 make it difficult to account for the fact that in the Laue photographs described below, first orders of reflection do not appear in planes having any even index. The more complicated arrangement derivable from O_h^8 has been discarded for a similar reason. The two types of arrangement derived from O^3 are identical with those from O_h^5.

In either arrangement derived from O_h^5 the coördinates[10] of the potassium and tin atoms, placing d_{100} equal to unity, are as follows.[11]

K: $(1/4, 1/4, 1/4)$ $(1/4, 3/4, 3/4)$ $(3/4, 1/4, 3/4)$ $(3/4, 3/4, 1/4)$ $(3/4, 3/4, 3/4)$ $(1/4, 3/4, 1/4)$ $(3/4, 1/4, 1/4)$ $(1/4, 1/4, 3/4)$.

Sn: $(0, 0, 0)$ $(1/2, 1/2, 0)$ $(1/2, 0, 1/2)$ $(0, 1/2, 1/2)$.

There are two possible arrangements for the chlorine atoms, as follows.

Arrangement I. Cl: $(1/4, 1/4, 0)$ $(1/4, 3/4, 0)$ $(3/4, 1/4, 0)$ $(3/4, 3/4, 0)$ $(3/4, 1/4, 1/2)$ $(3/4, 3/4, 1/2)$ $(1/4, 1/4, 1/2)$ $(1/4, 3/4, 1/2)$ $(0, 1/4, 1/4)$ $(0, 1/4, 3/4)$ $(0, 3/4, 1/4)$ $(0, 3/4, 3/4)$ $(1/2, 3/4, 1/4)$ $(1/2, 3/4, 3/4)$ $(1/2, 1/4, 1/4)$ $(1/2, 1/4, 3/4)$ $(1/4, 0, 1/4)$ $(3/4, 0, 1/4)$ $(1/4, 0, 3/4)$ $(3/4, 0, 3/4)$ $(1/4, 1/2, 3/4)$ $(3/4, 1/2, 3/4)$ $(1/4, 1/2, 1/4)$ $(3/4, 1/2, 1/4)$.

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[8] Schönflies, "Krystallsysteme und Krystallstructure," Teubner, Leipzig, 1891, p. 229.

[9] Niggli, "Geometrische Krystallographie des Diskontinuums," Gebrüder Borntralger, Leipzig, 1919, p. 40; also *Physik. Z.*, 19, 229 (1918).

[10] The coördinates for these special cases were derived from those for the general case given by Schönflies (Ref. 8, p. 549).

[11] The tin atoms might be placed at $(1/2, 1/2, 1/2)$ $(1/2, 0, 0)$ $(0, 1/2, 0)$ $(0, 0, 1/2)$; but the resulting arrangement would, with a suitable alteration in the value of u in Case II, be identical with that given.

Arrangement II.   Cl: (u, 0, 0)   (ū, 0, 0)   ($1/_2$ + u, $1/_2$, 0)   ($1/_2$−u, $1/_2$, 0)   ($1/_2$ + u, 0, $1/_2$)   ($1/_2$−u, 0, $1/_2$)   (u, $1/_2$, $1/_2$)   (ū, $1/_2$, $1/_2$)   (0, u, 0)   (0, ū, 0)   (0, $1/_2$ + u, $1/_2$)   (0, $1/_2$−u, $1/_2$)   ($1/_2$, $1/_2$ + u, 0)   ($1/_2$, $1/_2$−u, 0)   ($1/_2$, u, $1/_2$)   ($1/_2$, ū, $1/_2$)   (0, 0, u)   (0, 0, ū)   ($1/_2$, 0, $1/_2$ + u)   ($1/_2$, 0, $1/_2$−u)   (0, $1/_2$, $1/_2$ + u)   (0, $1/_2$, $1/_2$−u)   ($1/_2$, $1/_2$, u)   ($1/_2$, $1/_2$, ū).

To distinguish between these two possibilities, use will be made of the expression $I = f(d/n) (A^2 + B^2)$. Here I is the intensity of reflection, $f(d/n)$ will be assumed simply to have smaller values, for a given wavelength, the smaller is d/n. In all cases under consideration, $B = 0$. The following are the values of A for the (110) and (111) planes.

Arrangement I.

(110) $A = 2\,\overline{Sn}\,(1 + \cos \pi n) + 4\,\overline{K}\,(1 + \cos \pi n) +$

$$4\,\overline{Cl}\left(1 + \cos \pi n + 2 \cos \frac{\pi n}{2} + 2 \cos \frac{3\pi n}{2}\right).$$

(111) $A = 4\,\overline{Sn} + 4\,\overline{K}\left(\cos \frac{\pi n}{2} + \cos \frac{3\pi n}{2}\right) + 12\,\overline{Cl}\,(1 + \cos \pi n).$

Arrangement II.

(110) $A = 2\,\overline{Sn}\,(1 + \cos \pi n) + 4\,\overline{K}\,(1 + \cos \pi n)$

$$+ 4\,\overline{Cl}\left(1 + \cos \pi n + 2 \cos 2\pi n u + 2 \cos 2\pi n \left(u + \frac{1}{2}\right)\right).$$

(111) $A = 4\,\overline{Sn} + 4\,\overline{K}\left(\cos \frac{\pi n}{2} + \cos \frac{3\pi n}{2}\right) + 24\,\overline{Cl} \cos 2\pi n u.$

An inspection of these equations shows that for odd values of n the value of A becomes identically zero for the (110) plane but not for (111), and that
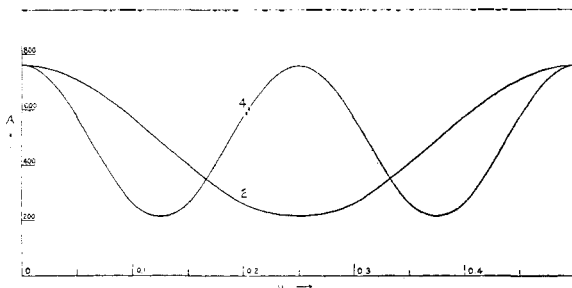
Fig. 1.—Values of A for K_2SnCl_6 (110).

for even values of n the value of A does not become zero   This agrees with the observations.

Since the intensity of the fourth order from (110) was actually greater than that of the second, it is clear, even without any quantitative assumption as to the "normal decline" of intensity, that A for the fourth order should be greater than A for the second.   By similar reasoning, for (111), A for the fourth order should be much greater than A for the third, and

A for the second should probably be greater than A for the first.[12] Actually, all these conditions are satisfied by the first arrangement. Taking the reflecting powers as proportional to the atomic numbers, for (110), $A_2:A_4 = 216:760$, and for (111), $A_1:A_2:A_3:A_4 = 200:456:200:760$. In order to determine whether any value of u can be found which gives suitable values of A with the second arrangement, the values of A for the various reflections have been plotted against u, all possible values of which lie between 0.0 and 0.5. These plots for (110) and (111) are given in Figs. 1 and 2, respectively. It will be seen that for a range of values of u in the neighborhood of $^1/_4$, all the conditions are satisfied. The numeri-
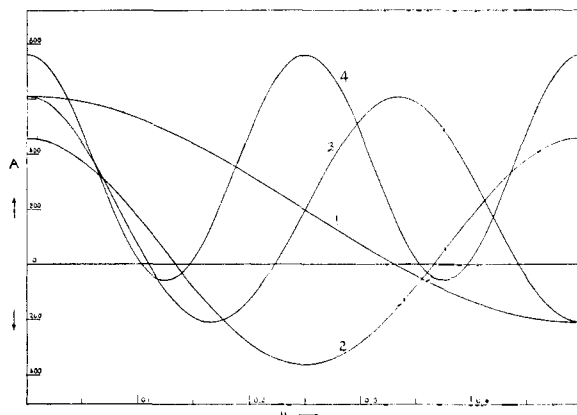

Fig. 2.—Values of A for K_2SnCl_6 (111).

cal values of A when $u = {}^1/_4$ are : for (110), $A_2:A_4 = 216:760$, and for (111), $A_1:A_2:A_3:A_4 = 200:360:200:760$. It is concluded that either Arrangement I or Arrangement II is possible, and that if II is the correct arrangement, the value of u lies between 0.2 and 0.3. To discriminate between these two arrangements and to apply further tests to the structure arrived at, use was made of Laue photographs.

IV.   Laue Photographs of Potassium Chlorostannate.

The source of X-rays for the Laue photographs was a Coolidge tube with a tungsten target, operated at a peak voltage of approximately 54,000. The shortest wave length present, calculated from the well-known relation $Ve = h\nu$, was accordingly 0.23 Å. Photographs were made with an X-ray beam passed at small inclinations from the perpendicular to the (111) and (100) faces, the crystals being 5 cm. from the plate. One was made with the beam closely perpendicular to (111).

On these photographs 250 or more spots ordinarily appeared. Gno-

[12] The very small angle of reflection of the first order from (111) makes its intensity less reliable than the others.

monic projections were made graphically[13] from the photographs, and from these projections the indices of each spot were obtained. The distance of each spot on the photograph from the central image, combined with the distance from crystal to plate, determined each angle of reflection. The value of $n\lambda$ for each spot was then calculated using the expression

$$n\lambda = \frac{2\,d_{100}\,sin\,\theta}{\sqrt{h^2 + k^2 + l^2}}$$ putting d_{100} equal to 9.96 Å. as found in Section II.

The smallest value of $n\lambda$ found for any plane having all odd indices was 0.26, and for any plane having any even index, 0.57. Thus no planes with any even index were found reflecting in the first order. That these facts are accounted for by either of the structures given in the previous section may be seen from an examination of the values of A. The planes may conveniently be divided into three classes according to the character of the indices.

Arrangement I.

 Class 1. All indices odd. $n = 1$; $A = 4\,\overline{Sn}$.

 Class 2. One index even. $n = 1$; $A = 0$. $n = 2$; $A = 4\,\overline{Sn} + 8\,\overline{K} - 8\,\overline{Cl}$.

 Class 3. Two indices even. $n = 1$; $A = 0$. $n = 2$; $A = 4\,\overline{Sn} - 8\,\overline{K} - 8\,\overline{Cl}$.

Arrangement II.

 Class 1. All indices odd. $n = 1$; $A = 4\,\overline{Sn} + 8\,\overline{Cl}(cos\,2\pi hu + cos\,2\pi ku + cos\,2\pi lu)$.

 Class 2. One index even. $n = 1$; $A = 0$. $n = 2$; $A = 4\,\overline{Sn} + 8\,\overline{K} + 8\,\overline{Cl}\,(cos\,4\pi hu + cos\,4\pi ku + cos\,4\pi lu)$.

 Class 3. Two indices even. $n = 1$; $A = 0$. $n = 2$; $A = 4\,\overline{Sn} - 8\,\overline{K} + 8\,\overline{Cl}\,(cos\,4\pi hu + cos\,4\pi ku + cos\,4\pi lu)$.

The relative intensities of spots due to planes of Class I will now be considered. Numerous instances were found in which a plane reflected in the first order somewhat more strongly than another plane having a larger spacing. For instance, a plane of the form $\{911\}$, with spacing 1.09 Å., was found to reflect more strongly than one of the form $\{731\}$, with spacing 1.30 Å., both, of course, at the same wavelength, and a plane of the form $\{953\}$, with spacing 0.929 Å., reflected at least twice as strongly as one of the form $\{773\}$, with spacing 0.963 Å. In some cases where two forms which it was desired to compare gave no planes reflecting the same wavelength, the method of plotting estimated intensities against wavelength was employed; it was necessary to exercise care in making comparisons in the neighborhood of the critical absorptions of tin ($\lambda = 0.424$ Å.) and of silver ($\lambda = 0.485$ Å.). In this way the instances given in Table II were noted where one plane clearly reflected more strongly than another having the same or a larger spacing.

If Arrangement I were correct, it would be expected that the intensity of reflection would always be less the smaller the spacing of the plane. Since the observations are not in accord with this, it remains to be deter-

 [13] Wyckoff, *Am. J. Sci.*, **50**, 322 (1920).

TABLE II

ABNORMAL INTENSITY RELATIONS FOR POTASSIUM CHLOROSTANNATE

Forms giving		Corresponding spacings of planes		Corresponding values of A calculated for $u = 0.245$	
(1) greater observed intensity	(2) smaller observed intensity	(1)	(2)	(1)	(2)
{911}	{731}	1.093	1.298	247	162
{953}	{773}	0.866	0.922	247	128
{951}	{755}	0.931	1.006	264	213
{553}	{731}	1.688	1.688	230	162
{551}	{711}	1.952	1.952	247	179
{931}	{753}	1.093	1.200	230	179
{911}	{751}	1.200	1.327	247	196
{973}	{11.3.3}	0.717	0.772	196	128
{995}	{11.5.3}	0.532	0.642	298	162
{13.5.1}	{11.5.3}	0.511	0.642	281	162
{13.3.1}	{11.7.3}	0.511	0.556	281	110
{13.3.1}	{11.7.3}	0.556	0.556	247	110
{973}	{11.3.1}	0.717	0.760	196	145

mined whether a value of u can be found in the second arrangement which accounts systematically for the observed abnormalities.

The values for A for a number of planes given in Table II are shown in Fig. 3 plotted against u. An examination of these plots shows that the
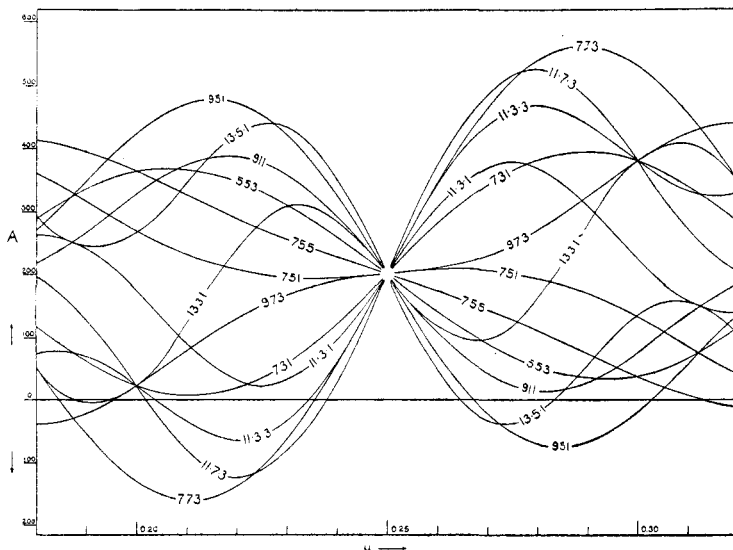

Fig. 3.—Values of A for first order reflections of various planes of Class 1 of K_2SnCl_6 or $(NH_4)_2SnCl_6$.

value of u cannot be just 0.25, but must lie below 0.25. Indeed all of the inequalities given in Table II are satisfied if u is given some value immediately below 0.25, and it was not found possible to establish any

inequalities that were not thus satisfied. The conclusion that u lies only a little below 0.25 receives some support from the fact that no very great abnormalities were found in the intensities.

Since first-order reflections are entirely absent in Classes 2 and 3, spots due to planes in these classes have been interpreted as pure second-order reflections for values of $n\lambda$ below 0.96. When the planes of Class 2 were examined among themselves it was not found possible to establish with certainty inequalities in the manner done for Class 1. This fact is explicable if u is only a little below 0.25; for not only is the value of A the same for each plane of Class 2 when $u = 0.25$, but also dA/du is zero at this point. The same is true for Class 3.

It is of interest that under comparable conditions planes of Class 2 reflected with about the same intensity as those of Class 3. In the immediate neighborhood of $u = 1/4$, all planes of Class 2 have $A = 4\overline{Sn} + 8\overline{K} - 8\overline{Cl}$, and those of Class 3, $A = 4\overline{Sn} - 8\overline{K} + 8\overline{Cl}$. These two expressions become equal if $\overline{K} = \overline{Cl}$ as has been found to be at least approximately the case in potassium chloride.[14] If Arrangement I were correct, Class 2 might be expected to reflect more strongly than Class 1.

The various tests afforded by the data, which involve no quantitative assumption concerning "normal decline" of intensity, and only rough assumptions as to the relative reflecting powers of the atoms, lead then to the conclusion that the coördinates of the atoms are given by Arrangement II, the value of u being probably not far from 0.245.

V. Spectral Photographs of Ammonium Chlorostannate.

No previous crystallographic work on ammonium chlorostannate was found in the literature. The crystals were prepared in the same manner as those of the potassium compound. The form chiefly developed was the octahedron with a frequent occurrence of cube faces. Two density determinations each gave the value 2.39 g. per cc., in good agreement with 2.387 given by Schröder.[15] Small crystals appeared optically isotropic when examined between crossed nicols in the polarizing microscope. A very good octahedral cleavage was observed.

Spectra from the (100) and (111) planes were photographed. In the latter case potassium chlorostannate was used as the reference crystal. The only noticeable difference in the relative intensities of the (111) spectra of the two substances was a weakening of the second order in the ammonium salt. The results of these measurements are given in Table III.

In applying the theory of space groups to ammonium chlorostannate account must be taken of the hydrogen atoms. If these be assumed to be all equivalent, then 32 positions are required for them in addition to

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[14] W. H. and W. L. Bragg, "X-rays and Crystal Structure," G. Bell and Sons, Ltd., London, 1916, p. 188.

[15] Schröder, *Jahresber.*, **1874,** 177.

TABLE III

REFLECTION DATA FOR AMMONIUM CHLOROSTANNATE

Plane	Line	Observed angle of reflection	n	d_{100}	Intensity
(100)	β	3° 7′	2	(10.03)	
	α_1	3 32		(9.98)	Medium
	β	6 15	4	10.02	
	α_1	7 2		10.00	Strong
	β	9 23	6	10.03	
	α_1	10 33		10.03	Weak
	β	12 32	8	10.05	
	α_1	14 8		10.03	Medium weak
(111)	β	2 41	1	(10.09)	
	α_1	3 1		(10.07)	Strong
	β	5 23	2	10.07	
	α_1	6 4		10.03	Medium strong
	β	8 4	3	10.09	
	α_1	9 7		10.04	Weak
	β	10 48	4	10.08	
	α_1	12 10		10.06	Medium

Mean   10.05Å.

Calc. from density   10.05

the 8, 4, and 24 positions as in the case of potassium salt. The space-groups O^3 and O_h^5 satisfy the conditions, and both lead to the same arrangement, namely, the tin, and chlorine atoms are located as in the potassium salt, the nitrogen takes the place of the potassium, and the hydrogen atoms are arranged on cube diagonals, the determination of one parameter being required to fix their position. This parameter could be given such a value that the hydrogen atoms would be grouped close to the nitrogen so as to form a tetrahedron, as they have been supposed to do in ammonium chloride.[16] In the following treatment the reflecting power of the hydrogen atoms has been assumed to be negligible. The expressions for A then become like those of the previous case except that $\overline{N}$ replaces $\overline{K}$.

From the relative intensities of the spectra given in Table III, it is clear that for (100), A for the fourth order must be greater than A for the second, and A for the eighth order must be greater than A for the sixth. And for (111), A for the fourth order must be greater than A for the third. These conditions are all satisfied if u has a value near $1/4$. At $u = 1/4$, the relative values of A for the (100) spectra, come out $280:664:280:664$, and for the (111) spectra $200:264:200:664$.

VI. Laue Photographs of Ammonium Chlorostannate.

Crystal plates were ground a few degrees from parallel to the planes (111) and (100). The Laue photographs obtained with them were treated

[16] Langmuir, THIS JOURNAL, 41, 1547 (1919).

in the same way as the previous ones. Only planes having all odd indices were found reflecting in the first order.

For the planes of Class 1 it was found possible to establish a series of inequalities in the same manner as for potassium chlorostannate. The instances noted are given in Table IV.

TABLE IV

ABNORMAL INTENSITY RELATIONS FOR AMMONIUM CHLOROSTANNATE

Forms giving		Corresponding spacings of planes		Corresponding values of A calculated for $u = 0.245$	
(1) greater observed intensity	(2) smaller observed intensity	(1)	(2)	(1)	(2)
{951}	{773}	0.972	0.972	264	128
{951}	{755}	0.972	1.010	264	213
{553}	{731}	1.310	1.310	230	162
{975}	{773}	0.808	0.972	230	128
{975}	{973}	0.808	0.852	230	196
{973}	{11.3.3}	0.852	0.852	196	128
{975}	{11.5.1}	0.808	0.829	230	179
{13.5.1}	{11.5.1}	0.720	0.829	281	179
{13.5.1}	{11.3.3}	0.720	0.852	281	128
{13.3.3}	{11.3.3}	0.735	0.852	230	128
{911}	{751}	1.103	1.161	247	196
{911}	{753}	1.103	1.103	247	179
{13.5.1}	{11.7.5}	0.720	0.720	281	145
{13.5.1}	{11.5.5}	0.720	0.768	281	196
{995}	{11.5.5}	0.735	0.768	298	196
{953}	{771}	0.938	1.010	247	145
{951}	{771}	0.972	1.010	264	145
{13.5.1}	{11.5.3}	0.720	0.807	281	162
{975}	{11.5.3}	0.807	0.807	230	162

Since no attempt was made to have the crystals of the two substances oriented in the same way when the photographs were taken, the pairs of planes which happened to permit comparisons were not always the same. But just as with the potassium salt, all of the inequalities which were established were satisfied by values of u slightly less than 0.25.

When planes of one of the classes 2 or 3 were examined among themselves, it was not found possible to establish inequalities in the values of A. From the same arguments as in the previous case the value of u is concluded to be not far from from 0.245.

When spots due to planes of Class 2 were compared with those from Class 3, it was found that, unlike the result with the potassium salt, those of Class 3 were distinctly more intense than those of Class 2. For instance, on two different photographs planes of the form {621}, $d/n = 0.778$, reflected more strongly than those of form {521}, $d/n = 0.910$, in spite of the smaller value of d/n; similarly {601} $d/n = 0.819$, reflected more strongly than {501}, $d/n = 0.977$. To explain this with the above struc-

ture it is necessary to assume no more than that the reflecting powers $\overline{Sn}$, $\overline{Cl}$, and $\overline{N}$ differ appreciably in the order named, that of tin being greatest. For the expressions for A are substantially: *Class 2*, $A = 4\,\overline{Sn} - 8(\overline{Cl} - \overline{N})$; *Class 3*, $A = 4\,\overline{Sn} + 8(\overline{Cl} - \overline{N})$.

If this interpretation of these intensities is correct, the value of A for planes of Class 2 is appreciably less than $4\,\overline{Sn}$, and for planes of Class 3 appreciably greater than $4\,\overline{Sn}$. Now the planes of Class 1 may be subdivided into: (1a) those for which the calculated value of A is $4\,\overline{Sn}$ plus a positive increment due to chlorine atoms alone, and (1b) those for which it is $4\,\overline{Sn}$ plus a negative increment due to the chlorine atoms. Certainly then planes of Class 1a should reflect a given wavelength more strongly than planes of Class 2 having the same value of d/n, and those of Class 1b should reflect less strongly than those of Class 3. A number of intensity comparisons were found possible which confirmed these conclusions. For instance, a plane of the form $\{951\}$, $d/n = 0.972$, reflected at $n\lambda = 0.45$ more strongly than one of the form $\{431\}$, $d/n = 0.986$, reflected at $n\lambda = 0.90$, and a plane of the form $\{421\}$, $d/n = 1.197$, reflected around $n\lambda = 0.60$ more strongly than one of the form $\{731\}$, $d/n = 1.703$, at $n\lambda = 0.30$ in spite of the more favorable value of d/n in the latter form. No inequalities in the reverse sense were found.

The X-ray data for ammonium chlorostannate thus lead to the same type of structure that was deduced for the potassium salt and, as far as can be determined, to about the same value of u.

VII. Discussion of the Crystal Structures.

The structure deduced for potassium chlorostannate involves the following relations. Each potassium atom has 4 tin atoms equally distant from it. Each tin atom has 8 potassium atoms equally distant from it. Each chlorine atom has 4 potassium atoms equally distant, and each po-
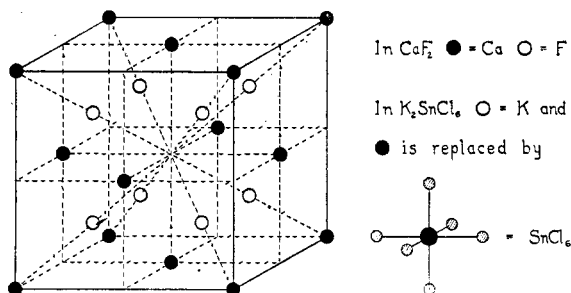

In CaF$_2$ ● = Ca O = F

In K$_2$SnCl$_6$ O = K and

● is replaced by

[structure] = SnCl$_6$

Fig. 4.—Arrangement of the atoms in CaF$_2$ and in K$_2$SnCl$_6$.

tassium atom has 12 chlorine atoms equally distant, but each chlorine atom is at a shorter distance from one tin atom than from any other, and each tin atom has 6 chlorine atoms at this distance from it. The structure

may thus be regarded as an assemblage of potassium atoms and $SnCl_6$ groups.

If the potassium atoms and $SnCl_6$ groups be considered electrically charged so that the crystal is built up of K^+ and $SnCl_6^=$ ions, the structure is then ionically similar to that of calcium fluoride,[17] K^+ replacing F^-, and $SnCl_6^=$ replacing Ca^{++}.

These relations are illustrated by Fig. 4.

The cohesional relations of a polar substance may well be presumed to depend to a considerable extent upon the electrostatic attractions and repulsions of the constituent ions; and since the arrangement of the ions is the same in the chlorostannates as in calcium fluoride, it is not surprising that, in spite of the dissimilarity in atomic constitution, these substances show the same cleavage, namely, along the octahedral planes.[18]

The shortest distances between the various unlike atoms are given in Table V. These distances are accurate to within a few tenths of 1%, except the distance from the tin to the chlorine atoms, whose calculation involves the value of u. It is possible that this distance is several per cent. too high, but it can hardly be much too low.

TABLE V

DISTANCES BETWEEN THE ATOMS IN 10^{-8} CM.

Substance	d_{100}	Sn and Cl	K or N and Sn	K or N and Cl
K_2SnCl_6	9.96	2.44	4.31	3.52
$(NH_4)_2SnCl_6$	10.05	2.46	4.35	3.55

VIII. Summary.

With the aid of spectral photographs and unsymmetrical Laue photographs, the crystal structures of potassium chlorostannate and ammonium chlorostannate have been determined; and these structures have been shown to be closely similar to each other. It was found possible to carry out the analyses without making any quantitative assumption concerning "normal decline" of intensity, and with only rough assumptions as to the relative reflecting powers of the atoms. The results lead to the conclusion that 6 equivalent chlorine atoms are grouped about each tin atom; and the structure is accordingly regarded as built up of $SnCl_6^=$ ions and K^+ or NH_4^+ ions, in the way shown in Fig. 4. The similarity of these substances, in structure and cleavage, to calcium fluoride is pointed out, as being in accordance with this conclusion.

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[17] W. L. Bragg, *Proc. Roy. Soc.*, **89A**, 474 (1914).
[18] Ref. 2, p. 206.