ART. XVII.—*The Crystal Structure of the Alums;*[1] by RALPH W. G. WYCKOFF.

Introduction.—Besides some early Laue photographic measurements[2] an extended spectrometric study[3] has been made of the crystal structures of four alums—the potassium-aluminum, potassium-chromium, ammonium-aluminum and ammonium-iron alums. On the basis of these measurements a complicated structure was assigned. Because in this atomic arrangement the sulphate group appeared to have lost its identity another structure[4] developed from these same data has been suggested. For this second atomic grouping the corresponding space group is T_h^2.

In the course of some measurements made by the writer upon a Laue photograph of potassium-aluminum alum, data were obtained which pointed to T^6 rather than to T_h^2 as the corresponding space group. In view of the definite character of the spectrometric observations it thus became necessary to determine whether these observations themselves were in error or whether greater limitations must be applied to the use of the criteria for distinguishing between cubic space groups[5] than had been supposed requisite. The following studies of Laue and spectrum photographs of potassium- and of ammonium-aluminum alums were undertaken with this end in view.

Laue Photographic and Spectrographic Data.—Crystallographic information has given to the alums the symmetry of the paramorphic hemihedral (pyritohedral) class of the cubic system. Figure 1 is a practically symmetrical Laue photograph of potassium-aluminum alum taken with the X-rays normal to an octahedral face. The hemihedral character of this photograph is immediately evident; the crystal class defining the symmetry of the arrangement of the atoms in this alum must consequently be either T or T^h. A

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[1] A somewhat more detailed account of these experiments is being published in the Zeitschrift für Krystallographie.

[2] T. Terada, Proc. Math. Phys. Soc. Tokyo 7, 290, 1914.

[3] L. Vegard and H. Schjelderup, Ann. d. Physik 54, 146, 1917.

[4] P. Niggli, Physikal. Z., 19, 225, 1918.

[5] Ralph W. G. Wyckoff, this Journal, 4, 175, 1922.

distinction[6] between various of the space groups having these symmetries should be possible from a study of reflections from planes with one index zero. For atomic arrangements developed from T_h^2 odd order reflections will be missing for planes of the forms {*0kl*} where *k* is even and *l* is odd. Those obtained from T_h^6 will also lack odd order reflections from planes of the forms {*0hl*} where both *h* and *l* are odd.

FIG. 1.

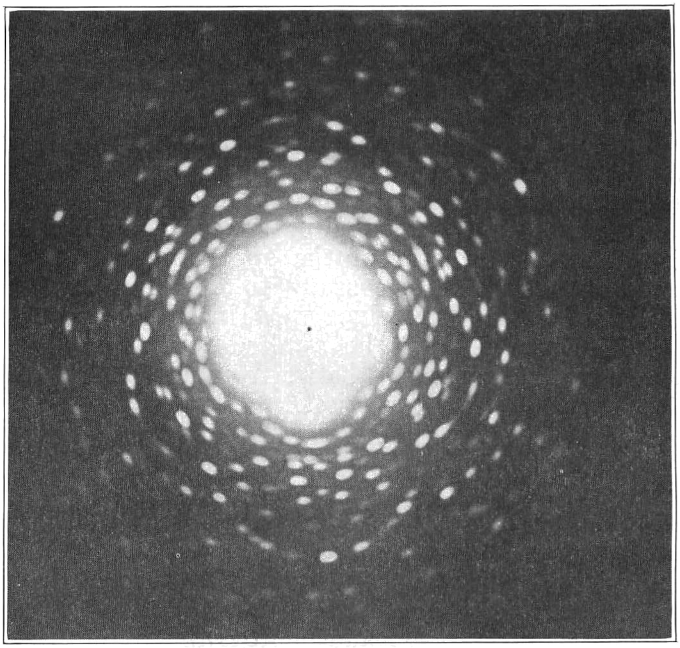

FIG. 1.—A print from a practically symmetrical (111) Laue photograph of potassium-aluminum alum.

Laue photographs were analyzed in the usual manner[7] from the (111) face of ammonium-aluminum alum and from the (100) and (110) faces of potassium-aluminum alum. A gnomonic projection of one of these is shown in fig. 2. Table I gives data from the photograph of

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[6] Ralph W. G. Wyckoff, op. cit.
[7] Ralph W. G. Wyckoff, this Journal, 50, 317, 1920.

TABLE I.—Laue Photographic Data from Photograph No. 4 of $NH_4Al(SO_4)_2 \cdot 12\ H_2O$ (111) face.

Plane	Distance	Intensity	$n\lambda$	Form
$80\bar{5}$	2.15	f	0.513	058
$09\bar{7}$	2.40	ab	.468	097
$07\bar{6}$	1.95	m	.482	076
$\bar{7}\ 12\ 0$	3.42	f	.511	0 7 12
$\bar{7}90$	1.95	ab	.391	079
$\bar{5}60$	1.65	m	.485	056
$\bar{4}07$	1.60	f	.458	074
$\bar{4}\ 0\ 13$	3.60	f	.540	0 13 4
$0\bar{3}7$	1.95	ab	.583	037
$0\bar{4}9$	1.80	ab	.419	049
$15\ \bar{4}\ 0$	3.90	f	.500	0 15 4
$08\bar{7}$	1.85	ab	.400	087
$\bar{6}70$	1.50	ab	.378	067
$7\bar{4}0$	1.50	f	.431	074
$5\bar{3}0$	1.27	ab	.510	053
$\bar{5}08$	1.33	ab	.330	085

this figure for first order reflections from planes one of whose indices is zero. The spacing obtained from either the spectrometric[8] or from spectrographic measurements combined with the known densities shows that either four or 32 chemical molecules must be contained within the unit cube. The recorded values of $n\lambda$ were calculated on the assumption of the smaller unit. Since no $n\lambda$ less than the shortest wave length known to be present in the X-ray beam was found, this smaller unit may be taken as the correct one. From this table it will be observed that though various planes of the forms $\{k0l\}$ are present and though other planes were in position suitable for reflection neither those of the forms $\{0kl\}$ nor planes with both integers odd give any effect. The study of other Laue photographs brought other planes into positions to reflect in the first order region. The data from these photographs, however, agree with those of Table I in fulfilling exactly the requirements for a corresponding space group T_h^6.

The measured intensities of reflection from the (110) face of the potassium- and ammonium-aluminum alums as determined by the spectrometer have been recorded as follows:

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[8] L. Vegard and H. Schjelderup, op. cit.

FIG. 2.

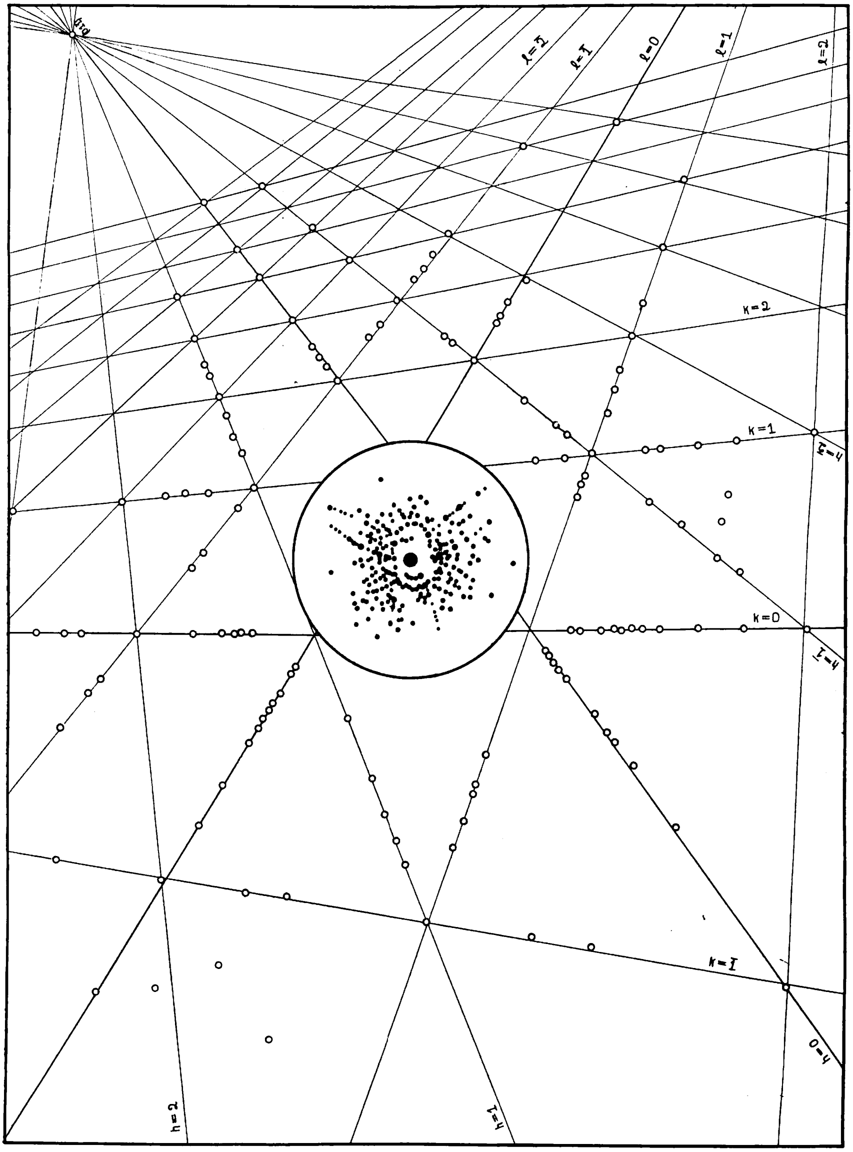

FIG. 2.—A gnomonic projection of some of the reflections in a (111) Laue photograph of ammonium-aluminum alum. All planes having one zero index are shown in the central reproduction of the Laue photograph. With this projection and Table I an approximation to the original data can be obtained.

Crystal	Intensity in *n*th Order.							
	$n=1$	2	3	4	5	6	7	8
$KAl(SO_4)_2 \cdot 12H_2O$	9	100	38	30	0	41	0	20
$NH_4Al(SO_4)_2 \cdot 12H_2O$ ..	6	100	50	31	3	53	3	24

FIG. 3.

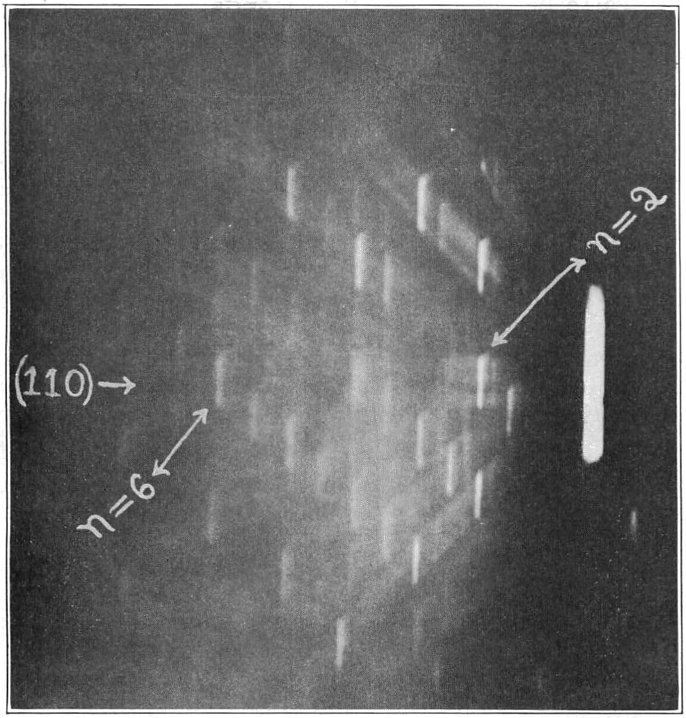

FIG. 3.—A spectrum photograph, using molybdenum radiation, from the (110) face of potassium-aluminum alum acting as the principal reflecting face. The crystal was set so that the plane containing the normals to the two (111) planes adjacent to the (100) reflecting face was perpendicular to the plane of the X-ray beam.

If, as the Laue photographs indicate, the space group is T_h^6 there will of course be no odd order reflections from this plane. Spectrographic observations with (110) as the principal reflecting face were made with both of these alums in the attempt to account for the large odd order spectrometric results. Figure 3 shows the spectrum observed when a crystal of potassium-aluminum alum is continuously rotated through an angle of 20° from the position in which the slit beam of X-rays parallels the (110) face. In this photograph the plane containing the normals to the two (111) faces adjacent to the principally reflecting (110) face was perpendicular to the axis of rotation. No odd order reflections from (110) are to be found. Many secondary spectra of considerable intensity are present, however, and it will be observed that some of them lie directly above and below the positions where odd order (110) reflections would occur. It seems probable that reflections from other than (110) thus were received into the ionization chamber during the spectrometer measurements and gave results which were attributed to odd orders of this principal spectrum. The nature and positions of the secondary spectra will change with a rotation of the crystal about an axis normal to the (110) face. Reflections from other planes may nevertheless always be expected to interfere to a greater or less extent with the spectrometer measurements. Similar spectrographic observations upon the (110) face of ammonium-aluminum alum likewise showed no traces of odd order reflections from the principal spectrum.

The alums thus furnish a striking practical illustration of the inability of the unaided spectrometer technique to serve as a faithful basis for the determination of the structures of crystals. This is shown even more vividly in fig. 4 than by fig. 3. The orientation of the crystal for the production of this last spectrum was similar to that for the previous one except that the crystal was turned slightly about the normal to the (110) face and was rotated through a somewhat larger angle which did not permit a return to parallelism between crystal face and the X-ray beam; as a consequence reflections through small angles have not been recorded. The large numbers of extraneous effects which would interfere with the routine observations upon this comparatively simple plane are immediately obvious.

The Crystal Structures of the Alums.—The spacings calculated from the spectrographic observations are in approximate agreement with those determined by the spectrometer and no new accurate measurements have been made. Since the corresponding space group has been established as T_h^6 and there are four molecules of the composition $R'R'''(SO_4)_2.12H_2O$ in the unit, the atoms of these alums must have the following positions:[9]

FIG. 4.

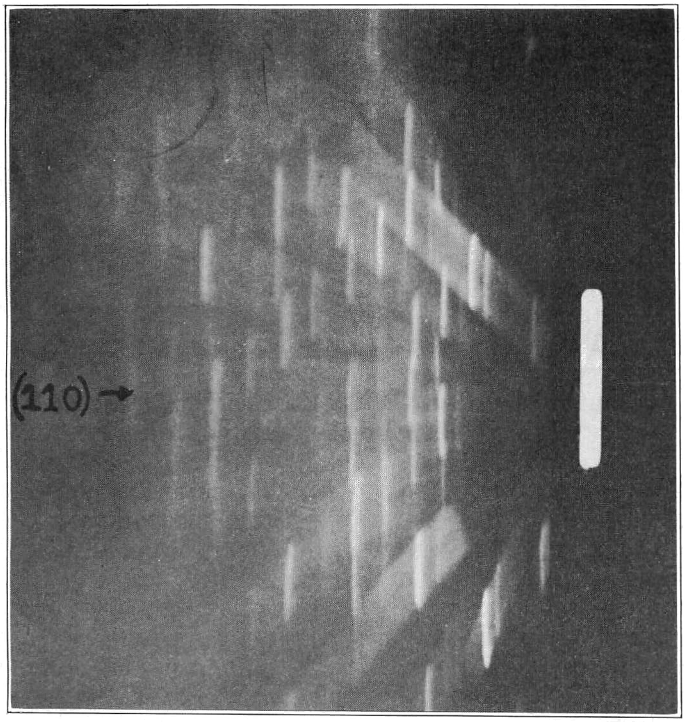

FIG. 4.—A spectrum photograph from the (110) face of ammonium-aluminum alum. The crystal was turned somewhat about the normal to the (110) face from the symmetrical position of fig. 3. During the rotation the crystal did not return to the zero position so that reflections at small angles did not have the opportunity of recording themselves.

K or N atoms 4b: $000;\ 0\tfrac{1}{2}\tfrac{1}{2};\ \tfrac{1}{2}0\tfrac{1}{2};\ \tfrac{1}{2}\tfrac{1}{2}0.$
Al atoms 4c: $\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2};\ \tfrac{1}{2}00;\ 0\tfrac{1}{2}0;\ 00\tfrac{1}{2}.$
S atoms 8h: $uuu;\ u+\tfrac{1}{2},\tfrac{1}{2}-u,\bar{u};\ \bar{u},u+\tfrac{1}{2},\tfrac{1}{2}-u;\ \tfrac{1}{2}-u,\bar{u},u+\tfrac{1}{2};$
$\bar{u}\bar{u}\bar{u};\ \tfrac{1}{2}-u,u+\tfrac{1}{2},u;\ u,\tfrac{1}{2}-u,u+\tfrac{1}{2};\ u+\tfrac{1}{2},u,\tfrac{1}{2}-u.$

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[9] P. Niggli, Geometrische Krystallographie des Discontinuums (Leipzig, 1919); Ralph W. G. Wyckoff, Carnegie Institution of Washington, Publication No. 318, 1922.

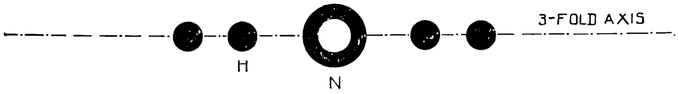
Sulphate oxygen atoms: Since this space group does not provide for 32 equivalent positions, all four of the sulphate oxygen atoms cannot be exactly alike. A reasonable structure would not be provided by making the four unlike and placing them all on the body diagonals of the unit cube. Consequently eight oxygen atoms must have the arrangement 8h (with the value of u different from that for sulphur) and 24 must occupy the generally equivalent positions of $T_h{}^6$. It will thus be noted that in this crystal three of the oxygen atoms of the sulphate group are alike but different from the fourth.

Water molecules: Similarly the 48 water-oxygen atoms must be divided into two groups, each of which occupies generally equivalent positions of $T_h{}^6$. The hydrogen atoms naturally go into four other groups of generally equivalent positions.

With 11 variable parameters defining the positions of sulphur and oxygen atoms, nothing could be gained with the present lack of knowledge of scattering through trying accurately to place any of these atoms within the unit.

The placing of the ammonium-hydrogen atoms in the ammonium alum presents an interesting difficulty. The only way these 16 hydrogen atoms can be located within the unit cell so that the symmetry will correspond to that of the crystal as a whole divides them into two groups of eight like atoms. This, however, would place the atoms on body diagonals so that an ammonium group would have the appearance of fig. 5. From a chemical standpoint such an ammonium group would seem so improbable as to suggest that perhaps the hydrogen atoms in the ammonium alums need not have a symmetry which conforms to that of the crystals as a whole. Such an uncertainty in the position of the ammonium-hydrogen atoms need not be in contradiction with either X-ray

Fig. 5.



data or the optically isotropic character of these crystals because of the very few electrons that are involved. It will be interesting to see whether other cases will arise which may require a similar assumption.

Summary.

It has been shown that Laue photographic and spectrum photographic studies give T_h^6 rather than T_h^2 as the corresponding space group for the alums. The manner of arrangement of the atoms within the unit cell is outlined though no attempt is made to locate those atoms having variable parameters. It is pointed out that the 12 water molecules fall into two groups of six each. The hydrogen atoms in the ammonium groups of the ammonium alums present an interesting problem in the impossibility of arranging them into a chemically plausible radical which will possess a symmetry in keeping with that of the rest of the crystal.

This structure is different from those previously assigned on the basis of spectrometer data. The spectrographic observations clearly show the practical inability of unaided spectrometer measurements to furnish reliable data for the determination of crystal structures.

Geophysical Laboratory,
Carnegie Institution of Washington,
January, 1923.