3. The specific heats of factors and products and the heat of dilution of the product needful for the attainment of these results were found experimentally.

4. The temperature coefficient of the heat of solution of cadmium in conc. hydrochloric acid is shown to be negative, −71 cal. per degree; probably even with dilute acid it amounts to as much as −30 cal. per degree.

CAMBRIDGE 38, MASSACHUSETTS

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 13]

THE CRYSTAL STRUCTURE OF AMMONIUM FLUOSILICATE

BY RICHARD M. BOZORTH[1]

Received March 22, 1922

1. Introduction

Ammonium fluosilicate, $(NH_4)_2SiF_6$, exists in two crystalline forms,[2] cubic and hexagonal. The cubic form is the stable one at ordinary temperatures, while the hexagonal form has been obtained[3] below 5°. It seemed probable that the cubic form has the same structure as ammonium chloroplatinate studied by Wyckoff and Posnjak,[4] and ammonium and potassium chlorostannate studied by Dickinson;[5] but complete evidence of iso-morphism was lacking.[6] It was therefore desirable to study its crystal structure, not only to determine whether it is the same as that of these other salts, but also to measure the size of the unit of structure and the distances between the centers of the various atoms.

Crystals of the fluosilicate were prepared by the spontaneous evaporation at room temperature of an aqueous solution containing an excess of hydrofluoric acid.

The methods employed for obtaining the X-ray data and for the interpretation of these data are essentially those used by Wyckoff and Posnjak and by Dickinson, to whose articles reference may be made for more detailed information.

I wish to express my thanks to Dr. R. G. Dickinson for valuable advice during the progress of this research.

2. Determination of the Size of the Unit-cube and the Number of Molecules in It

Photographs of line spectra from the (111) face of a crystal showed

[1] DuPont Fellow in Chemistry.

[2] Groth, "Chemische Krystallographie," Engelmann, Leipzig, **1906**, vol. 1, p. 485.

[3] Gossner, *Z. Kryst. Mineral.*, **38**, 147 (1904).

[4] Wyckoff and Posnjak, THIS JOURNAL, **43**, 2292 (1921).

[5] Dickinson, *ibid.*, **44**, 276 (1922).

[6] Ref. 2, p. 466.

five orders of reflection. From the values of the angles of the reflections and the density of the salt, determined to be 2.01, the smallest possible number of molecules in the unit of structure was found in the usual way to be 4, as in the other salts mentioned above.

Table I gives the angles of reflection, the orders of the reflections, and the length in Ångstrom units of the unit-cube based on this conclusion. In calculating the number of molecules in the unit and the length of the unit-cube the wave length[7] of the rhodium α_1 line was taken to be 0.6121 Ångstrom units.

TABLE I

THE X-RAY REFLECTIONS OF THE RHODIUM α_1 LINE FROM THE (111) FACE

Angle of reflection	Order of reflection	Length of unit-cube	Intensity of reflection
3° 38′	1	8.37	strong
7° 15′	2	8.40	strong
10° 56′	3	8.38	medium weak
14° 39′	4	8.38	medium weak
18° 26′	5	8.38	weak
	From the density	8.37	
	Final value	8.38	

3. The Laue Photographic Data

Laue photographs were then taken with a beam of X-rays passing through the (111) face, and these photographs analyzed by the usual methods.

The data which were useful in determining the positions of the fluorine atoms are given in Table II. The interplanar distances and wave lengths are expressed in Ångstroms. The smallest wave length calculated for any spot on a Laue photograph was 0.27 Ångstrom units. Wave lengths lower than 0.26 were considered to be absent from the spectrum.

TABLE II

DATA FROM THE LAUE PHOTOGRAPHS

Reflecting plane	Inter-planar distance	Photograph No. 1		Photograph No. 2		Photograph No. 3		Calculated amplitude for $u=0.205$
		Wave length of reflected X-rays	Intensity of spot produced	Wave length of reflected X-rays	Intensity of spot produced	Wave length of reflected X-rays	Intensity of spot produced	
		First-Order Reflections						
$(1\bar{3}5)$	1.42	0.40	0.9	0.47	3	..	..	1.2
$(5\bar{3}1)$	1.42	0.49	1.0	..	..	..	..	1.2
$(33\bar{5})$	1.28	0.48	0.3	0.50	0.4	..	..	0.2
$(35\bar{3})$	1.28	..	..	..	..	0.46	0.5	0.2
$(15\bar{5})$	1.17	0.52	1.5	0.49	4	..	..	2.8
$(11\bar{7})$	1.17	..	..	..	..	0.46	0.6	0.4
$(\bar{5}35)$	1.09	..	..	0.46	2.5	..	..	1.8
$(\bar{7}3\bar{1})$	1.09	0.31	0.0	0.42	0.05	..	..	0.5
$(\bar{3}7\bar{3})$	1.02	0.47	0.4	0.37	0.4	..	..	1.5

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

TABLE II (continued)

Reflecting plane	Inter-planar distance	Photograph No. 1. Wave length of reflected X-rays	Photograph No. 1. Intensity of spot produced	Photograph No. 2. Wave length of reflected X-rays	Photograph No. 2. Intensity of spot produced	Photograph No. 3 Wave length of reflected X-rays	Photograph No. 3 Intensity of spot produced	Calculated amplitude for $u=0.205$
			First-Order Reflections					
$(55\bar{7})$	0.84	0.46	0.4	0.47	0.6	..	..	1.7
$(3\bar{5}9)$	0.78	0.36	0.2	0.40	0.3	..	..	0.9
$(\bar{5}9\bar{3})$	0.78	0.32	0.1	..	..	0.46	0.5	0.9
$(\bar{7}75)$	0.76	0.50	0.0	0.44	0.0	..	..	0.0
$(1\cdot\bar{1}\cdot 11)$	0.76	..	..	..	..	0.46	0.4	1.2
$(5\bar{5}9)$	0.73	0.45	0.3	0.49	0.5	..	..	3.0
$(19\bar{7})$	0.73	0.44	0.1	0.41	0.1	..	..	0.7
$(11\cdot\bar{1}\cdot\bar{3})$	0.73	0.46	0.05	0.52	0.1	..	..	0.2
$(11\cdot 1\cdot\bar{5})$	0.69	0.46	0.2	0.47	0.2	..	..	1.8
$(\bar{7}59)$	0.67	0.46	0.1	0.41	0.1	..	..	1.3
$(5\cdot\bar{5}\cdot 11)$	0.64	0.44	0.2	0.47	0.3	..	..	2.4
			Second-Order Reflections					
$(\bar{1}2\bar{1})$	3.42	..	..	0.40	0.4	..	..	0.3
$(\bar{2}12)$	2.79	..	..	0.48	0.2	..	..	0.0
$(1\bar{2}3)$	2.24	0.35	0.4	0.41	0.9	..	..	1.1
$(04\bar{3})$	1.68	0.45	0.1	0.41	0.1	..	..	0.5
$(\bar{3}24)$	1.56	0.52	0.0	0.47	0.0	..	..	0.1
$(\bar{3}50)$	1.44	0.48	0.5	0.41	0.5	..	..	3.2

4. Interpretation of the Data

The possible arrangements for ammonium fluosilicate permitted by the theory of space groups are those considered for ammonium chloroplatinate by Wyckoff and Posnjak, and for ammonium chlorostannate by Dickinson. The correct arrangement in this case is the same one that they have found, and can be proved in the same way. The intensity functions are accordingly of the same form.

For purposes of comparing intensities, planes may be divided into three classes, namely: (1) planes all of whose indices are odd; (2) planes having two odd indices and one even; (3) planes having one odd index and two even. Planes of Classes 2 and 3 reflect only in even orders.

The value of the parameter u, which fixes the position of the fluorine atoms, was first limited to the region between 0.19 and 0.25 by the following method. It was observed on the spectral photographs that the fourth-order reflections from the (111) face were as strong as the third-order reflections. It was therefore concluded that the fourth-order amplitude must be greater than the third-order ampli-

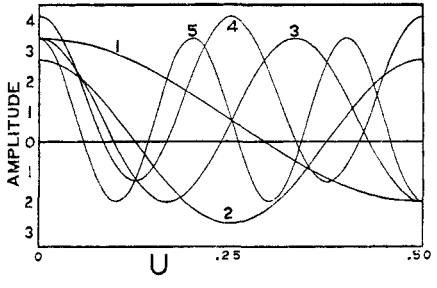

Fig. 1.

tude. The amplitudes calculated for all five orders from the (111) face are plotted for all distinct values of u in Fig. 1. The regions which show a greater fourth-order than third-order amplitude can be noted. It was concluded

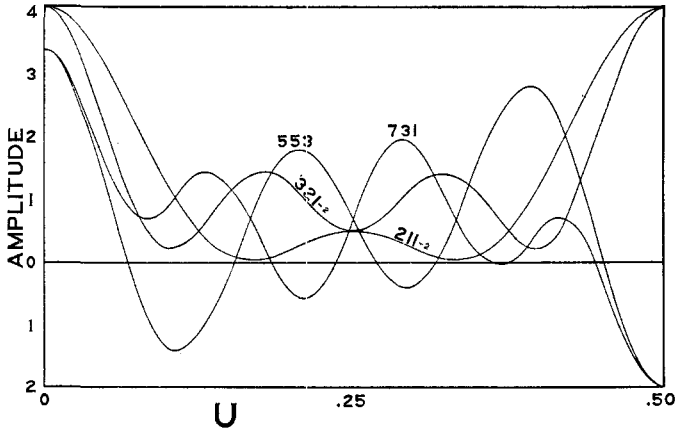

Fig. 2.

from Laue photographic data that (553) must have a larger amplitude than (731) in the first order, and (321) a larger amplitude than (211) in the second order. The calculated amplitudes of these forms are plotted for all distinct values of u in Fig. 2. It will be seen from Figs. 1 and 2 that the only values of u which account for these data are those between 0.19 and 0.25. To limit further the value of u a plot was made showing the amplitudes of planes of Class 1 for values of u between 0.19 and 0.25. The original plot included all planes having an interplanar distance of more than 0.64 Ångstrom units, which is the interplanar distance for (11·5·5), the most complex plane observed. In Fig. 3 are reproduced only those curves which were most useful. Certain inequalities in amplitude were established from the Laue photographic data, and the value of u more definitely determined with the aid of the figure. For example, since (11·5·1) > (971), $u < 0.218$;

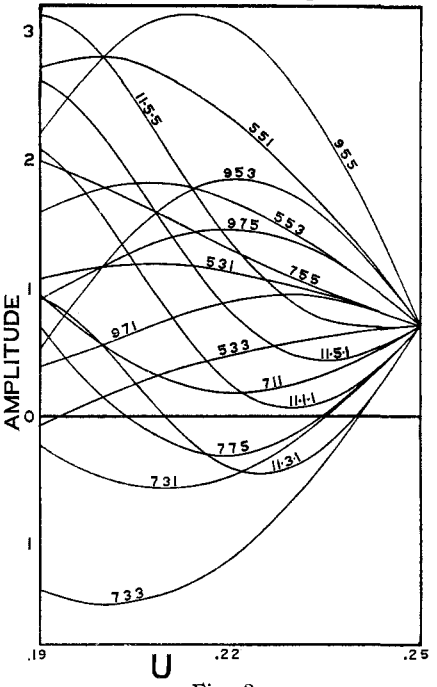

Fig. 3.

since $(11\cdot5\cdot1) > (975)$, $u < 0.211$; since $(711) < (533)$, $u < 0.218$; since $(955) > (11\cdot5\cdot1)$, $u > 0.195$; and since $(971) \geqq (11\cdot3\cdot1)$, $u > 0.200$. The value of u, therefore, lies between 0.200 and 0.208. The best value is considered to be 0.205.

In calculating the amplitudes given in the last column of Table II it has been assumed that the reflecting power of each atom is proportional to its atomic number; but the determination of u based on the comparisons that have been made is largely independent of this assumption, since any reasonable values of the reflecting powers would lead to the same conclusion. However, comparisons between planes of different classes, or even between planes of the same class where at least one of the amplitudes is small or opposite in sign to the other, can be made properly only with a good knowledge of reflecting powers. In view of these limitations all the comparisons which have been properly made are satisfied remarkably well when $u = 0.205$. Many of these comparisons may be made with the data of Table II, using the calculated amplitudes given in the last column.

5. Conclusions as to the Structure

Summary

The crystal structure of ammonium fluosilicate has been shown to be like that of ammonium chloroplatinate, ammonium and potassium chlorostannates, namely the structure is that[8] of calcium fluoride, CaF_2, in which each fluorine atom is replaced by an ammonium group, and each calcium atom by a fluosilicate group with the 6 fluorine atoms equidistant from the silicon atom in the directions of the axes of the crystal. The length of the cube constituting the unit of structure containing 4 molecules was found to be 8.38 Ångstrom units; the corresponding lengths for the three other complex salts just mentioned are 9.84 for ammonium chloroplatinate, 10.05 for ammonium chlorostannate, and 9.96 for potassium chlorostannate. The shortest distance between the centers of the atoms of fluorine and silicon is 1.72 Ångstrom units, while the sum of the Bragg radii[9] for these atoms is 1.84. The corresponding distances between the platinum or tin and the chlorine atoms in the other three salts are 2.3 Ångstrom units for ammonium chloroplatinate, 2.46 for ammonium chlorostannate and 2.44 for potassium chlorostannate.

PASADENA, CALIFORNIA

[8] See W. H. and W. L. Bragg, "X-Rays and Crystal Structure," G. Bell and Sons, Ltd., London, **1916**, p. 107.

[9] W. L. Bragg, *Phil. Mag.*, **40**, 180 (1920).