ART. XL.—*On the Crystal Structure of Ammonium Chloride*; by RALPH W. G. WYCKOFF.

Introduction.—Crystals of ammonium chloride are of interest because their symmetry as previously determined by the conventional methods of face development and etch figure formation are completely at variance with the symmetry of the arrangement of their atoms as found from studies of crystal structure using X-rays.

Studies of face development and of etch figures that seem fairly definite both agree in assigning crystals of ammonium chloride to the enantiomorphic hemihedral (plagihedral) class of cubic symmetry.¹ X-ray powder measurements² (and a single spectrometric observation),³ on the other hand, have been interpreted as yielding a structure which is possessed of hemimorphic hemihedral (tetrahedral) cubic symmetry. On the basis of space-group reasoning it has also been shown that the powder data are such as to seem to preclude the possibility of any atomic arrangement possessing enantiomorphic symmetry being in agreement with them.⁴ In view of the importance of the conclusion which must be drawn from these conflicting observations, both for crystal structure study and for crystallography itself, it has been considered desirable to study Laue photographs of ammonium chloride to see if the greater number of data which they can furnish will be in agreement with the powder measurements.

*Laue Photographic Data for Ammonium Chloride.*⁵—Clear optically isotropic crystals in the form of rectangular prisms several millimeters on one side and usually from one to two millimeters thick were obtained by desiccating a solution of ammonium chloride containing urea.

A measurement of the refractive index of one of these crystals for the purpose of insuring their purity was

¹ See P. Groth, *Chemische Krystallographie*, Vol. I, p. 182 (1906) for references.

² G. Bartlett and I. Langmuir, *J. Am. Chem. Soc.* 43, 84, 1921.

³ W. H. and W. L. Bragg, *X-rays and Crystal Structure*, p. 110 (London, 1918).

⁴ Ralph W. G. Wyckoff, *this Journal*, 3, 177, 1922.

⁵ Some of these experimental data were collected in the Gates Chemical Laboratory of the California Institute of Technology.

made by H. E. Merwin, to whom the writer wishes to express his sincere gratitude not only for this determination but also for discussions of the crystallographic

FIG. 1.

FIGURE 1. A Laue photograph of ammonium chloride produced by passing the X-rays in a direction roughly normal to a cube face.

aspects of this problem. He says: "The refractive index of ammonium chloride crystals grown from solution with urea was the same as that of the pure salt used for the solution, 1.639 ± 0.001 . This is lower than Grailich's rough value usually quoted. Contamination

by urea would presumably lower the index about 0.001 for each per cent.”

Passage of a beam of X-rays in a direction roughly normal to a cube (100) face of several of these crystals yielded a series of very beautiful Laue photographs. A reproduction of one of these is given in figure 1; the

FIG. 2.

FIGURE 2. A gnomonic projection of a Laue photograph of ammonium chloride which had very nearly the orientation of the photograph of Figure 1. With the aid of Table I (which refers to the photograph of Figure 2) and an enlargement of this projection it is possible to reconstruct the original data.

gnomonic projection of a photograph having an orientation very close to that of figure 1 is shown in figure 2. With the aid of these two figures and the plate distances of typical spots which have been recorded in Table I, it is possible to reproduce approximately the original data found upon this second photograph.

From the powder photographic data⁶ the length of

⁶ G. Bartlett and I. Langmuir, *op. cit.*

the side of the unit cube which would contain a single chemical molecule of NH_4Cl was found to be 3.859 Å.U. This information is of course all that is required to calculate the value of $n\lambda$, where n is the order of the reflection and λ is the wave length of the reflected X-rays, for each spot upon the Laue photographs. If this is done and if the true unit cube were a larger one containing not one but eight chemical molecules within it, then

TABLE I. Typical Laue Photographic Data
(for application to Figure 2).

Indices	Distance from Central Spot	Estimated Intensity	Wave Length ($n\lambda$)
231	2.35 cm	7	0.450 Å.U.
$\bar{2}31$	2.32	7	.445
$\bar{2}\bar{5}1$	2.65	0.5	.340
431	2.62	1	.363
$\bar{1}31$	2.72	4	.573
031	2.87	10	.630
$\bar{2}\bar{3}1$	3.75	6	.650

some reflections should be found with a value of $n\lambda$ less than 0.24, which is the smallest wave length in the X-ray beam employed in these experiments. On none of the photographs, one of which was given an exposure from four to five times as long as usual in order to bring out faint reflections, were any spots found having such a low value of $n\lambda$; the Laue photographic data are thus in agreement with the powder data in assigning one chemical molecule to the correct unit cell for this form of ammonium chloride crystals. The approximate intensity calculations, carried out in the usual manner,⁷ are readily shown to be in accord with the only structure containing one molecule within the unit which the theory of space-groups indicates as possible. There can consequently be no legitimate doubt of the correctness of the usual structure assigned to ammonium chloride. In this structure the atoms have the following positions:

Nitrogen atoms: $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

Chlorine atoms: 000.

Hydrogen atoms: uuu ; $\bar{u}\bar{u}u$; $\bar{u}u\bar{u}$; $u\bar{u}\bar{u}$, where the value of u is not determinable. The arrangement is shown in Figure 3.

⁷ Ralph W. G. Wyckoff, this Journal, 50, 317, 1920.

Conclusions.—The conclusions which were given previously can now be stated in even more definite terms.⁸ If the hydrogen atoms of ammonium chloride have an arrangement which conforms to the symmetry of the crystal as a whole, then this symmetry must be hemimorphic hemihedral (tetrahedral); if, as is perhaps conceivable, the hydrogen atoms have a more or less hap-

FIGURE 3. The unit cube of ammonium chloride.

hazard distribution about the nitrogen atoms, its symmetry will be holohedral. In no case, however, can the symmetry of the arrangement of the atoms of this crystal agree with the enantiomorphic hemihedry which studies of both face development and etch figures assign to it. If these crystallographic data are correct, it will therefore be necessary to conclude that such studies even when carried out under ideal conditions to yield the maximum amount of data conceivable can not always indicate the symmetry of the arrangement of the atoms within a crystal.

This conclusion is not only of significance to crystallog-

⁸ Ralph W. G. Wyckoff, this Journal, 3, 177, 1922.

raphy itself but it is of the greatest import to students of crystal structure. By making uncertain a choice of the appropriate class of symmetry in advance of X-ray studies, it considerably lengthens the problem of crystal structure determination.

The difficulties of crystallographic description in the case of crystals to which different symmetry characteristics are assigned by different methods of study have recently been emphasized.⁹ It has been suggested that such crystals should be especially segregated into a group by themselves and that a complete description of their symmetry will include both a statement of the symmetry of the crystal as obtained by such "physical" methods as a study of the electrical or optical properties or the X-ray diffraction effects and a statement of the "latent" symmetry which is supposed to be made evident by the "chemical" means of etch figures and growth forms. The creation of this additional classification is not satisfactory if only for the reason that the concept of "latent" symmetry is not precise. The symmetry of a crystal as deduced by the various "chemical" means is different in many instances not only for these various methods but it may even be different for the same method carried out under changed external conditions. Thus the symmetry deduced from the face development upon scheelite (for face development must be reckoned among the "chemical" means of symmetry determination) is hemihedral though the etch figures that have been obtained are strictly holohedral¹⁰; or in the case of dolomite etch figures have been produced which show sometimes holohedral¹¹ and sometimes hemihedral¹² characters. From the point of view of those students of crystal structure who have felt the force of the difficulties into which such cases as this one of ammonium chloride have led them, the symmetry characteristics which have here been called "latent" are probably determined not by the symmetry of the crystal itself but rather by certain properties inherent in the constituent atoms. Etch figures, face development and the like are therefore to be considered as essentially surface phenomena, and

⁹ E. T. Wherry, this Journal, 4, 237, 1922.

¹⁰ H. Traube, Zeitsch. f. Kryst. 30, 398, 1899.

¹¹ P. Gaubert, Bull. Soc. franc. de Min., 24, 326, 1901.

¹² P. Koller, Neues Jahrb. Min. Beil. Bel., 42, 488, 1919.

the internal symmetry of the crystal itself is only one of a number of important factors which bear upon the nature of these surface phenomena.¹³

For the crystal analyst, at least, the formal part of these difficulties must, however, be met by a greater precision in the definition of what is meant by the symmetry of a crystal. Symmetry, from this point of view, can only mean that of the arrangement of the constituent parts (the atoms) of which a crystal is composed.

This case of ammonium chloride seems to require that both the crystal analyst and the crystallographer must make a considerable revision in their estimate of the value of the usual crystallographic information relating to the symmetry of a crystal, and it is therefore worth while to reemphasize the desirability of a repetition of the purely crystallographic study of ammonium chloride.

SUMMARY.

It is shown that the Laue photographic data obtained from crystals of the low temperature form of ammonium chloride are in agreement with the powder data in assigning to it a structure containing one chemical molecule within the unit cube. The consequences introduced by the disagreement between the symmetry of this uniquely determined structure and the symmetry as obtained by ordinary crystallographic means are discussed. It is pointed out that it is not permissible to accept etch figure data and face development as definite indications of the symmetry of the arrangement of the atoms within a crystal.

Geophysical Laboratory,
Carnegie Institution of Washington,
Washington, D. C.
October, 1922.

¹³ It would seem that Wherry's views (*op. cit.*) are in accord with these, but it is not at all clear from his discussion that such is the case.