

ON THE CRYSTAL STRUCTURE OF AlCl_3

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The crystal lattice of AlCl_3 has been derived on the basis of crystal-geometrical considerations starting from the dimension of the unit cell and from the fact that in the crystal lattice, according to the electric conductivity measurement of BILTZ and VOIGT, there should be ionic bonds. The crystal lattice derived in this way proved to be the same as that given by KETELAAR and his collaborators in 1947. Therefore the statement seems to be justified that there cannot be Al_2Cl_6 molecules in the solid phase of AlCl_3 , as has been suggested by GERDING and SMIT on the basis of investigations of Raman spectra. In the lattice a graphic picture is given for the mechanism of transition of the crystal lattice to the Al_2Cl_6 molecules of the liquid or vapour phase, and also for the mechanism of transition in the reversed direction.

KETELAAR [1] in 1935 was the first to determine the crystal structure of AlCl_3 . In this the cubic close-packed arrangement of the Cl atoms proved later to be correct. The hexagonal cell assignable in the anion frame is

$$\begin{aligned} a_H &= 5,92 \text{ \AA}, \\ c_H &= 18,22 \text{ \AA}. \end{aligned} \tag{1}$$

The Al ions are placed in the holes of the given frame so that a monoclinic symmetry should take place. The axis c of the monoclinic unit cell is one third of the smaller body diagonal of the hexagonal cell, therefore data of this are

$$\begin{aligned} a &= 5,92 \text{ \AA}, \\ b &= 10,22 \text{ \AA}, \beta = 180^\circ - \text{arc tg} \left(\frac{c_H}{a_H} \right) = 108^\circ, \\ c &= 6,16 \text{ \AA}. \end{aligned} \tag{2}$$

KETELAAR placed the Al ions originally in pairs into each octahedron, in which case the distance between such two Al ions would be $0,64 \text{ \AA}$. Such a close arrangement of the Al ions is entirely impossible this, however, cannot be discovered in the X-ray diagram, since the scattering of the Al ions makes only a small contribution to the intensity of the reflexions.

In the first structure given by KETELAAR Al_2Cl_6 molecules were present. PALMER and ELLIOT [2] showed by the electron diffraction method, that in the saturated steam of AlCl_3 such molecules are present which consist struc-

turally of two AlCl_4 tetrahedra with a common edge. GERDING and SMIT [3] also give an account of the existence of Al_2Cl_6 molecules on the basis of Raman-spectroscopical investigations carried out with liquid and solid AlCl_3 .

KETELAAR and coworkers [4] in 1947 have shown that the measured intensities of the X -ray reflexions can be approached much better by calculation if, in place of the tetrahedral molecule arrangement, the Al ions are placed in individual octahedral cavities. They abandoned existence of the Al_2Cl_6 molecule in the solid phase and attained the layer lattice given by them recently which is in contradiction to the statement of GERDING and SMIT. Partly, however, owing to the better agreement of the intensities and partly because of the fact that the Raman spectra obtained in solid and liquid phase do not agree as well as those obtained in the case of AlBr_3 and AlI_3 (GERDING and SMIT) the conclusion may be drawn that the existence of Al_2Cl_6 molecules in the solid state may not be considered as established. Therefore KETELAAR's newest structure must be taken as correct.

In the present paper the author wants to show that the structure, given recently by KETELAAR, can be attained on the basis of the close packing in the ionic crystals, which has been treated elsewhere [5, 6].

Let us start from the data of the unit cell, considering that the conductivity measurements of BILTZ and VOIGT [7] indicate the presence of an ionic bond in the crystal.

From the data of the unit cell the volume $v_{\text{Cl}} = 29,7 \text{ \AA}^3$ for one Cl ion is essentially smaller than that of Cl ions with radii of $1,81 \text{ \AA}$ in closest packing ($35,5 \text{ \AA}$). KETELAAR therefore was led to the statement that the structure is based on the closest packing of the Cl ions.

In a regular close-packed anionic plane the two axes of the assignable orthorhombic cell are

$$\begin{aligned} a &= a' \cdot \sqrt{3}, \\ b &= 3 \cdot a', \end{aligned}$$

if a' is the distance between two adjacent ions. If these two axes are identified with those of the monoclinic cell a and b given by KETELAAR [2] we obtain from both equations similarly

$$a' = 3,42 \text{ \AA}. \quad (3)$$

This does evidently mean that in the anionic planes the Cl ions are arranged regularly but are closer to each other than the distance ($3,62 \text{ \AA}$) calculated from the ionic radius of the Cl ion.

The cations are placed in the spatial cavities of the close-packed anionic frame in such an arrangement that the monoclinic symmetry should be obtained.

For the tetrahedral cavities of a regular close-packed anionic frame

$$r_A + r_X = a' \sqrt{\frac{3}{8}} = 2,22 \text{ \AA}, \quad (4)$$

if $a' = 3,62 \text{ \AA}$. This is small compared with $r_{\text{Cl}} + r_{\text{Al}} = 1,81 + 0,57 = 2,38 \text{ \AA}$, thus the lattice has to be extended if the Al ions should find room in the tetrahedral cavities. On the other hand, however, the lattice is contracted according to the value $a' = 3,42 \text{ \AA}$. This is the reason why the tetrahedral arrangement of the Al ions has to be rejected.

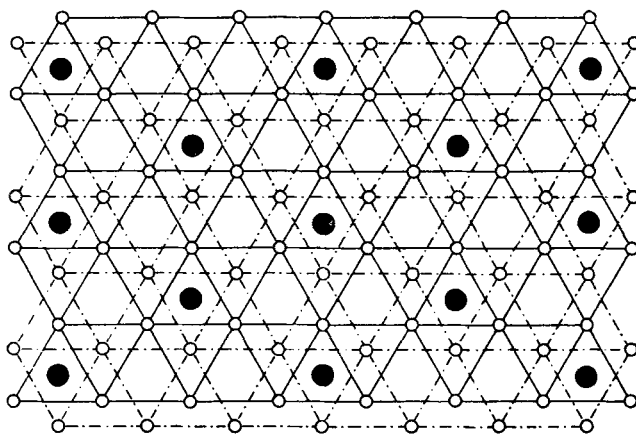


Fig. 1. Hexagonal close-packed anion frame perpendicular to the close-packed planes. One third of the octahedral cavities are filled with Al ions and build columns perpendicular to the planes

We can assume that the Al ions occupy octahedral cavities. The number of the octahedral cavities in the close-packed anionic frame is here thrice the number of the Al ions. If we want to place the Al ions in these, considering Pauling's coordination principle, then every corner of the octahedra filled by Al ions has to be common with another octahedron.

Assuming a hexagonal close packing of the anions, a realization of this could be obtained in such a way that a third of the octahedral columns with common sides are filled up by Al ions (Fig. 1). This cation distribution is unrealizable because the identity in the direction c would then be a sixth of the value found. Since, however, the identity c is equal to the distance of seven successive close-packed anionic planes we must reject the possibility of a hexagonal close packing of anions. There remains for the anions the possibility of a cubic close packing. In this the octahedra are connected to each other only by edges or corners and Pauling's coordination principle can only be satisfied when $2/3$ of the octahedral cavities within the plane intervals are

filled up by Al ions. In this way only every second plane interval can be occupied by Al ions and in the direction of the axis c_H merely every fourth of these occupied layers will be identical with the first which is just in accordance with the identity measured in the direction c_H .

Accordingly, the AlCl_3 can only be a layer lattice with layers known in CrCl_3 and $\text{Al}(\text{OH})_3$. All subsequent layers can be only geometrically identical, but considering their relative position, two different cases can be distinguished.

Placing the cation arrangement, as above described, in every second plane interval of the cubic close-packed anion frame layers are obtained between which every two adjacent layers can be transferred into each other by a parallel displacement. This displacement of the given cationic arrangement, is always parallel to the smaller body diagonal of one of the hexagonal unit cells, which can be set up in the cubic close-packed anionic frame. As this hexagonal unit cell can be chosen in three different ways, differing by 120° , the position of the adjacent layers can also be of three different kinds. The cationic arrangement of the subsequent layers within a crystal lattice can be selected so that either each of the three directions of the displacement is playing a part or, throughout the whole lattice the neighbouring layers are transferred one into the other by a shift in the identical direction. By these two possibilities two different crystal lattices can be obtained.

Carrying on in the cubic close-packed anionic frame the cationic arrangement of a starting layer in the subsequent layers so that each of the three kinds of displacements takes place in some order, the subsequent layers, dependent upon the order of the displacement, can be transferred into each other by a right- or left-handed threefold screw axis (3_1 or 3_2). Fig. 2 represents schematically the sequence of layers. The cation distribution of layers is easily recognizable on the right in the Fig. Here the horizontal lines signify the close-packed anionic planes in a projection parallel to the layers — the three different positions of the close-packed anionic planes succeeding each other in the manner of cubic close-packing are represented by three different notations — the circles show the notation of the three cation distributions following one another between the anionic plane-pairs. In Fig. 2 the basis of the three different hexagonal cells is marked and the numbered arrows signify the projection perpendicularly to the layers, of the threefold sliding direction. The order of slidings is given by the numbers beside the arrows. The displacements of the starting layer given here result in a crystal lattice of hexagonal symmetry the unit cell of which is identical with that mentioned above. This case is found in the structure of CrCl_3 .

If the subsequent layers are shifted into each other throughout the whole crystal lattice, always in one direction (Fig. 3), and it is taken into consideration that the mentioned displacement of the cationic arrangement

leads always to an anionic environment identical with the former, then $1/3$ of the body diagonal of the hexagonal cell — the length of one displacement —

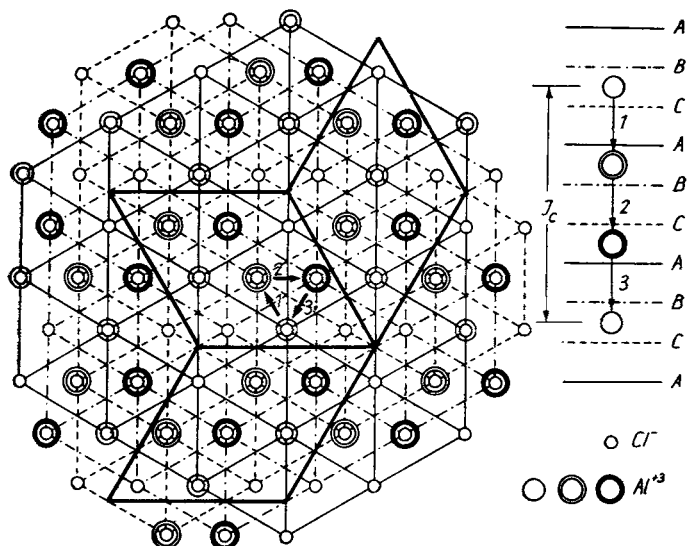


Fig. 2. Ionic arrangement of CrCl_3 . The right side of Fig. 2 shows the sequence of the anion planes and cation arrangement

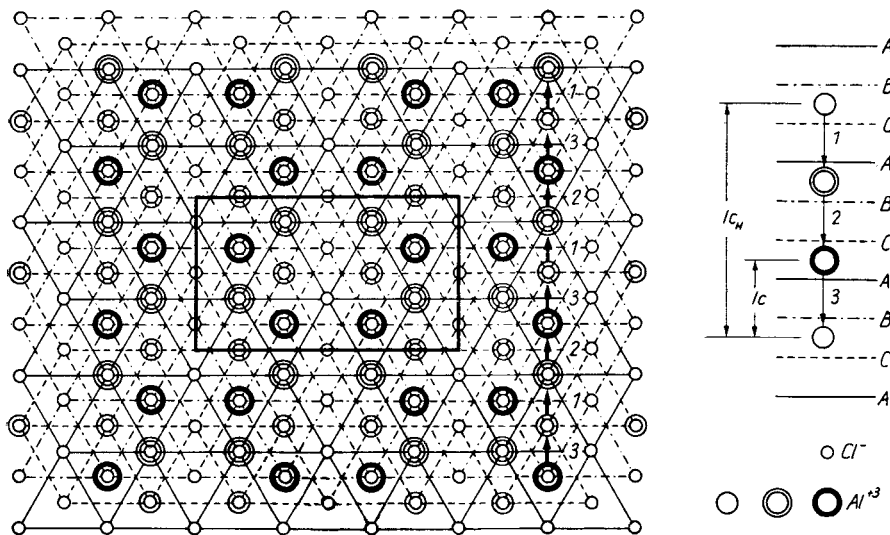


Fig. 3. Ionic arrangement of AlCl_3 perpendicular to the close-packed anion planes. The right side of Fig. 3 shows the sequence of the anion planes and cation arrangement

is the identity. This will be the real axis c of the unit cell and instead of the hexagonal cell we attain a monoclinic cell. This is the case with AlCl_3 .

The dimension of the unit cell and the ion coordinates in the lattice deduced in such a way can only be given approximately. Exact numerical values of the coordinates have to be determined from reflexion intensities, but this causes no essential change in the lattice structure.

Mere geometrical considerations lead therefore to the structure of AlCl_3 which — as has been mentioned — has recently been determined by KETELAAR [1] on the basis of X-ray diffractions. Accordingly, Al_2Cl_6 molecules do not exist in the solid phase and this is the reason why it has not been possible to give a convincing proof of the existence of molecules in the solid phase even by Raman spectra [3].

We are able now to picture the mechanism of the Al_2Cl_6 molecule formation which follows when the solid phase ceases to exist.

When by an increase of temperature solid AlCl_3 melts, breakdown of the crystal lattice can be imagined in the following way: first the loose bonds between the layers are interrupted and afterwards the layers fall apart owing to a re-arrangement of the Al ions which takes place within the loosened layers from octahedral to tetrahedral cavities and so Al_2Cl_6 molecules are formed. The mechanism of this re-arrangement of cations and the formation of molecules is shown in Fig. 4 in which one layer of the AlCl_3 crystal lattice is represented schematically in the projection perpendicularly to the layer. The Al ions are shifted during the re-arrangement in the direction of the arrows into the adjacent tetrahedral cavities and the formation of Al_2Cl_6 molecules given by PALMER and ELLIOT [2] occurs practically without a change of the position of the anions in the layer. The Al_2Cl_6 molecules formed in the layers in this way are in the Fig. separated from each other by dotted lines. It may be imagined that the layers cease to exist only after the formation of the molecules, as soon as the bonding force between them ceases to exist.

From the fact that AlCl_3 is easily sublimable and at a slow precipitation small crystal plates appear the conclusion may be drawn that some insignificant bonding force between the molecules must be present, and the layer only falls apart when the bonding energy is outbalanced by the heat motion. On the other hand, at precipitation with diminuation of the heat motion the small forces between the molecules are prevailing and the molecules will occupy their places beside each other corresponding to the former layers. And, by the inversion of the above mechanism the layers will be formed during the temperature decreasing when the Al ions are transferred again to octahedral cavities. This kind of layers placed one under another leads to macroscopic crystalline plates.

The mechanism given in Fig. 4 is a reversible one, which means that the mostly ionic bonding of the solid phase occurs prevalently in covalent bonds when during the increase of temperature Al_2Cl_6 molecules are formed and, on the other hand, the prevalently ionic bond returns during the decrease

of temperature, when the Al ions occupy again the octahedral cavities. This phenomenon is only then comprehensible, if we assume that the interaction which Al and Cl atoms produce upon each other becomes apparent in the alteration of the electron configuration, but this effect changes with the influence of temperature so that the partial atomic bond turns into a poor

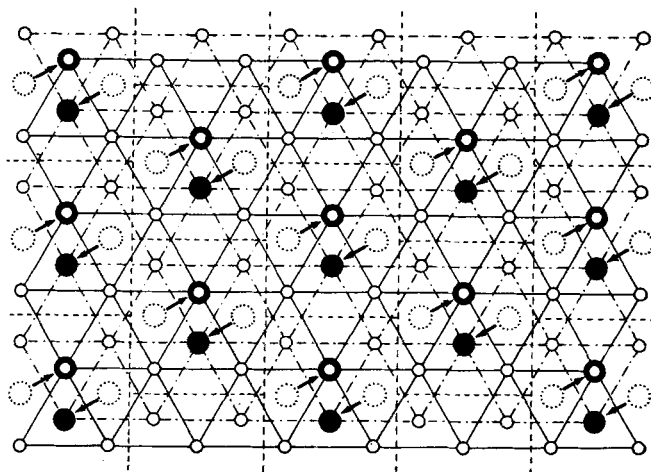


Fig. 4. A layer of the crystal lattice of AlCl_3 . The dotted circles represent the cation arrangement in the crystal lattice; the circles in full line give the re-arranged cation distribution after building Al_2Cl_6 molecules at the temperature of sublimation. The manner of cation re-arrangement is outlined by arrows

atomic bond and vice versa. Unfortunately we are not yet sure of the existence of such an effect, however, by lattice-structural considerations it becomes obvious that factors of this kind are playing a role in the formation of lattice geometry and its alteration.

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О КРИСТАЛЛИЧЕСКОЙ СТРУКТУРЕ $AlCl_3$

К. ШАШВАРИ

Резюме

Решетка $AlCl_3$ выведена на основе кристалло-геометрических соображений, исходя из размеров элементарной ячейки и из факта, что согласно измерениям электрической проводимости, произведенным Бильцем и Фойгтом, имеется и ионная связь. Решетка, выведенная этим способом, оказалась идентичной с выведенной Кетэллар и сотр. решеткой в 1947 году. Это, кажется подтверждает, что в твердой фазе $AlCl_3$ нет молекул Al_2Cl_6 , как предлагали Гердинг и Смит, на основе исследований спектров комбинационного рассеяния. Дана наглядная картина механизма перехода решетки в молекулы Al_2Cl_6 , характеризующие жидкую и паровую фазы.