

Citation:

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of both phenomena in ammonium-chloride may not be considered however as a statement of these results. For VOIGT¹⁾ finds the connexion

$$\frac{n_1 \kappa_1 - n \kappa}{n_2 \kappa_2 - n \kappa} = -2,$$

where $n \kappa$ is the absorption coefficient outside the field, $n_1 \kappa_1$ and $n_2 \kappa_2$ the absorption coefficients for the ordinary and the extraordinary rays. For ammonium-chloride it has been found here however, that the vibrations along both of the principal directions are absorbed stronger, so that the above fraction is *positive*.

A plausible representation of these phenomena may be obtained however by the assumption of an orientation of the somewhat elongated particles of the ammonium-chloride.

The phenomena of Case I (see 9) are analogous to phenomena of this kind: fine lines on glass or corrosion figures on crystals are seen clearly, when the length direction of the lines or figures is perpendicular to the plane through the incident ray and the line of observation²⁾. In Case II the eye has the most disadvantageous position to receive light of the orientated particles. In Case IV the incident light has a disadvantageous direction for the deflexion. Case V is easily derived from IV. The dispersion only cannot be explained by the orientation. For in the case of a slit-width below a wavelength we should expect just the opposite from what has been observed.³⁾

Finally I wish to express my indebtedness to Prof. ZEMAN for his encouragement and powerful assistance in this research.

Amsterdam, June 1916.

Chemistry. — “*The Interpretation of the Röntgenograms and Röntgenspectra of Crystals*”. By PROF. A. SMITS and DR. F. E. C. SCHEFFER. (Communicated by Prof. J. D. VAN DER WAAALS).

(Communicated in the Meeting of June 24, 1916.)

1. LAUE'S researches³⁾ and those by W. H. and W. L. BRAGG⁴⁾ about the diffraction of Röntgenrays by crystals have given rise to a view about the arrangement of the atoms in the solid substance, which, though sufficiently in agreement with the *physical properties* of the substance, cannot be reconciled with our *chemical ideas*.

¹⁾ Loc. cit. p. 58s.

²⁾ Compare CORTON et MOUTON, Les ultramicroscopes, les objets ultramicroscopiques. Paris 1906, p. 167.

³⁾ Sitzungsber. d. Bayer. Akad. d. Wiss., Juni 1912.

⁴⁾ Proc. Cambridge Phil. Soc. 17 (1912) 1, 45.

The quintessence of this new view is this, that the atoms of a solid substance occupy in a definite way the places of points of a lattice, in which arrangement the molecules no longer occur as separate particles, so that the idea of a molecule would undergo a fundamental modification for the solid substance, for it is immediately seen that according to this view every solid phase both in physical and in chemical sense had to be looked upon as one large molecule.

2. It strikes the chemist immediately that as the forces which occur - e. g. between, Na and Cl atoms in the solid phase have certainly to do with the valency, it would follow from the model designed by BRAGG for solid NaCl that Na just as Cl has a valency of six. This fact is so very remarkable for this reason that importance is attached to the fact that the quadri-valency of the carbon atom would follow from the model for diamond.

Also the model given by BRAGG for calcium-carbonate leads to remarkable conclusions. It appears namely from this model that every Ca-atom is surrounded by six oxygen-atoms, and that the distance between the centres of Ca and O is smaller than that between Ca and C. Along the sides of the calcspar rhomboheder there prevails no chemical force, for there is every reason from chemical side to assume in CaCO_3 no binding between Ca and C, but to do so between Ca and O. Led by the distances in the model of BRAGG we might distinguish CO_3 -groups; then, however, it is remarkable that every Ca-atom would always be connected with one O-atom of six CO_3 -groups, whereas we should have expected that every Ca-atom would be bound to two oxygen atoms of the *same* CO_3 -group. These remarks suffice, therefore, to show that this model cannot be reconciled with our idea of valency.

This objection can be thus further elucidated. In the representation given by the BRAGGS model of the solid substance the considerations are perfectly ignored which have led to the *firm conviction* that the atoms in the molecule are bound by forces which are characterized by their localized nature and by their definite number.

Thus BOLTMANN writes ¹⁾: "Wir erklären die Existenz der aus zwei Atomen zusammengesetzten Molekule durch eine, zwischen den Atomen thatige anziehende Kraft, welche wir die chemische Anziehung nennen. Die Thatsachen der chemischen Valenz oder Wertigkeit machen es wahrscheinlich, dass die chemische Anziehung keineswegs einfach eine Funktion der Entfernung der Mittelpunkte der Atome ist, dass sie viel mehr bloss an verhältnissmassig kleine Bezirke auf

¹⁾ Vorlesungen über Gastheorie, I, 177.

der Oberfläche der Atome gebunden ist. *Man kann auch nur unter der letzteren, keineswegs unter der ersteren Annahme ein der Wirklichkeit entsprechendes Bild der Gas-dissociation erhalten.*"¹⁾

Accordingly BOLTZMANN assumes that the chemical attraction resides in a sensitive region (empfindlicher Bezirk) or bulging out of the atom, which gives rise to the origin of a space called by him critical space (kritischer Raum). When now the centre of the second atom lies in the critical space of the first, and the sensitive regions of the two atoms partially overlap, the two atoms are certainly chemically bound to each other.

As BOLTZMANN showed we are now compelled to assume that the sensible region is found locally and not uniformly round the whole atom, as this latter assumption would lead to absurdity. Accordingly the conclusion at which BOLTZMANN has arrived is this: "In dem jetzt betrachteten Falle, wo der kritische Raum über die ganze Oberfläche der Deckungssphäre gleichmässig verteilt ist, würden sich, sobald die Atome sich überhaupt zu verbinden anfangen, sofort mit Vorliebe Aggregate bilden, die eine grössere Atomzahl enthalten. Es würde daher sogleich etwas Aehnliches, wie bei der Verflüssigung eines Gases eintreten".²⁾

That the chemical attraction acts locally, is certain, and whether we accept BOLTZMANN's view about the chemical attractive force or the newer view of STARK³⁾, of BOHR⁴⁾, or of J. D. VAN DER WAALS JR.⁵⁾, this is entirely indifferent at the moment, we only wish to state here very clearly *that the chemical attractive force is a local force, acting in points the number of which is determined by the valency.*

That this chemical force governs the atom bindings in the molecule also in the solid state, and the valency must manifest itself in this phase as well as in any other, may be considered as firmly established, so that any representation which leaves out of account these circumstances so exceedingly important from a chemical point of view, must be erroneous.

At last a third objection may be pointed out. The present representation of the solid substance is not able to account for the existence of internal equilibria in the solid phase.

3. It appears therefore, clearly from the foregoing that the cur-

¹⁾ The italics are ours.

²⁾ l. c. p. 215.

³⁾ Prinzipien der Atomdynamik III.

⁴⁾ Phil. Mag. (6) 26, 1, 476. 857 (1913).

⁵⁾ These Proc. XVI p. 1082.

rent representation of the solid substance must undergo a modification, so that the fundamental objections mentioned here, are obviated. How this is possible, we shall consider now.

In the very first place it should be pointed out that the Röntgenogram gives us only the relative situation of the centres of gravity of the atoms, and does not teach us anything about the value of the distances *between* the atoms with respect to the parameter of the lattice.

About this question, which is of so great importance for us, we can get to know something by way of estimate.

In the first place the representation that LINDEMANN¹⁾ formed of the atom movement in the solid substance yields a value for the distance between the atoms, which is negligible with respect to the atom radius; it becomes even so small that the compressibility cannot be taken into account without assuming compressibility of the atoms.

Another indication of the smallness of the distances between the atoms resting on a firmer ground, is furnished by what follows. From the determinations of the critical data follows that for normal substances the critical volume is about 2,4 times the value of the b from VAN DER WAALS SR.'s equation of state.

If b is given the value which holds for the rarefied gaseous state, i.e. four times the volume of the molecules, the real value of the volume will certainly be found too small, as the factor 4 decreases for smaller volumes. The minimum value v_m for the volume of the molecules is, therefore, given by the equation $v_k = 9,6 v_m$, in which v_k represents the critical volume.

For ether the critical density is 0,26 according to YOUNG, and at 0° the density of the liquid is 0,72. Hence the following relation exists between the volume at 0°, v , and the volume of the molecules:

$$v = \frac{0,26}{0,72} 9,6 v_m = 3,5 v_m.$$

It follows from this that in liquid ether at least 2/7 of the volume is filled by the molecules. The temperature of 0° C. being about 0,6 times the critical temperature of ether, the just calculated ratio will always exist between the volume of the liquid and the volume of the molecules at a reduced temperature of 0,6 according to the law of corresponding states.

If the molecules are now considered to be spheres, which are arranged cubically, then the free distance between the spheres in the

¹⁾ Physik. Zeitschr. 11, 609 (1910).

direction of the side of the cube is at most 0,4 times the radius of the molecule.

From J. D. VAN DER WAALS Sr.'s new considerations published in this number of the Proceedings, follows quite in accordance with our calculations that the distance between the molecules of a liquid as ether will be *smaller* at 0° than 0,4 of the radius of the molecule.

It follows, therefore, from this that in a liquid phase there exists only a small difference between the distance of the centres of gravity of the molecule and the diameter of the molecule.

If we now consider that as a rule the solid phase possesses a greater density than the liquid phase, it follows immediately from the above calculation that the said difference will be still somewhat smaller for the solid phase.

Accordingly the distance between the molecules in the solid phase is small.

An important conclusion may be drawn from this for the *solid substance*, which runs: *the distance between the atoms which belong to different molecules, will depart very little from the distance between the atoms in the same molecule, which engenders the possibility that these small differences do not find expression in the Röntgenogram.*

The objections advanced here can be entirely obviated by assuming that there exist molecules also in the solid phase, and that the distance between the atoms in the molecule is of the same value as the distance between the atoms of different molecules.

Considered in this light there is no reason to be astonished that the Röntgenogram does not teach us anything about the existence of molecules in the solid phase.

Still it is possible that on refinement of the method of research or on enlargement of the Röntgen image the spots betray a composite character, and in this case the difference between chemical and physical binding might still find expression. Besides the size of the spots is often not negligible with respect to the distances between the spots, so that variations are certainly possible in the distances.

4. It is clear that when special forces make their appearance, always between one Na and one Cl atom the symmetry of the common salt crystal can change. Now as BRAGG himself observed ¹⁾, the model NaCl given by him is not in harmony with the symmetry. It does not seem improbable to us that the occurrence of the special chemical bindings is just in connection with this lower sym-

¹⁾ Proc. Roy. Soc. A **89**, 468 (1913); Zeitschr. f. anorg. Chem. **90**, 216, 1914.

metry¹⁾. However this may be, it seems to us that a model of the crystal cannot be satisfactory, unless the idea of molecule and the lower symmetry find expression in it.

Also the occurrence of internal equilibria must be revealed by the crystal model, which is impossible with the prevalent conception. If we consider e. g. a mixed crystal of two molecule kinds, one of which is a polymer of the other, it must be possible that definite atoms are alternately bound or not bound to others. Of course it is possible that in the formation of double molecules the distances are little modified, if at all, so that this chemical process is not expressed in the Röntgenogram, but then we should at least come to the conviction that the Röntgenogram does not teach us anything about the chemical forces which interest us most, so that in other words we cannot make out whether two neighbouring atoms are chemically bound or whether they are not.

Thus it is e. g. possible that by means of the Röntgenogram no difference is found between a mixed crystal and a chemical binding, when they possess the same symmetry in solid state, though chemically there exists a very great and exceedingly important difference between them.

We thought it incumbent upon us to make these remarks, because from physical side the problem of the atom arrangement in the solid substance seems to be considered as all but solved, though the given solution is entirely incompatible with the most essential element, viz. with the chemical properties.

5. The chemical requirements, therefore, include that the *valency* is expressed, while there are indications for NaCl and KCl that the symmetry is lower than has been assumed in BRAGG's model.

Accordingly BRAGG's model for these chlorides must be subjected to a considerable modification; every atom lying on an axis of symmetry would have to be multivalent on the assumption of chemical bindings, unless the binding lies on the axis itself. To this is added that the valency would depend on the circumstance whether the atom is situated on a 2, 3, or 4 fold axis, or in the centre.

When designing a new model for NaCl we have further been led by the assumption that the distance between the chemically bound atoms will not be greater than that between not bound atoms, and the chemical force, therefore, never acts in a diagonal direction. Further by the assumption that the chemical binding, undoubtedly, is one of the factors that determine the class of symmetry of the

¹⁾ If NaCl should be holoedrical, then it will hold in each case for KCl.

crystal. We have taken these circumstances into account in the following model. There is no atom in the centre of the figure, because when it were present, it would be an atom of a valency of six. For the reason mentioned above the places have been left vacant on the 2 and 3 fold axes. The four-fold-axis has been perfectly covered with molecules in our model, except in the centre.

Just as in BRAGG's model the planes (111) are alternately exclusively covered with Na resp. Cl-atoms. The planes (100) and (110) all contain both Na and Cl-atoms. In every section there occur vacant places, the number of which will relatively decrease as the crystal gets larger. The condition for interference will, however, get more complicated here than in BRAGG's model, because parallel planes are not perfectly equally covered. Testing by observation is rendered less simple in consequence of this. It is, however, clear that among other things the explanation for the difference between the interference images of NaCl and KCl also perfectly applies to our model.

To construct this model one can start from the inner cube, indicated by fig. 1, the side of which is the double parameter of the lattice. There are only homonymous atoms in the centres of the side planes of this cube; these atoms are chemically bound with the atoms lying in the centres of the planes of the second cube (fig. 2), the side of which is four times the parameter of the lattice. The other net-points of the second cube are all as much as possible covered with atoms. The four atoms that lie nearest about the central atom in each plane, are bound with atoms of the third cube, fig. 3. Each plane of the third cube contains 5 atoms, which are bound with the following one. We can now imagine, that the crystal is built up of two kinds of crystal molecules of the size of fig. 2 or fig. 3 or of still greater dimensions. These crystal molecules are derived of the innercube indicated by fig. 1, with Na resp. Cl atoms in the centres of the side planes.

Anorg. Chem. Lab. of the University.

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A. SMITS and F. E. C. SCHEFFER: "The Interpretation of the Röntgenograms and Röntgenspectra of Crystals".

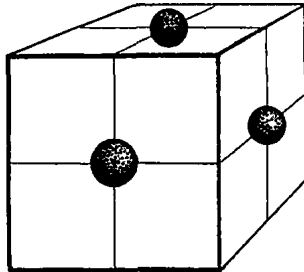


Fig. 1.

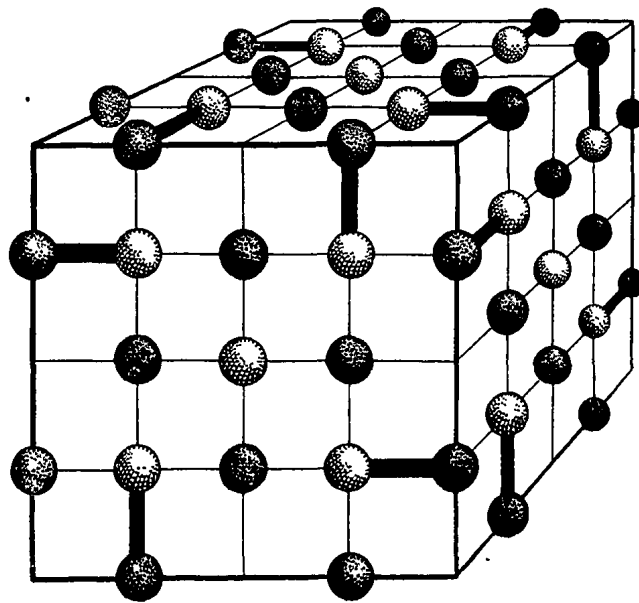


Fig 2.

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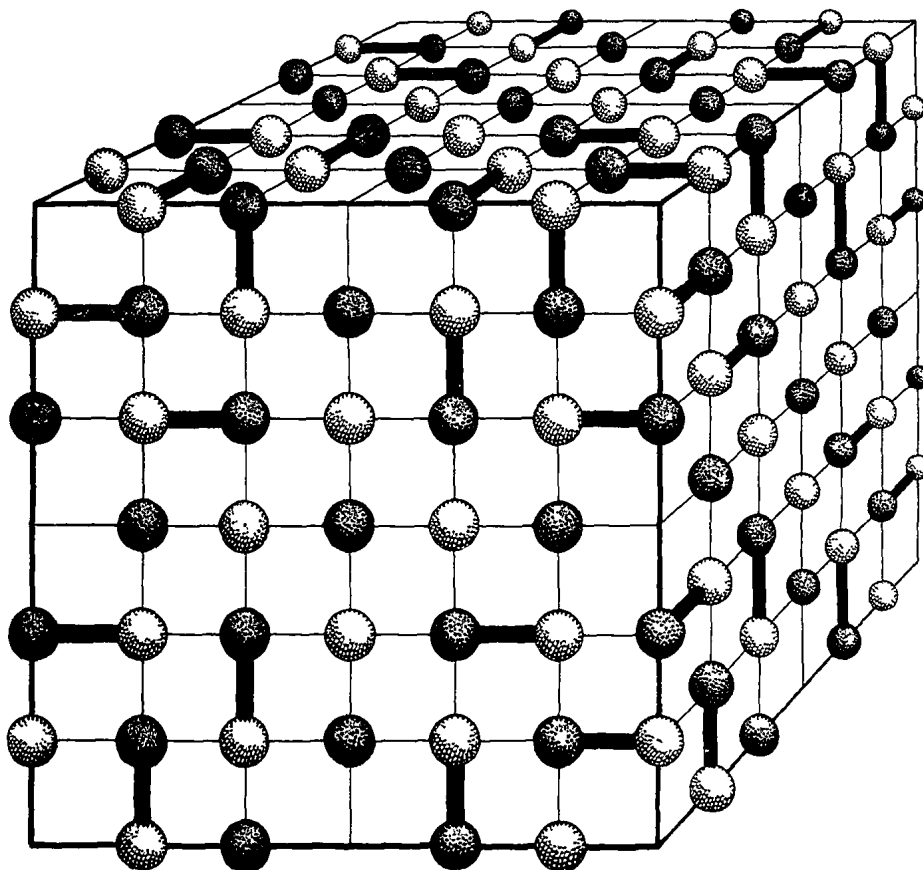


Fig 3.

Proceedings Royal Acad. Amsterdam, Vol. XIX.