Chemistry. — *On the Symmetry and Structure of the cubic Nitrates of Calcium, Strontium, Barium and Lead.* By Prof. Dr. F. M. Jaeger and F. A. van Melle.

§ 1. Between the results of the crystallographical and the Roentgen-spectrographical investigations on the true symmetry of the isomorphous series of cubic *nitrates* of the metals *calcium, strontium, barium* and *lead,* there are still a number of discrepancies, which cause the question to be quite unsettled.

As far as concerns the geometrical form of these crystals, all data obtained by the different crystallographers seem to indicate, that the symmetry is truly the *tetrahedral-pentagonedodecahedral* one. The *Ca*-salt was obtained by Retgers [1]) in apparent octahedra from the monoclinic *tetrahydrate* on heating it at 150° C.; it is isomorphous with the *Sr*-salt. which also forms a monoclinic tetrahydrate, but which may also be obtained directly in an anhydrous cubic form, if crystallized from warm solutions. Wulff [2]) showed, that in most cases it crystallizes in apparent cubo-octahedra, but that its twins often manifest also a dodecahedron {210}. Scacchi [3]) stated, that a slight addition of Fe_2Cl_6 to its solutions, favours the development of this last form, and Wulff found the same fact, if $CaCl_2$ be added to the solution.

According to this author, the *Ba*-salt shows, besides both tetrahedra {111} and {1$\bar{1}$1} and the cube {100}, moreover a pentagonal dodecahedron {201} and a left-handed, positive tetrahedral pentagonedodecahedron, also in the case that *no* strange salts are added to the solutions. The development of this last form is favoured by an addition of $NaNO_3$ to its solution; while the presence of KNO_3, $NaNO_3$ and *saccharose* causes the appearance of the forms {211} and {221}, and that of *ferric nitrate* leads to the manifestation of {883} and {5$\bar{1}$1}. Lewis [4]) observed the tetrahedral pentagonedodecahedra: {3$\bar{5}$1}, {2$\bar{1}$4} and {214}, in addition to the usual limiting forms; and Henriques [5]) showed, that on addition of some *nitrophenol* to the solution, the pentagonal dodecahedron {201} becomes the predominant form. Although the study of the etching-figures has also led to results [6]), which agree with the symmetry mentioned above, they must now be considered as having only a feeble

[1]) J. W. Retgers, Zeits. f. Kryst., **21**, (1893), 257.

[2]) L. Wulff, ibid., **4**, (1880), 139.

[3]) A. Scacchi, Pogg. Ann. der Physik, **109**, (1860), 366.

[4]) W. J. Lewis, Zeits. f. Kryst., **2**, (1878). 64.

[5]) R. Henriques, Ref. ibid., **5**, (1881), 365.

[6]) H. von Baumhauer, Z. f. Kryst., **1**, (1877), 52. On {100} etching-figures were observed which correspond with a left-handed negative tetrahedral pentagonedodecahedron; also Wulff (loc. cit.) mentions the same fact.

conclusive force, because of the fact that in recent times it could be proved, that the presence of slight traces of impurities can have a strong influence upon this phenomenon in the case of KCl; in the older investigations this fact could, in general, not yet be sufficiently taken into account.

In the case of $Pb(NO_3)_2$ WULFF [1]) observed, on rapid evaporation of the solution, the tetrahedra $\{111\}$ and $\{1\bar{1}1\}$ in *un*equal development, besides $\{883\}$ and a tetrahedral pentagonedodecahedron, which approximately seemed to correspond with the symbol: $\{10.5.6\}$. According to this author, the appearance of this last form seems to be favoured by the presence of some $Zn(NO_3)_2$. An analogous influence was observed by SCACCHI with respect to the appearance of $\{201\}$, if traces of $NaNO_3$ were added to the solution. It may be remarked here, that we have observed this pentagonal dodecahedron also, in a well-developed form, if *no* other salts were added to the solution. According to MOREL [2]), the form $\{201\}$ would be favoured also by the presence of HNO_3.

As is well known, MARBACH as the first observed, that all these *nitrates* show an abnormal birefringency, which in the case of the *lead*-salt, for instance, is particularly strong, and which is studied several times in detail. It manifests itself by a division in optically-abnormal sections of the crystals and is often explained by the presence of internal strains in the crystalline individuals.

§ 2. On the contrary, there are also facts, which seem to prove *against* the tetrahedral-pentagonedodecahedral symmetry of these crystals. There is, for instance the peculiar circumstance, that never even a trace of circular polarisation could be detected with them, — not even in LONGCHAMBON's more recent and accurate investigations. Another difficulty is presented by the investigations of their pyro-electrical behaviour by HANKEL, who says that the forms $\{111\}$ and $\{1\bar{1}1\}$ may be discerned by their opposed pyro-electric polarity, — a fact which in the cubic system is, however, impossible [3]). On the other hand, no piezo-electrical phenomena are, up till now, observed with these crystals [4]).

But also from the results of the ROENTGEN-spectrographical study of these *nitrates* the conclusion seems to become evident, that they have another symmetry, the *dyacisdodecahedral* one. Besides some ROENTGEN-spectrographical observations made by NISHIKAWA and HUDUNIKI [5]) and some not published results of WYCKOFF [6]) obtained by means of LAUE-spectrograms, there are also calculations of the intensities made by

[1]) L. WULFF, loco cit.

[2]) J. MOREL, Bull. de la Soc. minér. **9**, (1886), 294.

[3]) E. RIECKE, vid. L. GRAETZ: *Handbuch der Elektrizität und des Magnetismus*, Bnd. **1**, (1918), 407.

[4]) Conf. e.g. P. TERPSTRA, Natuurw. Tijdschrift, **10**, (1928), 92; Congres Natuur- en Geneeskunde, Leuven, (1928).

[5]) S. NISHIKAWA and K. HUDUNIKI, Proceed. Math. Phys. Soc. Tokyo, **9**, (1917), 197.

[6]) R. W. G. WYCKOFF, *The Structure of Crystals*, (1924), 353.

VEGARD, Zeits. für Physik **9**, (1922), 395, from powder-spectrograms after HULL-DEBIJE. They all seem to lead to the conclusion, that the symmetry is *dyacisdodecahedral* and that the space-group is T_h^6. In the presence of such strongly diffracting atoms like those of *Ba* and *Pb*, such a calculation of the diffraction-intensities from powder-spectrograms has no significance whatsoever with respect to the placing of the (NO_3)-groups within the primary cell. To the space-group T_h^6, it is true, corresponds the simple cubic lattice; but no diffraction-images were found, which would be incompatible with those of a substance having a face-centred cubic lattice, because the *Ba*- and *Pb*-atoms which in the last case would have the positions: $[000]$, $[0\ ^1/_2\ ^1/_2]$, $[^1/_2\ 0\ ^1/_2]$ and $[^1/_2\ ^1/_2\ 0]$, are so predominant in their diffracting power, that no difference in both case is detectable. However, in the case of powder-spectrograms the choice between the groups T_4 and T_h^6 must be made by looking for the absence of reflections of the first order of $\{hko\}$, if h, as well as k are both *odd*. Now the predominant action of the *Ba*- and *Pb*-atoms in the corresponding *nitrates* already mentioned as well as the fact, that with *Ca*- and *Sr-nitrates only a single* diffraction-line of $\{hko\}$, namely *only* (210), was observed, — *makes it quite impossible to fix a choice between* T_4 *and* T_h^6 *by means of powder-spectrograms.* It was, therefore, necessary to repeat these investigations, making use this time of rotation-spectrograms.

§ 3. Rotation-spectrograms were made by means of an apparent cubo-octahedron of $Sr(NO_3)_2$, the directions $[1\bar{1}0]$ and $[100]$ being used as axes of rotation. Figure 1 shows the spectrogram obtained with $[1\bar{1}0]$
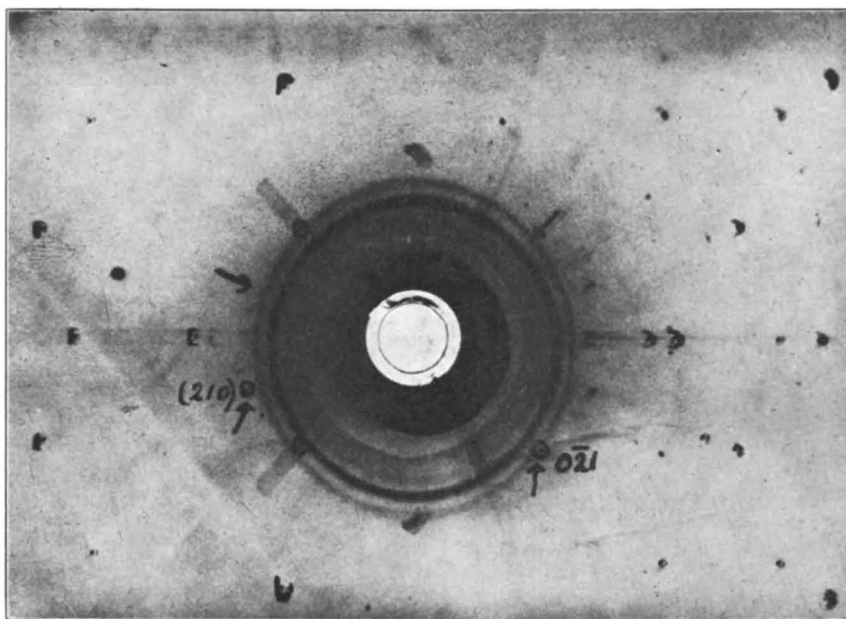
as axis of rotation, the mean position being such, that it made $15°$ with (001) and the crystal being rotated through $10°$ to both sides of it. From the reciprocal lattice it can be deduced, that (120), (201), (210), (0$\bar{2}$1), (110), (320), (330), and (100) will be in such positions, as to give the corresponding reflections. It appeared, that (210) and ($\bar{0}$21) were truly *present*, but that (120), (201), (110), (320) and (330) were *lacking*. In the case of the rotation-spectrogram round [100], the exposition was 3 hours, while the rotation occurred in such a way, that eventually (003) and (005), respectively (005) and (007) would possibly appear. Although the cube-face used was beautifully developed and very smooth, the said reflections of odd orders appeared, however, to be wholly *absent* in each case.

From these observations the conclusion must be drawn, that the fundamental lattice is the *simple cubic* one, with: $a_0 = 7.80$ A.U. and with 4 molecules $Sr(NO_3)_2$ in the elementary cell. Because, moreover, the first order of $\{hko\}$, h being *odd*, is *not* present here, this fact points to the space-group T_h^6.

§ 4. LAUE-spectrograms were now made in the case of *Sr-, Ba-*, and *Pb-nitrate*. (Tungsten-anticathode; 50 K.V. tension). It appeared that the spectrograms thus obtained by radiation $\perp$ to $\{111\}$, did *not* possess symmetry-planes passing through the trigonal axis; — a result, evidently quite in accordance with the unpublished results of WYCKOFF (conf. loco cit., p. 353). The LAUE-spectrograms of the three *nitrates* mentioned, showed the greatest possible analogy; it is most remarkable, that they do almost not deviate from those of a true holo-cubic crystal (three spots are the only ones, which are *un*symmetrically situated) with three symmetry-planes $\perp$ (111).

A rotation-spectrogram of $Ba(NO_3)_2$ with [100] as axis, proved again, that the reflections (001) and (003) were both *absent*; but there appeared here also a reflection of (210) in the 1st order, while (120) was *absent*. Therefore, it must be concluded from this, that the space-group of $Ba(NO_3)_2$ is also T_h^6, with: $a_0 = 8.10$ A.U. and with 4 molecules of the salt in the elementary cell.

§ 5. Now a rotation-spectrogram of $Pb(NO_3)_2$ was made with [100] as axis of rotation, the primary position of the crystal being such, that it was at $36°$ with (010), while the rotation occurred through an angle of $10°$ to both sides, i.e. from $26°$ to $46°$ with respect to (010). In this case (003), (005) and (007) had an opportunity to reflect. But, although the crystal used had a beautiful, smooth face of several mm^2 surface, *no other* reflections than that of (004) and (006) could be obtained, not even after prolongated exposition: also in this case all reflections of *odd* order appeared to be *absent*.

BRAGG-spectrograms, obtained by exposition during several hours and by rotating through a small angle in such a way, that the images of (001), (002) and (003) could be expected, gave *no* images of any appreciable intensity, safe (002), the others having intensities certainly less than

$\frac{1}{100}$ th part of that of (002). Also from these data it becomes almost certain, that the space-group is T_h^6, having thus *dyacisdodecahedral* symmetry.

On (210) a BRAGG-spectrogram gave the 1st order image of (210); from our spectrograms, — *calcite* being used for the purpose of comparison, — the value of a_0 was deduced to be: 7.80 till 7.81 A. U. $\pm$ 0.01, in stead of VEGARD's value: 7.84 A. U.

§ 6. The attempts to fix the positions of the *N*- and *O*-atoms in this case by a calculation of the intensities, can only have any significance in the case of the *Ca*-salt. In that of the *Ba*- and *Pb*-salts it would be only possible perhaps to obtain better information about the true positions of these atoms by means of accurate measurements with an ionisation-spectrometer; *but it is excluded in these cases to obtain any reliable results from powder-spectrograms.*

Better than powder-spectrograms, these LAUE-photo's indicate the severe difficulties present here for the calculation of the four parameters of the structure. For, as the great majority of the diffraction-spots is compatible with the holo-cubic symmetry, — even in the case of $Sr(NO_3)_2$, where the number of electrons of the metal is about the same as that of the (NO_3)-groups, — it is highly probable, that the *oxygen*-atoms *approximatively*, and the *metal*-atoms *rigorously*, have positions in the structure of these crystals, which are compatible with those present in one of the classes of holo-cubic symmetry (for instance, position 24a of WYCKOFF's list). The possibility seems, therefore, excluded beforehand, of fixing the true positions of the *N*-atoms with their relatively small number of electrons, in the midst of the seven times greater number of the electrons of the other constituents of these salts. Exactly because the method based upon the diffraction of ROENTGEN-rays is still a method of small sensitivity, as regards the differences between heavier and lighter-atoms, diffère nécessairement de l'ensemble de tous les points de R, de sorte que l'ensemble fermé $F_\alpha = R - \overset{\alpha}{\underset{\beta=1}{\varSigma}} G_\beta$ est non vide, quel que soit $a > \Omega_\tau$. — the possibility, that yet a tetrahedral-pentagonedodecahedral arrangement with the symmetry T_4, — but *very nearly approaching* to an arrangement with the symmetry T_h^6, — may be present here, needs still to be considered in future: the facts revealed by all crystallographers seem, as was pointed out before, to indicate the symmetry of the group T.

Certainly it is necessary to investigate the complete structure of these nitrates in detail. For, notwithstanding the results obtained here with respect to the symmetry and space-group, a number of physical discrepancies remain.

In every case VEGARD's conclusion about a *dyacisdecohedral* symmetry can now be considered as being right, notwithstanding the fact that *no proof* was given by him. The further investigation of the structure of these *nitrates* can be continued now, starting from the data here obtained.

Groningen, Laboratory for Inorganic and
Physical Chemistry of the University.

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