Chemistry. — *"Some Remarks on the Crystalform of Boron-nitride and on the eventual Ambiguity in the Analysis of Powder-spectrograms."* By Prof. F. M. JAEGER and H. G. K. WESTENBRINK.

§ 1. *Boron-nitride*: $(BN)_x$ commonly occurs in the form of a white, tallowy powder, which in literature is described as amorphous [1]). Even on magnifying 500 times, no crystalform of the particles present in the powder studied [2]) is observed under the microscope. There is no doubt, however, about the fact, that the compound is really microcrystalline; this was, a short time ago, experimentally proved for the first time by TIEDE and TOMASCHEK [3]). It is, however, impossible to provide better developed crystals by recrystallization from a solvent or molten mass, or by sublimation; therefore, on studying the substance by means of *X*-rays, it is *only* possible here to make use of powder-spectrograms after HULL-DEBIJE's method, without our having any opportunity to test the results obtained in any other way. In the following pages it is emphasized once more, how ambiguous results from the interpretation of such spectrograms may follow, if no other method in ROENTGEN-analysis can be made use of, or if neither goniometric measurements, nor sufficient data about the crystallographic symmetry are available for further control.

Another difficulty presented itself here in the fact, that the specific weight of the substance is not, or at least very inaccurately, known and its exact determination is much hampered by the peculiar nature of the compound. As the original preparation appeared to be not completely homogeneous under the microscope, but to contain small black grains, — it was necessary to separate these by fractional sedimentation with water. They consist principally of crystallized *boron*, which has a higher specific weight than the principal mass of the preparation. From the remaining mass about five fractions of a different degree of dispersion could be separated by fractional sedimentation; the last fraction gave with water a colloidal solution, from which the colloidal substance by addition of a trace of hydrochloric acid could be coagulated. After drying

[1]) L. MOESER and W. EIDMANN, Ber. d. d. chem. Ges., **35**, 536, 1902; A. STOCK and M. BLIX, Ber. d. d. Chem. Ges., **34**, 3039, (1901).

[2]) W. H. BALMAIN, Phil. Mag. (3), **21**, 170, (1842); **22**, 467, (1843), **23**, 71, (1843); **24**, 191, (1844); Journ. für prakt. Chemie, **27**, 422, (1842); **30**, 14, (1843). F. WÖHLER, Ann. der Chem. **74**, 70, (1850); Pogg. Ann., **79**, 467, (1851).

[3]) E. TIEDE and H. TOMASCHEK, Zeits. f. Elektrochemie, **29**, 303, (1923); cf. also: E. TIEDE and F. BÜSCHER, Ber. d. d. chem. Ges., **53**, 2206, (1920).

at 100° C., also this last preparation was studied in the same way: it appeared, however, that all preparations gave *identical* ROENTGEN-spectrograms. The specific weight of these different fractions, however, differed considerably and appeared to decrease with an increasing degree of division. Perhaps this fact might be related to the particular circumstance, that the molecular weight of *boron-nitride* is, according to most investigations, certainly a *multiple* of the most simple formula: *BN*; the dissociating power of the water may be the cause of the occurrence of a mixture of several kinds of such polymeric molecules. The last three fractions obtained showed finally only a small difference of their specific weights, so that its final value with near approximation could be fixed at $d_{40}^{18°} = 1,99$. But as will become clear, this value presents again a new difficulty for the exact interpretation of the true crystalstructure.

§ 2. A considerable number of diffraction-lines could be observed on the well developed spectrograms, which were obtained after HULL-DEBIJE's method in using the *K*-radiation of a *copper*-anticathode. The lines showed strongly different intensities on the film. The principal ones are reviewed in the following table; assuming a *cubic* symmetry as the most probable one in respect to the chemical composition, the indices were calculated from the suitable quadratic equation. Such a cubic arrangement may a priori be considered as probable here, taking

TABLE I.					
Number of the lines:	Intensity:	Double distance to the centre in mm;	$sin^2 \frac{\theta}{2}$:	Calculated values of $sin^2 \frac{\theta}{2}$:	Indices: (MILLER)
1	9	18.0	0.0321	0.0321	(111)
3	10	23.5	0.0542	0.0535	(102)
4	3	25.8	0.0651	0.0642	(112)
5	4	36.5	0.1275	0.1284	(222)
3	3	38.7	0.1425	0.1391	(320)
8	4	48.4	0.2166	0.2140	(420)
9	1	52.1	0.2477	0.2568	(422)
12	4	66.4	0.3794	0.3852	(600)

Quadratic equation: $sin^2 \frac{\theta}{2} = 0.0107 \ (h^2 + k^2 + l^2)$ (α-radiation).

$R = 25$ mm. For the lines N⁰. 2 and 7, cf. Table II.
Tension: 55000 Volt; time of exposure: 6 hours.

into consideration the relatively small difference in atomic number of the boron- and nitrogen-atoms [1]).

From the indices of the scattering atomic planes, which evidently occur in all possible combinations of odd and even numbers, it follows, that the underlying grating is a *simple cubic* one, the characteristic translation of it (edge of the cubic cell) a_0 being calculated, with respect to the wave-length used, as 7,44 A.U. But from the value for $d = 1,99$, the number n of molecules BN present in such a cell, results as:

$$n = \frac{(7,44)^3 \times 1,99 \times 10^{-24}}{1,64 \times (11 + 14) \times 10^{-24}} = 20.$$

Therefore, within each cell 20 *boron-* and 20 *nitrogen-*atoms should necessarily find their places, — a number, which can hardly be considered to be in accordance with that of the equivalent positions, characteristic for the space-groups of cubic symmetry.

§ 3. However, as follows from Table II, the results of the measurements can be interpreted with the same degree of accuracy, also on the assumption, that here a *tetragonal* grating is present. (See Table II following page).

Supposing *this* interpretation to be the right one, *boron-nitride* appears to be tetragonal, with a grating built up from *simple tetragonal cells.* The edges of the cell are: $a_0 = 4,295$ A.U. and $c_0 = 5,176$ A.U.; so that the axial ratio has the value: $a : c = 1 : 1,2052$. If again the value of d_0 at 18° C. be considered as: 1,99, the number n of molecules BN per elementary cell is calculated as: $n = \dfrac{(4,295)^2 \times 5,176 \times 1,99 \times 10^{-24}}{1,64 \times 25 \times 10^{-24}}$ $= 4,6$; so that 4 or 5 *boron-*atoms and the same number of *nitrogen-*atoms must be present in each cell. The first number is certainly, but the second not in accordance with the number of equivalent positions compatible with the special symmetry of the tetragonal space-groups.

§ 4. As all further necessary data are lacking, it is impossible here to fix our choice and to decide, whether *boron-nitride* has *cubic or tetragonal* symmetry. An analogous case of ambiguity in the interpretation of powder-spectrograms occurred recently in the study of *thallium* by LEVI [2]). This author attributed to the metal, with respect to his results obtained by the HULL-DEBIJE-method only, a hexagonal structure (trigonal closest packing), with the grating-constants: $a = 3,47$ A.U.; $c = 5,52$ A.U.; and $a : c = 1 : 1,59$. TERPSTRA [3]) drew, however, attention to the fact, that

[1]) The case of a trigonal structure, which could be supposed, appeared only to be compatible with the results of the measurements, if the axial ratio were $a : c = 1 : 1,225$. Then, however, α must be 90°, and no difference is present then with a cubic grating, considered in the direction of a trigonal symmetry-axis.

[2]) G. R. LEVI, Nuovo Cimento, May, June, (1924); Zeits. f. Kryst. **61**, 561, (2925).

[3]) P. TERPSTRA, Zeits. f. Kryst. **63**, 318, (1926).

					TABLE II.			
Number of the lines:	Intensities (estimated)	Double distance to the centre in mm :	$\theta/2$:	$sin^2\dfrac{\theta}{2}$:	$sin^2\dfrac{\theta}{2}$:	Calculated values of $sin^2\dfrac{\theta}{2}$:	Indices (MILLER).	Remarks:
1	9	18.0	10°19′	0.1791	0.0321	0.0321	(100)	
2	2	21.2	12°9′	0.2105	0.0443	0.0442	(101)	β-line.
3	10	23.5	13°28′	0.2329	0.0542	0.0542	(101)	
4	3	25.8	14°47′	0.2552	0.0651	0.0642	(110)	Only present on one film.
5	4	36.5	20°55′	0.3570	0.1275	0.1284	(200)	
6	3	38.7	22°10½′	0.3774	0.1425	0.1505	(201)	
7	2	43.8	25°6′	0.4242	0.1799	0.1768	(202)	β-line.
8	4	48.4	27°44′	0.4654	0.2166	0.2168	(202)	
9	1	52.1	29°51′	0.4977	0.2477	0.2489	(212)	
10	1	63.9	36°37′	0.5965	0.3558	0.3586	(321)	β-line.
11	3	65.8	37°42′	0.6115	0.3740	0.3773	(302)	Only observed on one film.
12	4	66.4	38°3′	0.6164	0.3799	0.3857	(104)	
13	5	71.8	41°8′	0.6579	0.4327	0.4394	(321)	
14	1	76.4	43°46′	0.6917	0.4785	0.4878	(303)	Only present on one film.
15	3	87.9	50°22′	0.7701	0.5931	0.5999	(331)	

Quadratic form: $sin^2\dfrac{\theta}{2} = 0.0321\,(h^2 + k^2) + 0.0221\,l^2$ (α-radiation);

and $sin^2\dfrac{\theta}{2} = 0.0262\,(h^2 + k^2) + 0.0180\,l^2$ (β-radiation).

$R = 25$ mm. Tension: 55 Kilovolt; time of exposure: 6 hours.
Line N⁰. 2 is the β-image of N⁰. 3; line 7 that of N⁰. 8; N⁰. 10 that of N⁰. 13; all other lines are α-images.

these observations of $sin^2\dfrac{\theta}{2}$ could as well, if not better, be calculated from a quadratic equation for a tetragonal grating, whose parameters are: $a_0 = 5,2$ A.U. and $c_0 = 8,2$ A.U. Only after the Italian author[1] had recently been able to obtain LAUE-spectrograms of cathodically deposited, very small *thallium*-crystals, it was possible for him to prove beyond any doubt, that the symmetry is certainly *hexagonal*. As the calculated and observed intensities for the structure of *thallium* attributed by him,

[1] G. R. LEVI, „Nuovo Cimento", October (1926).

do not agree, however, a reviewed investigation of this crystalstructure remains highly desirable.

These data and those given in this paper, may, therefore, be once more considered as a warning, not to draw conclusions about crystal-structures, where *only* the results of powder-spectrograms can be used. If it is required to give a final solution of problems concerning the crystalstructure of the compounds investigated, such data can only be considered as valuable, if used in connection with the results of other spectrographic methods and of crystallographic measurements.

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