

Chemistry. — The Allotropism of Beryllium. Bij F. M. JAEGER and J. E. ZANSTRA.

(Communicated at the meeting of June 24, 1933).

§ 1. In a previous paper¹⁾, in which the remarkable behaviour of crystalline lumps of *beryllium* was described, when the metal is heated above a certain temperature, we already mentioned that from the experiments hitherto made, it must be concluded that some allotropic change in the metal seems to take place, although evidently no *direct* connection between this phenomenon and the abnormal calorimetric behaviour exists. In a following publication we intend to return to these calorimetric phenomena, since it was discovered that also samples of this metal occur that do *not* manifest the said behaviour; while, on the other hand, we observed the phenomena described also in the case of some other metals, in the first place with *zirconium*. In the present paper we only wish to publish the results of the investigation of the metal by means of *X-rays*, which has led us to the discovery of a new modification of *beryllium*, —this being probably a metastable form of the metal with respect to the ordinary *α-beryllium*.

The structure of *beryllium* has been determined by G. MEIER and by Mc KEEHAN²⁾; according to the latter, *α-beryllium* has a closest-packed hexagonal arrangement, with $a_0 = 2,283 \text{ \AA}$. and $c_0 = 3,61 \text{ \AA}$. and with two atoms of *Be* within its simple parallelepipedic cell; $d_0 = 1,827$. There is, however, no complete agreement between the observed and the calculated intensities of the different reflecting forms; moreover, the author already mentions the occurrence of a number of unexplained lines in his spectrograms, whose presence he partially attributes to the admixture of a small quantity of beryllium-oxide, and partially tries to account for by assuming the presence of an unknown substance.

At our disposal we had two very pure samples of *beryllium*¹⁾: the one in the form of very beautiful crystal-aggregates, the other in the shape of a massive cylindrical rod, which *inter alia* was used by E. J. LEWIS³⁾ in his experiments on the electrical conductivity of the metal and which most kindly was put at our disposal by Prof. E. MEERRITT of Cornell-University. The results obtained with these two samples are

¹⁾ F. M. JAEGER and J. E. ROSENBOHM, These Proceedings Amsterdam, 35, (1932), 1055; conf. p. 1061.

²⁾ G. MEIER, Thesis Göttingen, (1921); L. W. Mc KEEHAN, Proc. Nat. Acad. of Science, 8, (1922), 270; M. C. NEUBURGER, Zeits. f. Kryst., (A), 85, (1933), 325.

³⁾ E. J. LEWIS, Phys. Review, 34, (1929), 1577.

practically identical, so that in the following no special distinction between them is made.

§ 2. *α-Beryllium.*

From the sample of pure, well crystallized *beryllium*, provided by SIEMENS, some single crystals, showing the face {0001} and some others, showing a hexagonal prism, could be isolated. Rotationspectrograms were made with the *c*-axis and the orthohexagonal *b*-axis, respectively, as axes of rotation. Also oscillation-spectrograms on {0001}, after BRAGG's method, were prepared, — calcite being used as a standard-material. The analysis of the rotationspectrograms was made by means of BERNAL's method.

A. *Rotation-spectrogram round the c-axis.*

Copper-*α*-radiation; 50 m. Amp. hours. The spectrogram showed a principal and the first accessory spectrum.¹⁾

Principal spectrum: (110) = (01 $\bar{1}$ 0); (310) = (11 $\bar{2}$ 0).

1st Access. Spectrum: (111) = (01 $\bar{1}$ 1). $I_c = 3,64 \text{ \AA}$ (corrected; see C). No abnormal reflections were observed with these crystals.

B. *Rotation-spectrogram round the orthohexagonal b-axis.*

Principal spectrum: (200) = (10 $\bar{1}$ 0); (002) = (0002); and (202) = (10 $\bar{1}$ 2).

1st Access. Spectrum: (111) = (01 $\bar{1}$ 1); and (112) = (01 $\bar{1}$ 2). $I_b = 2,28 \text{ \AA}$. No abnormal reflections were found.

C. An oscillation spectrogram on {0001} was obtained by means of *molybdenum*-radiation; a second order reflection was found, calcite being used for the purpose of comparison. From the observed value: $d_{(0001)} = 1,82 \text{ \AA}$., I_c is calculated to be: $3,64 \text{ \AA}$.

The axial ratio of *α-beryllium* is, therefore, calculated at: $a:c = 1:1,5877$.

As the specific weight of the metal is about 1,83, the single parallelepipedic cell contains *two* atoms of beryllium; $d_{calc.} = 1,816$.

§ 3. Although many of the powderspectrograms prepared showed, — as was already mentioned, — a number of extra-diffraction-lines, some of them, however, proved to be completely free from those.

Thus a powderspectrogram, prepared with *Cu*-radiation ($R = 57,2 \text{ m.M.}$; exposure = 32 m. Amp. hours) showed the following lines (*hkl*), as calculated from the angles θ (see Table I).

The values of $\sin^2 \theta$ are calculated from the formula:

$$\sin^2 \theta = 0,1515 (h^2 + hk + k^2) + 0,0453 \cdot l^2.$$

Of the lines (100) and (101) also β -images were occasionally observed.

¹⁾ The orthohexagonal indices being ($h_0 k_0 l_0$) and the hexagonal ones (BRAVAIS) being ($h k l$), we have the relations: $h_0 = 2h + k$; $k_0 = k$; $l_0 = l$ and consequently: $2h = h_0 - k_0$; $k = k_0$; $2l = h_0 + k_0$ and $l = l_0$. The orthohexagonal axes are: $a_0 \sqrt{3}$; a_0 ; and c_0 .

TABLE I. Powderspectrogram of α -Beryllium.				
Int.:	θ :	$\sin^2 \theta$: (observ.)	$\sin^2 \theta$: (calcul.)	($h k l$) (BRAVAIS):
7	22° 15'	0.1516	0.1515	(100) = (10 $\bar{1}$ 0)
6	25 32	0.1856	0.1812	(002) = (0002)
10	26 30	0.1986	0.1968	(101) = (10 $\bar{1}$ 1)
6	35 34	0.3378	0.3327	(102) = (10 $\bar{1}$ 2)
6	42 35	0.4556	0.4544	(110) = (11 $\bar{2}$ 0)
4	48 40	0.5696	0.5593	(103) = (10 $\bar{1}$ 3)
3	51 33	0.6131	0.6060	(200) = (20 $\bar{2}$ 0)
6	53 20	0.6417	0.6358	(112) = (11 $\bar{2}$ 2)
5	54 10	0.6551	0.6516	(201) = (20 $\bar{2}$ 1)
4	63 14	0.7972	0.7875	(202) = (20 $\bar{2}$ 2)
3	69 8	0.8731	0.8765	(104) = (10 $\bar{1}$ 4)

§ 4. From these data it must be concluded, that α -beryllium has, indeed, the structure indicated by Mc KEEHAN, — the parameter in the direction of the c -axis being $\frac{1}{2} c_0$. However, the calculated and observed intensities do *not* agree in all respects: thus, for instance, the calculated intensity of (100) is smaller than that of (002). But it must be emphasized that the beryllium-crystals used showed a most distinct *mosaic*-structure; and also other peculiarities of the crystals: e. g. the existence of cleavage- and glidingplanes, — are not taken into account in the calculations of the intensities.

The LAUE-pattern on {0001}, obtained by means of a *tungsten*-anticathode showed a hexagonal symmetry, but simultaneously a remarkable *asterism*.

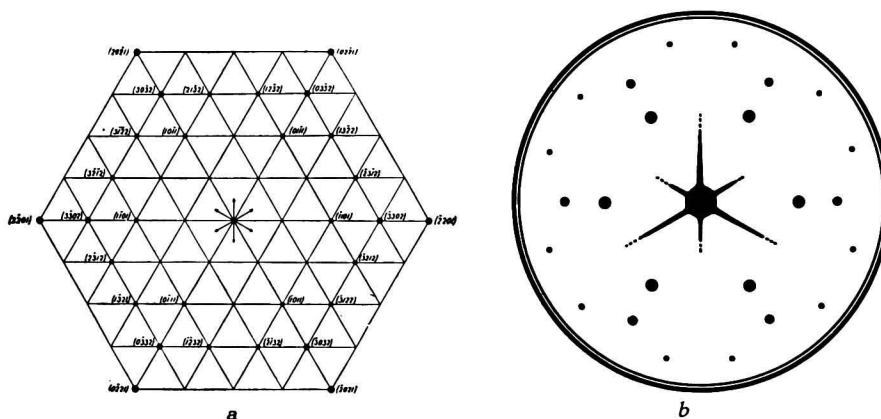


Fig. 1. Gnomonic Projection (a) of the LAUE-pattern (b) of Beryllium on {0001}, obtained with $W\alpha$ -radiation.

As the voltage used was 40 K.V., the maximum wave-length is about 0,9 Å, the minimum wave-length perhaps 0,3 Å. The most intensive spot ($\overline{2201}$) corresponds to: $\lambda = 0,461$ Å; the other spots are: ($330\overline{2}$), $\lambda = 0,4165$ Å; ($\overline{2312}$), $\lambda = 0,3995$ Å and ($\overline{2202}$), $\lambda = 0,3415$ Å.

The asterism observed might perhaps indicate that a *ditrigonal* symmetry D_{3d}^3 is really present; in that case the two Be-atoms in the cell would have the positions: $[\frac{1}{2} \frac{2}{3} u]$ and $[\frac{2}{3} \frac{1}{3} u]$, in which u is equal to: 0,25.

§ 5. *β-Beryllium*. In a considerable number of cases the powder-spectrograms of *beryllium* prove to contain a set of accessory lines, which cannot be inserted within the normal spectrum of the *α-beryllium*. Such extra-lines were also observed by other investigators; they were attributed either to an admixture of beryllium-oxide or to "unknown" impurities. However, the relative intensities of these accessory lines with respect to the others, made it highly improbable, that they would correspond to the oxide; many of them did, moreover, not coincide with the diffraction-lines of the oxide, which was studied by using the same radiation (*iron*) as that used in the study of the metal itself¹⁾.

One of the lines observed by us was the same as that formerly attributed by Mc KEEHAN to an "unknown" element *X*; it was met with as well in the case of the American, as in that of the German sample. However, it soon appeared more probable that these extra-lines would correspond to another modification of the metal, the existence of which was previously suspected by us²⁾ for other reasons.

Preliminary investigations had taught us that the extra-lines appeared most distinctly after a prolonged heating of the metal above 500° or 700° C.; the most favorable results were obtained by heating at 630° C. in a perfect vacuum for 10 hours. The same crystals which were used in the former experiments at ordinary temperature, — they, therefore, yielding no other lines than the normal ones mentioned above, — were embedded in a layer of carefully calcined magnesia, contained in a small tube (0,1 cm.) of pyrex-glass; during the heating the tube was evacuated, the pressure remaining under about 0,1 mm. of mercury. By this treatment the crystals proved to be changed in no way; they preserved their original lustre and yielded the same sharp reflections as before, while the glass-tube was neither attacked by the metal, — this being isolated from the walls of the tube by the protecting layer of magnesia.

A'. *Rotation-spectrogram round the c-axis*.³⁾

The most intensive spots of this spectrogram were the same as those

¹⁾ Berylliumoxide is also hexagonal: $a_0 = 2,694$ Å.; $c_0 = 4,392$ Å. There are 2 molecules in the elementary cell.

²⁾ F. M. JAEGER and E. ROSENBOHM, These Proceed. 35, (1932), 1055.

³⁾ Some of these spectrograms were prepared in this laboratory by Mr. BEINTEMA.

of the normal, not heated crystal, mentioned sub A. Besides these, however, a number of *new* spots proved to be present, which are rigorously orientated with respect to the original ones. They were arranged in a principal spectrum and the 1st, 2nd, 3^d and 5th accessory spectra:

Principal spectrum: *(200) or *(110); *(310); (400); (420); (600).

1st *Access. spectrum*: (201) or (111).

2nd *Access. spectrum*: *(202) or *(112); (402).

3^d *Access. spectrum*: (203) or (113); *(313); (423); (623).

5th *Acc. spectrum*: *(205) or (115).

The indices mentioned correspond to orthohexagonal axes, deduced from the row-lines, with $a_0 = 7,1 \text{ \AA}$ and $b_0 = 4,1 \text{ \AA}$; while the identity-distance I_c is $10,8 \text{ \AA}$, i. e. $3 \times c_0$ of the α -modification.

The 1st spectrum is weak, the 4th is absent, while the 3^d and 5th spectra are rather intensive; the directions of the c_0 -axes of the two forms coincide. Evidently the orthohexagonal lattice is centred in its basal plane, as triplets with $(h + k) = \text{odd}$, do not occur.

B'. *Rotationspectrograms round the b-axis* ($= 4,1 \text{ \AA}$).

The four spectrograms prepared all showed two or three spectra; the orthohexagonal indices of the spots observed were:

I. *Principal spectrum*: *(200); (400); (402); (201); (202); *(203).

1st *Access. spectrum*: *(111); (311); *(111); *(112); (313).

2nd *Access. spectrum*: (222).

II. *Principal spectrum*: *(002); *(003); (005); (205); (203); (205).

1st *Access spectrum*: *(115); *(112); (113); (313).

2nd *Access spectrum*: (221); (220).

III. *Principal spectrum*: *(202); (203); (402); (205).

1st *Access spectrum*: (111); (313); (112); (113); *(115).

2nd *Access spectrum*: (221); (220).

IV. *Principal spectrum*: (203); (006); (002); (003); (005).

1st *Access spectrum*: *(112); (113); (313); (113); *(115).

All occurring spots are accounted for by means of an orthohexagonal elementary parallelepipedic cell of the dimensions:

$$I_a = 7,1 \text{ \AA}; \quad I_b = 4,1 \text{ \AA}; \quad I_c = 10,8 \text{ \AA}.$$

§ 6. In this way it now became possible to find the indices-triplets of the extra-lines observed by us in the different powder-spectrograms and also those already observed by MC. KEEHAN. This investigator used a *molybdenum*-anticathode, whose β -radiation was considerably weakened by selective absorption. The observed three abnormal lines, whose $\sin^2\theta$, — calculated for *Fe*-radiation, — corresponded to 0,1945; 0,2179 and 0,0977. The two first he attributed to the presence of *beryllium-oxide*; but this is highly improbable, because their intensities here are much too great, considering the minimal traces of the oxide present in our preparations. Moreover, the line with $\sin^2\theta = 0,1722$ (*Fe*-radiation) in the spectrum of *Be* 0 has the *same* intensity as that with $\sin^2\theta = 0,2179$

(=0,2208); so that it is inconceivable, why the reflection with $\sin^2\theta=0,1722$ does not equally well appear amongst the extra-lines. The line with $\sin^2\theta=0,1945$ might correspond to $\beta(100)$ of *a-beryllium*; but the observed intensity (=6) is then much too great in comparison with that of the corresponding α -line. The third line, with $\sin^2\theta=0,0977$ is the one, attributed by MC. KEEHAN to an "unknown substance X"; it was, however, constantly observed by us in all powerspectrograms of *beryllium*, which showed such extra-lines. As chemical analysis proved that the two samples of *beryllium* used by us contained at least 99,5% Be and only traces of Fe, while no iron-lines were ever observed, — it is most probable that the reflections observed are really characteristic of *beryllium* itself. Moreover, the intensities of the extra-lines are still greater, if a previously heated *beryllium*-crystal be taken as an object and, if then after powdering, a powerspectrogram is made.

The coefficients of the quadratic equations, derived from the values: $a_0 = 4,1 \text{ \AA}$ and $c_0 = 10,8 \text{ \AA}$ and calculated for Cu_α - and Cu_β -radiation, are:

$$\begin{aligned} \sin^2\theta &= 0,0470. (h^2 + hk + k^2) + 0,00505. l^2 \text{ (\alpha-radiation), and} \\ \sin^2\theta &= 0,0382. (h^2 + hk + k^2) + 0,00409. l^2 \text{ (\beta-radiation).} \end{aligned}$$

The occurring extra-lines with $\sin^2\theta = 0,0349$; 0,0621; 0,0840 and 0,1135 can, however, not correspond to these equations; if, however, the other possible value of a_0 , i. e. $7,1 \text{ \AA}$, be taken, these quadratic equations become:

$$\begin{aligned} \sin^2\theta &= 0,0157. (h^2 + hk + k^2) + 0,00505. l^2 \text{ (\alpha-radiation) and} \\ \sin^2\theta &= 0,0127. (h^2 + hk + k^2) + 0,00406. l^2 \text{ (\beta-radiation);} \end{aligned}$$

and now the interpretation of the diffraction-lines mentioned no longer presents any real difficulty.

Two samples of *beryllium*, previously heated for 10 hours at 650° C. and for 20 hours at 800° C. respectively, yielded, — besides the normal lines of *a-beryllium*, — the following extra-lines ($R = 44.4 \text{ mm.}$; exposure: 50-56 m. Amp. hours).

The intensities (see Table II on following page) were estimated relatively to that of (101) of the α -modification, this intensity being taken = 10. To the lines having greater values of $\sin^2\theta$, many possible indices-triplets can be attributed; so that these symbols become rather arbitrary.

A powdered sample of ordinary, not previously heated, metal was studied by means of *iron*-radiation (70 m. Amp. hours); the rather strong secondary radiation in the camera was prevented by screening off with a very thin aluminium-foil. The spectrogram (see Table III on following page) showed the following extra-lines, — all corresponding with the lines for *copper*-radiation already mentioned and indicated by *; the lines indicated by ** were those also observed by Mc. KEEHAN, who in his experiments used a *molybdenum*-anticathode.

TABLE II.
Diffractionlines of β -Beryllium.
(Copper-radiation).

Int. :	θ :	$\sin^2 \theta$ (observed) :	Indices $\{hkl\}$ calculated from the quadratic formula :
3	10° 46'	0.0349**	(102)
2	11 56	0.0428*	(110) and (003)
3	13 25	0.0538*	(111)
2	15 6	0.0679**	(112)
2	16 10	0.0755*	(113)
1	16 56	0.0848*	(202)
2	17 51	0.0940*	(113)
3	19 51	0.1087*	(203) and (210)
2+	20 30	0.1227*	(005)
1+	21 36	0.1355**	(204)
1	32 52	0.2945	(403) and (320)
1	34 16	0.3170	(225)
1	34 49	0.3260	(410), (306) and (008)
1	38 44	0.3915	(307)

TABLE III.
Diffractionlines of β -Beryllium.
(Iron-radiation).

Int. :	θ :	$\sin^2 \theta$ (observed) :	$\sin^2 \theta$ (for copper- α -radia- tion) observed :	Indices $\{hkl\}$ calculated from the formula :
2	16° 6 $\frac{1}{2}$	0.0769	0.0488	(110) and (003)
3	16 56	0.0848	0.0538	(111)
2	18 5 $\frac{1}{2}$	0.0982**	0.0622	(200)
1*	20 23 $\frac{1}{2}$	0.1214	0.0775	(113)
1	21 46	0.1375	0.0848	(202)
2	22 55	0.1516	0.0940	(113)
3	24 23	0.1704	0.1087	(203) and (210)
3	25 5	0.1797	0.1135	(211)
4	26 15	0.1945**	0.1231	(005)
4	27 6	0.2075	0.1311	(212)
3	27 50	0.2179**	0.1355	(204)
1	32 3	0.2816	0.1781	(115)
3	39 6	0.3978	0.2518	(313) and (400)

The calculation of the indices of lines with greater values of $\sin^2\theta$

becomes rather arbitrary, as many possibilities occur; the relative intensities were visually estimated, that of (101) of the α -form being taken = 10 also in this case.

The indices were, — for $a_0 = 7,1 \text{ \AA}$ and $c_0 = 10,8 \text{ \AA}$; — calculated from the corresponding quadratic formula for copper-radiation :

$$\sin^2\theta = 0,0157 \cdot (h^2 + hk + k^2) + 0,00505 \cdot l^2$$

and from the analogous equation for the β -radiation.

The majority of the lines observed in these powerspectrograms is also met with in the rotation-spectrograms, as may be seen, if the indices of the latter be transformed into those corresponding to the lattice with $a_0 = 7,1 \text{ \AA}$ and $c_0 = 10,8 \text{ \AA}$. The following examples are a proof of this fact, although a number of spots on the rotationspectrograms do not equally occur in the powerspectrograms:

Spots on rotation-spectrograms:	Corresponding lines on powder-spectrograms:	Spots on rotation-spectrograms:	Corresponding lines on powder-spectrograms:
A. round [0001]:		B. round the <i>b</i> -axis:	
(200)	(110)	(111)	(111)
(110)	(110)	(200)	(110)
(420)	(410)	(201)	(111)
(201)	(111)	(202)	(112)
(111)	(111)	(203)	(113)
(202)	(112)	(112)	(112)
(112)	(112)	(003)	(003)
(203)	(113)	(005)	(005)
(113)	(113)	(113)	(113)
(205)	(115)		
(115)	(115)		

§ 7. There can hardly be any doubt, therefore, that the β -modification of *beryllium* has also hexagonal symmetry, with $a_0 = 7,1 \text{ \AA}$ and $c_0 = 10,8 \text{ \AA}$, — its axial ratio thus being: $a : c = 1 : 1,5211$, which is a little smaller, therefore, than that of the α -form. The β -form is probably monotropic; at temperatures in the vicinity of 650° C . it is produced with an observable velocity, but the content of this β -form in the metallic phase is certainly not greater than about 10% , — as may be deduced from the relative intensities of the diffraction-lines. Once produced, the β -form, although metastable, remains present in the metal even at ordinary temperatures, — its transformation into the α -modification obviously being impeded by strong passive resistances.

Beryllium-powder, which yielded strong abnormal spectrograms, was

repeatedly and during a long time, cooled in a mixture of solid carbon-dioxide and acetone, and every time a powder spectrogram of the cooled metal was prepared. In this way it could be stated that the intensities of the extra-lines gradually diminished, although they never completely disappeared. Perhaps this fact can serve as a proof, that at least a "partial" transformation of the β -modification into the stabler α -form is possible. By previous measurements¹⁾ with heated *beryllium*, we gathered the impression, that the specific weight does *not* considerably alter in this transformation; probably it is a little increased (1,91). If this be true, then the number of the atoms within the elementary cell must be about 60. As the β -modification, however, cannot be prepared in a pure state and its quantity in the metallic phase always remains very limited, more certain data about this question could, at this moment, not be obtained.

The ordinary metal seems always to contain a certain percentage of the metastable modification; this fact, most probably, accounts for the irregular and inconstant physical properties of *beryllium*, as observed by different investigators.²⁾

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¹⁾ F. M. JAEGER and E. ROSENBOHM, loco cit., p. 1060.

²⁾ Conf. E. J. LEWIS, loco cit.

Plantkunde. — *Temperatuur en Tijd van den Bloemaanleg bij Bol-Irissen.*
(Mit Zusammenfassung). Door A. H. BLAAUW. (Mededeeling
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te Wageningen).

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In de levensgeschiedenis van een volledige knop hebben wij de bladvormende, de bloemvormende en de strekkingsperiode onderscheiden. Wanneer het ooit mogelijk zal zijn over de periodiciteit in de ontwikkeling der gewassen een beter begrip te krijgen in verband met de heerschende groeifactoren, dan dient in de eerste plaats die periodieke vorming en strekking van blad en bloem bij verschillende uiteenlopende gewassen goed bekend en *beschreven* te zijn. Daarna volgt een *vergelijking* en zoo mogelijk een *rangschikking* in verschillende typen van ontwikkeling. Dan pas is er een grondslag om te zoeken, of er eenig begrijpelijk *verband* is te vinden tusschen bepaalde periodiciteitstypen en de omstandigheden, waaronder die gewassen het jaar doorbrengen; zoowel in de cultuur onder vaak sterk gewijzigde omstandigheden als in het land, waar zij wild voorkomen en waarvan zij het klimaat dus sinds onheuglijke tijden als hun natuurlijk milieu