TABLEAU II.

Courbe de fusion de l'hydrogène.					
T °K.	p kg/cm²	p at	T °K.	p kg/cm²	p at
14	1.7	1.6	21	272.4	263.8
15	33.2	32.2	22	318.6	308.5
16	67.3	65.2	23	366.1	354.5
17	103.6	100.3	24	414.5	401.4
18	142.2	137.7	25	464.2	449.6
19	183.1	177.3	26	518	502
20	227.6	220.4	27	572	554

qu'en combinaison avec une courbe donnant ces différences en fonction de la température. C'est de cette manière que nous avons déduit le tableau II. D'autres formules, proposées par TAMMANN [1]), par JÄNECKE [2]) et de nouveau par SIMON et GLATZEL, ne représentent pas nos mesures d'une manière plus satisfaisante.

Nous tenons à adresser nos vifs remerciements à M. C. J. MATTHIJS, nat. phil. cand., de son assistance pendant les observations et à M. L. NEUTEBOOM, technicien 1re classe au laboratoire cryogène, de son aide pendant les expériences.

[1]) G. TAMMANN, Kristallisieren und Schmelzen, 1903, p. 90.
[2]) E. JÄNECKE, Zs. f. physik. Chem. A. 156, 161, 1931.

Chemistry. — *The Structure of Potassium-Osmiamate.* By F. M. JAEGER and J. E. ZANSTRA.

(Communicated at the meeting of May 28, 1932.)

§ 1. In this paper the results of the spectrographical study of *potassium-osmiamate*: $KOsNO_3$ will be communicated and the structure of this salt in the crystalline state, as deduced from them, will finally be discussed.

The compound was obtained in the way indicated in 1847 by its discoverers FRITZSCHE and STRUVE [1]) by treating a solution of OsO_4 in potassiumhydroxide at 40° C. with strong ammonia. Its real chemical structure remained, for a long time, unsettled, until in 1901 WERNER and DINKLAGE [2]) proved that it is *no nitroso*-compound, but a derivative of

[1]) J. FRITZSCHE and H. STRUVE, Journ. de Pharm. et Chim. (3) **12**, (1847), **304**; A. JOLY, Compt. rend. Paris, **112**, (1891), 1442; L. BRIZARA, Ann. de Chim. et Phys., (7), **21**, (1899), 369; Bull. Soc. Chim. Paris, (3), **21**, (1899), 170.
[2]) A. WERNER and K. DINKLAGE, Ber. d. d. chem. Ges., **34**, (1901), 2698.

*octa*valent *osmium*, to which they ascribed the formula: $\left\{O=\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Os}}=NK\right\}$ of the tautomeric form: $\left\{O=\overset{\overset{O}{\|}}{\underset{\underset{N}{|||}}{Os}}-OK\right\}$. As we shall see, neither of these formulae is the correct one for this substance in the solid state, as the spectrographical data prove, that here we have to deal with a complex salt entirely built up by ions, all of them having the electronic configuration of inert gases.

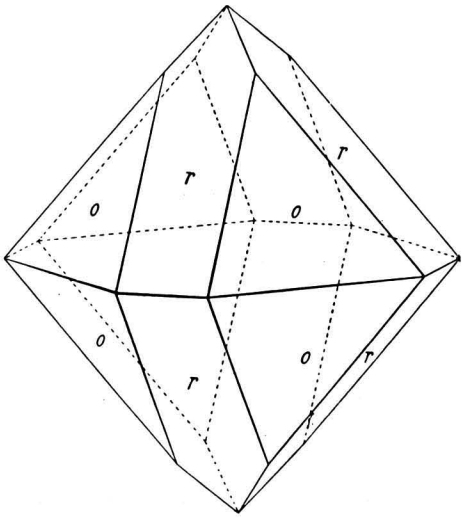

Fig. 1. Potassium-Osmiamate.

§ 2. *Crystallographical data.*

Potassium-Osmiamate crystallizes from a cold aqueous solution in the form of yellow crystals, which are mostly opaque, very brittle and often only rudimentarily developed. It is advisable to recrystallize the salt in a *vacuum*-exsiccator *in the dark* and at a *low* temperature, so as to prevent the compound from being partially decomposed under formation of a finely divided black precipitate of *osmium* or OsO_2.

The crystals are, as we shall soon see, *tetragonal-bipyramidal*, with an axial ratio: $a:c=1:2.3123$; the symmetry is, however, only very slightly different from a *di*tetragonal-bipyramidal one and this deviation is in no case manifested by the external form of the crystals.

Forms observed: $r=\{101\}$, predominant, lustrous; $o=\{112\}$, in most cases narrower and less developed than r, but yielding good reflections. The habitus is either bipyramidal or flattened parallel to two opposite faces or r.

Angular values	*Observed*	*Calculated (from the spectr. data)*
$o:r=(112):(011)$	$=40°27'$	$40°28'$
$o:o=(112):(11\bar{2})$	$=62\ 48$	$62\ 54$
$o:o=(112):(\bar{1}12)$	$=74\ 11$	$74\ 12$
$r:r=(101):(10\bar{1})$	$=46\ 50$	$46\ 46^1/_2$

No distinct cleavability was observed.

The measurements are practically identical with those published in 1891

by DUFET [1]) ; in his publication the crystals are, however, turned round the *c*-axis through 45°, so that the axial ratio, calculated from our angular values, becomes: $a' : c' = 1 : 1.6350$ in that case. It is, however, advisable, as we shall soon see, to adopt the choice of the indices, as here suggested in the crystallographical measurements.

In convergent polarized light a crystal plate cut parallel to {001} showed the normal axial image of a uniaxial crystal of positive character and without circular polarisation. The specific gravity of the crystals at 18° C. was found to be: 4.49—4.51.

Corrosion-figures were obtained by means of a mixture of water and alcohol: on the faces (112) and $(11\bar{2})$ they had the shape of apparently isosceles triangles situated in such a way, that the presence of a plane of symmetry perpendicular to the tetrad axis was confirmed. If the triangles are really isosceles ones, also the presence of vertical planes of symmetry would be indicated by this fact. As we shall soon see, this is, however, *not* true; but it is worth while already here to draw attention to the fact, that the absence of the vertical symmetry-planes is neither revealed by the limiting faces of the crystals, nor by the corrosion-figures mentioned above.

By the resonance-method of GIEBE and SCHEIBE [2]) the absence of a symmetry-centre could *not* be proved. All these facts indicate, that either a ditetragonal-bipyramidal, or a tetragonal-bipyramidal symmetry is present in this case.

A LAUE-pattern on {001}, obtained with *tungsten*-radiation (44000 Volts) passing a small crystal in the direction of the *c*-axis, at first sight seemed to possess a tetrad axis and $2 + 2$ symmetry-planes passing through this axis. On closer examination, however, it appeared that the spots of the inner circle, corresponding with {321} ($\lambda = 0.371$ Å.) showed differences in intensity, which were quite analogous to those observed in the cases of *wulfenite, potassiumperiodate,* etc., excluding therefore the presence of vertical planes of symmetry and proving the existence of only a tetrad axis (Fig. 2). The crystals are, therefore, hemihedral; their symmetry is that of the *tetragonal-bipyramidal* class C_{4H}. In Fig. 2^B the corresponding LAUE-pattern on {110} is reproduced, showing two perpendicular symmetry-planes.

The deviation from the symmetry D_{4H} evidently is, also in this case, only very small.

§ 3. *Rotation- and Oscillation-Spectrograms.*

A rotation-spectrogram by means of *copper*-radiation, with the *c*-axis as axis of rotation, showed a principal and six accessory spectra, the spots of the

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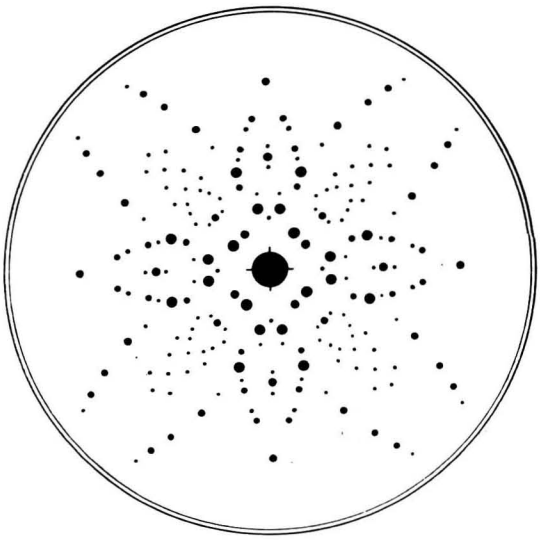
[1]) H. DUFET, Bull. Soc. minéral. franc., **14** (1891), 214: vid. also: NORDENSKJÖLD, Journ. f. prakt. Chem., **41**, (1847), 104. The axial ratio found by DUFET is: $a' : c' = 1 : 1.6319$.

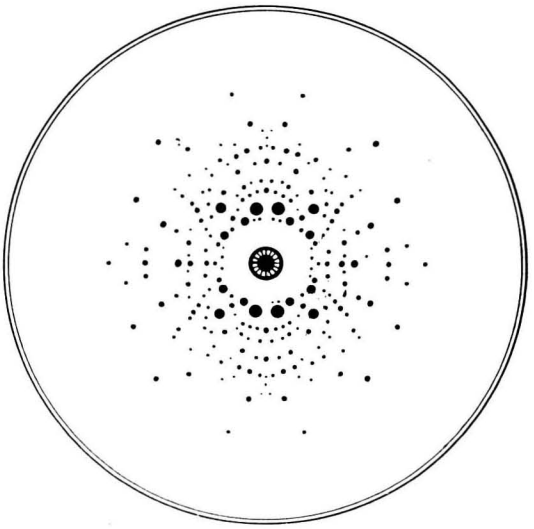
[2]) E. GIEBE and A. SCHEIBE, Zeits. f. Phys. **33**, (1925), 760; A. HETTICH and A. SCHLEEDE, ibid., **46**, (1928), 147.

even spectra being considerably more intensive than those of the odd ones. The 6th spectrum was, moreover, stronger than the 4th, this last more intensive



Laue-Pattern on {001} of Potassium-Osmiamate.

Fig. 2A



Laue-Pattern on {110} of Potassium-Osmiamate

Fig. 2B

than the 2nd; etc. From the distances of the subsequent spectra, the value I_c in the direction of c-axis could be determined to be: 12.95 Å.U. A BRAGG-spectrogram on the face (001), — *calcite* being used as a standard of comparison, — gave a fourth order image, yielding $d_{(001)} = 3{,}27$ Å.; from this follows the correct value of $I_c = 13{,}08$ Å. Although the time of exposure was much increased (8 m. Amp. hours; *Cu-α*-radiation), *no* other spectrum than (004) could ever be obtained.

In the same way a rotation-spectrogram was prepared round [110]; a principal and four accessory spectra were here observed, of which the even ones also showed more intensive spots than the odd ones. From this the distance $I_{(110)}$ is calculated to be: 7.99 Å.U. An oscillation-spectrogram on (110), — *calcite* again serving as a standard, — gave $d_{(110)} = 4.00$ Å.U.; no other spectral line than this second order image could be observed, so that the true value of $I_{(110)}$ must be: 8.00 Å.

A rotation-spectrogram obtained by rotating the crystal round [100], however, showed a principal and three accessory spectra; the third spectrum consisted only of Cu_β-images. In the direction of the axis of rotation, I_a appeared to be: 5.59 Å.U.; the true value, corrected by means of a BRAGG-spectrogram was: $I_a = 5.65$ Å. The axial ratio $a : c$ thus becomes: 1 : 2,3123, — as was found from the direct crystallographical measurements.

The volume of the elementary cell is 417,6 Å^3.; as the density at 20° C. is 4,51, the cell evidently contains a mass represented by: $K_4Os_4N_4O_{12}$.

The true specific gravity of the crystals at 0° C., therefore, must be: 4,616.

A BRAGG-spectrogram on the face (112) only showed a first order spectrum, $d_{(112)}$ being found to be: 3,414 Å.U.; moreover, $d_{(101)}$ was determined at: 5,15 Å.U., while $d_{(101)}$ was calculated to be: 5,19 Å.U. The spacings parallel these faces are, therefore, not halved.

A more detailed analysis of these rotation-spectrograms was now made by means of BERNAL's method. The spectrogram round [001] was excellently suited for this purpose, not only because it was very sharp and quite symmetrically built, but because, — as a consequence of the small value of I_a (=5.65 Å.), — the row-lines of this image are rather far apart, so that the indices of the spots could be determined with a fairly high degree of accuracy. On the other hand, the accessory spectra appear at a rather small distance from each other, I_c being very large; as a consequence the α- and β-spots on the first and second accessory spectra appear very close together.

1. The following α-diffraction-images unambiguously were observed:

Principal Spectrum: (200); **(220); (400); **(420); (440).
First acc. Spectrum: (101); *(211); (301); (321); *(411); (431); *(501); (521).
Second acc. Spectrum: **(112); (202); (222); **(312); (332); (422); (512).
Third acc. Spectrum: *(103); (213); (303); (323); *(413); (433).
Fourth acc. Spectrum (114); **(204); **(224); (404); **(424).
Fifth acc. Spectrum: (105); (215); (305); (325); (415); (435).
Sixth acc. Spectrum: **(116); **(316); (336).

From this it instantly becomes clear, that only reflections occur of such planes (hkl) for which $(h+k+l)$ is an *even* number. Although, for instance, the planes (111) and (110) in these experiments ($\varphi = 31° + 31°$) came into positions favourable for "reflection", *no* images of both these sets of planes occur in odd orders.

This fact proves that the fundamental grating of this structure is that of *the bodily-centred tetragonal cell* Γ_t'.

2. In the same way the rotation-spectrogram round [100], obtained with *copper*-radiation and an exposure of 20 m. Amp. hours, showed the following diffraction-images:

Principal Spectrum: (013); **(004); (024); (015); (033); (008); (035); (028); **(042); (019); (037); (044); (046) or (0.2.10); (039); (0.1.11); (0.0.12); (053); **(048); (055).

First acc. Spectrum: *(101); *(112); (105); (123); *(116); (125); (107); (127); (109); (136); (143); (129); (1.1.10); (138); *(147); (1.2.11).

Second acc. Spectrum: **(211); (213); (204); (215); **(206); **(224); (217); (226); (235); **(228); (237); (2.0.10); (244); (2.2.10); (239); (248).

Third acc. Spectrum: *(303); (321); (323); (316); (332); (307); (318); (336).

The right interpretation of this spectrogram was more difficult than in the case of the rotation-spectrogram round [001]. However, several spots occur in unsymmetrical positions, they being present only to the left or only to the right of the median plane. As the angle of oscillation is known, this fact can help us to fix the choice of the indices in ambiguous cases by means of graphical construction.

3. Especially well suited for analysis was the rotation-spectrogram obtained by rotating about the axis [110]; the indices are found by the transformations: $2h' = h + k$; $2k' = h - k$; $l' = l$.

Principal Spectrum: **(1$\bar{1}$2); (004); (1$\bar{1}$6); **(2$\bar{2}$4); (008); (2$\bar{2}$6); **(3$\bar{3}$2); (1$\bar{1}$8); (2$\bar{2}$8); (1.$\bar{1}$.10); **(336); (0.0.12).

First acc. Spectrum: *(101); (103); (105); (2$\bar{1}$3); (2$\bar{1}$5); (107); (109); (3$\bar{2}$5); (2$\bar{1}$9); (3$\bar{2}$7); (4$\bar{3}$1); (433); (1.0.11).

Second acc. Spectrum: **(112); (202); **(204); **(1$\bar{1}$6); (3$\bar{1}$2); **(206); **(208); (3$\bar{1}$6); (4$\bar{2}$2); (3$\bar{1}$8).

Third acc. Spectrum: (211); (213); (301); (215); (303); 305); (307); (217); (4$\bar{1}$1); (4$\bar{1}$3); (4$\bar{1}$5); (309); (4$\bar{1}$7); (2.1.11); (5$\bar{2}$1).

Fourth acc. Spectrum: **(312); (400); (402) or (316); (404); (406).

Also in the cases **2** and **3,** the even spectra are the most intensive ones; (101) occurs in *all* orders, but (114) is absent, its intensity in reality being very weak, as we shall soon see. The reflections: (112) and (224) are very strong; indeed, (112) is a fundamental direction of growth of the crystals.

§ 4. *Powder-Spectrograms.*

Several powder-spectrograms of the salt after HULL-DEBIJE's method, were obtained as well by means of *copper-*, as by means of *iron*-radiation. The data obtained with *iron*-radiation are recorded in Table I.

§ 5. *Analysis of the* LAUE*-pattern on (001).*

The LAUE-pattern on (001), of which a gnomonic projection is

TABLE I.
Powder-Spectrogram of Potassium-Osmiamate.

No. of Line:	$2l$ in m.M.:	Estim. Intens.:	Wave-length λ:	Angle Θ	$sin^2\Theta$ (observed):	$sin^2\Theta$ (calculated):	Indices (hkl):
1	38.94	3	β	9° 45′	0.0287	0.0285	(101)
2	43.30	9	α	10 51	0.0354	0.0348	(101)
3	59.74	4	β	14 58	0.0667	0.0662	(112) or (103)
4	62.50	1	β	15 39	0.0728	0.0719	(004)
5	65.71	10	α	16 27	0.0802	0.0806 0.0789	(112) or (103)
6	68.94	3	α	17 16	0.0881	0.0877	(004)
7	73.43	2	β	18 8	0.0969	0.0962	(200)
8	80.60	4	α	20 11	0.1191	0.1175	(200)
9	82.95	1	β	20 47	0.1259	0.1249	(211)
10	87.24	1	α	21 51	0.1385	0.1394	(202)
11	92.24	3	α	23 6	0.1539	0.1524	(211)
12	97.33	3	α	24 23	0.1704	0.1692	(105)
13	105.50	2	α	26 25	0.1979	0.1962	(213)
14	108.23	5	α	27 6	0.2075	0.2055	(204)
15	109.53	1	β	27 26	0.2123	0.2104	(222) or (116)
16	116.21	3	α	29 6	0.2365	0.2351	(220)
17	122.19	5	α	30 36	0.2591	0.2571 0.2560	(222) or (116)
18	129.24	3	α	32 22	0.2866	0.2862	(215)
19	132.74	3	α	33 14	0.3004	0.2998	(107)
20	136.88	5	α	34 16	0.3170	0.3148 0.3158 0.3137	(206), (312) or (303)
21	138.71	2	α	34 44	0.3246	0.3230	(224)
22	145.69	1	α	36 29	0.3536	0.3507 0.3542	(008) or (226)
23	153.90	3	α	38 32	0.3881	0.3873	(321)
24	157.62	2	α	39 28	0.4040	0.4051	(118)
25	160.62	2	α	40 13	0.4169	0.4156	(217)

TABLE I. (*Continued*).

No. of Line:	$2l$ in m.M.:	Estim. Intens.:	Wave-length λ:	Angle Θ	$sin^2\Theta$ (observed):	$sin^2\Theta$ (calculated):	Indices (hkl):
26	164.22	3	α	41° 7′	0.4324	0.4322	(226)
27	169.09	1	β	42 20	0.4535	0.4565	(404)
28	173.08	4	α	43 20	0.4709	0.4699	(400)
29	178.06	4	α	44 35	0.4927	0.4918	(316) or (402)
30	180.81	1	α	45 17	0.5049	0.5048	(411)
31	184.26	1	α	46 8	0.5198	0.5192	(325)
32	187.57	1	α	46 58	0.5467	0.5486	(413)
33	191.20	3	α	47 53	0.5503	0.5506	(332)
34	192.74	4	α	48 16	0.5569	0.5576	(404)
35	199.72	4	α	50 1	0.5871	0.5874	(228) or (420)
36	205.16	3	α	51 23	0.6105	0.6094	(316) or (422)
37	210.94	1	α	52 49	0.6340	0.6365	(415)
38	217.44	2	α	54 28	0.6623	0.6657	(335)
39	220.53	4	α	55 13	0.6746	0.6751	(424)
40	232.81	2	α	58 18	0.7239	0.7259	(336)
41	236.57	2	α	59 14	0.7383	0.7397 0.7395	(431) or (501)
42	248.87	4	α	62 19	0.7842	0.7847 0.7836	(426), (433) or (503)
43	260.9	3	α	65 20	0.8258	0.8206	(408)
44	267.6	5	α	67 1	0.8475	0.8500	(514)
45	276.0	2	α	69 7	0.8729	0.8736	(505)
46	286.1	2	α	71 39	0.9009	0.9010	(523)
47	302.9	4	α	75 51	0.9402	0.9398	(440)
48	313.4	4	α	78 28	0.9599	0.9605 0.9617	(516) or (442)

Radius of Camera: 57.2 mM. Exposure: 14 m. Amp. hours.
Wave-Length: $\lambda_\alpha = 1.9366$ Å.; $\lambda_\beta = 1.7527$ Å.;
Quadratic Equation: $sin^2\Theta = 0{,}02937.\ (h^2 + k^2) + 0{,}005481.\ l^2$ . . . . . (α)
$sin^2\Theta = 0{,}02406.\ (h^2 + k^2) + 0{,}004492.\ l^2$ . . . . . (β)
Parameter of the Lattice: $a_0 = 5{,}65$ Å.; $c_0 = 13{,}08$ Å. Bodily-centred, tetragonal cell Γ'_t.
Specific Weight: 4,626 at 0° C.; 4 Molecules pro cell.

represented in Fig. 3, was analyzed in the usual way. The data obtained are collected in Table II.

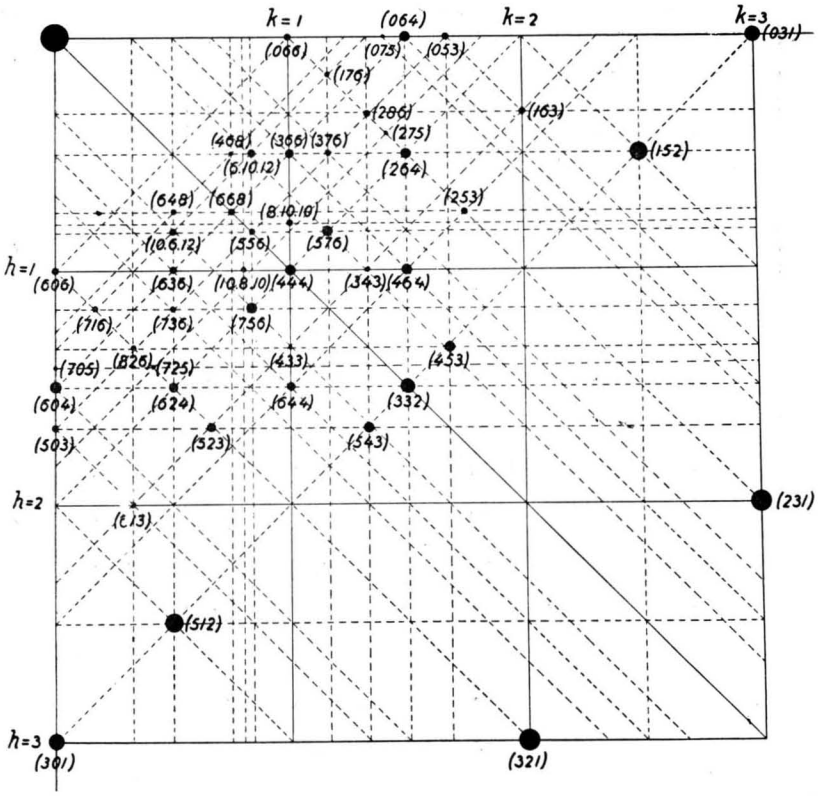


Fig. 3. *Gnomonic Projection of the* LAUE*-pattern on (001) of Potassium-Osmiamate.*

The sum of the indices $(h + k + l)$ of the images observed proves always to be an *even* number; the fundamental lattice, therefore, is the *bodily-centred* one Γ_t'', as already previously stated.

§ 6. *The Structure of Potassium-Osmiamate and the Calculation of the Parameters.*

From the study of the occurring indices-triplets, the special space-group to which the structure of *potassium-osmiamate* must belong, can be deduced by the following reasonings.

As the crystals of the *potassium*-salt have a centre of symmetry and do not possess piezo-electrical properties, the classes S_4, C_4, V, D_4 and C_{4v} are beforehand excluded. The LAUE-pattern on {001} excludes D_{4H}; so that only C_{4H} remains. The corresponding space-groups can only be: C_{4H}^5 and C_{4H}^6. In the first group no extinctions, — besides those of $\{h\ k\ l\}$, in which $(h + k + l)$ is odd, — need occur. But we found, that (002) is absent, only (004), (008), (00.12) being met with; moreover, all spacings

TABLE II.

1st Order Symbols of the Spots:	Estim. Intens.:	Glancing Angle θ:	λ (1st order):	λ (2nd order):	λ (3rd order):	λ (4th order):	λ (5th order):	λ (6th order):
(512)	10	9° 23′	0.3658	—	—	—	—	—
(301)	9	8 5	0.5325	—	—	—	—	—
(321)	9 and 7	6 28	0.3710	—	—	—	—	—
(332)	8	11 23	0.5219	—	—	—	—	—
(312)	7	15 3	(0.9123)	0.4562	—	—	—	—
(302)	5	16 18	(1.0038)	0.5019	—	—	—	—
(111)	5	16 43	(2.2370)	(1.1185)	(0.7457)	0.5593	—	—
(523)	4	13 17	0.4784	—	—	—	—	—
(212)	4	20 59	(1.7023)	(0.8512)	0.5674	—	—	—
(101)	3	23 12	(4.1216)	(2.0608)	(1.3739)	(1.0304)	(0.8243)	0.6869
(322)	3	13 17	(0.7117)	0.3558	—	—	—	—
(433) (503)	2	14 11 14 24	0.5501	—	—	—	—	—
(413)	2	17 6	(0.7856)	0.3928	—	—	—	—
(334)	2	22 9	(0.9323)	0.4662	—	—	—	—
(324)	1	25 20	(1.2522)	0.6261	—	—	—	—
(455)	1	14 11	0.5355	—	—	—	—	—
(716)	2	19 40	0.5174	—	—	—	—	—
(736)	2	18 26	0.5061	—	—	—	—	—
(705)	1	16 54	0.4558	—	—	—	—	—
(613)	1	11 38	0.3794	—	—	—	—	—
(536)	3	23 57	(0.7274)	0.3637	—	—	—	—
(556)	2	20 7	0.5174	—	—	—	—	—
(725)	1	20 11	0.4241	—	—	—	—	—
(756)	4	16 44	0.3636	—	—	—	—	—
(543)	3	11 25	0.3439	—	—	—	—	—

The wave-lengths produced at this voltage have a minimum of 0.28 Å., a maximum of about 0.63 Å.

$$\lambda = \frac{2 \cdot c_0 \cdot l}{(h^2 + k^2)\frac{c_0^2}{a_0^2} + l^2}$$

of $\{h\ k\ O\}$ are halved. No reflections: (110), (330), (310) were observed. *The only possible space-group is, therefore,* C_{4H}^6 [1]). Indeed, the structure of the salt is, as we shall see, quite analogous to that of *scheelite, stolzite, powellite, wulfenite,* of $NaIO_4$, KIO_4, $KReO_4$, etc. [2]). Also in these cases the overwhelming number of properties of these compounds appear to be in accordance with the higher symmetry D_{4H}, except the quite analogous deviations in the intensities of the inner spots of the LAUE-patterns on {001}. These deviations are only caused *by the unsymmetrical position of the four oxygen-atoms.* As a consequence of their feeble diffracting power these atoms contribute only little to the intensities of these reflections, especially in the higher orders, so that the symmetry of the LAUE-pattern of the *osmiamate* is chiefly determined by the position of the *K-* and *Os-*atoms, in the same way as it is determined by that of the *Ca-, Pb-, K-,* and the *W-, Mo-, I-,* and *Re*-atoms in the compounds just mentioned. The *oxygen*-atoms of these salts occupy positions which are in agreement with the observed intensities; but this is no longer true, if the symmetry of the space-group D_{4H}^{19} is assumed as the right one, as is, for instance, the case [3]), with *zircone:* $ZrSiO_4$.

There is no doubt as to the exactness of C_{4H}^6 as the right space-group of all the compounds mentioned, although the deviations from the symmetry D_{4H}^{19} are in some cases, as, for instance, in those of *scheelite* and *potassium-osmiamate,* rather small.

The four *osmium-* and *potassium*-atoms (or-ions) can be distributed over the two possible *four*fold places in the elementary cell. The *oxygen-* and *nitrogen*-atoms (or-ions), with the atomic numbers 8 and 7 respectively, and with equal electronic configurations for O'' and N''' in the complex ion: $\{(O'')_3Os^{VIII}(N''')\}^1$ can be distributed over a *sixteen*fold position;

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[1]) In this connection, it must be remarked, that the criteria given for C_{4H}^6 by H. MARK, *Die Verwendung der Roentgenstrahlen in Chemie und Technik,* (1926), p. 390, are *erroneous,* as they are appropriate only in the case of the face-centred cell of double volume. C_{4H}^5 is, as already demonstrated, *not* in accordance with the observed reflections: as (002) is absent, the *K-* and *Os*-atoms can only have the position (e) in R. W. G. WYCKOFF, *The Analytical Expression,* etc., (1922), p. 82, with $u = \frac{1}{8}$ and $\frac{5}{8}$. But then (110) must be very intensive, which is *not* true. With respect to the behaviour of the (NH_4)- *Rb-,* and *Cs-Osmiamates* to be described later on, it would be possible, that the *K*-salt also possesses a lower symmetry. But at the moment there is no reason for supposing this.

[2]) On *scheelite, powellite, stolzite, wulfenite* and the corresponding *Ba*-salts, conf.: R. G. DICKINSON, Journ. Amer. Chem. Soc., **42**, (1920), 85; P. NIGGLI and K. FAESY, Zeits. f. Kryst. **59**, (1924), 473; L. VEGARD, Skrift. Norsk. Vidensk. Ak.-Oslo, **1**, Mat. Kl. (1925), N°. **11**; Phil. Mag., **1**, (1926), 1151; T. BARTH, Norsk. Geol. Tidskr., **9**, (1926), 24; L. VEGARD and A. REFSUM, Skrift, N. Vid. Ak. Oslo, (1927), N°. 2; on $NaJO_4$ and KJO_4: L. M. KIRPATRICK and R. G. DICKINSON, Journ. Amer. Chem. Soc., **48**, (1926), 2327; E. HYLLERAAS, Zeits. f. Phys., **39**, (1926), 203; on $KReO_4$: F. MACHATSCHKI, Zeits. f. Kryst., **72**, (1930), 541; E. BROCH, Zeits. f. phys. Chem., **6**, B, (1929), 22.

[3]) R. W. G. WYCKOFF and S. B. HENDRICKS, Zeits. f. Kryst., **66**, (1927), 73.

a *twelve*fold position does *not* occur [1]) in the space-group C_{4H}^6, nor would there be any other fourfold position available, after the *osmium-* and *potassium*-ions once are fixed in:

a) Four *Os* at: $[0\ \frac{3}{4}\ \frac{1}{8}]$; $[0\ \frac{1}{4}\ \frac{7}{8}]$; $[\frac{1}{2}\ \frac{1}{4}\ \frac{5}{8}]$; $[\frac{1}{2}\ \frac{3}{4}\ \frac{3}{8}]$

b) Four *K* at: $[0\ \frac{3}{4}\ \frac{5}{8}]$; $[0\ \frac{1}{4}\ \frac{3}{8}]$; $[\frac{1}{2}\ \frac{1}{4}\ \frac{1}{8}]$; $[\frac{1}{2}\ \frac{3}{4}\ \frac{7}{8}]$

The twelve *oxygen-* and four *nitrogen*-ions together, therefore, obtain the parameters:

$[x\ ,y\ ,z]$; $[\frac{1}{4}-y\ ,\frac{3}{4}+x\ ,\frac{1}{4}+z]$; $[\frac{1}{2}+x\ ,\frac{1}{2}+y\ ,\frac{1}{2}+z]$; $[\frac{3}{4}-y\ ,\frac{1}{4}+x\ ,\frac{3}{4}+z]$.

$[\bar{x}\ ,\frac{1}{2}-y\ ,z]$; $[\frac{3}{4}+y\ ,\frac{3}{4}-x\ ,\frac{1}{4}+z]$; $[\frac{1}{2}-x\ ,\bar{y}\ ,\frac{1}{2}+z]$; $[\frac{1}{4}+y\ ,\frac{1}{4}-x\ ,\frac{3}{4}+z]$.

$[\frac{1}{4}+y\ ,\frac{3}{4}-x\ ,\frac{1}{4}-z]$; $[\frac{1}{2}-x\ ,\frac{1}{2}-y\ ,\frac{1}{2}-z]$; $[\frac{3}{4}+y\ ,\frac{1}{4}-x\ ,\frac{3}{4}-z]$; $[\bar{x}\ ,\bar{y}\ ,\bar{z}\ ]$.

$[\frac{3}{4}-y\ ,\frac{3}{4}+x\ ,\frac{1}{4}-z]$; $[\frac{1}{2}+x\ ,y\ ,\frac{1}{2}-z]$; $[\frac{1}{4}-y\ ,\frac{1}{4}+x\ ,\frac{3}{4}-z]$; $[x\ ,\frac{1}{2}+y\ ,\bar{z}\ ]$.

Now $(\frac{3}{4}+x)$ must *differ* from y; for the second order of (101) is present, although with a small intensity. For $(\frac{3}{4}+x)=y$, $|S|^2_{(202)}$ would be *zero*, as $S_{(202)}=\cos 2\pi\{(2x+2z),\ (-2x+2z),\ (2y-2z),\ (-2y-2z),\ (-2y+2z),\ (2y+2z),\ (-2x-2z),\ (2x-2z),\}=2\,.\cos 2\pi\{(2x+2z),\ (-2x+2z),\ (2y+2z),\ (2y-2z)\}$, while all sinus-functions are zero. For $y=\frac{3}{4}$, $|S|$ would be: $2\cos 2\pi\{(2x+2z),\ (-2x+2z),\ (\frac{1}{2}+2z),\ (\frac{1}{2}+2z)\}$. From the radius of the *O*-ion follows, that x must be very close to: 0,25; but for $x=0{,}25$, the intensity of (202) would be very great, and this is not true. In the same way, for $y=\frac{3}{4}$, the intensities of (114) and (118) would be *zero*, which neither is the case [2]).

The right values for x, y and z appear to be:

$$x=0{,}23\ ;\quad y=0{,}80\ ;\quad z=0{,}06.$$

The parameters of the *oxygen-* and *nitrogen*-ions thus become:

[0,23 ; 0,80 ; 0,06] ; [−0,55 ; 0,98 ; 0,31] ; [0,73 ; 0,30 ; 0,56] ; [−0,05 ; 0,48 ; 0,81]

[−0,23 ; −0,30 ; 0,06] ; [0,55 ; 0,52 ; 0,31] ; [0,27 ; −0,80 ; 0,56] ; [0,05 ; −0,02 ; 0,81]

[−0,05 ; 0,52 ; 0,19] ; [0,27 ; −0,30 ; 0,44] ; [0,55 ; 0,02 ; 0,69] ; [−0,23 ; −0,80 ; −0,06]

[−0,05 ; 0,98 ; 0,19] ; [0,73 ; 0,80 ; 0,44] ; [−0,55 ; 0,48 ; 0,69] ; [0,23 ; 0,30 ; −0,06]

Bij a translation of these positions by adding $(0,\ -\frac{3}{4},\ -\frac{1}{8})$ to these values, the final positions of all the ions considered become:

a) Four Os^{VIII}-ions at: $[0\ 0\ 0]$; $[0\ \frac{1}{2}\ \frac{3}{4}]$; $[\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}]$; $[\frac{1}{2}\ 0\ \frac{1}{4}]$.

b) Four *K*-ions at: $[0\ 0\ \frac{1}{2}]$; $[0\ \frac{1}{2}\ \frac{1}{4}]$; $[\frac{1}{2}\ \frac{1}{2}\ 0]$; $[\frac{1}{2}\ 0\ \frac{3}{4}]$.

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[1]) R. W. G. WYCKOFF, *The Analytical Expression, etc.* Washington, (1922), 82, under *a*, *b* and *f*. For the purpose of comparison wirh the co-ordinates of KIO_4 as given in literature, these positions must be shifted over $-\frac{3}{4}$ for y and $-\frac{1}{8}$ for z.

[2]) For $y=\frac{3}{4}$, $|S|_{(211)}=-|S|_{(2\bar{1}\bar{1})}$, so that (211) and $(2\bar{1}\bar{1})$ would have equal intensities. But this would exactly be the 16-fold position *h* of D_{4H}^{19}.

f) Twelve O''-ions + four N'''-ions at:

[0,23 ; 0,05 ; —0,065] ; [0,73 ; —0,45 ; 0,435] ;
[—0,23 ; —0,05 ; —0,065] ; [0,27 ; —0,55 ; 0,435] ;
[0,05 ; —0,23 ; 0,065] ; [0,55 ; —0,73 ; 0,565] ;
[—0,05 ; 0,23 ; 0,065] ; [—0,55 ; —0,27 ; 0,565] ;

[—0,55 ; 0,23 ; 0,185] ; [—0,05 ; —0,27 ; 0,685].
[0,55 ; —0,23 ; 0,185] ; [0,05 ; —0,73 ; 0,685].
[0,27 ; —0,05 ; 0,315] ; [—0,23 ; —0,55 ; —0,185].
[0,73 ; 0,05 ; 0,315] ; [0,23 ; —0,45 ; —0,185].

The sequence of the intensities of $\{h\ k\ l\}$, calculated by means of these parameters [1]), prove to show a perfect parallelism with those estimated visually, as may be seen from the Fig. 4, in which the relative intensities of the different planes $\{h\ k\ l\}$ are, for both cases mentioned, graphically plotted against the sixfold glancing angle 6 . (Θ) for each plane.

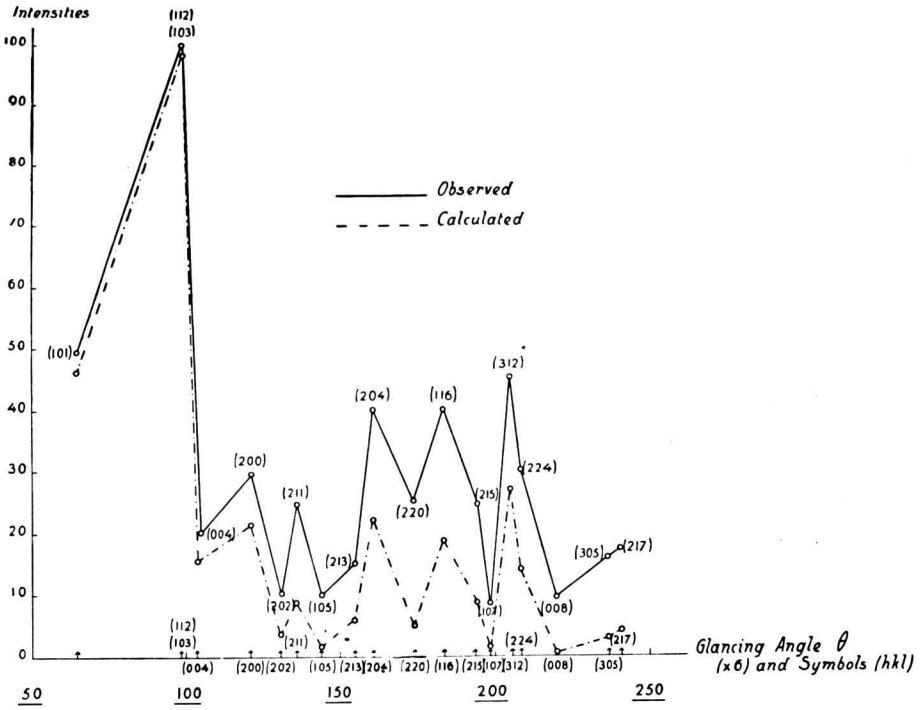

Fig. 4. *Estimated and Calculated Intensities of the Diffractionlines of Potassium-Osmiamate.*

[1]) The diffracting power of the *Os*-ion is proportional to (76—8) = 68; that of both the *O*- and *N*-ions proportional to (8 + 2) and (7 + 3) respectively, i.e. to 10; that of the *potassium*-ion to (19—1) = 18. The *O*- and *N*-ions, in couples, are situated in planes, which only make a very small angle with (100) and (010). If they were exactly situated *within* these planes, the symmetry would be D_{4H}^{19}, as in the case of *zircone*.

The *nitrogen-* and *oxygen-*ions are, therefore, arranged round the very small central *Os-*ions in such a way that they are situated in the corners of a tetragonal bisphenoid which is *very close to a regular tetrahedron, but the latter somewhat compressed in the direction of the c-axis.*

The symmetry C_{4H}^6 in this case only is manifested as a consequence of the particular circumstance, that with respect to the action of the *X*-rays, the *O''-* and *N'''-*ions *cannot* be distinguished from each other in the *potassium-*salt, although the electrical charges of their nuclei are not the same (8 and 7 respectively). If, however, these ions be considered as *not completely identical,* the true symmetry of the crystals can never be tetragonal-bipyramidal: for in the latter case, — i.e. if the *N'''-* and *O''-*ions be considered as *different,* — no horizontal symmetry-plane can be present. Then the highest possible symmetry could either be the tetragonal-pyramidal or the monoclinic one. As the absence of a symmetry-centre could *not* be proved, — while apparently the *K-*salt certainly exhibits a symmetry with respect to a horizontal plane [1]), — the first possibility

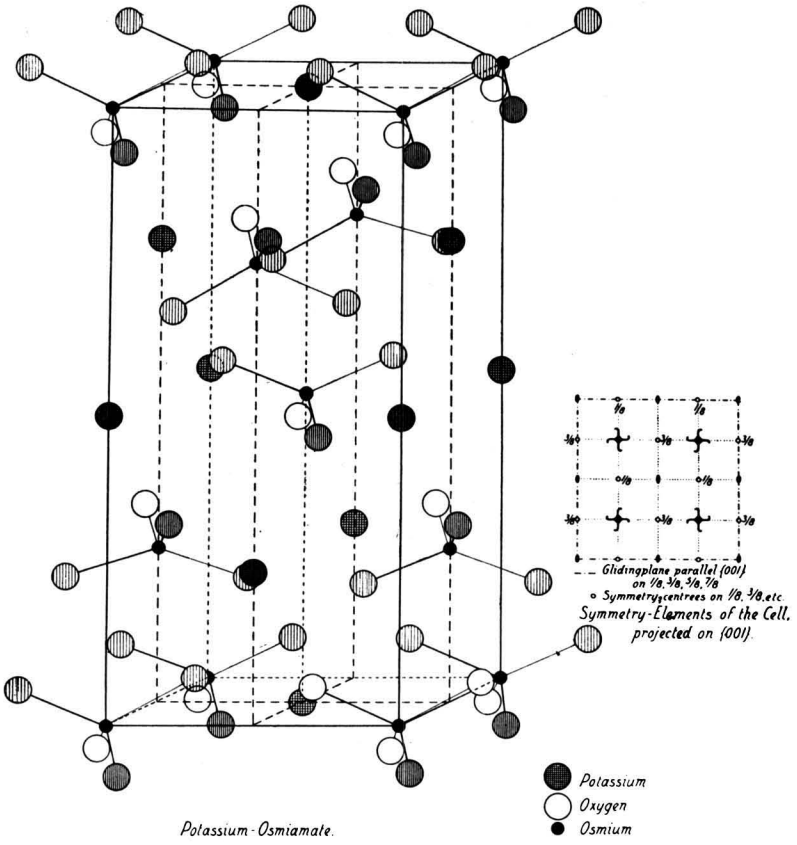

Fig. 5. *The Structure of Potassium-Osmiamate.*

[1]) The presence of this horizontal plane of symmetry excludes the possibility of *potassium-osmiamate* being rhombic-bisphenoidal.

must most probably be excluded, and the crystals, therefore, should be considered as really monoclinic. The tendency to form complexes of pseudo-tetragonal symmetry then, however, proves to be so great and this pseudo-tetragonal symmetry proves to be so perfect, that it is by no means any more possible to distinguish the crystals from really tetragonal ones. As we shall soon see, this pseudo-tetragonal character is equally well preserved in the case of the other *alkali*-salts of this type, which themselves certainly have a lower symmetry than the *K*-salt.

If a comparison is made between *potassium-osmiamate* and the other tetragonal-bipyramidal salts before mentioned, then it becomes clear, that in *potassium-periodate*: KIO_4 the planes of the couples of O''-ions make the greatest angle with the planes (100) and (010); that in the case of *tungstate of lead* (*wulfenite*): $PbW0_4$ that angle is somewhat smaller; in that of *potassium-osmiamate* still smaller; and in that of *scheelite*: $CaWO_4$ exceedingly small, — so that in its LAUE-pattern on (001) almost no deviation from a holohedral symmetry is any more observable. Finally, in *zircone*: $ZrSiO_4$, the couples of O''- and N'''-ions are situated *within* the planes (100) and (010), and the symmetry now becomes perfectly *di*tetragonal, corresponding to the space-group D_{4H}^{19}. Evidently these particularities are connected with the different electrostatic attractions of the ions $K+$, $Pb++$, $Ca++$ and Zr^{IV} for the surrounding O''-ions on the one hand, and those of the central ions I^{VII}, Os^{VIII}, W^{VI}, and Si^{IV} on the other hand. As we shall soon see, the result of such influences is still more clearly exhibited in the case of the other *alkali-osmiamates*.

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

Physics. — *Die Gleichung der Schmelzkurve.* Von J. J. VAN LAAR.

(Communicated at the meeting of May 28, 1932).

I.

Bekanntlich hat schon SIMON bei seinen Versuchen über die Schmelzkurven von verschiedenen Stoffen[1]) die empirische Gleichung $\underline{p+a=CT^c}$ aufgestellt, und dieselbe an seinen Beobachtungen bei *He*, *Ne*, *Ar*, H_2 und N_2 geprüft. Wir werden im folgenden versuchen eine theoretische Beziehung herzuleiten; wobei sich herausstellen wird, dass diese fast

[1]) SIMON und GLATZEL, Z. anorg. allg. Chem., **178**, 309—316 (1929); SIMON, RUHEMANN und EDWARDS, Z. f. physikal. Chem. (B) **2**, 340—344 (1929), **6**, 62—77 (1929) (*He I* und *II*); Ibid. **6**, 331—342 (1930) (H_2, *Ne*, N_2 und *Ar*); SIMON und STECKEL, BODENSTEIN-Festband, 737—744 (1931) (Schmelzwärme und Dichte *He*).