Notwithstanding these relatively small differences, the *differential* function $\frac{dQ}{dt}$, shows a quite different slope from ours. The fact, that at about 770° C. their value of c_p becomes identical with ours, seems to make it probable, that also in this case an *un*stabilized condition of the *gold* used may, at least partially, have been the cause of the said discrepancies. In this case, however, the latter are situated in the opposite direction, as was the case with the *silver* under analogous circumstances.

From the results here obtained with *platinum, silver, copper* and *gold* under different conditions it becomes, moreover, finally evident, that *no* predictions can be made as to the direction, in which the specific heats of worked and non-worked metals will be changed: the worked metal can show as well *smaller,* as *greater* values of c_p than the normal metal does. With respect to these phenomena, theoretical considerations [1]) still appear untimely, as in the momentaneous state of affairs doubtlessly a considerable number of still unknown factors play a decisive rôle in them.

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[1]) J. A. M. VAN LIEMPT and W. GEISS, Zeits. f. anorg. Chem., **171**, (1923), 317; *Die Natuiwiss.*, **19**, (1931), 705.

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

(Communicated at the meeting of June 25, 1932).

§ 1. In two previous papers [1]) the structure of *potassium-, ammonium-, rubidium-* and *thallium-osmiamate* have been discussed in detail. In the present paper we wish to publish the results of the analogous investigation of the corresponding *cesium-osmiamate,* which, although equally showing a truly pseudo-tetragonal character, yet in many respects appears to have a different structure.

Crystallographical Data.
From a hot aqueous solution it crystallizes in pale yellow, flat needles, much alike the *rubidium*-salt. From a cold solution, on slow evaporation in the dark, thin flat tables are obtained.

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[1]) F. M. JAEGER and J. E. ZANSTRA, these Proceedings, **35**, (1932), 610;

The crystals of the *cesium*-salt are represented in Fig. 1. They are *rhombic-bisphenoidal* and *pseudo-tetragonal*; their orientation with respect
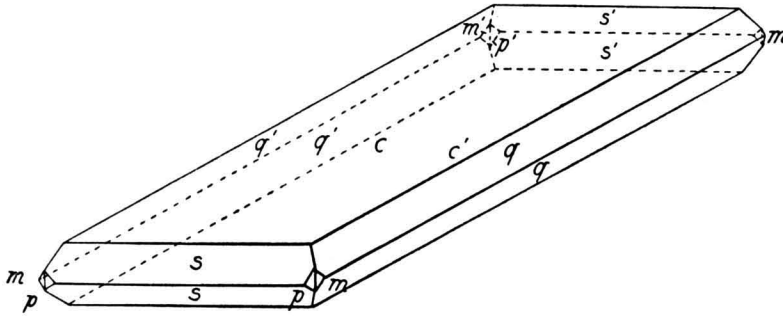

Fig. 1. Cesium-Osmiamate.

to the other pseudo-tetragonal salts is, however, such, that their *a*- and *b*-axis have the direction of the zone-axes [110] and [1̄10] in the crystals of the *potassium*-salt; as we shall see, also their spacings in these directions are completely comparable with those of the other *osmiamates* parallel to [110] and [1̄10]. The axial ratio is:

$$a : b : c = 0,9759 : 1 : 1,7157.$$

The angular values are not constant, but oscillate within rather wide limits.

As we will see, the ratio $b : c$ must rather be taken: $1 : 0,8577$, so that $s = \{101\}$ and $q = \{021\}$.

Forms observed: $c = \{001\}$, predominant, yielding very good reflections; $s = \{102\}$ and $q = \{011\}$, about equally well developed and giving sharp images; $m = \{110\}$ and $p = \{210\}$, subordinate and small, yielding rather dull reflections. The habitus is that of tabular crystals parallel to $\{001\}$ or of flat needles with their elongation parallel to the *a*-axis.

Angular Values:	*Observed:*		*Calculated:* (from the spectrosc. data):
$c : s = (001) : (102) =$	41° 0′ − 41°56′		40° 19′
$c : q = (001) : (011) =$	59 18 − 60 50		59 46
$s : s = (102) : (10\bar{2}) =$	96 18 − 97 56		97 22
$q : q = (011) : (01\bar{1}) =$	59	21	60 28
$m : p = (110) : (210) =$	18	13	18 17
$p : p = (210) : (2\bar{1}0) =$	51	4	52 1½
$m : m = (110) : (1\bar{1}0) =$	87	30	88 36

Perfect cleavability parallel to $\{001\}$.

Weakly birefringent; the double refraction is negative. The plane of the optical axes is parallel to {100}; the optical angle is only small, but greater than in the case of the *rubidium*-salt. Also the dispersion, although strong and abnormal, seems to be less than that of the *Rb*-salt. The specific weight at 16° C. is: 5.20.

From some optical particularities, which later-on will be described in a more detailed paper and from the corrosion-figures obtained, it must be deduced that the symmetry of the crystals is *rhombic-bisphenoïdal*.

§ 2. A LAUE-pattern on {001} was prepared by means of *tungsten*-radiation. The image showed rhombic symmetry (Fig. 2) and was analysed
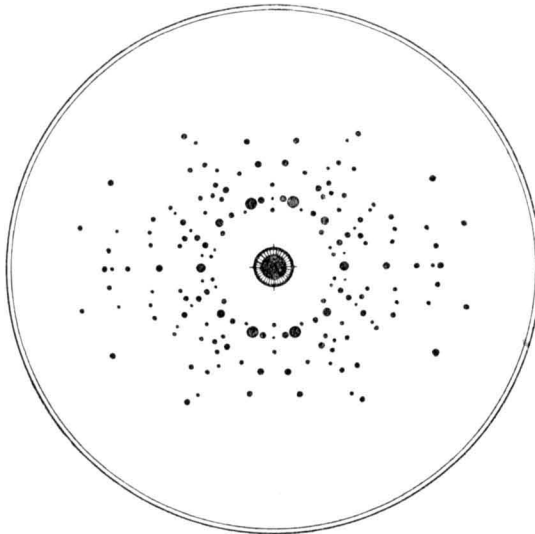

Fig. 2. LAUE-pattern on {001} of Cesium-Osmiamate.

in the usual way, after a gnomonic projection (Fig. 3) had been made. The results are collected in Table I.

The wave-lengths used lie between 0,3082 Å. and 0,75 Å. The fundamental lattice is the simple rhombic one.

From this follows, that (311), (301), (031), (142), (322), (513), (053), (253), (533) and (131) reflect in no lower than the second order, (121), (021) and (032) is no lower than the third order.

§ 3. Rotation-spectrograms were prepared by turning the crystals round the *a-*, *b-* and *c*-axis respectively. From these spectrograms the axial ratio: $a_0 : b_0 : c_0 = 8{,}08 : 8{,}35 : 7{,}22$ was deduced, which furnishes: $a : b : c = 0{,}9676 : 1 : 0{,}8648$; this axial ratio is in sufficient agreement with that found by the direct crystallographical measurements, if to *s* and *q* the symbols: $s = \{101\}$ and $q = \{021\}$ be attributed.

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			TABLE I.		
		Analysis of the LAUE-pattern on (001) of the Cesium-Salt.			

1st Order Symbols of Spots:	Estimated Intens.:	Glancing Angle θ:		(1st Order):	(2nd Order):	(3d Order):
(231)	2	9°	5$^1/_2$′	0.7146	—	—
(632)	2	9	38$^1/_2$	0.4018	—	—
(311)	10	10	11$^1/_2$	0.8968	0.4484	—
(452)	5	10	11$^1/_2$	0.4484	—	—
(542)	2	10	15	0.4437	—	—
(612)	1	10	36	0.4819	—	—
(301)	1	10	43	0.9984	0.4942	—
(162)	1	10	50	0.5034	—	—
(031)	7	10	59	1.0360	0.5180	—
(432)	2	12	53	0.7126	—	—
(494)	1	13	14	0.3749	–	-
(121)	3	14	29	1.7952	0.8976	0.4488
(854)	2	13	39	0.3964	—	—
(834)	3	14	57	0.4741	—	—
(502)	1	12	56$^1/_2$	0.7010	—	—
(814)	2	15	43$^1/_2$	0.5256	—	—
(474)	1	15	58	0.5433	—	—
(142)	1	15	43$^1/_2$	1.0512	0.5256	—
(585)	1	16	58$^1/_2$	0.4899	—	—
(3.11.6)	1	16	58$^1/_2$	0.4069	—	—
(2.11.6)	1	17	17	0.4224	—	—
(021)	2	16	8$^1/_2$	2.2296	1.1148	0.7432
(274)	1	17	42	0.6600	—	—
(876)	1	17	56	0.4520	—	—
(322)	1	17	35	1.3068	0.6534	—
(513)	2	18	29	0.9578	0.4789	—
(754)	1	14	54	0.4727	—	—
(053)	1	19	12$^1/_2$	1.0346	0.5173	—
(032)	1	21	10	1.8680	0.9340	0.6227
(184)	1	16	5	0.5491	—	—
(294)	1	19	9	0.4270	—	—
(394)	1	13	44	0.4036	—	—
(253)	1	17	52$^1/_2$	0.8998	0.4499	—
(856)	1	19	56	0.5559	—	—
(342)	1	13	0	0.7218	—	—
(533)	1	16	23$^1/_2$	0.7577	0.3789	—
(764)	1	13	57	0.4167	—	—
(131)	4	10	23	0.9492	0.4746	—
(252)	3	12	10	0.6455	—	—

1. The rotationspectrogram round the a-axis showed a principal and four accessory spectra. $I_a = 8.08$ Å. The most intensive spots ($\varphi = 30°$) appeared to be: (021); (044); (211); (232); (244) and (421). The even spectra were more intensive than the odd ones.
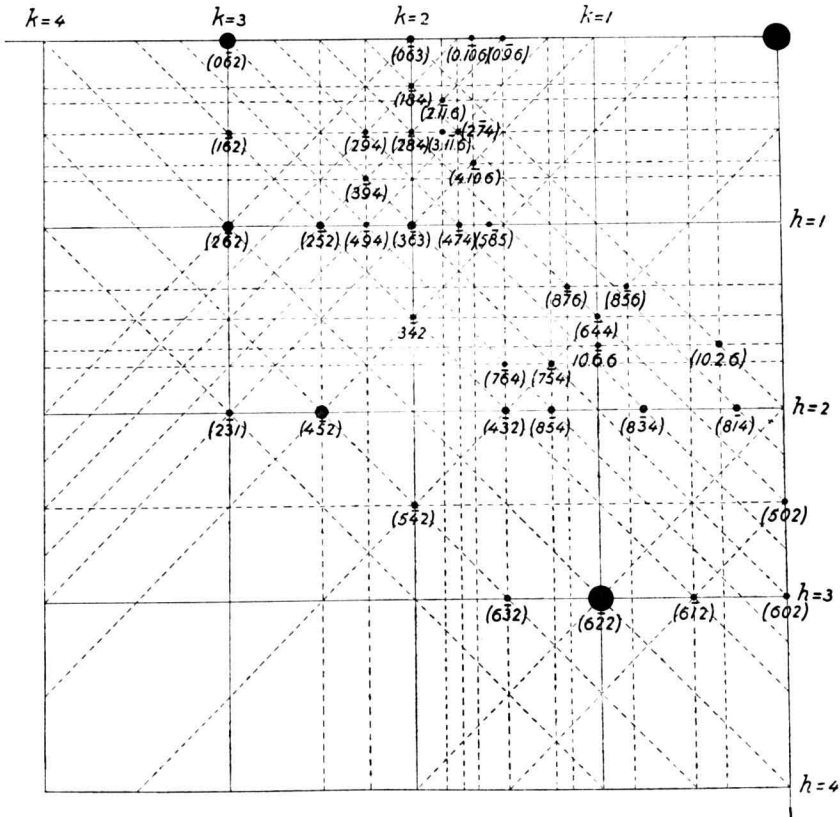

Fig. 3. Gnomonic Projection of the LAUE-pattern on $\{001\}$ of Cesium-Osmiamate.

2. The spectrum obtained by rotating round the b-axis ($\varphi = 60°$) also showed a principal and four accessory spectra. $I_b = 8.35$ Å. The most intensive images were: (002); (004); (105); (206); (602); (113); (214); (215); (216); (310); (410); (413); (513); (021); (023); (225); (126); (423); (623); (233); (234); (235); (330); (531) and (245).

3. The rotationspectrogram round the c-axis ($\varphi = 90°$) showed a principal and three accessory spectra. $I_c = 7.22$ Å. The most intensive spots observed were: (040); (460); (640); (021); (251); (351); (461); (421); (621); (042); (252); (212); (402); (412); (602); (642); (023); (233); (253); (353); (213); (413); (423) and (623).

§ 4. Also a powder-spectrogram was obtained which showed a great number of lines. However, this spectrogram was not used for the purpose of comparison of the calculated and observed intensities, for the same

reason as indicated in the case of the *rubidium*-salt. The general results were in agreement with those obtained by the rotation-spectrograms; a full description will be given in the more detailed paper to be published in the *Recueil des Trav. d. Chim. d. Pays-Bas.*

§ 5. *The structure of the Cesium-Salt.*

The discussion of the results obtained led to the conclusion, that the space-group in this case is V^2; the elementary cell contains a mass: $Cs_4Os_4N_4O_{12}$, the crystallographical axes having the direction of the zone-axes $[110]$ and $[1\bar{1}0]$ in the *potassium*-salt.

Also in this case it seems advisable to start the determination of the structure by first fixing the positions of the *Os*- and *Cs*-ions, because these ions contribute for the greater part to the intensities observed.

The argumentation leading to the final positions of these atoms will be discussed later-on in detail in our paper in the *Receuil*. Here we will only communicate the results.

1. The parameter in the direction of the *c*-axis is, as well for the *Os*-ions, as for the *Cs*-ions, equal to: $\frac{1}{2}$; layers of the *Os*-ions, and also those of the *Cs*-ions, are in this direction $\frac{1}{2} . c_0$ apart from each other.

2. In the direction of the *b*-axis, as well layers of ions with mutual distances of: $y = 0 . b_0$ and $y = \frac{1}{2} . b_0$, as layers of other ions with distances of: $y = \frac{1}{4} . b_0$ and $y = \frac{3}{4} . b_0$ must be present.

3. In the direction of the *a*-axis, each time a couple of *Os*-ions is situated on rows having the direction of the *a*-axis, which rows are alternately shifted with respect to each other over $\frac{1}{4} . b_0$. The distances of the *Os*-ions, — and in the same way that of the *Cs*-ions from each other, — must very closely correspond to $\frac{1}{2} . a_0$.

From all data mentioned, the most probable parameters of these ions become:

For the 4 *Os*-ions: $[000]$; $[\frac{1}{2}00]$; $[0\frac{1}{4}\frac{1}{2}]$; $[\frac{1}{2}\frac{1}{4}\frac{1}{2}]$.
For the 4 *Os*-ions: $[\frac{1}{4}\frac{1}{2}0]$; $[\frac{3}{4}\frac{1}{2}0]$; $[\frac{1}{4}\frac{3}{4}\frac{1}{2}]$; $[\frac{3}{4}\frac{3}{4}\frac{1}{2}]$.

Indeed, the intensities of the reflections calculated from these values, in so far as only the action of the *Os*- and *Cs*-ions is taken into account, agree very well with the intensities actually observed, as may be seen from Fig. 4, in which these intensities are compared for the spots of the rotation-spectrogram round $[010]$, plotted against $\sqrt{\dfrac{h^2}{a_0^2} + \dfrac{l^2}{c_0^2}}$ as abscissae.

The contribution of the $(3O + N)$-ions, it is true, cannot be neglected; but it is certainly much less than that of the heavy ions mentioned. For fixing their positions, *twelve* parameters must be determined. It is a hopeless task to find out the right combination of their values. The orientation of the $(3O + N)$-complex round an *Os*-ion at $[000]$, must differ somewhat from that round the *Os*-ion at $[\frac{1}{2}00]$; otherwise reflections as: (333) and (335), which are really present, could never occur. This different

orientation must be caused by the fact that the N'''-ions with their 10 electrons will be more greatly deformed by the influence of the eight-valent, central Os-ion, than the O''-ions will be.
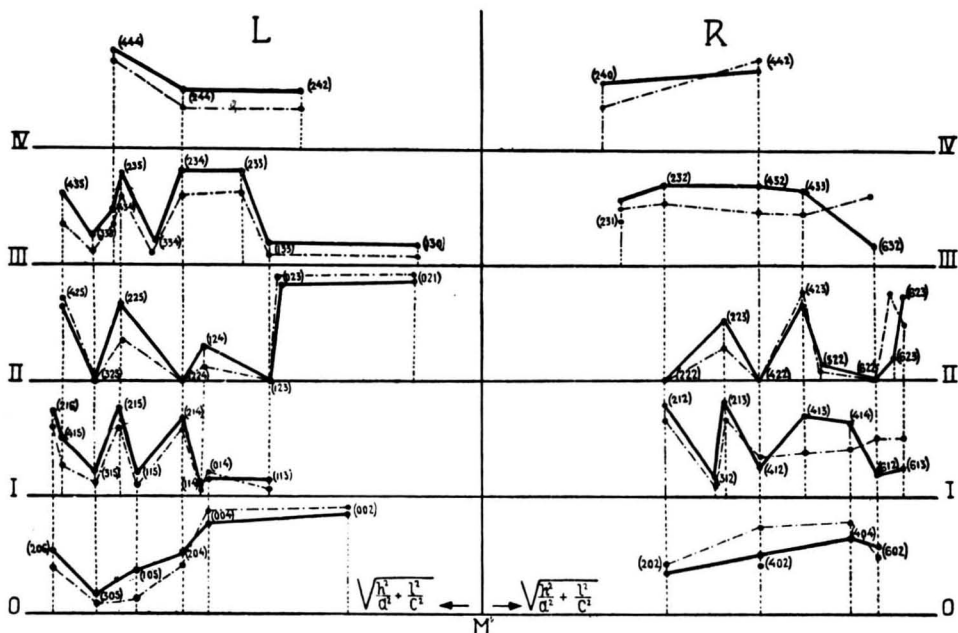

Fig. 4. Rotation-Spectrogram of Cesium-Osmiamate round [010].

The space-group of the *Cesium*-salt is V^2; V^2 must be the right one, as V^4, — the other alternative, — is excluded by the values of the parameters of its fourfold positions in the direction of the b-axis. The Os-ions in V^2 occupy the two possible twofold positions c) and d) [1]), with $u = \frac{1}{8}$; the Cs-ions the fourfold position e), with $x = \frac{1}{4}$, $y = \frac{5}{8}$ and $z = \frac{1}{4}$. A comparison of the structures of the Cs- and Rb-salts with that of the K-salt [2]) teaches us, that, while in the latter each ion $\{OsO_3N\}'$ is in the basal plane surrounded by $4 K^{\cdot}$-ions in such a way, that the distance between a $K^{\cdot}$- and Os-ion is 4.0 Å. In the Rb-salt the distances between two $Rb^{\cdot}$-ions already proved to be somewhat different in two directions: 5.57 and 5.84 Å. respectively, the distance between a $Rb^{\cdot}$- and Os-ion becoming: 4.07 Å. When the $(3O + N)$-complex is still somewhat more rotated round the direction of the c-axis, the original arrangement of the K-salt becomes unstable, because it no longer corresponds to a closest packing: now the elementary cell gets expanded in one direction [110] of the original K-salt, contracted in the other [1̄10] and the new structure of the Cs-salt is produced, in which the distance between a Cs'- and Os-ion is 4.6 Å., while the dimensions of the sub-cell (half the original one)
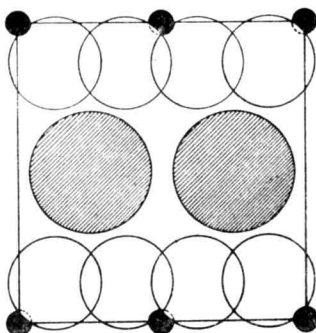
[1]) R. W. G. WYCKOFF, loco cit., p. 57.
[2]) F. M. JAEGER and J. E. ZANSTRA, these Proceedings, 787, (1932).

become: 4.02 and 8.35 Å. Two Cs-ions now get each time more distant from each other by two intercalated O''-ions. The surface occupied in the
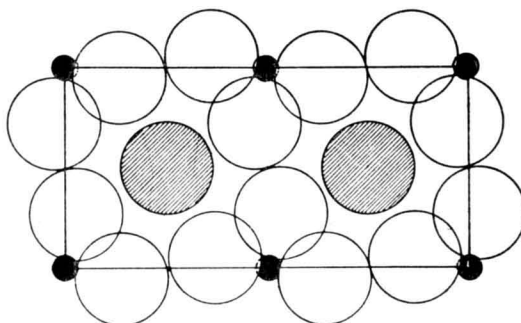
A Potassium-Osmiamate

B. Cesium-Osmiamate.

Fig. 5. Comparison of the Structure in (001) of the K- and Cs-salts.

basal plane by 1 molecule $K Os O_3 N$ was: 31.9 Å², that occupied by 1 molecule $Rb Os O_3 N$ is: 32.2 Å²; and that occupied by 1 molecule $Cs Os O_3 N$ is: 33,1 Å². The latter surface is smaller than in the case that the Cs-salt had preserved the original structure of the K-salt.

The co-ordination-number of the eight-valent Os-ion proves to be 6; there are 4 O''-ions surrounding it in the basal plane, one above and one below that plane. Also the apparent pseudotrigonal arrangement of the atoms in the plane (100) of the Cs-salt, — as it is, for instance, also revealed in the angular values of the crystals in the zône [100], — is clearly visible in this structure. Hence the mutual relations between the tetragonal K-salt and the rhombic, but truly pseudo-tetragonal (NH_4)-, Rb-, Tl- and Cs-salts are fully explained by the crystalline structures deduced for all these salts.

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