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De kristalstructuur der alkaliperrhenaten en -perjodaten.

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SUMMARY.

In connection with the investigation of some *alkali-osmiamates* carried out in this laboratory, the crystal structure of a number of *perrhenates* and *periodates* was investigated.

It was found that the *"scheelite structure"*, which was already met with in the cases of $KReO_4$, $AgReO_4$, $NaIO_4$, KIO_4 and $AgIO_4$, was also present in those of $NaReO_4$ and of the NH_4 - and Rb-salts. On the contrary, the Cs-salts belong to a different structure-type; the latter is, however, closely related to the *"scheelite"* type and can be derived from it by a slight deformation, which causes the symmetry of the latter to be changed from a *tetragonal*, to a *pseudotetragonal*, orthorhombic one.

 $TIReO_4$ has a transition temperature at 123° C. Above this temperature, it possesses the "scheelite" structure; below this temperature, it is rhombic and isomorphous with the *Cs*-salt in the present case, the pseudo-tetragonal character of this second modification of the *Tl*-salt is, moreover, particularly clearly expressed.

The dimensions of the elementary cell of all these salts were accurately determined:

Tetragonal Salts:

	a ₀ (Å)	$c_0(\text{\AA})$
$NaReO_4$	$5,362 \pm 0,001$	$11,718 \pm 0,002$
NH_4ReO_4	$5,871 \pm 0,003$	$12,942 \pm 0,007$
$RbReO_4$	$5,803 \pm 0,003$	$13,167 \pm 0,007$
$TlReO_4$	$5,761 \pm 0,005$	13,33 ± 0,01
NH ₄ IO ₄	$5,983 \pm 0,003$	$12,790 \pm 0,007$
<i>RbIO</i> ₄	5,874 ± 0,003	$12,938 \pm 0,007$

Orthorhombic Salts:

	$a_0(\text{\AA})$	<i>b</i> ₀ (Å)	$c_0(\text{\AA})$
CsReO ₄	$5,737 \pm 0,003$	$5,968 \pm 0,003$	$14,241 \pm 0,007$
$TlReO_4$	$5,623 \pm 0,003$	$5,791 \pm 0,003$	$13,295 \pm 0,007$
CsIO ₄	$5,838 \pm 0,003$	6,014 ± 0,003	$14,364 \pm 0,007$

The spacegroup of these orthorhombic salts is V_h^{16} .

The following positions were ascribed to the Cs- or, as the case may be, to the Tl-atoms, and to the Re- or I-atoms:

4 Cs (Tl): $[u, \frac{1}{4}, \frac{1}{8}]$ $[\overline{u}, \frac{3}{4}, \frac{7}{8}]$ $[u + \frac{1}{2}, \frac{1}{4}, \frac{3}{8}]$ $[\frac{1}{2} - u, \frac{3}{4}, \frac{5}{8}]$. 4 Re (1): $[\overline{u}, \frac{1}{4}, \frac{5}{8}]$ $[u, \frac{3}{4}, \frac{3}{8}]$ $[\frac{1}{2} - u, \frac{1}{4}, \frac{7}{8}]$ $[u + \frac{1}{2}, \frac{3}{4}, \frac{1}{8}]$. The value of the parameter u in CsReO₄ is: 0,042; in TlReO₄ it is: 0,00 and in CsIO₄ it is: 0,030.

A rational explanation of the striking fact that the Cs-salts in the series of the perrhenates and periodates have the same structure as the (NH_4) -, Rb- and Tl-salts in the series of the osmiamates, — has been given, in which considerations about the relative deformabilities of the three kinds of complex ions more especially are brought to the fore.