Generally one may say that structures where the AlF₆-octahedra are linked together, will not be stable at higher temperatures because of the increased vibrational energy. As can be seen from the three reactions above, the compounds always decompose into more energetically favourable compounds.

In the electrolytic production of aluminium, one often operates with additions of both CaF₂ and AlF₃ to the molten cryolite bath. Since calcium fluoride-aluminium fluoride mixtures seem to have some complex forming properties, it might be possible for the Ca²⁺-ions in an acid bath to take part in the conductivity process together with the Na⁺-ions, as indicated by the conductivity measurements by Yim and Feinleib.⁴

**Experimental.** The samples were first homogenized by mixing aluminium fluoride and calcium fluoride in the right proportion in 100 % alcohol in a glove box. The aluminium fluoride was prepared by vacuum sublimation of anhydrous AlF₃ (A.D. Mackay, Inc. U.S.A.) in a high-frequency heated furnace. The method has been described in detail by Rolin.⁵ Calcium fluoride a.r. from Mallinckrodt Chemical Works, U.S.A., was dried at 400°C in a vacuum furnace before use.

The DTA heating and cooling curves were recorded by a Speedomax G X–Y recorder and by use of a D.C. Microvolt Amplifier (range 50–2000 microvolt, Leeds and Northrup, U.S.A.).

At the eutectic temperature, 828°C, and peritectic temperature, 881°C, equilibrium crystallization occurred only for compositions with more than 40 mol% AlF₃ at cooling rates of about 3–5°C/min. On the CaF₂-side of the system the temperature therefore had to be taken from the heating curves.

The X-ray investigations were carried out with a Philips Wide Range Goniometer PW 1050/25, connected to a Philips PW 1051 recorder (Philips, Eindhoven, Holland), and with a Nonius type Guinier camera using CuKα radiation, λ(Kα₁) = 1.5405 Å.

The density of the 50:50 sample was determined by use of a vacuum pycnometer method using Shell Odourless Kerosene as a displacement liquid.

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**Shear Structure of the Wolfram Oxide WO₂⁻⁹⁵**

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The preparation of a wolfram oxide, intermediate in composition between WO₂ and W₂O₅, and from its chemical analysis found to have the formula WO₂₋⁹⁵, was recently reported by Imre and one of the present authors.¹ Structural studies using X-ray single-crystal and powder data have given the following results.

The single-crystal photographs of the new oxide were found to show very close similarities with those of W₂O₅,² indicating that WO₂₋⁹⁵ is actually another representative of a wolfram oxide with crystallographic shear occurring in a ReO₃-type arrangement of atoms. Detailed inspection disclosed that the structural parameters within the planes of shear, i.e. the a and b axes of the monoclinic unit cells, are practically identical in the two oxides. WO₂₋⁹⁵, however, showed in comparison with W₂O₅ approximately a

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doubling of the parameter corresponding to the spacing of the shear planes.

The unit-cell dimensions of $\text{WO}_{2.95}$ were found to be

$$a = 11.9 \, \text{Å}, \quad b = 3.815 \, \text{Å}, \quad c = 49.4 \, \text{Å}, \quad \beta = 106^\circ 4. $$

The density obtained from the apparent loss of weight in benzene (7.1 g/cm$^3$) corresponds to a unit-cell content of $W_{40}O_{118}$ ($\delta_{\text{calc}} = 7.12 \, \text{g/cm}^3$). This composition evidently fits the general formula $M_nO_{8n-3}$ characteristic of any phase with the kind of shear plane present in $W_{40}O_{118}$. From general expressions previously given, the following "ideal" unit-cell parameters are obtained for a phase with $n = 40$, if the space-diagonal of the metal-oxygen octahedron is assumed to be 3.750 Å.

$$a = 11.86 \, \text{Å}, \quad b = 3.750 \, \text{Å}, \quad c = 49.02 \, \text{Å}, \quad \beta = 106^\circ 6. $$

A minor structural difference between $W_{40}O_{118}$ and $W_{40}O_{118}$ is revealed by a slightly different character of their Weissenberg photographs $h11$ and $h22$. The symmetry of the former oxide phase is $P2_1/m$ with all the wolfram atoms in a mirror plane. In $W_{40}O_{118}$ the wolfram atom arrangement is slightly puckered and the symmetry consequently changed ($P2_1$).

The oxide $W_{40}O_{118}$ falls in the same compositional range as a phase observed in the reduction of wolfram trioxide with hydrogen. Studies on the latter reduction product have shown that crystallographic shear in a ReO$_3$-type arrangement of atoms is the structural principle active also in this phase. The spacing of the parallel planes of shear is, however, a random one in contrast to what is the case in $W_{40}O_{118}$ and $W_{40}O_{118}$. The existence of another wolfram oxide, $WO_{5.54}$, within the present region of composition has been reported by Ackermann and Rauh. Structural studies on this compound have led to an atomic arrangement of the formula $WO_{5.54}$ related to but definitely different from that of $W_{40}O_{118}$.

The various investigations recently carried out of slightly reduced wolfram trioxide specimens have demonstrated the importance of crystallographic shear as the structural principle common to such materials. Depending on the conditions of formation of the reduced oxides, parallel shear planes may adopt a random distribution or they may arrange themselves at regular intervals of different extension. The latter case will give rise to phases of stoichiometric compositions although with quite complicated formulae. Similar structural models originating from such considerations, including several transition-metal oxide systems, have been presented elsewhere.

The immense possibilities of geometrical variations imaginable in the structural pattern present in this group of compounds naturally suggest the very likely existence of further wolfram oxide phases. Studies on the molybdenum-oxygen system by Kihlberg have shown that several oxides form only within rather limited intervals of temperature or under quite special conditions in a metastable state. It seems rather likely that the wolfram-oxide system will be found to behave similarly. Evidence was obtained during the preparative work that trace amounts of potassium, aluminium, or nickel have some stabilizing effect on $WO_{2.95}$. The possibility should therefore be considered that the presence of minute quantities of other elements may stabilize or promote the formation of further wolfram oxide phases.

Full details on this study will be published elsewhere.

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