Tunnel Structure of $K_2W_4O_{13}$

By MADELEINE SELEBORG
(*Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden*)

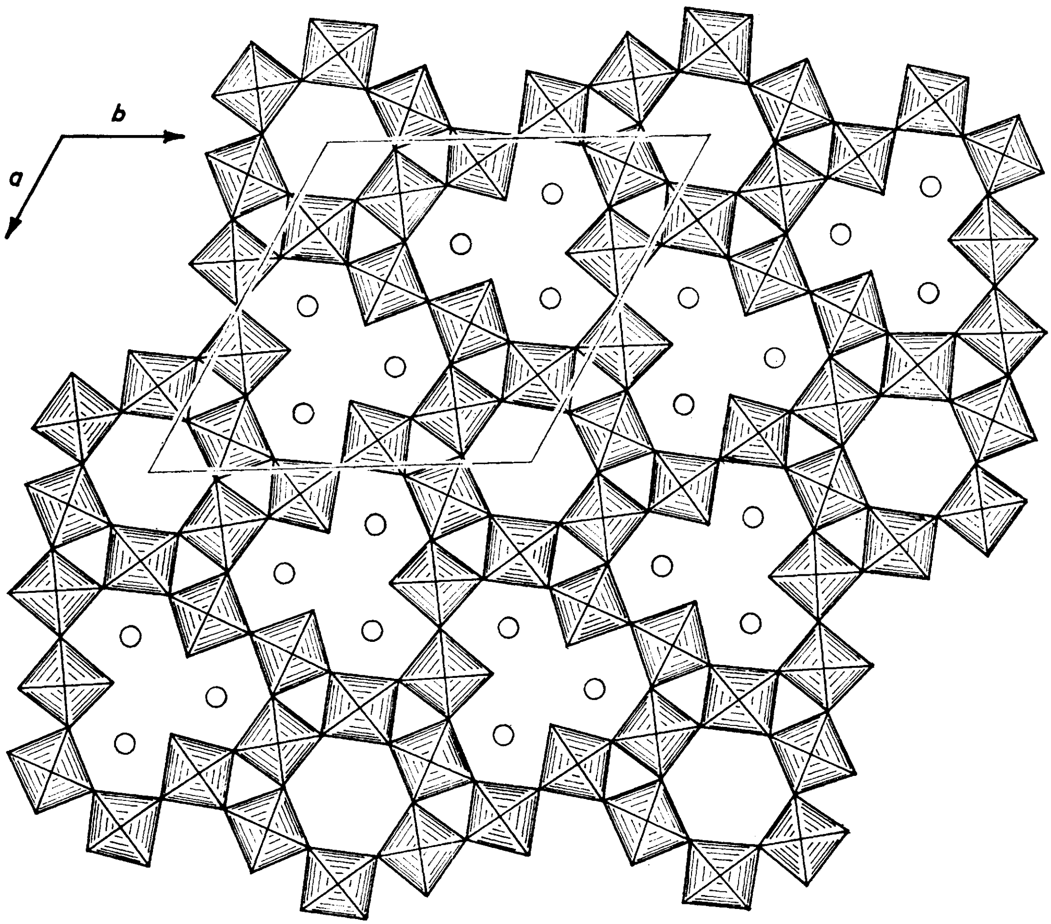
THE existence of a phase $K_2W_4O_{13}$ was pointed out by Hoermann[1] and later confirmed by Gelsing *et al.*[2] For the present investigation this compound was prepared by heating an intimate mixture of tungsten trioxide and a surplus of potassium tungstate at 750° in a platinum crucible. The crystals were faintly green, long, extremely thin needles adhering very strongly to each other. The Guinier powder photograph agrees well with powder data of $K_2W_4O_{13}$ as given by Gelsing *et al.*[2]

The present structure was derived from three-dimensional Weissenberg data using Cu-K_α radiation. The 434 independent reflections were estimated visually. No attempt to correct for absorption effects has been made as yet. The results are $K_2W_4O_{13}$, hexagonal, $a = 15{\cdot}530 \pm 0{\cdot}003$, $c = 3{\cdot}8502 \pm 0{\cdot}0007$ Å, $Z = 3$; space group: $P6$ (No. 168).

The structure was derived from a Patterson synthesis and refined by least-squares techniques to a present R-factor of 0·134. Only observed intensities were included in the refinement.

The structure is built of WO_6 octahedra which by shared corners form six-membered rings. Through the centres of these rings are formed tunnels of infinite extension running in the direction of the short axis. This is a structural feature which several tungsten compounds have in common. The hexagonal tungsten bronzes,[3] which are represented by a potassium bronze and also by rubidium and cæsium bronzes have tunnel structures. In these compounds the tunnels enclose the statistically distributed alkali ions. The pseudo-hexagonal tungsten trioxide,[4] which has a superlattice due to the substitution of one molybdenum for every twelfth tungsten, contains six-edged empty channels running parallel to the c-axis which in this case is 3·834 Å. Empty tunnels of infinite extension are also found in the tungsten oxide $W_{18}O_{49}$.[5]

In the tetratungstate, the six potassium ions are probably placed in a six-fold position, thus occupying interstices of a somewhat complicated shape The one-fold position $00z$ would also be a plausible site in analogy to the conditions in the tungsten bronzes. That this in fact may be the case is indicated by the difference Fourier syntheses and consequently by least-squares refinements based on that assumption. The five remaining potassium ions would then be statistically distributed over the six-fold position. That the two types of tunnel interstices arise in the tetratungstate, only one of which is present in the structurally similar tungsten bronzes is due to the coupling of the WO_6 octahedra in the two structures. While in the latter structure the six-membered rings are sharing octahedra with



FIGURE

The structure of $K_2W_4O_{13}$ *projected along the* c-*axis. The extent of one unit cell is indicated. The six-fold position of potassium is symbolized by circles.*

adjacent rings, in the tetratungstate the rings which here may be regarded as "double", have no octahedra in common. They are more loosely connected sideways through shared corners, thus forming additional tunnels of a more irregular shape in between them.

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