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Note on the Crystal Structure of Trivanadium Pentoxide

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The existence of a vanadium oxide V_3O_5 The existence of a various communication 1. The compound was found to be monoclinic with the symmetry C_2/c or Cc and with the unit cell dimensions

$$a = 9.98 \text{ Å}, \qquad b = 5.03 \text{ Å}, c = 9.84 \text{ Å}, \qquad \beta = 138.8^{\circ}.$$

Slight deviations in the parameter values have been observed indicating that the range of composition of the oxide has a finite width.

The observed density of 4.6 is in accordance with a unit cell content of 4 units of

V₃O₅ (calculated density 4.75).

The crystal structure has been derived on the basis of single-crystal data registered by one of us (G.A.) using MoK radiation. The following preliminary values were thus obtained:

12 V and 20 O in 8 sets of point positions 4(a) of space-group Cc (No. 9): (0,0,0; $\frac{1}{2},\frac{1}{2},0) + x,y,z; x,y,\frac{1}{2} + z.$

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4 V_1: x = 0.088,
                           y = 0.250.
                                             z = 0.464
 \begin{array}{llll} 4 & V_2; & x = 0.412, & y = 0.250, \\ 4 & V_3; & x = 0.000, & y = 0.750, \\ \end{array} 
                                             z = 0.536
                                             z = 0.250
4 O_1: x = 0.04_4,
                           y = 0.60,
                                             z = 0.10_2
4 O_3: x = 0.13_9,
4 O_3: x = 0.36_1,
                           y = 0.10,
                                             z = 0.31_1
                                             z = 0.18_{\bullet}
                           y = 0.90,
4 O_4: x = 0.45_6,
                           y=0.40
                                             z = 0.39
4 O_5: x = 0.25_0
                           y = 0.40.
                                             z = 0.00
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The arrangement of the metal atoms is centrosymmetrical (C2/c) while that of the oxygen atoms (derived by S.A.) is not.

The structure is built up of VO, octahedra which are mutually joined by sharing corners, edges and faces. By means of the latter kind of connection, "double-octahedra" (containing V_1 and V_2 atoms) result which are similar to those occurring in the corundum-type structures, e.g. V₂O₃. The "double-octahedra" are mutually joined by edges to form parallel rows extending infinitely through the structure. These rows are coupled together by "singleoctahedra" (containing V3 atoms). The V-V distance of octahedra joined by faces is 2.74 Å, while the V-V distances of octahedra sharing edges are 2.96 and 3.10 Å. The V-O and O-O distances, which so far are less accurately known, occur within the ranges 1.9-2.2 and 2.5-3.1 Å, respectively. Refinement of the structure is in progress.

X-Ray studies at temperatures up to 1 000°C did not show any indications of

phase transformations in V₃O₅.

The structure of V₃O₅ is essentially different from those of low- and high-Ti₃O₅. The V₃O₅ structural type has, however, been found to be present in a phase TiCr, O, obtained in low yield by melting a mixture of the pure oxides in an electric arc furnace under an inert atmosphere 3. (This phase seems to be stabilized by minor contents of aluminium.)

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