

CRYSTALLOGRAPHY

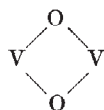
Structure of Vanadium Dioxide

GOLDSCHMIDT¹ came to the conclusion that vanadium dioxide had a rutile structure in which, in its idealized form, each vanadium would be surrounded by a regular octahedral arrangement of oxygen atoms. In fact, in actual rutile structures, the regular octahedral arrangement must always be lost² (as is in fact observed), though the unit cell will remain tetragonal, because four of the metal oxygen (or halogen) distances will remain equal. The other two could be different without any loss of symmetry, but it is found that usually they have virtually the same length as the other four (for example, in titanium dioxide four of 1.94 Å. and two of 1.99 Å. and in magnesium fluoride four of 2.00 Å. and two of 1.98 Å.)³. The arrangement of the six cations around a metal atom in a tetragonal rutile structure may therefore be visualized as "one at the north pole, one at the south, and four on the equator as a rectangle".

The structure of vanadium dioxide is sufficiently like this for Goldschmidt to have believed that it had a true rutile structure. However, it has been found more recently that the structure is distorted and is, in fact, monoclinic⁴. A detailed examination shows that the oxygen atoms lie very close to what may be described as the 'rutile positions' but that the vanadium atoms are somewhat displaced, the six VO distances being 2.03, 2.01, 2.05, 1.87, 1.86, 1.76 Å. Considerable stress has been placed on the fact that while in a rutile structure the metal atoms lie, equally spaced, on straight lines, the vanadium atoms in vanadium dioxide are spaced alternately 2.65 Å. and 3.12 Å. apart (instead of at regular intervals of about 2.87 Å.; the vanadium atoms are no longer quite on one straight line). As a result it has been proposed that there is metal-metal bonding⁵, the vanadium atoms being bonded in pairs.

It has been claimed that evidence for this type of bonding is provided by the correlation of: (a) the axial ratios for rutile type phases; (b) the metal-metal bond-lengths, with the number of valence electrons supposedly available for each metal-metal bond. It is of course very possible that the degree of distortion may be dependent on the number of valence electrons present on each metal centre—but this may or may not be related directly with metal-metal bonding. It seems to us that there is no evidence that it is so related and in fact that metal-metal bonding does not appear likely to occur in vanadium dioxide or to provide a probable reason for the particular structural distortion that occurs.

The two close vanadium atoms are in a situation which can be represented by:



the four atoms being coplanar. Moreover these two oxygen atoms shown are particularly close to one another. Consequently, the space between the two vanadium nuclei is very much occupied by the electron clouds of the two oxygen atoms, and it is difficult to suppose that there is direct bonding between them in any ordinary sense. Moreover, if metal-metal bonding were the cause of the distortion it would be expected that the two vanadium atoms would be displaced directly towards one another. This is

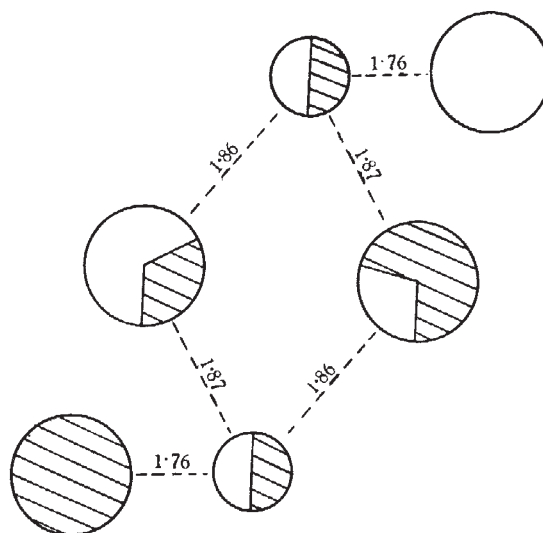


Fig. 1. Diagram showing the arrangement of atoms in the 'V₂O₄ units'. Large circles represent oxygen atoms, small ones vanadium atoms. The degree of shading represents the relative distances of the centres of the circles below the plane of the paper. The numbers give distances between centres (in Å.)

quite definitely not so. The vanadium atoms are displaced partly towards one another, or alternatively towards the oxygens lying between them, but even more towards one of the other oxygen atoms. It is as if there is a displacement of the vanadium atoms from their rutile positions so that a V₂O₄ molecule is beginning to be formed, with the structure shown in Fig. 1. The four oxygen atoms are approximately in a single plane, being close packed in that plane, the two vanadium atoms being placed so that each forms three pyramidally directed bonds, one vanadium being on one side of the oxygen plane and the other vanadium being on the other side. The whole structure is then a particular interlocking pattern of these V₂O₄ units. However, it must be stressed that the structure is really intermediate between this and a true rutile structure since the other three distances (2.01, 2.03, 2.05) are only a little greater than those in the V₂O₄ groupings (1.76, 1.86, 1.87), the incipient V₂O₄ units representing the way in which the true rutile structure is distorted.

This structure will be analysed in more detail elsewhere and a comparison with the structures of VO, V₂O₃ and V₂O₅ will then be made.

R. HECKINGBOTTOM
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¹ Goldschmidt, V. M., *Skrifter Norske Videnskaps-Akad., Oslo*, (I) *Mat. Natur.*, K1, No. 1 (1926).

² Pauling, L., *Z. Kristallog.*, **67**, 377 (1928).

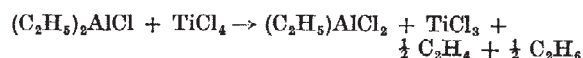
³ Baur, W. H., *Acta Cryst.*, **9**, 515 (1956).

⁴ Andersson, G., *Acta Chem. Scand.*, **10**, 623 (1956).

⁵ Magneli, A., and Merinder, B.-O., *Acta Chem. Scand.*, **11**, 1635 (1957).
Andersson, G., and Magneli, A., *Acta Chem. Scand.*, **9**, 1378 (1955). Pauling, L., *The Nature of the Chemical Bond*, third ed., 438 (1960).

Crystal Structure of β-TiCl₃

β-TiCl₃ is usually prepared according to the reaction:



by mixing heptane solutions of the reactants. The