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Studies on the Vanadium Pentoxide — Molybdenum Trioxide System. I. The Relation between the Crystal Structures of the two Oxides

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The crystal structure of vanadium pentoxide has been investigated by Ketelaar [1] and, quite recently, by Byström, Wilhelmi, and Brotzen [2]. The atomic arrangement derived by the latter authors differs from that given by the former by being centro-symmetrical (space-group *Pmnm* instead of *Pmn*) and introduces considerable adjustments especially of the oxygen parameters, leading to oxygen-oxygen distances of plausible lengths throughout.

Byström and his co-workers favoured the centro-symmetrical space-group after examining the symmetry of etch-figures on crystals of the substance. Mr. Erik Blomgren and Mr. Johannes Bæcklund of this Institute have kindly tested a specimen of vanadium pentoxide for piezoelectricity, but in spite of using very sensitive methods no such effect could be detected. This negative result may also be considered as an argument in favour of the centro-symmetrical arrangement, although the possibility of the crystal lattice lacking a centre of symmetry cannot be definitely excluded in this way.

According to the new structural scheme the vanadium atoms of the lattice have five adjacent oxygen atoms at distances of 1.54, 1.77, 1.88 (two atoms), and 2.02 Å. If a sixth oxygen atom, situated 2.81 Å from the vanadium atom, is included in the coordination polyhedron, this will form a very distorted VO_6 octahedron (*cf.* Fig. 1a and b). Byström and his co-workers, however, prefer to exclude this remote oxygen atom and consider the lattice as built up of trigonal VO_5 bipyramids.

The vanadium-oxygen distances of 1.8—2.0 Å agree fairly well with those derived by Aebi [3] for the VO_6 octahedra of $V_{12}O_{26}$ (1.85—2.50 Å), by Brandt [4] for the VO_4 tetrahedra of $CrVO_4$ (1.72 and 1.80 Å), and by Sundberg and Sillén [5] for the VO_4 tetrahedra of KUO_2VO_4 (1.7 Å). The close similarity

between the short vanadium-oxygen distance of 1.54 Å and that obtained by Palmer [6] from electron diffraction studies on $VOCl_3$ (1.56 Å) is remarkable, but the conditions in the two compounds are fairly different and hardly allow of a direct comparison.

We have carried out a calculation of the *ab* projection of the electron density function of vanadium pentoxide, on the basis of carefully estimated intensity data obtained from zero layer line Weissenberg photographs of a minute crystal rotated around (001) and using multiple film technique. This projection is centro-symmetrical irrespective of the symmetry being *Pmn* or *Pmnm*. The parameter values of the vanadium atom and of the oxygen atom in question, obtained in this way, agree with those reported by Byström and his coworkers. Provided that the actual space-group is *Pmnm*, which is most probably the case, the corresponding interatomic distances given by these authors are thus fully confirmed.

The crystal structure of molybdenum trioxide is well known through the work of Braekken [7] and N. Wooster [8]. A determination of accurate atomic positions has recently been carried out at this Institute [9]. The structure is built up of distorted MoO_6 octahedra, joined by sharing edges to form zigzag shaped rows. The rows are mutually connected by corners to form layers, which are placed on top of each other without having atoms in common (*cf.* Fig. 1c and d).

If the lattice of vanadium pentoxide is considered to be built up of VO_6 octahedra (*v. supra*), it is obvious that there exists a close relationship between this structure and that of molybdenum trioxide (*cf.* Fig. 1). The former compound may also be described as containing zigzag shaped rows, running parallel to the *c* axis, composed of VO_6 octahedra sharing edges (*cf.* the double chains of VO_4 tetrahedra suggested by Machatschki [10]). The rows are mutually connected to form layers of infinite extension normal to the *a* axis, by having corners of the octahedra in common. Contrary to what is the case in molybdenum trioxide, the layers in the vanadium pentoxide structure are also mutually joined by octahedra sharing corners to form a three-dimensional network. Geometrically, an idealized arrangement of octahedra corresponding to the lattice of molybdenum trioxide may be transformed into that of vanadium pentoxide by giving every second layer of the structure a translation of $^1/_2\ (a + c)$.

That this relationship between the two oxide structures is not merely a formal, geometrical one is strikingly demonstrated by the ability of the vanadium pentoxide lattice to take up considerable quantities of molybdenum trioxide in solid solution [11]. Vanadium atoms are then statistically replaced by molybdenum atoms, the correct number of metal atom positions being left

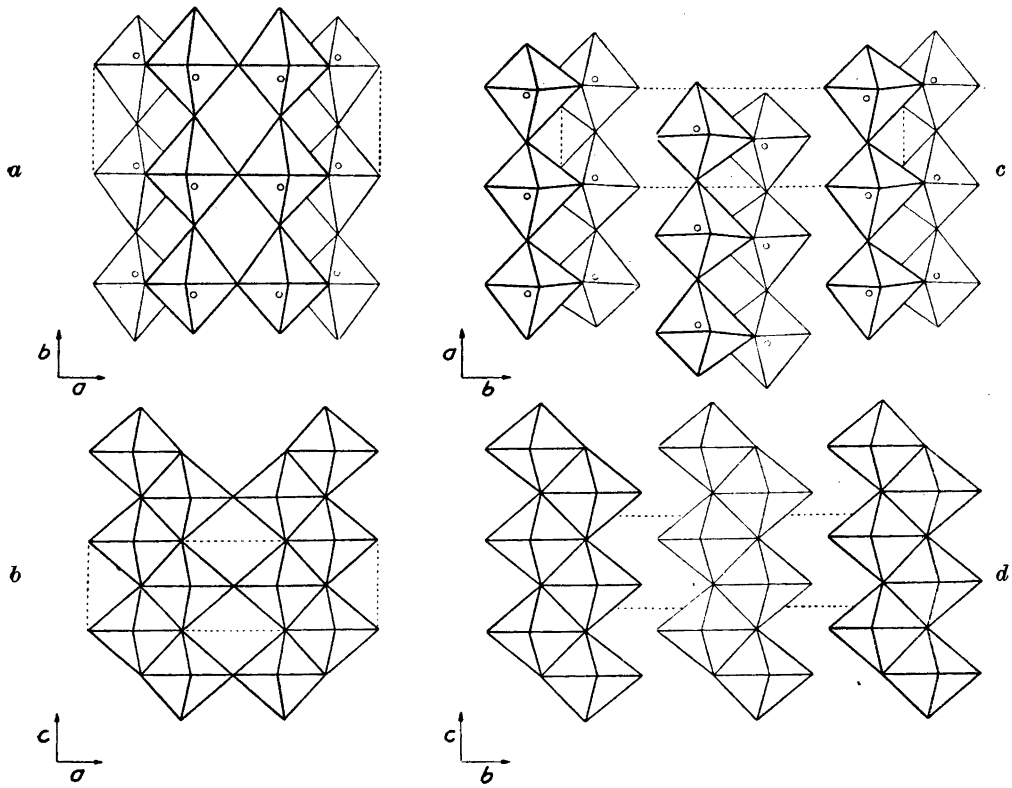

Fig. 1. The crystal structures of vanadium pentoxide (a, b) and molybdenum trioxide (c, d) represented in terms of the octahedra, which are obtained by joining the centres of the oxygen atoms coordinated with each metal atom. Octahedra indicated by heavy lines are situated at a higher level than those drawn with thin lines. In a) and c) the positions of the metal atoms within the octahedra are marked with small rings.

vacant in order to maintain electroneutrality. At about 700° C, 17 % of the vanadium atoms of vanadium pentoxide may be substituted in this manner. It is probable that the abundance of vacant metal atom positions causes the phase to break down at a higher molybdenum content. In contrast the solubility in vanadium pentoxide of tungsten trioxide crystallizing with a deformed ReO_3-structure, is negligible if any [12]. Similarly, tungsten trioxide is not soluble in molybdenum trioxide [13].

With increasing content of molybdenum atoms in the vanadium pentoxide phase there is a continuous increase of the lengths of the *a* and *c* axes, while the *b* axis steadily diminishes. This decrease of the distance between adjacent

rows of the structure evidently implies that the metal-oxygen polyhedra gradually change towards a more pronounced octahedral arrangement (*cf.* Fig. 1). Full data on this subject will be published in the near future.

A solubility of vanadium pentoxide in the molybdenum trioxide lattice would imply either the insertion of vanadium and oxygen atoms in interstices in the lattice or substitution of molybdenum atoms by vanadium atoms, the latter alternative being accompanied by the appearance of holes in the oxygen lattice of the original structure in order to maintain electroneutrality. However, addition of extra atoms or subtraction of oxygen atoms is highly improbable in this case for crystallochemical reasons. This supposition has been verified by experimental evidence which has shown that vanadium pentoxide is insoluble in the molybdenum trioxide phase [11].

SUMMARY

It is pointed out that there exists a remarkable relationship between the crystal structures of vanadium pentoxide and molybdenum trioxide. This kinship is manifested in an extended solubility of molybdenum trioxide in the vanadium pentoxide phase. The changes of the unit cell dimensions accompanying this process indicate that the metal-oxygen polyhedra of this phase — be they considered as triangular bipyramids of MeO_5 with an additional, remote oxygen atom or as highly distorted MoO_6 octahedra — are gradually modified towards a more regular octahedral arrangement.

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