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# Metal-Metal Bonding in Some Transition Metal Dioxides

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Short metal-metal distances found in the rutile-type phases in the systems $(Ti,V)O_2$ and $(V,Mo)O_2$ indicate the presence of bonds between the metal atoms. There is a close relation between the axial ratio of these compounds and the number of free valence electrons available per bond. A comparison is made with the bonds observed in the dioxides of $MoO_2$-type and in orthorhombic rhenium dioxide and also in some complex ions containing transition metals of valence numbers lower than their maximum ones.

In the dioxides of $MoO_2$-type, *i.e.* vanadium, molybdenum, wolfram, technetium and rhenium dioxide, and in the orthorhombic modification of the latter, short metal-metal distances have been observed which indicate the presence of bonds between the metal atoms. All these oxides contain metal atoms with valence numbers lower than their maximum ones, which implies that there are valence electrons not engaged in metal-oxygen bonding. It has been pointed out in previous articles that there exists a qualitative relation between the metal-metal bond distances and the number of free electrons available per bond [1,2].

In order to throw further light on this relationship a few systems of mixed transition metal dioxides have been studied [3]. These systems have contained representatives of the structure types mentioned above and titanium dioxide (rutile type). A surprising result of this investigation was the occurrence of extended regions of rutile-type structure not only in pseudobinary systems containing titanium dioxide as a component, *e.g.* $TiO_2$-$VO_2$, but also in systems that did not contain a component of rutile structure, *e.g.* $VO_2$-$MoO_2$.

The structure types of rutile, molybdenum dioxide and orthorhombic rhenium dioxide are alike in being built up of metal-oxygen octahedra joined by corners and by edges. The short metal-metal distances are associated with the octahedra sharing edges. For the rutile type this distance is simply equal to the length of the $c$ axis of the unit cell, while the calculation of the metal-metal distances for the two other structure types requires the knowledge of the actual values of the metal atom parameters.

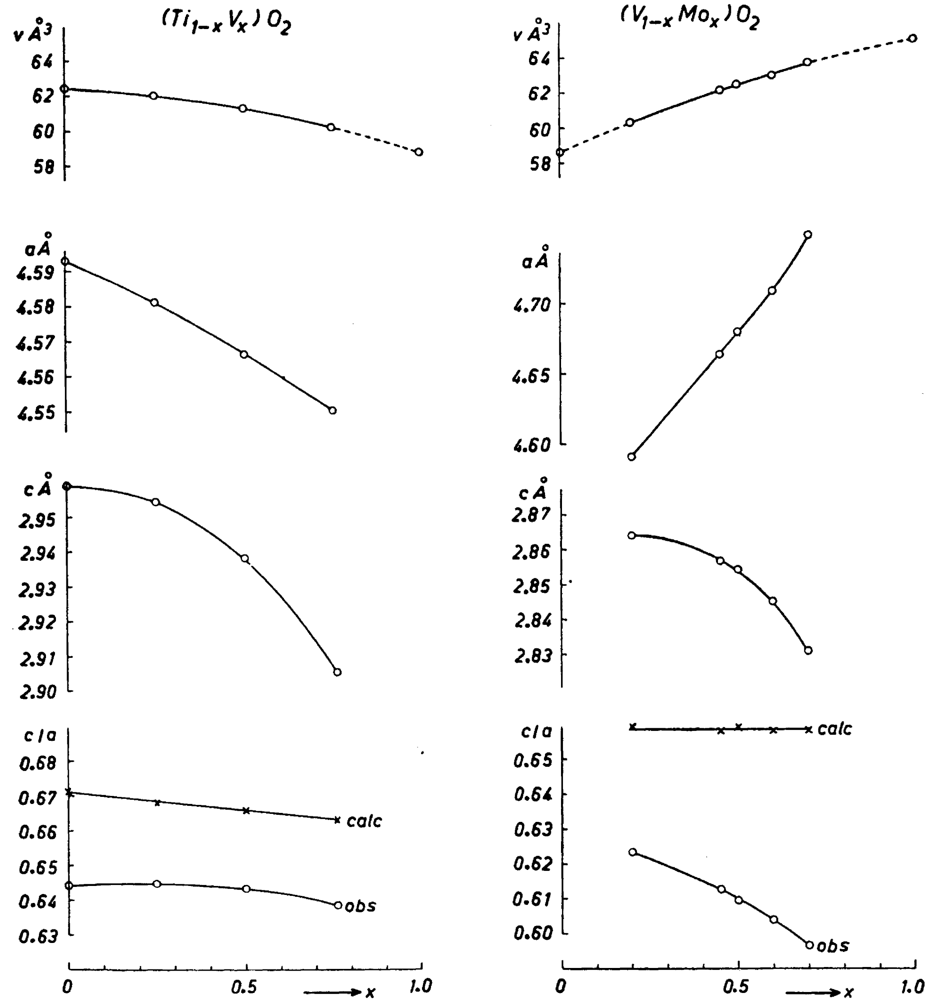

*Fig. 1.* Lattice parameters of the rutile-type phases in the systems (Ti,V)$O_2$ and (V,Mo)$O_2$.

The factors determining the length of the close metal-metal approach may be rather complicated in nature but for a simplified discussion the following factors will be considered:

1) The geometrical relations connected with the ratio of the metal and oxygen atom radii.
2) The repulsive forces caused by the charges of the atoms.
3) The bonding forces between the metal atoms.

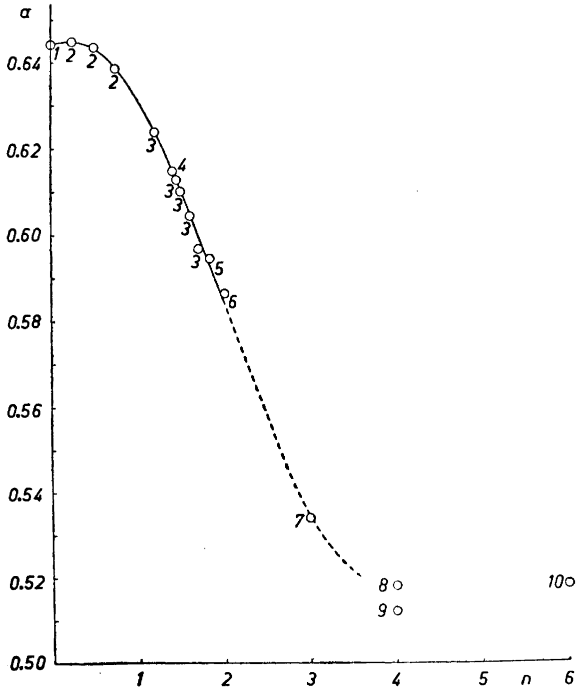

*Fig. 2.* Axial ratios of rutile-type phases and equivalent quantities for other types of transition metal dioxides ($a$) *versus* number of valence electrons available per metal-metal bond ($n$). The figures correspond to the following samples: 1-$TiO_2$, 2-$(Ti,V)O_2$, 3-$(V,Mo)O_2$, 4-$(Re,V)O_2$, 5-$(Re,Mo,V)O_2$, 6-$VO_2$, 7-$ReO_2$ (orthorhombic), 8-$MoO_2$, 9-$WO_2$, 10-$TcO_2$ and $ReO_2$ ($MoO_2$-type).

The lattice parameters of the rutile-type phases in the systems $(Ti_{1-x},V_x)O_2$ and $(V_{1-x},Mo_x)O_2$ are represented in Fig. 1 as functions of the composition. The decrease with increasing $x$ of the volume per formula unit ($v$) of the former is in accordance with the formula volumes of the pure components. The same is true for the increase with $x$ of the volume of the $(V_{1-x},Mo_x)O_2$ rutile phase.

For $(Ti,V)O_2$ both the $a$ and $c$ axes decrease with increasing $x$. At about $x = 0.4$ the shortening of $c$ seems to be slightly accelerated. For $(V,Mo)O_2$ the increase of the $a$ axis with $x$ parallels the change of the formula volume, while the $c$ axis shows a simultaneous shortening. The results indicate the presence in $(V,Mo)O_2$ of considerable attractive forces between neighbouring metal atoms, increasing in strength with the molybdenum content. They also suggest the possibility of slight attraction in $(Ti,V)O_2$ for high vanadium contents.

Pauling [4] has given an expression for the axial ratio of rutile-type crystals considering the influence of the ratio of the atomic radii and of the anion-anion repulsive forces. The metal-metal interaction was considered negligible.

Fig. 1 also shows the axial ratio derived by this formula, $c/a$ (calc), and those obtained from the experimental data, $c/a$ (obs). For $(Ti,V)O_2$ the calculated and experimental ratios differ by approximately the same amount as that found by Pauling for pure titanium dioxide. The deviating slope of the observed ratios for $(V,Mo)O_2$ indicates that a contracting force acts between the metal atoms in the $c$ direction and that this effect increases with increasing molybdenum content.

It appears that the axial ratio may provide a suitable "normalized" measure of the metal bond length present in these phases. Fig. 2 gives the values of $c/a$ (obs) for the various samples of $(Ti,V)O_2$ and $(V,Mo)O_2$ as a function of the number of valence electrons available per metal-metal bond, *i.e.* the number of valence electrons not engaged in metal-oxygen bonding divided by the number of short metal-metal distances. The corresponding data for two samples of rutile structure obtained in the $(V,Re)O_2$ and $(V,Mo,Re)O_2$ systems also fit the smooth curve.

Fig. 2 also contains data for the various dioxides of $MoO_2$-type (deformed rutile structure) and for the orthorhombic rhenium dioxide. For these substances a different normalized bond length had to be chosen instead of the axial ratio used for the rutile-type structures. Thus, for the monoclinic $MoO_2$-type compounds, the quotient $d/\sqrt{bc\sin\beta}$ was adopted as an appropriate equivalent of $c/a$ (rutile). In this expression, $d$ denotes the length of the metal-metal bonds which extend approximately parallel to the $a$ axis of the unit cell, this direction corresponding to that of the unique axis of the ideal rutile lattice. For the orthorhombic rhenium dioxide where the bonds form zig-zag strings through the structure, the bond length was analogously divided by the square root of the unit mesh area projected parallel to the bond direction.

It must be emphasized that the bond lengths of the pure dioxides are less accurately known than those present in the rutile-type structures. This is especially so for the technetium and rhenium dioxides. The $d$ values for these two compounds have thus been roughly estimated assuming the metal atom positions to be the same as those found for molybdenum dioxide.

The change of direction of the curve for high number of electrons is very likely associated with the considerable electrostatic repulsion between the metal atoms at the very short metal-metal distances present in these compounds which are significantly shorter than those occurring in the metals.

It seems probable that similar but not identical curves may be given by other mixed oxide systems. Thus niobium dioxide, the structure of which is a superstructure of the rutile type [5], gives an axial ratio of the subcell falling considerably below the curve given in Fig. 2. This may indicate the existence of stronger bonds in this compound than those found in the present investigation. On the other hand tantalum dioxide of rutile structure [6] shows an axial ratio rather close to that of titanium dioxide, which may be an indication of weak or no bonding between the tantalum atoms. Similar values of the axial ratio (0.642—0.673) are also shown by several rutile-type structures found by Brandt [7] among mixed oxides of antimony, niobium or tantalum with aluminium, gallium or transition elements which are likely to be present in a trivalent state (chromium, iron and rhodium). The group of trirutile structures, studied by Byström, Hök and Mason [8], and comprising mixed

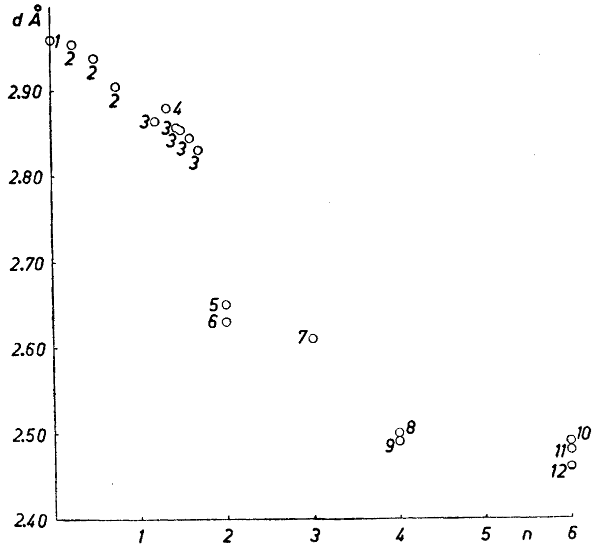

*Fig. 3.* Metal-metal bond lengths for various transition metal compounds ($d$) *versus* number of valence electrons available per bond ($n$). The figures denote the following substances: 1-$TiO_2$, 2-$(Ti,V)O_2$, 3-$(V,Mo)O_2$, 4-$(Ta_6Cl_{12})^{2+}$, $(Ta_6Br_{12})^{2+}$ and $(Nb_6Cl_{12})^{2+}$, 5-$VO_2$, 6-$(Mo_6Cl_8)^{4+}$, 7-$ReO_2$ (orthorhombic), 8-$MoO_2$, 9-$WO_2$, 10-$ReO_2$ ($MoO_2$-type), 11-$TcO_2$, 12-$(W_2Cl_9)^{3-}$.

oxides $ASb_2O_6$ and $ATa_2O_6$, where A is magnesium, zinc, iron, cobalt or nickel, likewise gives high values for the ratio $c/3a$ (0.645—0.665). X-Ray studies on further systems of mixed transition metal dioxides are in progress. It is also planned to start magnetic investigations of these substances in the near future.

Very short metal-metal distances have also been found in other transition metal compounds, *e.g.* the ions $W_2Cl_9^{3-}$ and $Mo_6Cl_8^{4+}$ studied by Brosset [9–11] and the ions $Nb_6Cl_{12}^{2+}$, $Ta_6Br_{12}^{2+}$ and $Ta_6Cl_{12}^{2+}$ investigated by Vaughan, Sturdivant and Pauling [12]. The geometrical conditions present in these compounds are of course quite different from those in the dioxides. It is, however, interesting to note that the rough qualitative relation found to connect the metal-metal distances with the number of valence electrons available per metal-metal bond in the dioxides also seems to be valid for these complex ions (*cf.* Fig. 3).

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