This paper presents a brief survey of the structures and properties of early transition-metal oxides containing d⁰ and d¹ cations. Transition-metal oxides constitute a fascinating class of inorganic solids that have attracted the attention of solid-state/materials chemists from the early days. Among them, oxides of the early transition-metals (periodic groups 4, 5, 6 and 7) containing d⁰ and d¹ electronic configuration are a special subclass, distinctly different from the other transition-metal oxides, showing several unique features. For example, the crystal structures of d⁰ metal oxides consist of distorted metal–oxygen (MO₆) octahedra where the cation is displaced from the centre of the octahedron (Fig. 1). Several of the interesting features of these oxides can be directly traced to this distortion. The occurrence of layered structures and distinct oxide hydrates for VO₂, MoO₃ and Re₂O₇ is a direct consequence of the distortion. The high static relative permittivity and the consequent ferroelectric behaviour, the presence of soft phonon modes and the ability to accommodate oxygen-deficient non-stoichiometric (e.g. WO₂₋ₓ, TiO₂₋ₓ) without oxygen vacancies could all be traced to a soft M−O potential that is again a direct consequence of the out-of-centre distortion of MO₆ octahedra in d⁰ metal oxides. Another special feature is that the d⁰ cation, which is in its highest oxidation state, can be reduced partially or wholly in many instances, where the electronic configuration of the metal is now d¹ or d². Two classes of reduced oxides containing d¹ d² configuration are well known. They are the oxide bronzes typified by the tungsten bronzes, AₓWO₃ (A=alkali metal), which exhibit metal-like properties and the reduced oxides such as WO₂₋ₓ, and TiO₂₋ₓ, with an apparent anion deficiency. A unique structural principle called crystallographic shear (CS) that operates in the latter materials eliminates the oxygen vacancies without changing the octahedral coordination of the metal atom, as a consequence, highly ordered homologous series of mixed-valent phases of the formulae, W₂O₅₋ₓ, W₃O₇₋ₓ and Ti₃O₆₋ₓ, are obtained instead of grossly non-stoichiometric phases. Well-known among the oxides containing d¹ electronic configuration are Ti₂O₃, VO₂ and Re₂O₇. Besides these early transition-metal oxides which have been known for quite some time, several new binary and multinary ones have been uncovered in the recent decades. In addition to the ferroelectric (d¹) and metallic (d² d³) properties to which we have already referred, these oxides exhibit a whole range of interesting materials properties that include Brønsted acidity, catalytic, and photocatalytic reactivity, non-linear optical response, metal–non-metal transitions, charge-density-wave instability and superconductivity. The purpose of this paper is to focus attention on the structure and properties of early transition metal oxides containing d⁰ and d¹ d² cations, especially on the recent developments, and to point out potential new directions in this growing area of inorganic materials chemistry.
and HfO

The oxygen coordination around vanadium can be regarded as literature using ATOMS software. MoO

‡ Although group 3 oxides, Sc2O3, Y2O3, and La2O3 belong to this category, we do not consider them here because of the large separation between the empty d states and filled oxygen 2p and 2s states, which makes the d states chemically insensitive.

† The structures are drawn from the crystallographic data given in the literature using ATOMS software.

4

Fig. 2 Structures of (a) Re2O7 and (b) Cr2O3. In (c), the atomic positions of the Cr2O3 structure are shown, revealing the highly distorted octahedral coordination around CrVI.

5

dOxides

Early transition metals of the periodic groups 3‡–7, whose valence electrons are well screened by the rare-gas inner core and hence readily ionized, form dOxides where the metal atom is in its highest oxidation state. The following are the well known ternary oxides containing dOxidations: TiO2, ZrO2, HfO2, V2O5, Nb2O5, Ta2O5, Cr2O3, MoO3, WO3; Mn2O7, Re2O7, Re2O8. The structures of many of these oxides (TiO2, V2O5, Nb2O5, MoO3 and WO3) are built up of MO6 octahedra which are connected through corners and edges.4 The structures of other oxides consist of different polyhedra: while ZrO2 and HfO2 contain MO4 polyhedra, Ta2O5 consists of both TaO6 octahedra and TaO6 pentagonal bipyramids. The structures of Cr2O3, Mn2O7 and Te2O6 consist of only MO6 tetrahedra. The unique layered structure of Re2O7 on the other hand contains corner-sharing ReO6 octahedra and ReO4 tetrahydroxide. We show in Fig. 1 and 2 representative structures of dOxides.

A characteristic feature of all the octahedral structures is that the MO6 octahedra are considerably distorted in such a way that the cation is displaced from the centre of the octahedron creating unequal M–O bonds.19 With the V2O5 structure, one of the V–O bonds is so long (2.79 Å) that the oxygen coordination around vanadium can be regarded as square pyramidal rather than octahedral.20 Similarly, although the structure of Cr2O3 is conventionally described as consisting of chains of CrO2V2O7 tetrahedra,21 inclusion of two additional oxygens from adjacent chains would give a highly distorted octahedral coordination around CrVI (Fig. 2). We see that the characteristic out-of-centre distortion of MO6 octahedra in dOxides increases with increasing charge-to-size ratio of the cations.

Out-of-centre distortions of MO6 octahedra in dOxides, which are crucial to many of the interesting properties of these materials, have an electronic origin.22 To understand the origin, let us consider the electronic structure of a typical dOxide, viz., WO3, in its undistorted form (Fig. 3). The valence band (which corresponds to the highest occupied molecular orbitals, HOMOs) is mainly anionic (oxygen 2s and 2p), and the conduction band (which corresponds to the lowest unoccupied molecular orbitals, LUMOs) is mainly cationic, arising from the empty d states. For small and highly charged dOxidations, the separation between the HOMO and the LUMO states becomes sufficiently small so as to permit a mixing between them that stabilizes the occupied states at the expense of the unoccupied states through a second-order Jahn–Teller effect.23,24 The effect manifests in the form of out-of-centre distortion of MO6 octahedra that gives rise to unsymmetrical M–O–M linkages in extended structures. The smaller the HOMO–LUMO gap, the larger is the distortion. For dO in n(0) configuration, the distortion is rapidly suppressed with increasing n value. The model readily explains the observed structural features of dOxides.25 Thus, for small and highly charged cations such as VVI, CrVI and MoVI, the distortion is large, and for large and relatively less charged cations such as ZnII, HfIV and ScIV, there is less or no distortion at all around their MO6 octahedra.

Between cations of same charge and similar size such as NbV, TaV or TiIV and NbVI, the distortion is lesser for the heavier ions because of the larger HOMO–LUMO gap. In chemical terms, the variation of the HOMO–LUMO gap and hence the distortion of MO6 octahedra could be related to polarization of anions by highly charged cations. This effect could thus be understood in terms of Pearson’s concept26 of ‘hardness’. In ternary and multinary phases containing dOxidations, the magnitude of the distortion is modulated by the presence of other cations and the actual crystal structure which may either buttress or suppress the effects of distortion.27,28

We shall now turn to the consequences of the distortion of MO6 octahedra in dOxides. An obvious consequence is that the oxygens of the long M–O bonds are relatively more ionic (more basic) than the oxygens of the short M–O bonds. The long M–O bonds become vulnerable to sission and the basic oxygens susceptible to electrophilic attack, for example, by protons. Formation of well defined hydrates of WO3, MoO3, and Re2O7 is a direct manifestation of the reactivity of long M–O bonds of the distorted MO6 octahedra. Interestingly, the hydrates possess lower dimensionality structures as compared to the parent anhydrous oxides; thus WO3·H2O is layered,29 while WO3·2H2O has a molecular structure (Fig. 4), while Re2O7·2H2O has a layered structure.24 A more dramatic illustration of the reactivity of long M–O bonds is provided by the formation of layered MOPO4 hydrates (M=V, Nb) here the anhydrous MOPO4 phases possess a three-dimensional structure21 consisting of chains of corner-connected MO6 octahedra with alternating long and short M–O bonds along the chain, while the hydrates possess a layered structure26,27 where the oxygens of the long M–O bonds are replaced by water of hydration (Fig. 5). Interestingly, the layered oxide hydrates WO3·H2O, MoO3·H2O and NbOPO4·H2O are all strong Bronsted acids30–32 intercalating basic organic molecules such as n-alkylamines through acid–base interaction:

\[ \text{O}^+\text{M}^+\text{OH}^- \overset{\text{[O}^+\text{M}^+\text{OH}^-]\text{H}^+}{\text{[O}^+\text{M}^+\text{OH}^-]} \text{RNH}_2 \overset{[\text{O}^+\text{M}^+\text{OH}^-]}{\text{[O}^+\text{M}^+\text{OH}^-]+\text{H}_2\text{N}^+\text{R}}} \]

Another manifestation of the acidity of these oxide hydrates is the formation of higher hydrates,33,34 WO3·2H2O, MoO3·2H2O, VOPO4·2H2O and NbPO4·3H2O (s=2–3).

metal cations in the interlayer region, topochemical ion exchange readily occurs in aqueous acids yielding the corresponding protonated derivatives. A particularly interesting class of such materials are the ion-exchangeable layered perovskites\textsuperscript{38–41,46} of the general formulae, $\text{A}_{x}$\textsubscript{1−1/3}$\text{M}_{x}$\textsubscript{1/3}$\text{O}_{2+x}$, and $\text{A}_{x}$\textsubscript{1/3}$\text{M}_{x}$\textsubscript{1/3}$\text{O}_{2+x}$, where $\text{A}$ denotes interlayer alkali cations, $\text{A}’$ calcium, lanthanum, etc., and $\text{M}$, is $\text{Nd}^3^+$ and $\text{T}^6$. Typical examples are $\text{CsCa}_{3}\text{Na}_{2}\text{O}_{10}$ (ca. 0.56) and $\text{LiMMoO}_{2}$ (0.56) of which the last are Ruddlesden-Popper phases\textsuperscript{42} related to Sr$_2$Ti$_2$O$_7$.

In all these cases, the interlayer alkali-metal ions are readily exchanged with protons to yield protonated derivatives. It must be mentioned that first results of ion-exchange in this series were obtained by Tournoux et al.\textsuperscript{44} with $\text{CsCa}_{3}\text{Na}_{2}\text{O}_{10}$.

We show the crystal structures of these oxides in Fig. 6. We see that the MO$_2$ octahedra are distorted to give short terminal $\text{M}–\text{O}$ bonds (ca. 1.70–1.75 Å) which point to the interlayer region.\textsuperscript{38,41} In the protonated derivatives such as $\text{HL}_{2}\text{La}_{2}\text{NbO}_{2}$ (La = La, Nd) and $\text{Ca}_{3}\text{Na}_{2}\text{O}_{10}$, the protons (or $\text{H}_2\text{O}^+$ ions) are attached to the short terminal $\text{M}–\text{O}$ bonds. The strong acidity of the terminal oxygens renders the interlayer protons highly acidic and, accordingly, these materials display Brønsted acidic properties intercalating n-alkylamines and other organic bases.\textsuperscript{38–41}

An interesting consequence of the distortion of Ti$_6$ octahedra is seen in the $n$=1 Ruddlesden-Popper phases

<table>
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<th>parent oxide</th>
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<td>43</td>
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Table 1 Oxide solid acids containing $\text{d}^0$ cations and their parents

Fig. 4 Structures of (a) WO$_3$·H$_2$O and (b) Re$_2$O$_7$·2H$_2$O

Fig. 5 Structures of (a) VOPO$_4$·H$_2$O and (b) VOPO$_4$·2H$_2$O

where the additional water molecules are held in between the layers through hydrogen bonding.\textsuperscript{42} The consequences of the short $\text{M}–\text{O}$ bonds in $\text{d}^0$ oxides are more impressive. Since the oxygen of the shortest $\text{M}–\text{O}$ bond in a distorted octahedron is acidic relative to other oxygens, protons (or $\text{H}_2\text{O}^+$ ions) attached to this oxygen acquire a distinct Brønsted acidity. Several protonated oxides of this kind have been synthesized in recent years. We list them in Table 1 along with their parent alkali-metal analogues from which the protonated derivatives are obtained by ion exchange. Since the parent compounds are all layered, containing alkali-metal cations in the interlayer region, topochemical ion exchange readily occurs in aqueous acids yielding the corresponding protonated derivatives. A particularly interesting class of such materials are the ion-exchangeable layered perovskites\textsuperscript{38–41,46} of the general formulae, $\text{A}_{x}$\textsubscript{1−1/3}$\text{M}_{x}$\textsubscript{1/3}$\text{O}_{2+x}$, and $\text{A}_{x}$\textsubscript{1/3}$\text{M}_{x}$\textsubscript{1/3}$\text{O}_{2+x}$, where $\text{A}$ denotes interlayer alkali cations, $\text{A}’$ calcium, lanthanum, etc., and $\text{M}$, is $\text{Nd}^3^+$ and $\text{T}^6$. Typical examples are $\text{CsCa}_{3}\text{Na}_{2}\text{O}_{10}$ (La = La, Nd)\textsuperscript{38,39} and $\text{La}_{3}\text{TiO}_{10}$ (La = Na, K)\textsuperscript{41} of which the last are Ruddlesden-Popper phases\textsuperscript{42} related to Sr$_2$Ti$_2$O$_7$.

In all these cases, the interlayer alkali-metal ions are readily exchanged with protons to yield protonated derivatives. It must be mentioned that first results of ion-exchange in this series were obtained by Tournoux et al.\textsuperscript{44} with $\text{CsCa}_{3}\text{Na}_{2}\text{O}_{10}$.

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*Corresponds to the lowest $pK_a$-base that the acid can intercalate.

![Fig. 4 Structures of (a) WO$_3$·H$_2$O and (b) Re$_2$O$_7$·2H$_2$O](image1)

![Fig. 5 Structures of (a) VOPO$_4$·H$_2$O and (b) VOPO$_4$·2H$_2$O](image2)

![Fig. 6 Structures of layered perovskite oxides: (a) $\text{K}_2\text{La}_{3}\text{TiO}_{10}$, (b) $\text{Ca}_{3}\text{Na}_{2}\text{O}_{10}$, (c) $\text{KLa}_{3}\text{NbO}_{10}$, and (d) $\text{NaTiO}_2$.](image3)
NaLaTiO$_3$ (Ln = lanthanide) originally synthesized by Blasse and Van den Heuvel.\textsuperscript{35} The crystal structure of these solids reveals an unique ordering of Na and Ln atoms. Instead of a random distribution of these atoms at the interlayer sites of the parent Sr$_2$Ti$_2$O$_6$ structure, the Na and Ln atoms are ordered in the sequence Na-La-Ln-Ln along the c-direction.\textsuperscript{36} (Fig. 6) This ordering is clearly dictated by the distortion of the TiO$_6$ octahedra, the oxygen of the short Ti–O bonds pointing towards the Na layer. As a result, the sodium ions are readily ion-exchanged with protons to give another novel series of protonated oxides,\textsuperscript{37} HL$n$TiO$_2$ + H$_2$O. It must however be mentioned that an electron microscopic study\textsuperscript{38} of the structure of Na$_2$TiO$_3$ revealed the presence of double perovskite layers, Na$_2$Ti$_2$O$_5$, separated by [Y–NaO–Y] triple rock-salt layers. Structurally, this phase appears to be closer to TiBa$_2$Cu$_3$O$_7$ than to Ruddlesden–Popper phases.\textsuperscript{39}

The Aurivillius family of layered perovskite oxides having the general formula (B$_2$O$_3$)$_n$(A$^n$–$M^m$O$_{3n+1}$)$_n$, where $A$ is a Sr, Ba, Na, W, etc., is crucial to the structure, stability and properties.\textsuperscript{40}–\textsuperscript{46} Recent crystal structure refinements\textsuperscript{47} of representative members of this family, B$_2$O$_3$K$_n$B$^2$Ti$^6$O$_{3n+1}$ and B$_2$O$_3$Ba$^2$Ti$^6$O$_{3n+1}$, have revealed that cooperative displacements of both the lone-pair Bi$^6+$ cations as well as the $D^0$ cations at the octahedral sites give rise to the observed structures and ferroelectric properties. Interestingly, ion-deficient members of this family have disordered oxygen vacancies around the $D^0$ cations exhibiting high oxide ion conductivities.\textsuperscript{48}

HMMO$_x$ (M = Nb, Ta, M = Mo, W) and their hydrates constitute a novel series of layered oxides containing $D^0$ cations.\textsuperscript{49,50} We have synthesized these solids by ion exchange from the well known tetragonal tungsten bronze (TTB) structure or results in a layered structure, in which the short M–O bonds are connected to form a well known layered structure consisting of layers of MO$_6$ octahedra alternating with MO$_6$ octahedra in the c-direction.\textsuperscript{51} From the structure of Li$_2$Nb$_2$O$_6$ we see that all the three metal–oxygen octahedra are strongly distorted.\textsuperscript{52} Since Li atoms are arranged in sheets perpendicular to the c-direction, its removal by exchange with protons in aqueous acids octahedra. Oxides of this composition crystallize either with point to the interlayer region where the H$^\infty$ bases like 4-nitroaniline ($pK_a = 0.4$), quinoxaline ($pK_a = 0.56$) and pyrrole ($pK_a = 0.4$). It may be relevant to point out here that the strong Bronsted acidity of heteropoly acids\textsuperscript{53} such as H$_2$PM$_2$O$_{11}$H$_2$O (M = Mo, W) has its origin in the distorted MO$_6$ octahedra and the presence of short M–O terminal bonds. The phosphomolybdic-anion, PM$_2$O$_{11}^-$, consists of 12 edge-shared Mo$_6$O$_{18}$ octahedra surrounding a PO$_4$ tetrahedron. The Mo atoms are displaced towards terminal oxygen giving short (1.70 Å) M–O bonds.\textsuperscript{54} The protons and water molecules present in the interconnected space around the heteropolyanion ions make the solid highly acidic. The phosphomolybdc acids are also fast proton conductors.\textsuperscript{55}

Another consequence of the distortion of d$^0$ MO$_6$ octahedra is that the M–O bonds are polarized, creating a net dipole moment. When such distorted octahedra are connected up unsymmetrically to give a non-centrosymmetric extended network, the crystal exhibits a macroscopic spontaneous polarization. This polarization is the origin of several ferroelectric properties\textsuperscript{56} which include ferroelectricity and non-linear optical (NLO) behaviour such as second harmonic generation (SHG) of electromagnetic radiation. Typical examples of d$^0$ oxides showing these properties\textsuperscript{57} are BaTiO$_3$, KNbO$_3$, LiNbO$_3$ and KTiOPO$_4$. The ferroelectric properties of BaTiO$_3$ were first investigated by Merz.\textsuperscript{58} The distortions of MO$_6$ (M = Ti, Nb) octahedra in ferroelectric perovskites, BaTiO$_3$ and KTiOPO$_4$, which involve displacement of the M atoms to create one short, two short and three short M–O bonds have been successfully modelled by electronic structure calculations.\textsuperscript{59,60}

While the calculations clearly show that an admixture (hybridization) between the metal d states and the oxygen 2p states is essential for ferroelectricity, questions relating subtle bonding effects due to A cations on the structure and properties of AMO$_x$ perovskites (e.g. SrTiO$_3$ does not show a ferroelectric transition; PbTiO$_3$ exists in a tetragonal phase that is stable up to 766 K) as well as the relative stabilities of the various perovskite phases are yet to be quantitatively understood.\textsuperscript{61}

Besides d$^0$ perovskites, oxides of the general formula, $A$$_n$M$_3$O$_{3n+2}$, where $A$ is a short M–O bond (such as Na, Tl, as well as Mo, W) and B are electropositive cations (such as Ba, Na, etc.) exhibit ferroic and non-linear optical properties,\textsuperscript{62} which are again related to the distortions of d$^0$ MO$_6$ octahedra. Oxides of this composition crystallize either with the well known tetragonal tungsten bronze (TTB) structure or with the orthorhombic tungsten bronze (OTB) structure. Typical examples belonging to these structure types are respectively Ba$_2$Na$_2$Nb$_2$O$_7$ (bannana) and Cs$_2$Na$_2$Nb$_2$O$_7$, whose ferroic properties are comparable.\textsuperscript{63,64}

As we have already mentioned, LiNbO$_3$ and KTiOPO$_4$ (KTP) are among the well known inorganic NLO materials\textsuperscript{65} whose NLO response could be directly traced to the presence of distorted MO$_6$ octahedra which are unsymmetrically connected. In KTP the TiO$_6$ octahedra are connected cis-trans creating chains of alternating short (1.70–1.75 Å) and long (2.10–2.15 Å) M–O bonds along the polar axis (Fig. 8). Another structural motif that gives NLO properties among d$^0$ oxides is the presence of trans-connected MO$_6$ octahedral chains again containing alternate long and short M–O bonds.

NaLaTiO$_3$, Li$_2$TiO$_3$, KTiOPO$_4$, BaTiO$_3$, KNbO$_3$, LiNbO$_3$, and KTiOPO$_4$ are representative members of this family. These oxides show ferroelectric properties, the presence of short M–O bonds and high oxide ion conductivities. The ferroelectric properties of BaTiO$_3$, KNbO$_3$, LiNbO$_3$ and KTiOPO$_4$ have been successfully modelled by electronic structure calculations. While the calculations clearly show that an admixture (hybridization) between the metal d states and the oxygen 2p states is essential for ferroelectricity, questions relating subtle bonding effects due to A cations on the structure and properties of AMO$_x$ perovskites (e.g. SrTiO$_3$ does not show a ferroelectric transition; PbTiO$_3$ exists in a tetragonal phase that is stable up to 766 K) as well as the relative stabilities of the various perovskite phases are yet to be quantitatively understood.

Fig. 7 Schematic structures of (a) LiNbWO$_6$, and (b) H$_2$SiWO$_6$. Open circles around metal atoms denote oxygens. Large open circles at (b) denote water molecules.
Typical examples of this kind of structure are\textsuperscript{68,69} $K_2\text{NiSO}_4\text{Si}_2\text{O}_8$ (Fig. 8) and $\text{ANbO}_3\text{B}_3\text{O}_7$ ($\text{A}\text{"K}, \text{Rb}, \text{Cs}$).

The crucial role of $d^n$ cations in the NLO properties of KTP-type materials has been revealed\textsuperscript{70} by synthesizing non-$d^n$ analogues such as $\text{KSnOPO}_4$ and $\text{KSnSO}_4$ which do not exhibit a significant SHG response. In contrast, considerable substitution of $d^0$ Nb$^+$ for Ti$^{4+}$ in the KTP structure does not adversely affect the SHG response of $\text{KTIOPO}_4$\textsuperscript{71} LiMn$^{4+}$O$_2$ oxides ($M = \text{Nb}, \text{Ta}; M = \text{Mo}, W$)\textsuperscript{72},\textsuperscript{73},\textsuperscript{74},\textsuperscript{75},\textsuperscript{76} a crystalline SHG response that is not destroyed by ion-exchange of lithium by proton.\textsuperscript{77} The result clearly reveals that the SHG response of this material is due to the MMO$_x$ octahedra, the lithium atoms making little contribution to the hyperpolarizability of this material.

Another important property of $d^n$ oxides is their ability to selectively catalyze oxidation of organic molecules.\textsuperscript{78} Selective oxidation of propene to acrolein by bismuth molybdates $[\text{Bi}_6\text{Mo}_{12}\text{O}_{39}]^3\text{−}$ and bromines of the type $[\text{Bi}_6\text{O}_5\text{Mo}_{12}\text{O}_{39}]^{3\text{−}}$ and of $n$-butane to maleic anhydride by vanadium phosphates $\left[\text{VOPO}_4\right]_n\left[\text{VO}_2\text{P}_2\text{O}_7\right]_{3n}$ are two of the industrially important catalytic conversions, where the role of $d^n$ cations (Mo$^{7+}$ and V$^{5+}$) in the catalysis has been established. In recent times, $d^n$ oxides have been found to exhibit photocatalytic reactivity towards such important reactions as photodecomposition of water\textsuperscript{79} and methanol.\textsuperscript{80} Although TiO$_2$ itself was known for long to split water into hydrogen and oxygen in a photoelectrochemical cell,\textsuperscript{81} the use of ion-exchangable layered perovskites, such as $\text{RbNb}_{2}\text{O}_{4}\text{TiO}_3$ and $\text{RbLa}_{2}\text{Ti}_{3}\text{O}_{9}$ photocatalysts, in these reactions is a significant new development. In addition, Nd$_2\text{Ti}_3\text{O}_7$, an anion-deficient layered perovskite derived from $\text{K}_2\text{Nd}_{2}\text{Ti}_3\text{O}_7$, shows a persistent photocatalytic activity with a slow decay rate, that appears to be related to oxygen vacancies.\textsuperscript{82}

Curiously, the recently discovered negative electronic temperature coefficients of $\text{K}_2\text{LiTaO}_3$ and $\text{ZrV}_2\text{O}_7$ are two of the industrially important oxides exhibiting fine variations in electronic properties which are attributable to the radius and acidity of $\text{Ln}^{3+}$ cations $\text{LnTiO}_3$; $\text{CeTiO}_3$ and $\text{PrTiO}_3$ seem to belong to one set showing a weakly correlated, antiferromagnetic ordering of $d^n$ spins, while $\text{GdTiO}_3$ and $\text{YbTiO}_3$ are strongly correlated ferromagnetic materials; reportedly,\textsuperscript{83} NdTiO$_3$ is unique showing no magnetic ordering down to 4.2 K. Hole dopants, such as $\text{La}^{3+}, \text{Si}^{4+}$, destroys magnetic ordering and induces metallic behaviour in these systems. None of the hole-doped ($d^0$) perovskite titanates however exhibit superconductivity.\textsuperscript{84}

The electronic properties of two other transition($m$) oxides, $\text{LiTiO}_3$ and $\text{LiTi}_2\text{O}_3$, stand in marked contrast to those of $\text{LiTi}_2\text{O}_5$ perovskites. While $\text{LiTi}_2\text{O}_5$ having an ordered rocksalt (hexagonal) structure is metallic and Pauli paramagnetic,\textsuperscript{85} $\text{LiTiO}_3$ having the spinel structure is metallic and superconducting ($\text{T}_c = 13$ K). This difference in electronic properties reveals the importance of crystal structure: while the perovskite structure of $\text{LiTiO}_3$, which permits linear ($\mu < 180$) $\text{Ti}^3\text{−}\text{O}\rightarrow\text{Ti}\text{−}\text{O}$ interaction the $3d^0$ electron in the n-bonding $\text{TiO}_6$ tetrahedra, the rocksalt and the spinel structures permit 90$\text{°}$ $\text{Ti}^3\text{−}\text{O}\rightarrow\text{Ti}$ as well as direct Ti$^3\text{−}\text{O}$ interactions. The difference in electronic properties of perovskite-like $\text{LiTiO}_3$ and rocksalt and spinel-type $\text{LiTi}_2\text{O}_5$ and $\text{LiTi}_2\text{O}_3$ could at least be qualitatively understood in terms of the difference in bonding possibilities between the two types of structures. This difference in bonding also points to the futility of looking for direct analogies between $d^n$ and $d^0$ perovskites and $\text{K}_2\text{NiF}_4$ oxides, in the wake of the discovery of high-temperature superconductivity in copper oxides.\textsuperscript{86}

$\text{V}^0\text{d}^0$ forms a rich variety of oxides whose properties bring out the influence of structure and dimensionality. While the $\text{X}$-d cubic perovskite $\text{SrVO}_3$ is metallic\textsuperscript{87} having no localized moment associated with $\text{V}^0\text{d}^0$, the 2-D $\text{Sr}_2\text{VO}_7$ (ref. 109)
having the K$_2$NiF$_4$ structure \( [n=1 \text{ member of the Ruddlesden-Popper (R-P series), is semiconducting and antiferromagnetic below 10 \text{ K}. Sr}_nV_3O_{3n+1} \text{ (ref. 92a) and Sr}_nV_4O_{3n+2} \text{ (ref 93, 110) (n=2 and n=3 members of the R-P series) are metallic down to 4.2 \text{ K}. While the effect of dimensionality on the electronic properties of these d$^0$ oxides is obvious, there seems to be a correlation between the degree of distortion of the VO$_6$ octahedra and the electronic properties.}^{100} \) For this purpose, the degree of distortion is expressed as \( \{V—O_{\text{metal}}—(V—O_{\text{nonmetal}})\}—V—O_{\text{plane}}. \) For metallic SrV$_4$O$_9$, the distortion is exactly zero since all the six V—O bond lengths (1.92 \text{ Å}) are equal. For semiconducting SrO$_x$ which has elongated VO$_6$ octahedra with four planar V—O bonds at 1.917 \text{ Å} and the two apical V—O bonds at 1.986 \text{ Å}, the degree of distortion is 0.036. For the metallic Sr$_2$V$_3$O$_8$, there are two kinds of VO$_6$ octahedra, the terminal and the central;
the distortion indices are, respectively, 0.021 and 0.004, suggesting that the d electrons of the central octahedra are delocalized and those of terminal octahedra are localized. Magnetic susceptibility data lend support to this possibility. Similar correlation between the degree of distortion and electronic properties seems to exist in LaTiO$_3$ perovskites.\textsuperscript{195}

It is interesting to compare the distortion of VO$_x$ octahedra in two other vanadium(IV) oxides, (VO)$_2$P$_2$O$_7$ (ref. 94) (Fig. 10) and KVOP$_3$ (ref. 95). (VO)$_2$P$_2$O$_7$ possesses 1-D double-chains of VO$_x$ octahedra which are linked by P$_2$O$_7$ groups, whileKVOP$_3$ adopts the KTP structure (Fig. 8) containing unsymmetrically connected chains of VO$_x$ octahedra. In both the structures, the VO$_x$ octahedra are considerably distorted, the metal atom moving away from the centre, indicating that for low-dimensional vanadium(IV) oxides which are insulating, the out-of-centre distortion of VO$_x$ octahedra persists even for d$^0$ electronic configuration.

Oxides containing 4d$^1$ NbO$_3$ octahedra are less numerous. Rutile-like NbO$_3$\textsuperscript{18} exhibiting semiconducting behaviour is similar to VO$_x$, where the 4d electrons of NbO$_3$ octahedra are tied into metal-metal bonds across the edge-shared octahedra of the rutile structure. Among the binary oxides containing Nb$^{IV}$, Nb$_2$O$_5$, is well characterized.\textsuperscript{17} It has a 3 x 4 x $\infty$ block structure (Fig. 11) consisting of pillars of ReO$_3$ structure bridged by edge-sharing octahedra at the pillar boundaries. This oxide is unique in that it is an itinerant electron antiferromagnet exhibiting both metallic conductivity and antiferromagnetic ordering at 12 K. While there are no definite perovskite-type niobium(IV) oxides known at present, an $n$=2 member of the R$^0$P$^2$ phase, R$_2$InP$_2$O$_7$, has been reported.\textsuperscript{196} Its electronic property is not known, but extended Hückel calculations predict 2-D metallic properties for this material. It has however been reported recently\textsuperscript{197} that a lithium-intercalated layered perovskite, KCa$_4$Nb$_2$O$_9$, exhibits a superconducting transition around 1 K.

Unlike niobium, molybdenum forms a variety of oxides where the electronic configuration of the metal is 4d$^3$–4d$^4$. LnMoO$_3$ (Ln=Gd–Lu, Y) oxides\textsuperscript{198, 199} are unique among them in that they contain isolated tetrahedral MoO$_4$\textsuperscript{2–} ions in the scheelite structure. The cubic tungsten bronze analogues of molybdenum, $\alpha$-M$_2$MoO$_6$ (A = Na, K; x = 0.90–0.97), which are prepared under high (65 kbar) pressure,\textsuperscript{200} are metastable under ordinary pressure and temperatures. These materials are similar to the cubic tungsten bronzes, showing metallic behaviour without spontaneous magnetism.

Under ordinary pressures, molybdenum forms several novel quasi-low-dimensional oxides and oxide bronzes containing 4d electrons.\textsuperscript{201–205} These materials have attracted considerable attention during the last decade in view of the unique low-dimensional electronic properties which include CDW driven metal-insulator transitions, sliding CDWs and insulator–superconductor transitions.

CDW and superconductivity are two most fascinating properties exhibited by a number of low-dimensional transition-metal compounds having small d electron counts.\textsuperscript{21, 22} Both the phenomena arise from a common origin, namely strong electron-phonon interaction. The possibility of a CDW accompanied by a lattice distortion was first predicted by Peierls\textsuperscript{22, 23} and Frohlich\textsuperscript{24} for a 1-D metal. The distortion and the associated electronic transition arise from a coupling of conduction electrons and phonons at 2K$_x$ (where K$_x$ is the Fermi wavevector corresponding to the reciprocal unit cell dimension); the coupling leads to a spontaneous lattice distortion and a modulation of the charge density (hence the name CDW) at $T > 0$ K, if the gain in electronic energy due to opening of a gap at the Fermi surface is greater than the potential energy cost of the lattice distortion. In a strictly 1-D metal, the gap opening is complete and the transition is a clean metal–non-metal (Peierls) transition. For quasi-low-dimensional systems, the CDW transition is associated with partial gap openings at the Fermi surface and therefore one finds metal–metal transitions rather than metal–non-metal transitions.

CDW was first experimentally realized\textsuperscript{24, 25} in the niobium and tantalum chalcogenides such as NbSe$_2$, TaS$_2$, and TaSe$_2$. When CDW was discovered in the blue molybdenum

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig10}
\caption{Fig. 10 Structure of (VO)$_2$P$_2$O$_7$. For clarity, P atoms are not shown.}
\end{figure}
bronze\textsuperscript{11} \( K_4 \text{MoO}_3 \), which is chemically and structurally different from the niobium and tantalum chalcogenides, it gave rise to considerable excitement and impetus to the study of low-dimensional molybdenum oxides and bronzes. Investigations over the last decade have established the occurrence of CDW and related electronic properties in at least three distinct types of molybdenum oxides: the blue bronzes, \( A_3 \text{MoO}_4 \), the purple bronzes, \( A_3 \text{MoO}_4 \), and \( \text{MoO}_3 \). Since these developments have been authoritative discussed in the literature\textsuperscript{11,12} we recount only the salient features here.

Among the three structure types of molybdenum oxides which exhibit CDW related instabilities, the blue molybdenum bronzes, \( A_3 \text{MoO}_4 \) \((A = K, \text{Rb and Tl})\) possess essentially a 1-D structure (Fig. 12) consisting of clusters of ten edge-sharing \( \text{MoO}_3 \) octahedra linked by corners. A complete study of the structure and properties of the blue bronze, \( \text{K}_3 \text{MoO}_4 \), has been carried out by Ganne et al\textsuperscript{13}. The purple bronzes, \( A_3 \text{MoO}_4 \) \((A = \text{Na, K, Tl})\), of which the potassium compound is prototypical, crystallize in a layered structure consisting of four sheets of \( \text{ReO}_3 \)-like \( \text{MoO}_3 \) octahedra which are capped by corner-sharing \( \text{MoO}_3 \) tetrahedra (Fig. 12). The potassium atoms are located in the interlayer positions. While the effective valence of tetrahedral-site molybdenum is 6+, the valences of octahedral-site molybdenums are 5.1+ and 5.8+ for the two crystallographically non-equivalent molybdenum atoms. The purple molybdenum bronze, \( \text{K}_2 \text{MoO}_4 \), exhibiting a Peierls distortion at 120 K, is truly stoichiometric whose structure has been accurately refined \((R=0.02)\) in the space group \( P\overline{1}n1 \) (ref. 119). The effective valence of the tetrahedral-site molybdenum is 6+, while the valences of the octahedral site molybdenums are 5.0+ and 5.6+ in this compound. Clearly, the tetrahedral molybdenum is the key to whether the 4d electrons exhibit CDW-related phenomena. All the three types of molybdenum oxides: the blue bronzes, orthorhombic MoO\textsubscript{3}, and \( \text{MoO}_3 \), exhibit CDW related instabilities, which are further substantiated by X-ray diffuse scattering studies and band structure calculations\textsuperscript{110}. These results unambiguously reveal that confinement of 5d electrons to \( \text{WO}_3 \) octahedra in 2-D structures can give rise to structural and electronic instabilities similar to those of molybdenum bronzes and oxides containing 4d electrons.

**Conclusion**

The brief survey of early transition metal oxides containing 4d and 5d-4d electronic configurations reveals an intimate relationship between the crystal structure and electronic properties. The characteristic out-of-centre distortion of metal-oxygen (\( \text{MoO}_3 \)) octahedra in many 4d oxides is at the heart of several of the interesting properties, including formation of
layered structures exhibiting ion-exchange and intercalation, Bronsted acidity, ferroelectric and non-linear optical response. Oxides containing d^0 MOs, octahedral exhibit a variety of electrical and magnetic properties that owe their origin to the nature of d-like states near the Fermi level. While 5d^1 and 4d^1 electrons in three-dimensional (3-D) structures give rise to itinerant electron magnetism and conduction, 3d^6 electrons in low-dimensional structures are localized. The properties of d^1 (tinomium) oxides possessing perovskite, rocksalt and spinel structures show an interesting correlation with crystal structure and bonding that reveals the futility of looking for d^1 analogues of superconducting cuprates. Molybdenum oxides and borates containing 4d electrons, which are confined to low-dimensional structures, exhibit characteristic CDW-driven electronic instabilities arising from a strong electron-phonon interaction. Recent investigations reveal that similar instabilities can be induced in low-dimensional tungsten oxides containing 5d electrons.

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References


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